Alfred Bader fonds

Correspondence

Purdue Univ.
1993-1996

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PURDUE UNIVERSITY

DEPARTMENT OF CHEMISTRY

Trip file
April 97

August 21, 1996

Dr. Alfred Bader
924 East Juneau, Suite 622
Milwaukee, WI 53202

Dear Alfred:

Thank you for your letter of August 14.

I am pleased to learn that you and Mona Berg have started working together for an art exhibition. I have just formally asked both Mona Berg and Derek Davenport to work with you on this matter. Of course, three of you as well as your wife are cordially invited to the Saturday Banquet on April 5, and I am delighted to learn that you are willing to present an after-dinner talk.

We have reserved a deluxe double room at the Purdue Memorial Union Club for April 4 and 5, 1997 (Confirmation No. 336124).

With best regards,

Sincerely yours,

Ei-ichi Negishi
Professor of Chemistry

EN/mc

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PURDUE UNIVERSITY

DEPARTMENT OF CHEMISTRY

October 3, 1996

Dr. Alfred Bader
924 East Juneau, Suite 622
Milwaukee, WI 53202

Dear Alfred:

During the last H. C. Brown Lectures, you revealed to me your thoughts on endowing an ACS National Prize on Organoboron and Allied Chemistry in honor of Professor Brown. I thought it was timely and great idea. When I had an occasion to talk to Professor Brown recently, he revealed his desire to see the plan realized. You must be aware of the three new ACS Awards, all of which bear the names of prominent chemists. In particular, both **George A. Olah** and **Koji Nakanishi** are organic chemists. All in all, I believe that the time is ripe for installation of an ACS National Prize in honor of Professor Brown. And, your willingness to spearhead the drive toward this goal would be very much appreciated. It would be especially nice if it could be announced by you at the H. C. Brown/85th Birthday Activities on April 4/5, 1997. Of course, if there is anything that I can do to be of help, please do not hesitate to contact me. By the way, do you know what it would cost to have such a Medal/Award endowed and operated by the ACS? I look forward to hearing from you regarding this matter.

With best regards,

Sincerely yours,

Ei-ichi Negishi
Professor of Chemistry

EN/mc

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Dr. Alfred Bader
924 East Juneau, Suite 622
Milwaukee, Wisconsin 53202
Phone: 414/277-0730
Fax: 414/277-0709

A Chemist Helping Chemists

August 14, 1996

Professor Ei-ichi Negishi
Chairman, H.C. Brown Lectureship Committee
Purdue University
1393 Brown Building
West Lafayette, IN 47907-1393

Dear Ei-ichi:

We look forward to next April's Brown Symposium and have already discussed with Mona Berg, the director of the Purdue Art Gallery, a possible show of paintings in honor of Herb.

Last April, we stayed with the Browns, but that must have been a burden on them, even though I think we all enjoyed it.

Could you please make reservations for us at the Purdue Union for the Friday and Saturday nights of the next symposium?

Also, might you like me again to give an after-dinner talk? You probably know that the best way to my heart is to invite me to speak!

Best regards, as always,

AB/cw

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PURDUE UNIVERSITY

DEPARTMENT OF CHEMISTRY

August 29, 1996

Dr. Alfred Bader
924 East Juneau, Suite 622
Milwaukee, WI 53202

Dear Alfred:

My students and I described the fast reaction of diborane with alkenes to give organoboranes in 1957. The academic chemistry advanced rapidly. I received the ACS Award for Creative Research in 1961 and the Nobel Prize in 1979.

But progress in the industrial aspects of this development was much, much slower. I tried repeatedly to interest industrial organizations in the commercial possibilities. Initial interest was frequently evidenced. An expensive market survey would be made. When this survey revealed that borane chemicals were not being manufactured and chemical organizations could not estimate their needs in the coming year or two, the interest vanished.

Then in 1972 I turned to you. You invited me to Milwaukee and I spoke to you and your staff. You were immediately intrigued by the possibility. We entered into an agreement and four people, Dr. Harvey Hopps, Dr. Clinton F. Lane and 2 B.S. chemists went to work. Sales were $10,000 the first year. Now it is in the millions. Moreover, with this entry into borane/organoborane area, Aldrich became a center for the industrialization of organometallics.

I have always felt that your contribution to the commercialization of borane/organoborane chemistry has not received the attention it deserved. At the recent meeting of BUSA-V in Guanajuato, Mexico I presented the matter to the International Committee.

It was unanimously voted to give you a special commendation for your contributions to the borane field. Since the next meeting, 1998, was scheduled to be held at the University of Georgia, Athens, Georgia, with Professor R. B. King in charge, you were invited to speak, and to put on an art exhibit should you desire. Athens, Georgia is not far from Atlanta and there would be no difficulty in having you and Isabel picked up at the Atlanta Airport and brought to Athens, returning the same way.

You have done so much, in so many areas, you may be surprised by the depth of our appreciation for your major contribution to boron chemistry. I hope you will find it possible to come to the meeting and receive our recognition and appreciation.

Sincerely,

Herb

Herbert C. Brown

PURDUE UNIVERSITY
Department of Chemistry *inter-office memorandum*

TO: Chemistry Faculty

FROM: E. Negishi E. Negishi

DATE: May 7, 1996

SUBJECT: 14th H.C. Brown Lectures

The 14th H. C. Brown Lectures is scheduled for Saturday, April 5, 1997. I am pleased to inform you that the following 4 outstanding organic chemists including one of our former colleagues have accepted our invitation. The theme for the symposium is: "Frontiers in Organic Synthesis".

Dale L. Boger (Scripps)
Larry E. Overman (UC Irvine)
Paul A. Wender (Stanford)
Hisashi Yamamoto (Nagoya, Japan)

It promises to be another exciting event. We also plan to celebrate Herb's 85th birthday on that day. As part of our celebration, **Dr. Alfred Bader** (former president of Aldrich Chemical Co.). has already agreed to stage an art exhibition. Other events are also being planned. Any suggestions you may have will be appreciated by us.

PURDUE UNIVERSITY

DEPARTMENT OF CHEMISTRY

March 12, 1996

Dr. Alfred Bader
924 East Juneau, Suite 622
Milwaukee, WI 53202

Dear Dr. Bader:

Please forgive my delayed response to your letter dated February 28, 1996. I was away for one week.

I am delighted to learn that you and you wife (I presume) will be able to attend the 13th H. C. Brown Lectures. Although the final program is not yet available, the event begins at 8:30 or 9:00 am, April 13 (Saturday). There will be a banquet that evening. Accordingly, we have made a reservation for a room for April 12 and 13 at the Holiday Inn North at SR 43 and Interstate 65 (West Lafayette). Unfortunately, both Purdue Memorial Union Hotel and University Inn are fully booked for these nights.

If I may, I would like to ask you to present a banquet talk on a topic of your choice, chemistry, art, or life.

There will be six Brown Lecturers this year:

H. Alper (U. of Ottawa)
C. P. Casey (U. of Wisconsin)
R. H. Crabtree (Yale U.)
R. H. Grubbs (CIT)
T. Marks (Northwestern U.)
R. R. Schrock (MIT)

As you note, the symposium promises to very exciting.

I look forward to seeing you in April.

Sincerely yours,

Ei-ichi Negishi
Professor of Chemistry

EN/mc

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PURDUE UNIVERSITY

HERBERT C. BROWN

March 13, 1996

Prof. Dr. Walter Siebert
IX International Meeting on Boron Chemistry
University of Heidelberg
Anorganisch-Chemisches Institute
Im Neuerheimer Feld 270
D-6 Heidelberg, Germany

Dear Professor Siebert:

I am somewhat surprized by your reluctance to recognize the major contributions of Dr. Alfred Bader and Dr. Clinton F. Lane in commercializing borane reagents and intermediates. German chemistry has long provided an outstanding example of the advantages to be gained by a close cooperation between the chemical industry and academic chemists.

Before I approached Aldrich, I approached a number of major chemical organizations. Invariably interest was expressed, but a market survey quickly cancelled that interest. After all, these new chemicals were not yet being manufactured and sold. How could an established market exist? But Aldrich was not discouraged by the absence of an existing market, Aldrich undertook to manufacture these chemicals and the market now exists.

Enclosed is a 4 page copy of a brochure from Aldrich, "Boron Reagents from Aldrich".

Boron chemists throughout the world have found their research greatly assisted by the commercial availability of these boron reagents and boron intermediates.

I believe the pioneering efforts of Dr. Alfred Bader and Dr. Clinton F. Lane deserve recognition by IMEBORON IX.

I would recommend "Award for Pioneering Efforts in Commercializing Borane Reagents and Chemicals." But if the International Committee prefers to give them Certificates of Recognition for their Pioneering Efforts in Commercializing Borane Reagents and Chemicals, I should accept their decision. I feel that we, as Boron Chemists, should recognize their exceptional contribution in advancing Boron Chemistry and Research by making so many Borane Reagents and Chemicals readily available.

Sincerely,

Herbert C. Brown

Herbert C. Brown

HCB:jc

cc: International Advisory Committee BCC: Alfred Bader/Clinton F. Lane

Enc.

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PURDUE UNIVERSITY

March 26, 1996

[illegible]
Dr. Alfred Bader
[illegible]
[illegible]

Dear Alfred

On the day we landed in Honolulu, Dec. 17, where I was scheduled to speak to the Meeting of the Paci[illegible] Rim Chemical Societies, we had no inkling of any problem. That night Sarah awoke at 1:00 AM comp[illegible] about an excruciating pain in her upper abdomen. I immediately called 911 and took her to the Kuakini Hospi[illegible] (founded in 1900 by Japanese immigrants). It is a teaching hospital which specializes in heart surgery. She [illegible] her operation on Dec. 20 (single by-pas[illegible]

I [illegible] that it takes men about 3 months to recover from this operation. For some reason women take longer. And for people approaching 80 recover is slower still. But Sarah has beaten these warnings. Sh[illegible] now approaching full recovery, so I am now finding time to handle nearly 3 months accumulation of ma[illegible]

In 1992 the University celebrated my 80th birthday concurrently with the 9th H. C. B. Lectures. Many [illegible] students and coworkers came from around the world. We had a wonderful time. But the occasion had an eff[illegible] on Sarah that I had not anticipated. She suddenly realized that I was not the youngster she had married 55 [illegible] earlier. She insisted that we must leave our home of 45 years to build a new home in a Retirement Village [illegible] medical services would be readily available (for me). This home is in West Lafayette, only 3/4 mile from our previous home. It is somewhat larger. We have a large unoccupied bedroom.

Since Ei-ichi was unable to make a reservation for you at the Purdue Memorial Union or one of the [illegible] Motels in West Lafayette, I hope that you and Isabel will agree to stay with us. The bedroom is a combined library and spare bedroom, larger than the bedroom you kindly provided for us in your home, and is adja[illegible] complete washroom. We are only 3 miles from the central campus.

Since I have a reserved parking [illegible] campus adjacent to the Chemistry Building and [illegible] Center, where the lectures will be held, it would be a far more convenient place than the Holiday Inn a[illegible] [illegible]

Please let me know your decision. If you decide to accept, I will ask Negishi's sec[illegible] present reservation at the Holiday Inn. If you are driving in, I will give you specific instructi[illegible] home a[illegible]

If you and Isabel prefer to fly Milwaukee/Indianapolis, or Milwaukee/Chicago/Lafayette, you and I[illegible] will be picked up at the appropriate airpo[illegible]

[illegible]

Herbert C. Brown

E. Negishi P. V. Ramach[illegible]

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Dear Wilfred: Once I started
reading your autobiography
I couldn't put it down until
the end.
Love to
[illegible]
Don't you miss Purdue anymore?
S.

1393 Herbert C. Brown Building
PURDUE UNIVERSITY

November/December 1995

Dear Family, Former and Present Coworkers and Friends ——

My pessimistic wife has again been surprised by our achieving the arrival of another year in reasonably good health. We have traveled somewhat less than in the past. However, we did travel to Europe to attend the triennial get-together of the Nobel Laureates in Chemistry at Lindau, Germany, in June. We went to Seoul, Korea in September to participate in the Global Convention for Restoration of Morality and Humanity. This provided an opportunity to see our friends in Korea. We are currently planning a trip to the Hawaiian Isles to participate in the Meeting of the Pacific Rim Chemical Societies, December 12-22. Finally, we participated in a two-week trip in California in connection with the Pre-OMCOS Meeting at U. Cal. Davis (commemorating George Zweifel's retirement) and the OMCOS Meeting at U. Cal. Santa Barbara. That trip, with the tours arranged by Professor E. Negishi, made it possible to revisit Yosemite (see photo).

We had an interesting experience at the ACS Meeting in Chicago where HCB participated in a Symposium on "Reductions in Organic Chemistry." When we first arrived at the lecture hall, we were astonished. It was large, with a rated capacity of 750 people. Since there were some 50 different programs going on simultaneously, we thought the hall would be nearly empty, possibly with only the speakers in attendance. But we were wrong. When HCB gave his talk, the hall was full with a large group of 100 to 150 people standing in the back. Perhaps they were attracted by the unusual sight of a chemist, who at 83, is still active in research.

A number of you sought explanations for our statement last year that we had celebrated our 57 years of marriage (now 58) and our 136th Wedding Anniversary (now 139). We had intended to include our explanation, but there is no more room, so it will have to wait until next year, if the Fates permit.

With best wishes to all, Sincerely,

Herb and Sarah

Herbert C. and Sarah B. Brown

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Dr. Alfred Bader
924 East Juneau, Suite 622
Milwaukee, Wisconsin 53202
Phone: 414/277-0730
Fax: 414/277-0709

A Chemist Helping Chemists

December 14, 1995

Professor and Mrs. Herbert C. Brown
Chemistry Laboratories
Purdue University
1393 Brown Building
West Lafayette, IN 47907-1393

Dear Sarah and Herbert:

Thank you for your wonderfully encouraging notes.

Of course, Isabel and I very much look forward to attending the next Brown Lectures in April.

With all good wishes for 1996, I remain,

Yours sincerely,

AB/cw

Dr. Alfred Bader
924 East Juneau, Suite 622
Milwaukee, Wisconsin 53202
Phone: 414/277-0730
Fax: 414/277-0709

A Chemist Helping Chemists

February 28, 1996

Professor Ei-ichi Negishi
Chairman, H.C. Brown Lectureship Committee
Purdue University
1393 Brown Building
West Lafayette, IN 47907-1393

Dear Professor Negishi:

Isabel and I much look forward to being with you for the Herbert Brown Symposium on the weekend of April 13th.

Could you please send me a schedule and could you please make reservations for us at the Purdue Union?

With all good wishes, I remain,

Yours sincerely,

AB/cw

PURDUE UNIVERSITY

DEPARTMENT OF CHEMISTRY

November 6, 1995

Dr. Alfred Bader
924 East Juneau, Suite 622
Milwaukee, WI 53202

Dear Dr. Bader:

A copy of your letter of October 13 for Prof. Grutzner has been forwarded to me.

As you may have heard from Dr. Grutzner, we will have six prominent organometallic chemists (H. Alper, C. P. Casey, R. Crabtree, R. H. Grubbs, T. J. Marks, and R. R. Schrock) for the 13th H. C. Brown Lectures (April 13, 1996). Furthermore, we are also planning to celebrate Professor Brown's 85th birthday in the spring of 1997. As in the past, we would be delighted and thankful to you if you would kindly stage an exhibition of your art collection. With your permission we would be planning it for the 14th Brown Lectures in 1997. (1)

If you could attend the 13th Brown Lectures on April 13 (Sat) next year, we would also like to ask you to present an after dinner talk on a topic of your choice. We have always greatly appreciated your participation in various event associated with Professor Brown and our Organic Division. (2)

I look forward to hearing from you about the matters mentioned above.

With best regards,

Sincerely yours,

Ei-ichi Negishi
Chairman
H. C. Brown Lectureship Committee

EN/mc

Dear Prof. Negishi:

I am just leaving for England – and am so happy to receive your letter just now.

I am honored & the answer to (1) & (2) is of course yes.

Best wishes
Alfred Bader
10 XI 95.

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PURDUE UNIVERSITY

HERBERT C. BROWN

December 1, 1995

Prof. Dr. W. Siebert
Anorganisch-Chemisches Institut
Im Neuenheimer Feld 270
D-69120 Heidelberg, Germany

Dear Professor Siebert:

I note your requirement for a one-page abstract early in 1996 and a photo-ready manuscript of my lecture to be submitted by mid-July.

The time you propose to be the first Session Lecture of Session B (Organic/Medicinal) on Monday, July 15, 1996 at 11:00 h is entirely satisfactory.

I have another proposal for you to consider. It is presented in the accompanying letter.

Sincerely yours,

Herbert C. Brown

Herbert C. Brown

bcc: Alfred Bader
Clinton F. Lane

1393 Herbert C. Brown Building

PURDUE UNIVERSITY

HERBERT C. BROWN

December 1, 1995

Prof. Dr. W. Siebert
Anorganisch-Chemisches Institut
Im Neuenheimer Feld 270
D-69120 Heidelberg, Germany

Dear Professor Siebert:

At the time we were developing hydroboration and hydroboration reagents, I tried to interest a number of industrial organizations in the desirability of making these new products readily available for research chemists and possibly commercially available for industrial application. I had no success. Companies such as Metal Hydrides and the Ethyl Corporation considered my proposal, but decided against making the effort, often after an expensive market survey.

Finally, I presented the opportunity to Aldrich Chemical Company. Their President, Alfred Bader, was enthusiastic. We entered into an agreement. He hired one of my students, Clinton F. Lane, and things developed rapidly. Now sales are in the multi-million dollar range and research in this area has been greatly facilitated by the ready availability of borane reagents.

I am enclosing a copy of Borane Reagents (Aldrich).

I believe it is desirable that IMEBORON recognize this effort, which has advanced the area of borane chemistry so greatly. I suggest that you consider the desirability of giving Dr. Alfred Bader and Dr. Clinton F. Lane an appropriate recognition for what they have achieved in advancing borane chemistry.

I hope you will consider my suggestion and discuss it with your associates in IMEBORON IX.

With all best wishes,

Sincerely yours,

Herbert C. Brown

Herbert C. Brown

encl.
bcc: Alfred Bader
Clinton F. Lane

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Dr. Alfred R. Bader
2961 North Shepard Avenue
Milwaukee, WI 53201

Dr. Alfred Bader
924 East Juneau, Suite 622
Milwaukee, Wisconsin 53202
Phone: 414/277-0730
Fax: 414/277-0709

A Chemist Helping Chemists

December 14, 1995

Professor Herbert C. Brown
Chemistry Laboratories
Purdue University
1393 Brown Building
West Lafayette, IN 47907-1393

Dear Professor Brown:

Thank you for the copies of your letters of December 1st sent to Dr. Bader.

He is in England through the end of December and will reply personally upon his return to Milwaukee.

Best wishes,

Cheryl Weiss
Office Manager

Dr. Alfred Bader
924 East Juneau, Suite 622
Milwaukee, Wisconsin 53202
Phone: 414/277-0730
Fax: 414/277-0709

A Chemist Helping Chemists

March 12, 1996

Professor Herbert C. Brown
Chemistry Laboratories
Purdue University
1393 Brown Building
West Lafayette, IN 47907-1393

Dear Herbert:

I was truly shaken by your letter and news about Sarah's bypass operation. We very much hope that by the time of our visit next month Sarah will have fully recovered.

Thank you for sending me the reprint.

With all good wishes to both of you, as always,

AB/cw

PURDUE UNIVERSITY

HERBERT C. BROWN

March 7, 1996

Dr. Alfred Bader
924 East Juneau, Suite 622
Milwaukee, Wisconsin 53202

Dear Alfred:

Fortunately we still had an original reprint of my article on Kekulé and Couper, *J. Chem. Ed.* 36, 104-110 (1959). It is enclosed.

Sarah and I are currently recovering from a difficult time, explained in the enclosed memoranda of Jan. 18 and Feb. 1. Her progress has been remarkable, so I am in turn making progress in catching up on my two-month accumulation of mail.

At the rate she is progressing she should be back to normal by the time of your visit. We will be delighted to see you and Isabel again.

With all best wishes,

Sincerely,

Herb

Herbert C. Brown

HCB:jc

Enc.

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924 East Juneau, Suite 622
Milwaukee, Wisconsin 53202
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Fax: 414/277-0709

A Chemist Helping Chemists

March 5, 1996

Professor Herbert C. Brown
Chemistry Laboratories
Purdue University
1393 Brown Building
West Lafayette, IN 47907-1393

Dear Herbert:

Isabel and I much look forward to being with you the weekend of April 13th.

Do you keep old reprints of your papers? If you happen to have a reprint of your paper on Kekulé and Couper which appeared in the *Journal of Chemical Education* in 1958, I would very much appreciate a copy.

With fond regards to you and Sarah, I remain,

Yours sincerely,

AB/cw

Enclosure

PURDUE UNIVERSITY

DEPARTMENT OF CHEMISTRY

April 16, 1996

Dr. Alfred Bader
924 East Juneau, Suite 622
Milwaukee, WI 53202

Dear Alfred:

Let me first thank you and Isabel, your able assistant, for a most fascinating and entertaining lecture on Loschmidt, Anschütz, and Kekulé. I also read some parts of your book the next day and was thoroughly fascinated by it.

We sold all 12 copies of your book, 11 copies for $25 each and 1 copy sold to a graduate student for $12.50. You have graciously agreed to charge us only $12.50 per copy. Accordingly I am enclosing a check in the amount of $150. The balance in the amount of $137.50 will be deposited in a discretionary account which is used to promote research-related activities among Organic Graduate Students and handled through our business office. I do not know at this time how many other students would like to purchase your book for $12.50, but I have sent a memo to that effect to students and postdoctoral associates.

As you note in a copy of my letter to Dale Boger, the 14th Brown Lectures is scheduled for April 5 (Saturday), 1997. We would be most grateful if you and Isabel could kindly participate in this very special event. An art exhibition you suggested to me is most attractive. It would also be very attractive if you could present an art-related talk either Friday evening (April 4) or during the luncheon on April 5. I will make sure to invite Derek Davenport, Dorothy Murphy, and Mona Berg.

Once again, thank you very much for your participation. I have already heard many very favorable comments on your presentation.

With best personal regards,

Sincerely yours,

Ei-ichi Negishi
Professor of Chemistry

EN/mc

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PURDUE UNIVERSITY

DEPARTMENT OF CHEMISTRY

March 22, 1996

Dr. Dale L. Boger
Department of Chemistry
Scripps Research Institute
10666 N. Torrey Pines Road
La Jolla, CA 92037

Dear ~~Dr. Boger:~~ Dale

On behalf of the Organic Division of Purdue University I would like to extend to you an invitation to deliver a lecture (45-50 min) at the **14th Herbert C. Brown Lectures** scheduled for **April 5 (Saturday)**, 1997, on the theme of **Frontiers in Organic Synthesis**. We hope to have several prominent and currently very active chemists in the field such as yourself. Following our recently established "tradition", we ask our invited speakers to arrive here in time for an informal Friday dinner and social. The Brown Lectures typically begin at 9:00 a.m. the next morning and end sometime in the afternoon, and the event concludes with a Saturday evening banquet. Next year, Herb Brown will be a research active 85-year old chemist. We hope to be able to celebrate this rare accomplishment with this event.

We will be happy to provide a modest honorarium in addition to covering your travel expenses. In view of the very unpredictable and widely ranging current airfare structure, we need to ask you to seek an economy-class airfare, preferably at the super-saver rate.

We sincerely hope that you will be able to accept our invitation and look forward to hearing from you soon, preferably by April 12, regarding this matter.

Sincerely yours,

Ei-ichi Negishi
Professor of Chemistry
Tel: 1-317-494-5301
E-mail: NEGISHI@CV3.CHEM.PURDUE.EDU

EN/mc

EIICHI OR SUMIRE NEGISHI
4956 TAFT RD. PH. 317-463-4439
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9067

April 15 19 96

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PAY TO THE ORDER OF Dr. Alfred Bader $ 150.00

One Hundred Fifty Only ———— DOLLARS

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Lafayette, Indiana

Preferred One℠

MEMO

Eiichi Negishi

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9068

April 15 19 96

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PAY TO THE ORDER OF Purdue University $ 112.50

One Hundred Twelve & 50/100 — DOLLARS

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Lafayette, Indiana

Preferred One℠

MEMO

Eiichi Negishi

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PAY TO THE ORDER OF Purdue University $ 25 00

Twenty Five ———— DOLLARS

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Bank One, Lafayette, NA
Lafayette, Indiana

MEMO

Dr. Henry Feuer

⑆074900974⑆ 0 170 240 6⑈ 0756

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PURDUE UNIVERSITY

HERBERT C. BROWN

April 19, 1996

Professor Sheldon G. Shore
Department of Chemistry
The Ohio State University
100 West 18th Avenue
Columbus, OH 43210-1185

Dear Sheldon:

At the time we discovered hydroboration and, shortly afterward, asymmetric hydroboration with Ipc_2BH, I tried to interest a number of large chemical companies in exploring the commercial possibilities of boron chemicals. They would express interest, make an expensive market survey, and discover that borane chemicals were not being marketed. How could a company consider entering a field where no market was currently in existence?

Finally, in 1972 I suggested this possibility to Alfred Bader, then President of the Aldrich Chemical Company. He exhibited the imagination and courage we expect of our research people and decided to explore the market possibilities. He hired one of my students, Clinton F. Lane. Their efforts have greatly contributed to the advance of boron chemistry.

I have in front of me a brochure, "BORON REAGENTS - The widest selection of quality boron products." The 20 pages of the brochure lists hundreds of boron reagents. I realize it involves a break with precedence, but I believe we should also recognize exceptional contributions to the field by industry. In the past all of our recognitions have gone to academic people!

Among the academic people, I recommend George Kabalka and Bakthan Singaram. Incidently, in your letter it should be Donald S. Matteson (note the e).

With all best wishes,

Sincerely,

Herb

Herbert C. Brown

HCB:jc

bcc: Alfred Bader —
Clinton F. Lane

(OVER)

H. C. BROWN AND R. B. WETHERILL LABORATORIES OF CHEMISTRY
1393 BROWN BUILDING • WEST LAFAYETTE, IN 47907-1393 USA
PHONE: (317) 494-5316 • FAX: 07-1-317-494-0239 • E-MAIL: HCBROWN@CHEM.PURDUE.EDU

THE OHIO STATE UNIVERSITY

Department of Chemistry

100 West 18th Avenue
Columbus, OH 43210-1185

Phone 614-292-2251
FAX 614-292-1685
TELEX 332911
Answer Back Code: OSU CHEM UD

April 12, 1996

Professor Herbert C. Brown
Department of Chemistry
Purdue University
1393 Brown Building
West Lafayette, IN 47907-1393

Dear Professor Brown:

I am writing to ask your recommendations in selecting recipients of the BUSA award to be presented at BUSA-V-MEX. The award consists of an engraved plaque that recognizes distinguished accomplishments in the field of boron science by the awardee. Awards have been presented at each of the earlier BUSA meetings.

Please recommend no more than two individuals, not necessarily those in your area of research, whom you believe deserve special recognition and indicate reasons for your selections. While the award specifically cites distinguished accomplishments, we should also consider contributions to the promotion of boron science.

Please let me have your recommendations by May 8, 1996. Awardees will be selected by past recipients of the award.

Previous recipients of the BUSA award:

Thomas Fehlner
Donald Gaines
Russel Grimes
Frederick Hawthorne
Donald Mattson
Thomas Onak
Sheldon Shore
Larry Sneddon
Albert Soloway
Robert Williams

Sincerely yours,

Sheldon

Sheldon G. Shore
Professor of Chemistry

(over)

PURDUE UNIVERSITY

Dr. P. V. Ramachandran
Research Scientist
DEPARTMENT OF CHEMISTRY

Purdue to B file

March 28, 1996

Professor Walter Siebert
IX. IMEBORON Secretariat
Anorganisch-Chemisches Institut
Universitat Heidelberg
Im Neuenheimer Feld 270
69120 Heidelberg
GERMANY

Dear Professor Siebert:

Enclosed please find the following:

1. Registration form (duly filled) for Professor Herbert C. Brown and Mrs. Sarah B. Brown.
2. Abstract form (duly filled) and the abstract for Professor Brown's Session Lecture entitled, "Recent Developments in Our Sixty Year Program on Diborane and Organoboranes for Syntheses".
3. Registration form (duly filled) for myself.
4. Abstract form (duly filled) and the abstract for a talk entitled, "Efficient Syntheses of 1,2- and 1,3-diols via Intramolecular Asymmetric Reductions of α- and β-hydroxy ketones" that I wish to present at the IMEBORON-IX.
5. A bank draft for DM 1200.00 towards the Registration Fee for Prof. and Mrs. Brown and myself.

You should have already received copies of all of these by fax. I am awaiting the necessary papers to apply for an entry visa to attend the meeting. Looking forward to a wonderful conference, I remain

Sincerely,

P. Ramachandran

P. V. Ramachandran

cc: H. C. Brown

P.S. HCB has asked me to send you a copy of the recent Aldrich catalog entitled, "Boron Reagents" to emphasize his point that Aldrich (Alfred Bader and Clinton F. Lane) has contributed to the advancement of boron chemistry by making available numerous boron intermediates for the chemical community.

bcc: Dr. Alfred Bader ✓, Dr. C. F. Lane

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WEST LAFAYETTE, IN 47907-1393 • FAX (317) 494-0239

CURRENT DEVELOPMENTS IN OUR SIXTY YEAR PROGRAM ON DIBORANE AND ORGANOBORANES FOR SYNTHESES

Herbert C. Brown

H. C. Brown and R. B. Wetherill Laboratories of Chemistry
Purdue University, West Lafayette, IN 47907-1393, U. S. A.

It is a rare experience to have had the opportunity to carry out research on a selected topic for 60 years. Research normally proceeds at a slow pace. Day by day and week by week it is difficult to see much progress. But research is cumulative. Each discovery makes possible advances in many areas.

On my graduation from the University of Chicago in 1936, my classmate, Sarah Baylen, gave me a graduation gift, a copy of "The Hydrides of Boron and Silicon" by Alfred Stock (Karlsruhe). This book persuaded me to do my Ph. D., with Professor H. I. Schlesinger and Dr. A. B. Burg, exploring the chemistry of diborane.

The Ph. D. study of the reaction of diborane with aldehydes and ketones opened up the hydride era of organic reductions. The study of this reaction led to the discovery of alkali metal borohydrides. Study of the reducing characteristics of the borohydrides led to the discovery of hydroboration. Hydroboration provided a simple synthetic route to organoboranes. Investigation established that these compounds have a most versatile chemistry. This study provided in 1961 the first non-enzymatic asymmetric synthesis in high ee and opened this new active research area to chemists. Clearly, we had discovered a Major New Continent of Chemistry.

1. Beginnings
2. Volatile Compounds of Uranium
3. Alkali Metal Route to Diborane
4. Alkali Metal Borohydrides
5. Selective Reductions
6. Hydroborations.
7. Versatile Organoboranes
8. Asymmetric Hydroboration
9. Asymmetric Synthesis Made Easy
10. α-Pinene: Superior Chiral Auxiliary
11. Asymmetric Reductions
12. Asymmetric Allyl- and Crotylboration
13. Asymmetric Opening of Meso Epoxides
14. Asymmetric Enolborations

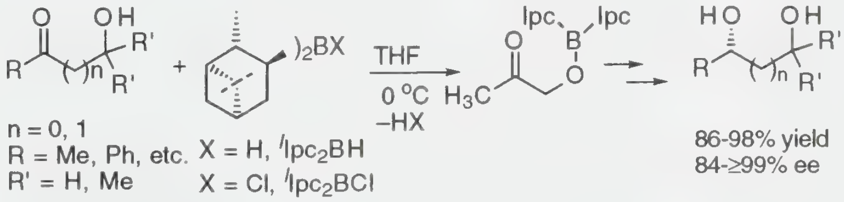
Some recent developments, to be discussed, reveal that we have not yet completed the exploration. It will require a new generation of chemists to continue this exploration and apply the riches of the New Continent for the good of Mankind.

EFFICIENT SYNTHESES OF 1,2- AND 1,3-DIOLS VIA INTRAMOLECULAR ASYMMETRIC REDUCTION OF α- AND β-HYDROXY KETONES

P. Veeraraghavan Ramachandran and Herbert C. Brown
H. C. Brown and R. B. Wetherill Laboratories of Chemistry
Purdue University, West Lafayette, IN 47907-1393, U. S. A.

The unique structural features of α-pinene contribute to its facile elimination from *B*-isopinocampheyl-9-borabicyclo[3.3.1]nonane (Aldrich: Alpine-Borane) and make possible Midland's successful application of this trialkylborane for the asymmetric reduction of aldehydes and acetylenic ketones, although the reduction of the carbonyl groups by trialkylboranes typically require relatively extreme conditions.[1] Application of Midland's reagent to the reduction of acetophenone and acetylcyclohexane is much less satisfactory. Reasoning from the probable reaction mechanism that an increase in the Lewis acidity of the boron atom might be beneficial, we tested (–)- and (+)-*B*-chlorodiisopinocampheylboranes (^{d} and ^{l}Ipc$_2$BCl, Aldrich: (–)- and (+)-DIP-Chloride) and established them as successful reagents for the reduction of a variety of representative prochiral ketones.[2] During a systematic study of the compatibility of DIP-Chloride with the presence of representative functional groups in the aromatic ring of acetophenone, we observed that an *o*-hydroxyl group provides the product, *o*-hydroxy-α-phenethanol, in the opposite optical isomer.[3] A similar effect was also noted for the presence of an *o*-carboxylic acid group in the acetophenone substrate.[4]

We have now found that treatment of α- and β-hydroxyketones with one equiv of diisopinocampheylborane or DIP-Chloride rapidly provides the corresponding ketoalkyl diisopinocampheylborinates, which then undergo facile intramolecular reduction. This reaction sequence, followed by oxidative workup, provides a general synthesis of optically active 1,2- and 1,3-diols in very high enantiomeric excess.



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[1] Midland, M. M. *Chem. Rev.* **1989**, *89*, 1553. [2] Brown, H. C.; Chandrasekharan, J.; Ramachandran, P. V. *J. Am. Chem. Soc.* **1988**, *110*, 1539. [3] Ramachandran, P. V.; Gong, B.; Brown, H. C. *Tetrahedron Lett.* **1994**, *35*, 2141. [4] Ramachandran, P. V.; Chen, G. M.; Brown, H. C. *Tetrahedron Lett.* **1996**, *37*, 0000.

Dr. Alfred Bader
924 East Juneau, Suite 622
Milwaukee, Wisconsin 53202
Phone: 414/277-0730
Fax: 414/277-0709

A Chemist Helping Chemists

March 21, 1996

Professor Ei-ichi Negishi
Chairman, H.C. Brown Lectureship Committee
Purdue University
1393 Brown Building
West Lafayette, IN 47907-1393

Dear Professor Negishi:

Isabel and I much look forward to being with you for the Brown Lectures, and I am honored that you have invited me to be the banquet speaker.

My title will be *"Richard Anschütz, the Chemist Detective"*. For that talk, I will require an overhead projector. How long would you like the talk to be?

As you perhaps know, my autobiography, *Adventures of a Chemist Collector*, is now out, and I enclose a couple of reviews. The book is being offered by the American Chemical Society, and many chemists at Purdue may have read it. But if you would like, we could easily bring a few copies along, in case you would like to arrange a book-signing. It retails for $25, but I need to be paid only $12.50 each - to cover the requirements of my contract with publisher and literary agent. The balance could be kept by whichever organization arranges the book-selling.

As you probably know, the book deals extensively with our happy collaboration with Sarah and Herbert.

With all good wishes, I remain,

Yours sincerely,

AB/cw

Enclosures

PURDUE UNIVERSITY

DEPARTMENT OF CHEMISTRY

March 12, 1996

Dr. Alfred Bader
924 East Juneau, Suite 622
Milwaukee, WI 53202

Dear Dr. Bader:

Please forgive my delayed response to your letter dated February 28, 1996. I was away for one week.

I am delighted to learn that you and you wife (I presume) will be able to attend the 13th H. C. Brown Lectures. Although the final program is not yet available, the event begins at 8:30 or 9:00 am, April 13 (Saturday). There will be a banquet that evening. Accordingly, we have made a reservation for a room for April 12 and 13 at the Holiday Inn North at SR 43 and Interstate 65 (West Lafayette). Unfortunately, both Purdue Memorial Union Hotel and University Inn are fully booked for these nights.

If I may, I would like to ask you to present a banquet talk on a topic of your choice, chemistry, art, or life.

There will be six Brown Lecturers this year:

H. Alper (U. of Ottawa)
C. P. Casey (U. of Wisconsin)
R. H. Crabtree (Yale U.)
R. H. Grubbs (CIT)
T. Marks (Northwestern U.)
R. R. Schrock (MIT)

As you note, the symposium promises to very exciting.

I look forward to seeing you in April.

Sincerely yours,

Ei-ichi Negishi
Professor of Chemistry

EN/mc

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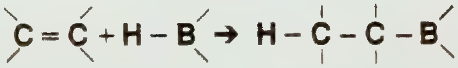
WEST LAFAYETTE, IN 47907-1393 • FAX (317) 494-0239

Herbert C. Brown

Lectures in Organic Chemistry



$$>C=C< + H-B< \rightarrow H-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-B<$$

1996

Department of Chemistry
Purdue University
West Lafayette, Indiana

Herbert Charles and Sarah Baylen Brown

THE THIRTEENTH
HERBERT C. BROWN
LECTURES IN ORGANIC CHEMISTRY

April 13, 1996

Department of Chemistry
Purdue University
West Lafayette, Indiana 47907

SCHEDULE OF EVENTS

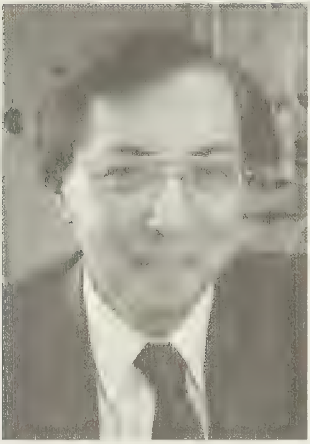
Saturday, April 13	**HERBERT C. BROWN LECTURES** *Frontiers in Organometallic Chemistry* Room 218, Stewart Center
9:00 - 9:10 a.m.	**Opening Remarks** **Richard A. Walton** Head, Department of Chemistry Purdue University
9:10 - 10:00 a.m.	**Howard Alper** University of Ottawa *Metal Catalyzed Organic Reactions: A Springboard to New and/or Improved Chemical Processes*
10:00 - 10:45 a.m.	**Coffee and Poster Session** Room 218, Stewart Center
10:50 - 11:40 a.m.	**Charles P. Casey** University of Wisconsin at Madison π*-Propargyl Metal Complexes*
11:40 a.m. - 12:30 p.m.	**Robert H. Crabtree** Yale University *Breaking the C-F Bond*
12:30 - 1:50 p.m.	**Luncheon** West Faculty Lounge, Memorial Union

1:50 - 2:40 p.m.	**Robert H. Grubbs** California Institute of Technology *Organic and Polymer Synthesis Using Ruthenium Carbene Complexes*
2:40 - 3:30 p.m.	**Tobin J. Marks** Northwestern University *Connections between Heterogeneous and Homogeneous Catalysis. The Case of Molecule-Based Olefin Polymerization Catalysts*
3:30 - 4:20 p.m.	**Richard R. Schrock** Massachusetts Institute of Technology *The Pluses (and Some Minuses) of Triamidoamine Ligands in High Oxidation State Chemistry*
4:20 - 4:30 p.m.	**Closing Remarks** **Herbert C. Brown** Purdue University
	Adjournment

BANQUET

Lafayette Country Club
1500 South Ninth Street
Lafayette

6:00 - 7:00 p.m.	**Social Hour** (cash bar)
7:00 p.m.	**Dinner** **Alfred Bader** *Richard Anschütz, the Chemist Detective*



HOWARD ALPER

PROFESSOR OF CHEMISTRY AND ASSISTANT VICE PRESIDENT, RESEARCH
UNIVERSITY OF OTTAWA

Howard Alper received his B.Sc. degree in 1963 from Sir George Williams University in Montreal, and his Ph.D. degree in 1967 with J. T. Edward at McGill University. Following a year spent as a NATO postdoctoral fellow with Paul Schleyer at Princeton, he joined the faculty of the State University of New York at Binghamton in 1968. He returned to Canada at the end of 1974, assuming the position of Associate Professor of Chemistry at the University of Ottawa where he has remained as full professor since his promotion in 1978. He served as Chair of the Department of Chemistry during 1982-85 and again from 1988-94. In addition to supervising his research group, Professor Alper is Assistant Vice-President, Research at the University of Ottawa. The research interests of Professor Alper extend from organic to inorganic chemistry with a strong focus on catalysis. Homogeneous, phase transfer and, more recently, heterogeneous catalysis by metal complexes are the keystones for his contributions in the areas of oxidation, reduction, carbonylation and cycloaddition reactions. Of particular note is his work on metal catalyzed ring expansion-carbonylation reactions of heterocycles, and the chiral synthesis of heterocycles by palladium catalyzed cycloaddition of aziridines and heterocumulenes. He has been able to isolate and characterize for the first time several of the key catalytic intermediates in the carbonylation of halides. Novel cobalt and ruthenium carbonyl catalyzed rearrangements and cyclization reactions applicable to the synthesis of alkaloids have also been discovered in his laboratories. Using metal complexes intercalated on clays (e.g. montmorillonite), he has developed efficient routes to urethanes and polyurethanes as well as regioselective methods for the hydroformylation of vinylsilanes. Finally, he is also interested in studying the chemistry of novel organometallic complexes and in the metal catalyzed functionalization of polymers such as polybutadiene and polyvinylacetylene.

In addition to having published over 360 papers, Professor Alper has received an impressive number of awards and distinctions. He is an E. W. R. Steacie Fellow of the Natural Sciences and Engineering Research Council of Canada (NSERC), a J. S. Guggenheim Fellow (1985-86), and a Killam Research Fellow (1986-88). He has also received the Catalysis Award of the Chemical Institute of Canada (1984), the Alcan Award for outstanding contributions to research in inorganic chemistry (1980), the Alfred Bader Award for outstanding achievement in organic chemistry (1990), a Commemorative Medal for the 125th Anniversary of Canada for significant contributions to Canada (1992), and an E. W. R. Steacie Award for Distinguished Contributions to Chemistry (1993). He was elected Fellow of the Royal Society of Canada in 1984, and is currently Vice-President of the Academy of Sciences of the Royal Society of Canada.

CHARLES P. CASEY

H. B. ADKINS PROFESSOR OF CHEMISTRY AND STEENBOCK PROFESSOR IN PHYSICAL SCIENCES

UNIVERSITY OF WISCONSIN AT MADISON

Charles P. Casey (born January 11, 1942) received his early education in St. Louis, Missouri (B.S. in Chem., St. Louis University, 1963). He began his graduate research as an NSF Fellow with George M. Whitesides at M.I.T. where he received the Eastman Kodak Award for his graduate studies with organocopper compounds After receiving his Ph.D. degree in 1967, he spent several months at Harvard University as an NSF Fellow in the laboratories of Paul D. Bartlett In 1968, he joined the faculty at the University of Wisconsin-Madison where he is now *Homer B. Adkins Professor of Chemistry and Steenbock Professor in the Physical Sciences*.

Professor Casey's research focuses on mechanistic organometallic chemistry. Current studies include reactions of metal-metal double bonds, carbene complexes, concerted organometallic reactions, and use of wide bite angle diphosphines in hydroformylation. He is author of more than 200 papers in organometallic chemistry

Professor Casey has served the American Chemical Society as a member of the Editorial Advisory Boards of the Journal of Organic Chemistry (1978-83) and of Organometallics (1985-87), as Chairman of the Wisconsin Section (1985), the Organometallic Subdivision (1986), and the Inorganic Division (1991), as a member of Advisory Board of the Petroleum Research Foundation (1992-94). He served on the N.I.H. Study Section on Metallobiochemistry (1984-88). He has been a lecturer in the ACS short course on *Frontiers of Organic Chemistry* since 1982

Casey is a member of the National Academy of Sciences (1993) and the American Academy of Arts and Sciences (1993) and a Fellow of the American Association for the Advancement of Science (1991). He has received the Alumni Merit Award from St. Louis University (1987), an Alexander von Humboldt Senior Award (1988), a Fellowship from the Japan Society for the Promotion of Science (1988), the Arthur C. Cope Scholar Award of the ACS (1988), the ACS Award in Organometallic Chemistry (1991), and was a National Science Council Distinguished Lecturer in Taiwan (1994)

ROBERT H. CRABTREE
PROFESSOR OF CHEMISTRY
YALE UNIVERSITY

Robert H. Crabtree, Professor of Chemistry at Yale University, was born in London and was educated at Oxford, where he worked with Professor Malcolm Green. At Sussex University, he studied nitrogen fixation under Professor Joseph Chatt for his Ph.D. degree. In 1973, he moved to the Institut de Chimie des Substances Naturelles at Gif-sur Yvette, France, where he worked with Dr. Hugh Felkin on homogeneous catalysis.

In 1977, he moved to Yale University as Assistant Professor and started his studies on C-H activation. Examples of stoichiometric and catalytic alkane C-H activation were discovered and, in 1985, the Mercat reaction that allows selective preparative scale synthesis of a wide variety of simple functional derivatives from alkanes and alkyl compounds via a radical route. The same period saw the discovery of halocarbon complexes and the directing effects of 'Crabtree's catalyst' that made it useful in synthetic organic chemistry.

The celebrated discovery of the dihydrogen complex by Kubas (1984) opened another chapter with the discovery in the Crabtree group of the T_1 method, now one of the standard methods for detecting H_2 complexes, as well as a variety of reactions involving H_2 complexation, notably deprotonation of bound H_2 and fluxional exchange between classical and nonclassical sites in complexes of the type $L_nMH(H_2)$. Many polyhydrides were shown to have such nonclassical structures. The distinction between 'stretched' and 'unstretched' σ-complexes was also made during this period.

The most recent period has been marked by the discovery of a new type of intra- (jointly with Bob Morris) and intermolecular interaction, the unconventional M-H...H-N 'dihydrogen bond'. This can perturb rates and equilibria in reactions of metal complexes. Strong B-H...H-N interactions explain the fact that BH_3NH_3 is a solid rather than a gas like the isoelectronic species C_2H_6. Conventional H-bonds can also speed up reactions of coordinated ligands, such as CO.

In the last few months, a series of reactions of saturated fluorocarbons has been found, including a convenient thermal method for the disposal of CFCs and for the aromatization of cyclic perfluoroalkanes and a photochemical method for the conversion of perfluoroalkanes to perfluoroalkenes.

He has been awarded a number of fellowships and prizes including the Organometallic Chemistry Awards of the ACS and the Royal Society of Chemistry. He is the author of a popular textbook in organometallic chemistry.

ROBERT H. GRUBBS

VICTOR AND ELIZABETH ATKINS PROFESSOR OF CHEMISTRY
DIVISION OF CHEMISTRY AND CHEMICAL ENGINEERING
CALIFORNIA INSTITUTE OF TECHNOLOGY

Robert H. Grubbs received his B.S., M.S., and Ph.D. degrees as follows: B.S., Chemistry, University of Florida, Gainesville, Florida, 1963; M.S., 1965; Ph.D., R. Breslow, Chemistry, Columbia University, New York, New York, 1968. He then was an NIH Postdoctoral Fellow, J. P. Collman, Chemistry, Stanford in 1968-69.

He is the Victor and Elizabeth Atkins Professor of Chemistry at the California Institute of Technology, Pasadena, California, USA, where he has been a faculty member since 1978. Before moving to Caltech, he was at Michigan State University from 1969 to 1978 achieving the rank of Associate Professor

The research group of Grubbs is involved in the design, synthesis, and mechanistic studies of complexes that catalyze useful organic transformations. The major focus of the group over the past few years has been on the olefin metathesis reaction. This reaction has been used to prepare families of new polymeric structures from the ring opening polymerization (ROMP) of cyclic olefins which have useful mechanical, electronic or optical properties. The key to this work has been the use of well-defined catalysts that grow living polymers. To optimize the utility of these catalysts, new catalysts have been developed that are extremely tolerant of organic functional groups. In addition to their use as initiators for polymerizations, these catalysts have been found to have numerous applications in organic synthesis.

Professor Grubbs' awards have included Alfred P. Sloan Fellow, 1974-76, Camille and Henry Dreyfus Teacher-Scholar Award, 1975-78, Alexander von Humboldt Fellowship, 1975, ACS National Award in Organometallic Chemistry, 1988, the Arthur C. Cope Scholar Award, 1990, and the ACS Award in Polymer Chemistry (Mobil Chemical Company), 1995. He was elected to the National Academy of Sciences in 1989, and Fellow of the American Academy of Arts and Sciences in 1994.

TOBIN J. MARKS

C. E. & E. H. MORRISON PROFESSOR OF CHEMISTRY

NORTHWESTERN UNIVERSITY

Tobin J. Marks, Charles E. & Emma H. Morrison Professor of Chemistry at Northwestern University, where he also holds a chair in Materials Science and Engineering, was born in Washington, D. C. on November 25, 1944. He received his B.S. degree from the University of Maryland in 1966, and his Ph.D. degree from the Massachusetts Institute of Technology in 1970, under the guidance of F. Albert Cotton. After acquiring his doctorate, he joined the staff of Northwestern as an assistant professor.

He has contributed very significantly to advances in three areas, *i.e.*, organometallic chemistry, bioinorganic chemistry, and solid-state chemistry. He was among the first to develop the organometallic chemistry of the lanthanides and actinides, a field now under very active study throughout the world. He also applied physical chemical methods to elucidate the molecular structure and bonding in transition metal borohydride complexes. In recent times he has developed new catalysts for olefin polymerization and hydrogenation based on novel cationic metallocene complexes. He was the first to use polypyrazolylborate ligands as models for protein multi-imidazole metal binding environments, thereby providing important information on several important classes of copper metalloproteins. In solid-state chemistry he has developed rational methods for synthesizing macromolecules of great significance in the development of polymeric materials having unusual electrical and/or nonlinear optical properties and has developed metal-organic precursors for the growth of high temperature superconducting films.

Dr. Marks has received many awards and honors. He is a fellow of the American Academy of Arts and Sciences and a member of the U.S. National Academy of Sciences. He has received the American Chemical Society awards for Organometallic Chemistry (1989) and for Inorganic Chemistry (1994). He has been an Alfred P. Sloan Fellow, a Camille and Henry Dreyfus Teacher-Scholar, and a Guggenheim Foundation Fellow. He is an associate editor of the ACS journal *Organometallics* and a member of the editorial advisory boards of several international journals. He is a Corporation Member of Inorganic Syntheses, and a member of the Governing Council of the Gordon Conferences. He has been a distinguished visiting lecturer at universities throughout the United States, and has given invited lectures in Canada, France, Germany, Great Britain, Israel, Italy, Japan, Portugal, and Taiwan. He is the author of more than 450 publications.

RICHARD R. SCHROCK

FREDERICK G. KEYES PROFESSOR OF CHEMISTRY
MASSACHUSETTS INSTITUTE OF TECHNOLOGY

Richard R. Schrock was born in Indiana, but spent his high school years in San Diego, California. He obtained his B.A. degree in 1967 from the University of California at Riverside, where he spent his summers working on gas phase photochemistry in the group of James Pitts. He attended graduate school at Harvard University, from where he received his Ph.D. degree in inorganic chemistry in 1971 He spent one year as an NSF postdoctoral fellow at Cambridge University working in the group of Lord Jack Lewis. In 1972 he was hired by Earl Muetterties of the Central Research and Development Department of E. I. duPont de Nemours and Company. After three years in the group of George Parshall he moved to M.I.T. in 1975 where he became full professor in 1980 and in 1989 the Frederick G. Keyes Professor of Chemistry. His interests include the inorganic and organometallic chemistry of high oxidation state early metal complexes (especially those that contain an alkylidene or alkylidyne ligand), catalysis and mechanisms involving alkylidene or alkylidyne species, the chemistry of high oxidation state dinitrogen and related complexes, and the controlled synthesis of polymers using well-defined organometallic initiators. He is perhaps best known as the discoverer of "high oxidation state carbene" (alkylidene complexes) by α hydrogen abstraction reactions in high oxidation state metal alkyl complexes. In the last few years he has applied alkylidene chemistry toward polymer synthesis, in particular ring-opening-metathesis polymerization (ROMP) of cyclic olefins, the synthesis of ordered polymers containing organic or inorganic semiconductors or metal clusters, and the controlled polymerization of acetylenes to give polyenes of potential interest as non-linear optical materials

R.R. Schrock has been an Alfred P. Sloan Fellow, a Camille and Henry Dreyfus Teacher-Scholar, the Royal Society Centenary Lecturer and Medalist in 1991, and an Alexander von Humboldt Fellow (1995). He received the ACS Award in Organometallic Chemistry (1985), the Harrison Howe Award of the Rochester ACS section (1990), and the ACS Award in Inorganic Chemistry (1996). He has been elected to the American Academy of Arts and Sciences and the National Academy of Sciences. He was Associate Editor of *Organometallics* for eight years, and has published more than 290 research papers

PROFILES OF THE FOUNDERS
OF THE
HERBERT CHARLES AND SARAH BAYLEN BROWN FUNDS

Herbert C. Brown was born in London on May 22, 1912, but was brought to the U.S. at age two and grew up in Chicago. He enrolled in Crane Junior College in 1933, where he met Sarah Baylen, now his wife of more than 59 years. When Crane closed for lack of funds in June 1933, they continued their training in the home laboratory of one of their teachers, Nicholas D. Cheronis. When new colleges were opened in 1934, they attended Wright Junior College, where Sarah autographed his yearbook with the inscription, "To a future Nobel Laureate." They then entered the University of Chicago in 1935 as juniors. H. C. Brown completed two years of work in one year and graduated in 1936. A graduation gift from Sarah, Alfred Stock's Baker Lectures on "Hydrides of Boron and Silicon," was in part responsible for his choosing H.I. Schlesinger as his graduate research advisor at Chicago. His Ph.D. thesis (1938) dealt with the reduction of carbonyl compounds with diborane. After a year of postdoctoral work with M.S. Kharasch, he became assistant to Schlesinger (with rank of instructor) and codiscovered sodium borohydride. He became assistant professor at Wayne (now Wayne State) University in 1943, exploring steric strains. He was promoted to associate professor in 1946. In 1947 he moved to Purdue University as professor. He was promoted to R. B. Wetherill Professor in 1959 and R. B. Wetherill Research Professor in 1960. He received an Honorary Ph.D. from the University of Chicago in 1968. Since his "retirement" in 1978, he has been R. B. Wetherill Professor Emeritus, supervising a research group of approximately 10 postdoctoral associates, a secretary, and visiting scholars. He has published five books and over 1170 scientific publications. He has won the majority of major awards in his field, including the Nobel Prize for Chemistry in 1979, the ACS Award for Creative Research in Organic Chemistry (1960), the National Medal of Science (1969), the Roger Adams Award (1971), the Preistley Medal (1981), the Perkin Medal (1982), the American Institute of Chemists Gold Medal Award (1985), the National Academy of Sciences Award in Chemical Sciences (1987), the Emperor's Decoration (Japan): Order of the Rising Sun, Gold and Silver Star (1989), Oesper Award, Cincinnati ACS Section (1990), Honorary Scholar of the University of Wales, Swansea (1994), and Honorary Professor of the Institute of Organometallic Chemistry, Chinese Academy of Science (1994). Both Herbert and Sarah Brown enjoy good health and make frequent trips that typically combine lectures and other scientific commitments including manuscript preparation, sightseeing, and photography, as well as occasional visits to their grandchildren in California.

LIST OF HERBERT C. BROWN LECTURES

1984
G. Stork
S. Danishefsky
P. A. Grieco

1985
J. I. Brauman
F. G. Bordwell
P. Kebarle

1986
C. H. Heathcock
A. I. Meyers
S. Masamune
K. B. Sharpless

1987
R. G. Bergman
T. Mukaiyama
B. M. Trost

1988
D. H. R. Barton
N. J. Leonard
K. Mislow

1989
A. G. Brook
I. Fleming
J. Michl

1990
N. Nakanishi
G. D. Prestwich
K. L. Rinehart

1991
P. B. Dervan
S. M. Hecht
P. A. Kollman
R. Noyori

1992
R. R. Holmes
R. C. Larock
G. A. Molander
L. M. Stock
Y. Yamamoto

1993
F. N. Diederich
D. A. Dougherty
J. M. McBride

1994
P. A. Bartlett
B. O. Fraser-Reid
A. B. Smith, III

1995
F. A. L. Anet
P. Lauterbur
D. E. Wemmer

H.C. BROWN LECTURESHIP COMMITTEE

E. Negishi, Committee Chairman and Co-organizer
I. Rothwell, Co-organizer
M. Coree, Secretary

Dr. Alfred Bader
924 East Juneau, Suite 622
Milwaukee, Wisconsin 53202
Phone: 414/277-0730
Fax: 414/277-0709

A Chemist Helping Chemists

April 29, 1996

Professor and Mrs. Herbert C. Brown
1014 Lincoln Trail
West Lafayette, IN 47906

Dear Sarah and Herbert:

Isabel and I want to thank you most sincerely for your wonderful hospitality. It was so good to be back with you at Purdue after four years, and we already look forward to the next H.C. Brown Symposium next April 5th.

Enclosed are the two manuscripts on Couper and Loschmidt, which will be published by Plenum, together with all the other talks given at the Loschmidt Symposium.

With fond regards, I remain,

Yours sincerely,

AB/cw

Enclosures

Dr. Alfred Bader
924 East Juneau, Suite 622
Milwaukee, Wisconsin 53202
Phone: 414/277-0730
Fax: 414/277-0709

A Chemist Helping Chemists

April 29, 1996

Professor Ei-ichi Negishi
Chairman, H.C. Brown Lectureship Committee
Purdue University
1393 Brown Building
West Lafayette, IN 47907-1393

Dear Ei-ichi:

You will have realized how very much Isabel and I enjoyed the H.C. Brown Symposium. We already look forward to next year's, which we understand will be on Saturday, April 5th.

Thank you for your help in selling 122 copies of my autobiography. I am allowed to sell these at $12.50 each, and if more students would like some, please just let me know and I will send them.

With all good wishes, I remain,

Yours sincerely,

AB/cw

PURDUE UNIVERSITY

PURDUE UNIVERSITY GALLERIES

April 16, 1996

Dr. Alfred Bader
2961 N. Shepard
Milwaukee, WI 53211

Dear Alfred,

David and I returned Sunday night from a weekend in Chicago to find your message on our answering machine. I'm sorry to have missed your visit. I don't think I have seen you since we returned your artwork following the exhibit in 1992. You were in town this weekend, I imagine, for the H. C. Brown lecture series.

Derek Davenport lent me his copy of your autobiography and I have been meaning to write to tell you how much I have enjoyed reading it-- even the chapters about chemistry. What an extraordinary life you have led and are still leading. Your accounts about acquiring paintings are as exciting as a good mystery novel. I had read the *Art & Auction* article about the pilfered Adriaen van Ostade painting, so it was interesting to learn that it might have been yours.

The installation photo you included of *From Private Collection to Corporate Identity* started me thinking that Herb Brown's 85th birthday will soon be upon us and I wonder if that may have been the reason behind your call. If so, I am definitely amenable. There is still some flexibility in the 1996-97 exhibition schedule but I will be firming the calendar by the end of May.

I look forward to hearing from you. Please give my best to Isabel.

Kind Regards

Mona

Mona Berg
Purdue Galleries

PURDUE UNIVERSITY GALLERIES • SCHOOL OF LIBERAL ARTS • 1396 PHYSICS BUILDING, ROOM 205
WEST LAFAYETTE, IN 47907-1396 • (317) 494-3061

ALFRED BADER FINE ARTS

DR. ALFRED BADER

ESTABLISHED 1961

April 29, 1996

Ms. Mona Berg
Purdue University Galleries
School of Liberal Arts
1396 Physics Bldg., Room 205
West Lafayette, IN 47907-1396

Dear Mona:

Thank you so much for your letter of April 16th. Of course you were right that I wanted to discuss with you the possibility of another art exhibit to honor Herbert Brown on his 85th birthday in April of 1997.

I will call you before long to discuss what kind of exhibit might be suitable.

With all good wishes, I remain,

Yours sincerely,

AB/cw

By Appointment Only
ASTOR HOTEL SUITE 622
924 EAST JUNEAU AVENUE
MILWAUKEE WISCONSIN USA 53202
TEL 414 277-0730 FAX 414 277-0709

PURDUE UNIVERSITY

HERBERT C. BROWN

To: My Colleagues in Chemistry
From: H. C. Brown
Re: Further Developments
Date: February 1, 1996

Sarah is making excellent progress, not as fast as she would like (she lacks my patience), but faster than the Doctors had predicted.

But consider my problem.

When we married, Sarah agreed that I would handle the chemistry in the family and she would handle everything else. But consider what happened to me. My secretary of 27 years resigned suddenly in the middle of December. Sarah had her operation on December 20. Suddenly, I had to do all of her work, all my secretary's work, and all of my own work. For the first time in my life I had to wash clothes, make meals, etc., etc. Three things made this bearable. First, there is Sarah's rapid progress which promises that she soon will be able to handle her usual activities. Second, friends such as Shiela Wolinsky, Louise Klatch, and Sarah Axelrodt provided delicious dishes which greatly facilitated my preparation of meals. Finally, my energetic associate, P. V. Ramachandran, outdid himself in helping me with all kinds of obligations. A new secretary will start on February 5 and Ramachandran will teach her the routine of my office. I will then be able to catch up with the manuscripts my students have given me (5), the manuscripts sent to me for review (4), and the numerous manuscripts we have promised for meetings, past and future.

Herb

(OVER)

H. C. BROWN AND R. B. WETHERILL LABORATORIES OF CHEMISTRY
1393 BROWN BUILDING • WEST LAFAYETTE, IN 47907-1393 USA
PHONE: (317) 494-5316 • FAX: 07-1-317-494-0239 • E-MAIL: HCBROWN@CHEM.PURDUE.EDU

To: My Colleagues in Chemistry
From: H. C. Brown
Re: Sarah's By-Pass in Honolulu
Date: January 18, 1996

I was scheduled to speak at the Meeting of the Pacific Rim Chemical Societies, Dec. 17-22. Accordingly, on Sunday, December 17 Sarah and I flew in to Honolulu and checked in at the Hilton Hawaiian Village, where I was scheduled to speak on Thursday, Dec. 21. We went to bed as usual, at ~11:00 PM.

At 1:00 AM Sarah woke up, complaining of an excruciating pain in her upper abdomen. I called 911 and an ambulance arrived to take us to the Kuakini Medical Center.

There, over the next two days the problem was diagnosed as involving her heart. The pain recurred several times, but was prevented from developing into a major heart attack.

On Wednesday, she had an angiographic examination. One of the heart arteries showed a complete blockage. So angioplasty could not be used. Morover, I was told that under her present condition she probably could not survive a long airplane trip with its reduced atmospheric pressure. We had to proceed to a by-pass. That was done as a continuation of the angiographic examination.

There was good news. The surgeon told me that there was no sign of damage to the heart. Only a single by-pass was necessary. He also expressed surprize that the vein he harvested appeared to be from a female of forty years, not eighty.

This is an extraordinary difficult operation. It is a major triumph of medical science to have achieved this development. But recovery is very slow, requiring 3 to 4 months. Sarah is making excellent progress, but much slower than her impatient nature desires. But I am very happy. I thought I was going to lose the girl I had known for 64 years, since we had met in a junior college chemistry class. Now I am very hopeful of retaining her.

I thought that by sending you this note, I would answer the questions in your mind and avoid repeating the story to many of you.

Herb

(OVER)

PURDUE UNIVERSITY

HERBERT C. BROWN

March 13, 1996

To
Dr C LANE

Prof. Dr. Walter Siebert
IX International Meeting on Boron Chemistry
University of Heidelberg
Anorganisch-Chemisches Institute
Im Neuerheimer Feld 270
D-6 Heidelberg, Germany

Dear Professor Siebert:

I am somewhat surprized by your reluctance to recognize the major contributions of Dr. Alfred Bader and Dr. Clinton F. Lane in commercializing borane reagents and intermediates. German chemistry has long provided an outstanding example of the advantages to be gained by a close cooperation between the chemical industry and academic chemists.

Before I approached Aldrich, I approached a number of major chemical organizations. Invariably interest was expressed, but a market survey quickly cancelled that interest. After all, these new chemicals were not yet being manufactured and sold. How could an established market exist? But Aldrich was not discouraged by the absence of an existing market, Aldrich undertook to manufacture these chemicals and the market now exists.

Enclosed is a 4 page copy of a brochure from Aldrich, "Boron Reagents from Aldrich".

Boron chemists throughout the world have found their research greatly assisted by the commercial availability of these boron reagents and boron intermediates.

I believe the pioneering efforts of Dr. Alfred Bader and Dr. Clinton F. Lane deserve recognition by IMEBORON IX.

I would recommend "Award for Pioneering Efforts in Commercializing Borane Reagents and Chemicals." But if the International Committee prefers to give them Certificates of Recognition for their Pioneering Efforts in Commercializing Borane Reagents and Chemicals, I should accept their decision. I feel that we, as Boron Chemists, should recognize their exceptional contribution in advancing Boron Chemistry and Research by making so many Borane Reagents and Chemicals readily available.

Sincerely,

Herbert C. Brown

Herbert C. Brown

HCB:jc

cc: International Advisory Committee BCC: Alfred Bader✓/Clinton F. Lane

Enc.

H. C. BROWN AND R. B. WETHERILL LABORATORIES OF CHEMISTRY
1393 BROWN BUILDING • WEST LAFAYETTE, IN 47907 1393 USA
PHONE: (317) 494-5316 • FAX: 07-1-317-494-0239 • E-MAIL: HCBROWN@CHEM.PURDUE.EDU

PURDUE UNIVERSITY

DEPARTMENT OF CHEMISTRY

November 6, 1995

Dr. Alfred Bader
924 East Juneau, Suite 622
Milwaukee, WI 53202

Dear Dr. Bader:

A copy of your letter of October 13 for Prof. Grutzner has been forwarded to me.

(1) As you may have heard from Dr. Grutzner, we will have six prominent organometallic chemists (H. Alper, C. P. Casey, R. Crabtree, R. H. Grubbs, T. J. Marks, and R. R. Schrock) for the 13th H. C. Brown Lectures (April 13, 1996). Furthermore, we are also planning to celebrate Professor Brown's 85th birthday in the spring of 1997. As in the past, we would be delighted and thankful to you if you would kindly stage an exhibition of your art collection. With your permission we would be planning it for the 14th Brown Lectures in 1997.

(2) If you could attend the 13th Brown Lectures on April 13 (Sat) next year, we would also like to ask you to present an after dinner talk on a topic of your choice. We have always greatly appreciated your participation in various event associated with Professor Brown and our Organic Division.

I look forward to hearing from you about the matters mentioned above.

With best regards,

Sincerely yours,

Ei-ichi Negishi

Ei-ichi Negishi
Chairman
H. C. Brown Lectureship Committee

EN/mc

Dear Prof. Negishi:

I am *just* leaving for England — and am so happy to receive your letter just now.

I am honored & the answer to (1) & (2) is *of course yes*.

Best wishes
Alfred Bader
13 XI 95

1393 HERBERT C. BROWN LABORATORY OF CHEMISTRY • RICHARD B. WETHERILL LABORATORY OF CHEMISTRY
WEST LAFAYETTE, IN 47907-1393 • FAX (317) 494-0239

Dr. Alfred Bader
924 East Juneau, Suite 622
Milwaukee, Wisconsin 53202
Phone: 414/277-0730
Fax: 414/277-0709

A Chemist Helping Chemists

October 13, 1995

Professor John B. Grutzner
Department of Chemistry
Purdue University
1393 Herbert C. Brown Laboratory of Chemistry
West Lafayette, IN 47907-1393

Dear Professor Grutzner:

Many thanks for your thoughtful letter telling me about the H.C. Brown lectures next April 13th.

I have not been to these lectures for three years and very much hope to be able to attend these.

Do you know whether the Department plans some special event for Herb's 85th birthday, akin to the gala events for his 75th and 80th birthdays? If so, you might like to suggest to your Department of Art that an exhibition of paintings might again be appreciated.

Also, you might sometime like to consider inviting me to give a talk describing Richard Anschütz' discoveries of the works of Archibald Scott Couper and Josef Loschmidt. I enclose some material relating to recent lectures.

Incidentally, Herbert wrote an important paper on Couper and might be well be interested in this history.

With best regards to you and your associates, I remain,

Yours sincerely,

AB/cw
Enclosures

PURDUE UNIVERSITY

DEPARTMENT OF CHEMISTRY

October 10, 1995

Dr. Alfred Bader
2961 N. Shepard Avenue
Milwaukee, WI 53211

Dear Alfred:

Last Spring you inquired about the 1996 H. C. Brown lectures and I promised to let you know. The enclosed note from Dr. Negishi gives the preliminary information on the event. We hope that you will be able to attend. Please feel free to contact me if I can be of assistance.

Best wishes,

John B. Grutzner
Professor of Chemistry

JBG/scj

Enclosure

1393 HERBERT C. BROWN LABORATORY OF CHEMISTRY • RICHARD B. WETHERILL LABORATORY OF CHEMISTRY
WEST LAFAYETTE, IN 47907-1393 • FAX (317) 494-0239

PURDUE UNIVERSITY
Department of Chemistry

inter-office memorandum

TO: Chemistry Faculty

FROM: E. Negishi, Chairman, H.C. Brtown Lectureship Committee

DATE: October 9, 1995

SUBJECT: 13th Brown Lectures
Frontiers in Organometallic Chemistry

I am pleased to inform you that the following distinguished chemists have agreed to participate in the **13th H.C. Brown Lectures, Saturday, April 13, 1996.** It promises to be an exciting event, and I urge you to attend it. Please also mark your calendar for the event.

Howard Alper (U. of Ottawa)
Charles P. Casey (U. of Wisconsin)
Robert H. Grubbs (CalTech)
Tobin J. Marks (Northwestern U.)
Richard R. Schrock (MIT)

Addition of one more chemist is being considered.

PURDUE UNIVERSITY

DEPARTMENT OF CHEMISTRY

12/4/95

Dear Alfred: Herewith one of Herb Brown's few essays in the history (as opposed to self-history) of chemistry. However he once told me that manuscript of a popular history of chemistry that he wrote with Sarah in the late 1930's still exists. I've never seen it. It was good to see you and Isabel again.

Yours sincerely,

Derek

HERBERT C. BROWN/RICHARD B. WETHERILL LABORATORIES OF CHEMISTRY
WEST LAFAYETTE, IN 47907-3699

Herbert C. Brown

Lectures in Organic Chemistry

1994

Department of Chemistry
Purdue University
West Lafayette, Indiana

Herbert Charles and Sarah Baylen Brown

THE ELEVENTH
HERBERT C. BROWN
LECTURES IN ORGANIC CHEMISTRY

April 8-9, 1994

Department of Chemistry
Purdue University
West Lafayette, Indiana 47907

SCHEDULE OF EVENTS

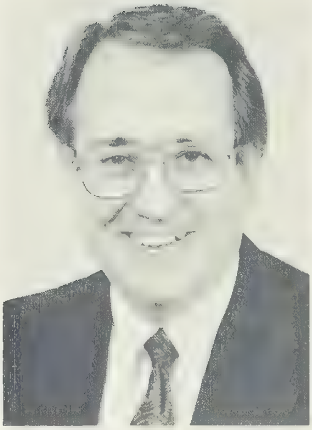
Friday, April 8

	Banquet	
6:15 p.m.	**Social Hour** (cash bar)	Lafayette Country Club 1500 South Ninth Street Lafayette, Indiana 47905
7:00 p.m.	**Dinner**	

Saturday, April 9

	Herbert C. Brown Lectures in Organic Chemistry *Synthesis of Natural and Unnatural Organic Compounds*
9:00 - 9:15 a.m.	**Opening Remarks** **Richard A. Walton** Head, Department of Chemistry Purdue University
9:15-10:15 a.m.	*The Design, Synthesis, and Crystal Structure of a Pyrrolinone-Based β-Strand Peptidomimetric: Application to the Design of Renin and HIV Protease Inhibitors* **Amos B. Smith, III** Professor of Chemistry University of Pennsylvania
10:15-10:55 a.m.	**Coffee and Poster Session** West End Lobby, Stewart Center

11:00 a.m. -12:00 noon	*Control of Peptide Conformation Through Macrocyclization and Helix Templates* **Paul A. Bartlett** Professor of Chemistry University of California, Berkeley
12:00-1:30 p.m.	**Luncheon** Faculty Lounge, Memorial Union
1:30-2:15 p.m.	*Research Presentations by:* **Pat Bishop, Kristi Dell, and Jae Jeong**
2:15-3:15 p.m.	*A Contemporary Case of Serendipity: The Chemistry of n-Pentenyl Glycosides* **Bertram O. Fraser-Reid** Professor of Chemistry Duke University
3:15-3:30 p.m.	**Closing Remarks** **Herbert C. Brown** R. B. Wetherill Research Professor Emeritus
	Adjournment



AMOS B. SMITH, III

RHODES-THOMPSON PROFESSOR OF CHEMISTRY
UNIVERSITY OF PENNSYLVANIA

Amos B. Smith, III (born August 26, 1944) received his early education in Lewisburg, Pennsylvania. In 1966 he was awarded Bucknell University's first combined four-year B.S.-M.S. degree in Chemistry. After a year in medical school (University of Pennsylvania), he earned his Ph.D degree (1972) and completed a year as a Research Associate at Rockefeller University. In 1973, he joined the Department of Chemistry at the University of Pennsylvania; currently, he is the Rhodes-Thompson Professor of Chemistry, Chairman of the Department, and Member of the Monell Chemical Senses Center and the Laboratory for Research on the Structure of Matter (LRSM)

Smith's research interests encompass three diverse areas: natural product synthesis, bioorganic chemistry and materials science. Current synthetic targets include antitumor, pesticidal, immunosuppressant, and fungicidal agents To date, more than 60 architecturally complex natural products have been prepared in his Laboratory. In addition, Smith, in collaboration with Ralph Hirschmann, has executed the design and synthesis of non-peptide peptidomimetics of protease enzymes (i.e., renin and the AIDS protease) and haptens for the production of catalytic antibodies capable of peptide bond formation At Monell, he pioneered the use of computerized pattern recognition techniques for the analysis of chemical communication. Collaborative programs at the LRSM include the chemistry and physics of novel liquid crystals and the fullerenes. Seminal synthetic contributions in the fullerene area include the first fluorinated fullerenes, the first fullerene epoxide ($C_{60}O$), and the parent fullerene cyclopropanes ($C_{61}H_2$ and $C_{71}H_2$)

Smith has been a Visiting Professor at both Columbia and Cambridge Universities. Editorial Board memberships include the *Journal of the American Chemical Society* (1988-1993), the *Journal of Organic Chemistry* (1982-1986, 1994-), *Journal of the Chemical Society, Perkin Transactions I* (1992-), *Organic Reactions* (1987-), *Organic Synthesis* (1990-), and *Fullerene Science and Technology* (1993-). He has also served as member of the NIH Medicinal Chemistry A Study Section, the Executive Committee of the Organic Division of the American Chemical Society, and as Chairman of the Organic Reactions and Processes Gordon Conference. He is co-author of over 275 publications and has delivered over 230 invited lectures, including plenary lectures at the National Organic Chemistry Symposium, numerous Gordon Research Conferences, the Royal Society Christmas Lectures (Edinburgh, Scotland and Cardiff, Wales), and the 3éme Cycle en Chimie at the French Speaking Universities in Switzerland. His honors and awards include the Camille and Henry Dreyfus Teacher Scholar Award, the NIH Career Development Award, The John Simon Guggenheim Memorial Foundation Fellowship, The Japan Society for the Promotion of Science Fellowship, The Kitasato Institute Medal, the Arthur C. Cope Scholar Award, the Alexander von Humboldt Research Award for Senior U.S Scientists, the Alumni Award for Outstanding Professional Achievement (Bucknell University), and the ACS Ernest Guenther Award.

PAUL A. BARTLETT

PROFESSOR OF CHEMISTRY

UNIVERSITY OF CALIFORNIA, BERKELEY

Paul A. Bartlett was born on January 5, 1948, did his schooling in the Boston area, and graduated with an A.B. (Phi Beta Kappa) and an A.M. in Chemistry from Harvard University in 1969. As an undergraduate, he did research with David Dolphin on the synthesis of the alkaloid ipalbidine. His graduate years were spent as an NSF Predoctoral Fellow at Stanford University, working under the direction of William S. Johnson on an ester cleavage reagent and a synthesis of estrone by cationic olefinic cyclization. After receiving his Ph.D. in 1972, Dr. Bartlett spent a year as an NIH Postdoctoral Fellow in the laboratory of S. Jonathan Singer of the Biology Department at UC-San Diego developing a cleavable protein crosslinking reagent and a water-soluble, derivatizable heavy-metal cluster for specific electron microscopic staining purposes. In 1973, he joined the faculty of the Chemistry Department at the University of California, Berkeley, where he is currently Professor. He has been honored with fellowships from the NSF, NIH, and the Alfred P. Sloan Foundation, and he has been the recipient of the Alexander von Humboldt Senior Scientist Award, the Stuart Pharmaceuticals Award, the Buck-Whitney Medal, and the Cope Scholar Award.

Dr. Bartlett's early research interests involved the development of synthetic methods and their application to problems in natural products chemistry. The focus of this work was on methods of stereocontrol via cyclization reactions, with syntheses of the antibiotics nonactin, tirandamycin A, and polyether targets as representative examples. His recent research emphasis has been the application of organic synthesis to biological problems, including the synthesis and study of enzyme inhibitors and metabolic intermediates. This work has involved the development of potent inhibitors of enzymes from a number of classes, in particular the development of tetrahedral phosphorus derivatives as transition state analog peptidase inhibitors. Dr. Bartlett has also addressed issues surrounding the principles of transition state analogy and the influences that structural alterations have on the kinetic and thermodynamic aspects of enzyme-inhibitor interaction. A second domain of interest to his group is the shikimate-chorismate biosynthetic pathway; his group has synthesized and evaluated intermediates and inhibitors for a number of enzymes in the sequence. A third research focus at present concerns the use and development of structure-based approaches and computer graphics for the design of three-dimensional peptide mimics and enzyme inhibitors. To aid in this work, he and his group have developed the program CAVEAT and a number of 3-D structural databases, including TRIAD and ILIAD.

The two questions that he is asked most frequently begin with "Are you related to..." and "Do you still jump out of..."; the answer to both questions is no.

BERTRAM O. FRASER-REID

James B. Duke Professor of Chemistry

Yale University

Bert Fraser-Reid was born in Jamaica and received his primary and secondary schooling there. After working for five years he went to Canada and entered Queen's University, Kingston, Ontario, enrolling in chemistry in spite of the fact that the subject had not been offered at his high school. He obtained Bachelor's and Master's degrees at Queen's and then was awarded a NRC (Canada) Fellowship for Ph.D. studies at the University of Alberta with Professor R.U. Lemieux. He spent from 1964 to 1966 as an NRC Overseas Postdoctoral Fellow with Professor Sir Derek Barton at Imperial College of Science and Technology in London. In 1966 he returned to Canada as an Assistant Professor at the University of Waterloo. He moved to the University of Maryland in 1980 and two years later joined Duke University where he is currently a James B. Duke Professor of Chemistry.

Fraser-Reid's interests span all aspects of the organic chemistry of carbohydrate derivatives. As one of the pioneers in the use of these substances for natural product synthesis, Fraser-Reid played a primary role in bringing the attention of the wider chemistry community to this class of compounds. Rather than focusing merely on the merits of their chirality, his work sought to emphasize, demonstrate, and exploit their unique structural and conformational properties, and the relativity reactivity differences with their carbocyclic counterparts. The work in his laboratory ranges from natural products and oligosaccharide synthesis, to free radical and photochemical methodology, to physical organic and theoretical mechanistic investigations. His work has been described in over 250 publications and he has been a constant plenary lecturer at major national and international symposia for over fifteen years.

He has served on several review panels for the NIH, was a member of NSF Advisory Committee on Chemistry, and currently serves on the NRC's Board on Chemical Sciences and Technology. He is currently on the Editorial Advisory Boards of the Journal of the American Chemical Society, the Journal of Carbohydrate Chemistry, Natural Products Letters, and Carbohydrate Letters. He has been a Chairman of the Carbohydrate Division of the American Chemical Society

In 1989 Fraser-Reid received a Senior Scientist Award from the Alexander von Humboldt Foundation of Germany. In 1990 he was winner of the American Chemical Society (Claude S. Hudson) award for carbohydrate chemistry, and also received a citation from the Jamaican National Foundation for a service by a Jamaican national in the United States. In 1991 he received the Percy Julian Award of the National Organization of Black Chemists and Chemical Engineers, the R.E. Jeffrey Medal from the New South Wales Chemical Society of Australia, was elected a Fellow of the American Academy of Arts and Sciences, and was named the 13th North Carolina Distinguished Lecturer by the N.C. Division of the American Chemical Society. In 1993 he received the President's Medal of Charles R. Drew University of Medicine and Science. He has been awarded a 1993-94 Fellowship from the Japan Society for the Promotion of Science, and he has been selected as the 1995 recipient of the Haworth Memorial Medal and Lectureship of the Royal Society of Chemistry of the United Kingdom.

Dr. Fraser-Reid is an accomplished musician on the pipe organ and piano.

PROFILES OF THE FOUNDERS OF THE HERBERT CHARLES AND SARAH BAYLEN BROWN FUNDS

Herbert C. Brown was born in London on May 22, 1912, but was brought to the U.S. at age two and grew up in Chicago. He enrolled in Crane Junior College in 1933, where he met Sarah Baylen, now his wife of more than 57 years. When Crane closed for lack of funds in June 1933, they continued their training in the home laboratory of one of their teachers, Nicholas D. Cheronis. When new colleges were opened in 1934, they attended Wright Junior College, where Sarah autographed his yearbook with the inscription, "To a future Nobel Laureate." They then entered the University of Chicago in 1935 as juniors. H.C. Brown completed two years of work in one year and graduated in 1936. A graduation gift from Sarah, Alfred Stock's Baker Lectures on "Hydrides of Boron and Silicon," was in part responsible for his choosing H.I. Schlesinger as his graduate research advisor at Chicago. His Ph.D. thesis (1938) dealt with the reduction of carbonyl compounds with diborane. After a year of postdoctoral work with M.S. Kharasch, he became assistant to Schlesinger (with rank of instructor) and codiscovered sodium borohydride. He became assistant professor at Wayne (now Wayne State) University in 1943, exploring steric strains. He was promoted to associated professor in 1946. In 1947 he moved to Purdue University as professor. He was promoted to R.B. Wetherill Professor in 1959 and R.B. Wetherill Research Professor in 1960. Since his "retirement" in 1978, he has been R.B. Wetherill Research Professor Emeritus, supervising a research group of approximately 15 postdoctoral associates, a secretary, and visiting scholars. He has published seven books and over 1150 scientific publications. He has won the majority of major awards in his field, including the Nobel Prize for Chemistry in 1979, the ACS Award for Creative Research in Organic Chemistry (1960), the SOCMA Medal (1960), the National Medal of Science (1969), the Roger Adams Award (1971), the Priestly Medal (1981), the Perkin Medal (1982), the American Institute of Chemists Gold Medal Award (1985), the National Academy of Sciences Award in Chemical Sciences (1987), and the Emperor's Decoration (Japan): Order of the Rising Sun, Gold and Silver Star (1989). Both Herbert and Sarah Brown enjoy good health and make frequent trips that typically combine lectures and other scientific commitments including manuscript preparation, sightseeing, and photography, as well as occasional visits to their grandchildren in California.

LIST OF HERBERT C. BROWN LECTURES

1984

G. Stork
S. Danishefsky
P.A. Grieco

1985

J.I. Brauman
F.G. Bordwell
P. Kebarle

1986

C.H. Heathcock
A.I. Meyers
S. Masamune
K.B. Sharpless

1987

R.G. Bergman
T. Mukaiyama
B.M. Trost

1988

D.H.R. Barton
N.J. Leonard
K. Mislow

1989

A.G. Brook
I. Fleming
J. Michl

1990

N. Nakanishi
G.D. Prestwich
K.L. Rinehart

1991

P.B. Dervan
S.M. Hecht
P.A. Kollman
R. Noyori

1992

R.R. Holmes
R.C. Larock
G.A. Molander
L.M Stock
Y. Yamamoto

1993

F.N. Diederich
D.A. Dougherty
J.M. McBride

H.C. BROWN LECTURESHIP COMMITTEE

M. Andrus
M. Lipton
E. Negishi, Chairman
M. Coree, Secretary

On the Unimportance of A Liberal Arts Education

An address by
Dr. Alfred Bader

To the Academy of Letters and Science University of Wisconsin-Stevens Point

Ask a thousand students on any campus in the country why they are attending a university, and more than 900 will reply "to acquire a profession"—to become an engineer, a scientist, a medical person, to study business administration and so on. And what do they think of a liberal arts education? Generally little, unless they want to become teachers. But doesn't everybody know that teachers earn less than plumbers and auto mechanics?

So it was with me, when I entered a university in Canada. I chose engineering because my grandfather had been an engineer, and so had the man who adopted me. I am totally unmechanical, just not interested in motors and very poor in math. But I loved chemistry, organic chemistry, and so I chose chemical engineering, emphasizing chemical. Engineers then as now looked down on the students in arts—soft, sissy types, rich perhaps, no need to work.

It took a while to realize how wrong we were—with me that conversion started at a university but wasn't completed until years later. It began innocently enough: by my third year in college I had discovered the joys of dating—an expensive pastime, and so by March of that year I was short of cash. Looking through the university calendar, I saw a scholarship in public speaking—$50! How silly could I get? Public speaking—and me with a thick German accent! Still, $50 was $50, and so I tried and won. One of the judges, the vice principal of Queen's University, urged me to join the debating society—something engineers just never did. Sissy stuff, close to liberal arts. Still, I joined and that year won the Dominion of Canada debating championship—German accent and wartime notwithstanding.

Public speaking. Debating!

Perhaps nothing in life is as essential to success as the ability to express yourself clearly and succinctly. You wouldn't believe how many reports I have read by Ph.D.'s in chemistry in just awful English. There is such beauty in brevity, yet often technically well-educated people neither write nor speak well. And often they have no idea just how bad they are.

As I said, at first to me, such liberal arts pursuits had purely utilitarian uses. Fifty dollars for the public speaking scholarship, the transient glory of winning debates. Then, through two bits of luck the enjoyment of liberal arts dawned on me.

One was the opening of a two-volume work of the collected essays of Thomas Babington Macaulay. What language, what arguments, what history. I still own those two volumes, which I had carefully bound in paper, the Scotch tape to hold it now turned dark brown. The thrill of opening it now—after reading it from cover to cover several times in the 1940s—is much like seeing an old friend in a museum, a great Dutch painting not seen for many years. Much later I read somewhere that Macaulay was a second rate historian—that many of his "facts" were in fact mistaken. Sydney Smith said of Macaulay that he not only overflowed with learning, but stood in the slop. Pfui on you, harsh critic. His language, his arguments are brilliant—how often have I said to myself, "If only I could speak and write like that!" And thinking that, I would try.

The other bit of luck came at Harvard. At Queen's there had been no art history, no art gallery. At Harvard there was a great museum, and great teachers—men like Jakob Rosenberg, lecturing on Rembrandt. I remember once, I think in 1948, I was leaving the chemistry department in the middle of the day, and my chemistry professor, Louis Fieser, asked me where I was going. I said, "Over to the Fogg where Jakob Rosenberg is lecturing on Rembrandt." Fieser replied in mock disgust, "Alfred, you haven't made up your mind yet whether you want to be a chemist or an art historian." Well, some forty years later, I still haven't and I am much the happier for it.

There is such pleasure in looking at a great painting—it is really indescribable. I am sure that my blood pressure goes up, my pulse quickens, I feel good all over. These physical manifestations are very selective: old masters, of all kinds, not just Dutch—they work. Late Picassos and abstract art—no effect. Some 19th century art, yes, and some no. Some realistic works, like those of Bouguereau make me physically sick, and I turn away quickly. That great music critic, Winthrop Sargent, said that to him music was art that invited intuitive and passionate reactions, rather than cold-blooded appraisals. So, to me, it is with paintings. I can make cold blooded appraisals only with paintings I don't really care for.

Thus, to sum up, a liberal arts education is totally unimportant—unless you want to succeed in life—when the use of language is essential—or want to enjoy life to its maximum potential. You cannot do that until you have been exposed to the arts—literature, music, theater, painting, sculpture—and have realized just what appeals *to you* the most. You can lead a reasonable life being good professionally and enjoying beer and football on weekends—and you will never know just how much you are missing.

CASTLE

Allow me to digress for a minute and speak about business in America. You may be hard put to think of a connection between business life and a liberal arts education—yet I am sure there is, or at least I feel there should be.

There are three things fundamentally wrong with much in American business, and the three illnesses are related. The first is the glorification of the "image," rather than paying attention to the reality of good service. Companies spend billions advertising how good they are, and they often spend very little on really good service, preferring to let clerks send form letters to complaining customers. "Send the bastard form letter No. 37" is a sick joke, awfully close to the truth in many companies. Customers are not always right, but they are always individuals, human beings, who have the right to have their complaints considered individually, on a personal basis.

The second illness is the enormous attention paid to the *next* bottom line. Of course, one must pay attention in business to the bottom line—if there is no profit, no earnings, eventually there will be no business. But it is not terribly important whether the company's next quarterly earnings will be up 10 or 15 or 20 percent, as long as management works so successfully that earnings will be up substantially five and ten years from now.

Unlike many American businessmen, I do not admire the Japanese. Their lifestyle is terrible—why they don't even have room in their tiny houses to hang old master paintings—and I wouldn't want to trade with the richest of them for even a day. But in two business aspects they are way, way ahead of us. One is their long-term view of business, the other their loyalty to each other—employers to employees and vice versa.

Our third sickness in business is the deification of bigness. Big is beautiful. This is utter nonsense. If anything, in business small is beautiful. Because when the operation is small, the manager can pay attention to his product, his employees, his customers. When bigness becomes an end in itself, then it leads to the excesses you have witnessed in the last years. Endless mergers—not because the products will be improved or the lives of the employees—but because the egos of the top people demand it. The vulgarity of these excesses is truly ugly. There is something fundamentally wrong when you see—as we have seen even in Wisconsin, not just in New York or California—top managers of large, rapacious companies earning a million or more in salaries, while at the same time thousands of employees are laid off. Every single layoff is a personal tragedy, causing trauma in the affected family, and it is almost always caused by poor management. Yet it is seldom the managers who are penalized. There again, the Japanese are way ahead of us.

The deification of bigness. Mistaking great wealth for happiness. Would I really be happier if I were twice as wealthy? I don't think so.

And I know what would make me a great deal unhappier—loss of my family, my friends, the great people I work with, my health—none related to bigness.

Somehow I believe that a person who has really enjoyed great literature would understand all this and would do far better in business than many MBA's to whom bigness is god.

My friends speak of the ABC of my life: art, Bible and chemistry. How I came to art and chemistry is clear. To the Bible, I came more circuitously. We had neighbors in Vienna, wonderful people, orthodox Jews who invited me to their Sabbaths and Passover meals—accompanied by learned discussions about biblical passages, but I don't remember actually looking at a Bible until I was 14. Two weeks after I turned 16 I had the good fortune of being put into a prisoner of war camp. Of course, it took years before I realized what good fortune it was. The British suspected me and many others of being Nazi spies, and we were sent to Canada. I was the youngest in the camp, and on our first day there, the camp commandant questioned me carefully, surprised that a youngster of 16 had parachuted into England. When I tried to explain that I was not a parachutist, but was a Jew who had fled to England, he just laughed and assured me that he did not believe me, and anyway, he didn't like Jews either. In the next 18 months, I learned a lot about the Bible. What a book it is—no wonder it has been the best seller, the most translated book ever. What inspiration. When I read Moses' speech at the end of Deuteronomy (30:11-14):

> *For this commandment which I command thee this day, it is not hidden from thee, neither is it far off.*
>
> *It is not in heaven, that thou shouldest say, Who shall go up for us to heaven, and bring it unto us, that we may hear it, and do it?*
>
> *Neither is it beyond the sea, that thou shouldest say, Who shall go over the sea for us, and bring it unto us, that we may hear it, and do it?*
>
> *But the word is very nigh unto thee, in thy mouth, and in thy heart, that thou mayest do it.*

It is to me as if I were listening to Moses. And when I look at Leviticus 19, I see the most important commandment for ethics in business: you shall not put a stumbling block before the blind—do not mislead your customers—and the most important commandment for civil rights: do not stand idly by the blood of your neighbor.

with

Amos

arts

This leads to one aspect of a liberal education which is, I believe, the most important of all, as it affects our relationship to others. Some call it religion, or philosophy or sociology—it is really some of each of these. It encompasses the most fundamental questions in life: why are we here—is there in fact a reason at all—or are we all here by chance, and is it best just to get the most out of life and be gone?

Politicans from all sides mouth platitudes about democracy—but why should democracy be superior to other forms of government? Obviously we are not created equal—some are very much stronger than others—some are far more intelligent. Why not an elitist government of the ablest? Only with a liberal arts education are you likely to think about such questions.

And only if we believe that God has created all of us, that there is some of God in all of us, must we come to the conclusion that each of us should have equal opportunity. Democracy. Justice for all. Moses put it so clearly—justice, justice you shall seek—and Amos so beautifully: Let justice well up as waters, and righteousness as a mighty stream.

Turn to the very opposite, evil, true evil, men killing indiscriminately, the millions killed by the minions of Hitler and Stalin, the killings in South Africa and Central America. What can persuade a man to kill another in cold blood? I am sure that it is popularly believed that the men killing millions in concentration camps of eastern Europe were brutes, sadists, men easily distinguished from the rest of us. I am afraid that this just is not so. Only recently I read the autobiography of Rudolph Hoess, the commandant of Auschwitz, the man who perfected the use of cyclone B in the gas chambers where hundreds of thousands of women and children were killed. Hoess was the son of deeply religious Catholics; he rebelled against his parents, joined the German army at 16 and the Nazi party after the first world war. He worked in several concentration camps and in 1940 became commandant of Auschwitz. After the war he spoke to psychiatrists, and wrote a detailed autobiography. What we see is a shockingly average human, without imagination, believing in authority, believing without question when Hitler assured Germany that the extermination of millions was right. The author of the book, "Menschen in Auschwitz" who knew Hoess, wrote that under other circumstances, Hoess could have been the painstaking director of a post office. He was one of millions, and not just in Germany. Some of you will remember and all of us will want to forget My Lai, Americans killing women and children in Viet Nam, and the atrocities of the KKK. But if we got to know the people involved, we would realize that by and large they are not sadists, not monsters, not, in fact, so different from the people around us. What they lack is imagination, the ability to think themselves into the position of others, traits developed by a liberal arts education.

Japanese

One of the first stories I remember hearing when I was a boy was of a very religious Jew coming, deeply depressed, to his rabbi, saying, "Rabbi, what can I do, no matter how much I study I will never be as great and as wise as Moses." To which the Rabbi replied, "Sam, when you come before the heavenly Judge, he will not ask you, 'Sam, why were you not as great and wise as Moses?' All the Almighty is going to ask you is, 'Sam, why were you not as great and as wise as you, Sam, could have been.' "

My friends, a total education should prepare you for a better life as well as a better livelihood. Perhaps you can be able scientists, competent engineers, good doctors without a liberal arts education—though that may be questionable. But without it, I am quite certain you will not be as great and as wise as you might be, and will miss a great deal of the enjoyment of life.

Dr. Alfred Bader, scientist, industrialist, art historian and philanthropist, was born in Vienna in 1924. Wartime stays in England and Canada led to Queens University (Ontario) where he earned a B.Sc. in Chemical Engineering, a B.A. in History, and a M.Sc. in Organic Chemistry. After working as a chemist for Murphy Paint Company, he went to Harvard, completed his Ph.D. in Chemistry, and returned to Murphy (owned by Pittsburgh Plate Glass Company) which transferred him to Milwaukee. In 1951, he began Aldrich Chemical Company, which he ran part-time out of a garage. He resigned from PPG in 1954 to devote full time to Aldrich which ultimately became the world's foremost supplier of high-quality fine organic chemicals. Aldrich merged with Sigma Chemical Company in 1975, creating the Sigma-Aldrich Corporation of which Bader is currently chairman.

Bader's contributions to chemistry include numerous publications and patents. Contributions to profession, community and state have been recognized with honorary degrees (UW-Milwaukee and Madison, Purdue, Queen's University), and numerous other awards of distinction.

Generous with his time and talents, Dr. Bader continues to share his knowledge and experiences with others. (One of his most popular speeches combines two of his loves—art and chemistry—and deals with the chemistry involved in the restoration of art.) His participation in this lecture series reaffirms the tradition of distinction for the series.

Dr. Alfred Bader
2961 North Shepard Avenue
Milwaukee, Wisconsin 53211

April 19, 1995

Professor Derek Davenport
Department of Chemistry
Purdue University
West Lafayette, IN 47907-3699

Dear Derek:

Thank you so much for your note of April 12th and for sending me a copy of Herbert Brown's 1959 paper entitled "Foundations of the Structural Theory".

I have now known Herb for over twenty years, and as you will see from *Adventures of a Chemist Collector*, we have worked happily together and yet I had no idea that Herbert was interested in the history of chemistry.

Like Bob Woodward, Herb admires Cooper as does everyone who studies his work. What a pity that neither Herb nor Bob knew much about Loschmidt, though I hope that both you and he will enjoy Chapter 16 on Loschmidt and Couper in my autobiography.

I just wish that I had known Herb's 1959 article when I was writing that chapter, because if I had known it, I would certainly have included it in the bibliography on page 203.

With all good wishes, I remain,

Yours sincerely,

AB/cw

cc: Professor Herbert Brown

Dr. Alfred Bader
2961 North Shepard Avenue
Milwaukee, Wisconsin 53211

March 21, 1995

Professor John B. Grutzner
Department of Chemistry
Purdue University
1393 Herbert C. Brown Laboratory of Chemistry
West Lafayette, IN 47907-1393

Dear Professor Grutzner:

Thank you so much for your invitation to attend the Herbert C. Brown Lectures in Chemistry at the end of this month. I wish that Isabel and I could attend, but have to be at the ACS meeting in Anaheim to receive the Parsons Award.

As soon as you know the exact date of next year's lectures, could you please let me know, because we would very much like to come to Purdue then.

With many thanks for your help and best regards, I remain,

Yours sincerely,

AB/cw

Herbert C. Brown

Lectures in Organic Chemistry

$>C=C< + H-B< \rightarrow H-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-B<$

1995

Department of Chemistry
Purdue University
West Lafayette, Indiana

Herbert Charles and Sarah Baylen Brown

THE TWELFTH
HERBERT C. BROWN
LECTURES IN ORGANIC CHEMISTRY

March 31 - April 1, 1995

Department of Chemistry
Purdue University
West Lafayette, Indiana 47907

SCHEDULE OF EVENTS

Friday, March 31

	Banquet	
6:15 p.m.	**Social Hour** (cash bar)	University Inn 3001 Northwestern Avenue West Lafayette, Indiana 47906
7:00 p.m.	**Dinner**	

Saturday, April 1

	Herbert C. Brown Lectures in Organic Chemistry **Nuclear Magnetic Resonance Spectroscopy** Wetherill Room 104
9:00 - 9:15 a.m.	**Opening Remarks** **Richard A. Walton** Head, Department of Chemistry Purdue University
9:15-10:15 a.m.	*Isotopic Perturbation of Conformational Equilibria* **F. A. L. Anet** Professor of Chemistry University of California, Los Angeles
10:15-10:55 a.m.	**Coffee and Poster Session**

11:00 a.m. -12:00 noon	*The Interplay of NMR Structural Studies and Synthesis in Developing Sequence Specific Minor Groove Ligands of DNA* **David Wemmer** Professor of Chemistry University of California, Berkeley
12:00-1:30 p.m.	**Luncheon** West Faculty Lounge, Memorial Union
1:30-2:15 p.m.	*Research Presentations by:* **Christophe Copéret and Zhendong Jin**
2:15-3:15 p.m.	*Virtual Sample Tubes for NMR Spectroscopy in Living Things* **Paul C. Lauterbur** Professor of Chemistry University of Illinois
3:15-3:30 p.m.	**Closing Remarks** **Herbert C. Brown** R. B. Wetherill Research Professor Emeritus
	Adjournment

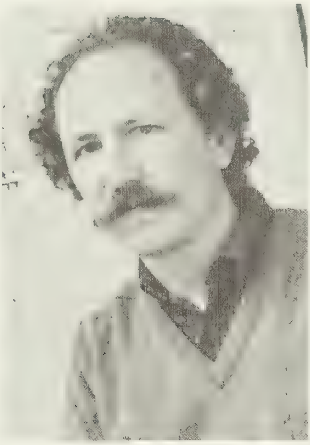
FRANK A. L. ANET

EMERITUS PROFESSOR OF CHEMISTRY
UNIVERSITY OF CALIFORNIA, LOS ANGELES

Frank A. L. Anet was born in France on October 24, 1926, and his family emigrated to Australia in 1937. Between 1945 and 1950 he attended the University of Sydney where he was introduced to structural studies on natural products and obtained B.Sc. (Hon) and M. Sc. degrees. He went to England in 1950 on a 1851 Exhibition scholarship and earned a D.Phil. degree from Oxford University in 1952 working with Sir Robert Robinson on *Strychnos* and *Rauwolfia* alkaloids. After postdoctoral work at Oxford University and at the National Research Council of Canada in Ottawa, he joined the faculty at the University of Ottawa in 1954, rising to professor of chemistry in 1962. Following a visiting professorship during 1963 at the University of California, Los Angeles, he became a professor of Chemistry at UCLA in 1964. He retired in 1991 to become an Emeritus Professor of Chemistry. He was a member of the Editorial Board of the *Journal of Magnetic Resonance* between 1968 and 1975 and presently serves on the Editorial Boards of *Magnetic Resonance in Chemistry* and *Magnetic Resonance Reviews*. He has been closely associated with the Experimental NMR Conferences and he chaired and organized the 25th ENC in 1984. He has been involved as a member (and sometimes as a chairman) of many committees dealing with NMR facilities for the NSF and NIH. In 1982 he was a member of an International Evaluation Committee on Physical Organic Chemistry in Sweden for the Swedish Natural Science Research Council. He received the H. N. McCoy Award from UCLA in 1968 and was elected a Fellow of the American Association for the Advancement of Science in 1988.

Anet has made major contributions to the chemistry of indole and *Lycopodium* alkaloids, including a pioneering investigation of transannular interaction between nitrogen and carbonyl groups. Shortly after joining the University of Ottawa, he became interested in reaction mechanisms and high-energy intermediates, such as singlet and triplet methylene, and in highly strained molecules, such as derivatives of benzocyclopropene. He discovered some highly unusual water-stable σ-bonded organochromium compounds that are intermediates in chromous salt reductions of organic halogens compounds. He applied nuclear magnetic resonance spectroscopy to numerous problems and has become a leading expert in the interpretation of complex and unexpected spectral features. He demonstrated the power of dynamic NMR to probe conformational and/or fluxional states in molecules such as cyclooctatetraene and its iron-tricarbonyl derivatives. Numerous six- to sixteen-membered rings, including most of the parent cycloalkanes, were investigated in conjunction with molecular mechanics, to give a clear picture of their static and dynamic conformational properties. Anet built high-field FT NMR spectrometers necessary for his research before such instruments were commonly available. His work on cryogenic trapping of high-energy conformations provided the first direct spectroscopic detection of the boat form of cyclohexane and the cisoid form of 1,3-butadiene. In collaboration with Professor Kurt Mislow, a molecular analog of "La Coupe du Roi" was found.

Relaxation in NMR has been a long standing interest where Anet has made important contributions, including the first application of the nuclear Overhauser effect (NOE) to obtain stereochemical information, and an experimental demonstration that T_2 can be greater than T_1. He has applied the method of isotopic perturbation of conformational equilibria to deuteriated cyclohexanes and heterocyclic analogs and developed an NMR method for the assignment of configuration in CHDT groups by direct tritium NMR spectroscopy. His most recent work, done in collaboration with Professor Martin Saunders, deals with the NMR detection of helium-3 encapsulated in various fullerene molecules.



DAVID E. WEMMER
PROFESSOR OF CHEMISTRY
UNIVERSITY OF CALIFORNIA, BERKELEY

David Wemmer was born in California in 1951 and grew up there, receiving his B.S. in Chemistry and Mathematics from the University of California at Davis in 1973. The combination of studies in mathematics and chemistry lead to interest and undergraduate research in both theoretical chemistry and spectroscopy. His graduate studies were done with Prof. Alex Pines at the University of California at Berkeley, his thesis work developing and applying new methods in solid state NMR spectroscopy leading to a Ph.D. in 1979 After a postdoctoral year in Germany with Prof. Michael Mehring, again in solid state NMR and molecular physics, he moved to Stanford to help operate the NIH funded NMR center there and turned his attention to biological molecules. Research along these lines continued after moving to the University of Washington where attention was especially focused on DNA oligomers and their interactions. Finally in 1985 he returned to Berkeley joining the Chemistry faculty as Assistant Professor and established a wide ranging research program involving application of NMR to problems of biomolecular structure and function He is now Professor of Chemistry and Assistant Dean of the College of Chemistry at Berkeley, and is also active as a Member of the Lawrence Berkeley Laboratory where he serves as Director of the National Tritium Labeling Facility, an NIH funded Research Resource, as well as directing his own research group

Wemmer's research interests have grown around the rapid development of multidimensional NMR methods and the ability to chemically and genetically prepare large amounts of a variety of nucleic acids and proteins for biophysical studies. NMR methods now complement x-ray diffraction as an alternative high resolution structure determination method. A central theme for much of the group's work has been trying to understand the basis for specific interactions between biological molecules, and how they contribute to biological function. At the present time the work divides into two major areas: design and characterization of sequence specific DNA binding ligands, and proteins which are involved in regulation of genetic expression. In the first area structural studies of complexes of the natural product distamycin with DNA oligomers rich in A-T base pairs lead to the realization that there is a strong coupling between the DNA structure and the binding mode. By understanding the relationship between structure and binding mode a design for modified analogs of distamycin which would bind at G-C base pairs was developed and successfully tested. The recent extension of this work has given a molecule now specific for a central GCGC target sequence. Progress is also being made on extending the length of the target sequence, and enhancing the sequence specificity. The second major area of work is structural analysis of regulatory proteins, especially transcription factors. Many proteins must contact both DNA and other proteins in order to control expression of various genes These proteins are often modular in structure, some modules responsible for DNA binding and others for assembly of the active transcription complex. Structures have been solved for several modules, including the DNA binding domain of HSF and a regulatory domain from NTRC. Other proteins, such as Sxl a message splicing control factor and FUR a protein regulating iron uptake in bacteria, are also being studied

When not in the lab, or at home with his wife and daughters, Wemmer can generally be found roaming the hills of the East Bay on a bicycle

PAUL LAUTERBUR

PROFESSOR OF CHEMISTRY
UNIVERSITY OF ILLINOIS

Paul Lauterbur was born on May 6, 1929 in Sidney, Ohio. His early interests in chemistry, including rocket fuels and organosilicon compounds, led him to major in that subject at Case Institute of Technology, where, among other things, he tried to determine whether Ph_3CSiPh_3 would dissociate into free radicals. After receiving his B.S. in 1951, he went to the Mellon Institute to work on organosilicon chemistry, including silicone rubbers, while taking graduate work at the University of Pittsburgh. A stint in the Army, from 1953-1955, allowed him to pursue an interest in NMR studies of molecular structures that had developed a year earlier. Upon his return to the Mellon Institute, he persuaded Dow Corning Corporation to set up an NMR lab there, and began work using the spectra of ^{29}Si, ^{13}C and other nuclei to study the structures, properties and reactions of organic and inorganic molecules. In 1962 he received his Ph.D. from the University of Pittsburgh, and shortly joined the young State University of New York at Stony Brook as Associate Professor of Chemistry, where he continued such studies, including work on shielding tensors in single crystals, and isotope effects on chemical shifts. His turn toward high resolution NMR of biological molecules, including ^{13}C protein spectroscopy, isotopic labelling and tritium labelling, was cut short by his realizing, in 1971, that NMR could be used to make pictures. That idea, sometimes referred to as NMR zeugmatographic imaging, led to a variety of developments. The most visible of these is clinical MRI (magnetic resonance imaging). Others include the development of magnetic contrast agents, both molecular and particulate, NMR microscopy, and various forms of spatially resolved NMR spectroscopy. In 1985 he moved to the University of Illinois, where he is currently Center for Advanced Study Professor of Medical Information Science, Chemistry, Physiology, Biophysics and Bioengineering, and in the Beckman Institute, and Director of the Biomedical Magnetic Resonance Laboratory at the Urbana-Champaign campus, and Distinguished University Professor in the College of Medicine at the Chicago campus. His work there is primarily in the areas of image processing, NMR microscopy, neuroscience, and new types of magnetic contrast agents.

Dr. Lauterbur has been awarded five honorary degrees, is a member of the National Academy of Science, and has been awarded, among other honors, the National Medal of Science, the National Medal of Technology, the Albert Lasker Clinical Research Award, the Bower Award and Prize, and the Kyoto Prize

PROFILES OF THE FOUNDERS OF THE HERBERT CHARLES AND SARAH BAYLEN BROWN FUNDS

Herbert C. Brown was born in London on May 22, 1912, but was brought to the U.S. at age two and grew up in Chicago. He enrolled in Crane Junior College in 1933, where he met Sarah Baylen, now his wife of more than 58 years. When Crane closed for lack of funds in June 1933, they continued their training in the home laboratory of one of their teachers, Nicholas D. Cheronis. When new colleges were opened in 1934, they attended Wright Junior College, where Sarah autographed his yearbook with the inscription, "To a future Nobel Laureate." They then entered the University of Chicago in 1935 as juniors. H. C. Brown completed two years of work in one year and graduated in 1936. A graduation gift from Sarah, Alfred Stock's Baker Lectures on "Hydrides of Boron and Silicon," was in part responsible for his choosing H.I. Schlesinger as his graduate research advisor at Chicago. His Ph.D. thesis (1938) dealt with the reduction of carbonyl compounds with diborane. After a year of postdoctoral work with M. S. Kharasch, he became assistant to Schlesinger (with rank of instructor) and codiscovered sodium borohydride. He became assistant professor at Wayne (now Wayne State) University in 1943, exploring steric strains. He was promoted to associate professor in 1946. In 1947 he moved to Purdue University as professor. He was promoted to R. B. Wetherill Professor in 1959 and R. B. Wetherill Research Professor in 1960. He received an Honorary Ph.D. from the University of Chicago in 1968. Since his "retirement" in 1978, he has been R. B. Wetherill Professor Emeritus, supervising a research group of approximately 15 postdoctoral associates, a secretary, and visiting scholars. He has published five books and over 1170 scientific publications. He has won the majority of major awards in his field, including the Nobel Prize for Chemistry in 1979, the ACS Award for Creative Research in Organic Chemistry (1960), the National Medal of Science (1969), the Roger Adams Award (1971), the Preistley Medal (1981), the Perkin Medal (1982), the American Institute of Chemists Gold Medal Award (1985), the National Academy of Sciences Award in Chemical Sciences (1987), the Emperor's Decoration (Japan): Order of the Rising Sun, Gold and Silver Star (1989), Vesper Award, Cincinnati ACS Section (1990), Honorary Scholar of the University of Wales, Swansea (1994), and Honorary Professor of the Institute of Organometallic Chemistry, Chinese Academy of Science (1994). Both Herbert and Sarah Brown enjoy good health and make frequent trips that typically combine lectures and other scientific commitments including manuscript preparation, sightseeing, and photography, as well as occasional visits to their grandchildren in California.

LIST OF HERBERT C. BROWN LECTURES

1984

G. Stork
S. Danishefsky
P.A. Grieco

1985

J.I. Brauman
F.G. Bordwell
P. Kebarle

1986

C.H. Heathcock
A.I. Meyers
S. Masamune
K.B. Sharpless

1987

R.G. Bergman
T. Mukaiyama
B.M. Trost

1988

D.H.R. Barton
N.J. Leonard
K. Mislow

1989

A.G. Brook
I. Fleming
J. Michl

1990

N. Nakanishi
G.D. Prestwich
K.L. Rinehart

1991

P.B. Dervan
S.M. Hecht
P.A. Kollman
R. Noyori

1992

R.R. Holmes
R.C. Larock
G.A. Molander
L.M Stock
Y. Yamamoto

1993

F.N. Diederich
D.A. Dougherty
J.M. McBride

1994

P.A. Bartlett
B.O. Fraser-Reid
A.B. Smith

JOURNAL OF ORGANOMETALLIC CHEMISTRY

We have received the manuscript of the article described below. We shall notify you of our decision concerning publication as soon as possible. Any enquiries should be addressed to the Regional Editor, Professor C. Eaborn, School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ, UK. Fax: (0273) 677196.

[illegible]

Herb: I will arrange for this to be the first in Vol 500, and leave a note for my successor to do the same for your contribution to Vol 1000! With best wishes

Colin

Professor H.C. Brown
Chemistry Laboratories
Purdue University
West Lafayette
Indiana 47907
USA

Date 10/2/95

Paper No. 95/45

Title

Versatile α-pinene-based borane reagents for asymmetric syntheses.

Authors

H.C. BROWN and V. Ramachandran

Editor C Eaborn

ELSEVIER SEQUOIA S.A., c/o Elsevier Editorial Services
Mayfield House, 256 Banbury Road, Oxford, OX2 7DH, UK

Dr. Alfred Bader
2961 North Shepard Avenue
Milwaukee, Wisconsin 53211

September 16, 1994

Prof. Herbert C. Brown
1393 Brown Building
Purdue University
West Lafayette, Indiana 47907 1393

Dear Herbert,

I am sorry that a trip to Spain has delayed my thanking you for your letter of August 15th.

My autobiography will be published by Weidenfeld and will be available next April. It is entitled *The Adventures of a Chemist-Collector*.

All good wishes to both of you from both of us.

As always,

1393 Brown Building
PURDUE UNIVERSITY

HERBERT C. BROWN

August 15, 1994

Dr. Alfred Bader
2961 North Shepard Avenue
Milwaukee, Wisconsin 53211

Dear Alfred:

I greatly enjoyed reading the copies of the two articles, "Portrait of a Connoisseur Chemist" and "Queen's and the Castle." The first one had the third page missing, but *Chemistry in Britain* is in my library, so I had good, clear copies made. Enclosed are two for your collection. Unfortunately, there are parts of the second article which are so faint as to be difficult to read, but I don't know where *Saturday Night (July/August)* is published.

I am sorry to say that I did miss the first item in *Chemistry in Britain*. But I no longer have the time and energy to keep up with the massive literature. I appreciate your calling it to my attention.

I look forward to reading your Autobiography. When will it be available?

Since the Agreement you made for me gave the patents in the borane area to Aldrich, I do not feel that it would be appropriate for me to write a letter to *Chemistry in Britain* re the Callery Letter. I am confident that Clint and Aldrich, with the legal advice they have access to, will do a first-rate job resolving the question with Callery. I remain ready to give Clint and Aldrich any advice I can regarding the chemistry involved.

Please give our love to Isabel.

With all best wishes from both Sarah and me,

Sincerely,

Herbert C. Brown

encl.
cc: Clinton F. Lane

H. C. BROWN AND R. B. WETHERILL LABORATORIES OF CHEMISTRY
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Dr. Alfred Bader
2961 North Shepard Avenue
Milwaukee, Wisconsin 53211

August 9, 1994

Professor Herbert Brown
1393 Brown Building
Purdue University
West Lafayette, Indiana 47907-1393

Dear Herb,

Thank you for your gracious letter of August 2nd.

Surely Callery is off base in their argument, and I was wondering whether you should write a letter to *Chemistry in Britain*, setting them straight.

Isabel and I negotiated the purchase of the castle, but then gave the funds to Queen's University. A couple of explanatory articles are enclosed. Most of the details will also appear in the last chapter of my autobiography, which has a great deal to say about you and your help.

Fond regards to you and Sarah.

As always,

c: Dr. Clinton Lane

1393 Brown Building
PURDUE UNIVERSITY

HERBERT C. BROWN

August 2, 1994

Dr. Alfred Bader
2961 North Shepard Avenue
Milwaukee, Wisconsin 53201

Dear Alfred:

With the increasing years, I am experiencing decreasing energy. I owe you several letters, but they are buried in a mass of unanswered correspondence.

Fortunately, I had seen the exchange of correspondence between Clint and the Callery people in *Chemistry in Britain* and had sent a copy by FAX to Clint. Nonetheless, your thoughtfulness is appreciated.

Sarah and I returned on July 17 from a week in Swansea and London. The primary purpose of the trip was to be installed as an Honorary Fellow at the University of Wales, Swansea. (I do not clearly understand the meaning of this new "honor," since I received an Honorary Doctorate from the University of Wales back in 1981, but since they have been very good friends, I did not feel I should ask questions.

While in London, Sarah and I visited Ralph and Muriel Emmanuel for an erev shabbes dinner. He told me about the beautiful castle you had bought and your plan to present it to Queen's University for use as a campus-in-England. Congratulations! It is nice to be able to buy such a castle in your neighborhood on the spur of the moment for such a worthwhile purpose. (If you have a news article on the incident, I would like a copy for your file.)

I hope all is well with you and Isabel. Sarah and I hope we can find an opportunity to get together in the not-too-distant future.

With all best wishes,

Sincerely,

Herb

Herbert C. Brown

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Dr. Alfred Bader
2961 North Shepard Avenue
Milwaukee, Wisconsin 53211

April 26, 1994

Professor Ei-ichi Negishi
Department of Chemistry
Purdue University
1392 H. C. Brown Laboratory of Chemistry
West Lafayette, Indiana 47907 1393

Dear Ei-ichi,

Thank you for your thoughtful letter of April 13th.

Of course, Isabel and I would have liked to attend the H. C. Brown Lectures and hope that you will be able to give us ample notice for next year's lectures. Is the date already fixed?

All good wishes.

Sincerely,

PURDUE UNIVERSITY

DEPARTMENT OF CHEMISTRY

April 13, 1994

Dr. Alfred Bader
2961 N. Shephard Ave.
Milwaukee, WI 53201

Dear Alfred:

I was very sorry to learn that the announcement of the 11th H. C. Brown Lectures, April 8 and 9, 1994, was not sent to you. I must confess that, due to my absence for about a month before the meeting, it was more difficult for me to get involved in some detailed aspects of our preparation than usual. Be that as it may, it was a serious oversight on our part, which we fully intend to avoid in the future. Certainly, it was unintentional and "anti-intentional". Please accept our deep apology.

With best regards,

Sincerely yours,

Ei-ichi Negishi
Professor of Chemistry

EN/mc

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Dr. Alfred Bader
2961 North Shepard Avenue
Milwaukee, Wisconsin 53211

August 25, 1993

Prof. Herbert C. Brown
1014 Lincoln Trail
West Lafayette, Indiana 47906

Dear Herb:

What an unexpected pleasure to see you and Sarah at my Loschmidt presentation.

As you will see from the enclosed, there has been some very severe criticism of our views about Loschmidt, and I would be most interested in having your reaction.

I am working on my autobiography and enclose a rough draft of the story of our happy collaboration. May I impose you to look it over to make sure that I have not made any factual mistakes.

Fond regards to you and Sarah.

Sincerely,

Enclosures

PURDUE UNIVERSITY

DEPARTMENT OF CHEMISTRY

August 11, 1993

Dr. Alfred Bader
2961 N. Shepard Avenue
Milwaukee, WI 53211

Dear Alfred,

Thank you for taking the time to write. I very much approve of your support for disadvantaged students. Bart is a great chemist and I am just trying to help him get started. The next time you visit Purdue I hope you will have a chance to meet him. I'm sure you would enjoy each other.

Madeline Kahr is indeed a relative. She is Bart's great aunt. He has never met her however.

Thanks for your many fine contributions to Chemistry. The world is better for your presence.

Best wishes,

John B. Grutzner
Professor of Chemistry

JBG/scj

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Dr. Alfred R. Bader
2961 North Shepard Avenue
Milwaukee, Wisconsin 53211

August 6, 1993

Prof. John B. Grutzner
Department of Chemistry
Purdue University
West Lafayette, Indiana 47907

Dear John:

I am sorry that a very long trip to Europe has delayed my responding to your thoughtful letter of May 28th.

I am certain that Bart Kahr is an excellent man, but I don't believe that I should be supporting individual postdoc positions. In the last few years, my family and I have tried to concentrate more on helping disadvantaged students through projects such as Project SEED and a similar scheme which we are trying to initiate in Britain. I do hope you will understand.

Incidentally, is Prof. Kahr the son of Andrew Kahr, formerly financial vice president at of Ventron, and of Madeline Kahr, and art historian who has published widely on Dutch 17th century paintings?

Best personal regards.

Sincerely,

1393 Brown Building

PURDUE UNIVERSITY

HERBERT C. BROWN

7/1

June 21, 1993

Dr. Alfred Bader
2961 North Shepard Avenue
Milwaukee, Wisconsin 53201

Dear Alfred:

Following your urging, I invited John Frost in to discuss his problem here. Things went well. When he left, I had the distinct impression that he had decided to remain at Purdue. However, about a month later, there was an official notice that he was leaving for a Research Institute at Michigan State. I do not believe that the position involves actual membership in the Faculty of the Michigan State Chemistry Department. Unfortunately, his discussion of the opening there did not leave me with a clear picture of the organization and mission of the Research Institute. I am disappointed, but I hope he finds his move beneficial to his career.

At the celebration here of my 80th birthday, Arno Cahn told me of a program which had appeared on Canadian Public Television about the refugees who had escaped to England from Hitler's clutches, only to be shipped to Canada as enemy aliens for internment. I expressed an interest, and [illegible]

Sarah and I watched it last night and found it fascinating.

Since you had been involved, I thought it would be of special interest to you. Do you know about the program? Have you seen it?

With all best wishes,

Sincerely,

Herb

Herbert C. Brown

1393 Brown Building

PURDUE UNIVERSITY

June 21, 1993

HERBERT C. BROWN

Dr. Arno Cahn
72 East Allison Avenue
Pearl River, New York 10965

Dear Arno:

I deeply appreciate your sending me a copy of the video tape which describes the experiences of those who escaped to England from Hitler's Europe, only to be interned as enemy aliens and then transported to Canada. Sarah and I watched it with fascination last night.

Why did it take us nearly a month to see it?

As you know, we recently built a new home in the Westminster Retirement Village here in West Lafayette (less than a mile from our previous home). We discovered we don't have the energy of our younger years. We moved on January 28, and it has taken over four months to get things fully organized. But now we can relax and watch not only your fascinating tape, but also the tape of the H. C. Brown 80th Birthday Celebration.

I was happy to learn that your Consulting Services, Inc. is keeping you busy.

Give our love to Blossom.

Sincerely,

Herb

Herbert C. Brown

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FAX TRANSMITTAL SHEET

FROM: DR. ALFRED BADER

2961 North Shepard Ave.
Milwaukee, Wisconsin 53211

PHONE: (414) 962-5169

FAX: (414) 962-8322

TO: Prof. John W. Frost
Department of Chemistry
Purdue University

DATE: July 29, 1993

FAX 317 494 0239

Dear John:

We and our young friend, George Seoane, plan to drive from Milwaukee to Indianapolis this coming Sunday, leaving Milwaukee at around 9 o'clock in the morning. Thus, we could visit you in the afternoon on Sunday, but then must be at our motel in Indianapolis around 6:00 p.m. to meet an old friend. Thus, we would really have very little time, and I would much prefer to have an hour or two.

My last talk in Indianapolis is from 9--10 on Tuesday morning, and we plan to return home shortly thereafter. Thus, I could be with you late on Tuesday morning, and perhaps you and your wife could join us for lunch and talk much more leisurely. Would this be possible?

In either case, please let me know where we can meet.

Fond regards and good wishes,

PURDUE UNIVERSITY

DEPARTMENT OF CHEMISTRY

May 28, 1993

Dr. Alfred W. Bader
2961 N. Shepard Avenue
Milwaukee, WI 53233

Dear Alfred:

Herb Brown reminded me that over the years, you have been an active supporter of young chemists, in addition to your many years of support for Purdue chemistry. I am writing to alert you to a special opportunity that exists for my exciting young colleague, Bart Kahr.

Bart is the kind of chemist that you would enjoy meeting. He has a dual degree in Chemistry and Art. He is creative and a truly intellectual individual in the mold of Jim Brewster and his mentors, Kurt Mislow and Mike McBride. You will gain an insight into these talents from the enclosed reprint from *Angew. Chemie*. Bart was both the discoverer of the origin of optically anomalous crystals and the author of this article. He was a finalist in the NSF Presidential Scholars Awards, but just missed out. He is very productive and multitalented as you will see from his publication list. He is full of ideas. What he lacks most at this point is one or two experienced co-workers to develop those ideas. That is why I am writing to you. Would you be willing to be the initiator for his explosion onto the chemical scene by providing the money for Bart to hire a postdoc?

Bart has just received an application for a postdoc from Mr. Thomas Miebach. He is an experienced synthetic organic chemist and x-ray crystallographer (Diplom with Dr. R. Boese, U. Essen; Ph.D. candidate with Dr. Brunker, SUNY Binghamton). This is just the type of individual Bart needs. Bart's current group consists of an Indian postdoc who Bart has trained from scratch, six of our brightest and best undergraduates, and three beginning graduate students. As you know, Purdue attracts a limited number of intellectually sophisticated graduate students and so Bart, like Jim Brewster before him, has had trouble building his research group. The addition of Mr.Miebach would provide the critical expertise to start the snowball.

Bart currently has funding from NSF and the Petroleum Research Fund and is actively seeking additional support. However, he has no funds at present to seize the opportunity of hiring Mr. Miebach. In my opinion, this is one of those very rare opportunities where a timely investment could launch an outstanding career. I hope you will be intrigued enough to come and see for yourself and to seriously consider donating the funds to Purdue for Bart's research. I

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WEST LAFAYETTE, IN 47907-1393 • FAX (317) 494-0239

would be happy to assist the process in anyway. My phone number is (317)494-5247, and FAX number is (317)494-0239.

You are a connoisseur of fine chemistry, fine art, and fine people. Bart combines those qualities in a unique way. I trust that he will stimulate your eye for fine investing as well.

Best wishes,

John Grut

John B. Grutzner
Professor of Chemistry

jbg/mb

Dr. Alfred R. Bader
2961 North Shepard Avenue
Milwaukee, Wisconsin 53211

June 7, 1993

Professor John B. Grutzner
Department of Chemistry
Purdue University
West Lafayette, Indiana 47907 1393

Dear Professor Grutzner:

Your letter to Dr. Bader of May 28th has been received while he is out of the country until the end of July.

In the meantime, I have forwarded a copy to him in England.

Cordially,

Marilyn Hassmann

Curriculum Vitae for BART EVAN KAHR

Personal

Born October 28, 1961, New York City

Education

B.A.	Middlebury College (*magna cum laude*) Department of Art (*highest honors*) Department of Chemistry (*high honors*)	1983
M.S.	Princeton University	1985
Ph.D.	Princeton University Thesis Advisor: Professor Kurt Mislow Dissertation: *The Length of the Central Bond in Hexaarylethanes*	1988

Professional Experience

Crystallographer, Princeton University	1987
Postdoctoral, Yale University (with Professor J.M. McBride)	1988-90
Assistant Professor, Purdue University	1990-

Honors

Phi Beta Kappa (Middlebury College)	1983
American Institute of Chemists' Prize (Middlebury College)	1983
Hugh Stott Taylor Prize (Princeton University)	1984

Societal Affiliations

American Chemical Society, American Crystallographic Association, American Association for Crystal Growth, History of Science Society, Sigma Xi

Research Interests

Mechanisms of crystal growth, mixed crystal structure, electrical, magnetic, and optical properties of solids, structure and internal dynamics of non-natural products, reactive intermediates, history of chemistry and crystallography.

Current Research Group

Postdoctoral: Prakash Gopalan, Sei-Hum Jang (to begin in June)

Graduate students: Mike Kelley (analytical), Guy Crundwell (inorganic), Christine Mitchell (organic)

Undergraduates: Jason Chow, Matthew Peterson, Jay Molstad, Steven Antonelli, Mary Jennifer Jay, Richard Arkin

Teaching (1992-1993)

CHM 668 - Physical Organic Chemistry

CHM 696B - Solid State Chemistry

CHM 490 - Junior/Senior Honors Seminar

PUBLICATIONS - Bart Kahr (Purdue University)

1. *A New Preparation of α - Cycloheptatrienyl Ketones*, I.D. Reingold, H.A. Trujillo, B.E. Kahr, J. Org. Chem. **1986**, *51*, 1627.

2. *The Length of the Ethane Bond in Hexaphenylethane and Its Derivatives*, B. Kahr, D. Van Engen, K. Mislow, J. Amer. Chem. Soc. **1986**, *108*, 8305.

3. *Molecular Structure of Hexakis(dichloromethyl)benzene*, B. Kahr, S.A. Biali, W. Schaefer, A.B. Buda, K. Mislow, J. Org. Chem. **1987**, *52*, 3714.

4. *Structure, Resolution and Racemization Decakis(dichloromethyl)biphenyl*, S.E. Biali, B. Kahr, Y. Okamoto, R. Aburatani, K. Mislow, J. Am. Chem. Soc. **1988**, *110*, 1917.

5. *Twisted Polycyclic Aromatic Hydrocarbons. Structural Studies of Protic and Deuteriated 1,2,3,4-Tetraphenyltriphenylenes*, R.A. Pascal, Jr., D. Van Engen, B. Kahr, W.D. McMillan, J. Org. Chem. **1988**, *53*, 1687.

6. *Stereochemistry of Hexakis(dimethylamino)benzene and its Dication*, J.M. Chance, B. Kahr, A.B. Buda, J.P. Toscano, K. Mislow, J. Org. Chem. **1988**, *53*, 3226.

7. *Determination of the Central Bond Length in Hexaarylethanes by Nutation NMR Spectroscopy*, N. Yannoni, B. Kahr, K. Mislow, J. Am. Chem. Soc. **1988**, *110*, 6670.

8. *Linkage of Alkylidyne, Carbonyl, and Alkyne Ligands at a Tungsten Center to Form a Metallacyclopentadienone and an η^3-Oxocyclobutenyl Complex*, A. Mayr, K.S. Lee, B. Kahr. Angew. Chem., Int. Ed. Engl. **1988**, *27*, 1730.

9. *Severely Warped Benzene Ring due to Push-Pull Electronic Demands and Steric Distortions in 1,3,5-tris-N,N-dialkylamino-2,4,6-trinitrobenzenes*, J.M. Chance, B. Kahr, A.B. Buda, J.S. Siegel, J. Am. Chem. Soc. **1989**, *111*, 5940.

10. *Occurrence and Interconversion of High-Mass Fullerenes*, D. Ben-Amotz, R.G. Cooks, L. Dejarme, J.C. Gunderson, S.H. Hoke II, B. Kahr, G.L. Payne, J.M. Wood, Chem. Phys. Lett. **1991**, *183*, 149.

11. *Gas-Phase Reactivity of Fullerene Anions*, L.S. Sunderlin, J.A. Paulino, J. Chow, B. Kahr, D. Ben-Amotz, R.R. Squires, J. Am. Chem. Soc. **1991**, *113*, 5489.

12. *Oxygen and Methylene Adducts of C_{60} and C_{70}*, J.M. Wood, B. Kahr, S.H. Hoke II, L. Dejarme, R.G. Cooks, D. Ben-Amotz, J. Am. Chem. Soc. **1991**, *113*, 5907.

13. *Evidence for an Externally Bound Fe^+-Buckminsterfullerene Complex, FeC_{60}^+, in the Gas Phase*, L.M. Roth, Y. Huang, J.T. Schwedler, C.J. Cassady, D. Ben-Amotz, B. Kahr, B.S. Freiser, J. Am. Chem. Soc. **1991**, *113*. 6298.

14. *Aromatic Hydrocarbon Derivatives of Fullerenes,* S.H. Hoke II, J. Molstad, G.L. Payne, B. Kahr, D. Ben-Amotz, R.G. Cooks, Rapid Commun. Mass Spectrom. **1991**, *5*, 472.

15. *Optically Anomalous Crystals*, B. Kahr, J.M. McBride, Angew. Chem., Int. Ed. Engl. **1992**, *31*, 1.

16. *Disorder in the Crystal Structures of Hexakis(dimethylsilyl)benzene and its Tricarbonyl Chromium, Molybdenum, and Tungsten Complexes*, B. Kahr, J.M. Chance, K. Mislow, Mol. Cryst. Liq. Cryst. **1992**, *210*, 195.

17. *Comparison of Twists in Isosteric Propellers: X-ray Structures of Tris(2,6-dimethoxyphenyl)borane, tris(2,6-dimethoxyphenyl)methyl Cation, and Tris(2,6-dimethoxyphenyl)methyl Radical*, B. Kahr, J.E. Jackson, D.L. Ward, S.-H. Jang, J. Blount, Acta Cryst., Sect. B, **1992**, *B48*, 324.

18. *Interrupted σ-Bonds in Materials with Colligative Magnetic Properties*, S.-H. Jang, R.A. Bertsch, J.E. Jackson, B. Kahr, Mol. Cryst. Liq. Cryst. **1992**, 211, 289.

19. *Structures for Polymorphs of Triphenylchloromethane. Triphenylacetic Acid Illustrates the Isomorphous Stable Modification*, B. Kahr, R.L. Carter, Mol. Cryst. Liq. Cryst. **1992**, 219, 79.

20. *Reaction of Fullerenes and Benzyne*, S.H. Hoke II, J. Molstad, D. Dilettato, M.J. Jay, B. Kahr, R.G. Cooks, J. Org. Chem. **1992**, *57*, 5071.

21. *Reevaluating Structures for Mixed Crystals of Simple Isomorphous Salts: $NaBr_xCl_{1-x}O_3$*, P. Gopalan, M. L. Peterson, G. Crundwell, B. Kahr, J. Am. Chem. Soc. **1993**, *115*, 3366.

22. *Reevaluating Structures for Mixed Crystals of Simple Isomorphous Salts: $Ba_xPb_{1-x}(NO_3)_2$*, P. Gopalan, B. Kahr, J. Solid State Chem. **1993**, 0000.

23. *Crystal Structure and Magnetic Susceptibility of a Hydrocarbon Free Radical: Tris(3,5-di-tert-butylphenyl)methyl*, B. Kahr, D. Van Engen, P. Gopalan, Chem. Mat. **1993**, 0000.

24. *Correlation of Structure and Internal Dynamics for Tris(2,6-dimethoxyphenyl)methyltin Trihalides: A Homologous Series of Seven-Coordinate Tin Compounds*, S. Dostal, S.J. Stoudt, P. Fanwick, W. Sereatan, B. Kahr, J.E. Jackson, Organomet. **1993**, 0000.

25. *Organic Hourglass Inclusions*, B. Kahr, J.K. Chow, M.L. Peterson, J. Chem. Ed. **1993**, 0000.

26. *Aryl Ring Twists in Tris(2,6-dimethoxyphenyl)-Z Tripod Ethers: Why is the Radical (Z=C·) Different?* S.J. Stoudt, P. Gopalan, J.E. Jackson, B. Kahr, J. Chem. Soc. Chem. Commun. submitted.

27. *Jacobson and Heintschel Peroxides*, S.-H. Jang, P. Gopalan, J.E. Jackson, B. Kahr, Angew. Chem. to be submitted.

28. *Critical Analysis of Crystal Growth Inhibition by Dyes*, J.K. Chow, M. Kelley, B. Kahr, Mol. Cryst. Liq. Cryst. to be submitted.

Manuscripts in Preparation

29. *Effect of Habit Modification on Mixed Crystal Fine Structure*, P. Gopalan, G. Crundwell, M.L.Peterson, B. Kahr.

30. Chromoisomerism *and Polymorphism in 9-Phenylacridinium Hydrogensulfate,* P. Toma, M. Kelly, B. Kahr, S.R. Byrn.

31. *Tripod-ether Ionophores*, S.S. Stoudt, P. Gopalan, B. Kahr, J.E. Jackson

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International Edition in English

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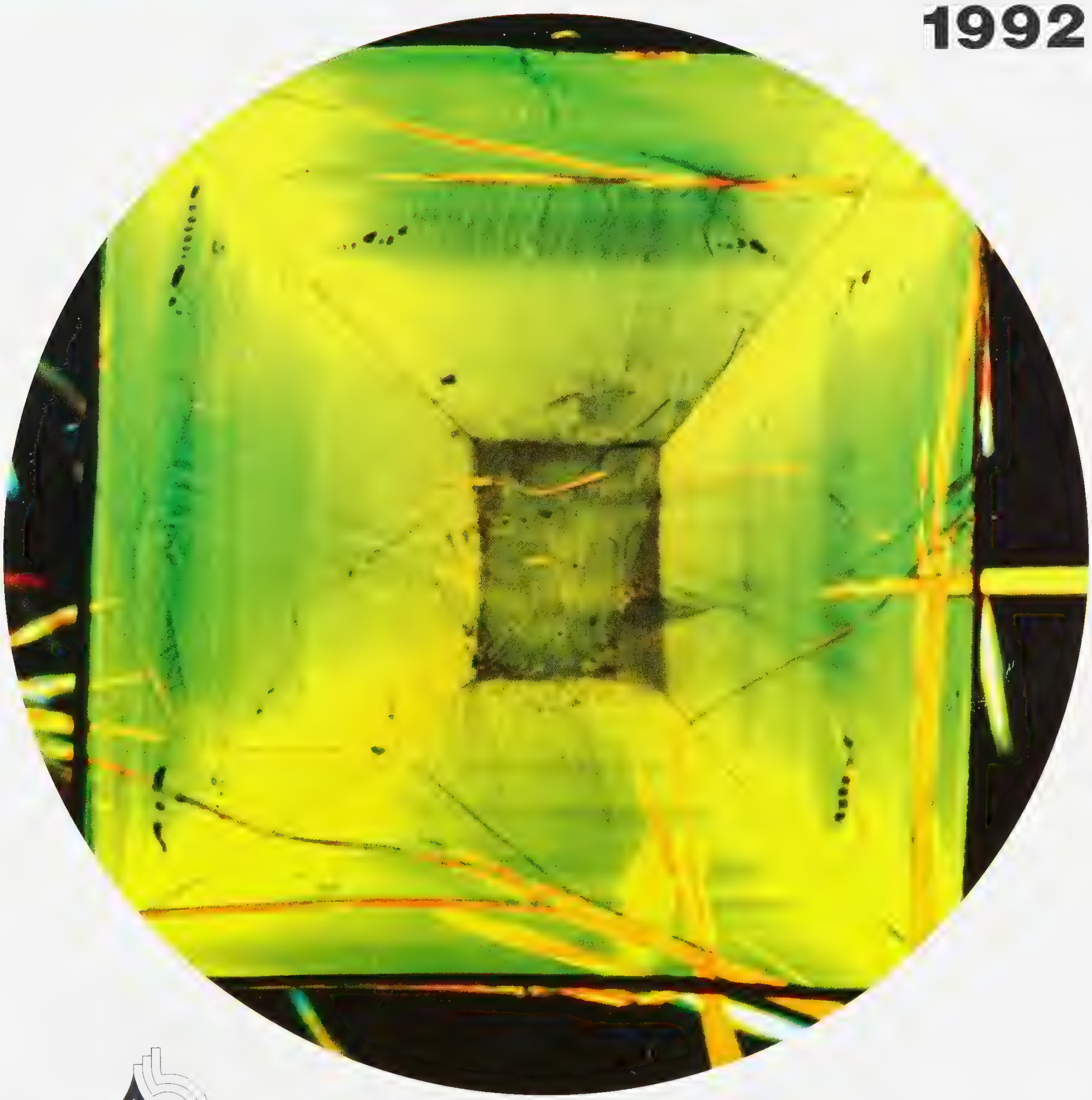

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Optically Anomalous Crystals

By Bart Kahr* and J. Michael McBride*

The optical symmetry of many crystals is lower than would be expected from their external form and X-ray diffraction data. Recently such *optical anomalies* have been attributed to nonequilibrium structures resulting from kinetically controlled crystal growth. Impurities are incorporated to different extents at various surface sites that would otherwise have become symmetry-related within the bulk crystal. After their discovery by Brewster in 1815, optically anomalous crystals were the subject of lively debate throughout the 19th century among some of the most distinguished contributors to the development of crystallography including Biot, Berzelius, Herschel, Mitscherlich, Frankenheim, Pasteur, Mallard, Klein, Groth, Wyrouboff, Barlow, Brauns, Rinne, Pockels, and Friedel. From a sea of wild speculation two conflicting postulates emerged: that the symmetric form resulted from accidental twinning of segments with lower symmetry, or that the optical peculiarities resulted from stress due to impurities or external perturbations. Neither postulate expresses the present view. Interest in this research waned at the turn of the century, and after 1917 no one pursued Tammann's alternative correct insight. The problem of anomalous double refraction attracted no attention for more than half a century until its recent solution. This review discusses both mineral and organic systems with particular emphasis on the phyllosilicate apophyllite and on 1,5-dichloro-2,3-dinitrobenzene. These nonequilibrium structures relate to questions of crystal order, crystal growth, molecular recognition, and the design of new materials. The review provides a reminder of the enduring value of the polarizing microscope as a research tool in chemistry.

1. Introduction

1.1. What is an Optically Anomalous Crystal?

In a literal sense any crystal whose optical properties deviate from expectation could be called optically anomalous. Descriptions of optical anomalies are scattered throughout the crystallographic literature. Examples from the work of David Brewster, a pioneer in crystal optics at the beginning of the 19th century, range from interference patterns associated with fluid inclusions in diamonds[1] to the variegated interference colors in some types of quartz.[2] However, a phenomenon that seems anomalous to one generation can seem commonplace to a succeeding generation with more sophisticated expectations. For example, some minerals were considered optically anomalous because their sequence of interference colors in convergent light does not follow Newton's scale of colors.[3] Such behavior is now assigned to variation of refractive index with wavelength in highly dispersive minerals.

The most common type of optical anomaly occurs when a crystal's optical symmetry is lower than its apparent structural symmetry, as established by measuring dimensions of the bulk crystal or by X-ray diffraction. Such cases have been

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recognized for 175 years but have remained mysterious until quite recently. In this paper we use *optically anomalous* or *anomalous* to refer only to this type of crystal.

The optical symmetry of a crystal can be determined by measuring its refractive index tensor, which depends on its electric polarizability. Most crystals are biaxial (Fig. 1a); they have one direction of maximum polarizability and refractive index (***M***), and a perpendicular direction of minimum polarizability (***m***). Within the plane defined by ***M*** and ***m*** there are four other directions (***i'***) whose intermediate polarizability matches that in the third orthogonal direction (***i***). Pairs of these directions together with ***i*** define a *circular section*, a plane within which the polarizability is constant in all directions. The normal to a circular section is called an *optic axis* (***oa***). Plane-polarized light can propagate along an optic axis without becoming elliptically polarized. A crystal is called biaxial when it has two circular sections and two optic axes.[4b]

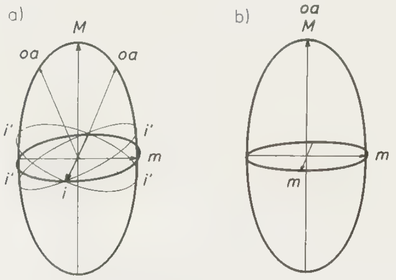


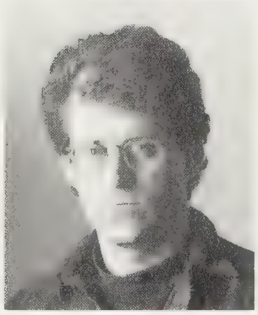
Fig. 1. Refractive index tensors (indicatrices) of a biaxial and a uniaxial crystal.

Figure 1b shows an *axially symmetric* anisotropic crystal (a crystal with only one axis of three-, four-, or sixfold symmetry) in which one polarizability extremum (***M***) must lie along the axis, while the other two orthogonal axes are equivalent in polarizability (***m*** and ***m***). Such a crystal has a single optic axis, parallel to the symmetry axis, and is called *uniaxial*. Crystals with higher symmetry have the same polarizability in all directions and are called *isotropic*. By observing the passage of polarized light through a crystal with a polarizing microscope, or in favorable circumstances with the eye, it is possible to establish its symmetry as biaxial, uniaxial, or isotropic.[4a] When this symmetry is lower than that revealed by morphology or some other technique, the crystal is optically anomalous.

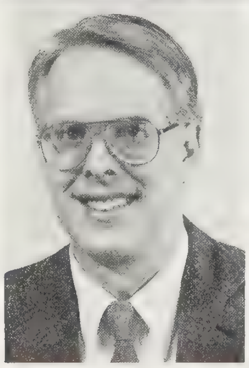
Anomalous crystals are usually twinned. They possess several distinct homogeneous regions, or *sectors*, whose number and relative orientation appear to be determined by the rotational symmetry of the crystal morphology. For example, a crystal with four- or sixfold symmetry should be uniaxial. Anomalous crystals with four- or sixfold morphological symmetry are typically composed of four or six biaxial segments, these being rotated from one another by 90° or 60°, respectively (see Fig. 2). Such twinning is called mimetic, because the composite crystal mimics a single crystal of higher symmetry and shows no reentrant angles between the constituent segments. Most of the hundreds of crystals described as optically anomalous in the literal sense fall into this specific class.

1.2. How Crystal Growth Causes Optical Anomalies

In 1988, while studying the growth of mixed crystals of fatty acid diacyl peroxides in this laboratory, Steven Bert-



Bart Kahr was born in New York City in 1961. He developed an interest in structural chemistry working with David Reingold at Middlebury College. At Princeton University he studied stereochemically unusual molecules with Kurt Mislow, obtaining a PhD degree in 1988. During graduate school he was fortunate to have shared a laboratory with Jeffrey Chance. After two years of crystallographic research in J. M. McBride's laboratory at Yale University, he joined the faculty of Purdue University as Assistant Professor of Chemistry.



Michael McBride was born in Lima, Ohio, in 1940. After undergraduate work at the College of Wooster and Harvard College, he earned the Ph.D. for research on free radical chemistry under Paul D. Bartlett at Harvard University. Since 1966 he has been on the faculty of Yale University. His research on organic solids has emphasized spectroscopic studies of free radical reactions in single crystals and the relationship among molecular structure, reactivity, and the mechanical properties of organic solids. He has an active interest in the history of organic chemistry. In 1987 he shared the Nobel Laureate Signature Award for Graduate Education with his student M. D. Hollingsworth. In 1990 he was Jacob and Erna Michael Visiting Professor at the Weizmann Institute of Science.

man recognized an optically anomalous crystal.[5] Square plates of pure di-11-bromoundecanoyl peroxide have true fourfold symmetry and are thus uniaxial. Inclusion of 5–15% of structurally analogous molecules of an impurity also gave square plates, but examination of these mixed crystals with the polarizing microscope showed that they were mimetic twins. Typical crystals were divided diagonally into four biaxial sectors interrelated by 90° rotation (Fig. 2). X-ray diffraction of single sectors showed that the fourfold symmetry had been broken. We attributed this desymmetrization to selective incorporation of impurity molecules among otherwise symmetry-related sites of the host lattice.

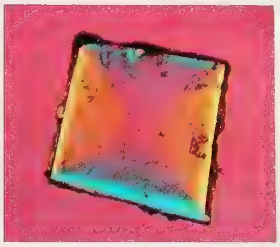


Fig. 2. Sectoring in a mixed crystal of di-11-bromoundecanoyl peroxide containing 15% of the analogue in which one terminal bromine atom is replaced by hydrogen; viewed along [001] between crossed polarizers with first-order red retarder (γ at 45°) [5]. Change in color from one growth sector to the next is due to a difference in orientation of the monobrominated compound caused by kinetic control of molecular addition to the lateral faces. (This same crystal was illustrated in [5], where the impurity was incorrectly identified as having one terminal bromine replaced by a *methyl* group. The effect of the impurity is nearly the same whether bromine is replaced by hydrogen or methyl.)

We were delighted by the prospect of using crystal optics to study this subtle aspect of crystal growth. But we were not surprised by the selectivity, because we had been attempting to apply to our crystals the elegant techniques of Addadi, Lahav, Leiserowitz, and their collaborators, whose comprehensive studies have revealed and exploited analogous selectivity in less symmetrical systems.[6]

It is easy to imagine that enantiomorphous lattice sites should be differently populated by a resolved chiral impurity, since the two kinds of defects must have different energies. It may at first seem surprising that impurity populations should also differ among sites related by a proper symmetry element, such as rotation. Such defects have identical energies, and thermodynamics requires their concentrations to be equivalent in a dilute solid solution at equilibrium. However most real crystals, especially those of solid solutions, are *not* at equilibrium. Once a molecule becomes incorporated into the crystal lattice, it is usually difficult for it to undergo a dramatic change in position or orientation. Thus many structural features of real crystals are controlled by the kinetics of growth rather than by equilibrium thermodynamics. To understand selective population one must recognize that growth occurs at the crystal surface and that most crystal faces lack the full symmetry of the three-dimensional lattice. For example, crystallographic axes are defined near a crystal face only when they are perpendicular to the surface; and even then the face must be flat and free of growth steps. Sites that should ultimately become equivalent by space group symmetry are thus different in structure and energy at the time impurities chose whether or not to occupy them.[7] Sectors of a crystal that have grown through different faces should have different impurity distributions and different optical properties, as illustrated in Section 2.3.2. When two crystal faces are related by symmetry, impurity distributions in the corresponding crystal sectors, resulting from growth through the two faces, should be related by the same symmetry.

After observing the optical anomaly in organic peroxides, we searched the literature for reports of analogous phenomena. We discovered that, although current texts give them little attention, descriptions were common in the 19th century when optical microscopy was the most powerful method of crystallographic analysis. Unsuccessful attempts to resolve these anomalies, which were observed in a wide variety of organic and inorganic crystals, form a consistent thread that parallels the development of crystallography generally. The present understanding of optical anomalies has emerged only over the last dozen years.

Section 2 of this paper outlines the history of the study of optically anomalous crystals within the context of the history of crystallography in the 19th and early 20th centuries. The mineral apophyllite is illustrated specifically. Section 3 discusses the present status of optical anomalies in inorganic and organic systems. Section 4 describes their relevance to current research on molecular recognition, on the kinetics and mechanism of crystal growth, and on rational approaches to designing crystalline materials for technical applications.

2. The History of Optical Anomalies

2.1. Crystal Classification according to Form

The mature development of any science requires a coherent classification of the objects under study. Thus progress in crystallography[8, 9] required classification of crystals. Crystals may be classified according to their external morphology, their physical and chemical properties, or their internal structure. All sorts of information may be relevant: shape, cleavage, chemical composition, color, hardness, density, refractive index, phase transition temperatures, space group symmetry, atomic positions, and many others.

Because the outstanding macroscopic feature of mineral samples is their polyhedral shape, attempts to classify crystals according to form trace back at least to the work of Nicolaus Steno (1638–1687),[10] who articulated a form of the Law of the Constancy of Interfacial Angles.[11] Maurice Cappeller (1685–1769) extended Steno's emphasis on form for the purpose of identification.[12] As in this botanical work, Carolus Linnaeus (1707–1778) sought to classify minerals within a system of genera.[13] Form was the most important organizing principle in his system. In an early attempt to approach the question of internal structure, A. G. Werner (1750–1817) sought a small group of *primary forms* to which the vast array of possible crystal shapes might be referred.[14]

Not everyone agreed that form should be the primary consideration in crystal classification. Romé de l'Isle (1736–1790) thought that form should be supplemented by chemical analysis, because shape alone was neither unique nor unambiguous. Not only can a single polymorph of a given chemical substance with a particular unit cell structure appear in many different shapes or *habits*, but also different substances can appear as isomorphs displaying the same form.[15] Through his Law of Rational Intercepts René Just Haüy (1743–1822) could relate the various shapes of a given polymorph by showing that crystal faces can be described by small integral indices when referred to three vectors. He further sought by successive cleavages to discover the unique building block, or *molécule intégrante*, for polymorphic crystals.[16] But Haüy sought idealized relationships among a crystal's dimensions and neglected precise goniometry (the quantitative measurement of form) when the results did not agree with his theory.[17] The limitations of his method were emphasized after Wollaston (1766–1828) invented the reflecting goniometer.[18] At the start of the 19th century it was clear that crystallography was in need of a physical method, independent of the measurement of form, that could assist in classification by confirming at least some of the qualitative aspects of crystal symmetry.[19]

2.2. Optical Classification of Crystals

The development of the science of crystal optics in the 19th century revealed the utility of birefringence in crystal classification. The first observation of birefringence or double refraction was reported by Erasmus Bartholinus (1625–1698), who noticed that within a crystal of calcite a single ray of light was split into two.[20] Christian Huygens (1629–1695) realized that one of these rays obeyed the ordinary law of refraction while the other did not and was always contained within a plane defined by the direction of incidence and a special axis, the direction of high rotational symmetry in the rhombohedral crystal.[21] Haüy, undoubtedly because of his own researches with calcite, undertook studies of double refraction and noticed that crystals of other substances with the form of a cube or octahedron lacked this property. Finally Johann Jacob Bernhardi (1774–1850) suggested explicitly that double refraction was directly related to a crystal's form.[22] However only two optical classes were distinguished at this time: crystals that were birefringent and those that were not. There was as yet no distinction between uniaxial and biaxial birefringent crystals.

In 1808 Etienne Malus (1775–1812), while examining a crystal of calcite in sunlight reflected from the windows of the Palais Luxembourg, noticed that the intensity of the two rays varied as a function of the crystal's orientation.[23, 24] He correctly recognized this as the phenomenon of polarization.[25] His discovery that the rays had different polarization greatly assisted studies of doubly refracting minerals, because researchers were no longer restricted to examining large, strongly birefringent crystals in which divergence of the two rays was readily visible.

In 1811 François Arago (1786–1853) discovered that brilliant colors sometimes are produced when a crystal is examined between two polarizers.[26] Immediately after Arago's discovery David Brewster (1781–1868)[27] and Jean-Baptiste Biot (1774–1862)[28] recognized the colors as a signature of *weak* birefringence and began systematic explorations of a wide variety of crystals and biological specimens.[29] Independently they distinguished between uniaxial and biaxial birefringent crystals. They also discerned the connection to morphology, since well formed uniaxial crystals always had three-, four-, or sixfold rotational symmetry.

This new method of analysis inspired Brewster to challenge Haüy's assignments of primive forms to eleven mineral substances[30] and to write:

> "If the physiology of mineral bodies shall ever attain the dignity of a science, its foundations must be laid upon optical results, and its progress directed by the unerring light of optical analysis."[31]

> "If we take a crystal... bounded by six equal square faces, the crystallographer will content himself with calling it a *cube*, but the optical mineralogist will only call it a *cube* when it has *no double refraction*."[30]

The optical classification of crystals as isotropic, biaxial, or uniaxial by Brewster[32] and Biot[33] in the second decade of the 19th century is still valid. One may further assign a biaxial crystal to one of three classes, where both, one, or neither of the directions of maximum and minimum polarizability are fixed by symmetry. This may be accomplished optically because principal directions that are not fixed by symmetry will in general differ for light of different wavelength.[34]

2.3. The First Observations of Optical Anomalies[35b]

2.3.1. Brewster's Initial Report

As Brewster was developing his optical classification scheme, he discovered several minerals that appeared to be exceptions and chose to treat them separately. In 1815 he announced to the Royal Society of Edinburgh:

> "Philosophers will no doubt be surprised to learn, that *muriate of soda, fluate of lime,*[*] *the Diamond, Alum* [despite their high symmetry][**] have actually the property of Double Refraction, but under circumstances of such a singular kind, as to entitle them to be regarded as a new class of doubly refracting crystals."[36]

He then described optically anomalous crystals of fluorspar (CaF_2, Fig. 3). To observe the indistinct low-order interference effects of a fluorspar crystal more clearly, he supplemented its birefringence by laying it on a plate of calcium sulfate which by itself between crossed calcite polarizers gave "a *brilliant blue* colour of the second order on Newton's scale." He was surprised to observe that

> "when the cube of fluor-spar remained stationary, there was one portion of it at *m*, which made the *blue* colour [of the $CaSO_4$] *red*... while another portion, at *n*, made the *blue* colour *green*."

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[*] sodium chloride, calcium fluorosilicate

[**] Square brackets in quotations indicate interpolations by the authors.

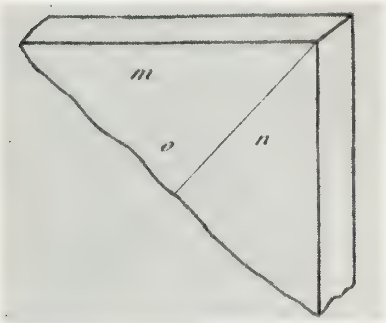


Fig. 3. Brewster's first illustration of an optically anomalous crystal (1815); when superimposed on a calcite crystal that gave a blue interference color, sectors *m* and *n* at the corner of the fluorspar crystal appear red and green, respectively [29].

In this first report of an optical anomaly, the cubic crystal was not only birefringent, it was not even homogeneous, but rather divided into sectors like those of the peroxide crystals (Fig. 2). Brewster speculated that the anomaly had probably originated during crystal growth:

> "If the laws which regulate the crystallisation of these minerals had been allowed an undisturbed operation, it is probable that the crystals would have had a perfect cube or an octahedron for their primitive form, and would have exhibited none of the phenomena of double refraction."

Brewster clearly understood that such optical properties imply a reduction from the symmetry of the crystal form. But he was in no position to identify the nature of the irregularities of growth which produce the deviations. During the next decade Brewster studied other optically anomalous minerals including chabazite,[37] garnet,[38] topaz,[39] and apophyllite.

2.3.2. Apophyllite

2.3.2.1. The Structural Basis for the Optical Anomaly of Apophyllite

It is worth interrupting the chronological narrative to describe apophyllite in greater detail, because its optical anomalies have been debated from Brewster's time until the present, and understanding these anomalies will help to focus the historical discussion.

Apophyllite is a silicate, empirical formula $KCa_4Si_8O_{20}F \cdot 8\,H_2O$, formed by hydrothermal recrystallization within cavities in rocks derived from lava.[40] The name (Greek: formed of leaves) reflects its ready cleavage perpendicular to the fourfold symmetry axis and its separation into layers on heating. The cleavage is consistent with the sheet structure revealed in 1931 by the X-ray study of Taylor and Náray-Szabó.[41, 42]

Silicate units form the covalent sheet shown in Figure 4. Each Si atom shares three oxygens with neighbors and is connected to a fourth, negatively charged oxygen by a bond that is roughly perpendicular to the sheet. Four silicate units make up a ring surrounding the crystallographic fourfold rotation axis that is perpendicular to the sheet, so that all four "axial" oxygens point toward the same side of the sheet. Axial oxygens of neighboring rings point toward the other side of the sheet.

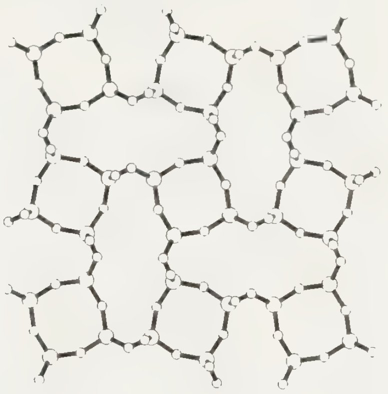


Fig. 4. Silicate units forming a covalent sheet in apophyllite, viewed along [001]. Axial oxygens of the rings in the center and corners of this figure point away from the viewer; those on the other four rings point toward the viewer.

Adjacent sheets are related by mirror symmetry (Fig. 5). Between silicate rings whose axial bonds point toward the mirror is a slightly flattened cube of negative oxygens; between those silicate rings whose axial oxygens point away from this mirror is a roughly spherical void with a diameter of about 8.5 Å. The void accommodates a potassium ion solvated by eight waters, and each cube of negative oxygens holds a square of four calcium ions surrounding a fluoride ion (Fig. 6). Potassium, calcium, and fluoride all lie on the mirror plane between silicate sheets.

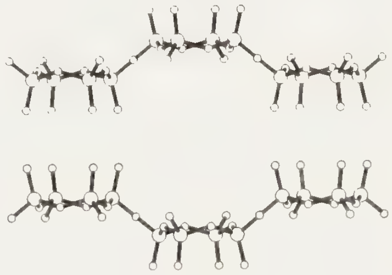


Fig. 5. Adjacent, mirror-related silicate sheets in apophyllite, viewed along [100].

As an apophyllite crystal grows, impurities from the hydrothermal medium can be incorporated into its lattice. Some possible substitutions are OH^- for F^- (hydroxyapophyllite), Na^+ for K^+ (natroapophyllite), Mg^{2+} for Ca^{2+}, and Al^{3+} for Si^{4+}.[43] Substitution for F or K does not disturb the local fourfold symmetry, since each lies on a fourfold axis,[44] but substitution for Ca or Si breaks the local symmetry. If growth occurs through a crystal face where a bias consistently inhibits substitution in some of the "symmetry-related" silicon (or calcium) sites, the fourfold

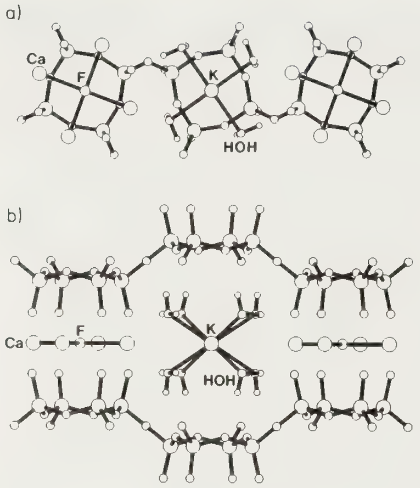


Fig. 6. View of the silicate sheets of apophyllite showing the positions of the water molecules and potassium, calcium, and fluoride ions between them: a) from the top along [001] and b) from the side along [100].

axis would disappear and the corresponding growth sector would be biaxial and optically anomalous.

Idealized patterns for thin sections cleaved perpendicular to the fourfold axis of optically anomalous apophyllite crystals are illustrated in Figure 7. They can be rationalized in terms of the growth of the crystal shown in Figure 8. The crystal displays three forms, or sets of symmetry related faces (Fig. 8a): two small square {001} or *basal* faces at the top and bottom, four hexagonal {110} or *prism* faces around the middle, and eight pentagonal {101} or *pyramid* faces between the basal and prism faces. Behind each face is a sector of the crystal that grew by deposition of material through that face. Figures 8b–d show the smaller crystal from which the crystal of Figure 8a grew, and the three classes of sectors that were involved in the growth. Figure 8b shows the two basal sectors, Figure 8c the four prism sectors, and Figure 8d the eight pyramid sectors. In indicating colors in Figure 7 we have assumed that when impurities are incorporated through the basal and prism faces they are not selectively ordered in a way that breaks the fourfold symmetry, but that those incorporated through a pyramid face are ordered so that the sector becomes biaxial, with axes oriented relative to the particular growth face. Thus when viewed through a polarizing microscope with a first-order red retarder, material from the uniaxial basal and prism sectors (Fig. 8b,c) appears red, while that from the biaxial pyramid sectors (Fig. 8d) is either yellow or blue.

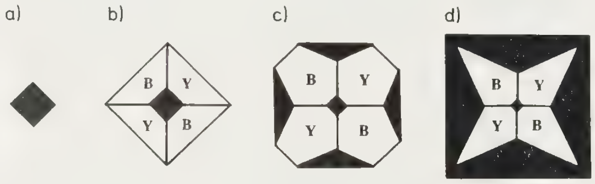


Fig. 7. Idealized patterns in thin sections of an apophyllite crystal (see Fig. 8) successively cleaved perpendicular to its fourfold axis and viewed with a first-order red retarder. Uniaxial sectors appear red (shown as black), biaxial sectors appear blue (B) or yellow (Y). For detailed explanation, see text.

The section of Figure 7a came from the very top of the crystal in Figure 8a, and thus includes only material from the uniaxial basal sector. Section 7b came lower in the crystal, so a somewhat smaller basal square is surrounded by trapezoidal portions from the four adjacent biaxial pyramid sectors. The octagonal section 7c came lower still so that it intersected both pyramid and prism faces. Thus the small central square is surrounded by hexagonal portions from pyramid sectors while the horizontal and vertical edges include triangular portions of uniaxial prism sectors. Section 7d originated so low in the crystal that it intersected only prism faces. The border is all material from uniaxial prism deposition. The center is a small square from the uniaxial basal sector which is surrounded by portions of four biaxial pyramid sectors.

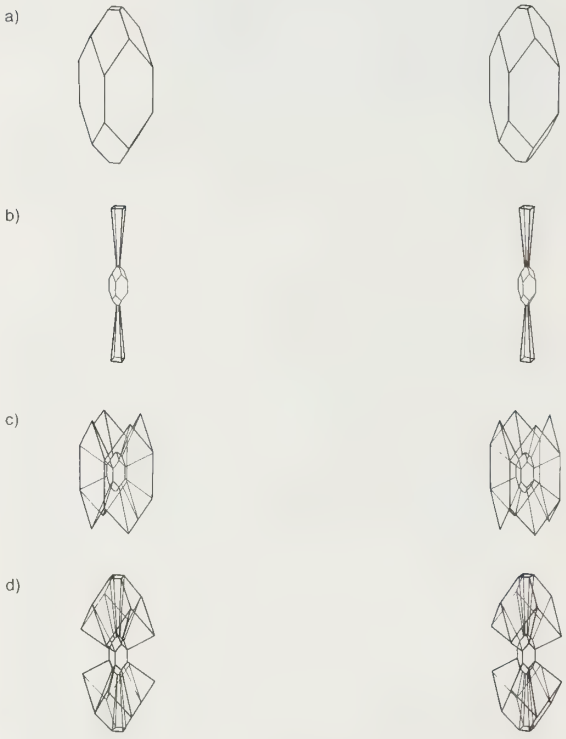


Fig. 8. Stereo views of a typical optically anomalous apophyllite crystal. a) The three sets of symmetry-related faces: two *basal* faces at the top and bottom, four *prism* faces around the middle, and eight *pyramid* faces between the basal and prism faces. b)–d) The smaller crystal from which the crystal of a) grew, and the three classes of sectors that were involved in the growth: b) basal sectors, c) prism sectors, d) pyramid sectors.

2.3.2.2. *Brewster and Apophyllite*

Sir David Brewster (Fig. 9), whose name is recalled in Brewster's angle, made many contributions to mineralogy, crystallography, and physical optics.[45] Besides inventing the lenticular stereoscope and the kaleidoscope, he became the first to suggest that spectroscopy be used for chemical

Fig. 9. David Brewster (1781–1868), a pioneer in the development of optics [45], first observed anomalous birefringence in crystals and speculated with keen insight on its origin.

analysis when, after observing that certain lines are removed from the solar spectrum when the light passes through NO_2 gas, he wrote of

> "a general principle of chemical analysis in which simple and compound bodies might be characterized by their action on definite parts of the spectrum."[46]

Brewster, who made so many fundamental scientific contributions, underlined the importance he assigned to his work on the optical anomaly of apophyllite in a striking, if indirect way. Since he held no academic appointment until his 56th year, he was forced to rely on editing and voluminous writing to support his family. In 1819 he launched a new enterprise by founding *The Edinburgh Philosophical Journal.* For the very first paper in this journal Brewster chose his own contribution *On a New Optical and Mineralogical structure exhibited in certain specimens of Apophyllite and other minerals.*[47]

Upon examining slices of apophyllite crystals cut normal to the unique axis of a tetragonal prism Brewster observed figures resembling "tesselated pavements" in which the presumed uniaxial crystal was actually composed of discrete biaxial tiles (Fig. 10a). "The interior conformation of Apophyllite," he conjectured, "presents us with the new fact in crystallography, that a regular crystalline form arises from the union of smaller crystals whose homologous sides are not parallel to each other… The tessellated structure which is possessed by [these crystals] is a property so singular and so distinctive, that I would propose to mark it by the name of *Tesselite.*"

In 1821 Brewster published a more detailed *Account of a Remarkable Structure in Apophyllite, with Observations on the Optical Peculiarities of that Mineral,*[48] in which he even used hand-colored plates to illustrate the sectoring. He described new specimens of anomalous apophyllite and drew remarkably prescient conclusions regarding the growth of these unusual objects. It seemed to him that crystal growth by orderly aggregation of identical minute particles must create a body that is

> "homogeneous throughout, possessing the same mechanical and physical properties in all parallel directions… The tessellated Apophyllite, however, could not have been formed by this process. It resembles more a work of art, in which the artist has varied, not only the materials, but the laws of their combination… The boundaries of these corresponding, though distant zones, are marked with the greatest precision, and all their parts as nicely adjusted, as if some skilful workman had selected the materials, measured the spaces they were to occupy, and finally, combined them into the finest specimen of natural Mosaic."

He went further to emphasize that ordinary twinned crystals

> "…and those compound groups which arise from the mutual penetration of crystals, are merely accidental deviations from particular laws, which govern the crystalliza-

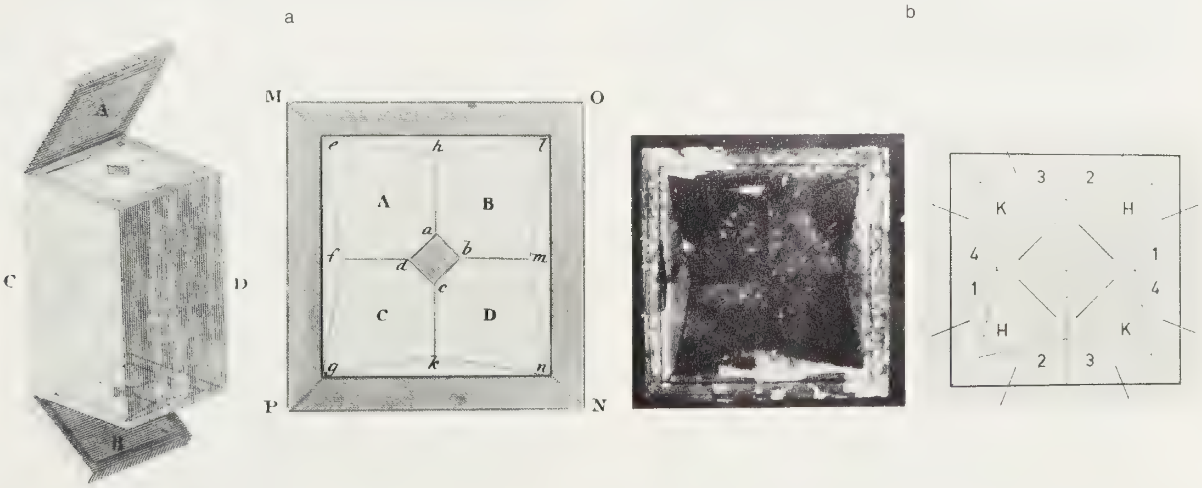


Fig. 10. a) The drawing of Brewster's apophyllite shows on the left a thin section being removed from a square prism, and on the right a projection of that slice revealing nine optically discrete tiles [48]. b) Photomicrograph and diagram of a similar apophyllite section reported in 1965 by Sahama, who attributed the optical inhomogeneities to "penetration twinning" [155].

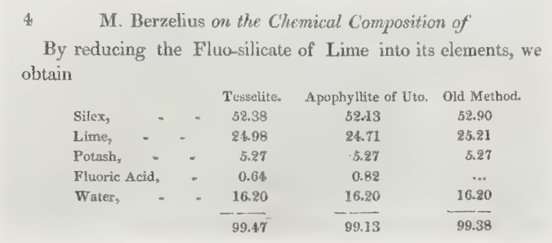
> tions in which they occur... The compound structure of the Apophyllite, however, cannot be referred to these capricious formations. It is itself the result of a general law, to which there are no exceptions, and when more deeply studied, and better understood, it must ultimately lead to the introduction of some new principle of organisation, of which crystallographers have at present no conception."

Brewster was almost correct when he supposed that tesselite must have been assembled in concentric stages (first a uniaxial core, then surrounding biaxial tiles, and finally a uniaxial border), but he was unable to suggest the "new principle of organisation" that could rationalize this sequence of events.

2.3.3. *Berzelius's Chemical Analysis*

Since there might have been a chemical difference between tesselites and other apophyllites, Brewster asked Jöns Jakob Berzelius (1779–1848) to compare their chemical compositions. Not only was Berzelius Europe's leading analytical chemist, he had also been the first scientist to propose a chemical classification of minerals.[49] He recognized silica as capable of forming a "negative" constituent and identified the Silicates, of which apophyllite was an example, as those minerals that contained it.[50] In 1822 Berzelius reported that analyses of anomalous and normal apophyllites agreed for every component within 0.3% (Fig. 11) and he added:[51]

> "Differences of this kind, however great be the influence which they exercise upon light, can never constitute differences of species in mineralogy, differences which can only be founded on a real diversity of composition."



4 M. Berzelius *on the Chemical Composition of*

By reducing the Fluo-silicate of Lime into its elements, we obtain

	Tesselite.	Apophyllite of Uto.	Old Method.
Silex, - -	52.38	52.13	52.90
Lime, - -	24.98	24.71	25.21
Potash, - -	5.27	5.27	5.27
Fluoric Acid, -	0.64	0.82	...
Water, - -	16.20	16.20	16.20
	99.47	99.13	99.38

Fig. 11. Analyses by which Berzelius established the chemical identity of Tesselite with apophyllite, as published in Brewster's journal [51]

This assertion drew a stern retort from Brewster:[52]

> "Of the three methods of analysis, we conceive the crystallographic method [measuring crystal dimensions] to be the least perfect; the chemical method next to it; and the optical method decidedly superior to both... When the chemist determines that two bodies have the same ingredients, he is ignorant of the manner in which these ingredients are combined. If the analysis of a quadruped and a bird indicated the same elements, he could not discover that these elements formed hair and horn in the one, while in the other they displayed themselves in the finest plumage. The chemist, indeed must fail in detecting structures, because he commences his process by destroying them."

Thus long before chemists spoke of structure Brewster criticized the analyst's neglect of possible isomerism. Berzelius was not to not coin the word "isomer" for another eight years.[53] Insisting on the uniqueness of tesselite Brewster continued:

> "It would be a strange abridgment of the privileges of the optical observer, if he were not permitted to designate by a new name a body which possesses one of the most remarkable structures that has ever come under the notice of the mineralogist."

2.3.4. *Biot's Initial Interpretation*

Brewster's work on optical anomalies went largely unnoticed.[54] The only contemporary comments on his observations came from the two other authorities on crystal optics, J. F. W. Herschel (1792–1871)[55] and J.-B. Biot (Fig. 12), a leading French physicist and crystallographer, whose name is recalled in the Biot and Biot-Savart Laws of electromagnetism.

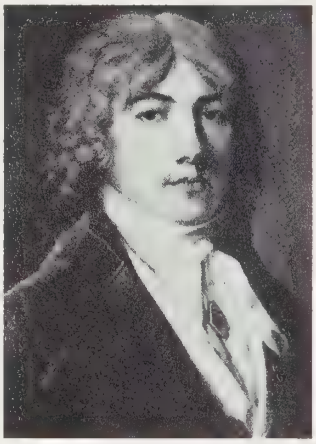


Fig. 12. Jean-Baptiste Biot (1774–1862) attempted the first comprehensive explanation of optical anomalies in crystals with his *Mémoire sur la polarisation lamellaire* (1841) [59, 61]. This theory of Lamellar Polarization was popular but not successful.

Biot and Brewster were rivals of a sort. They exchanged visits and correspondence, referred to one another in writing in the most respectful terms, and tried to collaborate, but they seem to have been fundamentally incompatible. Representatives of nations recently at war, they had a number of common interests which put them at loggerheads, including the mental health of Isaac Newton.[56] Biot took a deep interest in Brewster's "new class of doubly refracting crystals." He attributed the optical anomalies that Brewster had "accidentally" observed to stress caused by rapid cooling or evaporation during crystal growth.[57] For support Biot cited Brewster's own observation that pressure could generate analogous birefringence in animal gelatin and glass (Fig. 13).

Brewster was offended that the fruit of his systematic studies should be termed "accidental" and responded:[36]

> "Had M. Biot repeated the experiments to which he alludes... and compared the results with those produced by

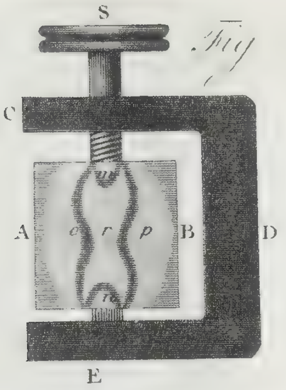


Fig. 13. A piece of glass rendered birefringent by pressure (Brewster, 1815) [81 a]. The letters mark progressive changes in the interference colors between pressure points *m* and *n*. A, B = white; *o*, *p* = yellow; *r* is of higher order

> heat and rapid evaporation, he would have instantly seen that the two classes of phenomena are essentially distinct, and could not possibly have the same origin."

Brewster objected both because the birefringence was too strong to be explained plausibly by stress and because the sector boundaries were so regular. In his view some higher law must be at work. Much later Brewster wrote that he had convinced Biot, in a private communication, that the phenomenon was not due to extreme external conditions.[58]

2.4. Twinning Hypotheses

2.4.1. *Biot's Lamellar Polarization*

Biot undertook an extensive study of optical anomalies that culminated[59] in 1842 in what Brewster called an "elaborate Memoir peculiarly marked by the genius and sagacity of that distinguished philosopher."[60] Biot presented this theory of *polarisation lamellaire* in three lectures to the Academy of Sciences in Paris.[61] In fact lamellar polarization was not theory at all, but rather the hint of an analogy. He suggested that, if a stack of glass slides can impart plane polarization to transmitted light by repeated refraction, it would not be surprising if a stack of crystal lamellae could impart elliptical polarization. Thus a set of lamellae might possess birefringence that individual layers lacked. Biot's distinction between contributions due to the elementary molecular particles and contributions due to the macroscopic crystal structure was central to his theory.

The ready cleavage of apophyllite made it a natural candidate for Biot's analysis. He wrote:

> "...aucune corps jusqu'ici connu ne s'est montré plus désespérant pour les cristallographes, ni plus riche en effects optiques pour les physiciens... Sans cette analyse intime et complète, le minéralogiste qui s'arrête aux formes ne connaît pas plus un cristal d'apophyllite, qu'on ne connaît une lettre par son enveloppe, un livre par sa couverture, un écrin par l'étui où il est renfermé... Tous les phénomènes optiques opérés par les diverses variétés de cristaux d'apophyllite résultent de la simultanéité des actions moléculaires... Les premiers dépendant de leur axe double réfraction unique... et les autres de l'existence des systèmes lamellaires..."[*]

Because of the optical complexity of some tesselite samples Biot began to invoke intricate systems of *hypothetical* lamellae, first in apophyllite and then in anomalous crystals of other minerals that showed no independent sign of layering. He proposed that the phenomenon provided a new structural tool:[62]

> "Cette manière simple de pénétrer dans l'intime structure du cristal total, décèle une infinité d'accidents de pénétration que l'on ne soupçonnerait jamais par le seul aspect des faces externes."[**]

Biot observed that alum crystals containing ammonia were anomalous, and inferred from his theory that they must be layered. Brewster challenged this interpretation, because alum free of ammonia was optically normal. Since the two alums must be equally lamellar, Brewster reasoned, the double refraction must be due to an inherent property of ammonia and not to lamellar crystal structure.[63] Brewster asserted that despite Biot's ingenuity his lamellar structures were "scarcely to be reconciled with the principles of crystallography."[64]

During the 1820s neither Brewster nor Biot subscribed to the wave theory of light.[65b] Prior to its general acceptance sundry phenomena were explained by invoking new species of polarization.[25] Now defunct ideas of *chromatic polarization, alternate polarization,* and *proportionate polarization* proliferated in the early 19th century. *Mobile polarization* involving elaborate gyrations of the "luminous molecules" as they passed through crystals was another of Biot's bizarre inventions.[28, 66] Lamellar polarization was just such an ad hoc concept, and Biot made no attempt to put the analogy with polarization by a stack of glass slides on a theoretical foundation:[67]

> "...je n'ai pas cru devoir taire ces analogies, si éloignées qu'elles pussent être... j'ai pensé qu'il n'était pas inutile d'indiquer les connexions... afin de les présenter aux théoriciens qui auraient l'habilete de les rendre plus intimes, si elles peuvent le devenir."[***]

No theoretician was equal to this challenge. Nevertheless, Biot's reputation and authority attracted the attention of many crystallographers to the problem of optically anomalous crystals. In 1846 a leading German crystallographer Eilhard Mitscherlich (1794–1863) assigned the optical

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[*] ...no substance thus far known has been more exasperating for crystallographers, nor richer in optical effects for physicists... Without such an intimate and complete analysis the mineralogist who stops at forms would no more understand a crystal of apophyllite than one understands a letter by its envelope, a book by its cover, or a jewel by the box that contains it... All the optical phenomena... result from the simultaneity of molecular and nonmolecular effects... The former deriving from their unique axis of double refraction, and the others from the existence of lamellar systems

[**] This simple way of penetrating into the intimate structure of a total crystal reveals an infinity of accidental penetrations that one would never suspect from the external aspect of the faces

[***] I have not thought it appropriate to silence these analogies, however remote they might be [but rather to] present them to theoreticians who have the skill to make them closer, if possible

anomaly of sodium chlorate to lamellar polarization and communicated his observations to Biot, who reported them to the French Academy of Sciences.[68] In 1848, the revolutionary year in which he demonstrated resolution of racemate salts in Biot's Collège de France laboratory, the young Louis Pasteur (1822–1895) published a note on sector twinning in crystals of potassium sulphate.[69] M. L. Frankenheim (1801–1869) in Breslau, an independent inventor of the theory of point lattices,[70] also adopted a version of Biot's theory.[71]

2.4.2. *Microscopic and Macroscopic Views*

Over the next thirty years most references to lamellar polarization were in the context of alternative explanations of optical anomalies. Most of the propositions were of two types, *stress theories* and *twinning theories,* each of them related in a way to Biot's thinking.[72]

Stress theories resembled Biot's theory in attributing birefringence to a macroscopic physical source, rather than to a molecular source, but they differed in assuming that the source was anisotropic mechanical stress in a solid continuum, rather than lamellar discontinuities. For example, in his 1855 Breslau habilitationsschrift Marbach suggested that whether or not a crystal was lamellar, its optical anomalies were due to tension as in stressed glass.[73] In a hybrid theory of 1852 Wertheim proposed that crystals without lamellar polarization can acquire it if pressure causes their irreversible separation into layers.[74]

Twinning theories resembled lamellar polarization in supposing that anomalous crystals were composed of many domains, but differed in attributing birefringence to reduced symmetry at the molecular level within each domain. The most successful of these, Mallard's theory of network twinning, is discussed in Section 2.4.3.

During the quarter century that followed Biot's hypothesis, optical anomalies were sometimes attributed to twinning, sometimes to stress. In the decade following the Franco–Prussian War, these views became doctrinaire and strongly polarized along national lines.

2.4.3. *Mallard's Network Twinning*

Perhaps no researcher in the 19th century did more to encourage the microscopic view of the internal structure of crystals than Auguste Bravais (1811–1863). His theory of the point lattices showed how crystals with different external forms might be composed of repetitively translated elemental units. This work inspired Ernest Mallard (1833–1894), Professor at the École supérieure des Mines (Fig. 14),[75] in his efforts to understand anomalous crystals.[76]

Mallard became spokesman for the French view of optical anomalies in 1876 by publishing a comprehensive theory in the *Annales des Mines* that relied heavily on the existence of Bravais lattices.[77] After rejecting lamellar polarization because it depended on a weak analogy and hypothetical crystal fissures,[78] he presented a theory based on a different kind of domain structure.

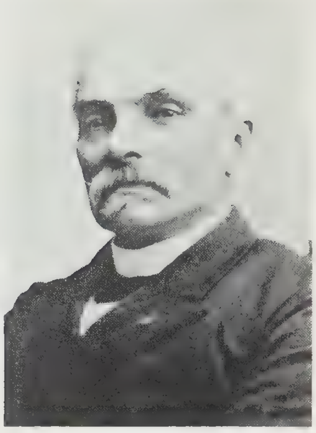

Fig. 14. Ernest Mallard (1833–1894) championed a "twinning model" in his 1876 treatise on anomalous birefringence [77]. Because it required the existence of hypothetical crystalline lamellae, it could be considered a successor to Biot's theory of Lamellar Polarization

Mallard assumed that optical anomalies and a number of other peculiarities are due to isomorphism. When two different unsymmetrical "integrant molecules" accidentally have similar cell dimensions it is possible to mix them in a single lattice. In the same way, when a single unsymmetrical "integrant molecule" has dimensions that are close to those for a symmetrical cell, it is possible to align differently oriented biaxial domains into a twinned structure that mimics higher symmetry. In Mallard's view, symmetrical crystals can arise from the interpenetration of isomorphous space lattices which have little or nor symmetry. He applied his analysis to several dozen mineral substances with cubic, hexagonal, and tetragonal morphologies.

One of these minerals was apophyllite. More than half a century after Brewster's original report Mallard wrote:[79]

> "L'apophyllite est une des substances dont les propriétés optiques ont le plus excité l'étonnement. Signalées pour la première fois par Brewster, qui a particulièrement examiné les surprenantes figures... à la lumière polarisée parallèle... ces anomalies optiques n'ont reçu encore aucune explication satisfaisante."[*]

Mallard then argued that Brewster's tesselite was simply a twin made up of biaxial sectors. He rationalized the uniaxial regions of apophyllite in terms of accidental compensation of birefringence between interleaved submicroscopic lamellae in different orientations. Had Brewster still been living, he would surely have objected that this "explanation" avoided the fundamental problem: what kind of law determined the exquisite twinning pattern? The modern interpretation explains the pattern in terms of orientation at the crystal surfaces through which different sectors grew, and indeed Mallard noticed that differently oriented sectors in garnet were related to the external growth faces. But he provided no explanation for the mechanism of orientation, and no aspect of his theory endured.

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[*] Apophyllite is one of the substances whose optical properties have aroused the most astonishment. Indicated first by Brewster, who examined particularly the surprising patterns... in parallel polarized light... these optical anomalies have still received no satisfactory explanation.

2.5. Stress Hypotheses

2.5.1. External Stress

Brewster had shown as early as 1814 that optically isotropic bodies, like glass and gelatin, become birefringent if stressed anisotropically by irregular heating[80] or compression.[81] A number of researchers assumed that stresses must account for the anomalous double refraction in regularly shaped crystals. Reusch, for example, proposed in 1867 that deposition on the surface of a growing crystal involved an intermediate state analogous to a colloid in that it would contract on solidification. This external stress from the crystal border could be the source of birefringence.[82]

From 1880 the various stress interpretations were dominant in Germany. Their principal exponents were Friedrich Klocke (1847–1884) and Carl Klein (1842–1907) (Fig. 15),[83] professors of mineralogy at the Universities of Marburg and Göttingen, respectively, and their students. Klocke followed the external stress interpretations of Marbach and Reusch[84] and showed the effects of anisotropic forces on the interference patterns of uniaxial crystals.[85] The stress hypothesis gained considerable impetus when Alfredo Ben-Saude, a student of Klein, allowed gelatins to dry rapidly in molds made in the shape of optically anomalous crystals (Fig. 16). Sections of the dried gelatins were birefringent and showed sectoring analogous to that of corresponding crystal sections.[86, 87] Ben-Saude assumed that rapid crystallization, like rapid drying of the gelatins, caused stress within the crystalline structure.

Fig. 15. Carl Klein (1842–1907) believed that external stresses resulting from catastrophic events in a crystal's history could account for anomalous birefringence

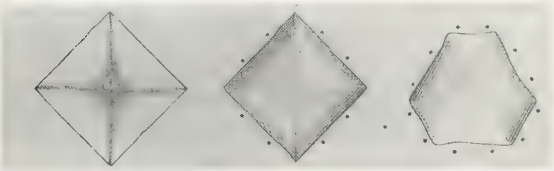

Fig. 16. Sections showing Ben-Saude's attempts to mimic anomalously birefringent crystals with rapidly dried, molded gelatin. Barbells in the center and right figures show indicatrix orientations in the different sectors as observed with crossed polarizers and a first-order red retarder [86]

Klein studied the effects of rapid heating and cooling on crystals, particularly the igneous minerals, boracite and leucite.[88] He subscribed to the theory that cataclysmic events in a crystal's history could account for the anomalies in many cases. As coeditor of the journal *Neues Jahrbuch für Mineralogie*, the principle forum for research on optical anomalies, Klein was an effective spokesman for this point of view, and was widely remembered as its leading proponent.[89]

Klocke, Klein, and Klein's student Friedrich Rinne (1863–1934) each studied and published on anomalous apophyllite. Like every predecessor except Brewster, each of them saw in apophyllite what he expected to see. Klocke[90] and Klein[91] both noted the relationship of the sectors to the external faces. The same relationship was used in Section 1.2 to support the modern view of sectoring by selective incorporation of impurities in apophyllite, but Klocke and Klein interpreted the relationship as evidence for stress exerted perpendicular to the growth faces. Rinne, noting that three different sectors participated in the same etch figure, inferred that they were not separated by the structural discontinuity that might have been expected from Mallard's twinning.[92]

2.5.2. Internal Stress Due to Impurities

Brewster's early speculation that the anomaly of apophyllite might be due to variation in its composition was refuted by the apophyllite analysis of Berzelius. In 1860 Leander Ditscheiner (1839–1903) revived interest in impurities when he suggested that optical properties could be adjusted over a wide range by averaging contributions from two isomorphous components in a mixed crystal.[93]

In 1882 Klocke encouraged his student Reinhard Brauns (1861–1931) (Fig. 17) to enter a university competition, which he won with a study of optically anomalous crystals.

Fig. 17. Reinhard Brauns (1861–1931) attributed anomalous birefringence to internal stress [112]. As a student in Marburg he launched his successful career in mineralogy by studying the role of impurities in this phenomenon.

Brauns continued this work and soon suggested that anomalous double refraction in some simple salts must be due to impurities.[94] Pure crystals of alum and barium nitrate were optically normal, but adding ammonium alum or lead nitrate, respectively, gave optically anomalous crystals. Since so many anomalous crystals were known to contain impurities, Brauns proposed that the cause of the anomalies could indeed be stress, but *internally* imposed stress resulting from a guest species acting upon the mismatched lattice of the host.

Klocke died suddenly in the summer of 1884 at the age of 37. Brauns continued the work in Marburg alone, developing his idea in a dissertation on optical anomalies in 1885,[95] and in a habilitationsschrift on the same subject two years later.[96] Although he focused on stress, in some ways Brauns's understanding of the relationship between impurities and optical anomalies by 1890 was quite similar to our present view:[97]

> "Die Spannungen entstehen durch den Eintritt der zwar isomorphen, aber doch chemisch und physikalisch etwas verschiedenen Substanz... Wenn wir uns vorstellen, dass bei dem Wachsen der Krystalle die Theilchen sich in Ebenen nach bestimmten Richtungen ablagern... so können wir hinzufügen: Die... auftretenden Kräfte ändern in den zu vorhandenen Krystallflächen gehörenden Anwachskegeln das optische Verhalten nach der geometrischen Symmetrie dieser Flächen."[*]

Our present view, like Ditscheiner's, assigns the optical effect to the direct contribution of an impurity rather than to its indirect mechanical influence on the host lattice. Ben-Saude, who showed that some mixed crystals with regular forms were optically normal, continued to favor the theory of external stress,[98] but Brauns faced a more serious challenge from France.

2.5.3. *Criticism of the Stress Hypothesis*

Stress as the explanation of crystal anomalies had been considered and rejected previously, when Brewster discounted Biot's suggestion in 1818.[36] Biot ultimately agreed and reported in his *Memoir on Lamellar Polarization*[59] that when he had shattered an anomalous crystal to relieve the hypothetical stress and reassembled the pieces, they produced the same anomalous effect on light as in the undamaged state.

Mallard published a rebuttal of the German interpretations in 1886.[99] He dismissed Klein's idea that anomalies are caused by rapid cooling, because the boundaries between sectors are sharp, and not gradual as in unannealed glass. He further contended that rapid cooling produces birefringence only in amorphous substances like glass and gelatin. Brauns quickly reported that birefringence is produced by sudden cooling of rock-salt crystals.[100] Mallard tried to dismiss Brauns's hypothesis involving isomorphous impurities by noting that many confirmed solid solutions are not optically anomalous.

Paul Groth (1843–1927) was atypical in Germany because he was inclined favorably toward Mallard's hypothesis.[101] His monumental *Physikalische Krystallographie* shows that he had a deeper appreciation of thermodynamic influence on crystal structure than his contemporaries.[102] Groth wondered how internal tensions could be the cause of the optical anomalies in simple salts grown from solution. He questioned the relevance of the gelatin experiments to crystalline materials because, in his view, any crystal must represent the most stable balance of forces among its constituent particles.[103]

Mallard's crowning achievement was his *Traité de cristallographie géométrique et physique*.[104] The first two volumes covered the geometrical and physical aspects of crystals. The third volume on crystalline assemblages would have addressed optical anomalies and answered his critics most fully. Although the manuscript had supposedly been completed, it was never found after the author's sudden death in 1894.[105]

2.6. The Golden Age of Optical Anomalies

2.6.1. *Explosion of Research on the Optical Anomalies*

The inauguration of Groth's *Zeitschrift für Krystallographie* in 1877 marked the emergence of crystallography as a mature science independent of geology.[106] Groth was concerned with the form and physical properties of all crystalline materials, mineral, organic, and synthetic, regardless of their origin. The *Mineralogical Magazine* was started by the Mineralogical Society of London in 1876. The *Bulletin de la Société Minéralogique de France* first appeared in 1878, as did Gustav Tschermak's *Mineralogische und Petrographische Mittheilungen* from Vienna. These new journals were required to accommodate the rapid expansion in crystallographic research. Mallard's comprehensive theory was new and controversial, and the time was ripe to support or criticize his hypothesis. Reports of optical anomalies and speculations on their source blossomed about 1880. Figure 18

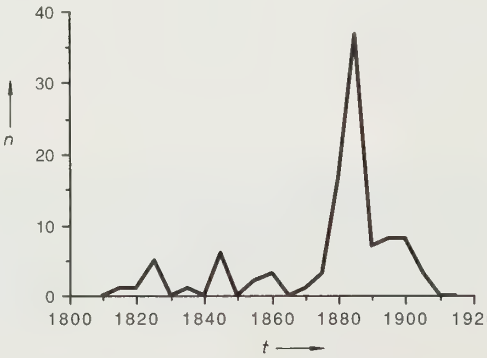

Fig. 18. The rise and fall of interst in research on optically anomalous crystals, based on the 99-reference bibliography of Johannsen (1919). n = number of citations, t = time in years

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[*] The stresses result from inclusion of a substance that is indeed isomorphous, but somewhat different chemically and physically... If we assume that during crystal growth the pieces are added in planes with given orientations.. we can conclude [that the stresses will] alter the optical properties of growth sectors related to given crystal faces according to the geometrical symmetry of these faces

plots the publication dates of the 99 significant papers on optical anomalies from 1815 to 1915 that were reviewed by Johannsen in 1918.[107] The steady stream of publication became a torrent in the 1880s, but it quickly shrank and disappeared about 1900.

The scientific significance of optical anomalies one hundred years ago is underlined by the professional stature of the principle researchers. From 1878 to 1892 six different active participants in the debate served as president of the French Mineralogical Society,[108] and all the principal crystallographic journals were edited by participants: Groth, Klein, Brauns, and Tschermak, as well as Rosenbusch, who edited *Neues Jahrbuch für Mineralogie, Geologie, und Paläontologie.*

2.6.2. Brauns's "Die Optischen Anomalien"

By 1890 the question of the cause and nature of optical anomalies had become so confused and contentious that, at the instance of Ferdinand Zirkel (1838–1912), professor of mineralogy at Leipzig,[109] the Fürstliche Jablonowski'schen Gesellschaft zu Leipzig[110] announced its competition[111] for

> "eine übersichtliche und kritische Zusammenstellung der auf die 'optischen Anomalien' der Krystalle bezüglichen bisherigen Forschungen, sowie die Ausführung neuer Untersuchungen, welche geeignet sind, die Ursachen jener anomalen Erscheinungen näher zu erläutern."[*]

The prize was awarded to Reinhard Brauns, now a privatdozent at Marburg, and his book, *Die Optischen Anomalien der Krystalle*, was published by the Society in 1891 (Fig. 19). This comprehensive 380-page monograph was an example of outstanding scholarship and served to launch Brauns's long and distinguished academic career that would include professorships in Karlsruhe, Kiel, Giessen, and Bonn.[112]

Although the book naturally represented Brauns's point of view, he discussed the contributions of others fully and for the most part fairly. For the title page he chose a motto from Goethe,[113] that evokes both the structure of anomalous crystals and the role he assumed as mediator:

> "Wo Parteien entstehen, hält Jeder sich hüben und drüben;
> Viele Jahre vergehn, eh' sie die Mitte vereint."[**]

He presented detailed discussions of some six dozen substances, most of which were anomalously birefringent crystals with optically discrete growth sectors (Fig. 20). In addition to apophyllite these included mixed crystals of barium nitrate and of alum as well as boracite, leucite, rock salt, garnet, analcime, chabasite, milarite, and pharmacosiderite. Brauns attributed most of these optical anomalies to internal stress resulting from inclusion of isomorphous impurities. But since many of the substances appeared to be pure, he did not insist that all optical anomalies conform to his model. He attributed many examples to external forces in the crystal's past history, such as mechanical compression, rapid cooling, or uneven heating. There were also categories for anomalies associated with solid–solid phase transitions, and for cases where no etiology could be identified.

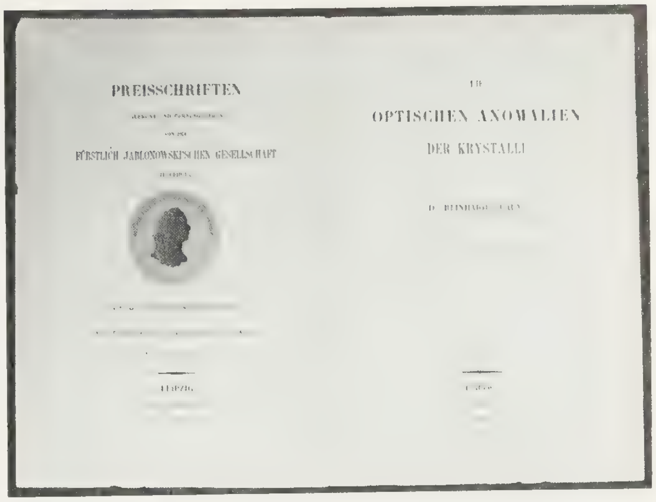
PREISSCHRIFTEN
FÜRSTLICH JABLONOWSKI'SCHEN GESELLSCHAFT
LEIPZIG
OPTISCHEN ANOMALIEN
DER KRYSTALLE

Fig. 19. Title page from Brauns's scholarly classic *Die Optische Anomalien der Krystalle* (1891). The book attempted, and for the most part succeeded, to present research on optically anomalous crystals as a closed subject [35a]

Notably absent was a category for network twinning. After discussing Mallard's hypothesis extensively, Brauns was emphatic in discarding it. He acknowledged that optical complexity could arise from differently oriented lamellae as in micas, but considered it fundamentally different from the sectoring produced by other mechanisms.[114] Despite this bias Brauns's book remains by far the most carefully reasoned, most objective, and most comprehensive source on the 19th century literature.

That Brauns had, for the first time, encapsulated all the experimental and theoretical observations on optical anomalies within a single volume may have given his work more authority than it merited. Subsequent writers frequently cited *Die Optischen Anomalien* as the definitive source,[115] and many of his assignments as to the cause of anomalous birefringence undoubtedly went unchallenged because of the impressive detail and scholarly excellence of the work.

2.6.3. Optically Anomalous Organic Crystals

Of all the anomalous crystals discussed by Brauns, only one was organic. This was strychnine sulfate hexahydrate, whose optical anomaly had been decribed in 1884 by Grigori Wyrouboff (1843–1913), a follower of Mallard in Paris,[116] then reinvestigated by Johannes Martin, a doctoral student of Klein[117] in Göttingen. Martin's dissertation was published in 1891,[118] the same year Brauns's text appeared. In addition to strychnine sulfate (Fig. 21) Martin described optical anomalies in pentaerythritol, benzil, and guanidinium carbonate. Two of these had also been discovered by Wyrouboff.

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[*] a critical collection and overview of previous research related to the 'optical anomalies' of crystals as well as of the results of recent research which are appropriate to explain more fully the source of these anomalous phenomena

[**] Where parties arise, each remains here or there:
Many years pass, before the middle unites them.

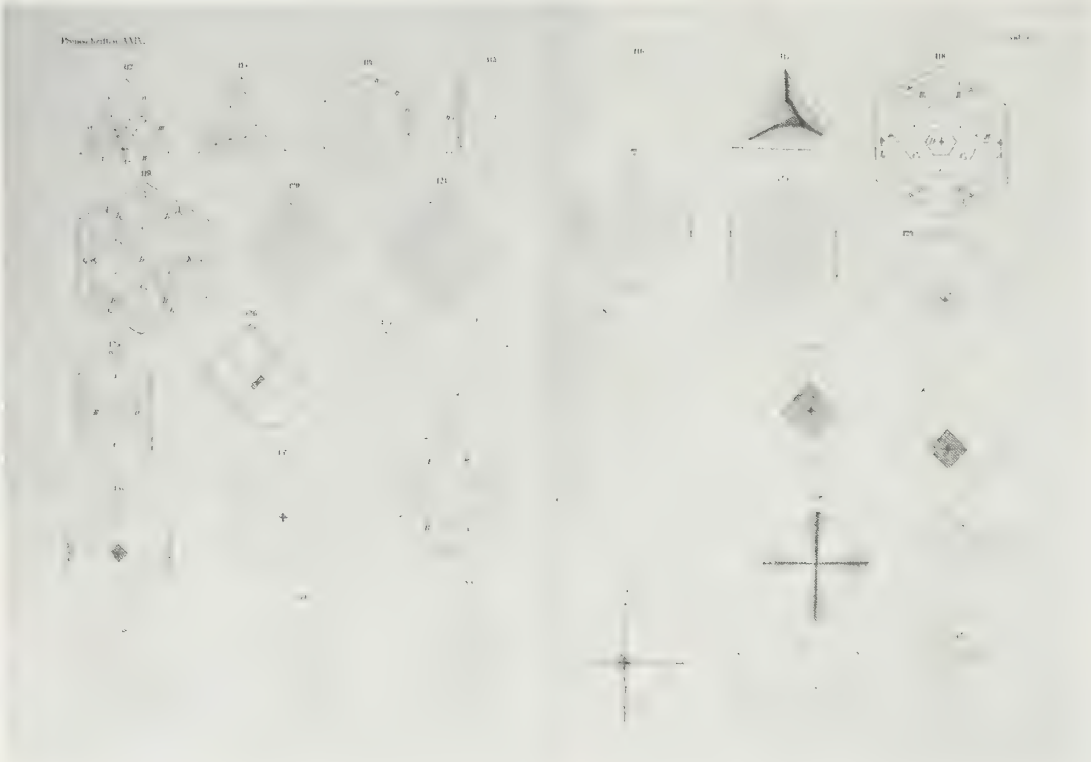

Fig. 20. Typical illustrations of optically anomalous minerals from Brauns's monograph [35a]. These figures, due among others to Mallard, Klein, and Brauns, show chabazite (112–115), apatite (116), diadelphite (117), corundum (118–119), vesuvianite (120–128a), apophyllite (129–132), an isomorphous solution of sodium ammonium sulfate and chromate (133), topaz (134), analcime (135–141), and eulytine (142).

Rejecting Mallard's theory, Martin was inclined toward the stress hypothesis, although he puzzled at how these ostensibly pure substances could give rise to the kind of optical anomaly that Brauns had attributed to solid solutions. To invoke external stress from drastic growth conditions seemed less appropriate for molecular crystals than for minerals. Martin suggested that the inherently isotropic particles were stressed by the "skeleton" of the crystal that had been previously laid down. Wyrouboff, who would later eulogize Mallard as the greatest philosopher of crystallography since Haüy,[106] excoriated Martin's dissertation, which he characterized as a stack of contradictory hypotheses.[119]

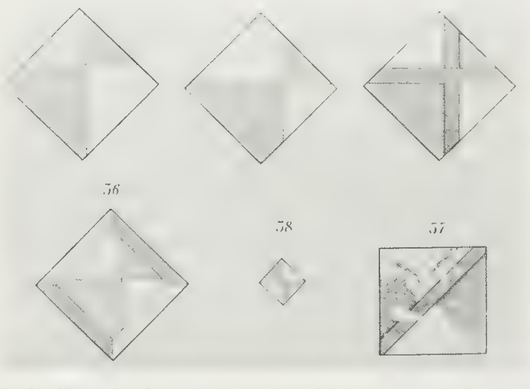

Fig. 21 Illustration from the dissertation of Johannes Martin showing sectored crystals of strychnine sulfate hexahydrate [118]. The complex pattern at the top right was interpreted as a superposition of the two layers with simple hour-glass figures on the left. The "picture-frame" pattern on the lower left has been observed for many substances (cf. Fig. 24c, 28c, d).

Other anomalous organic crystals were discovered at the end of the 19th century and will be discussed in Section 3.2.

2.6.4. Why the Research Waned

By the early 20th century optical anomalies had ceased to be a field for active research, even though the simple modern interpretation described in Section 1.2 had not been considered. Crystallography and mineralogy texts continued to include a short section on optical anomalies, usually deferring to one or more of the accepted hypotheses. In the absence of active research, hypotheses became dogma, even though none of them really explained the facts.

There are at least four reasons for the demise of this line of research:

1. Mallard died in 1894, and his successors in France did not have the prestige or interest to continue the debate.
2. Brauns's monograph was seen as so authoritative that many researchers, particularly in Germany, incorrectly considered the question to be closed.
3. The scientific community became bored with the polemic. Already in 1887 a review had begun, "The never-failing discussion of the optical anomalies of crystals is contin-

ued by R. Brauns, who combats the assertion of Mallard..."[120]

4. Interest in crystallographic research shifted away from bulk properties toward developing the kind of detailed structural model for crystals that had become so successful for molecules in organic chemistry.

2.7. Arrangement of Atoms within Crystals

Elaboration of the 230 space groups by Fedorov[121] and Schoenflies[122] in 1891 encouraged crystallographers to speculate in more detail about the internal structure of crystals. William Barlow (1845–1934), a self-taught crystallographer who would ultimately derive the space groups independently, tried to relate the external form of crystals to the symmetrical internal arrangement of their constituents.[123] Like other crystallographers since the days of Haüy, Barlow began by using spheres or other bodies to model crystal packing.[124] He ultimately realized that the variability of form reflected in the crystal kingdom could be more closely approximated by packing particles of different size. His close-packed models of dissimilar spheres agree remarkably well with modern models of simple binary salts.[125]

Barlow's 1897 treatment of the internal structure of crystals considered the problem of optical anomalies at length and relied heavily on the viewpoint of Brauns.[126] Like Brauns he believed that one class of optical anomalies derive somehow from solid–solid phase transitions that convert optically normal crystals into anomalous twins.[127] He also devised detailed geometric models that attempted to rationalize the contribution of isomorphous impurities to optical anomalies:[128]

> "Suppose that a linked group [of balls] has cubic symmetry, except that out of twenty-four outermost balls but twenty-two or twenty-three are similar and similarly situated, dissimilar balls making up the twenty-four and occupying places which are symmetrically situated, or nearly so; it is then conceivable that the closest-packing of a number of groups of this description may be one which disregards the slight irregularity and puts the groups together with their centres at the points of a cubic lattice, and with their predominating symmetrically arranged balls forming, as far as they go, a system in cubic symmetry.
>
> In a case of this kind the positions of the irregularities will not be symmetrically distributed; in other words the groups, when the deformities are taken into account, will be found variously orientated and the assemblage will not be strictly—i.e., mathematically—homogeneous, although, owing to the average effect of the deformities being the same in corresponding directions, the general symmetry will not be appreciably impaired."

Thus he visualized not only desymmetrization within each sector, but also the mimetic twinning of sectors that preserves the external morphology. He did not consider how the kinetics of crystal growth might make the desymmetrization systematic.

Writing in 1897 Barlow had little influence on the optical anomalies debate, which was already stale. However, optical anomalies were sufficiently common and considered sufficiently important that his new theory of the internal structure of crystals had to address them.

2.8. X-Ray Studies

X-rays, discovered in 1895, had been applied to crystal structure analysis by 1913. Speculation concerning the internal structure of crystals could now be tested directly. Within ten years optical crystallography had all but vanished as a subject for innovative research, and the problem of optical anomalies was swept aside by the rising tide of X-ray diffraction. In 1927 W. G. Burgers observed that because optical investigations "have led to different conceptions about the constitution [of certain anomalous samples], it is worthwhile to see how far X-rays are able to reveal the true nature of such crystals,"[129] suggesting that optical evidence may be ignored if it contradicts evidence from X-rays.

Apophyllite and other anomalous minerals were studied by X-rays in both Germany and France. By 1926 Friedrich Rinne, who as a student of Klein in Göttingen forty years earlier had studied apophyllite optically, was directing the Mineralogical Institute in Leipzig, where he transformed mineralogy "from a quaint determinative science to a modern branch of applied physics."[130] He was a pioneer in applying X-rays to mineralogy. His Laue photographs of apophyllite and other optically anomalous minerals showed no departure from the expected morphological symmetry (Fig. 22). For him this confirmed Klein's hypothesis that the anomalies were due to stress.[131]

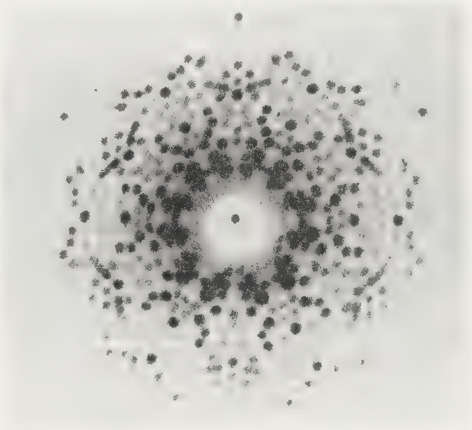

Fig. 22. Rinne's X-ray diffraction photograph of a single sector of optically anomalous milarite [131]. The density and resolution of such Laue photographs was inadequate to reveal small deviations from high symmetry.

In 1931, the year in which the atomic coordinates of apophyllite were first determined by X-ray diffraction,[41] Gossner and Kraus reported Laue photographs that seemed to confirm its tetragonal symmetry.[132] Gossner (1877–1937), a former student of Groth and his successor in Munich, surmised that because anomalous apophyllites have abnormal chemical composition, the substitution of impurities such as hydroxide for fluoride must cause the anomalies by creating local stress, as Brauns had suggested.

In his 1934 dissertation Raymond Hocart in Strasbourg wrote the last word in a controversy that had lasted sixty years and would soon be forgotten.[133] His research on optically anomalous minerals had been suggested by his adviser, the late Georges Friedel (1865–1933). In addition to formulating Friedel's Law, Hocart's teacher had made his life's work the study of twinned crystals that he had begun in Paris as a student of Mallard. Hocart's historical survey recalled criticisms of stress theories, such as the incompatibility between the existence of distinct birefringent sectors and the continuity of internal stress (Mallard), and the observation of Friedrich Pockels (1865–1913) that certain crystals fracture under considerably less pressure than would be required to generate their observed birefringence.[134] Hocart also noted[135] that

> "Rinne s'efforce de justifier la sensibilité médiocre de cette méthode en rapportant l'altération des propriétés optiques à une déformation des atomes; cette déformation est inaccessible aux rayons X."[*]

After reporting his own much more precise X-ray work Hocart concluded,[136]

> "...la théorie du mimétisme proposée par Mallard s'applique à un certain nombre de cas; dans les mêmes cas la théorie dite des tensions intérieures n'est d'aucun secours pour expliquer les faits connus... Si le cas de l'apophyllite est insuffisamment élucidé, il n'en est pas moins établi que dans les autres exemples cités ici la symétrie du cristal simple est au plus égale à celle qu'on peut déduire des propriétés optiques. Cette symétrie est inférieure à la symétrie extérieure apparente qui est manifestée par le groupement de plusieurs individus en un même édifice."[**]

Although X-ray results confirmed what was seen optically in several anomalous crystals—that for some reason the symmetry of individual sectors was lower than apparent external symmetry of the crystal—they did not address the source of the desymmetrization and the precision of the tesselation. In most anomalous crystals, optical detection of the desymmetrization is more sensitive than X-ray detection, as well as faster and easier. In Hocart's words,[137]

> "...il est regrettable que par l'application des rayons X à l'étude des cristaux l'attention ait été détournée des résultats acquis par les méthodes classiques de la cristallographie."[***]

Until very recently the long unsettled debate on optically anomalous crystals seems to have been almost completely forgotten. In 1943 Alfred Neuhaus (1903–1975), Professor of Mineralogy in Darmstadt, reported an optically anomalous sectoring of 1,8-dihydroxyanthraquinone that was not reflected in its X-ray patterns.[138] He cited none of the earlier literature describing crystals with precisely the same optical form, although there had been dozens of references to them in the same journal before he was born. His report was of an isolated phenomenon. In 1951 Neuhaus assumed the Professorship of Mineralogy in Bonn that had formerly been occupied by Brauns.[139]

Between 1945 and 1984 Brauns's classic book on optical anomalies, which remains the most comprehensive source in the field, was cited in the scientific literature only four times, and then only peripherally.[140]

2.9. Tammann's Insight

The closest approach to our present understanding of the phenomenon of optical anomalies was the isolated insight of a physical chemist who made pioneering contributions to the study of heterogeneous systems, crystallization, solid state reactions, and metallurgy.[141] In connection with his interest in alloys, Gustav Tammann (1861–1938, Fig. 23) in Göttingen published a series of papers on mixed crystals.[142] These papers focused on the equilibrium and nonequilibrium distribution of constituents in solid solutions.

Fig. 23. Gustav Tammann (1861–1938) suggested that optically anomalous crystals might be metastable "isomers" of more symmetrical normal crystals, but his prescient ideas were not well regarded by the crystallographic community, nor was X-ray crystallography sufficiently well-developed to test his hypothesis [142].

In a 1917 paper, *Die anomale Molekülverteilung in Mischkristallen als Ursache ihrer anomalen Doppelbrechung*,[*] Tammann discussed the theory of Brauns on internal stress from isomorphous impurities.[143] He speculated that although internal stress should play a role, the ordering of

---

[*] Rinne is forced to justify the mediocre sensitivity of [his X-ray] method by attributing the alteration of optical properties to a deformation of the atoms which is inaccessible to X-rays.

[**] the mimesis theory proposed by Mallard is applicable in a certain number of cases; in the same cases the so called theory of internal strain is of no use in explaining the known facts... If the case of apophyllite is still unclear, it is at least established that like other examples cited here [boleite, pharmacosiderite, boracite, and senarmontite] the symmetry of the simple crystal is at most equal to that which one would deduce from the optical properties. This symmetry is lower than the apparent external symmetry which results from the grouping of a number of individuals into a single structure.

[***] It is regrettable that by applying X-rays to the study of crystals, attention has been diverted from results obtained by the classical methods of crystallography.

[*] *The Anomalous Molecular Arrangement in Mixed Crystals as a Cause of their Anomalous Birefringence*

components alone would suffice to cause birefringence. Going further than Barlow he clearly indicated that the arrangements resulted from kinetic, not thermodynamic, control of crystal growth:

> "Die optisch anomalen Mischkristalle können als Isomere der optisch normalen Mischkristalle aufgefaßt werden. Der Grund der Isomerie ist hier eine verschiedene Verteilung der Moleküle in demselben Raumgitter, während er bei der gewöhnlichen Isomerie eine verschiedene Verteilung der Atome im Molekül ist. Die Mischkristalle abnormer Molekül- oder atomverteilung im Gitter sind aus atomistischen Gründen total instabile Phasen, denen kein Zustandsfeld zukommt, in dem sie stabiler als ihre Gitterisomeren mit normaler Molekülverteilung sind."[*]

Tammann did not consider what sort of mechanism might generate the observed asymmetry. In reviewing this paper Brauns criticized[144] its neglect of "die Abhängigkeit der optischen Symmetrie von der geometrischen Symmetrie einer Fläche, in dem Bezirk dieser, wenn sie vorhanden ist."[**] Brauns was almost certainly thinking of the face as a source of stress, rather than as a source of the molecular orientation during crystal growth that would have made Tammann's views congruent with our present understanding. He asserted correctly that there was insufficient evidence to support Tammann's views and concluded that the question should still not be considered settled.

No one developed Tammann's ideas on this subject. As Garner pointed out forty years ago,[141b] numerous aspects of Tammann's work were unconventional and "appear to many of us to be disconnected flights of genius, probably because their point of origin lies beyond our ken." Belated recognition of the correctness of Tammann's insight on optically anomalous crystals may help address Garner's concern that

> "[since] the changing language of scientific thought makes it uneconomic to absorb work done ahead of the time, [it is] problematical whether the theoretical investigations of Tammann will have any better success with a future generation of scientists than they have had with his contemporaries."

3. Current Status

3.1. Mineral Crystals

3.1.1. New Evidence and Understanding

Two kinds of zoning in which chemical composition varies from region to region within a crystal are familiar in mineralogy. One of them involves bands that are analogous to the growth rings of trees and result from changes in the composition of the fluid during crystallization. The other involves differences in composition between sectors that grew through faces that were not related by symmetry.[145] A third, less familiar type of zoning involves symmetry-related sectors that have identical composition but different impurity orientation. Tammann's views on lattice isomers are closely related to the latter and to the "order–disorder" concept which concerns phase transitions between structures with different patterns or degrees of atomic ordering.[146] One difference is that many discussions of order–disorder transitions assume reversibility, which Tammann specifically excluded.[147] Until recently there was no recognition that selective incorporation of impurities, or of disordered host molecules, among differently oriented lattice sites at the crystal surface should play an important role in generating a nonequilibrium structure. Optically anomalous crystals continued to be considered, in terms that had not changed for almost a century, as resulting either from stress or from some unexplained twinning mechanism.[148] Research over the last dozen years has begun to change that perception.

A neutron diffraction study of topaz in 1980 demonstrated symmetry lowering due to orientation of OH bonds.[149] In 1986 Rossman and Aines used polarized FTIR spectroscopy to demonstrate that the optical anisotropy of grossular garnets was associated with a selective orientation of OH ions that was assumed to have been established during crystal growth.[150] In 1988 Allen and Buseck reported X-ray results on similar garnets showing that during growth selective incorporation of Fe^{+3} for Al^{+3} and of Fe^{+2} for Ca^{+2} had lowered the symmetry of individual sectors to "$I\bar{1}$" from $Ia3d$,[151] confirming earlier observations by Takéuchi et al.[152] Although sectoring was easily observed by optical microscopy, it was invisible to the transmission electron microscope.

The most comprehensive recent work on optically anomalous minerals is due to Akizuki et al. In 1978 he explained optical observations on the anomalous feldspar adularia in terms of proposed differences among nominally symmetry-related unit cell sites at growth surfaces.[153] This was the first of a series of impressive papers in which he and his collaborators have rationalized the optical anomalies of more than a dozen minerals, including garnet, apophyllite, and a sample from Strontian, Scotland, of brewsterite, a rare strontium-containing zeolite named for Sir David Brewster.[154]

3.1.2. Present State of the Apophyllite Riddle

Until Akizuki's work, fundamental understanding of the optical anomaly of apophyllite had progressed little since its discovery by Brewster 175 years ago. In 1965 Sahama described an apophyllite from Finland with tesselation almost identical to that described Brewster[155] (Fig. 10b). His conclusions, coming on the sesquicentennial of the first report on optical anomalies, were not significantly more sophisticated that Brewster's. Noting that the optical properties were too regular to be attributed to strain, Sahama went no further than to invoke "penetration twinning" of orthorhombic

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[*] Optically anomalous mixed crystals can be understood as isomers of optically normal mixed crystals. Here the basis of the isomerism is a different arrangement of molecules in the same space lattice, while in normal isomerism it is a different arrangement of atoms in molecule. Mixed crystals with abnormal molecular or atomic arrangement in the lattice are on atomistic grounds totally unstable phases; there is no condition under which they are more stable than their lattice isomers with normal molecular arrangements

[**] the dependence of the optical symmetry on the geometrical symmetry of a face, in the sector in which it occurs

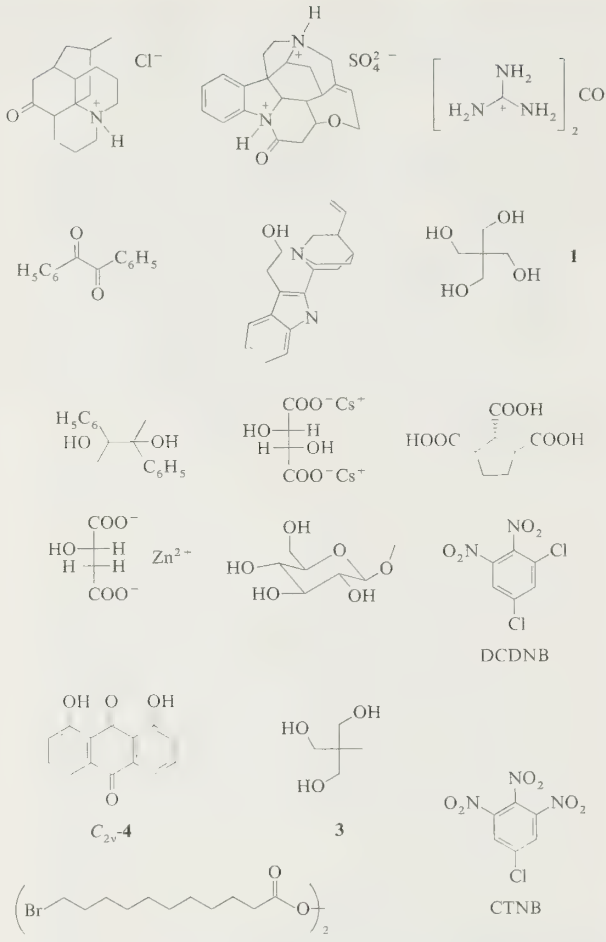
sectors whose "deviation from a strictly tetragonal symmetry must evidently be very slight." In his report of how growth conditions determine the morphology of apophyllite, Kostov mentioned the possible influence of impurities, but did not relate them to a mechanism of symmetry reduction.[156]

The paper of Akizuki and Konno, based on comprehensive, sophisticated optical observation of bulk and surface structures and on chemical analysis, presented a clear explanation of the way in which selective incorporation of impurities at growth sites on particular crystal facets could give rise to the tesselated structure.[157] Since substitution for K or F would not break the tetragonal symmetry, they favored selective substitution of Al for Si (or perhaps selective orientation of the O—H bond) as the source of desymmetrization. That neither of these orderings would have much influence on X-ray scattering is consistent with the failure of repeated efforts to detect the desymmetrization in apophyllite by X-ray diffraction. Although selective substitution of Al for Si seems plausible, there is still no direct evidence to confirm this explanation. We have recently studied growth banding in sectors associated with pyramid faces of an apophyllite from Bergen Hill, New Jersey. An electron microprobe analysis showed that in this sample the biaxial bands are actually *poorer* in aluminum than the uniaxial bands, although the opposite might be expected if biaxiality were due to inclusion of aluminum.[158] Thus Brewster's riddle is still not fully solved.

3.2. Organic Crystals

3.2.1. Literature Survey

Because of our desire to use optically anomalous organic crystals for studying molecular recognition during crystal growth,[5, 7] we surveyed the literature to identify promising systems. There must be a very large number of such crystals. Most axially symmetric organic crystals can probably be rendered optically anomalous by the presence of a suitable impurity. We searched crystal identification tables[159] for axially symmetric crystals that were not optically uniaxial.



Scheme 1. Structural formulas of compounds in Table 1 (in order from left to right).

Since optical properties are no longer commonly reported for organic crystals, it is not surprising that almost all of the cases we found were included in Groth's 72-year-old compendium of crystal data.[160]

Table 1 presents 16 reports of optically anomalous organic crystals in chronological order. In a number of cases we have

Table 1. Optically anomalous organic crystals.

Compound (see Scheme 1 also)	Morphology	Possible Source of Anisotropy	Year	Ref.
lycopodine-hydrochloride · H_2O	trigonal	?	1883	[a]
strychnine sulfate · 6 H_2O	tetragonal	ordering of water of hydration	1884	[176]
guanidinium carbonate	tetragonal	?	1884	[161]
benzil	hexagonal	impurities	1884	[161]
cinchonamine	trigonal	?	1887	[b]
pentaerythritol **1**	tetragonal	isomorphous impurities	1890	[118]
3,4-dihydroxy-3,4-diphenylbutane	tetragonal	?	1894	[c]
cesium tartrate	trigonal	cation impurity	1895	[169]
trans, trans-cyclopentane-1,2,3-tricarboxylic acid	hexagonal	?	1896	[d]
zinc (or magnesium) malate	tetragonal	impure salt	1898	[170]
β-methyl-D-glucoside	tetragonal	inclusion of α-anomer	1899	[162]
1,5-dichloro-2,3-dinitrobenzene (DCDNB)	tetragonal	selective disorder	1907	[184]
1,8-dihydroxyanthraquinone **4**	tetragonal	?	1943	[138]
deoxypentaerythritol **3**	tetragonal	incomplete disorder	1983	[166]
di(11-bromoundecanoyl) peroxide	tetragonal	monodebrominated impurity	1988	[5]
5-chloro-1,2,3-trinitrobenzene (DTNB)	tetragonal	brominated impurities	1990	[186]

[a] H. Söffing, Dissertation, University of Göttingen, **1883**; *Z. Krystallogr.*, **1884**, *9*, 620. [b] C. Friedel, *C. R. Hebd. Seances Acad. Sci.*, **1887**, *105*, 985; *Z. Krystallogr.*, **1889**, *14*, 605. [c] C. Riva, *G. Min. Crist. Petr. Sansoni.*, **1894**, *5*, 303; *Z. Krystallogr.*, **1886**, *26*, 218. [d] W. J. Pope, *J. Chem. Soc.* **1896**, *69*, 971.

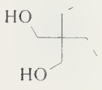
been able to confirm the anomalous phenomenon, and in some we can suggest its source on the basis of preliminary experiments described in this section. Section 3.2.2 summarizes the results from a more detailed study of one case.

For one compound of which we have obtained only uniaxial crystals and three others of which we have grown anomalous crystals, we suspect that the optical anomaly reported in the literature was due to selective incorporation of foreign or misordered molecules during crystallization. These substances are benzil, β-methyl-D-glucoside, pentaerythritol, and deoxypentaerythritol, respectively.

Our recrystallization of commercial benzil (Matheson) from carbon disulfide gave uniaxial hexagonal prisms, rather than the anomalous crystals reported by Martin[118] and by Wyrouboff.[161] His observations were probably due to an oriented impurity, although in our hands dissolving small amounts of benzoin or deoxybenzoin in the crystallizing solution did not give biaxial benzil crystals.

In 1899 Tietze[162] described optically anomalous β-methyl-D-glucoside crystals which he had obtained from Emil Fischer. The anomalous crystals were grown from mother liquors that remained after crystallization of the α isomer from the anomeric mixture of glucosides. The anomaly probably results from selective incorporation of residual α glucoside in the tetragonal lattice of the β anomer, since the α and β anomers of several carbohydrates cocrystallize.[163] We grew optically sectored crystals from an ethanol solution of β-methyl-D-glucoside (Sigma) in the presence of 17.5 mol% of the α anomer. The order of the interference colors in our crystals was considerably lower than in those described by Tietze, however.

Although Martin reported anomalous crystals of pentaerythritol (**1**),[118] pure crystals are genuinely tetragonal and uniaxial; molecules occupy sites of S_4 symmetry.[164] Pentaerythritol is difficult to obtain in pure form,[165] and crystals are almost invariably biaxial and sectored. Impurities of lower symmetry are probably oriented by selective incorporation on particular growth faces. R. L. Carter has grown anomalous crystals from pure pentaerythritol by adding 2-ethyl-2-(hydroxymethyl)butanol (**2**) as an impurity.[166]



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In 1983 Eilerman, Lippman, and Rudman reported that crystals of 2-(hydroxymethyl)-2-methyl-1,3-propanediol (deoxypentaerythritol, **3**) were isomorphous to pentaerythritol and appeared tetragonal by X-ray diffraction, suggesting that the methyl group was randomly disordered among the four hydroxymethyl sites.[167] However, by polarized microscopy they observed that the crystals were twinned, each plate being divided into four biaxial sectors. They inferred that each sector possessed a monoclinic C-centered cell containing four molecules. Together with Carter we have grown crystals from ethyl acetate and collected X-ray data from a single growth sector which shows a much more intricate structure.[168] Our triclinic supercell contains 32 independent molecules.

Traube described optically anomalous crystals of cesium tartrate[169] and of zinc malate.[170] For easy observation of deviation from axial symmetry, crystals should have well-developed faces perpendicular to the symmetry axis. We did not obtain appropriate crystals of these salts. A cation impurity, perhaps rubidium, is a likely source of Traube's observation. Crystals of cesium hydrogen tartrate, prepared from commercial purified CsCl in 1978, showed as much as 0.12% Rb by X-ray fluorescence.[171] Dicesium tartrate and dirubidium tartrate are isomorphous; a modern structure determination assigned the latter crystals to space group $P3_221$.[172]

We confirmed Wyrouboff's report that guanidinium carbonate is biaxial using crystals grown from the commercial salt (Aldrich). An ordered tetragonal structure of the salt in space group $P4_12_12$ has been reported with no mention of the optical anomaly.[173]

In the case of strychnine sulfate hexahydrate we have reproduced the reported anomaly, but we are again uncertain of its source. In 1857 this substance was used in the first demonstration that an organic crystal can rotate the plane of polarized light.[174, 175] Almost 30 years later Wyrouboff noted that the tetragonal crystals were optically anomalous and sectored,[176] an observation confirmed by Martin[118] and by Brauns[35a] (Fig. 21). Under conditions that apparently led to loss of an equivalent of water (heating, storage in desiccator, or long storage in air), the crystals became much more strongly birefringent. More remarkably, they often regained their original optical form on rehydration. We have confirmed these observations by growing crystals from cooled aqueous solution, exposing them to the air for dehydration, and returning them to the refrigerator for rehydration. X-ray data from a single growth sector of the hexahydrate crystal fit a tetragonal cell,[177] but the crystals diffracted poorly, and no further structural information was obtained. On standing at room temperature the crystals became so strongly birefringent that it was impossible to use a compensator to distinguish sectors with different directions of maximum polarizability.[178] The optical anomaly is certainly related to the state of hydration and perhaps to ordering of the waters of hydration. Brauns reported reversible changes in birefringence within a few minutes on transferring crystals between room air and a desiccator. Since a few minutes seems a short time to restore hydration and symmetry throughout a crystal, stress might play some role in this phenomenon.

We have reproduced the optical anomaly of 1,8-dihydroxyanthraquinone (**4**) but can offer no plausible explanation for the phenomenon. In 1943 Neuhaus reported optically sectored crystals.[138] These spectacular square, orange plates grow readily from acetone (Fig. 24). The solution ^{1}H NMR (500 MHz) spectrum from a single crystal of the quinone (Aldrich) showed no impurity peak larger than 0.5% of the hydroxyl signal from the pure compound. Previous structure determinations assigned the crystals to the space group $P4_1$.[179] Our structure, refined from X-ray intensities of one growth sector, showed no evidence of the desymmetrization that is implied optically.[180]

Rapid crystallization yields a metastable modification of 1,8-dihydroxyanthraquinone in the form of fine fibers. On the basis of vibrational spectroscopy Smulevich and Mar-

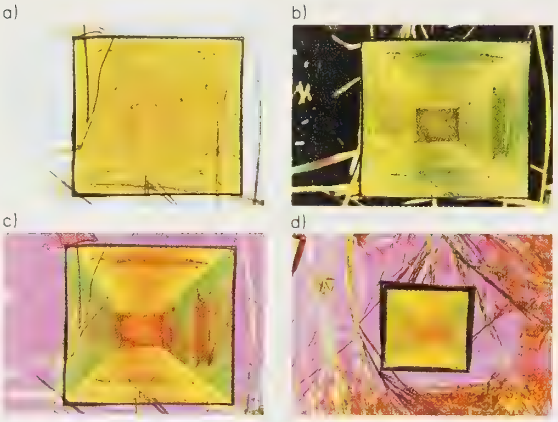
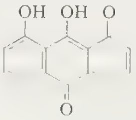


Fig. 24. Plate of 1,8-dihydroxyanthraquinone (**4**; 0.64 × 0.57 × 0.02 mm) grown within 30 minutes from acetone. View along [001] a) directly, b) between crossed polarizers (at 45°), and c) with a first-order red retarder (γ vertical). d) A smaller plate from the same batch. The source of anomalous birefringence in these crystals remains mysterious. Also visible are fine needles, the metastable modification

zocchi have argued that the predominant species in the two forms are the tautomers C_{2v}-**4** (see Scheme 1) and C_s-**4**.[181] The needles presumably contain the C_{2v} tautomer, while the plates have hydrogens bound to the oxygens at positions 1 and 9.[182] One might imagine that the minor species in the



C_s-**4**

optically anomalous plates is the C_{2v} tautomer, selectively included in some of the four lattice sites, and that tautomerization, although rapid in solution, is frozen out in the solid state. However, not only did solid-state ^{1}H and ^{13}C NMR spectra fail to reveal a second species in the anomalous plates, the needles and plates gave identical spectra.[183] In neither case was the resolution of the spectra sufficient to draw definitive conclusions.

3.2.2. 1,5-Dichloro-2,3-dinitrobenzene and Its Derivatives

After this preliminary survey of optically anomalous organic crystals, we studied the reported anomaly of 1,5-dichloro-2,3-dinitrobenzene (DCDNB) in much greater detail. DCDNB (see Scheme 1) is one of more than 70 substituted benzenes whose crystals were described by the mineralogist Ettore Artini (1866–1928) in a series of 10 papers between 1905 and 1918. Artini had undertaken this work in connection with the systematic investigation of aromatic compounds by the organic chemist Wilhelm Koerner (1839–1925), his colleague in Milan. Artini reported that although crystals of DCDNB from many solvents appeared to be tetragonal, microscopy of square (001) sections showed division along the diagonals into four distinctly biaxial sectors related to one another by rotation about [001], the apparent fourfold symmetry axis.[184] He also noted that departure from uniaxial character was small and variable "come spesso accade nelle sostanze otticamente anomale."[*]

We found that crystal plates from ether, chloroform, or benzene invariably showed the twinning described by Artini (Fig. 25). Refined lattice parameters from X-ray diffraction data on each of three of the sectors from a single plate showed an apparently orthorhombic cell with the principal axes in adjacent sectors rotated by 90° about *c*.[185] At a superficial level the absence of fourfold symmetry in this cell explains biaxiality and resolves the anomaly. That the crystals are multiply twinned may not be surprising, but why do they twin with precisely this pattern? Closer analysis reveals a novel mechanism for twinning that exemplifies the type of molecular recognition during crystal growth that we believe underlies most optical anomalies.

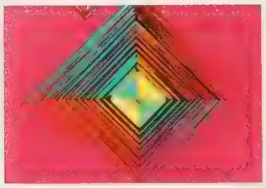


Fig. 25. Terraced plate of DCDNB (0.24 mm diagonal width, 0.024 mm thick at rim of central bright square) grown within 5 minutes by evaporation of $CHCl_3$ and viewed along [001] between crossed polarizers with a first-order red retarder (γ at 45°). In this pure crystal sectoring results from nonrandom disorder of a chloro and a nitro group.

An ordered crystal structure for DCDNB was refined to $R = 0.087$ in space group $P2_12_12_1$. This orthorhombic space group differs from the tetragonal group $P4_32_12$ by the absence of twofold rotational axes in locations close to the molecular C2 - C5 axis. Thus 5-chloro-1,2,3-trinitrobenzene (CTNB, see Scheme 1), the analogue of DCDNB in which the chlorine at position 1 has been replaced by a nitro group to make a molecular twofold rotation axis possible, gives crystals in space group $P4_32_12$ that are isomorphous with DCDNB.[186] If the growing crystal of DCDNB were totally unable to distinguish between the 3-chloro and 1-nitro groups flanking the 2-nitro position, the molecule would be incorporated from solution with complete rotational disorder about the C2–C5 axis, and the additional effective molecular symmetry would make the crystal truly tetragonal.

Close inspection of residual electron density after refinement of the $P2_12_12_1$ structure showed peaks consistent with this kind of disorder. Since other crystals have shown disorder from interchange of nitro and chloro positions,[187] it is not surprising that DCDNB has difficulty ordering these two groups. We refined the amount of rotational disorder independently in each of the four molecular sites which are nominally related by symmetry in space group $P2_12_12_1$. This five-parameter model gave much improved agreement with X-ray data collected from an untwinned crystal fragment ($R = 0.065$). The model showed that the minor molecular

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[*] as happens frequently in optically anomalous substances

orientation was present in substantial amounts that varied from site to site (32, 31, 15, and 18%, all ±1%).

These population differences that lower the crystal symmetry to $P1$ are due to differences in how molecules from solution were incorporated during growth into the different "symmetry-related" sites of this crystal fragment. The differences can be visualized by examining how molecules are oriented in one of the four molecular layers which stack along [001], the approximate fourfold screw axis of the unit cell. Figure 26a shows five molecules in one layer with the identity of the 1- and 3-substituents (Cl or NO_2) left ambiguous. The molecules are related by *a* and *b* translations. Figure 26b is a graph in which the central square symbolizes a growing crystal plate, and the four surrounding trapezoids represent the four growth sectors formed by adding molecules through the sides of the square to yield a final, larger crystal. Average orientation of the molecules within each sector is indicated by the shading of the circles standing for the 1- and 3-substituents. The ratio of dark to light area in a circle shows the ratio of NO_2 to Cl occupancy of the corresponding position. Ordering of the 1- and 3-substituents within the central square is irrelevant for the following argument, so they are shown as if fully disordered half light for chloro and half dark for nitro.

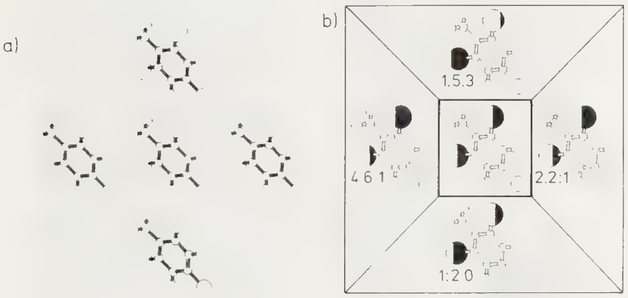
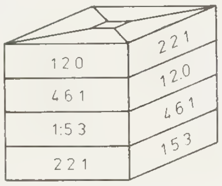


Fig. 26. a) Arrangement of neighboring molecules related by *a* and *b* translation within one layer of DCDNB. The approximate crystallographic fourfold screw axis is perpendicular to the paper, and the approximate molecular twofold symmetry axis joins the 2-nitro group at the upper left to the 5-chloro group at the lower right. The 1- and 3-substituents are indicated by large, nonspecified balls. b) Averaged molecular orientation in each trapezoidal growth sector of a macroscopic crystal. In real crystals the central square representing in the nucleus is much smaller. The average chloro:nitro population ratio at the 1-position is given explicitly for each sector.

In the bottom and right sectors orientation of chlorine to contact the growth surface of the central square is favored with a bias of ca. 2:1. At the top and left edges the bias is ca. 5:1 in the opposite direction, favoring contact of nitro with the growth surface. Apparently molecules from solution prefer to approach the bottom and right faces with their 1-chloro substituent toward the 5-chloro group of the surface molecules, and to approach the top and left faces with their 3-nitro group toward the 2-nitro group of the surface molecules. The bias favoring nitro–nitro contact (ca. 5:1) seems to be stronger than that favoring chloro–chloro contact (ca. 2:1). This naive picture ignores the role of molecules in adjacent layers and the specific structure of growth sites on the crystal surface (steps, kinks, etc.).[188] It also ignores the solvent. These additional factors will certainly be required to explain the small difference between top and left faces, and that between bottom and right faces.

Within the molecular layer of Figure 26 the resulting crystal is divided into four growth sectors surrounding the core. The division is along diagonal lines traced by corners of the expanding square plate. Each sector has a characteristic ratio of chlorine to nitro populations in position 1, as shown in Figure 26b. The same pattern arises by the same mechanism in the other three molecular layers of the unit cell, except that each is rotated by the fourfold screw axis that passes through the center of the original square. Thus under the 1:2.0 sector (top front in Fig. 27, bottom of Fig. 26) lies a 4.6:1 sector obtained by rotating the layer counterclockwise by 90° from the top layer. Next comes a 1:5.3 sector (180° rotation), and the cell is completed by a 2.2:1 sector (270° rotation). Each of the four sectors of the macroscopic 3-dimensional crystal is a stack of the same set of four different orientational populations in the same order, but from sector to sector the entire set is rotated by 90° and displaced by one layer (Fig. 27). The apparent rotation from sector to sector simply results from exchange of major and minor chloro:nitro populations among molecules with *identical framework orientation throughout the multiply twinned crystal.*

Fig. 27. Perspective view of a stack of four successive layers of DCDNB showing the sequence of chloro:nitro population ratios in the 1-position of molecules in each sector and layer. Adjacent growth sectors of a macroscopic crystal are rotated by 90 from one another and offset by one layer. This corresponds to the presence of a fourfold screw axis passing through the middle of the square.



Selective incorporation of misordered molecules in pure DCDNB is analogous to many cases where selective incorporation of impurities gives optically anomalous solid solutions. To support this analogy S. H. Tolbert prepared mixed crystals consisting of about 15% of 5-bromo-1,2,3-trinitrobenzene or 1-bromo-5-chlor-2,3-dinitrobenzene in CTNB, the isomorph of DCDNB with genuine fourfold symmetry.[189] Both solid solutions were optically anomalous, and in both cases X-ray diffraction from single growth sectors showed unsymmetrical distribution of the bromine substituent that differentiates guest from host. Bromine occupancy in sites that would have been related by symmetry in the pure host crystal varied from 1% to 27%. As might be expected, the sites with high bromine occupancy were oriented away from the crystal face that was active in growth of the sector.

4. Current Scientific Relevance of Optical Anomalies

4.1. The Challenge of Crystal Synthesis

One of the most challenging problems for modern chemistry is to develop tools for designing and assembling supramolecular structures that involve association of many molecules. Molecular crystals are a familiar and important class of these structures. Since the nonbonded interactions that hold molecular crystals together are weaker and less specific than the bonding interactions among atoms and groups within a single molecule, it is not surprising that methods for controlled crystal synthesis lag far behind those for molecular synthesis. Developing reliable methods for crystal synthesis is an important task, because the external habit and unit cell structure of crystals often determine crucial chemical and physical properties of commercially important solids ranging from pharmaceuticals to explosives, and from devices for nonlinear optics and integrated microelectronics to photographic emulsions. Optically anomalous crystals will assist in this effort both by serving as cases where the mechanism of crystal growth is particularly easy to study and by demonstrating new possibilities for tailoring crystal microstructure both at the growth sector and at the unit cell levels.

Twenty years ago Schmidt began discussing "Crystal Engineering" as the solid-state analogue of synthesis design.[190] Many concepts from molecular synthesis in the fluid phase have their analogues in the controlled preparation of crystals. Table 2 lists some comparisons. Specific growth sites at which new molecules add to a crystal surface play a role in the construction of nonbonds that is analogous to the role of reactive intermediates in the construction of bonds. In particular, the formation of a crystal nucleus, or of a screw defect or kink site on a crystal surface, is analogous to initiation of a free radical chain reaction; addition of a molecule to a kink so as to generate a new kink is analogous to propagation. Determining the structure and properties of these sites will be a key element in learning to control crystal growth.

Table 2. Some analogies between molecular and crystal synthesis.

Molecular Synthesis	Crystal Synthesis
synthetic strategy	crystal engeneering
bond construction	nonbond construction
reactive intermediate	growth site
initiation	nucleation
propagation	growth
termination	poisoning
chemoselectivity	guest discrimination
regioselectivity	habit modification
stereoselectivity	defect orientation
optical activity	birefringence

The growth of pure crystals and solid solutions provides several analogues to the types of selectivity that are sought in molecular synthesis. The choice between host and one or several guests for incorporation in a growing crystal is analogous to chemoselectivity. Purification by recrystallization is a familiar and dramatic example of this kind of selectivity. Addition to selected faces, which dictates the crystal habit, is analogous to regioselectivity. Incorporation of a guest in one among several symmetry-related host sites, as in optically anomalous crystals, is analogous to stereoselectivity.[5, 7, 191]

As in the case of molecular synthesis, the development of new techniques for crystal preparation will profit from an improved understanding of mechanism based on careful studies of prototypical cases. For mechanistic studies the birefringence of solid solutions can play a role analogous to that of optical activity in classical studies of fluid chemistry—it provides a permanent optical record of the course of the reaction. Optically anomalous crystals provide an excellent tool for studying the mechanism of crystal growth because the birefringence of individual sectors presents their growth history in a form that is easily read with a polarizing microscope. For example, while the crystal of Figure 2 grew as a square expanding from the center, the crystal of Figure 28a grew from a nucleus on the lower edge with molecules in the blue region adding through the right face and those in the yellow region through the top face, and the crystal of Figure 28b grew in a very complex way with blue regions growing through horizontal faces and yellow regions through vertical faces. The crystal of Figure 28c grew from at least five different nuclei at various times; four of the nuclei grew toward the front of the crystal and the one nearest the center, toward the rear. Enhanced birefringence in picture frames surrounding the crystals of Figure 28d indicates some change in crystallization mechanism.

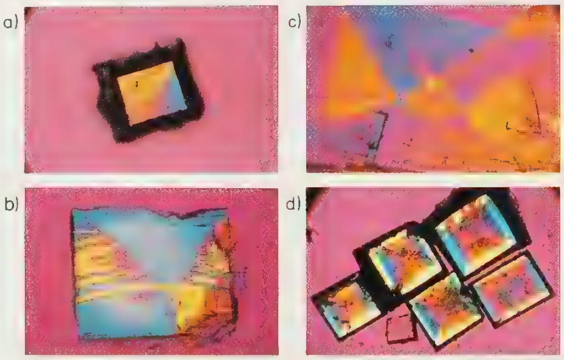


Fig. 28. Crystal plates with curious sectoring. a) Di-11-bromoundecanoyl peroxide containing 15% of the analogue in which one terminal bromine atom is replaced by a methyl group (11-bromoundecanoyl lauroyl peroxide). Although the shape of the rectangle may have been determined by a very thin crystal nucleated at the center, most of the thickening occurred from a nucleus near the left end of the lower edge. b) Pure 11-bromoundecanoyl lauroyl peroxide from acetone/$CHCl_3$. The bent stripes reveal a very complex pattern of crystal growth. c) The same peroxide mixture as in Figure 2. In this case growth occurred from at least five nuclei which occur at different depths in the crystal and thus were active at different times. d) Pure 11-bromoundecanoyl 11'-iodoundecanoyl peroxide. The source of the "picture frame" effect is not yet fully understood.

Birefringence shows not only which face was active during growth of a particular region, but also what kind of symmetry the growth site possessed and how effective it was at ordering the defects. For studies of dilute solid solutions the impurity may be thought of as an "indicator" whose incorporation reveals the growth history of the host. In principle, the same information is present in any solid solution, but strong intrinsic birefringence of the host lattice usually overwhelms the small contribution from unsymmetrically distributed defects. Isotropic or uniaxial hosts provide a blank background against which to view the effect of impurities.

4.2. Design of Desymmetrized Crystals

Optically anomalous crystals are common in both organic and inorganic materials and have even been observed in lunar samples.[192] They should be expected whenever growth kinetics can dictate a nonequilibrium distribution of defects in a high-symmetry crystal. The structure of solid solutions and disordered crystals should always be considered from this point of view. Even when a single crystal appears to have high symmetry, as in the case of DCDNB, single growth sectors can easily belong to the space group of lowest symmetry, *P*1. This realization relates to a general principle for designing crystalline materials: symmetry may be reduced selectively by the introduction of impurities. Symmetry reduction could be useful for developing new technological materials, especially for applications in nonlinear optics,[193] where high symmetry can be deleterious. With increased understanding of surface topography and the mechanisms of crystal growth, it should become possible to design and prepare mixed crystal with more finely tailored microstructures.

4.3. Study of Molecular Reorientation

In cases where a pure crystal is optically anomalous because of nonequilibrium orientation of disordered host molecules, there may be a temperature below the melting point at which the molecules can reorient to achieve the random, symmetrical orientation. The resulting change in birefringence could be used to follow the kinetics of molecular reorientation more easily and in smaller crystal regions than is possible with many spectroscopic techniques.

4.4. Mechanism of Crystal Twinning

The precise cause of crystal twinning is rarely understood.[194] Sometimes it has been attributed to growth of several crystals from a special seed with a higher symmetry than that of the individual crystallites.[194, 195] This cannot be the case for DCDNB because, when a seed cut from a single sector of a twinned crystal was placed in a supersaturated solution of DCDNB in chloroform, it grew into four sectors with the optical orientations predicted by the mechanism outlined in Section 3.2.2. In DCDNB twinning is a natural consequence of the growth kinetics and is not due to a special event or random mistake. The generality of this mechanism merits further study.

4.5. Molecular Recognition

There is great current interest in understanding the way in which weak intermolecular forces operate to allow the components of a supramolecular assembly to recognize one another. Since optical anomalies represent a breakdown of the recognition process during crystallization, investigating them carefully should yield valuable information on intermolecular forces and the mechanism of molecular recognition.

Information on molecular orientation from polarized microscopy is averaged over domains of at least micron dimensions. Standard X-ray diffraction results also represent spatial averages, as in the average Cl/NO_2 ratios depicted in Figure 26. Analysis of diffuse X-ray scattering can provide much more detailed information about molecular recognition by showing specific short-range pair correlations. For a given misordered molecule, diffuse scattering can provide the conditional probability that a particular neighbor is also misordered, rather than just the global probability that molecules in averaged sites are misordered. Following initial work by Flack and Glazer,[196] Welberry has made important theoretical and experimental contributions over the past fifteen years toward understanding short-range order in molecular crystals through diffuse scattering experiments.[197] He and his collaborators have found that local pair correlations can easily be two to four times larger than the average orientational preference revealed by normal Bragg scattering.[198] Optically anomalous, pure crystals like DCDNB, whose growth sectors are easily recognized and could be studied independently, should be particularly well suited for this type of study.

4.6. Value of the Polarizing Microscope

Current studies of optically anomalous crystals demonstrate the value of polarized light microscopy as clearly as investigations in the 19th century did.[199] Fifty years ago the microscope was still recognized as an important tool for chemistry, and students were routinely instructed in its proper use. Although microscopy persists in some areas, such as polymer, liquid crystal, and forensic chemistry, the rise of new analytical techniques and the concentration of academic chemistry on fluid phases have displaced microscopy from most chemistry curricula. McCrone has persistently advocated increased use of the polarizing microscope in analytical chemistry,[200] and growing interest in the solid state should favor a renaissance of this technique, particularly among organic chemists.

Although a microscope may cost 20 to 200 times less than newer tools for studying solids, it is unrivaled for rapid survey of transparent samples, particularly when they are inhomogeneous. Microscopy can be an indispensable adjunct for identifying regions in a solid that are worth more detailed study by other techniques. Without the help of the microscope to identify homogeneous growth sectors, X-ray diffraction can mislead by providing a crystal structure that is averaged over several domains. Microscopy can be as reliable as X-ray diffraction for determining the lattice orientation of a crystal being mounted for spectroscopic study, and it is much faster, but modern reports typically fail to provide relevant simple information on crystal birefringence.

Diffraction methods are unrivaled in providing quantitative structural detail at the atomic level. Still, it is instructive to note that many optical anomalies in mineral samples probably involve Al/Si ordering. These anomalies are easily seen with a microscope, but are nearly invisible to X-rays. Solid-state NMR or neutron diffraction could reveal Al/Si ordering, but both require samples some 10^7 times larger than those necessary for optical microscopy. Quantitative applications of optical microscopy in organic solid state chemistry would be helped greatly by improvement in simple models for predicting the electric polarizability of molecules.[20]

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[73] H. Marbach. *Ann. Phys. Chem.* **1885**, *170*, 412.

[74] W. Wertheim. *Ann. Phys. Chem.* **1852**, *86*, 325; **1852**, *87*, 498.

[75] For biographical information see G. Wyrouboff, *Bull. Soc. Min. Fr.* **1894**, *17*, 241; A. de Lapperant, *Ann. Mines. Mem. 9ème Ser.* **1895**, *7*, 267.

[76] A. Bravais, *On the Systems Formed by Points Regularly Distributed on a Plane or in Space* (translated by A. J. Shaler), Crystallographic Society of America, **1949**

[77] E. Mallard. *Ann. Mines. Mem. 7ème Ser.* **1876**, *10*, 60.

[78] See [77], pp. 65–66.

[79] See [77], pp. 121–122

[80] D. Brewster. *Phil. Trans. Roy. Soc. London* **1814**, *104*, 397, 436; **1815**, *105*, 1

[81] a) D. Brewster, *Phil. Trans. Roy. Soc. London* **1815**, *105*, 60; b) **1816**, *106*, 156; **1830**, *120*, 87, c) *Trans. Roy. Soc. Edinburgh.* **1818**, *8*, 218, 354.

[82] E. Reusch, *Ann. Phys. Chem.* **1867**, *208*, 618

[83] For biographical information see F. von Wolff, *Centralblatt. Mineral. A* **1907**, 640.

[84] F. Klocke. *Neues Jahrb. Mineral. Geol. Paläontol.* **1880**, *I*, 53.

[85] F. Klocke. *Neues Jahrb. Mineral. Geol. Paläontol.* **1881**, *II*, 249.

[86] A. Ben-Saude: *Neues Jahrb. Mineral. Geol. Paläontol.* **1882**, *I*, 41

[87] A. Ben-Saude, *Beitrag zu einer Theorie der Optischen Anomalien der Regulären Krystalle*. National Druckerei, Lissabon, **1894**.

[88] C. Klein. *Neues Jahrb. Mineral. Geol. Paläontol.* **1885**, *II*, 237; **1887**, *I*, 223

[89] A. Fock, *An Introduction to Chemical Crystallography* (translated by W. J. Pope), Clarendon Press, Oxford, **1895**, pp. 164–165.

[90] F. Klocke. *Neues Jahrb. Mineral. Geol. Paläontol.* **1881**, *I*, 204; see also [85].

[91] C. Klein. *Neues Jahrb. Mineral. Geol. Paläontol.* **1884**, *I*, 253.

[92] F. Rinne. *Neues Jahrb. Mineral. Geol. Paläontol.* **1885**, *II*, 19.

[93] L. Ditscheiner, *Sitzungsb. Kaiser. Akad. Wiss. Wien*, **1860**, *43*, 229. Brauns later pointed out that it would be difficult to mimic high symmetry by this means, because simultaneous compensation at all wavelengths would be unlikely. See also [35a], p. 26.

[94] R. Brauns. *Neues Jahrb. Mineral. Geol. Paläontol.* **1883**, *II*, 102.

[95] R. Brauns. *Neues Jahrb. Mineral. Geol. Paläontol.* **1885**, *I*, 96; *Dissertation*, Marburg, **1885**.

[96] R. Brauns, *Was wissen wir über die Ursachen der optischen Anomalien?* Habilitacion, Verein der preussischen Rheinlande und Westfalen, **1887**, p. 510

[97] See [35a], p. 257–258

[98] A. Ben-Saude, *Die Wahrscheinlichen Ursachen der Anomalen Doppelbrechung der Krystalle*, National Druckerei, Lisbon, **1896**. For a review by R. Brauns see *Neues Jahrb. Mineral. Geol. Paläontol. Ref.* **1897**, *II*, 249. For an earlier critique see R. Brauns, *ibid*, **1895**, *I*, 1, **1895**, 133.

[99] E. Mallard, *Bull. Soc. Min. Fr.* **1886**, *9*, 54

[100] R. Brauns. *Neues Jahrb. Mineral. Geol. Paläontol.* **1887**, *I*, 47.

[101] P. Groth reviewed Mallard's treatise. See: *Z. Kryst.* **1877**, *6*, 309.

[102] P. Groth, *Physikalische Krystallographie*, Wilhelm Engelmann, Leipzig, **1876**, (4th ed. 1905).

[103] See [35a], p. 55

[104] E. Mallard, *Traité de cristallographie géométrique et physique*, Paris, **1879–1884**.

[105] F. Wallerant, *Cristallographie*, C. Béranger, Paris, **1909**, p. I. Wallerant's book was intended to address some of the concerns in the lost volume, but it did not contain the polemic against the German view that might have expected from Mallard.

[106] G. Wyrouboff, *Mineral. Mag.* **1894**, *10*, 828

[107] A. Johannsen, *Manual of Petrographic Methods*, McGraw-Hill, New York, **1918**, pp. 510–514.

[108] Des Cloizeaux (1878, 1889), Mallard (1879, 1892), G. Friedel (1881), Bertrand (1886, 1901), Jannettaz (1887) and Wyrouboff (1891, 1902); also Wallerant (1899, 1905, 1916, 1930).

[109] See obituary notice of F. Zirkel, *Centralblatt Min.* **1912**, 513.

[110] The Society sponsored 14 other prize competitions in mathematics and the natural sciences between 1847 and 1911.

[111] See [35a], p. iv.

[112] For biographical information see *Festband Reinhard Brauns*: E. Kaiser, E. Lehmann, H. Schneiderhölm, O. Weigel, *Neues Jahrb. Mineral. Geol Paläontol. Beilage-Band* **1931**, *64* iv-xxii.

[113] J. W. v. Goethe, *Vier Jahreszeiten*, Werkstätten der Stadt Halle, Burg Giebichstein, **1937**

[114] See [35a], p. 57

[115] C. M. Viola, *Grundzüge der Kristallographie*, Wilhelm Engelmann, Leipzig, **1904**, pp. 269–274; M. Bauer, *Lehrbuch der Mineralogie*, E. Schweizerbart, Stuttgart, **1904**, pp. 325–328; F. Pockels, *Lehrbuch der Kristalloptik*, B. G. Teubner, Stuttgart, **1906**, pp. 488–490; A. Johannsen, *Manual of Petrographic Methods*, McGraw-Hill, New York, **1918** pp. 508–514; G. Tschermak, *Lehrbuch der Mineralogie*, Alfred Hölder, Wien, **1921**, pp. 256–260; E. S. Dana, *A Textbook of Mineralogy* J. Wiley, New York, **1932**, pp. 329–332; P. Ramdohr, *Klockmanns Lehrbuch der Mineralogie*, Ferdinand Enke, Stuttgart, **1948**, pp. 179–181; *History of Science in the Nineteenth Century* (Ed..: R. Taton; translated by A. J. Pomerans), Basic Books, New York, **1961**, p. 313.

[116] For biographical information, see F. Wallerant, *Bull. Soc. Min. Fr.* **1914**, *37*, 44.

[117] At least three previous dissertations from the Göttingen Mineralogical Institute had also dealt with anomalous organic crystals. (J. Zingel, 1883; H. Söffing, 1883; and O. Heintze, 1884), but their nature, and sometimes even the molecular structures, are unclear. They include methylbenzylhydroxamic acid, a paradinitrotoluidine $C_9H_{10}N_4O_6$ mixture, biphenyldodecachloride, and glucose sodium chloride (Traubenzuckerchlornatrium). See: C. Klein, *Neues Jahrb. Mineral. Geol. Paläontol.* **1885**, *II*, 237.

[118] J. Martin, *Beiträge zur Kenntniss der optischen Anomalien einaxiger Krystalle*, Dissertation, Universität Göttingen, **1890**; J. Martin, *Neues Jahrb Mineral. Geol. Paläontol. Beilage-Band* **1891**, *7*, 1 Reviewed by J. Beckenkamp, *Z. Kryst.* **1892**, *21*, 138

[119] G. Wyrouboff, *Bull. Soc. Min. Fr.* **1890**, *13*, 94

[120] H. A. Miers, *Mineral. Mag. Abs.* **1887**, *7*, 177.

[121] E. S. Fedorov, *Zap. Ross. Mineral. Obshchestva. Ser. 2*, **1891**, *28*, 345.

[122] A. Schoenflies, *Kristallsysteme und Kristallstruktur*, Leipzig, **1891**

[123] W. J. Pope, *J. Chem. Soc.* **1935**, 1328

[124] W. Barlow, *Nature* **1883**, *29*, 186, 205. See also editor's comments: *Crystal Form and Structure* (Ed..: C. J. Schneer), Dowden, Hutchison and Ross, Stroudsburg, PA, **1976**, pp. 54–55.

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[126] W. Barlow, *Scientific Proceedings of the Royal Society of Dublin, New Series* **1897**, *8*, 620–665

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[128] See [126], p. 663.

[129] W. G. Burgers, *Proc. Roy. Soc. London* **1927**, *A 116*, 553.

[130] J. W. Gruner, *Am. Mineral.* **1934**, *19*, 112

[131] F. Rinne, *Centralblatt Mineral. A* **1925**, 225; **1927**, 1; see also F. Rinne, *Z. Krist.* **1926**, *63*, 236.

[132] B. Gossner, O. Kraus, *Z. Krist.* **1928**, *68*, 595

[133] a) R. Hocart, *Contribution à l'étude de quelques cristaux à anomalies optiques*. Thèse Univ. Strasbourg, Paris, **1934**; b) *Bull. Soc. Min. Fr.* **1934**, *57*, 5–125

[134] F. Pockels, *Neues Jahrb. Mineral. Geol. Paläontol. Beilage-Band*, **1893**, *38*, 217

[135] See [133b], pp. 18–19

[136] See [133b], p. 125.

[137] See [133b], p. 7

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[141] a) *Dictionary of Scientific Biography, Vol. 13*, (Ed.: C. C. Gillispie), Charles Scribner's, New York, **1970**, p. 242; b) W. E. Garner, *J. Chem. Soc. 1952*, 1961; c) G. Masing, *Ber. Dtsch. Chem. Ges.* **1940**, *73*, 25

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[143] G. Tammann, *Nachr. Ges. Wiss. Göttingen Math-Phys. Kl.* **1917**, *2*, 216.

[144] R. Brauns, *Neues Jahrb. Mineral. Geol. Paläontol. Ref.* **1919**, 262.

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[147] M. A. Carpenter, *Phys. Chem. Miner* **1986**, *13*, 119

[148] See [4], pp. 321–322.

[149] J. B. Parise, C. Cuff, F. H. Moore, *Mineral. Mag.* **1980**, *43*, 943.

[150] G. R. Rossman, R. D. Aines, *Am. Mineral.* **1986**, *71*, 779

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[153] M. Akizuki, I. Sunagawa, *Mineral. Mag.* **1978**, *42*, 453

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[156] I. Kostov, *N. Jahrb. Min. Abh.* **1975**, *123*, 128

[157] M. Akizuki, H. Konno, *N. Jahrb. Min. Abh.* **1985**, *151*, 99

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[159] J. H. Donnay, H. M. Ondik, *Crystal Data, Determinative Table*, 3rd ed., U.S. Department of Commerce, National Bureau of Standards, and Joint Committee on Powder Diffraction Standards, **1972**, **1973**. M. W. Porter, R. C. Spiller, *The Barker Index of Crystals*, W. Heffer, Cambridge, **1956**.

[160] P. Groth, *Chemische Krystallographie*, Wilhelm Engelmann, Leipzig, **1906–1919**.

[161] The optical anomaly in benzil was first observed by Wyrouboff; see: G. Wyrouboff, *Bull. Soc. Min. Fr.* **1884**, *7*, 86. For a modern X-ray topographical study see: H. Klapper, *J. Cryst. Growth* **1971**, *10*, 13.

[162] O. Tietze, *Neues Jahrb. Mineral. Geol. Paläontol.* **1899**, *II*, 21.

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[165] For common impurities see: T. J. Simons, R. L. DeSilva, D. E. Creasy, *J. Chem. Tech. Biotechnol.* **1976**, *26*, 30; B. Clatworthy, S. Rehmatullah, A. B. A. Wahab; D. E. Creasy, *ibid.* **1982**, *32*, 518.

[166] R. L. Carter, unpublished.

[167] D. Eilerman, R. Lippman, R. Rudman, *Acta Crystallogr. Sect. B* **1983**, *B39*, 263.

[168] Space group $P1$, $a = 12.075$, $b = 27.054$, $c = 24.584$ Å, $\alpha = 131.22$, $\beta = 119.35$, $\gamma = 63.53^\circ$. R. L. Carter, B. Kahr, J. M. McBride, unpublished.

[169] H. Traube, *Sitz. Akad. Wiss. Ber.* **1895**, *10*, 198; *Z. Kryst.* **1898**, *30*, 403.

[170] H. Traube, *Neues Jahrb. Mineral. Geol. Paläontol. Beilage-Band* **1897**, *11*, 624. There is some confusion as to which salt of malic acid gives optically anomalous tetragonal crystals. Traube's later publication (*Z. Krystallogr* (**1898/1899**) 160) indicates that the interesting crystals are the magnesium salt

[171] L. K. Tempelton, D. H. Tempelton, *Acta Crystallogr. A* **1978**, *34*, 368.

[172] L. Bohaty', R. Fröhlich, *Z. Kristallogr. B* **1978**, *164*, 291.

[173] J. M. Adams, R. W. H. Smith, *Acta Crystallogr.* **1974**, *30*, 2191.

[174] Rotation is difficult to observe in biaxial crystals because of the simultaneous transformation from plane to elliptical polarization. In uniaxial plates it is easier to arrange for measurement along the optic axis, in which direction light can remain plane polarized.

[175] A. Des Cloizeaux, *Ann. Phys.* **1857**, *102*, 474.

[176] G. Wyrouboff, *Bull. Soc. Mineral. Fr.* **1884**, *7*, 10.

[177] $a = b = 7.61$, $c = 62.0$ Å.

[178] A monoclinic pentahydrate from ethanol has been studied, but it may differ from the dehydration product. C. Bokhoven, J. C. Schoone, J. M. Bijvoet, *Acta Crystallogr.* **1951**, *4*, 275.

[179] A. V. Jagannadham, *Z. Kristallogr.* **1957,** *108*, 457; A. Prakash, *Z. Krist.* **1965**, *122*, 272.

[180] B. Kahr, unpublished.

[181] G. Smulevich, M. P. Marzocchi, *Stud. Biophys.* **1984**, *104*, 105; *Chem. Phys.* **1985**, *94*, 99; *ibid.* **1986**, *105*, 159.

[182] The site symmetry of molecules in the plates is $C1$; it is not known for the needles.

[183] We thank Dr. K. Valentine at Princeton University for obtaining the ^{13}C CPMAS-NMR spectra and Dr. Bruce Hawkins at the NSF Regional NMR Facility at Colorado State University for the ^{1}H CRAMPS-NMR spektra.

[184] E. Artini, *Rendiconti Ist. Lomb. Sc. Lett.* **1907**, *11*, 1024.

[185] $a = 6.775(8)$, $b = 6.805(7)$, $c = 19.06(3)$ Å, $\alpha = 90.08(8)$, $\beta = 90.05(6)$, $\gamma = 89.98(5)^\circ$. B. Kahr, J. M. McBride, unpublished.

[186] $a = b = 6.7815(5)$, $c = 19.386(2)$ Å. However, 1,3,5-trichloro-2-nitrobenzene (space group $C2/c$) is not isomorphous with DCDNB and CTNB. B. Kahr, S. H. Tolbert, J. M. McBride, unpublished.

[187] Pentachloronitrobenzene: I. Tanaka, F. Iwasaki, A. Aihara, *Acta Crystallogr. Sect. B* **1974**, *30*, 1546; *p*-chloronitrobenzene: T. C. W. Mak, J. Trotter, *Acta Crystallogr.* **1962**, *15*, 1078.

[188] Other observations suggest that *inter*layer contacts between nitro groups not only establish the screw relationship between adjacent layers but also favor the pattern of *intra*layer contacts by an indirect mechanism.

[189] B. Kahr, J. M. McBride, S. H. Tolbert, unpublished.

[190] G. M. J. Schmidt, *Pure Appl. Chem.* **1971**, *27*, 647.

[191] H. E. Buckley, *Crystal Growth,* Wiley, New York, **1952**.

[192] U. B. Marvin, J. W. Carey, M. M. Lindstrom, *Science.* **1990**, *243*, 925.

[193] *Nonlinear Optical Properties of Organic Molecules and Crystals,* (Eds.: D. S. Chemla, J. Zyss), Academic Press, New York, **1987**; D. J. Williams, *Angew. Chem. Int. Ed. Eng.* **1984,** *23*, 690–703; I. Weissbuch, M. Lahav, L. Leiserowitz, G. R. Meredith, H. Vanherzeele, *Chem. Mater.* **1989**, *1*, 114.

[194] M. Senechal, *Comput. & Math. Appl.* **1986**, *12B*, 565.

[195] H. P. Zeck, *Nature, Physical Science* **1972**, *238*, 47.

[196] H. D. Flack, A. M. Glazer, *Philos. Trans. R. Soc. London* **1970**, *A266*, 559ff.

[197] T. R. Welberry, *Rep. Prog. Phys.* **1985,** *48*, 1543, and references cited therein.

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[200] W. McCrone, *Acc. Chem. Res.* **1990**, *23*, 77; F. W. McLafferty, *Acc Chem. Res.* **1990**, *23*, 63.

[201] S. S. Batsanov, *Refractometry and Chemical Structure* (translated by P. P. Sutton), Consultants Bureau, New York, **1961**.

6/1

[illegible]

PURDUE UNIVERSITY

DEPARTMENT OF CHEMISTRY

May 24, 1993

Dr. Alfred Bader
2961 North Shepard Avenue
Milwaukee, Wisconsin 53211

Dear Al,

Karen and myself would be delighted for you, Isabel and your traveling companion to visit us on Sunday, August 1. We look forward to your visit.

I have submitted my resignation to Purdue University and my acceptance of a full professor position at Michigan State University. Karen, myself, and the research group will be moving in mid December. The department and administration at Purdue failed to redress a single one of the problems which prompted my search for another professorial position. We would like to stay as positive as possible about Purdue even though events of recent months makes maintenance of a pleasant facade rather difficult.

Sincerely,

John

John W. Frost
PHONE: 317-494-0386
FAX: 317-494-0239

1393 HERBERT C. BROWN LABORATORY OF CHEMISTRY • RICHARD B. WETHERILL LABORATORY OF CHEMISTRY
WEST LAFAYETTE, IN 47907-1393 • FAX (317) 494-0239

Dr. Alfred R. Bader
2961 North Shepard Avenue
Milwaukee, Wisconsin 53211

June 7, 1993

Professor John W. Frost
Department of Chemistry
Purdue University
West Lafayette, Indiana 49707 1393

Dear Professor Frost:

Your letter to Dr. Bader of May 24th has been received while he is out of the country until the end of July. In the meantime, I have forwarded a copy to him in England.

Cordially,

Marilyn Hassmann

Dr. Alfred R. Bader
2961 North Shepard Avenue
Milwaukee, Wisconsin 53211

May 12, 1993

Professor John Frost
Department of Chemistry
Purdue University
West Lafayette, Indiana 47907

Dear John:

I am delighted to learn from Herbert Brown that matters have much improved.

Isabel and I look forward to being in Indianapolis on August 2 and 3. We will be driving with a young Spanish friend, the 13-year old son of Professor Carlos Seoane, a very able Spanish chemist.

Could we, perhaps, visit you in Lafayette on Sunday, August 1?

Fond regards,

PURDUE UNIVERSITY

DEPARTMENT OF CHEMISTRY

K

5/4/93

Dear Ulfried:

I have just received a flyer from Harvard U. describing a symposium in your honor on Monday, May 17. Congratulations! I would dearly love to be present, but Sarah and I are enroute to Moscow where we will participate in a Workshop to be held on the Bosom of the Volga — a new experience which we view with both interest and trepidation.

John Frost's problem appears to be largely resolved. Yesterday he gave me a huge mass of material which I am taking with me in the hope there will be time to read all about his unusual research program.

With warm affection from Sarah and me to Isabel and you —

Herb

HERBERT C. BROWN LABORATORY OF CHEMISTRY • RICHARD B. WETHERILL LABORATORY OF CHEMISTRY
WEST LAFAYETTE, IN 47907

Dr. Alfred Bader
2961 North Shepard Avenue
Milwaukee, Wisconsin 53211

March 18, 1993

Professor James Brewster
334 Hollow Wood Drive
West Lafayette, Indiana 47906

Dear Jim,

Isabel and I have been invited to speak at the ChemEd Conference in Indianapolis on Monday, August 2nd, and we would very much like to stop in West Lafayette on Sunday the first just to hold hands with Nathan's family. Could you please send me their addresses and telephone numbers and a little map showing how to get to their homes.

Many thanks and best wishes,

Dr. Alfred Bader
2961 North Shepard Avenue
Milwaukee, Wisconsin 53211

TO THE FAMILY AND FRIENDS OF
PROFESSOR NATHAN KORNBLUM

What can one say when one has lost and old and dear friend? The only words that come to mind are the words of Job, "Shall we take the good from God and not the bad?"

Nathan was one of the ablest chemists I have ever known--a man who helped Aldrich and many chemists around the world.

March 17, 1993

Dr. Alfred Bader
2961 North Shepard Avenue
Milwaukee, Wisconsin 53211

March 17, 1993

Professor James Brewster
334 Hollow Wood Drive
West Lafayette, Indiana 47906

Dear Jim,

I truly appreciate the thoughtfulness of your calling me to let me know of Nathan's passing. In a way it is a blessing, because certainly in the last year he was not his old self.

Please share the enclosed at the service.

All good wishes.

Sincerely,

Enclosure

Dr. Alfred Bader
2961 North Shepard Avenue
Milwaukee, Wisconsin 53211

March 17, 1993

Ms. Elizabeth Kornblum
328 Hollow Wood Drive
West Lafayette, Indiana 47906

Dear Ms. Kornblum:

I have just heard of the passing of your father, and I would like to tell you and your family how sad I am to have lost a good and long-time friend.

All good wishes.

Sadly,

Dr. Alfred Bader
2961 North Shepard Avenue
Milwaukee, Wisconsin 53211

March 8, 1993

Professor Phillip Fuchs
Department of Chemistry
Purdue University
West Lafayette
Indiana 47907

Dear Phil:

I was so happy to have your letter about hecogenin acetate, because I do want to continue to help chemists as much as I can.

Steroids sell better through the Sigma catalog, and the policy at Sigma and Aldrich is that the company selling more does the purchasing. Hence, it was Sigma who purchased hecogenin acetate, and they have over 5 kilos in stock. I do not quite know why someone at Aldrich decided to discontinue it--probably just Murphy's law--when a mistake can happen it will happen.

Hecogenin acetate could be purchased for a few hundred dollars per kilo, and material from China at approximately $1.00/gram is about right, but the Chinese are so unreliable.

You will find it easier bargaining with the people at Aldrich, but if you must talk to sales people in St. Louis it would be better not to mention my name.

Best wishes.

As always,

PURDUE UNIVERSITY

DEPARTMENT OF CHEMISTRY

To
Dr. Al Runquist
Please discuss
Thanks
Alfred
2/25.

Dr. Alfred Bader
2961 N. Shepard Avenue
Milwaukee, WI 53201

February 17, 1993

Dear Alfred,

Its just not the same dealing with Aldrich without you being there. I need a special favor. You may (or may not) recall that you gave us a special price ($975) on 500g of hecogenin acetate H20-6 on 11-08-91. We have make considerable progress converting this into some cephalostatin analogs which are showing interesting anti-cancer activity. We are running low and need a new infusion of starting material. Unfortunately, I have just been informed that Aldrich has discontinued this item as of May 1992.

Do you know anywhere I might look to find a new source? The best I have come up with so far is a guy named Kaj Arentz at Stearaloids who claims that Glaxco can supply kilo quantities. However, he doesn't seem to be able or willing to provide any price or delivery dates. When I last bugged him he claimed that he called Glaxco but the individual there reportedly "lost the paper" with the source location. Grr.

I really need some inside information here, I've tried all the Chem Sources places which are listed, but except for Stearaloids, no help there. KNK sells the material at $30/g; the interesting feature is their catalog number is **206**-544 (I bet the first number is just where they bought it--Aldrich).

If you can help, please call me at 317-494-5242 (or FAX at 494-7679, if you prefer).

Sincerely yours,

Phil

P. L. Fuchs
Professor of Chemistry

1393 HERBERT C. BROWN LABORATORY OF CHEMISTRY • RICHARD B. WETHERILL LABORATORY OF CHEMISTRY
WEST LAFAYETTE, IN 47907-1393 • FAX (317) 494-0239