

Alfred Baker Fonds

Chemistry and Art
More Adventures of a Chemist Collector

Chapter 15 -
Josef Koschmidt

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Josef Loschmidt

In Chapter 16 of the *Adventures of a Chemist Collector* I described Professor Christian Noe's and my efforts to follow in Bill Wiswesser's footsteps to bring Josef Loschmidt's chemical work to the attention of the world. In this we have, I think, succeeded and textbooks in chemistry are beginning to describe Loschmidt's work correctly.

I have summarized the literature through 1998, and the editor of the Bulletin for the History of Chemistry has permitted me to reprint this paper.

Professor Jiri Damborsky, the Loschmidt Professor of Chemistry at the Masaryk University in Brno has prepared a widely read website, www.loschmidt.cz

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The Wiswesser-Loschmidt Connection

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[The following article by me originally appeared in the *Bulletin of Historic Chemistry* 22 (1998). This reprinting has been slightly modified from the original.]

William Joseph Wiswesser (1914-1989) [fig. 1] graduated from Lehigh University with a BS in chemistry in 1936 and received an honorary DSc from that institution in 1974. He was employed by Hercules, the Trojan Powder Company, the Picatinny Arsenal, the Cooper Union, Wilson Products, the U.S. Army at Fort Detrick, and finally by the Agricultural Research Service of the USDA. Being interested throughout his varied career in simplifying chemical structure descriptions, he developed the Wiswesser Line Notation (WLN), which made possible the single-line depiction of every molecule, no matter how complicated. Research organizations in the 1980s had



BULLETIN FOR THE HISTORY OF CHEMISTRY

Division of the History of Chemistry of the American Chemical Society

NUMBER 22

1998





THE WISWESSER-LOSCHMIDT CONNECTION *

Alfred Bader, Milwaukee, WI

William Joseph Wiswesser (1914-1989) [Fig. 1] graduated from Lehigh University with a B.S. in chemistry in 1936 and received an honorary D.Sc. from that institution in 1974. He was employed by Hercules, the Trojan Powder Company, the Picatinny Arsenal, the Cooper Union, Willson Products, the U.S. Army at Fort Detrick, and finally by the Agricultural Research Service of the U.S.D.A., Being interested throughout his varied career in simplifying chemical structure descriptions, he developed the Wiswesser Line Notation (WLN), which made possible the single-line depiction of every molecule, no matter how complicated. Research organiza-



Figure 1. William J. Wiswesser

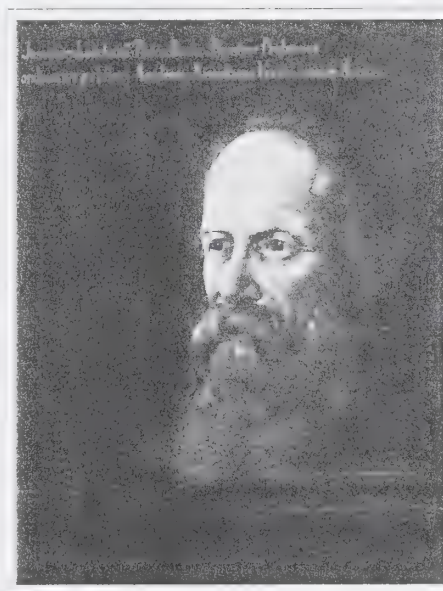
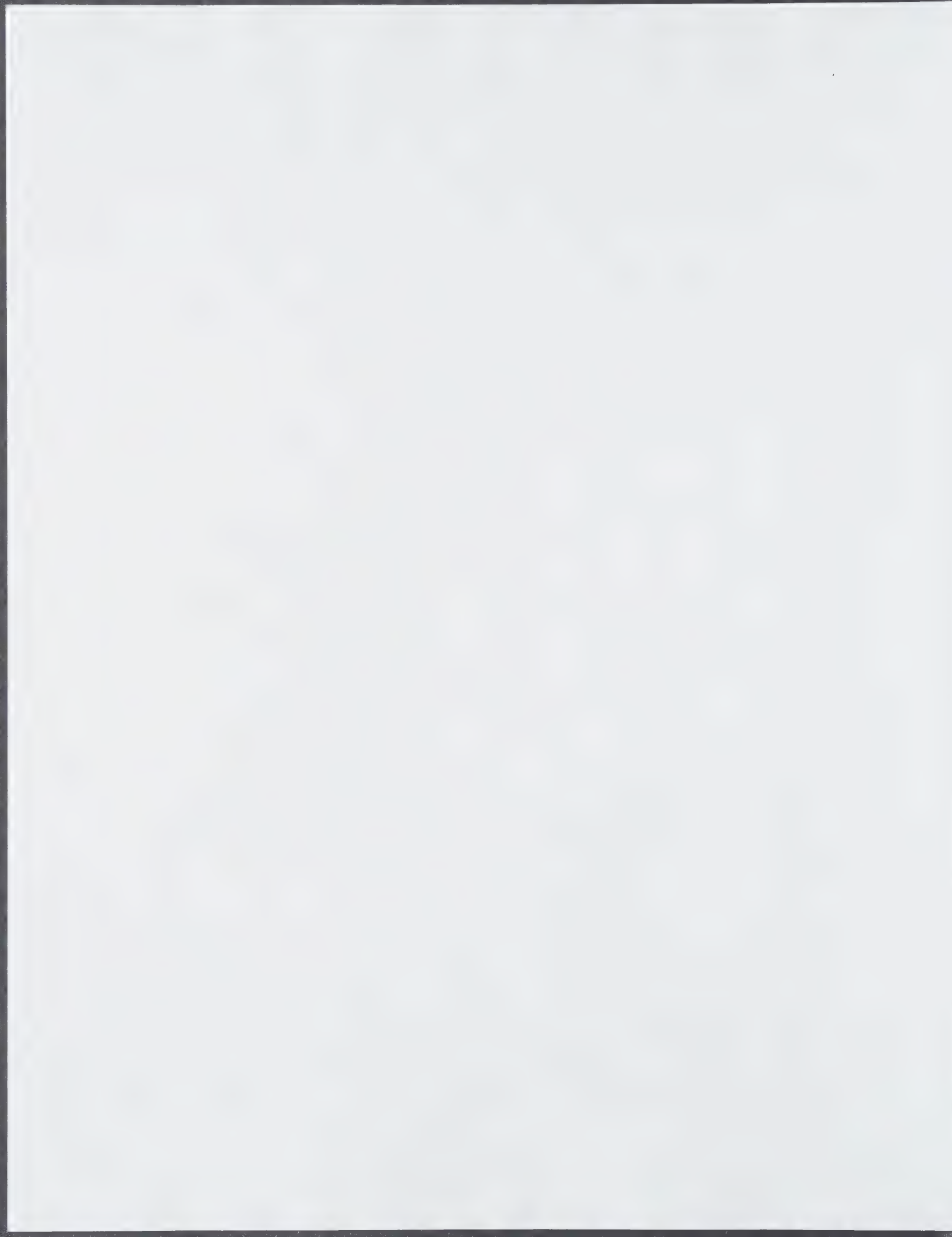


Figure 2. Josef Loschmidt

tions in the 1980's had millions of WLN records in their computers. The Aldrich Chemical Company even offered its catalog in WLN.

Wiswesser learned about the chemical work of Josef Loschmidt (1821-1895) [Fig. 2] from Moritz Kohn's paper in the *Journal of Chemical Education* (1), which is based on Richard Anschütz's paper (2) and reprint (3) of Loschmidt's 1861 volume (4). He felt that he had made a great rediscovery, also believing that this somewhat obscure chemist was the forerunner of the WLN; and he wanted the world to know about it.



He submitted a manuscript to the present author (A.B.) for the *Aldrichimica Acta*, which at the time was being distributed to over 200,000 scientists worldwide. Although the initial response was one of reluctance, I became enthusiastic about the subject after reading Loschmidt's book (3) and some letters, in particular one by Wiswesser to Linus Pauling (see Ref. 16), and collaborated to expand the paper, which appeared in *Aldrichimica Acta* in 1989 (5).

Wiswesser described Loschmidt's chemical firsts:

1. The first correct cyclic structure of benzene and of many aromatic chemicals, 121 in all.
2. The first representation of the allyl moiety.
3. The first representation of the vinyl moiety and of many others.
4. The first representation of cyclopropane, 21 years before it was made by Freund.
5. The first picture book of molecules, containing graphic displays with atomic domains, rather than abstract bond lines.
6. The first double- and triple-bond marks (within the overlaps).
7. The first realistic displays of atomic sizes and bond distances (largest overlap with triple bonds).
8. The first set of diagrams with correct C = 12, N = 14, O = 16 formulas.
9. The first textbook use of atomic-group symbols.
10. The first use of the valence prime marks on these and atomic symbols ("Valenz" was introduced by Wichelhaus in 1868, 7 years later).
11. The first LINE-FORMULA NOTATIONS ("rational formulas").
12. The first revelations of hexavalent and tetravalent sulfur.

The article also outlined Loschmidt's life and work, based largely on the biography Richard Anschütz published with the 1913 reprint. Wiswesser also prepared indices of Loschmidt and Anschütz citations, by author and subject. He translated Loschmidt's chemical names into English and collated structures with page numbers.

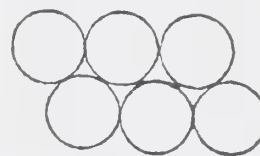
On the occasion of our last meeting in Reading, PA, Wiswesser gave me a great deal of his material on Loschmidt, even copies of the original plates, which he had hand-colored. Expressing concern about his own failing health, he urged me to continue his work on Loschmidt. I remember his pleasure upon receiving the *Acta* containing his article, just a few days before he died.

Since then, I have been trying to continue his work, by giving many lectures, first at the Boston American Chemical Society meeting in April 1990 (6), to which

he had been invited, and then at chemical society meetings and in chemistry departments, and finally by publishing several papers (7). All of these lectures and papers were based on Wiswesser's seminal paper in the *Aldrichimica Acta* (5). I have been greatly helped in these efforts by Professor Christian R. Noe, formerly at Loschmidt's alma mater, the Technical University in Vienna, and now at the J.W. Goethe University in Frankfurt.

Our papers have been attacked quite sharply by two historians of chemistry, Professors A.J. Rocke (8) and G.P. Schiemenz (9). Rocke presents three main arguments:

- (1) "Loschmidt clearly believed that the most probable structure for benzene (Schema 182) was a formula constructed from multiple fused cyclopropyl rings, using only single bonds. (8)"



Schema 182

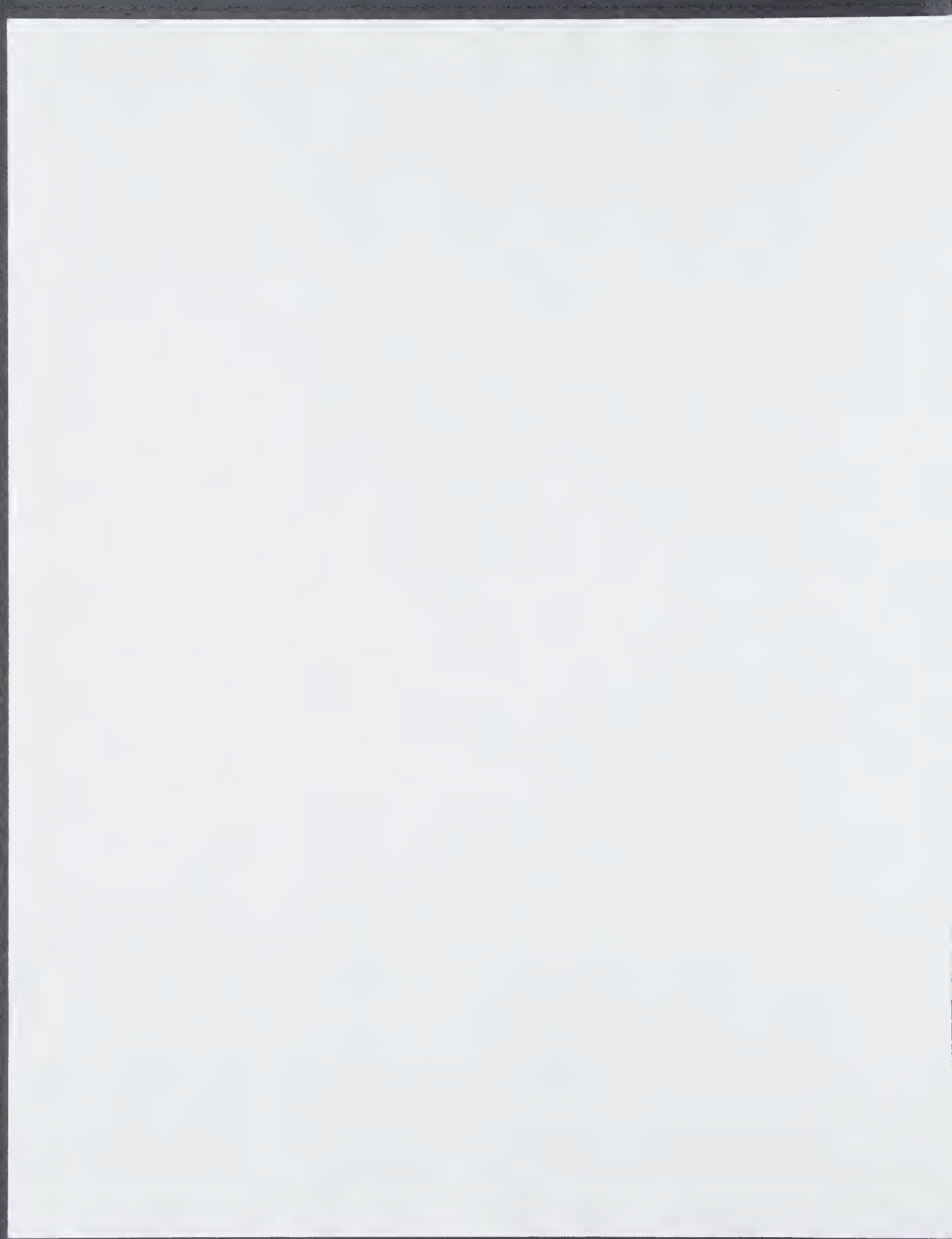
However, all of Loschmidt's more than 100 aromatic compounds are based on Schema 185 as the basic benzene structure.



Schema 185

- (2) "... Kekulé himself did not recognize Loschmidt as a predecessor for the benzene structure because he cited Loschmidt's benzene proposal in his first paper on the subject. If Kekulé had consciously taken the idea for benzene from this obscure source, or regarded the Loschmidt structure as similar to his own, the last thing he would have wanted to do was to draw attention to it. (8)"

Kekulé did not "cite" Loschmidt's proposal. All he said in one footnote in French (10) and one in German (11) was, "I prefer my structure to those of Loschmidt and Crum Brown." Aside from these denigrating footnotes - not citations - and one brief abstract (12), there were *no* references to Loschmidt's book in



the entire 19th century. Rocke points to the *Dictionary of Scientific Biography*, where more space is devoted to Loschmidt than to Kekulé. Loschmidt was indeed well known in the 19th century, but as a physicist, not a chemist. Not until Anschütz's first paper (2) was Loschmidt recognized as a highly competent chemist.

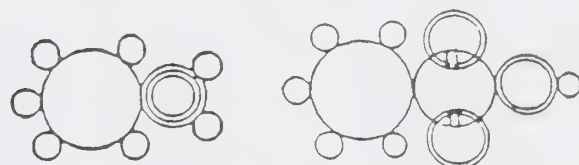
(3) "Even if Loschmidt had suggested a cyclical benzene structure in 1861, I would argue for its insignificance, because no empirical evidence could then be adduced to support the idea. (8)"

This is the kind of argument that can be made against much purely theoretical work.

Schiemenz criticized Wiswesser *inter alia* for claiming that Loschmidt was the first to consider a 6-carbon monocyclic structure for benzene, and also for stating that Loschmidt's book of 1861 was practically unknown and that he was "a shy and self-effacing man."

"Die Idee einer monocyclischen Anordnung der sechs C-Atome des Benzols kommt nach allem bei Loschmidt auch nicht andeutungsweise vor. (9a, 9c)"
 ["Nowhere is there in Loschmidt's book even the slightest hint of a monocyclic arrangement of the 6 carbon atoms in benzene."]

But consider the following structures to represent aromatic compounds aniline, benzenesulfonic acid, benzoic acid, and cinnamic acid.



Aniline

Benzenesulfonic Acid



Benzoic Acid



Cinnamic Acid

In a letter to *Chemistry and Industry*, Schiemenz wrote (9b):

This misunderstanding that Loschmidt's benzene structures might symbolize a monocyclic formula was already discussed by E. Rey in 1965, who aptly commented that one must interpret the circular symbol as what it really means and not as what it could be, and hence not as a circular array of six carbon atoms. The argument also holds true for all of Loschmidt's formulae (by the way, there were not 386!) which may have some superficial resemblance with modern molecular models. To date molecular modeling back to 1861 is just anachronistic.

Schiemenz's English summary of his longest paper states (9c):

In 1989, W. J. Wiswesser claimed that the correct, monocyclic structure of benzene was not conceived in 1865 by A. Kekulé, but already in 1861 by J. Loschmidt. It is shown that this view is neither correct nor new. As a symbol for the benzene nucleus C_6 , Loschmidt used a circle which Wiswesser believed to stand for a cyclic array of the six carbon atoms. In fact, this circle represents, in the two-dimensionality of the printed page, a sphere. Similar, but smaller 'circles' (*i.e.* spheres) represent hydrogen, carbon, nitrogen, oxygen and sulfur atoms. Their sizes are chosen so that the volumes of the corresponding spheres reflect the respective atomic weights (72 for C_6). This meaning soon passed into oblivion. As a consequence, gradually a misinterpretation developed which culminated in Wiswesser's view which recently has been popularized by C.R. Noe and A. Bader.

The most telling indication that Loschmidt thought of a monocyclic structure is in his Schema 229 for *p*-phenylenediamine (13):

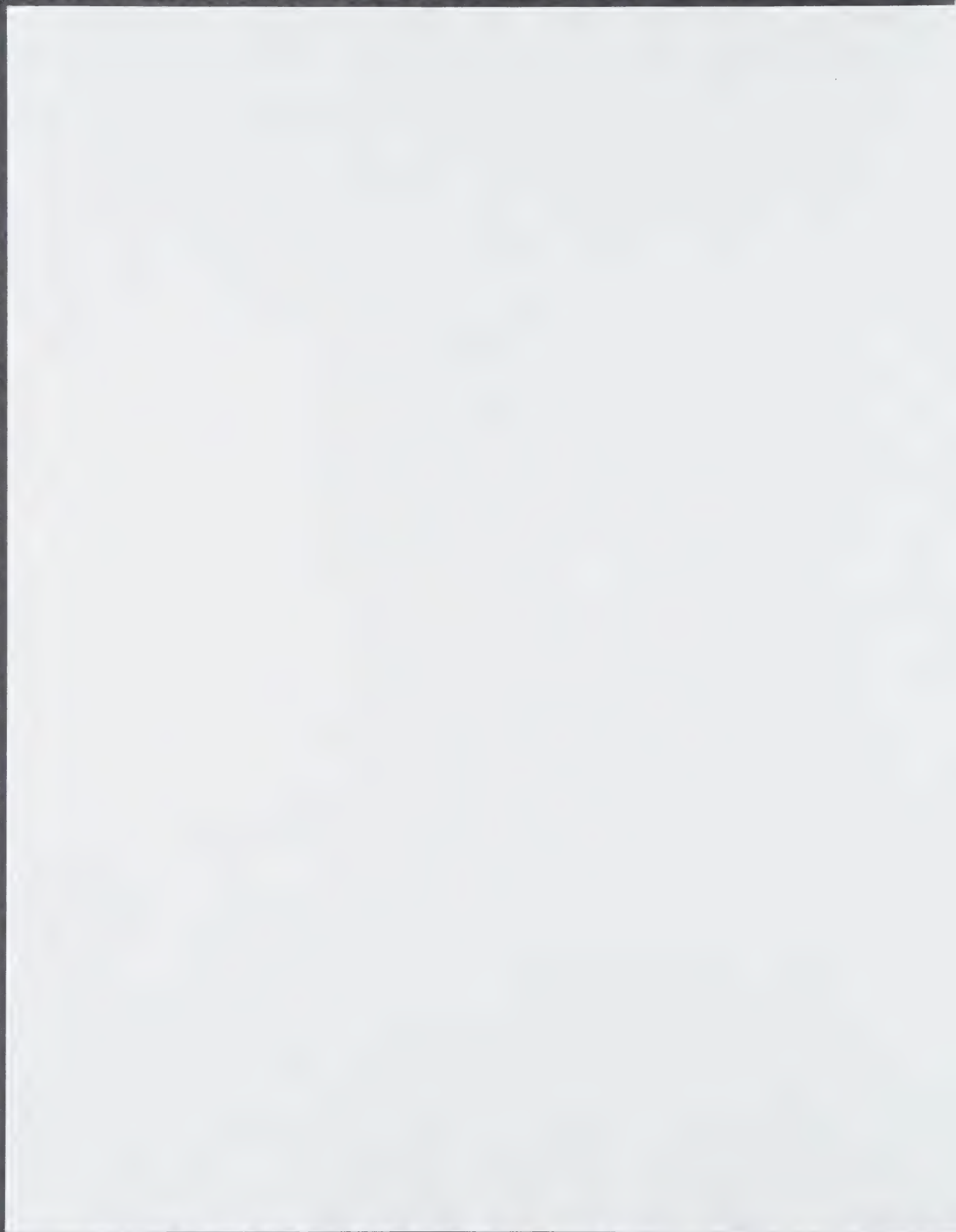
Schon der Anblick des Schema zeigt die Möglichkeit von isomeren Modificationen. ["Just looking at Schema 229 shows the possibility of isomeric modifications."]



Schema 229

Schiemenz counters (9d):

Auch eine Anmerkung Loschmidts zum 'Semibenzidam' = 'Azophenylamin' (Phenylendiamin), Schema 229, gehört hierher: 'Schon der Anblick des Schema zeigt die Möglichkeit



von isomeren Modificationen' (Loschmidt (1861), 34). Entgegen der Auffassung von Noe and Bader (*Chemistry in Britain* 29 (1993) 402, Corrigendum: S.573; vgl. dies., in Wötiz (1993), 233) einer Interpretation als o-, m-, p- Positionsisomerie noch nicht zugänglich (Anschütz (1913), 132), kann diese Bemerkung nur im Sinne einer Konstitutionsisomerie verstanden werden (vgl. Loschmidt (1861): *Isomerie*, S.8-11). Mithin muß bereits Loschmidt, der anderswo N-N- und auch O-O-Bindungen hat (Schema 176,178), an die Atomverknüpfung des Phenylhydrazins gedacht haben.

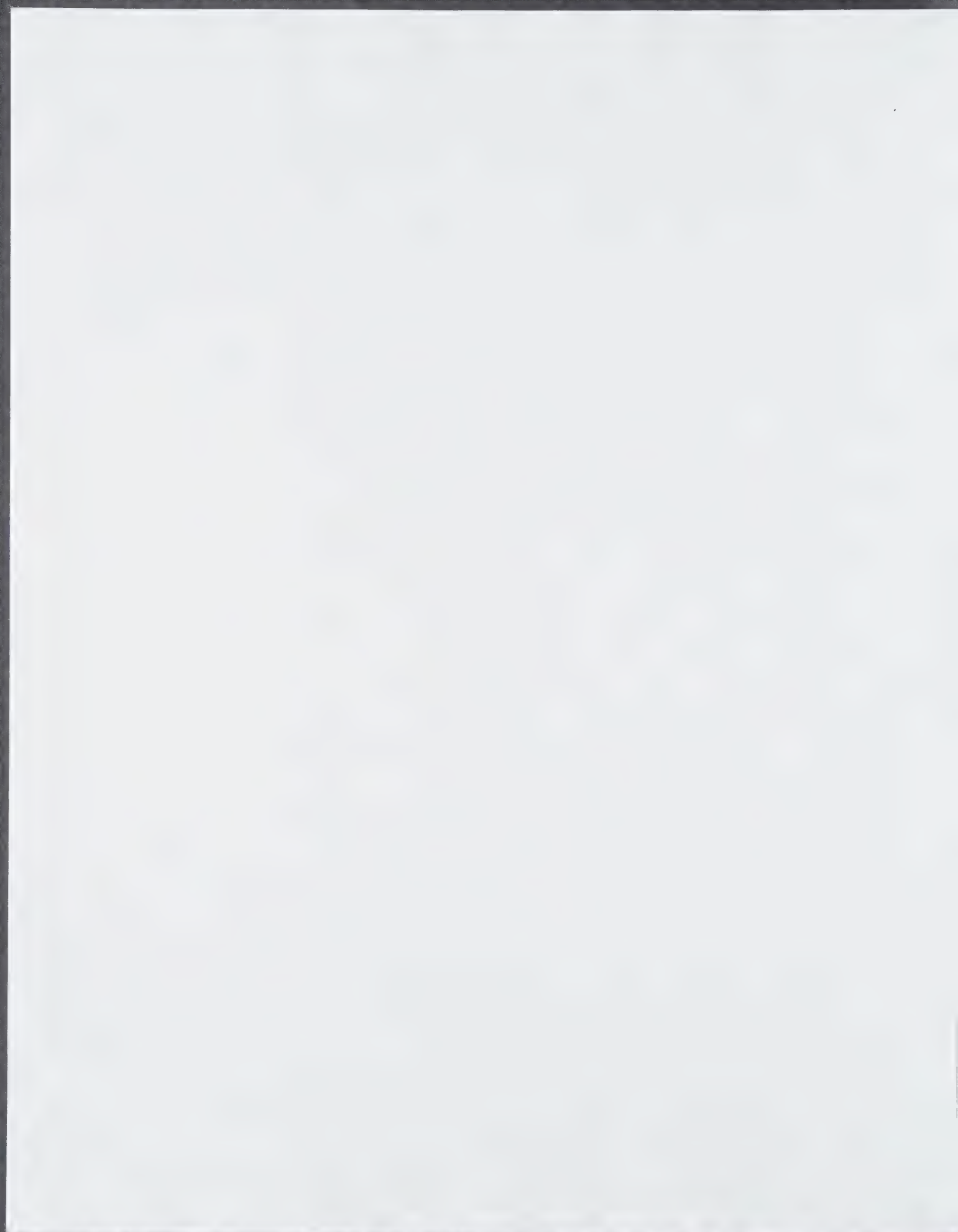
Thus, Schiemenz dismisses this argument by claiming that Loschmidt must have been thinking of an isomer like phenylhydrazine (which had not yet been made). However, in his discussion on isomerism, Loschmidt distinguished between isomers "im engern Sinne," like o-, m-, and p-isomers, and isomers "im weiteren Sinne," like phenylenediamine and phenylhydrazine. The former you can predict just by looking at them, but not the latter (14):

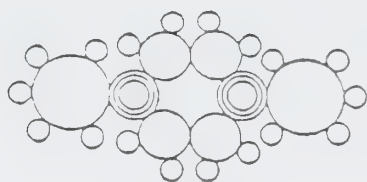
... wir **Isomerie im engern Sinne nennen**. Solche Isomerie findet statt zwischen Milchsäure und Paramilchsäure, zwischen **Alphatoluolsäure und Betatoluolsäure**. Die anderen Arten der **Isomerie im weiteren Sinne sind**: erstens jene Fälle, wo zwei Substanzen denselben Kern und dieselben Aufsatz-Atome haben, wo aber die letzteren zu anderen Aufsatzelementen gruppiert sind. **So haben Nitrotoluol und Benzaminsäure** [i.e., aminobenzoic acid] nicht nur dieselbe Zusammenstellung $C_7NH_3O_2$, sondern auch denselben Kern C_6^{VIII} und dieselben Aufsatzatome NH_2O_2 ." [Emphasis added]

Schiemenz points out that Loschmidt did think of six-atom monocycles such as his Schema 237, 1,4-diphenylpiperazine, and claims that this is "unambiguous proof that he did not think of such an array for [the C_6 nuclei]. (15)" Yet, in fact, Loschmidt came even closer to Kekulé's cyclohexatriene structure in his Schema 239 for the 1,3,5-triazine derived from aniline and 2,4,6-trichloro-1,3,5-triazine.

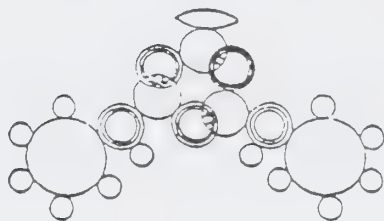
N^o 10 Kokele an Erlenmeyer verglichen 2. 1. 87
 Frankfurt 4. Jan 62.
 Lieber Erlenmeyer!
 Ihre gegenwärtige Kritik der Erdmann'schen Azyklischen Theorie habe ich
 erhalten (- Leisten dank!) und habe;
 ziemlich gleichförmig mit Loschmidt's Confessions
 formale. Ich bedauere, daß Sie nicht zu
 einer Kritik dieses Ihre Kritik aufzuführen;
 ich hätte natürlich lieber still yaffringan &
 ich glaube, sogar ich will wohl Ihre Auffor-
 derung still yaffringan. Ich würde mich ein

Figure 3. Letter from Kekulé to E. Erlenmeyer





Schema 237



Schema 239

Rather than being unambiguous proof that Loschmidt did not think of benzene as a six-carbon monocycle, it suggests that he must have considered such a structure but did not know how to do this without the inclusion of double bonds, hence, his decision to leave that “*in suspenso*. (16)”

Shortly after Loschmidt's book appeared on January 4, 1862, Kekulé wrote a letter to Emil Erlenmeyer [Fig. 3], in which he alluded to “*Loschmidt's Confusions formeln* (sic).” Why would Kekulé have chosen such a description for Loschmidt's structures? Because in 1861, Kekulé stated that you cannot write formulae of constitution, and so considered Loschmidt's structures “*formulae of confusion* (17):

Which of the different rational formulae one wants to use for specific cases is essentially a question of appropriateness. Based on the observations already given, there can be no doubt that one may use different rational formulae for the same substance. At the same time, one must also, of course, keep in mind that the rational formulae are only formulae of reactions (“*Umsetzungsformeln*”) and not formulae of constitution (“*Constitutionsformeln*”), and that they do not in any way describe the constitution, i.e., the position of the atoms in the compounds. This should be clearly stressed, because oddly enough some chemists still believe that by the study of chemical reactions, one can derive with certainty the constitution of compounds, and thus depict the positions of the atoms in the chemical formula. That the latter is not possible warrants no special proof ... Yet a basic task of natural science must of necessity be to discover the constitution of matter or in other words, the position of atoms; this, however, can only be at-

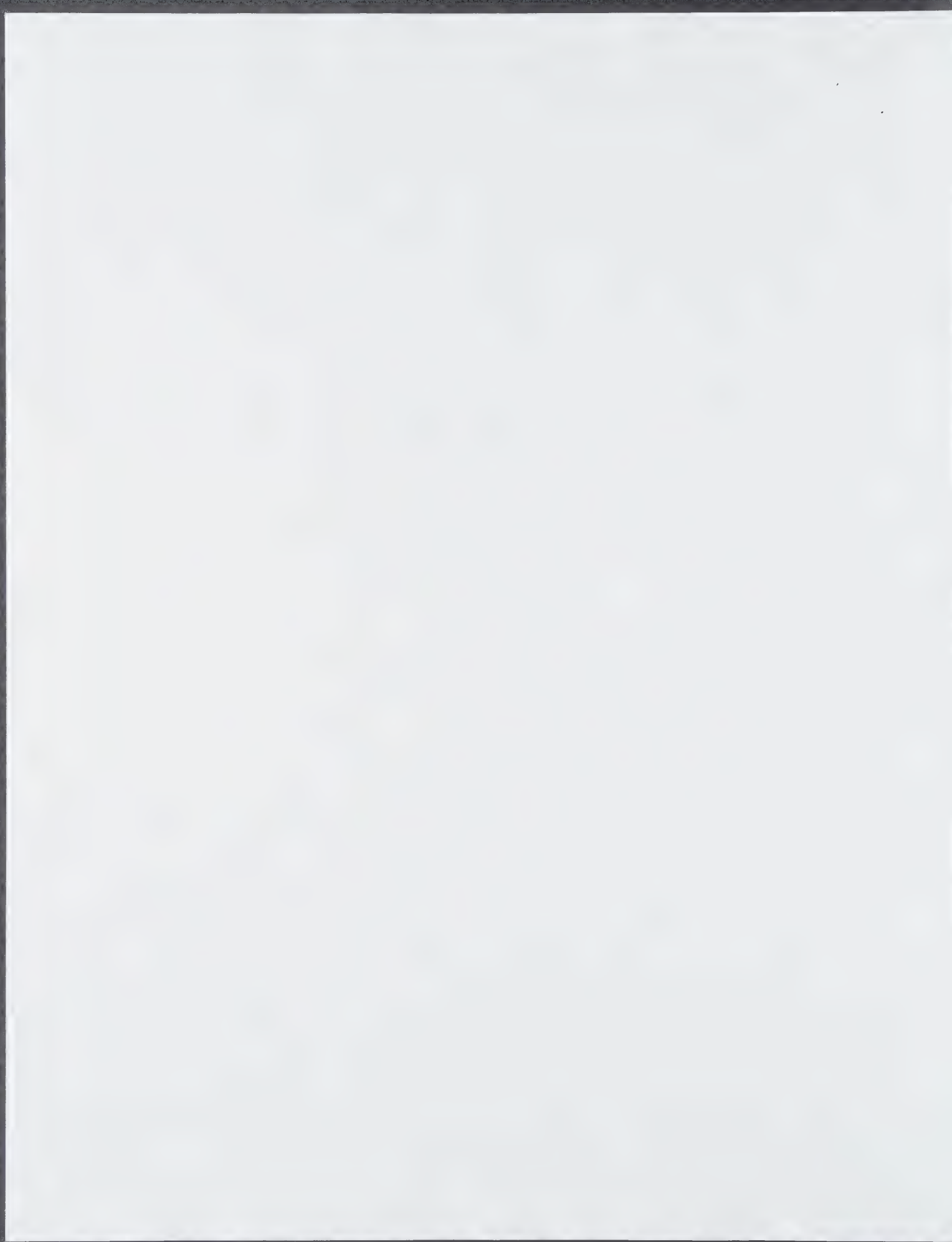
tained by the comparative study of physical properties of the existing compound and certainly not by the study of chemical reactions ... But even when we have succeeded in this, different rational formulae (“*Umsetzungsformeln*”) will still be appropriate. [Emphasis added]

As R.B. Woodward stressed in his 1972 Cope lecture (18):

He [Kekulé] was, in truth, too much under the influence of the theoretical and physical chemists of the time, who were inordinately opposed to the idea of fixed chemical structure—so much so that, until 1886, the infant *Berichte der Deutschen Chemischen Gesellschaft*, born in 1868, would only print structural formulae using dotted-and-dashed lines; the use of solid lines to represent the nearest neighbor relationships would have imputed too much reality to an hypothesis which leading theorists of the day simply would not accept.

Schiemenz (19) has claimed that Loschmidt's 1861 book became well known after its publication. As is clear from Kekulé's letter, he and Erlenmeyer knew of it (20). So did Herman Kopp who reviewed it briefly (12). Before Anschütz's publications of 1912 (2) and 1913 (3), however, there were only three references to it: two brief and disparaging footnotes (10, 11) in Kekulé's papers and Kopp's review (12). If indeed Schiemenz (19) is correct in asserting that Loschmidt's book was widely known, chemists may have “borrowed” from it without bothering to cite it; but that seems unlikely (21).

Schiemenz faults Wiswesser for describing Loschmidt as “a shy and self-effacing man.” How could a man “who was a member of the Imperial Academy of Sciences, founder of the Chemical-Physical Society, institute director and, at one time, dean of the faculty of philosophy of the University of Vienna be ‘a shy and self-effacing man’? (22)” Although this may indeed be difficult to understand, many who knew Loschmidt personally wrote about that very quality. Franz Exner, Loschmidt's successor as professor of physics at the University of Vienna, had known Loschmidt well for many years because Loschmidt had been a student and friend of Exner's father at the University of Prague. At the 100th anniversary of Loschmidt's birth, Exner wrote that Loschmidt had “a rare goodness of heart and modesty; totally without jealousy, he could enjoy the scientific successes of others just as much as his own. (23)” Alexander Bauer, the grandfather of the Nobel laureate Erwin Schrödinger, described his unsuccessful attempts to bring the *Chemische Studien* to the attention of scientists during a trip to England (24):



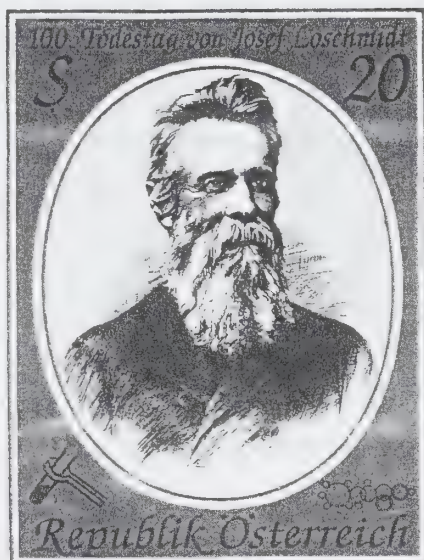


Figure 4. Commemorative Stamp

Only one, the mathematician Liouville (25) in Paris showed great interest and gave it a very favorable review. That publication [*Chemische Studien*] was quickly forgotten. It cannot be denied that its author was much to blame for that, because he later did nothing to draw attention to it, even though he had many opportunities.

Loschmidt's best friend, Ludwig Boltzmann, said, "...everywhere Loschmidt's excessive modesty prevented his being appreciated as much as he could and should have been. (26a)... He just could not stand it, when people talked about him and his merits. (26b)"

Richard Anschütz questioned why Loschmidt did not point to his own work of 1861 at the time of the *Benzolfest* in 1890 which celebrated the 25th anniversary of the correct benzene structure. Anschütz believed that Loschmidt's silence was "...because of the undemanding modesty which was an integral part of his character. The discovery of *Chemische Studien* ... his old, unnoticed and forgotten work, he left to chance (27)"—and, luckily, we must add, to Richard Anschütz and William Wiswesser.

A high point in Loschmidt's recognition as a chemist came at a symposium at the University of Vienna in June, 1995, at which many well known chemists paid tribute to Loschmidt, who had died 100 years earlier in July, 1895. Among the lecturers were Max Perutz, Carl Djerassi, and Sir Herbert Bondi, all originally from Vienna, and Ernest Eliel, Albert Eschenmoser, Christian Noe and Günter Schiemenz. The papers, which dealt

with chemistry and physics, have been published in English by Plenum (28). It was Wiswesser's recognition of Loschmidt's remarkable insights into chemical structure which sparked the renewed interest in and a greater understanding and appreciation of the *Chemische Studien*, culminating in the 1995 Symposium.

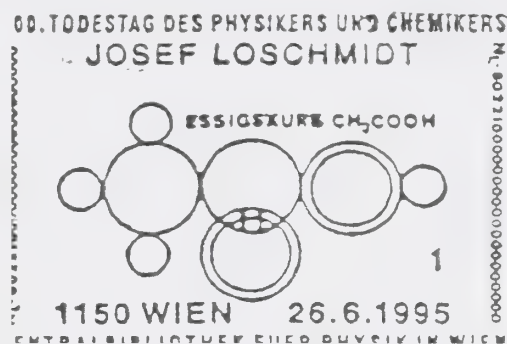


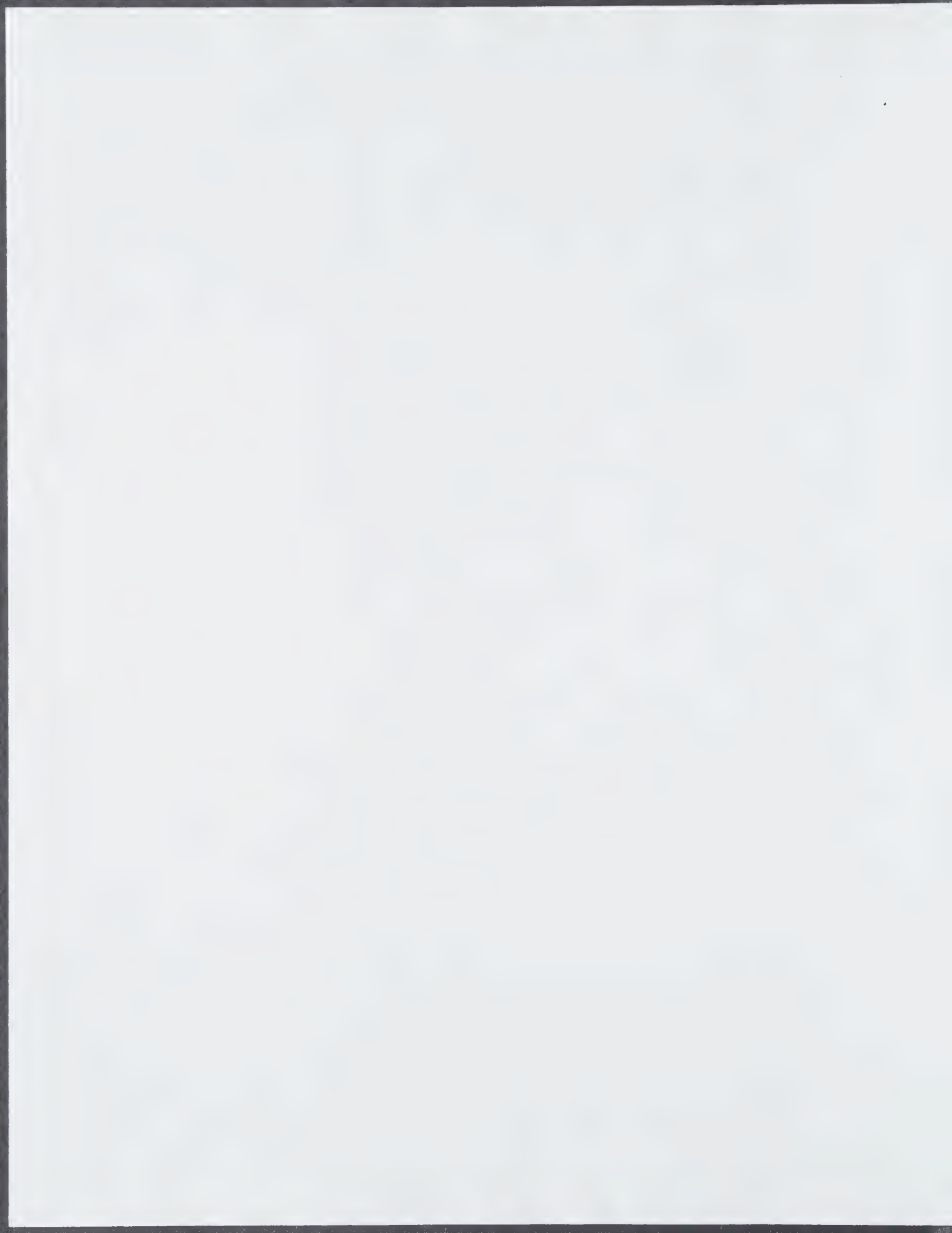
Figure 5. First-day Postmark

The Austrian postal service issued a commemorative stamp [Fig. 4] showing one of Loschmidt's many correct aromatic structures, that of cinnamic acid. The postmark of the first-day cover [Fig. 5] showed the structure of acetic acid, one of Loschmidt's many firsts.

Did Wiswesser make mistakes? Of the twelve "famous firsts," No. 1, "The first correct cyclic structure of benzene and of many aromatic chemicals, 121 in all," is somewhat of an overstatement. Loschmidt was the first to consider a monocyclic six carbon ring, but he did not know what to do with the double bonds. Kekulé's cyclohexatriene of 1865 appeared to be an improvement, but the puzzle about its unsaturation was still to be addressed (29). Wiswesser was correct in describing Loschmidt's other firsts and in ending his paper with, "...that tiny book of 1861 was really the masterpiece of the century in organic chemistry."

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12. Liebig's *Jahresbericht*, **1861**, 1, 335. [See Ref. 3, p. 100.]
13. Ref. 3, p. 68.
14. Ref. 3, p. 15.
15. Ref. 9b; Ref. 9c, p. 47.
16. I want to thank William F. Reynolds for pointing out that Loschmidt was probably reluctant to accept a benzene structure with double bonds, of which he was well aware, since this seemed inconsistent with the known chemistry of benzene. As Wiswesser pointed out in a letter to Linus Pauling (August 2, 1987, copy in author's personal collection), Loschmidt provided "amazingly perceptive graphical visualizations" in 1861 of increasingly tighter, overlapping bonding in ethane (Schema 9), ethylene (Schema 56, 57), and acetylene (Schema 59). Photocopies of this letter are available on request from either the author or the editor of the *Bulletin*.
17. A. Kekulé, *Lehrbuch der organischen Chemie*, F. Enke, Erlangen, 1861, p. 157.
18. R. B. Woodward, unpublished manuscript, courtesy of R. Hoffmann and the Chemical Heritage Foundation.
19. Ref. 9c, pp. 42-43.
20. "Knowing" and "understanding" are not always the same. In the heat of discussion during the Boston American Chemical Society meeting (6), I suggested that Kekulé may have plagiarized Loschmidt. I no longer think so. Kekulé 'knew' Loschmidt's book but did not 'understand' it as Anschütz and Wiswesser did. Loschmidt's Schema 185 for benzene may have led to Kekulé's snake dream, but we can never know for certain whether he even had that dream. The first six-carbon monocyclic benzene structure was Loschmidt's; the first cyclohexatriene Kekulé's. Most recently E. Heilbronner and K. Hafner have reviewed this controversy ("Bemerkungen zu Loschmidts Benzolformel," *Chemie Unserer Zeit*, **1998**, 32, 34). The authors approve particularly of Schiemenz' (Ref. 9c) "ausgezeichneten und akribisch recherchierten Richtigstellung" [Schiemenz' excellent and meticulously researched correction] and of Hafner's "August Kekulé, dem Baumeister der Chemie zum 150 Geburtstag," Justus von Liebig Verlag, Darmstadt, 1980. There (p. 76) Hafner wrote, "...again Kekulé succeeded brilliantly. His irresistible desire for clarity and his unusual power of imagination again helped. Basically the benzene formula is a logical conclusion from structural history. Today it seems obvious, but over a hundred years ago it was an extraordinary mental leap, comparable to the intellectual effort once necessary before man could exchange sled runners for the wheel. *The idea that a hydrocarbon might have a circular structure was totally foreign to chemists of that time. The circle was the symbol for the indivisible, the atom.*" [emphasis added]. But 13 years earlier Ferdinand Kirchhof ("Joseph Loschmidt und die Benzolformel," *Chem. Appar.*, **1967**, 91(2), 48) had written, "*The idea that a compound might have a circular structure was totally foreign to chemists of that time. The circle was the symbol for the indivisible, the atom, and the merit of having depicted the C₆ⁿ nucleus as a circle belongs unquestionably to Loschmidt.*" [emphasis added].
21. Recently, F. W. Lichtenthaler ("Emil Fischer's Proof of the Configuration of Sugars: A Centennial Tribute," *Angew. Chem. Int. Ed. Engl.*, **1992**, 31, 1541) has suggested that Adolf Baeyer, Hugo Schiff, and Rudolph Fittig were the first to depict sugars correctly, around 1870. Anschütz pointed out that Loschmidt was the



- first—nine years earlier—to show the correct structures of mannitol and other sugars (Ref. 3, pp. 119-120, footnotes 63, 66, 69, 70 and 72). But are Baeyer, Schiff, and Fittig likely to have known this?
22. Ref. 9c, p. 57.
 23. F. Exner, "Zur Erinnerung an Josef Loschmidt," *Naturwissenschaften*, **1921**, 9, Heft 11, March 18.
 24. A. Bauer, *Oesterreichische Chemiker-Zeitung*, **1913**, XVI, No. 18, 241, September 15.
 25. Jean Jacques has kindly pointed out that this was Joseph Liouville (1809-1882), but his review of *Chemische Studien* appears not to have been published.
 26. L. Boltzmann. "Zur Erinnerung an Josef Loschmidt," a eulogy presented to the Imperial Academy of Sciences in Vienna on October 29, 1895 and published by the executive committee for the erection of the Loschmidt monument, Vienna 1899; (a) p. 14; (b) p. 16.
 27. Ref. 3, p. 109.
 28. W. Fleischhacker and T. Schönfeld, Ed., *Pioneering Ideas for the Physical and Chemical Sciences*, Plenum Press, New York, 1997; see also Ref. 7g, h, 9e.
 29. For a clear discussion of Kekulé's benzene formulae, see G. P. Schiemenz' "Where did Kekulé Find 'his' Benzene Formula?" Ref. 7b, Ch. 9.

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