Josef Loschmidt, the Father of Molecular Modelling*

ALFRED BADER

One often hears anecdotal reports that this or that important work has been overlooked. This may be more common in art history – Jan Vermeer was forgotten for 150 years – but it happens even in the sciences.

One of the great discoveries of the nineteenth century, generally credited to August Kekulé, involved a much discussed dream of snakes biting their tails, leading to the circular structure of benzene. K. Hafner [1], the director of the Kekulé museum in Darmstadt, put it clearly in 1980: "... 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 theory. 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".

However, 13 years earlier, F. Kirchof [2] 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 C_6VI nucleus as a circle belongs unquestionably to Loschmidt" – Loschmidt, not Kekulé [3].

Who was this man, Loschmidt, referred to by Kirchof? Ask many chemists around the world, and few will know. Yet in every generation since Loschmidt died in Vienna in 1895 someone has discovered his work and has written about it, only to have it forgotten again.

The first to write extensively about Loschmidt was Richard Anschütz [4] who republished Josef Loschmidt's *Chemische Studien I* [5] of 1861. Anschütz reformatted [6] Loschmidt's work, eliminating the seven cumbersome fold-out plates, and placing the 368 graphic formulae with the text. Of these formulae, 121 are of aromatic compounds. Anschütz added many explanatory notes and a brief biography, and this reprint is much easier to use than the original.

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* This paper is based on work with the late Dr William Wiswesser and Professor Christian R. Noe.

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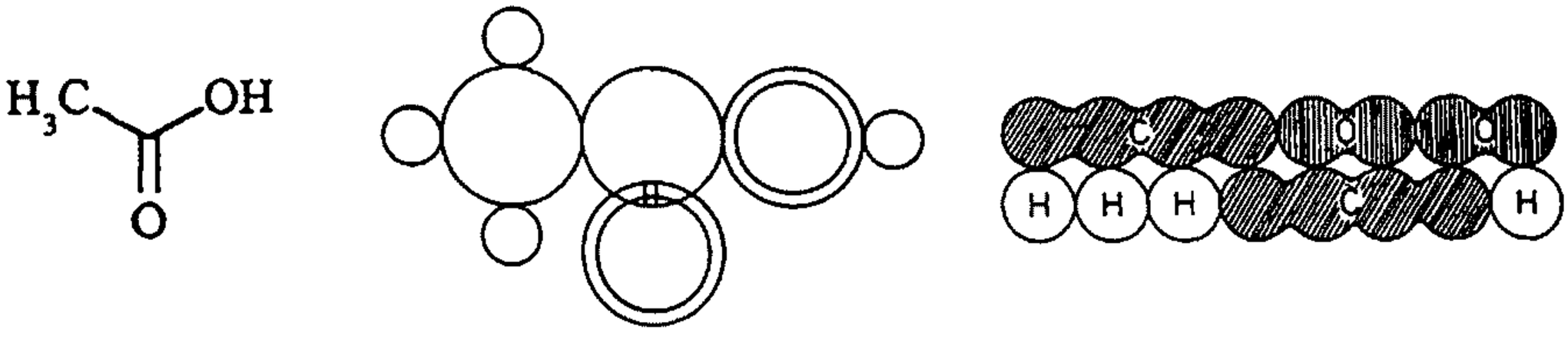
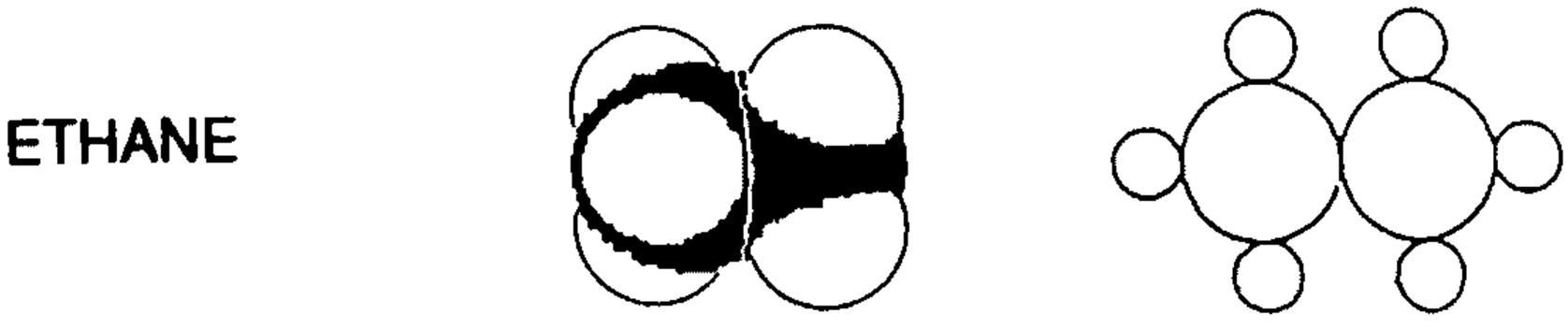


Acetic Acid Loschmidt 1861 Kekulé 1865

Figure 1



Molecular Modelling Today Loschmidt 1861

Figure 2

Anschütz's efforts were truly amazing. He was a Kekulé student, became his secretary and successor as professor of chemistry at the University of Bonn, and finally his biographer [7]. And reading Loschmidt's tiny book of 1861, he realised that Loschmidt's aromatic formulae preceded Kekulé's by four years! Yet he spent months reformatting and republishing Loschmidt's rare book, an act of atonement by a student for his teacher unparalleled in the annals of science.

Carbon Rings

... The second possiblility, that of another structure of the nucleus is shown in Figure 68 for C_3H_6. This linking of the carbon atoms is not unlikely, in view of the same linking with other polyvalent atoms; in fact, as we will see below with phenyl, it is in some cases the most acceptable supposition. One will be able to decide when we know whether there are two hydrocarbons, C_3H_6.

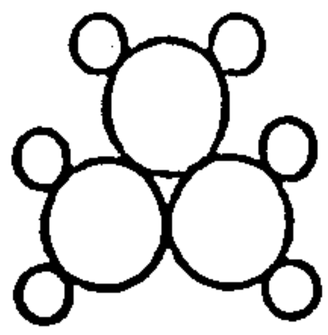


Figure 3 *J. Loschmidt, KONSTITUTIONSFORMELN der organischen Chemie in graphischer Darstellung - Kern C_3. Propylen - und Allyl - Reihe (translated).*

Anschütz favourably compared ([6], p.110) Loschmidt's structure for acetic acid with Kekulé's (Figure 1), and pointed out that Loschmidt was the first to depict double and triple bonds, with the overlaps (Figure 2), showed ozone correctly and cyclopropane (Figure 3) 21 years before it was first made by Freund in 1882. Loschmidt also showed many aromatic structures correctly (Figure 4), not just benzene, toluene, phenol, but more complicated structures like cinnamic acid (with the double bond trans!) and benzidine.

Of course Anschütz asked the obvious question: did Kekulé know Loschmidt's book of 1861? In a simple eight word sentence ([6], p.105) Anschütz denied that Kekulé had ever seen the work. What a bit of luck that Anschütz found Kekulé's reference to Loschmidt in footnote 2 of that famous paper [8] presented by Wurtz for Kekulé in Paris. There Kekulé stated that he preferred his structures to those of Loschmidt and Crum Brown. Had Anschütz not persevered and finally found, studied and reprinted Loschmidt's book, that seminal work in organic chemistry might still be unknown.

But surely, when a scientist states that he prefers his structures to another's, he must have studied that other's. Even more telling is a letter written by Kekulé to Erlenmeyer on January 4, 1862, just months after Loschmidt's publication, in which Kekulé refers to Loschmidt's *Confusionsformeln* ([7], p.305). Sometime between 1913, Anschütz's republication of Loschmidt's work [6] and his publication of the Kekulé biography [7] in 1929, Anschütz found this damning letter, and then admitted that Kekulé must have seen *Chemische Studien I*. Kekulé may not have understood that work fully, but, as J. Wotiz has pointed out ([3], chap.17), "Dreams do not come with footnotes and literature citations".

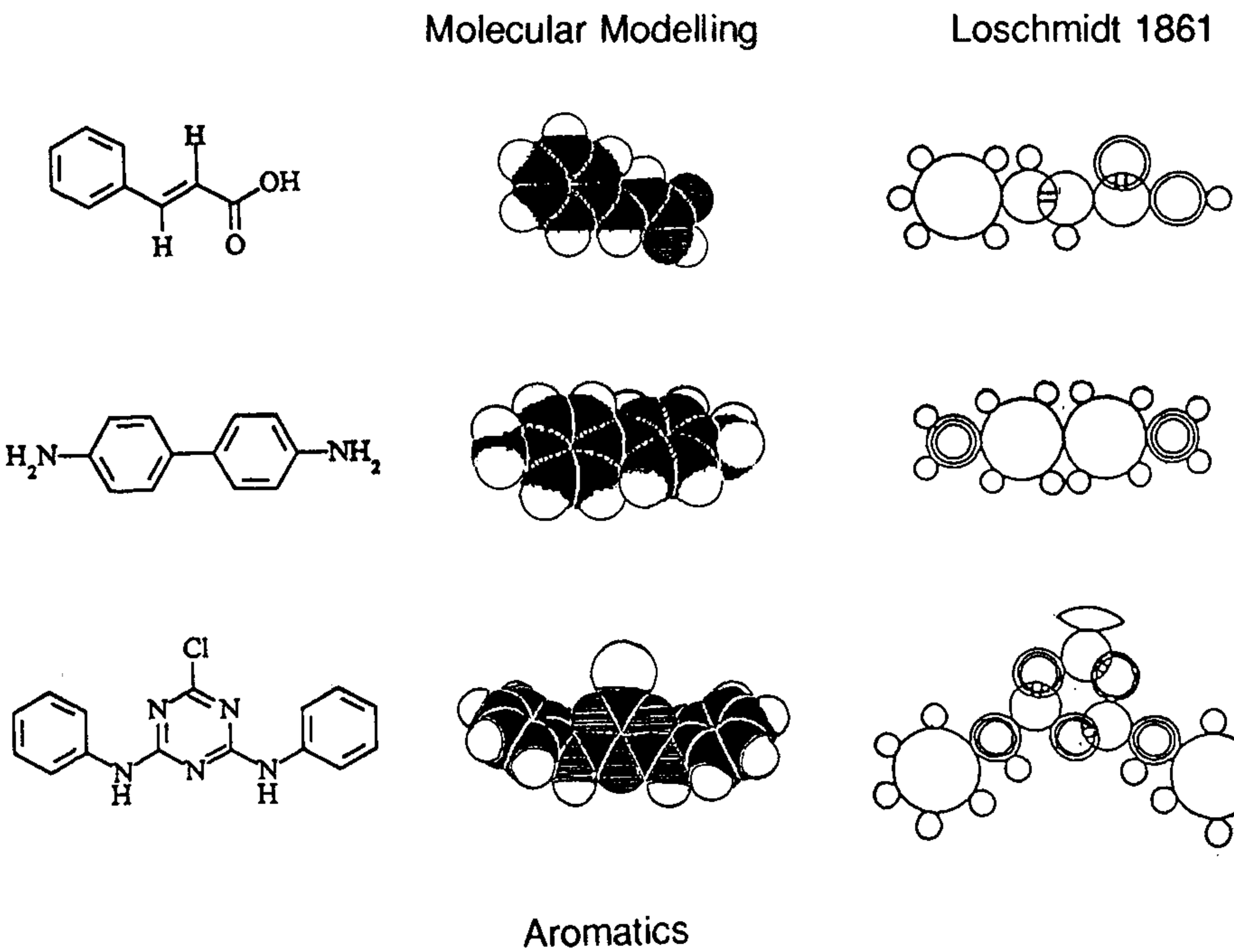


Figure 4

Anschütz stressed that it was a great pity that Loschmidt had not published his work in a widely read chemical journal, without asking which journal might have accepted this complicated 47 page treatise. It is doubtful that any learned journal at that time would have accepted a theoretical paper by an Austrian outsider, a high school teacher without a PhD, from Vienna where chemistry in the modern sense, accepted by the scientific community, had only been taught since the late 1840s. It was a time when Kekulé had stipulated that only "*Docenten der Chemie*", academics, should participate at the great chemists' conference in Karlsruhe in 1860 ([7], p.185).

And so Loschmidt did what few other chemists of meagre means would have done: he paid for the publication himself. But the book was for sale by the well-known Viennese publisher, Carl Gerold's Sohn, for 20 Neugroschen, was listed in the publisher's catalogue, and was purchased by the British Library which still has the soft-bound copy and the 1863 invoice from David Nutt, bookseller in the Strand.

The title is interesting. In the 1861 version in the British Library and in the Technical University in Vienna it is "*Constitutions-Formeln der organischen Chemie in graphischer Darstellung*" and Kekulé calling them

"*Confusions-Formeln*" was probably a play on words – Constitution – Confusion. To reprint the work, Aldrich obtained a microfilm from the National Library in Vienna, and there the title is "*Constitutions-Formeln der organischen Chemie in geographischer Darstellung*". Presumably that was a galley, changed from geographic to graphic in the final version. But geographic, describing the arrangement in space, was really a very apt description.

Anschütz's often repeated statement ([6], p.104) that Kekulé's 1865 depiction of benzene and its derivatives is preferable to Loschmidt's because the former could explain ring isomerism, is questionable. Discussing p–phenylenediamine (structure 229 on p.68 of [6]), Loschmidt stated that just looking at that structure suggested the possibility of isomers. Loschmidt called his book "*Chemische Studien I* "and must have planned a sequel, perhaps to deal with problems like isomerism, and was discouraged by the silence of his contemporaries, and the criticism of Kekulé.

Professor Noe and I were introduced to the work of Loschmidt by an essay of the late Dr W.J. Wiswesser [9], who had studied Loschmidt's structures in great detail, and saw them as the first 'rational formulae', close to his Wiswesser line notation, the WLN, widely used in the third quarter of this century. In April 1990, the American Chemical Society held a symposium at its meeting in Boston, commemorating the 100th anniversary of the Benzolfest in Berlin. The German Chemical Society had then honoured August Kekulé for his many achievements and for first showing the correct structure of benzene 25 years earlier. Dr Wiswesser, Professor Noe and I were invited to speak about Loschmidt at the Boston symposium but unfortunately Dr Wiswesser died the preceding December. Our presentation in Boston was criticised by some historians of science, who stated that Loschmidt used the circle for benzene just as a symbol and did not think of the six carbon atoms as being in a circle. One problem with Loschmidt's book is the author's extreme brevity. He did not repeat himself, and indeed in his chapter on benzene ([6], pp.58–77) did not state explicitly that he considered the six carbon atoms to be in a ring. But in the discussion of cyclopropane ([6], p.28), he said clearly (Figure 3) that while cyclopropane had not yet been made, such a ring was not improbable "as we will see below with phenyl, such a chain appears in some cases to be the most acceptable supposition". Equally persuasive is Loschmidt's depiction of six-membered heterocyclics, such as the heteroaromatic triazine 139 ([6], p.70).

Much has been written recently about fraud in science. Where does lack of understanding and forgetfulness end and fraud begin? The borderline is often fuzzy. Kekulé must have seen Loschmidt's book, but how much did he understand? Only with the psycho-analytical methods developed by another Austrian, Sigmund Freud, might we have been able to find out why Kekulé suppressed his first perception of benzene as a circular structure in Loschmidt's book, and transformed it into the story of a dream. Was it ambition or was it nationalism – the just developing conflict of Prussia with Austria which culminated in the war of 1866? We shall

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CHEMIKER-ZEITUNG CHEMISCHE APPARATUR

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Zu der GDCh-Hauptversammlung und Kekulé-Feier vom 13. bis 18. September 1965 übermitteln den in Bonn Versammelten die herzlichsten Grüße und Wünsche für einen ergebnisreichen Besuch

REDAKTION UND VERLAG
Chemiker-Zeitung / Chemische Apparatur

100 Jahre Benzoltheorie

Friedrich August Kekulé von Stradonitz zum Gedächtnis

Von Richard Lepsius

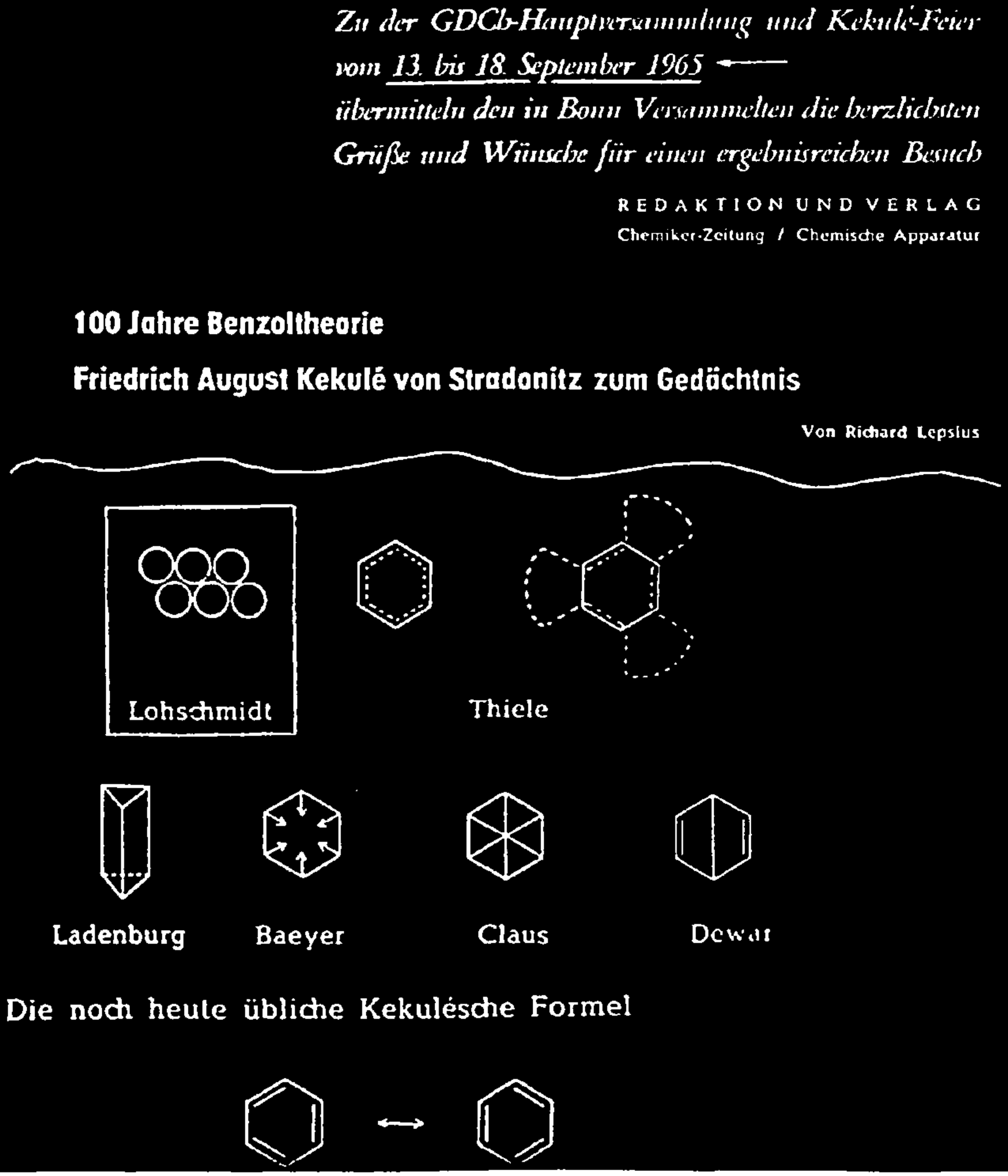
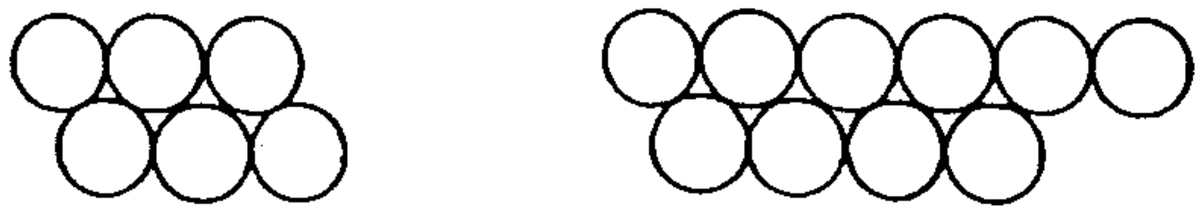
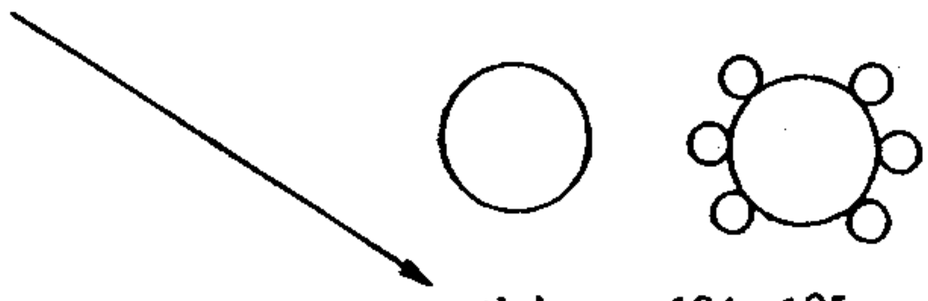


Figure 5

Under these circumstances one might almost be tempted . . . to think of Figure 182. From what we know so far, it is impossible to reach a definitive conclusion, and we can leave our decision in suspenso, particularly as our constructions are totally independent of this. We take for the C6 VI nucleus Figure 184, and treat it as if it were a hexavalent element.



Schema 182, 183.



Schema 184, 185.

Figure 6 *J. Loschmidt, Chemische Studien 1861 (translated)*

never know, though we can be certain that it was not forgetfulness; Kekulé had a wonderful memory ([7], p.468).

Or consider Richard Lepsius' depiction of various benzene formulae (Figure 5) published [10] by this academic grandson of Kekulé to commemorate the supposed 100th anniversary of the correct benzene formula. Kekulé certainly did not look at benzene in 1865 as there shown, and to misspell Loschmidt's name is a minor insult added to the major injury in alleging that Loschmidt looked on benzene as indicated. Loschmidt said (Figure 6, [6], p.59) that one might be tempted to look on benzene as Lepsius depicted, but he preferred the circular structure 185.

Whatever the motivation of Kekulé, the results are clear. Loschmidt probably learned of Kekulé's remarks and knew how disregarded his chemical studies were. And so most of his work from then on was in physics; his most important paper was on the calculation of the Loschmidt number, the number of molecules in a litre of an ideal gas [11]. In Loschmidt's obituary, Ludwig Boltzmann wrote [12] that Loschmidt's "work forms a mighty corner-stone which will be visible as long as science exists". That corner-stone was the calculation of the Loschmidt number. Presumably Boltzmann did not know much of Loschmidt's second corner-stone, in chemistry [5].

These two corner-stones are closely related. In an eight page essay on gas laws published with the *Chemische Studien* of 1861, Loschmidt described ([5], p.49) the purpose of all his work: "... to provide a deeper insight into the constitution of

matter". The calculation of the Loschmidt number gave the size of the molecules, the *Chemische Studien* their shapes.

If Kekulé had understood and praised Loschmidt's work, molecular modelling would have come to us a century earlier. Scientists around the world have been the losers.

Loschmidt the Man

Loschmidt was born on 15 March 1821, the son of poor farmers in a village near Karlsbad (Karlovy Vary) in Bohemia. The village priest recognised the boy's ability and persuaded his parents to send him to high school, and he then went to the university in Prague and the Polytechnic Institute in Vienna, now the Technical University. On graduation with the equivalent of a BSc in chemistry and physics, Loschmidt founded a company with a friend with whom he had developed the production of potassium nitrate. Unfortunately that company failed in 1849, and Loschmidt accepted various jobs, in Styria, Bohemia and Moravia before returning to Vienna in the early 1850s. First he worked as a private tutor and then, in 1856 qualified as a high school teacher in chemistry and physics. He became friends with two of Austria's ablest physicists, Josef Stefan and Ludwig Boltzmann, younger men who realised that this high school teacher studied some of the most important scientific problems, and Stefan helped him to become Privatdozent at the university in 1866. That was most unusual for a man without a PhD, corrected by his receiving an honorary doctorate in 1869. In 1868 he became associate professor, in 1872 full professor and in 1875 chairman of the physical chemistry laboratory and professor of physics to include physical chemistry. Two years later he became dean and in 1885 was elected to the senate of the faculty of philosophy. He died on 8 July 1895.

He must have been a shy and self-effacing man who was loved by his friends and admired by his students. His mind was far-ranging, in chemistry and in physics and also in social problems. He never pushed himself. His village priest, Stefan and Boltzmann, Anschütz and Wiswesser recognised his ability. Not even at the time of the Benzolfest, when German chemists celebrated 25 years of the correct benzene formula, did he point to his earlier work. Others would have claimed priority and stated that the Benzolfest was honouring the wrong man four years late.

Why do Professor Noe and I make this effort? Surely one of the great scientific achievements of this century is the realisation that molecules do in fact look as we depict them. Only in the last few decades have X-rays and NMR proven that molecular models correspond with reality. There were able scientists even at the beginning of this century who doubted the reality of molecular depictions.

So we must honour the man who was the first to depict so many molecules correctly, truly the father of molecular modelling. And we hope that in 1995 not only Czech and Austrian chemists but chemists all over the world will honour Loschmidt's memory on the 100th anniversary of his death. We also hope that our

great grandchildren will organise another Benzolfest in 2061, honouring the right man in the right year.

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