

Facts are better than dreams

Kekulé is always credited with predicting the circular structure of benzene. However, evidence suggests that an Austrian schoolteacher called Josef Loschmidt got there first.

If you ask any organic chemist about the 10 most important discoveries of the 19th century, they are likely to include the circular structure of benzene. This is said to have occurred to Kekulé in a dream, either on top of a bus in London or before a fire in Ghent, of snakes biting their tails, thus the circular structure of benzene. In later depictions of the dream, monkeys replaced snakes. Next to the six dreams related by and to Joseph, in *Genesis*, Kekulé's dreams are probably the most discussed in western writings, and are covered in hundreds of articles and many organic chemistry textbooks and psychology treatises.

The facts

These dreams, however, are irrelevant. Kekulé had seen a book,¹ written by a little known Austrian chemist/physicist called Josef Loschmidt, in 1861, four years before Kekulé published his circular benzene structure. This book includes 368 graphic formulae, 121 of which are aromatic compounds (*Fig 1*).

Sometimes tiny errors lead to detection, and this is what happened with Kekulé. In his most important paper, presented to the French academy in 1865, Kekulé included a footnote stating that he preferred his structures to those of Loschmidt and Crum Brown. Years later, Richard Anschütz, Kekulé's student, secretary, successor as professor of organic chemistry in Bonn and biographer, saw that footnote and wondered just who Loschmidt was.

Seldom in the history of chemistry has John F. Kennedy's dictum been more applicable: 'One man can make the difference and every man should try'. Anschütz discovered a brief reference in Liebig's *Jahresbericht* (a distant forerunner of *Chemical Abstracts*) of 1861 to a book by Loschmidt, and a Viennese bookseller finally supplied that book. Anschütz was flabbergasted: four years before Kekulé's predictions this book depicted many aro-

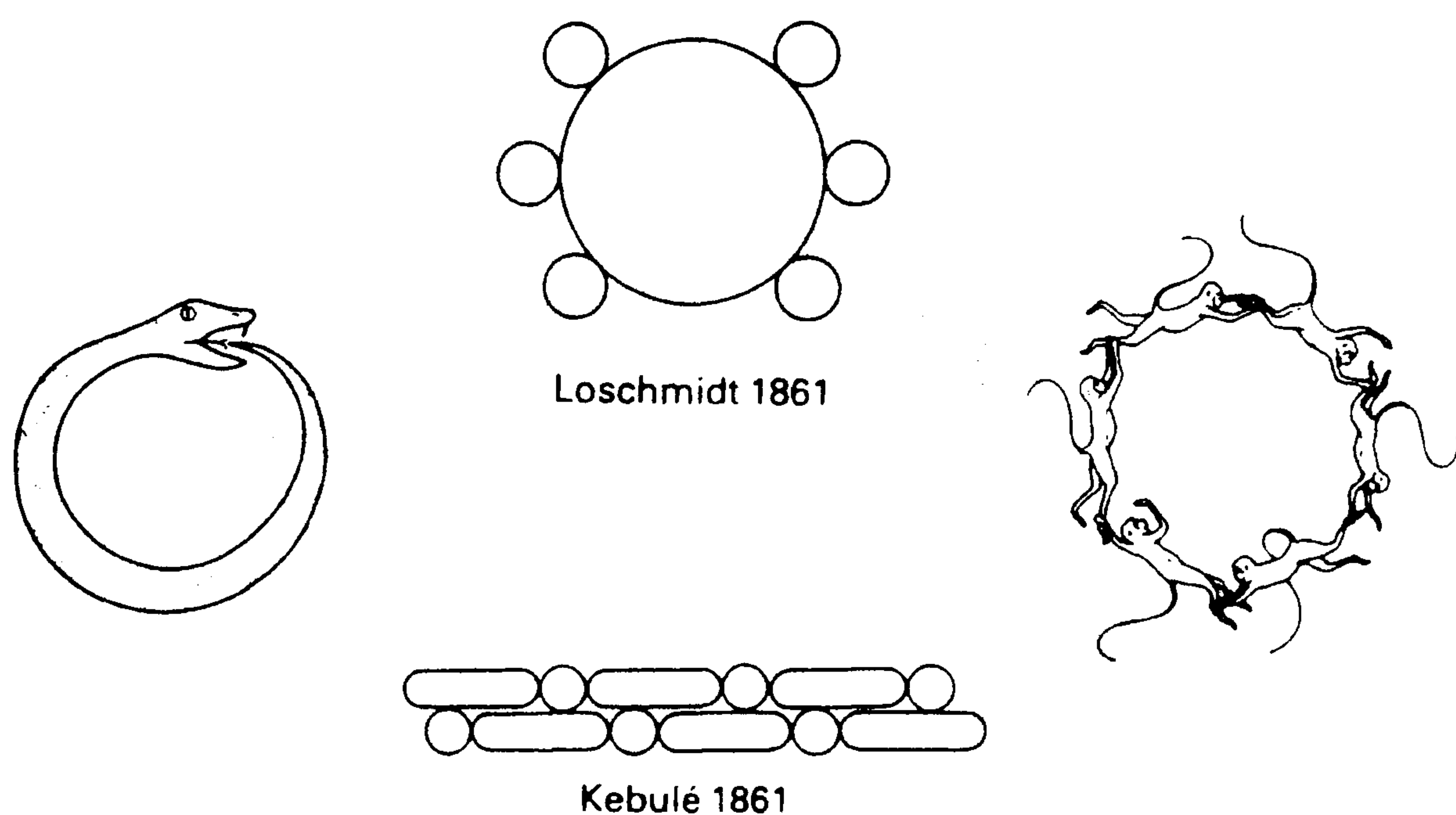
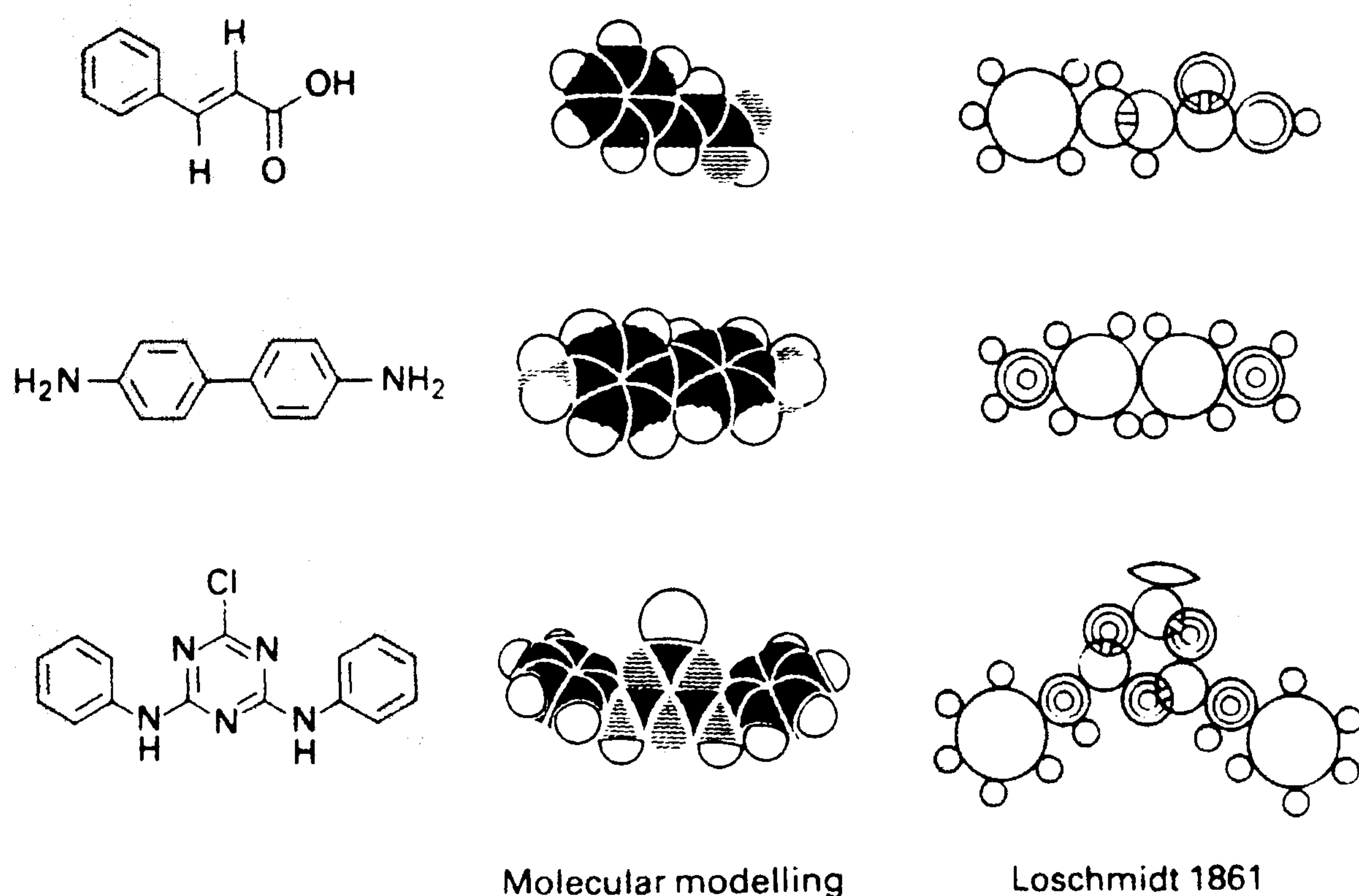


Fig. 1. Loschmidt's aromatic structures.



matic structures correctly, was the first to show double and triple bonds (Fig. 2) with the overlaps, the correct structure of ozone, and it predicted the existence of cyclopropane, 21 years before it was first made by another Austrian chemist, Freund. Of course Anschütz asked the all important question: Did Kekulé know Loschmidt's book? At first Anschütz denied this categorically.

Years later, he discovered a letter from Kekulé to Erlenmeyer, dated 4 January 1862, just months after the book appeared, in which Kekulé referred to Loschmidt's *Confusions-Formeln*—formulae of confusion. Loschmidt had called his book *Constitutions-Formeln der organischen Chemie*—confusion was Kekulé's snide remark. Kekulé had seen Loschmidt's book. This book is not easy to read. Its 47 pages deal with so many structures, tightly depicted in seven fold-out plates. It takes courage and patience to collate structures with text.

Making amends

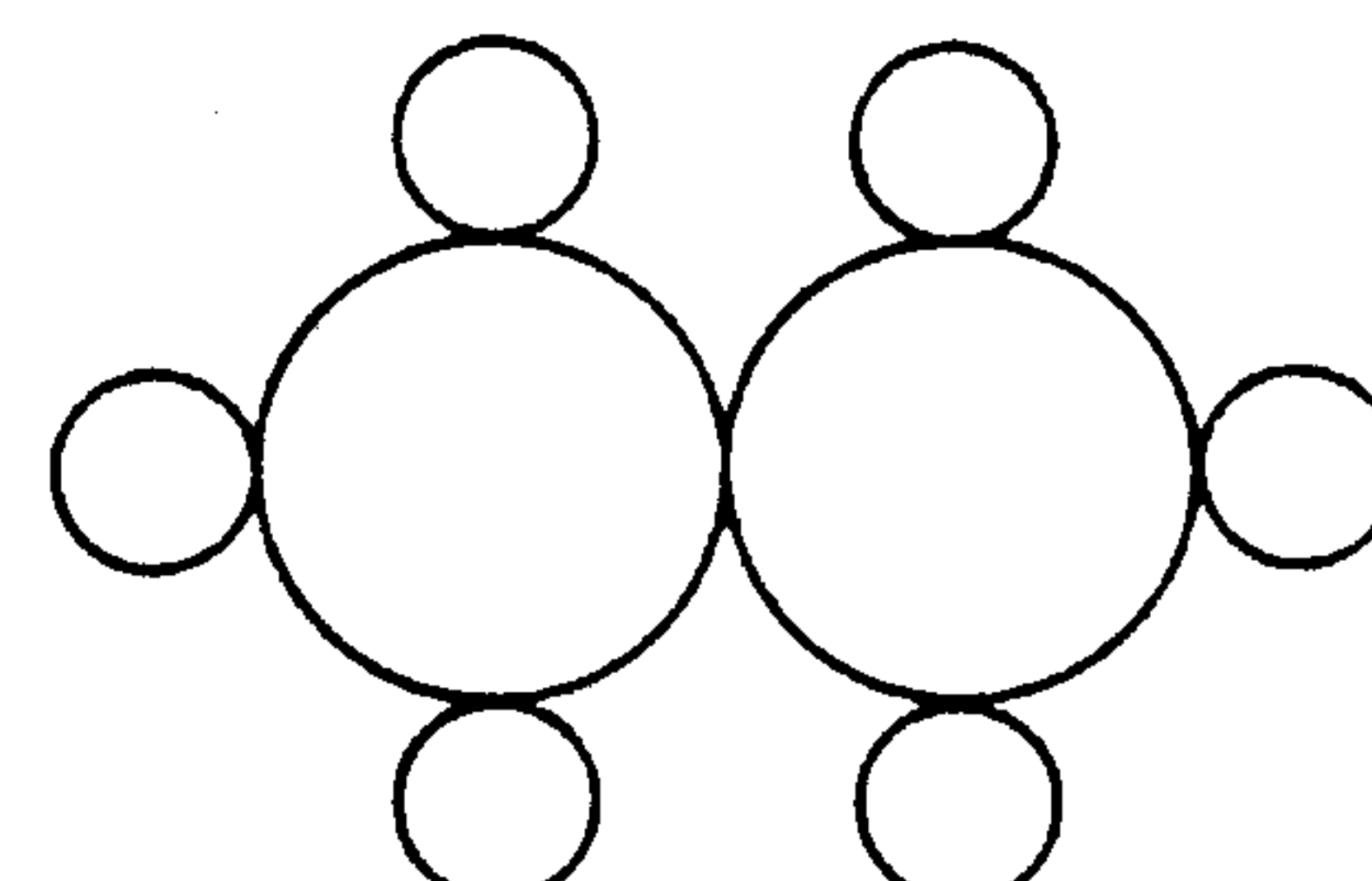
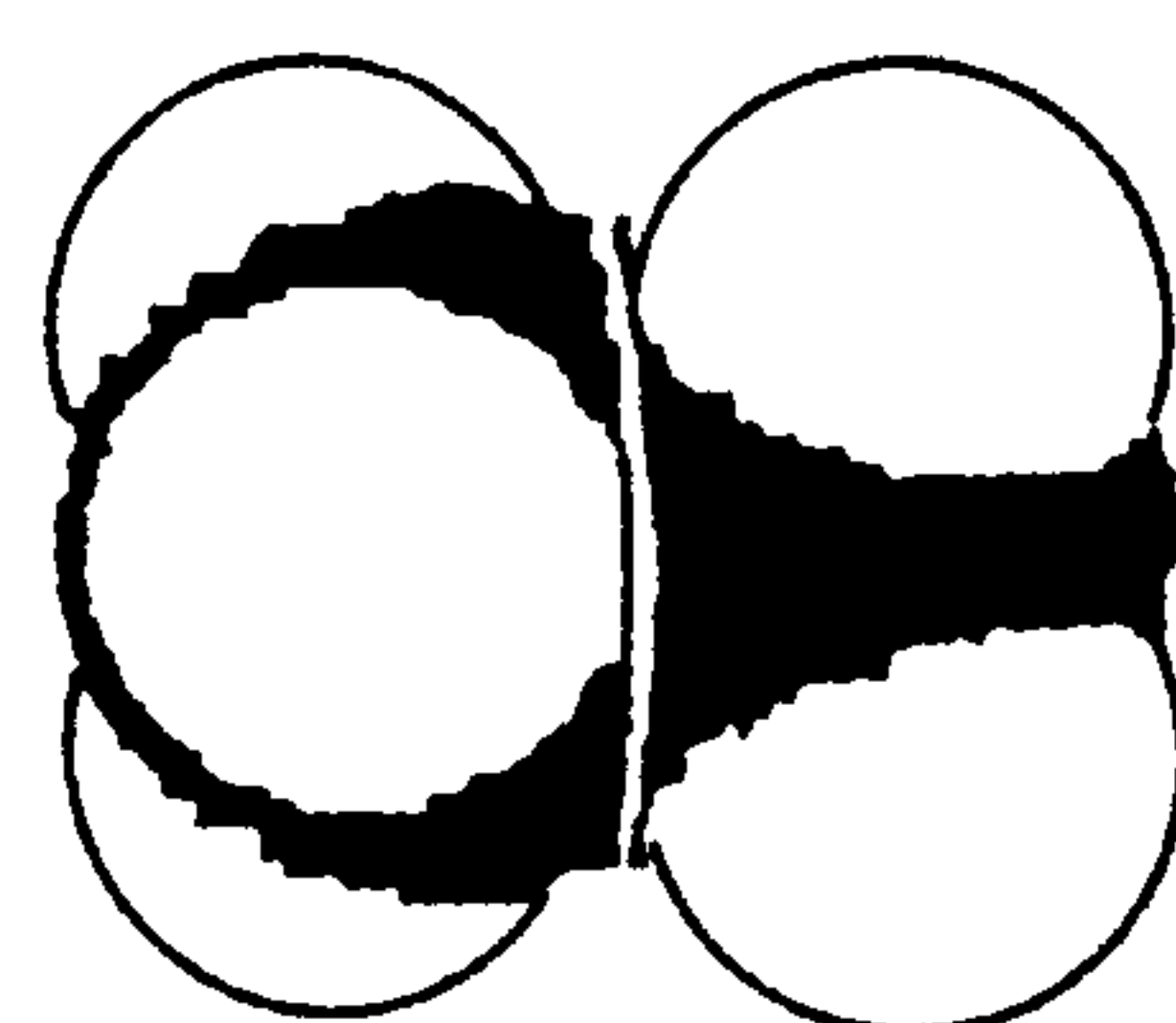
Anschütz spent months reformatting the book, so that structures accompany the text, and he added many explanatory footnotes and a biography. He published this more readable book² in a series of historically important works. It may be that Anschütz's enormous effort was close to an act of atonement by a student for the negligence of his teacher. The late William Wiswesser carefully studied Loschmidt's structures, the forerunners of his 'rational formulae', the Wiswesser Line Notation, and published an article on Loschmidt in the *Aldrichimica Acta* in 1989.³

In 1890 the German Chemical Society hosted an elaborate celebration, the *Benzolfest*, commemorating the 25th anniversary of August Kekulé's cyclic benzene formula. In April 1990, the American Chemical Society held a symposium to discuss that *Benzolfest* and invited Wiswesser and us to discuss the life and work of Josef Loschmidt. Sadly, Wiswesser died before that symposium and we presented the paper, expanded into a chapter in a book entitled *The Kekulé riddle, a challenge to chemists and psychologists*,⁴ detailing Loschmidt's work.

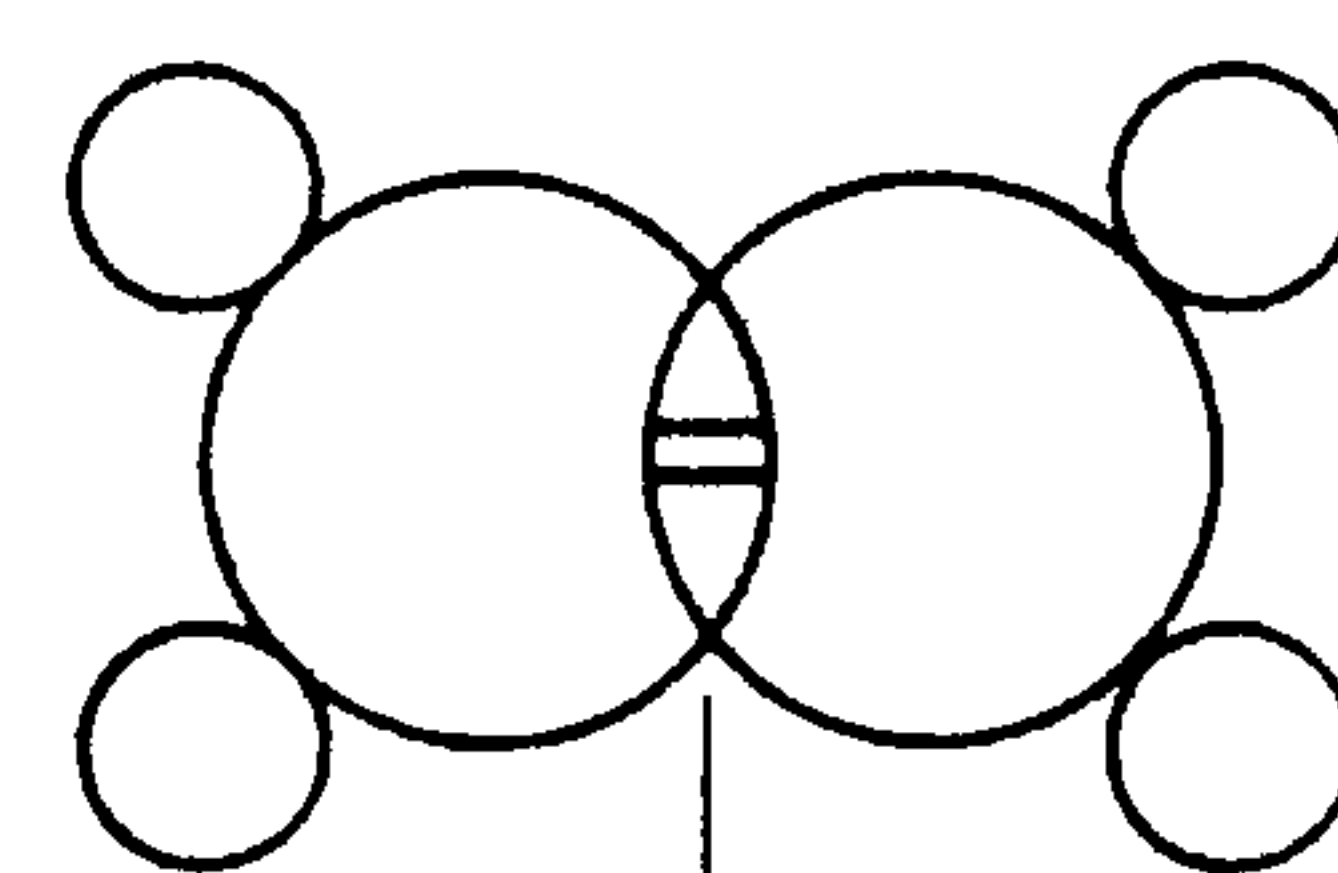
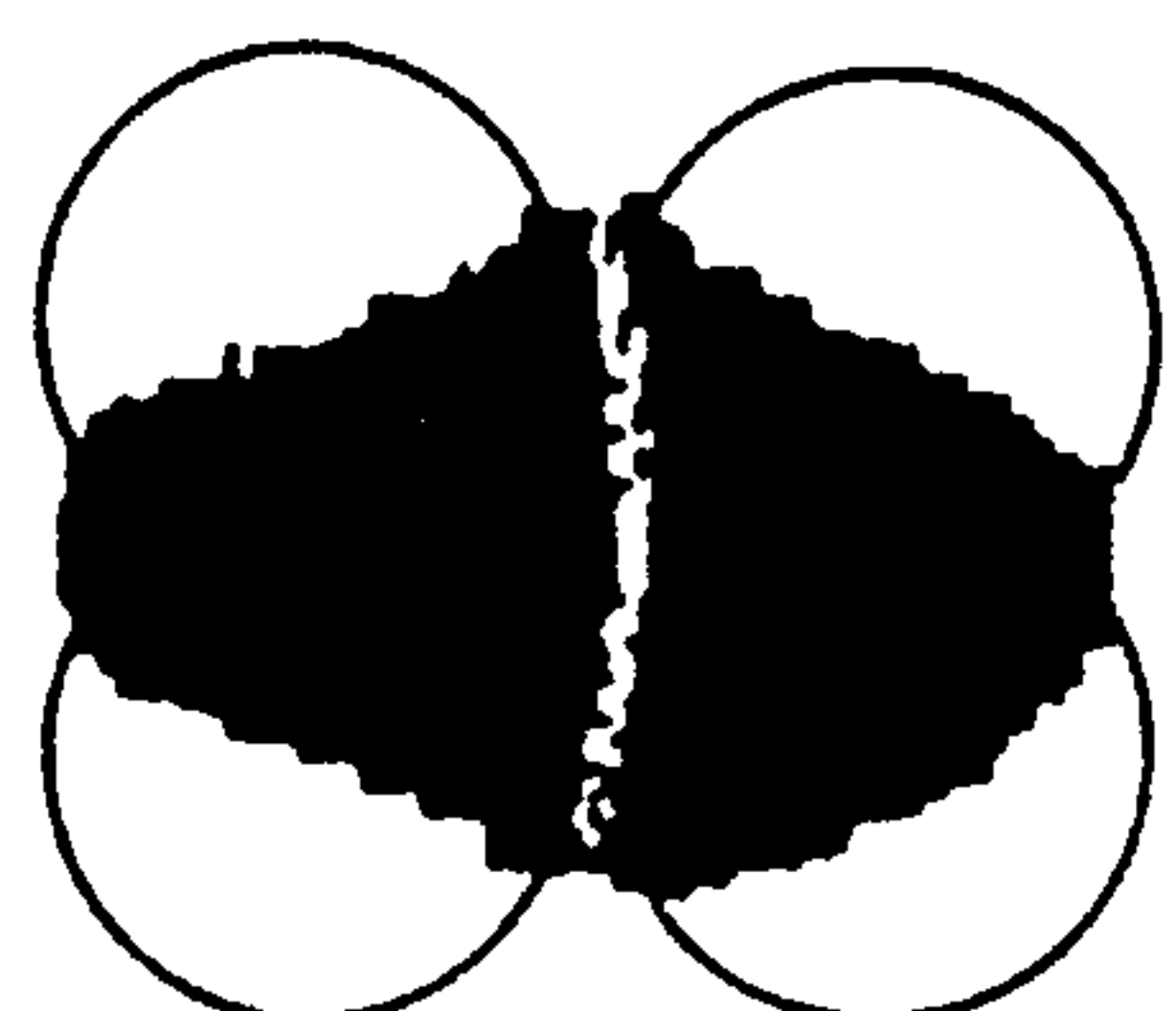
Some chemistry historians criticised our depiction of Loschmidt as the first to show the cyclic structure of benzene: Loschmidt had used the circle just as a symbol—he did not think of the six carbon atoms in a circle. In the chapter on benzene and its derivatives, Loschmidt did not state specifically that he thought of the six carbon atoms in a circle. The 47 page essay is so concise and Loschmidt did not repeat himself: in the discussion on the possibility of the existence of cyclopropane he said that such a carbocyclic ring seemed possible—'as we will see below with phenyl, it is at times the most plausible supposition'. Equally persuasive is Loschmidt's depiction of an aromatic six-membered heterocycle (Fig. 1). Thus it is certain that Loschmidt was the first to depict cyclic organic molecules—cyclopropane, benzene, heterocycles.

A German company has published an

Ethane

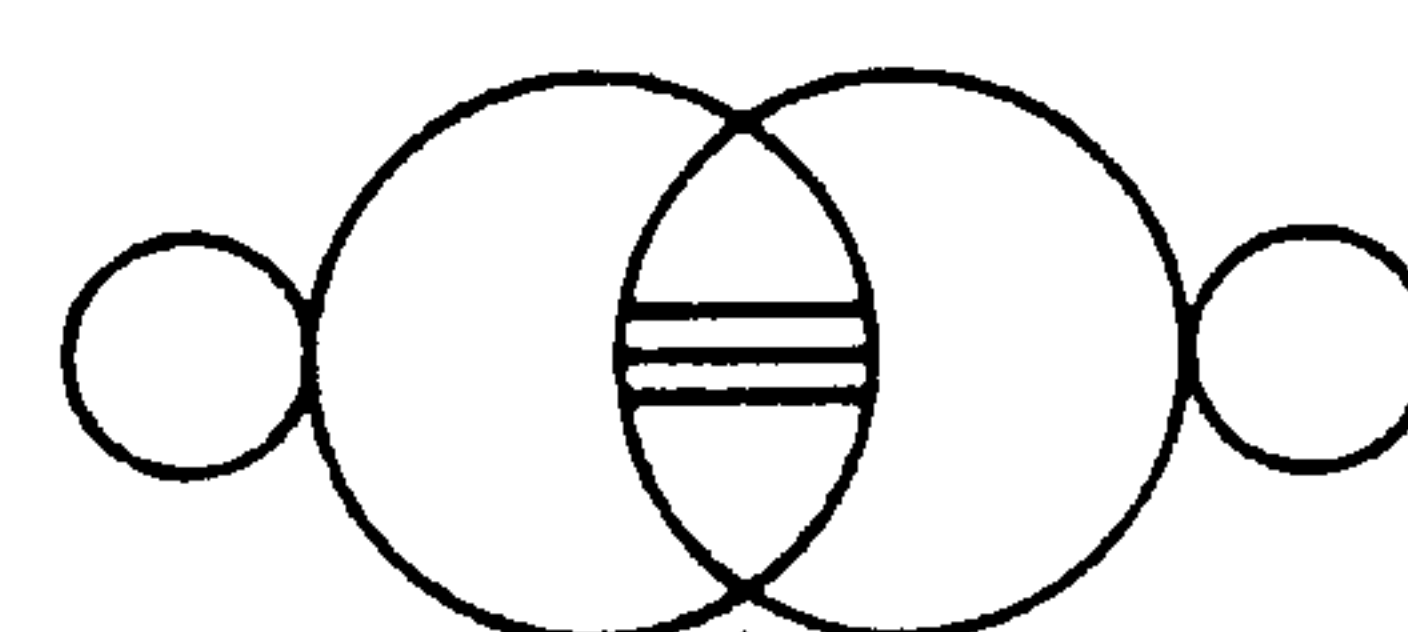
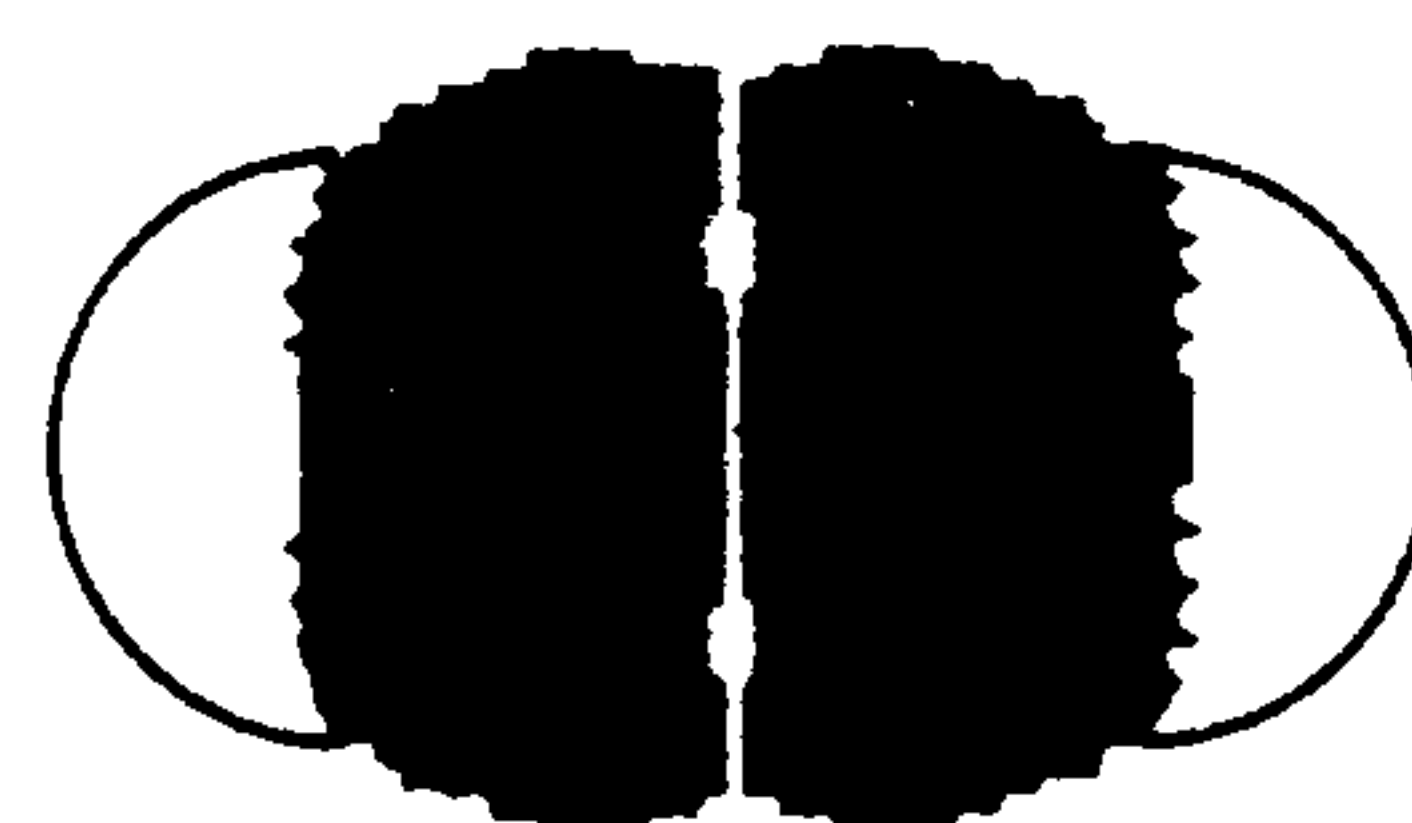


Ethene



Double bond

Ethyne



Triple bond

Fig. 2. A representation of double and triple bonds.

interesting table (Fig. 3), showing the greatest chemical discoveries, year by year. Those for 1865 include Kekulé's benzene formula and Loschmidt's number, leading to the actual size of the molecule. In 1811 Avogadro had predicted that this could be calculated; in 1865 Loschmidt had calculated it.

The relation between Kekulé, Loschmidt and the structure of benzene is now clear. Kekulé had failed to cite Loschmidt—as Wotiz⁴ has said, 'dreams do not come with footnotes and literature citations'. The relation of the structure of benzene to the Loschmidt number is not readily apparent, though just as real. Only few know about Loschmidt's motivation to calculate the number. He himself gave the answer: 'The main purpose of this work is to provide a deeper insight into the constitution of matter'. That key passage is not in his famous paper of 1865 calculating the size of the molecule, but in an eight page essay about gas laws accompanying the 47 page *Chemische Studien* of 1861. That essay includes Loschmidt's programme leading to the calculation of the Loschmidt number, deliberately published with the *Chemische Studien* which tried to depict molecules 'geographically'—ie in space. Liebig and many other chemists had doubted that actual atomic weights could be determined—a calculation made possible using the Loschmidt number. That number gave the weight; his molecular formulae of 1861 gave the structures.

It is fascinating to see how close Loschmidt is to our molecular modelling. Again, Anschütz is most helpful: he shows how superior Loschmidt's depiction of even the simplest molecules—eg acetic acid (Fig. 4)—is to that of Kekulé in the

same year, 1861. If only Kekulé had recognised and acknowledged Loschmidt's genius—rather than calling his structures *Confusions-Formeln*—molecular modelling would have been with us a century sooner.

Humble beginnings

Loschmidt grew to scientific prominence from a lowly background. He was born in 1821 in Bohemia. His village priest recognised his academic ability and persuaded his parents to send him to a high school. He then went to university in Prague and what is now the Technical University in

Fig. 3. An extract from a chronological table showing the Loschmidt number and Kekulé's benzene structures.

1865

Bestimmung der
Loschmidtschen Zahl

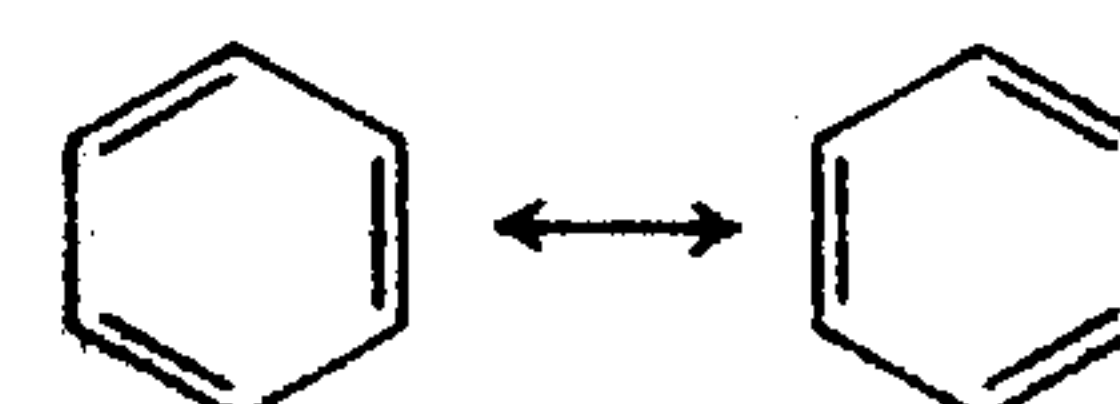
$$N_L = 6,02 \cdot 10^{23}$$

1865

Gründung der BASF

1865

Kekulé's Benzoltheorie



August
Kekulé



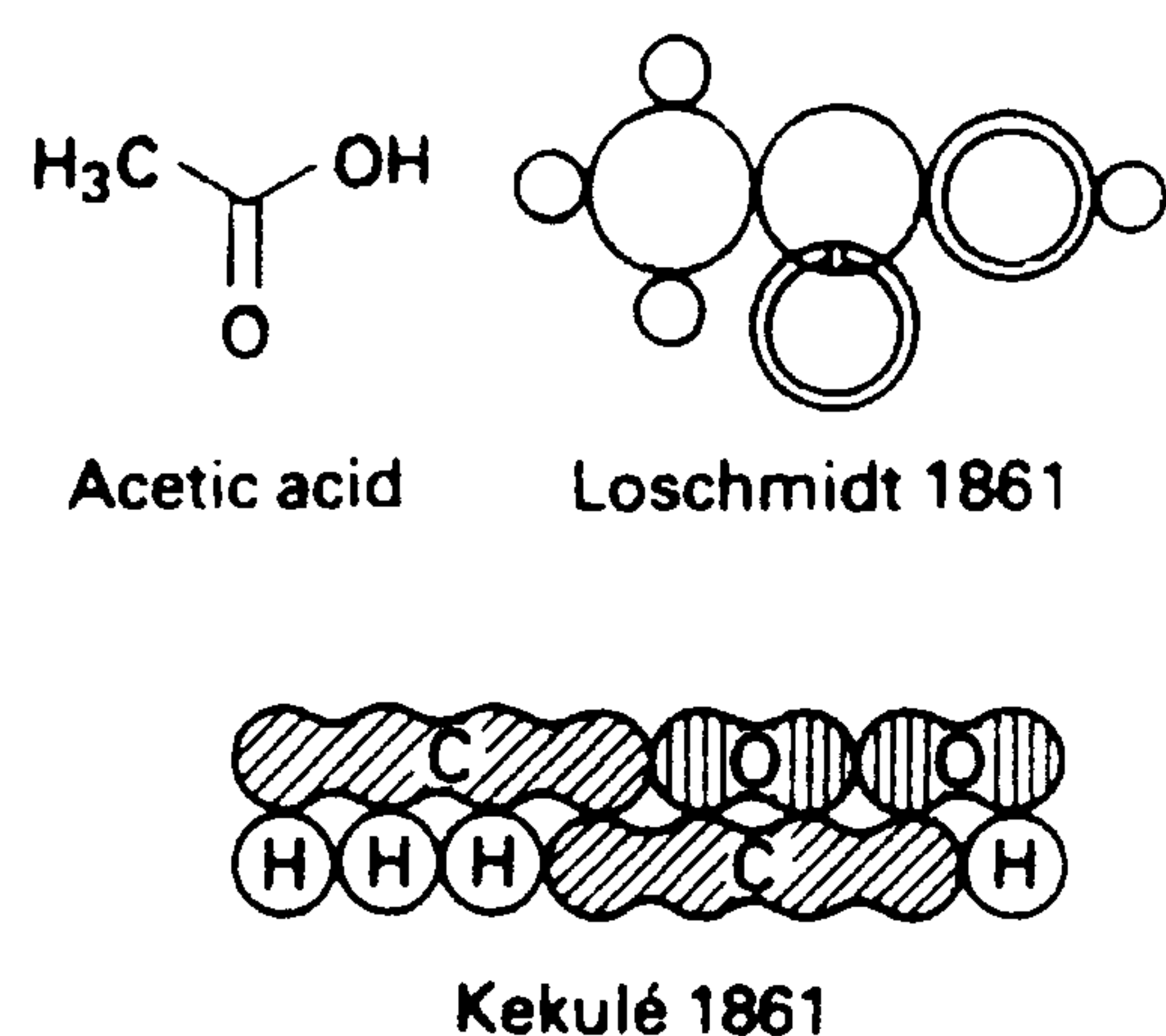


Fig. 4. The formula of acetic acid in 1861.

Vienna where he studied philosophy, chemistry and physics, graduating with the equivalent of a BSc. He then started his own company to make potassium nitrate and after its failure he worked for several chemical companies in Styria, Bohemia and Moravia. He then returned to Vienna in 1854, working first as a private tutor and then as a high school teacher in chemistry and physics.

Beginning with Anschütz, scientists have said 'If only Loschmidt had published his *Chemische Studien* in a widely read chemical journal'. But which journal in 1861 would have accepted such a theoretical treatise by an unknown Austrian high school teacher. Loschmidt paid for the publication of his two essays

himself, but this book was for sale by a well known printer, and could be bought for 20 Neugroschen—eg the British Library still has both the book and the invoice from 1863.

Greater things

Two of Vienna's ablest physicists, both younger than Loschmidt, Stefan and Boltzmann, recognised Loschmidt's genius, and Stefan helped him to become *Privatdozent** at the University of Vienna in 1866—unusual for a man without a PhD. Two years later he became associate professor. In 1869 he received an honorary PhD and in 1875 became full professor of physics, appointed to include physical chemistry. In 1877 he became dean of the faculty of philosophy, followed by election to the senate of that faculty in 1885.

Such a meteoric rise from high school teacher to dean may be unique in the annals of science. This recognition and the personal respect and admiration of his friends is based almost entirely on his work in physics. As Boltzmann said in Loschmidt's obituary: 'His work forms a mighty cornerstone which will be visible as long as science exists'. Boltzmann knew little about the *Chemische Studien* and should have said that Loschmidt's work forms two interrelated cornerstones, one in physics and one in chemistry. And so it

*A licensed university lecturer who receives student tuition fees but no salary.

is good to know that the Royal Society of Chemistry has established a Loschmidt award for work linking the two.

Why are we making such an effort with Loschmidt who was such a shy and self-effacing man, who never made the effort himself? One of the greatest achievements of this century is the proof—mainly through X-rays and NMR analysis—that molecules really look as the models show. And so, the true father of molecular modelling, Josef Loschmidt, must be honoured.

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References

1. J. Loschmidt, *Chemische Studien I*, Vienna, 1861. Reprinted by the Aldrich Chemical Co, 1989, catalogue no Z 18576-0.
2. J. Loschmidt, *Chemische Studien I*, republished by R. Anschütz in Ostwald's *Klassiker der exakten Wissenschaften*, Nr 190, Leipzig, 1913. Reprinted by the Aldrich Chemical Co, 1989, catalogue no Z 18577-9.
3. W. J. Wiswesser, *Aldrichimica Acta*, 22 (1), 17 (1989).
4. *The Kekulé riddle, a challenge to chemists and psychologists*, J. Wotiz (ed), Vienna, Illinois: Cache River, 1992.