

# Waking up to the facts?

The cyclical structure of benzene is a landmark achievement in chemistry. But who should rightfully be credited with its discovery?

Alan J. Roche

In a recent issue of *Chemistry in Britain* (1993, 29, 126), Christian Noe and Alfred Bader argue that the Austrian scientist Josef Loschmidt was the first to publish a correct cyclical structure for benzene, four years before August Kekulé's famous paper proposing a cyclohexatriene structure. They note that Kekulé was aware of Loschmidt's earlier suggestion, thus implying plagiarism by the great German chemist. Unfortunately, their arguments are deeply flawed.

## 'Confusions-Formeln'

As Noe and Bader correctly relate, Loschmidt privately published a pamphlet in 1861, containing no fewer than 368 proposed structures for organic molecules. He used a curious style of formula notation—referred to by Kekulé as *Confusions-Formeln* (formulae of confusion)—that takes some getting used to, and which must have caused some headaches for his contemporaries. Nonetheless, Loschmidt was perfectly consistent, and with practice one can translate the formulae without ambiguity into more conventional structures. When one does so, it becomes clear that Loschmidt was applying the principles of Kekulé's structure theory, which Kekulé had proposed three years earlier in the leading chemical journal of the day.<sup>1</sup>

Loschmidt's *Schema 68* (see Box) was proposed for the structure of 'propylene': a three-membered ring of carbon atoms that we now call cyclopropane. He adds that such a structure was by no means improbable; indeed, 'as we will see below regarding phenyl, it impresses one in many cases as the most acceptable supposition'.<sup>2</sup> From this, Noe and Bader have drawn the conclusion that Loschmidt also thought of benzene as a simple ring of carbon atoms. As this article attempts to show, however, this was not the case.

On the subject of benzene, Loschmidt discusses a possible diallene structure for the carbon nucleus of the molecule, but then argues against it because this does

not explain the non-existence of intermediary substances between the aliphatic and the aromatic series:

Under these circumstances one might almost be tempted to explain the unsaturated character of this nucleus not through compression [*Verdichtung*, i.e. double bonds], but rather through layering [*Schichtung*] of the carbon atoms, and to assign to the nucleus  $C_6$  something like *Schema 182*.

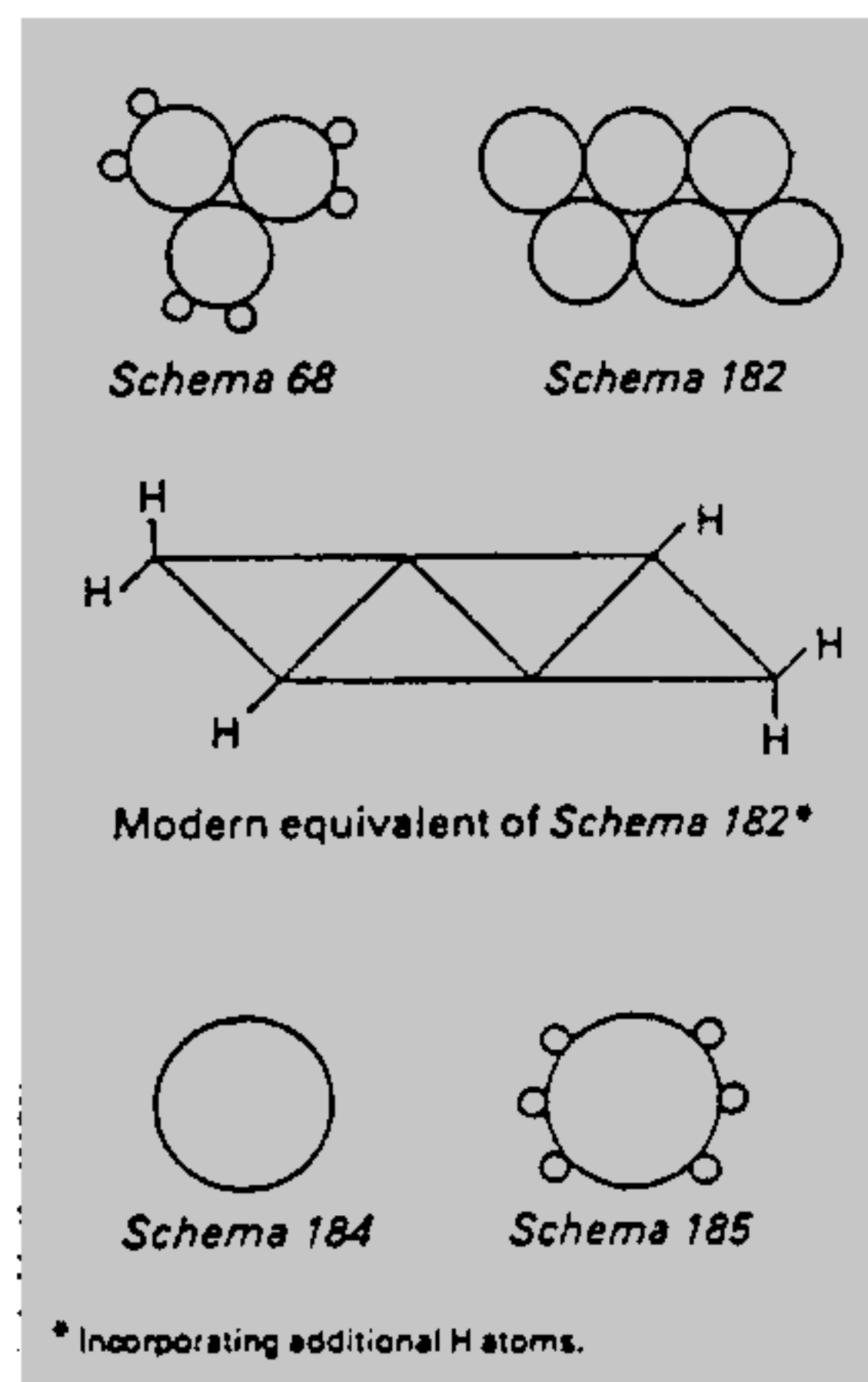
*Schema 182* depicts six adjacent circles (i.e. carbon atoms) in two close-packed layers of three circles each. Loschmidt discusses what the analogous formula for naphthalene would look like under this supposition, and then adds:

However, in the present state of our knowledge it is not possible to come to a definitive result in this matter, and we are all the more justified in suspending judgement, as our constitutions [structures] are fully independent of the question. We assume for the nucleus  $C_6$  the symbol *Schema 184* [a large unembellished circle], and treat the nucleus exactly as if it were a hexavalent element. Benzene,  $C_6H_6$ , *Schema 185*, is in the phenyl series what methane,  $CH_4$ , is in the methyl series. Just as the latter must be viewed as methyl hydride, so the former is phenyl hydride.<sup>3</sup>

## The wrong circles

What does all this mean? Loschmidt clearly believed that the most probable structure for benzene was a formula constructed from multiple fused cyclopropyl rings, using only single bonds: if one abstracts three hydrogen atoms from each of two cyclopropane molecules, then connects the two cyclopropanes with three carbon-carbon single bonds between four adjacent carbons, one arrives at the correct—indeed, the only possible—modern translation of Loschmidt's *Schema 182*. This is what Loschmidt meant when he said earlier that 'propylene' (regarded as cyclopropane) was relevant for benzene.

Significantly, however, Loschmidt provided no empirical justification for this structure (beyond the above quotations), and declared the issue still open. Although he clearly favoured the multiple



fused ring structure, he proposed to treat the benzene nucleus explicitly as structurally indeterminate; his large circle (*Schema 184*) was simply intended to signify this structural indeterminacy— $C_6$  as a 'hexavalent element'. In short, Noe and Bader's crucial *Schema 184* was not a proposal for cyclohexatriene, or for any other benzene ring structure. Loschmidt clearly intended that it was not any sort of structure at all—that was his point!<sup>4</sup>

As Noe and Bader state, Kekulé had read a copy of Loschmidt's pamphlet by 1862. Kekulé evidently understood and rejected the 'layered' structure for benzene that Loschmidt so clearly favoured but refused to defend. Loschmidt's cyclopropyl structures for propylene and benzene might have inspired Kekulé, possibly subconsciously, to think in terms of cyclical structures; indeed A. S. Couper, a more legitimate rival to Kekulé, had also suggested some cyclical structures even

before 1861. Clearly, Kekulé himself did not recognise 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.

## 'A bald speculation'

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. At that time everyone was convinced that there were two isomers of benzoic acid—the second one was called 'salylic acid'—and, likewise, that there were two isomers of each disubstituted benzene. Under such circumstances cyclohexatriene would have to be regarded as contra-factual. Only in 1864 did it become clear that 'salylic acid' was impure benzoic acid and that every disubstituted benzene has three isomers. Loschmidt could not have made a case for cyclical benzene in 1861—nor did he try to argue empirically for his multiple fused-ring structure. This was, as he quite openly admitted, a bald speculation.

According to Kekulé's famous dream anecdote, he got the idea of cyclohexatriene in Ghent, probably early in 1862, but only published it in early 1865. The delay has been suggested as a reason to disbelieve the anecdote. However, Kekulé published the theory immediately after it became possible, as a result of the new empirical data, to make a case for the structure. His experimental work during

1865–68 firmly established the theory.<sup>5</sup> I cannot assert unequivocally that the dream story is true, but it does fit all the available evidence, and there is no reason to disbelieve what Kekulé himself related to friends and colleagues.

## Fact or fiction?

Noe and Bader believe that *Facts are better than dreams*. Whether this is true or not, we must make certain that these facts are correct, and that means understanding the context from which important advances arise in history. Kekulé knew the facts; that was why he refused to publish in 1862 and proceeded only in 1865. It was Loschmidt, not Kekulé, who never progressed from beautiful dreams to hard arguments back up by data and new experiments.<sup>6</sup>

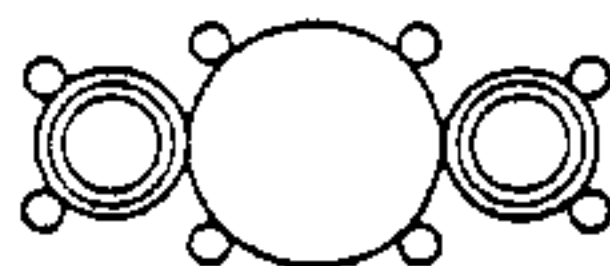
*Alan J. Roche is professor of history at Case Western Reserve University, Cleveland, Ohio 44106, US.*

## References

1. *Ann. chem. und pharm.*, 1858, 106, 129.
2. R. Anschütz, *August Kekulé*, vol 1, p296. Berlin: Verlag Chemie, 1929.
3. *Ibid.*, p303.
4. Similar arguments regarding Loschmidt's benzene proposal have been arrived at independently by Günter Schiemenz (University of Kiel).
5. A. Roche, *Ann. Sci.*, 1985, 42, 355; *idem*, *The quiet revolution: Hermann Kolbe and the science of organic chemistry*. Berkeley: University of California Press, 1993.
6. Here I am speaking only of Loschmidt's work in organic chemistry; he was also a distinguished physicist. Noe and Bader are wrong in believing that Loschmidt's work is not appreciated; in the *Dictionary of scientific biography*, more space is devoted to Loschmidt than to Kekulé.

*Professor Christian R. Noe and Dr Alfred Bader reply:* We believe that Professor Roche misunderstands our work, and that of Kekulé and Loschmidt. When Loschmidt published *Chemische Studien I* in 1861, Kekulé was working mainly with his 'rational formulí', stressing that these were not *Constitutionsformeln*,<sup>1</sup> ie they do not show the positions of atoms in molecules. He even doubted that anything could be learnt about the constitution of compounds by studying their reactions! Showing the positions of atoms in molecules was what Loschmidt excelled at, however, and Anschütz recognised the superiority of Loschmidt's structures.<sup>2</sup> In discussing benzene Anschütz wrote: '... four years before August Kekulé, Loschmidt considered the benzene nucleus as a structure containing the six carbon atoms in a ring [ringförmiger Bildung] ...'.<sup>3</sup>

When Loschmidt wrote 'one might almost be tempted ... to consider [Schema] 182' he did not mean that the latter was correct—indeed all his aromatic



Schema 229

structures are based on Schema 185. Consider, for example, *Schema 229* (see Box)—of which Loschmidt wrote: 'Just looking at this *Schema* shows the possibility of isomeric modifications, ie ortho and meta'.

We urge you to re-read Roche's article alongside our own and to decide for yourselves whose article is 'deeply flawed'.

## References

1. A. Kekulé, *Lehrbuch der organischen Chemie I*, p157. Erlangen: Verlag Ferdinand Enke, 1861.
2. J. Loschmidt, *Chemische Studien I*, Vienna, 1861; p110, footnote 3; all references to Loschmidt are from Anschütz's 1913 reprint.
3. *Idem*, p131, footnote 136.