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# It Began with a Daydream: The 150th Anniversary of the Kekulé Benzene Structure

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> ***“**I was sitting there, working on my textbook, but it was not going well; my mind was on other things. I turned my chair toward the fireplace and sank into half-sleep. Again the atoms fluttered before my eyes. This time smaller groups remained modestly in the background. My mind's eye, sharpened by repeated visions of a similar kind, now distinguished larger forms in a variety of shapes. Long lines, often combined more densely; everything in motion, twisting and turning like snakes. But look, what was that? One of the snakes had seized its own tail, and the figure whirled mockingly before my eyes. I awoke in a flash, and this time, too, I spent the rest of the night working out the consequences of the hypothesis.[1]**”***

Thus August Kekulé (1829–1896; Figure 1) described the circumstances surrounding his greatest inspiration—what one writer has characterized as “probably the most important dream in history since Joseph's seven fat and seven lean cows.”[2] At the time of this late-night daydream—it was probably early in 1862, if it happened as described[3]—Kekulé was Professor of Chemistry at the francophone University of Ghent. In January 1865, he revealed his molecular vision of benzene, without mentioning any of these personal details, in a short article presented at a meeting of the Société Chimique de Paris and published in their Bulletin (Figure 2).[4]

Kekulé's theory that benzene is structurally identical to cyclohexatriene was soon adopted by most German chemists, at least as a valuable heuristic convention, and the resulting burst of fame led to his call to the University of Bonn two years later, where he remained for the rest of his career. His celebrity was well deserved, for a precise understanding of aromatic compounds proved to be immensely consequential both for chemical science and chemical industry. Kekulé's older contemporary August Wilhelm von Hofmann—the founder of the Deutsche Chemische Gesellschaft, former President of the Chemical Society of London, and in many respects the superstar leader of German chemistry in the last third of the 19th century—later commented wistfully to a friend, “I would give all my discoveries for this one idea of Kekulé's.”[5]

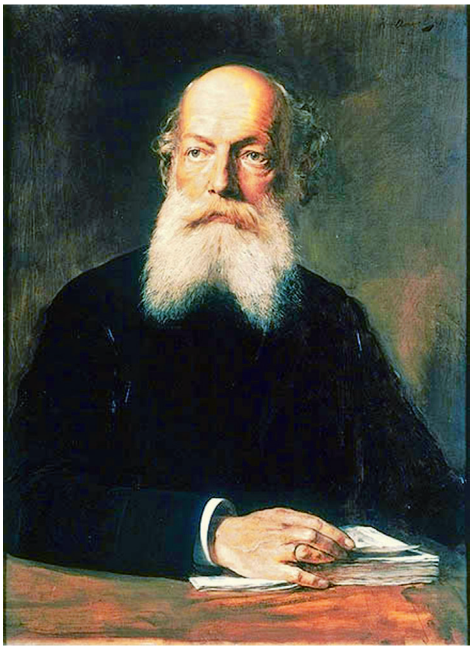

**Figure 1.** August Kekulé (1829–1896).

Kekulé told the story of his inspiration at the so-called “Benzolfest,” an elaborate celebration in Berlin to mark the 25th anniversary of the publication of his first paper on the structure of benzene.[6] Today, 150 years after that first paper, we can only agree with Hofmann's sense of the historic magnitude of Kekulé's great idea, and once again celebrate this landmark in the development of chemistry.

## The Background

In the first half of the 19th century, chemists did not recognize a special category of compounds corresponding to what we now call aromatic substances, partly because so few compounds in the benzene family were yet known. The earliest member of that family, benzoic acid, had long been recognized as a component of the fragrant commercial balsamic resin called “gum benzoin”, from whence it was named. In 1825, Michael Faraday isolated the hydrocarbon that would be called benzol or benzene from compressed illuminating gas. Gradually more compounds related to benzene and benzoic acid entered the chemical lexicon, and in 1855, Hofmann introduced the word “aromatic” to indicate

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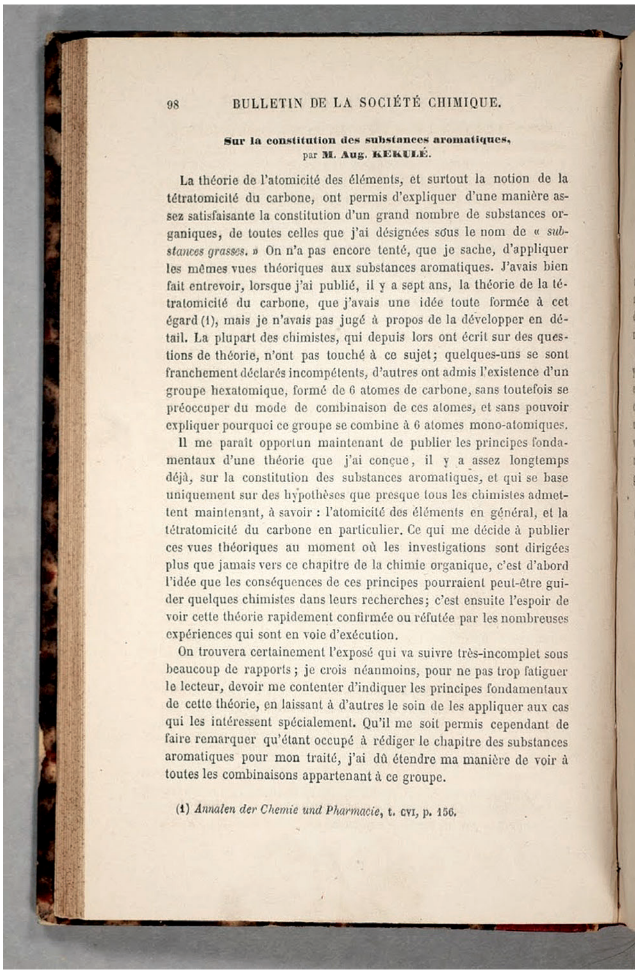

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**Sur la constitution des substances aromatiques,**
par **M. Aug. KEKULÉ.**

La théorie de l'atomicité des éléments, et surtout la notion de la tétratomicité du carbone, ont permis d'expliquer d'une manière assez satisfaisante la constitution d'un grand nombre de substances organiques, de toutes celles que j'ai désignées sous le nom de « *substances grasses.* » On n'a pas encore tenté, que je sache, d'appliquer les mêmes vues théoriques aux substances aromatiques. J'avais bien fait entrevoir, lorsque j'ai publié, il y a sept ans, la théorie de la tétratomicité du carbone, que j'avais une idée toute formée à cet égard (1), mais je n'avais pas jugé à propos de la développer en détail. La plupart des chimistes, qui depuis lors ont écrit sur des questions de théorie, n'ont pas touché à ce sujet; quelques-uns se sont franchement déclarés incompétents, d'autres ont admis l'existence d'un groupe hexatomique, formé de 6 atomes de carbone, sans toutefois se préoccuper du mode de combinaison de ces atomes, et sans pouvoir expliquer pourquoi ce groupe se combine à 6 atomes mono-atomiques.

Il me paraît opportun maintenant de publier les principes fondamentaux d'une théorie que j'ai conçue, il y a assez longtemps déjà, sur la constitution des substances aromatiques, et qui se base uniquement sur des hypothèses que presque tous les chimistes admettent maintenant, à savoir : l'atomicité des éléments en général, et la tétratomicité du carbone en particulier. Ce qui me décide à publier ces vues théoriques au moment où les investigations sont dirigées plus que jamais vers ce chapitre de la chimie organique, c'est d'abord l'idée que les conséquences de ces principes pourraient peut-être guider quelques chimistes dans leurs recherches; c'est ensuite l'espoir de voir cette théorie rapidement confirmée ou réfutée par les nombreuses expériences qui sont en voie d'exécution.

On trouvera certainement l'exposé qui va suivre très-incomplet sous beaucoup de rapports ; je crois néanmoins, pour ne pas trop fatiguer le lecteur, devoir me contenter d'indiquer les principes fondamentaux de cette théorie, en laissant à d'autres le soin de les appliquer aux cas qui les intéressent spécialement. Qu'il me soit permis cependant de faire remarquer qu'étant occupé à rédiger le chapitre des substances aromatiques pour mon traité, j'ai dû étendre ma manière de voir à toutes les combinaisons appartenant à ce groupe.

(1) *Annalen der Chemie und Pharmacie*, t. CVI, p. 156.

***Figure 2.*** The first page of the 1865 article.[4]

the chemical rather than olfactory characteristics of these substances.[7]

In 1858, Kekulé and Archibald Couper independently proposed the elements of what became known as the theory of chemical structure, and an international competition began to determine the molecular structures of familiar organic compounds.[8–10] In the 19th century this was no easy task, for chemists had to reason solely from macroscopic wet-chemical data; no instruments were yet available to provide intimate access to the molecular level. Proposals for the structures of simple aliphatic substances began to appear regularly in the literature, but more complex compounds were initially intractable.

The leading figure in early structural organic chemistry was Kekulé himself. He developed structural ideas not just in his journal articles, but also in the pages of his textbook, the first two volumes of which were published serially, in six installments that appeared between 1859 and 1866.[11] His announcement of structure theory (1858), and the first volume of his textbook (1859–1861), were devoted almost exclusively to aliphatic substances, though he did make vague reference to what he called "carbon-richer" (including aromatic) compounds, evidently thinking of structures containing multiple carbon–carbon bonds. He wanted to drop hints, but he was not ready to tackle aromatic structures head on.

Others were not so cautious. In the paper in which Couper announced his theory of structure, he provided a conjectural structure for salicylic acid which implied that benzene itself was the straight-chain diallene (1,2,4,5-hexatetraene).[9] In 1861, a then-unknown Viennese schoolteacher named Joseph Loschmidt mentioned the diallene hypothesis, but did not prefer it. Instead, he wrote, "one might be tempted" to imagine benzene as a planar array of what we would now consider to be four fused cyclopropane rings. However, he went on to point out that too little aromatic chemistry was yet known to be able to decide on *any* structure for benzene. Accordingly, thereafter he used a large circle to symbolize the yet-uncharacterized hexavalent aromatic nucleus.[12]

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## *Aromatic Studies before Cyclohexatriene*

The problem at that time was not to arrive at a *possible* structure for benzene, for if one assumed tetravalent carbon and monovalent hydrogen one could readily draw more than 200 isomers of the molecule whose empirical formula is $C_6H_6$.[13] As Loschmidt rightly pointed out, the real challenge was to propose a single structure that could be defended by empirical data known at that time. Neither Couper nor Loschmidt provided any such defense—understandably so, for too little was yet known about aromatic compounds in order to argue effectively for any single structural hypothesis.

The road was not an easy one, but progress was rapid.[10,14] In 1861 and 1862, chemists thought that they could distinguish two isomers of benzene, two of toluene, and two or even three of benzoic acid; moreover, a lower (five-carbon) homologue of benzene was thought to exist. A few disubstituted benzenes (such as nitrophenol or hydrobenzoic acid) were shown to exist in two isomers each. In the presence of all of these "facts," a cyclohexatriene hypothesis could not have survived, and would never have been proposed.

However, in 1863 and 1864, research by several chemists showed that these findings were in error. At the same time, additional isomers of disubstituted benzenes were being discovered. By 1864 it began to appear—to those who were paying close attention to such matters—that for every disubstituted benzene compound, three isomers would generally be found to exist, whereas it was now clear that monosubstituted benzenes, and benzene itself, occur in only one isomeric form. Moreover, by that time the minimum carbon content for aromatic molecules was known to be six atoms.

Kekulé was paying close attention to such details, partly because the time had come that he needed to treat aromatic compounds in his textbook—and also, no doubt, because aromatic compounds were becoming commercially important in the rising coal tar dye industry. If we can believe his later reminiscence, his benzene daydream occurred in 1862, when the situation was still quite confused, and it is not surprising that he moved slowly. When he finally did write a draft of his theory, he said that it “lay written among my papers nearly a year” until he was induced to publish it early in 1865;[1] this suggests that the draft was written in the first half of 1864. By that time, one could begin to assemble convincing empirical support for a cyclohexatriene hypothesis.

## The Personal Pathway to Discovery

Early in 1862, sitting by his fire in Ghent, overworked and dozing, it would be understandable that Kekulé’s “mind was on other things,” for he was about to be married. However, Stefanie Kekulé died during the birth of their first child, in May 1863. Kekulé was shattered by this tragedy, and for more than a year he could barely work. The appearance in August 1864 of a paper by Bernhard Tollens and Rudolf Fittig on isomeric relations of aromatic compounds[15] finally spurred him to act; rivals were obviously hard on his trail, and he might be scooped. He hired two capable private assistants, Carl Glaser and Wilhelm Körner, and prepared for a concerted research program.

But he still found himself unable to concentrate. He spent the first nine days of 1865 in Paris, “to at least somewhat shake myself from my lethargy” (as he put it to his good friend and former student Adolf Baeyer). While there, he visited with another good friend, fellow structuralist Adolphe Wurtz, Professor of Chemistry at the École de Médecine.[16] I suspect that he talked with Wurtz about his new theory, and asked Wurtz to present it at the next meeting of the Société Chimique, on January 27—which Wurtz did.

Back in Ghent, two weeks before the paper was presented, he wrote to Baeyer. Kekulé was depressed: he had no new experimental results from his own research, none from his research group, none even that he could see coming, and not a single line written on his textbook. “The main thing is that I feel so addled that I haven’t been able to bring myself to any solid work.” But since his return from Paris, he wrote, he felt a little better, and: “… I intend to make the most desperate efforts not to sink again. In these clear intermezzos I have dreamed a lot and sometimes even concocted theories; but I suffer from chemical constipation and am too lazy to write anything down. However!!! However, I will nevertheless soon let loose with some theoretical tinder … My plan is … to send off a swindle on the constitution of all aromatic substances to the Société Chimique. I won’t describe these publications to you, so they won’t lose the charm of novelty. But don’t expect too much: the good parts are not new, and the new parts not good.”[16]

That first short French paper on benzene theory[4,10,14] is surprising in some ways. For one thing, Kekulé continued to use the curious “sausage formulas” (Figure 3) that he had introduced six years earlier, in the first installment of his textbook. In these formulas, his sausage-shaped carbon atoms are four times longer than hydrogen atoms, for here length is proportional to valence. Since the formulas are essentially linear, he had to use arrows to indicate that the ends of the “open” carbon chain of the benzene molecule are to be imagined as connected together to make a kind of circular or “closed” chain. Three double bonds in the chain—where the carbon “sausages” are fitted more closely together—make cyclohexatriene. This ring he called the “chaîne principale,” but “chaînes latérales” could be attached, to make all the familiar aromatic substances then known.

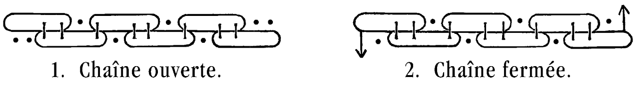

**Figure 3.** The 1865 “sausage” formulas showing open and closed chains in benzene (taken from reference [4]).

The other odd aspect about this first paper is its hesitancy. He certainly proposed that benzene, considered structurally, is what we call cyclohexatriene, and he argued for that structure from known empirical evidence. However, he only implied (and never stated explicitly) that it was a symmetrical molecule. He never stated or even implied here that the closed chain formed a hexagonal array. According to his theory, he wrote, there should be only one isomer of benzene and only one of monosubstituted benzenes, but “probably” three isomers of each di-, tri-, or tetra-substituted benzene. All of this is of course correct according to the theory—today we distinguish disubstituted *ortho*-, *meta*-, and *para*-isomers—but he left it to his readers to figure out *why* this should be the case. By this time enough was known about aromatic compounds to justify all these statements, but he was curiously shy about doing so.

This hesitancy quickly vanished. Just two months later, Kekulé’s passion for his work was finally back, and in fullest measure. On March 16 he wrote Baeyer, “There’s a great deal of activity in my laboratory right now and I hope it will come to something. We have started in on the aromatic side from A on [i.e., from the very beginning], guided by the ideas which I recently communicated to the Société Chimique and with which you are no doubt already familiar.”[17] And then on April 10 another report to Baeyer: “And now back again to my work! … Naturally, everything is aromatic. Facts to prove or disprove my recent aromatic theory, with which you have in the meantime no doubt become acquainted. … A great deal is in the works; the plans are unlimited, for the aromatic theory is an inexhaustible treasure trove. Now when ‘German youths’ need dissertation topics, they will find plenty of them here.”[18]

Early in 1866, Kekulé published a detailed and masterly German paper on his benzene theory that exhibited none of the diffidence of the French paper, and marshaled much additional empirical support.[19] Later that year, he published the final installment of the second volume of his textbook;

this installment was the size of a substantial monograph, and it was devoted exclusively to the new aromatic chemistry (Figure 4).[20]

Reactions from colleagues were almost uniformly favorable. Among those who immediately adopted the theory were Adolphe Wurtz, Adolf Baeyer, Emil Erlenmeyer, Friedrich Beilstein, Lothar Meyer, Carl Graebe, Edward Frankland, Alexander Crum Brown, and Alexander Williamson. The only prominent German chemist who unequivocally rejected the theory was Hermann Kolbe, whose bitter polemical writings of the 1860s and 1870s increasingly isolated him from his colleagues.

## Latter-Day Controversies

In recent years, some scholars have expressed doubts about the originality of Kekulé's benzene theory. It has been pointed out that occasional examples of ring structures can be found before 1865: two different ring compounds were proposed by Couper in 1858, and Loschmidt conjectured about cyclopropane in 1861. I mentioned above that Loschmidt used a large circle, similar to the "$x$" in algebra, to denote the then-unknown constitution of the aromatic nucleus—could this be interpreted as a ring structure? Finally, some have noted that in 1854 Auguste Laurent published a hexagonal symbol for the molecule of benzoyl chloride.[21] It is known that Kekulé was aware of all of these papers prior to the presumed date of his so-called "dream."[12b,22]

However, one must also consider the following circumstances. Laurent called his picture of benzoyl chloride a "polyèdre complet", not a ring of linked atoms; as part of his crystallographic molecular theory and predating valence theory, this image could hardly be interpreted as a hexagonal molecular structure in the post-1860 sense.[23] Couper's two-ring molecules both included heteroatoms, and neither ring was aromatic. Most telling, none of these authors even attempted to justify their proposals empirically. Kekulé's theory was not just the first cyclohexatriene proposal; it was also the first time anyone had even attempted to construct a robust empirical argument for any specific structure for the benzene molecule.[10,14]

Still, the critics have a point: any of these earlier contributions may well have made a conscious or even unconscious impression on Kekulé. Under the right psychological circumstances—as in his story of a late-evening reverie after intensive engagement with the problem—such an impression could have prompted a mental image of a cyclical molecular structure for benzene.

But did those circumstances even happen? When he told the stories, was he telling the truth as he remembered it? This has also recently been doubted. Kekulé's autobiographical reminiscences (including the story of his earlier "dream" of the first conception of molecular structure, while riding a London omnibus in 1855) were recorded only long after the respective events. Some have doubted that scientific inspirations could ever come in such a fashion. Some have argued that he was just inventing "tall tales" for the amusement of his audience. One scholar has even accused Kekulé of being a "fraud" and a "cheat" for thereby trying unjustly to claim priority over rivals such as Couper and Loschmidt.[24]

But I am strongly inclined to trust Kekulé's sincerity, for many reasons.[10] By 1890, no one, including Couper and Loschmidt, had ever contested Kekulé's priority for benzene theory; why would he want to invent false stories with the intention of asserting priority against rivals, when there were no rivals? Moreover, many scientists have told of sudden inspirations similar to Kekulé's, and in his speech Kekulé was careful to say that one must do much more than just "dream" in order to succeed in science. Furthermore, evidence shows that his audience took him seriously, and appreciated these stories as important elements of scientific discovery. And finally, Kekulé's demeanor throughout the "Benzolfest" was thoroughly thoughtful and serious, not lighthearted; he was a frail old man, speaking solemnly, for the ages. This was not an appropriate occasion to fabricate fables about one's life.

Others who have trusted in Kekulé's sincerity and believe in the truth of his story have offered speculative interpretations of his vision of the "snakelike form" that "whirled mockingly before [his] eyes." Some have argued that this figure is reminiscent of an ancient alchemical symbol, the "ouroboros" serpent that devours its own tail and is therefore a symbol of immortality. Kekulé's dream has even received Freudian and Jungian interpretations.[25] I believe that many of these psychological conjectures are improbable, even misleading. We do not need to know more than Kekulé himself knew about these mysterious sources of inspiration—which is little enough!

Of course, one can ever know with certainty whether Kekulé spoke truly about the origin of his ideas about benzene—not just because we cannot document a private mental event, but also because even if we credit his sincerity in telling the tale, we cannot be sure that his memory of the event was accurate. However, we can and should celebrate the development of the theory itself.

## Conclusions

It was a beautiful theory in its initial version of 1865–66, but Kekulé was well aware that it was not flawless. Cyclohexatriene had double bonds that did not behave like the double bonds in olefins; moreover, one might expect otherwise identical *ortho* compounds to have slightly different properties depending on whether the substituents bridged a single or a double bond in the benzene nucleus. In 1866, Kekulé abandoned his "sausage formulas" and began to write cyclohexatriene formulas in a manner that is easily recognized today (Figure 4).[26] Six years later, he suggested that the single and double bonds in the ring rapidly exchange places (Figure 5), producing the complete symmetry that the empirical chemistry of aromatic compounds seemed to call for.[27]

Kekulé's theory was a major reason why German chemistry became so powerful in the late nineteenth century. So many chemists (especially so many *German* chemists) turned to aromatic chemistry that by the early 20th century the large majority of all known chemical substances were aromatic. Moreover, so many industrially interesting sub-

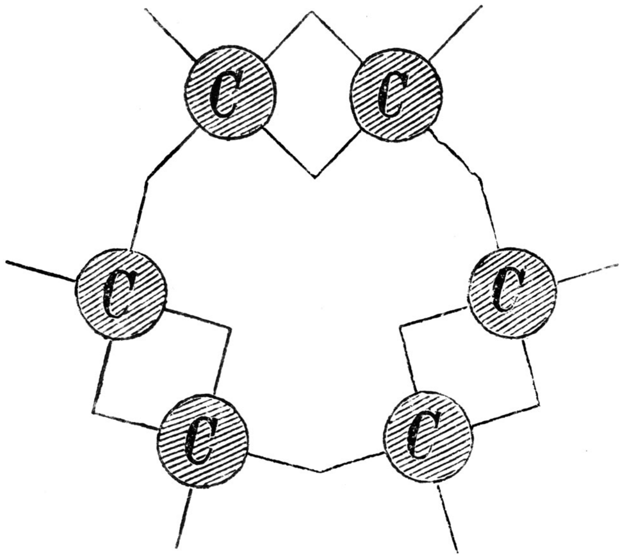

***Figure 4.*** Kekulé's 1866 ball-and-stick benzene formula (taken from reference [26a].

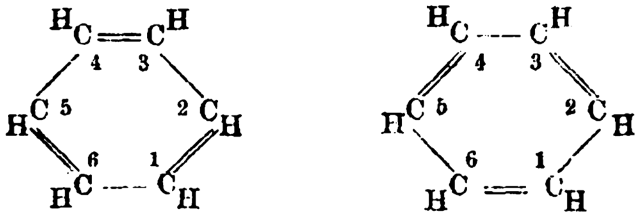

***Figure 5.*** Kekule's 1872 oscillating single and double bonds in benzene (taken from reference [27]).

stances—especially dyes and drugs—were aromatic, that Kekulé's theory became a master key to productive industrial research. Kekulé's theory was one of the most brilliant ideas of the nineteenth century, both for the development of the science, and for technological applications.

For decades after 1865, chemists proposed adjustments or alternatives to the theory, but Kekulé's great idea was never displaced. Eighty years ago, quantum-mechanical resonance gave new meaning to benzene structure. However, it speaks to the beauty and power of this theory that we still write "Kekulé structures" 150 years after Kekulé's first brief article was published.

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