

## 150 YEARS AFTER THEIR EMERGENCE: A NEW LOOK AT LOSCHMIDT'S REPRESENTATIONS OF BENZENE

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### Abstract

A new examination of structures that Loschmidt considered for benzene derivatives, notably naphthalene and “rings” doubly bonded to O or triply bonded to N, show conclusively that Loschmidt did not view benzene as a planar ring of six carbon atoms.

### Introduction

August Kekulé has long been credited with several major contributions to structural organic chemistry: recognizing the tetravalence of carbon (1857) (1,2); recognizing that carbon atoms combine with one another to form chains (1858) (3); and recognizing the structure of benzene (1865) (4), in the view of Japp, the “crowning achievement of the doctrine of the linking of atoms” (5). Kekulé's work on benzene provided a major stimulus to research in aromatic chemistry, causing an unprecedented growth in this field; it coincided with an explosive growth in the application of aromatic compounds, e.g., as synthetic dyes (6), pharmaceuticals (7), or explosives (8). The majority of Kekulé's contemporaries gave him credit for major accomplishments and, in essence, attributed to him the birth of structural organic chemistry.

Contemporary critics included the formidable Hermann Kolbe (9), and the science historian Ernst von Meyer (Kolbe's son in-law): Kolbe voiced opposition

to Kekulé's theories, because, in the summary of Alan Rocke, they were “at once too empirical and too speculative” (10); von Meyer criticized Kekulé for not giving credit to Frankland for the concept of valence or to Kolbe or for his many contributions (11).

More recent criticism has its roots in the work of Kekulé's biographer and successor on the Chair in Bonn, Richard Anschütz. While compiling material for his two-volume Kekulé biography (12), Anschütz found references to Couper (13), who had developed the idea of linking carbon atoms independent of Kekulé; he also noticed a footnote in Kekulé's 1865 paper concerning structural formulae by Loschmidt. This 1861 article (14) had been published outside of the established chemical literature and was not readily available. Anschütz noted that Loschmidt's booklet was hard to read (15); therefore, he had the entire work reprinted (16) with copious comments, including 208 footnotes with many references (Loschmidt's paper didn't cite any literature), and with several “improved,” i.e., revised structures. Most importantly he inserted the formulae into the text, making the work much easier to read.

In the 1980s new criticism arose from two quarters: Wotiz and Rudofsky attacked Kekulé's priority claims in general, and the benzene structure in particular (17); and Wiswesser, having discovered the work of Loschmidt, hailed him as a “forgotten genius” (18). This criticism reached its climax in *The Kekulé Riddle* (19), a 1993

volume with 19 contributions under the motto “Pravda vítězí” (“truth prevails”). Coincidentally, in 1995 a symposium was held to commemorate the centennial of Loschmidt’s death, in which 33 papers addressed his contributions to chemistry and physics (20).

The recent criticism of Kekulé focuses on a range of questions: (a) does Kekulé deserve credit for recognizing the tetravalency of carbon,  $C = 12$  (1,2), or does Kolbe, who implied tetravalency for the double-equivalent,  $C_2$  ( $C = 6$ ), just barely later (21)? (b) Does Kekulé deserve credit for realizing that carbon atoms can form chains (2,3) or does Couper (13), who developed the concept independently, whose formulae were “nearer to our present formulae” (5), and who “intended them to be constitutional formulae (5)? (c) Did Loschmidt (14) conceive a cyclic structure for benzene four years before Kekulé? And (d) was Kekulé inspired by dreams (22) or did he fashion his benzene structure after a pictogram of Loschmidt’s and fraudulently invent dreams to support his priority claims (17)?

In this paper I will review these issues, in particular the formulae that Loschmidt offered for benzene and selected derivatives to weigh whether they support the claim that Loschmidt viewed benzene as a cyclic array of six carbon atoms. An evaluation of the structures provides strong arguments that Loschmidt did not consider the nature of benzene in such terms. Some of these arguments, as far as I am aware, have not been advanced before.

### Tetravalence of Carbon and Linking of Carbon Atoms

In considering the first two points, recognizing the tetravalency of carbon (1) and realizing that carbon atoms can form chains (2,3), the opinion of Kekulé’s contemporary Ernst von Meyer, is illuminating. Meyer’s *Geschichte der organischen Chemie* (11), according to R. E. Oesper, is “among the late works that can rightfully be considered to be fairly complete” (23). Meyer (correctly) credited Frankland (24) with the concept of a specific valence for different atoms (25). He viewed Kekulé’s train of thoughts that led to the conclusion that carbon is tetravalent “almost identical” (“fast der gleiche”) to Frankland’s. Thus, he was unwilling to credit Kekulé with a *major* accomplishment in this area. Frankland (obviously) agreed with this conclusion; in his *Experimental Researches* (26) he correctly claimed credit

for the general concept of valence: “This hypothesis ...constitutes the basis of what has since been called the doctrine of atomicity or equivalence of elements; and it was, so far as I am aware, the first announcement of this doctrine.” It is hard to argue with the view pronounced by von Meyer or Frankland.

Still, von Meyer conceded that the scientific community was slow in reaching the obvious conclusion, and that a “specific valence of carbon had remained unformulated for an extended period of time” (“blieb die bestimmte Auffassung seiner Valenz längere Zeit unausgesprochen”) (25). The merit of having enunciated the tetravalence of carbon he accorded to Kekulé. Recent claims that Couper had “proposed the tetravalence of carbon” before Kekulé (15) are without merit as Kekulé’s 1957 paper (1a) was published a full year before Couper’s (13). Obviously, Loschmidt cannot be credited with having derived the tetravalency of carbon because his paper (14) appeared several years after Kekulé’s (1) as well as Couper’s (13), at a time when new insights were gained in rapid succession (27).

Concerning the linking of carbon atoms, von Meyer gave Kekulé credit for having developed this concept and, thereby, having advanced structural theory (25):

Kekulé’s merit ... lies in the fact that he tried to understand the way in which two or more carbon atoms link with each other and saturate their affinities. (Kekulé’s Verdienst ... muß darin gesucht werden daß er der Frage nach der Art wie sich zwei und mehr Kohlenstoffatome miteinander verbinden und ihre Affinitäten sättigen auf den Grund zu gehen suchte.)

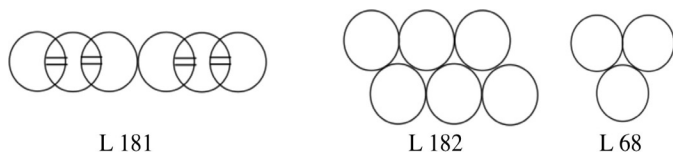
In the area of recognizing the ability of carbon atoms to form chains, both von Meyer (28) and Japp (5) argued that Couper deserves a share of the credit for having recognized this concept independently. Apparently, Couper’s work was not completely unknown in the 1890s, although, obviously, it was to Anschütz. A century later Bader (15) and Rocke (27) provided evidence that Couper gave his manuscript to Wurtz for presentation to the French Académie before Kekulé’s paper was published. Bader’s statement to the effect that “Wurtz failed to do that” (present Couper’s paper before the Académie) is, of course, correct; one should note, though, that Wurtz was not a member in 1858. In any event, Couper’s papers (13) appeared after Kekulé’s 1858 paper (3).

## Loschmidt's Benzene Formulae and Their Meaning



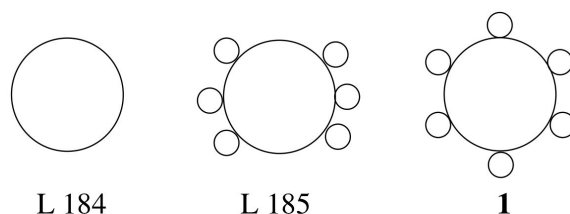
**Figure 1.** Johann Joseph Loschmidt, best known as a physicist for his 1865 estimate of the size of air molecules and for the determination of the number of molecules in a macroscopic sample. His contributions to organic chemistry were published outside of the scientific mainstream of his time and were essentially ignored by his contemporaries.

In 1861 J. J. Loschmidt (Figure 1) published a compilation of structures that allowed the direct visualization of the constitution of molecules, i.e., the connectivity of their atoms. This monograph (14) shows a detailed knowledge and deep understanding of many aspects of organic chemistry, though it does not contain a single reference. Among the numerous compounds for which Loschmidt offered structures, he recognized that benzene posed an especially difficult structural problem. He considered two structures in detail, describing them in 131 and 120 words, respectively. The first structure (29), 1,2,4,5-hexatetraene (bisallene, L 181), had been considered previously by Couper (13), and would “materialize” only more than 100 years later (30); the second structure was composed of fused three-membered rings without double bonds; tetracyclo[3.1.0.0<sup>1,4</sup>.0<sup>2,4</sup>]hexane, as current IUPAC nomenclature would name it, has yet to “materialize.” Loschmidt recognized that the known reactivity of benzene was incompatible with formula L 181; therefore he favored the tetracyclic structure, L 182.



He thought the “compressed” nature (“Verdichtung”) of benzene less important, but considered the layered nature (“Schichtung”) its key feature. He viewed this formula as a doubled allyl nucleus (“doppelte Allylkern”), i.e., composed of two fragments of L 68, an array he offered as an alternative structure for propylene and allyl derivatives.

Alas, Loschmidt refrained from taking a firm position on the details of the benzene structure because he didn't think that the available results (“nach dem bis jetzt vorliegenden”) supported formula L 182 unambiguously. Accordingly, he chose a non-committal formula, representing the benzene nucleus as a “hexavalent element” (“sechsstelliges Element”) (L 184) and benzene as L 185, describing the provisional character of this structure in a mere twenty words. In this context one should note that structure **1**, shown on the cover of *The Kekulé Riddle* (19) and a similar structure offered by M. Kohn (31) are deceptive adaptations without precedent in Loschmidt's work.



As Schiemenz (32,33) and Heilbronner and Hafner (34) have pointed out, the key to Loschmidt's benzene structure lies in his understanding of the term “element.” In the introductory pages of his booklet (35) Loschmidt unambiguously defined the “atom” as the center of a sphere, represented by a circle, i.e., its projection onto a plane. By this clear definition the circle in structures L 184 and L 185 represents an “atom,” not a “ring of six carbon atoms.” Significantly, this is exactly how Anschütz saw Loschmidt's structures (36): “in contrast to Kekulé he [Loschmidt] considered the benzene nucleus an array that behaves as a hexavalent element” (“im Gegensatz zu Kekulé sah er [Loschmidt] in dem Benzolkern ein Gebilde das sich wie ein sechswertiges Element verhält”).

Loschmidt's contemporaries either ignored or didn't know of Loschmidt's booklet. Textbooks of the second half of the 19<sup>th</sup> century did not cite Loschmidt's work (11, 27-39); only when Anschütz became editor of von Richter's text (40) were Loschmidt's formulae incorporated. However, Anschütz emphasized: “He does not address the equivalence of the six benzene hydrogens, it was incompatible with the assumption that benzene consists of two allyl-(trimethylene) rings ...” (“Ueber die

Gleichwertigkeit der sechs Benzolwasserstoffatome sagt er [Loschmidt] nichts aus, sie war bei der Annahme, dass das Benzol aus zwei geschichteten Allyl-(Trimethylen) Ringen besteht, ausgeschlossen ...”) Carl Graebe concluded: “His work was essentially ignored and has had no impact on the development of organic chemistry.” (“Seine Ausführungen [sind] so gut wie unbeachtet geblieben und haben auf die Entwicklung der organischen Chemie keinen Einfluss ausgeübt” (41).) Half a century later A. J. Ihde called Loschmidt’s work “an unheralded attempt to establish the theoretical foundations of structural chemistry ...because of its limited circulation [it] was never widely known” (42).

Beginning in the 1980s some authors (15,17,18,43) have chosen to ignore Loschmidt’s definition (and that of his 20<sup>th</sup>-century discoverer, Anschütz) and interpret the circle in L 184 as a ring of six carbons. If this assertion could be supported, Kekulé’s benzene structure of 1865 (4) would be a decided second to Loschmidt’s (14) and the commonly held historical view surely would have to be revised. However, the revisionist arguments have been met by several well-reasoned, thorough, and (at least to this author) convincing challenges.

G. Schiemenz followed the developing arguments for Loschmidt’s priority in detail, beginning with Anschütz’s revision, and summarized the results as “the birth of a legend” (32). He also surveyed the use of spheres for atoms in the mid-1800s and concluded that Loschmidt’s structures were not exceptional (33). Heilbronner and Hafner reviewed the development of structural chemistry in the 19<sup>th</sup> century (34); concerning Loschmidt’s benzene formula, and its recent interpretation as representing a ring of six carbons, they concluded: “it is hard to understand how an unambiguous statement [by Loschmidt] could be misunderstood so completely” (34) [by the authors of Refs. 15, 17, 18, and 43]. Rocke analyzed the use of structural images in the development of structural chemistry and concluded that Kekulé, and not Loschmidt, made significant contributions to the foundation of structural chemistry, including the benzene structure (27). The weight of these rebuttals appears strong, even overwhelming. Yet they have not silenced the revisionist view; in fact, new authors support this view (44,45), even if without additional arguments.

In a possibly vain attempt, to stem this tide, I wish to add to the argument in favor of Kekulé’s achievement; this attempt is based solely on Loschmidt’s structures and

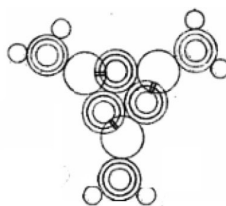
on the language he uses to describe them. In my view the priority claims in favor of Loschmidt are an interesting case of scientific anachronism. Loschmidt’s contemporaries were not prepared to see a connection between a circle (his “hexavalent element”) and an aromatic structure (even if they had studied the booklet in any detail); neither Anschütz nor Graebe viewed Loschmidt’s non-committal circle as a ring structure. Could it be that a half-century of exposure to the circle, that Robinson introduced in 1925 as a symbol of aromaticity (46), conditioned Loschmidt’s champions for their conclusion (15,17,18,43-45) and that their response could be seen as an example of a conditioned reflex?

The principal argument advanced in this paper against Loschmidt having conceived benzene as “a ring of six carbons” is based on the language Loschmidt uses to present structures L 184 and L 185. Loschmidt clearly conceded that it was “impossible to derive an unambiguous result from the available information (“ist es nach dem bis jetzt Vorliegenden unmöglich, hierüber zu einem definitiven Resultat zu gelangen”). Therefore, he postponed (held “in suspenso”) assigning a structure and chose a non-committal symbol. Loschmidt used the subjunctive (Konjunktiv) “as if it were a hexavalent element” (“als ob er ein sechsstelliges Element wäre”) [emphasis added] and fell short of using the affirmative indicative mode (Indikativ), such as, “Benzol hat die Ringstruktur 184” (“benzene has the ring structure 184”). Having refrained from assigning a structure he chose the circle (L 184) as a temporary representation without implying a relationship to the actual structure.

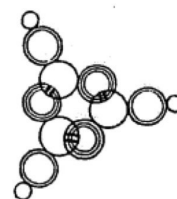
As a further argument we point to the failure to show the individual atoms. Loschmidt discussed and depicted the linear tetraene, L 181, and the tetracyclic benzene formula, L 182, in detail; he showed compounds, such as cyanuric acid, L 153, and melamine, L 154, as well as eleven of their derivatives as six-atom arrays. (Structures A 153 and A 154, reminiscent of Kekulé’s cyclohexatriene structure, are revisions created by Anschütz (16).) Loschmidt also showed all six individual carbon atoms for the perceived six-membered ring of “diethylenedi-



L 153



L 154

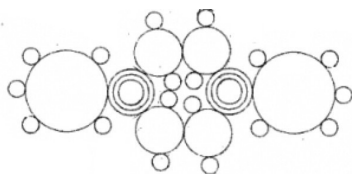


A 153

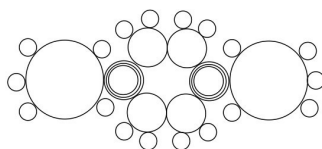


A 154

phenyl diamine,” L 237 (also “cleaned up” by Anschütz).

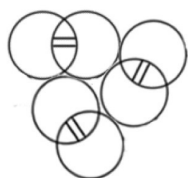
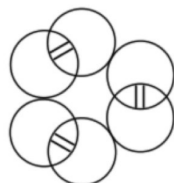


L 237



A 237

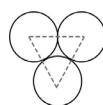
It appears inconceivable that Loschmidt would have failed to describe and depict the unprecedented planar cyclic benzene structure in similar detail, had he actually conceived of it. He surely would have given the revolutionary ring structure a more detailed pictogram, perhaps formula **2**, akin to L 153 and L 154, perhaps even a cyclohexatriene formula, **3**. The absence of any such formula for benzene argues strongly against Loschmidt understanding benzene as a planar monocycle.

**2****3**

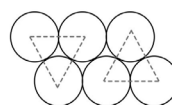
Furthermore, we note that Loschmidt did not comment on the arrangement of the carbon atoms in this “element”; he referred to the six-carbon unit as an “atom complex  $E_6$ ,” not once as a “ring.” Only in the discussion of the cyclic allyl structure, L 68, did he call a cyclic structure the “akzeptabelste Supposition” (“the most acceptable proposal”) for phenyl. However, there can be little doubt that the term “cyclic” refers to the cyclic allyl subunit (L 68) of the “doubled allyl” structure (L 182) and not to a benzene monocycle. He did discuss the putative “para”-isomer of benzene (“known” at the time, but soon discarded as erroneous); Loschmidt assumed for the “Kern” (nucleus) of para-benzene a “somewhat changed configuration.” This fact again supports the view that he saw benzene as a six-carbon cluster (with unspecified configuration).

Elaborating on his preferred benzene constitution, L 182, Loschmidt considered two unsaturated  $E$ -10 compounds, naphthalene ( $E_{10}H_8$ ) and “terpentin” ( $E_{10}H_{16}$ ); he recognized the terpene as “related to the vinyl function” and naphthalene as related to benzene. Alas, the relationship he envisioned between benzene and naphthalene does not support his understanding of benzene as a ring of six carbons. In analogy to the “layered” benzene,

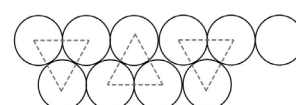
L 182, he considered naphthalene to be a “verdreifachtes” (threefold) allyl system, bearing a methyl group (L 183; Figure 2). In essence, he viewed naphthalene, as a homologue of toluene, the methyl-substituted “doubled allyl.” The proposed naphthalene structure, L 183, is irreconcilable with the notion of benzene as a “ring of six carbon atoms.”



L 68



L 182



L 183

Figure 2. Loschmidt's representation of cyclic allyl, benzene nucleus, and naphthalene nucleus; the dashed lines have been added to emphasize the “layered” “allyl” units.

To contemporaries wrestling with understanding the various structural representations of molecules, Loschmidt's preferred “layered” benzene formula (L182) may have been reminiscent of a structure that Kekulé offered for benzene in his textbook (47), in essence a three-dimensional cyclic version of the “benzine” (**4**) of his original publication (4) (Figure 3). Rotating the segments A and C around the C–C single bonds (denoted by red arrows) by  $120^\circ$  and  $-120^\circ$ , respectively, results in the triangular structure, **5**, where Kekulé's two black arrows (in structure **4**) form the final C–C bond closing the ring. Of course, it is obvious to today's reader that the perceived two-layer structure is an artefact of the “sausage” structures used by Kekulé.

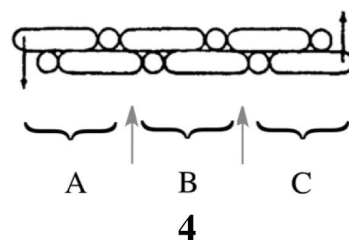
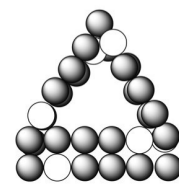
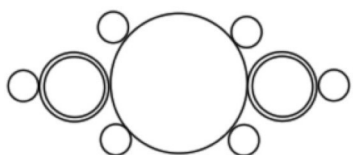
**4****5**

Figure 3. Two pictograms offered by Kekulé for benzene (4a,47). The first structure is dissected into two-carbon units; rotation of segments A and C by  $120^\circ$  and  $-120^\circ$ , respectively, around the single bonds (above the light arrows) allows the free valences (black arrows) to form the final C–C bond, closing the ring. In the second structure Kekulé's “sausage” C atoms are shown as linear arrays of four filled circles, H atoms as single open circles.

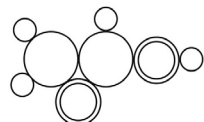
### Benzene Derivatives: Number of Isomers and Bonding to Di- and Trivalent Atoms

In the final section we probe Loschmidt's views of the benzene structure by his treatment of isomeric substituted benzenes and in the connection of di- and trivalent elements to benzene. Loschmidt did not comment on the symmetry of his "atom complex  $\text{E}_6$ ," he mentioned the possibility of isomerism, but not the number of possible isomers or the relative position of the substituents relative to each other. For example, he represented the two known isomeric "modifications" of "phenylglycol,"  $\text{E}_6\text{H}_4\text{Hd}_2$  [ $\text{Hd} = \text{OH}$ ], pyrocatechol (1,2-) and hydroquinone (1,4-), by the identical formula, L 188, in a streamlined "default" notation. Heilbronner and Hafner have pointed out, that (in nearly one hundred of his schemata), Loschmidt simply alternated the "Aufsätze" (substituents),  $=\text{O}$ ,  $-\text{H}$ , etc., between "up" and "down" to achieve streamlined ("sterisch möglichst gestreckt") formulae (34).

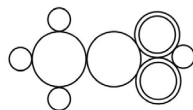


L 188

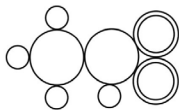
In the context of isomerism, we mention that Noe and Bader (43a) took exception to Kekulé's comment in a letter to Erlenmeyer, referring to "Loschmidt's Konfusionsformeln." Given the crowded Formeltafeln and, viewing just one example early in Loschmidt's paper, it perhaps is not too hard to understand the reaction of the cautious Kekulé (48). The pictograms considered for acetic acid include three structures, which in modern IUPAC nomenclature would be called oxiranol (L 23a) and dioxirane derivatives (L 23b and L (23b)), respectively. Loschmidt excluded the strained species as possible formulae for acetic acid, but expressly supported their presence in other carboxylic acids, specifically maleic acid.



L 23a



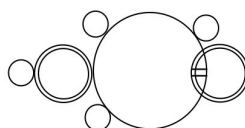
L 23b



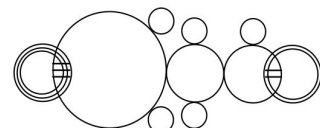
L (23b)

Less than four years after Loschmidt's publication Kekulé understood that the benzene ring could form only single bonds to (divalent) oxygen and (trivalent) nitrogen (47). In contrast, Loschmidt repeatedly depicted atoms

doubly or triply bonded to the "atom complex  $\text{E}_6$ ," i.e., in the formulae assigned to a total of twenty compounds containing as many as three " $\text{E}_6$  nuclei" with doubly- or triply-bonded atoms. We choose the formulae for "benzoquinone" (L 189) and "indigo" (L 270) as examples.

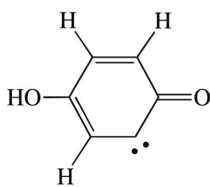


L 189

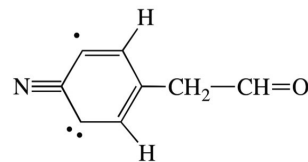


L 270

To accept the claim (15,17,18,40) that structures L 184 and L 185 represent a "ring of six carbon atoms" means to accept the presence of di-, tri-, and pentavalent carbons in formulae L 189 and L 270, which correspond to structures **7** and **8**, respectively. Structure **7** could be the first carbene, one year before Geuther's alkaline hydrolysis of chloroform (49). Structure **8** could be a carbene next to a pentavalent carbon next to an alkenyl free radical, almost forty years before Moses Gomberg's triphenylmethyl (50).

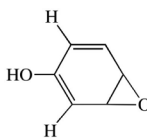


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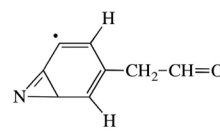


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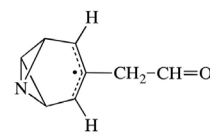
Replacing the CO double bond in **7** by two CO single bonds would yield a benzene oxide, **9**, but that clearly does not correspond to Loschmidt's pictogram, as it would ignore the specific double bond, one of Loschmidt's principal firsts in depicting organic structures. Similarly, converting the specific CN triple bond in **8** to a CN double plus a CN single bond or to three CN single bonds, would either yield a bicyclic azirene with an adjacent sigma radical, **10**, or an azabicyclobutane bridged by an allyl radical, **11**, respectively; again, neither **10** nor **11** reflects the pictogram, L 270.



9



10



11

Admittedly, the structure of indigo posed a serious puzzle to 19<sup>th</sup> century investigators; it took another

twenty years to solve (51), a very long period of time in an era when the science of organic chemistry was developing rapidly.

### Conclusion

In summary, I question the interpretation of Loschmidt's spherical benzene structure as a ring of six carbons for several reasons: (a) Loschmidt clearly favored the "layered" "doubled-allyl" structure (L 182); (b) the "triple-allyl" structure envisioned for naphthalene (L 183) supports this assignment; (c) his language clearly shows that the "cyclic" structure, L 185, was chosen as a noncommittal alternative because there was no clear evidence for structure L 181; (d) Loschmidt referred to the six-carbon unit as "atom complex  $\text{E}_6$ ," not as a "ring"; (e) given the detail in which Loschmidt described structures L 182, and the detail in which he depicted cyanuric acid, L 153, and melamine, L 154, as well as eleven of their derivatives, it is inconceivable that he wouldn't have described the revolutionary cyclic benzene structure in similar detail; and (f) he depicted over twenty cases of double and triple bonds to the "atom complex  $\text{E}_6$ ." I believe that the sum of these arguments show conclusively that Loschmidt did not view benzene as a planar molecule with six equivalent carbons and six equivalent hydrogen atoms.

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