

Crocker, Not Armit and Robinson, Begat the Six Aromatic Electrons

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1. Introduction

Aromaticity, long a cornerstone of organic chemistry, now extends equally well to inorganic or organometallic chemistry. *Chemical Reviews* dedicated a thematic issue to this topic¹ in 2001; this sequel on highly delocalized systems broadens the scope further. “Attacks” on aromaticity in the 1970s and since² have been based on its virtual (experimentally unmeasurable) character. Because there is no unique “yardstick”, aromaticity was regarded as a fuzzy notion that “had better be discarded.”³ But instead of withering away, aromaticity is blooming with increasing vigor, even after two centuries of existence. It is now appreciated that the continuous delocalization of electrons, which underlies aromaticity, is an extremely broad phenomenon, not confined merely to the π electrons of planar rings with sp^2 -hybridized atoms. Furthermore, there are an increasing number of powerful methods of assessing cyclic electron delocalization.

While there have been many historical accounts of the development of the aromaticity concept, none of these dwell on the two “unsung heroes” we feature in the present essay. The first, Henry Edward Armstrong, was certainly well-known as Professor at what is now Imperial College London. But it has not been generally appreciated that his remarkably detailed understanding of the nature of aromatic compounds⁴—well before the electron was discovered—anticipated both Robert Robinson’s “circle” notation and Eric Clar’s selective placement of such circles in polycycles. Our second hero, Ernest C. Crocker, is almost completely unrecognized. He was not a professor, a postdoc, or even a graduate student and never pursued a Ph.D. But his seminal 1922 *Journal of the American Chemical Society* paper⁵ described

accurately and in considerable detail the “six aromatic electron” structure of benzene, pyridine, and five-membered ring heteroaromatics. This was *three years* before the famous “aromatic sextet” paper⁶ of Armit and Robinson in 1925.

We hope that this historical essay will bring Armstrong’s and Crocker’s accomplishments to the fore, in much the same way that Loschmidt’s contributions⁷ are now much better appreciated.^{8b} We also emphasize in this appropriate forum that Kekulé’s final model for the structure of benzene was NOT the “oscillation hypothesis” so generally attributed to him. While this has been pointed out before,⁹ it remains overlooked by textbook writers as well by the general chemical public. In his earlier papers, Kekulé often described benzene as being “completely symmetrical.” In 1872, he reconciled this with the lower symmetry of cyclohexatriene by means of what is better described as a “vibration hypothesis”, whereby the intramolecular motion of the atoms resulted in fully symmetrical structure (the D_{6h} minimum). The so-called “oscillation hypothesis”, in which the two equivalent cyclohexatriene (D_{3h}) minima equilibrate rapidly through a fully symmetrical (D_{6h}) transition structure, was NOT what he intended. This later misinterpretation by others should not be attributed to Kekulé (see ref 50). He repeatedly referred to cyclohexatriene as “his benzene formula” (proposed in 1865–1866), but the final “Kekulé structure” (1872) was a regular hexagon.⁹

2. Pre-Electronic Theories of Aromaticity

Parallel to Galileo’s achievements in physics two centuries earlier, Lavoisier (around 1780) discarded the phlogiston pseudo-theory and raised chemistry to the rank of an experimental science based on quantitative measurements. The authors of the play *Oxygen*¹⁰ correctly bestowed Lavoisier the highest honor for this development. Had the revolutionaries not guillotined him, French chemistry might have competed more successfully with German and English achievements in the 19th century.

The atomic theory was based on firm experimental ground due to experimental and theoretical advances introduced by Dalton, Berzelius, Faraday, and other scientists. Organic chemistry developed into a separate discipline due to the demise of the dogma of the vital force (vitalism theory), to which Wöhler’s urea rearrangement (1828) contributed, due to Liebig’s methods of elemental analysis, and due to Avogadro and Cannizzaro’s distinction between atoms and molecules.

“Aromatic” had been used to classify odoriferous compounds, which often had high degrees of unsat-

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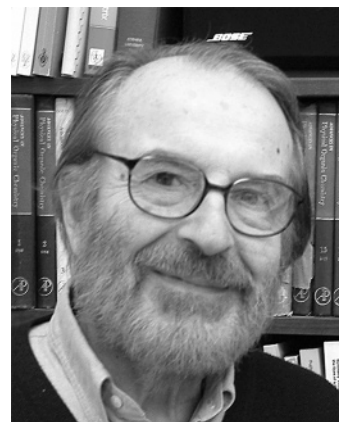


Alexandru T. Balaban, born in Timisoara, Romania, in 1931, is Professor at Texas A&M University at Galveston. Between 1956 and 1999, he taught Organic Chemistry at the Bucharest Polytechnic University, except for the period 1966–1969 when he was a Senior Research Officer at the Chemistry Section of the International Atomic Energy Agency in Vienna. He has held additional positions as Head of the Laboratory of Isotopically Labeled Compounds at the Bucharest Institute of Atomic Physics (1966–1974) and Vice-President of the Romanian Academy (1995–1998). His chemical research fields include new syntheses of aromatic heterocycles (oxazoles, indolizines, or pyrylium salts via the Balaban–Nenitzescu–Prail diacylation of alkenes) and of stable nitrogen free radicals, catalytic automerization of phenanthrene, electronic and steric components of secondary isotope effects, and chemical applications of graph theory (reaction graphs, enumeration of valence isomers of annulenes, topological indices, including the “Balaban index”, J , and a systematic nomenclature of diamondoid hydrocarbons coauthored with P. v. R. Schleyer). He has authored or edited 17 books, over 60 chapters in books edited by other authors, and over 650 papers published in peer-reviewed journals. He is a member of the Romanian Academy and of the American–Romanian Academy and an Honorary Member of the Hungarian Academy of Sciences. In 2005, he was elected as President of the International Academy of Mathematical Chemistry. Among his awards is the 1994 Skolnik Award of the Division of Chemical Information of the American Chemical Society.



Henry Rzepa received both B.Sc. and Ph.D. degrees from the University of London at Imperial College, the latter in the field of physical organic chemistry studying kinetic isotope effects in reactions of indoles. In 1974, he took up a postdoctoral fellowship in Austin, Texas, with Michael Dewar in an area which thereafter became known as computational chemistry. Since he has moved back to Imperial College London, where he is now Professor of Computational Chemistry, his research has developed in three main areas, the mechanisms of stereospecific reactions and properties of catalytic processes, the exploration of novel forms of aromaticity, and the semantic development of Internet-based publishing.

uration, since the beginning of the 19th century. But Faraday’s isolation and remarkably accurate characterization of benzene in 1825 dates the birth of the major branch of chemistry that we still designate



Paul von Ragué Schleyer was born in Cleveland, Ohio, in 1930. After education at Princeton and at Harvard (Ph.D. in physical organic chemistry with P. D. Bartlett), he returned to Princeton as Instructor in 1954 and was named Eugene Higgins Professor of Chemistry in 1969. Needing more computer time, he accepted in 1976 the Chair once held by Emil Fischer and became Co-Director of the Organic Institute of the University of Erlangen–Nuremberg, Germany. He founded its Computer Chemistry Center in 1993. Schleyer has been Professor Emeritus at Erlangen since 1998, but continues his career as Graham Perdue Professor of Chemistry at the University of Georgia, Athens. He has received honorary doctorates from the Universities of Lyon, France, Munich, Germany, and Kiev, Ukraine, as well as awards in seven countries and in different areas: physical organic, computational, boron, lithium, and most recently theoretical chemistry. He is past President of the World Association of Theoretically-Oriented Chemists (WATOC), a Fellow of the Bavarian Academy and the International Academy of Quantum Chemical Science, Coeditor Emeritus of the *Journal of Computational Chemistry*, and the Editor-in-Chief of the *Encyclopedia of Computational Chemistry*. His 12 books deal with carbonium ions, ab initio molecular orbital theory, lithium chemistry, and ab initio structures and involve collaborations with Nobel Laureates H. C. Brown, G. A. Olah, and J. A. Pople. A 1981–1997 survey identified him as being the third most cited chemist. He has published over 1100 papers.

Chart 1: Michael Faraday (1791–1867)

Faraday’s astoundingly broad-ranging discoveries rank him among the greatest scientists of the 19th century. The son of a blacksmith in a Sandemanian-faith Christian family, Faraday learned to read, write and reckon in a church Sunday school. At 14 he became a bookbinder’s apprentice. His interest in science was kindled by his reading and by lectures given at the Royal Institution in London by Sir Humphry Davy, who employed him as laboratory assistant in 1812. Davy was acclaimed as one of the greatest scientists for his discovery of two alkali metals (sodium and potassium), obtained by electrolysis of their molten salts. He also demonstrated the elemental nature of chlorine and invented the safety lamp, which did not cause explosions in coal mines. However, it has been said that Faraday was Davy’s greatest discovery.

Faraday began as a chemist. He liquefied chlorine, which had been assumed to be a “permanent gas,” like hydrogen, oxygen and nitrogen. He also was the first to prepare hexachloroethane and tetrachloroethene. His later discoveries in physics were the laws of electrolysis and electromagnetic induction (responsible for present-day electrical motors and dynamos), the Faraday effect, paramagnetism, and diamagnetism. Two units (the farad and the faraday) are named after him. He refused the offer of knighthood.

Faraday discovered benzene and established its empirical formula in 1825. Less well known is that Faraday’s sample was analyzed by the BP research laboratories on the occasion of the 200th anniversary of his birth, and presented at the Royal Institution in a videotaped talk given by Professor Sir John Cadogan (see www.armstrongwynne.org). The 99.7% purity found for Faraday’s sample could not have been attained by fractional distillation, and must have been achieved by fractional crystallization. Faraday reported a melting point within 0.1°C of the presently accepted value.

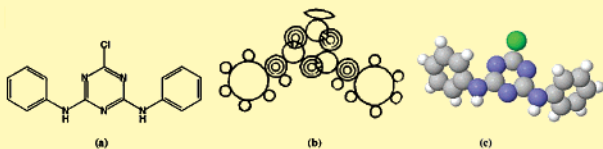
anachronistically as “aromatic”. Faraday (see Chart 1) named his substance “dicarburet of hydrogen”, that is, $(C_2H)_3$, since at the time the atomic weight of C was thought to be 6 and not 12. Faraday also isolated “carburet of hydrogen” (*trans*-2-butene) and estab-

Chart 2: Josef Loschmidt (1821-1895)

Biographical details of Loschmidt have been collected in a number of articles.⁵² Amongst many accomplishments, Loschmidt calculated correctly the number of molecules in one mole (known outside German speaking countries as "Avogadro's number"). In 1861 he published and circulated privately his extensive proposals for the structure of molecules, including many aromatic compounds, in the form of two pamphlets. One of these is a 60-page booklet containing hundreds of models of molecules; his fold-out pages of figures are amazing to behold today. The relatively recent "rediscovery" of Loschmidt's work (photo offset reproductions are sold by the Aldrich Co.) has helped fuel the debate about the relationship between Loschmidt's 1861 "constitution formulas" and Kekulé's 1865 benzene proposal.

Loschmidt employed circles not only to depict atoms, but also a larger circle to represent the (then unknown structure) of the "C₆^{VI}" six-carbon benzene nucleus *whatever its nature might be*. Loschmidt's representation of benzene, showing a large circle surrounded by six small circles for the hydrogens, seemingly hit upon nearly the correct solution. It anticipated the inscribed Armit-Robinson "aromatic sextet" circle by 74 years, and surely suggested a ring structure for benzene. However, the hydrogen spacing, based on "a union ally-like moieties,"^{9a} was not equal (as in the D_{6h} symmetry group), but was separated in two groups of three on the "top" and "bottom" (as in D_{2h} symmetry). More importantly, he did not suggest placements of the carbon atoms, even though he might well have done so (see below). His benzene circle notation was reflected by the later use of an elongated hexagon (also with D_{2h} symmetry), without double bonds or hydrogens, to represent benzene and its derivatives without specifying the nature of the bonding. This was the most commonly employed symbol in textbooks and journals for seven decades.

Unlike the cumbersome "sausage-like" representations of molecules used by Kekulé four years later (see Formula 1a and the 30 depictions of molecules in a fold-out figure in his 1866 *Annalen* paper),^{11c} all *without any spacial implications*, Loschmidt's are amazingly modern, and can be deciphered immediately. Perhaps the most remarkable is shown below as (a) a modern formula of a 2,4-disubstituted 1,3,5-triazene, (b) Loschmidt's drawing, and (c) a modern space-filled model (with covalent radii slightly decreased to match those implied by Loschmidt).



While (b) shows Loschmidt's usual representations of the phenyl substituents (but with nearly equal hydrogen spacings!), *the central triazene moiety obviously is depicted as a six-membered ring with three C=N double bonds!* Oddly, Loschmidt did not represent benzene similarly. One wonders why he did not make this connection, which is so obvious to us today. But nitrogen heterocycles (even pyridine) had not yet been included in the "aromatic" family. Nevertheless, Kekulé did not invent the concept of cyclic structures nor, it can be argued, the cyclohexatriene-like "three double bonds in a six-membered ring" motif. Loschmidt's pamphlets had circulated amongst European chemists for four years before Kekulé's first published proposal for the structure of benzene in 1865. It is incontrovertible that Kekulé knew and commented on Loschmidt's work (disparagingly in an 1862 letter to Erlenmeyer, ref 8a, p. 240).

lished the considerable difference in their chemical behavior. Despite its higher C/H ratio (greater unsaturation), benzene is much less reactive. Despite the relative simplicity of its composition, the structure of benzene was first proposed 4 decades after its discovery and nearly a decade after the development of the concept of "constitution" or "structure." But its unusual chemical properties continued to baffle the minds of the best chemists. How could the tetravalency of carbon, applied to a six-membered ring, be reconciled with the extraordinary stability of benzene? More than six further decades would elapse before a truly satisfactory explanation, based on quantum mechanics, was advanced.

While arguably others (notably Loschmidt, see Chart 2 and the discussion below) had preceded him, August Kekulé (1829-1896, Chart 3) is regarded as

Chart 3: August Kekulé (1829-1896)

August Kekulé was a student of Liebig in Giessen (Dr. Phil. 1852); he traveled widely professionally, and "became a scholar of Dumas, Gerhardt, and Williamson."⁹¹ As Privatdozent, he habilitated in Heidelberg in 1856. His fundamental papers on the tetravalency of carbon and the structures of molecules in 1857⁵⁴ led to his appointment as full Professor in Ghent (1858) where he published (1859) the first installment of his textbook of organic chemistry.

Organized by Kekulé in 1860 in Karlsruhe, the First International Congress of Chemistry was instrumental in disseminating Avogadro's assignment of the correct atomic weights to the then known elements. This enabled Mendeleev, who had attended the Congress, to construct his Periodic System of Elements. Mendeleev boldly deduced properties of three unknown elements. One can imagine his satisfaction when the discovery of gallium, germanium, and scandium confirmed these predictions.

In 1867, Kekulé accepted the offer to be Professor in Bonn and took charge of the largest chemical laboratory in the world at the time, already under construction. Dedicated a year later, Kekulé's Institute quickly became a Mecca for renowned visitors and attracted so many students that the building was expanded in 1873 and 1876. Consequently, Kekulé declined the offer (1873) to be Liebig's successor in Munich. Like Liebig and Wöhler, Kekulé was the doctoral mentor of many of the most prolific and influential chemists of the next and following generations. The development of the German dye industry owed much to Kekulé and his influence.

The fiftieth anniversary of the publication of Kekulé's benzene formula was celebrated in 1895 by the German Chemical Society.⁵⁵ Kekulé attended, and described his celebrated dream-like revelation of the ouroboros (snake biting its tail). He died a year later, in 1896. Several chemical societies organized symposia to commemorate the hundredth anniversary of Kekulé's benzene formula, and published the proceedings.⁵⁶

Kekulé's model (1b) has been credited by others erroneously as being the first representation of a cyclic molecule. However, Loschmidt had published⁷ many clear examples of 3, 5, 6, 8 and 10 membered rings in 1861. Thus, he depicted the then unknown cyclopropane by a triangle of three circles, representing the carbons; each had two smaller circles representing the hydrogens. A directly pertinent example is discussed in Chart 2. Couper had represented cyclic structures (including one for cyanuric acid) even earlier.^{9a} Kekulé's key postulate, a valence bond composite with averaged double and single bonds,⁵⁷ dates from 1872,¹² not 1865 as often is cited erroneously. To his credit, Kekulé visualized benzene as really having six equivalent CC bonds (see Appendix).⁹ He rationalized its apparent symmetry, but the unusual stability of benzene remained a mystery for 60 more years. Each ensuing generation, as represented in this essay by Armstrong, Thomson, Crocker, and Robinson, grappled with this central problem, until it was solved satisfactorily by Hückel.³⁸

being chiefly responsible for the aromaticity concept. His early papers (1865, 1866) and the second volume (1866) of his textbook outline the background of this term and define aromaticity on the basis of structural relationships to benzene. His general contributions to the development of the structural theory of chemistry (see Chart 3) may deserve comparison with Newton's influence on physics. Kekulé's ideas were the most influential, even when they were not the clearest in their time, nor even the first to be conceived; his structural representations were cumbersome, especially when compared to other proposals. Consequently, this has led to considerable controversy concerning priority, which continues today. The book of fascinating essays edited by John H. Wotiz, "The Kekulé Riddle",⁸ is aptly named. Several chapters (in particular, the critical appraisal by Schiemenz^{8c}) trace the evolution of Kekulé's benzene formulas, from his first depiction,¹¹ the "sausages" of 1865 (1a, Figure 1), to his last (completely misunderstood) proposal, the so-called "oscillating" valence structures of 1872.¹² (Snyder's historical account of "pre-electron events"^{9a} refutes this "oscillating" in-

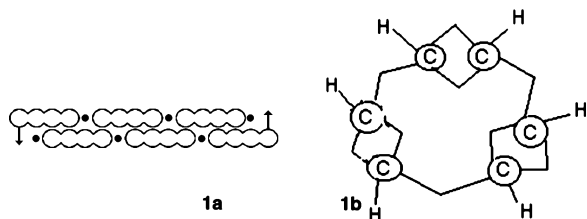


Figure 1. Kekulé's early cyclohexadiene-type benzene formulas. In **1a** (1865), Kekulé depicted the four valences of each carbon topologically by a two-dimensional rod four units in length, the hydrogens by dots (later by circles), and the closure by the arrows. Thereby each carbon has a double CC contact and single contacts to a H and a C. In his 1866 *Liebig's Annalen* paper, Kekulé explained that the two end carbons in **1a** were bound by a valence relationship (Verwandschaftseinheit) resulting in "a closed chain (a symmetrical ring), which still has six free valences." His 1866 textbook states that "the six carbons form a completely symmetrical atomic grouping, as in a ring." In **1b** (1866), Kekulé employed planar tetracoordinate dispositions of the carbon valences to represent benzene, which necessarily had alternating double and single valence connections in a ring.

terpretation (see ref 50). We do so in more detail here. For very comprehensive reviews of the history of the benzene problem, see, inter alia, Rocke,^{13a} Brush,^{13b} and Berson.^{9b,c}

Kekulé's first representation of a readily recognizable ring with alternating linkages (**1b**, Figure 1) dates from 1866.^{11c} Understandably, neither **1a** nor **1b** were adopted by Kekulé's contemporaries. Instead, they proposed more modern-looking benzene formulas not only after but also before Kekulé's 1865 "sausages". Laurent had employed hexagons (1854, 1855) in more general ways, but Loschmidt's 1861 depiction of a triazene with alternating single and double bonds in a hexagon is unmistakable (see Chart 2). However, Loschmidt evidently never recognized the possibility of representing benzene in the same manner; he employed only a nondescript large circle for the C₆ unit instead. Kekulé's **1a** was one-dimensional, a ring has to be imagined. At the same time as Kekulé (1865), Paul Havrez published his *Principe de la chimie unitaire* (albeit in a very obscure journal)¹⁴ in which he used rods and spheres to illustrate two versions of benzene rings three-dimensionally. Erlenmeyer (1866), Claus (1866), Butlerov (1868), Graebe (1868), and Ladenburg (1869)¹⁵ published various depictions of cyclohexatriene rings superior to **1b**. Kekulé adopted the last in the same year. Schiemenz^{8c} concludes, "Ladenburg's figure is [now] known as the *Kekulé formula*" [his emphasis]. "The main stream of the development [of valence bond formulas] had passed him by" [Schiemenz,^{8c} p 107]. But cyclohexatriene-based benzene formulas were not satisfactory. They did not represent the essential 6-fold symmetry necessary to account for experimental facts such as the existence of only single ortho- or meta-disubstituted isomers (see below). Despite his prescient rationalization of the 6-fold [*D*_{6h}] symmetry of benzene in 1872, Kekulé never conceived a suitable way to represent his "completely symmetrical" benzene by a single structure. His written description seems clear, but its meaning was not understood by his contemporaries or by posterity. "The *Kekulé formula*" was neither cyclohexatriene nor

a pair of "oscillating" cyclohexatrienes. Kekulé envisioned *D*_{6h} benzene!⁹

In 1872, Kekulé (who often had insisted that benzene had a "completely symmetrical" structure, see Figure 1 caption) proposed his "vibrating hypothesis," which did **not** involve the equilibration of two lower-symmetry cyclohexatriene structures so commonly (but erroneously) attributed to him (see ref 50). What Kekulé meant has generally been misinterpreted: rapidly "oscillating" geometries were **not** intended.⁹ Even in 1872, atoms in molecules were believed to vibrate while retaining their connectivity. Benzene was a special case, since, according to Kekulé, such vibrations would interchange the formal single and double bonds. He regarded benzene as having a single, symmetrical structure in which "every carbon atom...has exactly the same relationship to both of its neighbors" ["...jedes Kohlenstoffatom...zu deinen beiden Nachbarn genau in derselben Beziehung steht"]. Indeed, the B_{2u} vibration of benzene, much discussed by Shaik and Hiberty,¹⁶ distorts the *D*_{6h} minimum Kekulé envisioned toward two equivalent *D*_{3h} geometries. Kekulé's remarkable intellectual leap anticipated Pauling's much later use of the "Kekulé pair" [sic] as resonance contributors in an *electronic* theory of benzene. But Kekulé's idea was far ahead of its time, and his contemporaries were not wont to represent a single compound as some sort of composite of two formulas. Kekulé had tried earlier to solve this problem by using a fully symmetrical hexagon to represent the hydrogen (or substituent) placements^{11c} (also see ref 20), but this did not clarify the nature of the carbon skeleton.

Although an acceptable *single-formula* representation of benzene that captured the proper symmetry was not forthcoming until Robinson's circle notation of 1925,⁶ alternatives had been proposed as early as 1867. While Claus's diagonal formula **2** (a graph-theoretically nonplanar structure) was chemically impossible if each line corresponds to a covalent bond,¹⁷ it inspired Baeyer's¹⁸ and (independently) Armstrong's¹⁹ improved centric formula **3** (which did not imply cross-ring bonding). Although Lothar Meyer had proposed a similar centric formula in 1872, he regarded the inner valences to be "free" or "unsatisfied." In notable contrast, Armstrong stressed the mutual interaction of these "affinities" (the "resultants" directed toward the center) among one another. This concept would later correspond to the electron sextet by interpreting the "affinities" as π -electrons. Other formulas, now known experimentally as (CH)₆ valence isomers, were advanced by Ladenburg (triprismane or benzprismane, **4**)¹⁵ and by J. Dewar (bicyclo[2.2.0]hexadiene, **5**) (both only for discussion purposes, as often also has been misinterpreted).²⁰ Two more cubic graphs with six vertexes, benzvalene (**6**) and bis-cyclopropenyl (**7**), are possible.²¹ These (CH)₆ valence isomers (**4**–**7**) are now known to be much less stable than benzene owing to their high steric strain and lack of aromatic character. None have the necessary 6-fold symmetry (*D*_{6h}) to depict benzene (Figure 2).

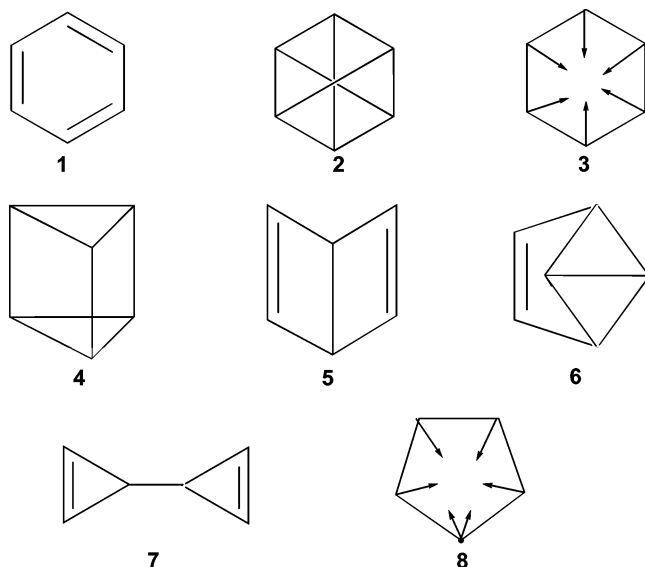


Figure 2. Early structural proposals for benzene (1–7). Of these, 4–7 are now known as (CH)₆ valence isomers. The centric formulation of five-membered ring heterocycles such as pyrrole and thiophene is shown as 8.

Wilhelm Körner²² had proposed a powerful method (“absolute”, i.e., independent of degradation to less substituted derivatives) for establishing the structure of polysubstituted benzene derivatives, by counting the numbers of different isomers resulting from introducing an extra substituent: thus, for benzene derivatives with identical substituents, meta-disubstituted compounds afford three trisubstituted isomers, ortho-disubstituted compounds afford two trisubstituted isomers, and para-disubstituted compounds afford only one trisubstituted isomer. The benzprismane (ignoring stereochemistry) and Kekulé’s formulas (including 6-fold equivalence of all CH groups) afford exactly the same numbers of isomers with any number of substituents because they yield the same cycle indexes associated with Polya’s method of computing these numbers. As seen from Figure 3, one can associate pairwise the triplets of di- and trisubstituted isomers of benzprismane and benzene, when ignoring stereochemistry in the former case and the distinction between single and double bonds in the latter case. However, Baeyer’s experimental investigations using the three isomeric benzene dicarboxylic acids and the corresponding cyclohexane dicarboxylic acids ruled out the prismane formula based on steric arguments. Having formulated his strain theory, Baeyer recognized the high steric strain of the prismane. He noted that the lack of optical activity in any ortho-disubstituted benzene derivative excluded the prismane structure.

In 1866, Erlenmeyer²³ proposed the first formula for naphthalene and introduced the concept that the reactivity should differentiate aromatic from nonaromatic compounds. This led to the first divergence among criteria for aromaticity. The reactivity of related aromatic substances could be used to predict the reactivity of an unknown compound. But the preparation of this compound was necessary to check whether it fulfilled the reactivity criterion. In the second volume of his *Textbook of Organic Chemistry*, published in 1866,²⁴ Kekulé insisted that aromaticity

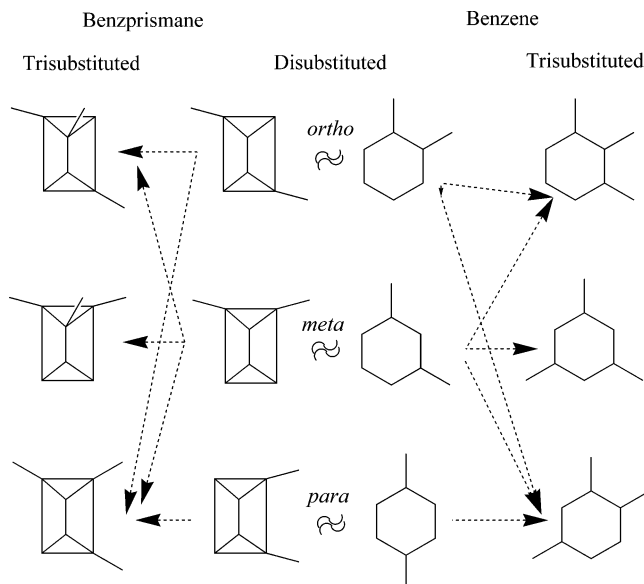


Figure 3. Correspondence between di- and trisubstituted isomers of benzene and benzprismane with identical substituents. Stereochemistry and bond multiplicity are ignored.

should be based on chemical structures. Hence, one would be able to classify as aromatic an unknown compound obeying the structural criterion, without having to prepare it and ascertain its reactions (but Kekulé might not approve of the purely computational predictions of new aromatic systems being published today, since he emphasized the primacy of experiment.)

Victor Meyer’s serendipitous discovery in 1883 that thiophene mimics closely the chemical and physical properties of benzene extended the aromatic concept beyond hydrocarbons to heterocyclic compounds with five-membered rings. Pyrrole and furan are similar to thiophene. Bamberger proposed the centric formula (8) for these five-membered heteroaromatics.²⁵ The two lines emerging from the heteroatom amount again to six lines directed toward the center. This implied that the nitrogen in pyrrole was pentavalent as it was considered, in those days, to be in nitro groups, RN(=O)₂ or in ammonium hydroxide. Bamberger’s experimental papers also are astonishing. Without the modern methods of purifying and characterizing substances, he was able to report numerous side products formed in very low yields.

Thiele, who also discovered the stability of the cyclopentadiene anion, elaborated in 1899 a theory of “residual valences” that compensated reciprocally in conjugated cyclic systems but not in acyclic systems. This concept explained the 1,ω-additions to acyclic conjugated systems.²⁶ Although flawed, this theory stimulated Willstätter²⁷ to synthesize cyclooctatetraene, which did not behave like an aromatic compound; he also tried unsuccessfully to obtain cyclobutadiene, as Kekulé himself had attempted 3 decades earlier.¹² For some time, it was believed that the absence of steric strain in a planar conjugated ring could account for the stability of benzene and for the instability of larger or smaller conjugated rings. The most modern view is that angle strain along with the lack of effective cyclic conjugation is

probably the reason for the instability (high reactivity) of “antiaromatics”.²⁸

In some mysterious way, the continuous conjugation of the three double bonds in a ring distinguished benzene from acyclic conjugated unsaturated compounds. But how to rationalize the exceptional behavior of the “aromatic” class of hydrogen-poor yet quasi-saturated hydrocarbons and their derivatives: their tendency to undergo substitution rather than addition reactions? Indeed, the substitution chemistry of benzene rapidly increased its importance and contributed to the flowering of the dye industry. Kekulé organized his organic chemistry textbook into aliphatic and aromatic sections; this practice continued for a century.

3. Electronic Theories of Aromaticity

J. J. Thomson's discovery of the electron in 1897²⁹ spawned numerous interpretations of valency in electronic terms by chemists, but these took nearly 2 decades to emerge. Thomson himself, Gilbert Newton Lewis, Irving Langmuir, and Walter Kossel all developed theories of chemical bonding during WWI. The development of quantum physics based on Schrödinger's equation (1926) occurred a decade later. Heitler and London performed the first calculations for the hydrogen molecule in 1927. Linus Pauling introduced the concepts of electronegativity, orbital hybridization, and resonance.³⁰ When applied to aromaticity, the last two concepts gave satisfactory results for benzene. Further elaboration however was necessary to explain why cyclooctatetraene and cyclobutadiene behave completely differently.

3.1. The π -Electron Aromatic Sextet

Robert Robinson (1886–1975) was a towering figure among England's organic chemists. He was appointed to the Waynflete chair of chemistry at the University of Oxford in 1930, a position he held till his retirement in 1955. Knighted in 1939, he was awarded the Nobel Prize for Chemistry in 1947 for his research on natural products (especially alkaloids and anthocyanines). He was responsible for introducing qualitative electronic theories for explaining many organic reactions; his well-known life-long scientific conflict with Christopher K. Ingold was due to the fight for primacy in this field.

Although various suggestions for explaining the bond equivalence of benzene had been made during the period 1908–1923, including concepts such as having the fourth valence of each carbon satisfied by a “mobile” electron associated with the ring,³¹ most such formulations were insufficient as theories of chemical bonding. A 1925 paper by James Wilson Armit, a doctoral student, and Robert Robinson entitled “Polynuclear heterocyclic aromatic types. Part II. Some anhydronium bases”⁷⁵ introduced the catchy term, “aromatic sextet”, clearly designated the “group of six electrons that resists disruption”, as well as the circle notation symbolizing this sextet. (The inscribed circle harks back to Loschmidt's benzene symbol, a circle but without an outer hexagon.) The sextet idea also was applied to five-membered aromatic rings, such as pyrrole and thiophene. Pyridine,

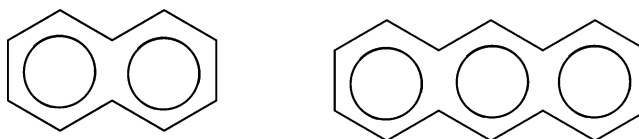


Figure 4. Armit and Robinson's 1925 pre-Hückel representations of naphthalene and anthracene with two and three “aromatic sextets”, respectively. The central bonds were omitted to satisfy the proper total electron count.

pyridinium, and pyrylium salts and their benzo-derivatives possessed aromatic sextets that did not involve the lone pair electrons of the heteroatoms. It seems reasonable to assume that Armit was responsible for the experimental work reported in the paper but that the ideas about aromaticity were Robinson's, as a part of his application of electronic theory to reaction mechanisms and the interpretation of organic chemistry. Armit pursued a career in industry and published little thereafter.

Even though the “aromatic sextet” is a logical extension of the earlier centric formulas for benzene and five-membered aromatics showing six lines pointing toward the molecule centers, relevant prior literature was not cited (see below). Moreover, sextet circles were drawn in all the rings of naphthalene and anthracene, requiring omission of the pairs of σ -electrons common to each pair of adjacent rings (Figure 4). This had a precedent in Bamberger's 1890 version of the centric formula for naphthalene, which (unlike Armstrong's; see below and Chart 4) had six “affinities” or “potential” bonds pointing toward the center of each ring but no central bond. That the valence bond structure of naphthalene had five double bonds and that of anthracene had seven also was ignored

These representations gave rise to confusion, perhaps even compounded by Robinson's attempted clarification, “...the deletion of the central connecting bonds is more apparent than real, because these attachments are by covalencies which involve the electrons of the sextets only.” In his brief retrospective personal account of “The Concept of the Aromatic Sextet”, given at the Sheffield Aromaticity Symposium in 1966³² Robinson stated, “The circle symbolized only the idea of association and implied no view about linking functions of the electrons. Naphthalene was represented (probably mistakenly) with two sextets, and the arithmetic of the electrons satisfied by deletion of the 9,10 carbon bond.” Robinson went on to discuss Clar's refinements in the use of the circle notation approvingly but did not take the opportunity of mentioning earlier contributions of Armstrong, Thomson, Crocker, Loschmidt, and others (see below).

The 1925 Armit–Robinson paper rapidly became the standard citation in discussions of aromaticity as being the (incorrectly credited) first recognition of the aromatic electron sextet, which was afterward generalized by the Hückel $4n + 2$ π -electron rule (with $n = 1$). In contrast, the prior work of an unknown American, Ernest C. Crocker, who identified the generality of six aromatic electrons clearly in 1922, has been almost completely overlooked. We only have found brief mention of Crocker in the Kekulé Cen-

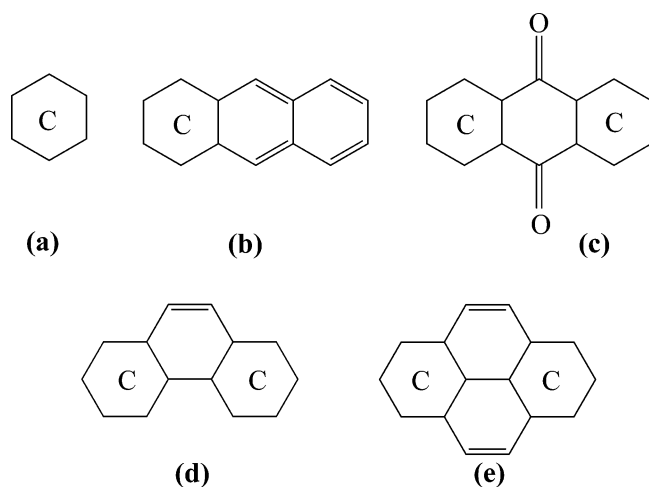


Figure 5. Armstrong's concise representations of (a) benzene, (b) anthracene, (c) anthraquinone, (d) phenanthrene, and (e) pyrene. His designation of only some of the rings with a "C" (centric) anticipates Clar's explicit use of inscribed circles in just the same way. Also see Chart 4, where Armstrong's actual structure of naphthalene is reproduced.

ennial (1966), J. P. Snyder's "pre-electron events" chapter (1969),^{9a,48f} Stranges's 1984 historical essay about G. N. Lewis,³³ S. Kikuchi's 1997 paper,³⁴ and Balaban's 2004 article on Clar structures.³⁵ But before turning to Crocker's contribution, let us consider Armstrong's even earlier prescient insights. He anticipated Robinson's aromatic "circle" even before the electron was discovered!

Henry E. Armstrong (1848–1937), a prominent British chemist, had represented the structures of polycyclic benzenoids correctly long before the discovery of the electron by applying the centric formulation of the six aromatic "affinities." Armstrong's representations (Figure 5) must be contrasted with Armit and Robinson's (Figure 4). Armstrong depicts naphthalene (see Chart 4) with 10 affinities (now recognized as being equivalent to electrons); the two affinities common to both rings "can act in two directions." His single "C" (centric) ring in anthracene and two "C's" in phenanthrene and pyrene (Figure 5) anticipate Clar remarkably. Armstrong's paper, "The structure of cycloid hydrocarbons,"⁴ also includes the following extraordinary descriptions, "the centric affinities act within a cycle rather than toward the center in the manner depicted"...*benzene*, according to this view, *may be represented by a double ring.*" [our emphasis] "When an additive compound is formed the inner circle of affinity suffers disruption, and ... the contiguous carbon-atoms to which nothing has become attached of necessity acquire the ethylenic or unsaturated condition." He concluded by speculating that "knowledge of the inner structure of the cycloid hydrocarbons" was required to settle many practical problems, citing as an example the rules governing the ortho/para- or meta-directing ability of benzene derivatives toward (electrophilic) substitution, which he had refined in 1887.

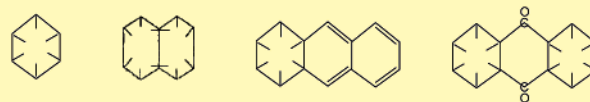
Ernest C. Crocker (1888–1964, Chart 5), then an employee at the Research Laboratory of Applied Chemistry of the Massachusetts Institute of Technology, published a paper in 1922 (three years before

Chart 4: Henry Edward Armstrong (1848–1937)

Armstrong was born (and lived all his life) in Lewisham, a suburb of London. A fascinating book, "The Theory of Words", apparently influenced his early schooling heavily and made him particularly critical of their meanings. In the spring of 1865 he entered, for no known reason, the Royal College of Chemistry in London (now the department of chemistry at Imperial College). Chemical training in those days was not lengthy, and after a year and a term, at the age of 18, Edward Frankland selected him to assist in research. Armstrong's project was to devise methods of determining organic impurities in sewage. His Ph.D. was awarded in 1869 on "acids of sulfur." A permanent appointment (1879) at City and Guilds of London Institute (now also part of Imperial College) followed. In 1884 at age 36, Armstrong became Professor of Chemistry at the Central Institution (another Imperial College precursor). He already had started on the systematic synthesis, degradation and structural constitution of many naphthalene derivatives (building on earlier work on benzene derivatives and Erlenmeyer's proposal for the structure of naphthalene) in 1881. W. P. Wynne was his most important collaborator; their collection of 263 naphthalene samples accrued over several decades is now preserved at Imperial College (see <http://www.armstrongwynne.org/>) This work gave impetus to the synthetic dye industry. His later research dealt with terpenes, particularly camphor, crystallography, and also with water purification, helping to eradicate typhoid fever.

In 1887, Armstrong became interested in classifying substituents of benzene in terms of their *meta*- and *ortho*-*para* directing influences. A footnote to an article on that theme proposed¹⁹ his centric formula for benzene in which six "affinities" act towards the centre of the ring (in the sense of vectors, or "resultants"). A similar representation had been proposed in 1872 by Julius Lothar Meyer but was suggested independently in 1887 by Adolf von Baeyer and employed often in his series of admirable papers, "On the Constitution of Benzene."¹⁸ However, unlike Armstrong, von Baeyer hardly extended its use beyond monocyclic benzene derivatives. An exception, phenanthrene, was symbolized with a long C9–C10 bond in the center. In contrast, Armstrong developed a much better way to generalize the centric formulas.

His early depictions of polycyclic molecules are shown below. Note how he applied the centric formalism, showing 10 affinities, correctly to naphthalene. He clearly indicates that there is only one affinity per carbon atom, but those in the center are shared by the two rings. Armstrong's somewhat different anthracene formulation also showed great insight, especially compared with von Baeyer's (and later, Robinson's) inferior representations: four double bonds and 6 special affinities (adding up to what we now describe as "14 π electrons") are clearly shown, and there is only one centric ring.



Armstrong's discussion of substituted benzenes also is noteworthy; "the introduction of a radicle [by which he meant atom or substituent on the benzene ring] doubtless involves an altered distribution of the affinity, much as the distribution of the electric charge in a body is altered by bringing it near to another body." Armstrong surely anticipates the polarizable distribution and the electronic nature of the charged particle ("affinity") now known as the electron but then of course undiscovered!

In 1890, Armstrong⁴ designated the six centric "affinities" by the letter C inscribed in a benzene ring, as shown in Figure 5 (had he chosen the letter O instead, he would have devised Clar-type formulas almost half a century earlier). He only used one C for anthracene, exactly as Clar did much later in his formula. Phenanthrene and pyrene, by contrast, had two C-rings, exactly as in Clar structures.

Citing Armstrong,¹⁹ (with our comments in square brackets): "the six carbon atoms [in benzene] are linked together by nine 'single bonds' and not in the manner indicated by Kekulé's well-known formula, by three single and three double bonds." "...Thompson's results⁵⁸ taken together with all that is known about benzene, must be held to prove that benzene is in no sense a compound of the same order as an olefine; and that Kekulé's formula, if used at all, must be literally interpreted to show that the carbon atoms are held together by nine affinities..." "... a symbol free from all objections may be based on the assumption that of the twenty-four affinities of the six carbon-atoms [the valence electrons], twelve are engaged in the formation of the six-carbon ring and six in retaining the six hydrogen-atoms, in the manner ordinarily supposed; while the remaining six react upon one another, acting towards a centre as if it were, so that the 'affinity' may be said to be uniformly and symmetrically distributed [A key hypothesis – the essence of benzene!]. I


would, in fact, make use of the symbol:  ... any one carbon-atom is directly connected with any other [carbon] atom not contiguous to it in the ring" [this anticipates the future development of the concept of multicenter bonding and MO theory].

Chart 5: Ernest C. Crocker (1888-1964)

Crocker was the son of a blacksmith and carriage maker. He had a telescope when he was 6 years old, his own chemistry laboratory at 12, and was one of the first to build an amateur radio station in New England. He tried unsuccessfully to persuade Orville Wright to put a wireless emitter on his flying machine. His mechanical skills and interest in science landed him a job at MIT at 19 and then permission to matriculate. He received his B. Sci. in 1914 after three years of study, went into industry, and then joined the war effort in 1917, working on poison gases and an idea of odor classification. After the war he returned to MIT and was employed by Robert E. Wilson in the Research Laboratory for Applied Chemistry. Crocker was not a graduate student and never pursued a Ph. D. degree, but was inspired by G. N. Lewis during their five years in common at MIT. Crocker's single author 1922 paper acknowledges the help of R. E. Wilson, J. F. Norris, and A. A. Blanchard.⁵

After joining the A. D. Little Company (also in 1922), Crocker developed his expertise on odors and flavors, and was reputed as "the man with the million-dollar nose." He authored a book "Flavors", a number of publications, held 16 patents, and chaired the Northeastern ACS Section in 1948-1949. A popular speaker, he lectured widely for the American Chemical Society.

It was acknowledged at the 1983 G. N. Lewis Symposium that Crocker had made the first use of Lewis's ideas for explaining the structure and reactivity of benzene and its derivatives. But Crocker did not elaborate on his 1922 paper or evidently complain about its lack of subsequent recognition by Robinson and others. Those who knew Crocker in later years did not suspect that he was the pioneer in applying G. N. Lewis's ideas to aromatic compounds.⁵⁹

Armit and Robinson) entitled "Application of the Octet Theory to Single-Ring Aromatic Compounds."⁷⁵ Crocker mentioned that Lewis, followed by Langmuir and others, first used cubic representations of first-row atoms initially with one electron at each apex to account for the closed shell (octet) of electrons that repel each other. Later, four sets of paired electrons were disposed at the corners of a tetrahedron, in agreement with the optical activity of many organic compounds. On the basis of these ideas, Crocker proposed the formula of benzene (Figure 6) comprised

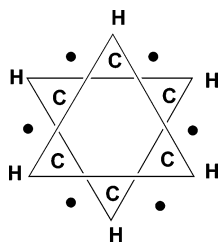


Figure 6. Crocker's 1922 "octet rule" benzene formula. The corners of each triangle represent carbon valences with two electrons each. The dots are the six aromatic electrons. In 1921, J. J. Thomson, the discoverer of the electron, similarly considered benzene to have three-electron bonding between each CH group.

of six carbon triangles with H's at each outer vertex and six inner CC contacts; this left six "aromatic electrons" (explicitly represented by dots) on the outside. Each of these electrons were interpreted to pair up either with one or the other of the two neighboring electrons, being in a "continuous vibration" in the plane of the ring.

Crocker acknowledged that Sir J. J. Thomson (see Chart 6) had arrived at a similar idea independently in a paper published in 1921.³⁶ Although Crocker never employed the term "aromatic sextet," he repeatedly emphasized that "six aromatic electrons" conferred stability to benzene and other aromatic compounds, particularly five-membered (furan, pyr-

Chart 6: Sir Joseph John (J. J.) Thomson (1856-1940)

Educated in Cambridge at the Trinity College in mathematics and physics, J. J. Thomson was elected as a Fellow of the Royal Society in 1884 and was appointed to the chair of physics at the Cavendish Laboratory. His 1897 discovery that all matter contained electrons was awarded the Nobel Prize for Physics in 1906. J. J. Thomson was knighted in 1908. In 1918, he became master of the Trinity College. Seven of his students later won Nobel Prizes for Physics. Like his namesake William Thomson (Lord Kelvin), who also was educated at Cambridge, Thomson contributed much to the development of physics into a modern science.

In a series of lectures at the Royal Institution between 1914 and 1919, Thomson presented his ideas about the role of electrons in chemical bonding. These ideas were published in 1921 under the title, "On the structure of the molecule and chemical combination."³⁶ Thomson's discussion of benzene and naphthalene assumed three-electron contact among the neighboring CH groups, "...With this arrangement we have complete symmetry, and it is analogous to the Armstrong and Baeyer or central [*i.e.* centric] theory of the benzene ring." For naphthalene, the "two cells round the two central carbons have two-electron contact, while the ten contacts between the outer cells are three-electron ones". Thomson's, like Armstrong's, anticipation of the 10 π electron structure of naphthalene went unheeded in Armit and Robinson's 1925 paper, in which 12 π electrons are implied by the two sextet rings (Figure 2).

Chart 7: Erich Hückel (1896-1980)

Erich Hückel was educated as a physicist; he never achieved recognition among chemists.⁶⁰ In contrast, his brother, Walter Hückel, became a well-known "Professor Ordinarius" (*i.e.* full professor) and authored a much-praised treatise, *Theoretical Basis of Organic Chemistry*, published first in 1931 and afterwards in many editions ("theoretical" was used in this context was to differentiate it from "practical"). Erich Hückel only was a "Professor Extraordinarius" (equivalent to an associate professor) until nearly the end of his career, when he was finally promoted to a personal Full Professorship. He had almost no coworkers, perhaps because he was a poor lecturer.⁶⁰ During most of his lifetime, Hückel was totally eclipsed by Linus Pauling and Wheland,⁶¹ who had elaborated Hückel's early valence bond (VB) method and devised the Resonance Theory, notwithstanding the fact that the VB method does not explain the Hückel $4n+2$ π -electron rule in simple terms. Hückel Molecular Orbital theory, elaborated by a number of more sophisticated π treatments, was disseminated in several influential books.⁶² Roald Hoffmann and William N. Lipscomb developed "Extended HMO theory," *i.e.*, into three dimensions.⁶³

On reading Erich Hückel's autobiography,⁶⁴ one is struck by the bitterness that he must have felt being so little recognized, when Nobel Prizes for chemistry were awarded to Peter Debye in 1936, Robert Robinson in 1947, Linus Pauling in 1954, and Robert S. Mulliken in 1966. In this autobiography, published five years before his death, Hückel complains that he suffered from being "between the chairs" of physics and chemistry. "Chemists don't understand my ideas, but physicists are not interested in chemical matters."

role, or thiophene) and six-membered heterocycles (pyridine). He also discussed ortho/para versus meta-orientation of aromatic substitutions in terms of electron-attracting or electron-repelling effects of substituents. Crocker's paper cited contributions by Lewis and Langmuir for the octet theory repeatedly. Crocker stressed both in the title and the text that all carbons in his representations involved electron octets.

Erich Hückel (Chart 7) achieved recognition by elaborating, together with Peter Debye, the theory of strong electrolytes in 1923³⁷ and later by applying a simplified version of quantum theory to π -electrons in conjugated molecules, which became known as Hückel molecular orbital (HMO) theory.³⁸ Although he never explicitly formulated a " $4n + 2$ rule" (see Berson, ref 60), this was obvious from his work. Hückel showed that monocyclic systems with continuous conjugation having 6, 10, 14, etc. π -electrons benefited from extra stabilization and were aromatic. But it is more accurate to refer to the "Hückel $4n + 2$ π -electron rule," rather than to "Hückel's rule."

4. Post-Hückel Developments in Theories of Aromaticity

After the elucidation of the structure of azulene³⁹ and Michael J. S. Dewar's proposal of the seven-membered tropolone formula for stipitatic acid explaining the mysterious behavior of these derivatives,⁴⁰ a flurry of synthetic efforts led to the preparation of aromatic cations such as tropylium⁴¹ and cyclopropenium.⁴² The doorway to the extensive research on nonbenzenoid aromatic compounds had been opened.⁴² Important examples include Franz Sondheimer's preparation of [18]- and many other annulenes⁴³ and Emanuel Vogel's syntheses of bridged [10]annulenes and their higher homologues.⁴⁴ All these developments vindicated the Hückel $4n + 2 \pi$ -electron rule.

A comment on the importance of good theories is relevant. Tropylium bromide had been obtained and its molecular formula established in 1891 by Merling, but, baffled by its water solubility, he could not deduce its structure.⁴⁵ William von E. Doering⁴¹ succeeded in demonstrating its aromatic tropylium ion character 66 years later!

Eric Clar, who had prepared and reviewed many new polycyclic benzenoid hydrocarbons, observed that resonance contributors that maximize the number of rings with three double bonds are the most important. On this basis, he developed *Clar structures*, which restrict inscribed circles only to benzenoid rings that have six π -electrons. Once electrons have been assigned to a ring, they cannot be used in another; hence, rings with inscribed circles do not share an edge.^{46,47}

Aromaticity is associated with enhanced electron delocalization resulting in increased stability, characteristic reactivity, equalization of interatomic bond lengths, and ring currents evidenced by magnetic consequences. Each of these manifestations of aromaticity has given rise to quantitative criteria of global or local aromaticity, amenable to experimental and theoretical determination. In addition to the aromaticity of familiar systems, antiaromaticity or hyphenated aromaticities (pseudo-, quasi-, etc.) were advocated. The three-dimensionality of fullerenes and of boron-based clusters, the homo-aromaticity of cationic systems, the important role of σ , in-plane, and double aromaticity as well as the aromaticity of Möbius and triplet state annulenes and of pericyclic transition states have enlarged the concept of aromaticity recently and made it clear that it must be measured with a variety of yardsticks. We have cited only a few among the many books⁴⁸ and papers⁴⁹ devoted to aromaticity.

5. Conclusions

We have reviewed part of the background of the concept of the six aromatic electrons, tracing its origins by emphasizing the remarkably modern cyclic representations of Loschmidt, the misunderstood Kekulé "vibrating", fully symmetrical structural proposal, Armstrong's description of the centric notation and its selective application to polycyclic aromatics (which anticipates both Armit and Robinson's circle notation and Clar's precise use of the circle in polyaromatic hydrocarbons), and Crocker's recogni-

tion (preceding Armit and Robinson) that six electrons were responsible for the aromatic character of benzene, pyridine, pyrrole, and thiophene. Justified questions arise. Why have chemists ignored Crocker's seminal paper published in the foremost American chemistry journal for 75 years? Why has Armstrong not received more recognition?

Our examples illustrate that credit for a scientific advance often is awarded to the most famous promulgator of an idea, rather than to its originator (even when the originator's concept was superior). Good structural depictions are important, but may not be decisive. The 30 sausage representations of simple benzene derivatives (based on **1a**) Kekulé published in 1866 are crude compared with Loschmidt's much larger catalog (1861) of diverse and remarkably modern-looking structures. But Loschmidt did not decipher the nature of the benzene "nucleus." He did depict a cyclohexatriene-type structure explicitly, albeit with three nitrogens in the ring, but did not apply this idea to represent benzene. Kekulé can be credited with the idea of a bond-alternating ring for benzene, although the hexagonal "Kekulé [cyclohexatriene] formula" attributed to him was arguably^{8c} first published by Ladenburg in 1869.¹⁵ Kekulé preferred to use empirical formulas instead.^{8c} Only nine of his 40 papers on aromatic species (1865–1888) employ hexagonal figures, and the earliest represent hydrogen (rather than carbon) placements. Nonetheless, Kekulé reconciled the *fully symmetrical* structure of benzene, indicated experimentally by the number of its substituted isomers, with the less symmetrical cyclohexatriene formula by means of his vibration hypothesis:⁵⁰ each carbon has exactly the same relationship to its two carbon neighbors. Despite the crudeness of his representations of structures, Kekulé insisted that benzene was "completely symmetrical" [D_{6h}]. The various centric formulas had 6-fold symmetry but were peculiar and cumbersome; they did not survive.

Armit and Robinson's simple solution, an inscribed circle signifying the "aromatic sextet" (1925), was universally adopted, but its correct extension to polycycles is problematical. Having taken no notice of Armstrong, Armit and Robinson misapplied it to naphthalene and anthracene. Armstrong's "affinities" (now equated with electrons) and his selective assignment of centric rings in aromatic polycycles anticipated Clar's precise use of the circle notation 70 years later. Like Armstrong with his six singular "affinities," Crocker emphasized (1922) the special character of the "six aromatic electrons" of benzene, pyridine, pyrrole, and thiophene and gave credit to Thomson's 1921 proposal for benzene. But Crocker's representation of benzene (Figure 3) was overly intricate and unappealing. Armit and Robinson (1925) did not cite these or any other prior contributions. Their discussion was less clear and their application to naphthalene and anthracene, unlike Armstrong's, was flawed. But Robinson's prestige, the easy to draw "circle," and the "catchy phrase," the *aromatic sextet*, captured the credit for the concept of the pre-Hückel electronic structure of benzene.

Indeed, from the very beginning of structural chemistry, good illustrations have often been the key to understanding; they provided the best means to present and to convey ideas. Chemists struggled for 60 years trying to find a truly satisfactory representation of the convention-breaking 6-fold symmetry of benzene. Loschmidt's formulas appear amazingly modern to us, but we are fully familiar with Robinson's circle notation and equate this with Loschmidt's. But Loschmidt intended his circle to be a nondescript symbol. As he had done for 1,3,5-triazabenzene, why did Loschmidt not represent benzene with the same motif: three double bonds in a hexagon? His contemporaries were evidently less impressed by his formulas than we are. Kekulé conceived the cyclohexatriene structure of benzene but formulated it clumsily (Figure 1). His failure to illustrate his "completely symmetrical" hypothesis adequately in 1872 led to the "oscillating" misinterpretation. Crocker's obscurity is due, at least in part, to his unduly complicated benzene symbol (Figure 6). If he had merely used a hexagon with six extra "dots" to signify the three-electron CC bonds, his contribution might have attracted more attention. Robinson finally invented a satisfactory benzene representation with his inscribed circle notation, but he erred in applying it to polycyclic aromatics (Figure 4). Armstrong already had done this correctly years before with his selective use of centric rings (Figure 5 and Chart 4). But the extra "centric" lines were bothersome to draw and the choices of the centric rings must have puzzled his contemporaries. Armstrong's real insights, which anticipated Clar by many years, were unappreciated and forgotten. Neither Robinson nor even Clar⁴⁶ cited Armstrong's papers. Hückel's inability to communicate his ideas understandably and visually to chemists contributed to his lack of recognition. "Making use of the catchy ($4n + 2$) slogan" (see Berson, ref 60) and a simple scheme, like Frost and Muslin's polygons inscribed in a circle,⁵¹ might have sufficed.

6. Acknowledgment

We thank F. D. Greene for information concerning E. C. Crocker and G. N. Lewis, as well as A. Roche, R. Huisgen, D. Lenoir, and the reviewers for warranted criticisms, helpful comments, and suggestions. NSF Grant CHE-0209857 supported this work in Georgia and an Arts and Humanities Research Board grant that in London.

7. Appendix: What Benzene Model Did Kekulé Propose in His 1872 *Annalen* Paper?

The problem of interpreting the benzene model Kekulé actually proposed in *Liebig's Annalen*, 1872,¹² can be expressed in modern terms as a choice between two alternatives:

OSC, The Oscillating Model. Two equivalent D_{3h} cyclohexatriene minima equilibrate rapidly through a fully symmetrical (D_{6h}) transition structure. This is generally represented in the literature by two full equilibrium arrows between the two minima. Kekulé never mentioned this model, even though it continues to be attributed to him. He never used the word "oscillating" or a rapidly equilibrating process in his paper. Another interpretation of "oscillating", closer

to but also not what Kekulé intended, is that the single bonds in benzene "switch back and forth."

VIB, The Collision or, Better Put, Vibrating Model. The structure only has a single, fully symmetrical (D_{6h}) minimum, but this vibrates (the b_{2u} spectroscopic mode) toward the bond-alternating D_{3h} forms. This is now represented by a double-headed resonance arrow between the two cyclohexatriene structures. Although the resonance concept lay far in the future, this model is very close to what Kekulé actually proposed.⁹ The ready in-plane deformation of benzene has been much discussed in recent years by Shaik and Hiberty,¹⁶ who have presented convincing arguments that the D_{3h} geometry, preferred by the π distortivity, would be adopted were it not for the σ framework. While Kekulé did not use the word "vibrating", the normal motion of atoms within molecules is described in detail and is central to his reasoning.

Kekulé's article,¹² "Theoretical considerations and historical notes on the constitution of benzene", summarizes his earlier views. He considered his first proposal—a ring with alternating single and double bonds—to be the simplest hypothesis, but only one among others. "When a possible equilibrium (Gleichgewichtslage) or a possible closely packed structure [as we now would call it] with symmetrical bonds [e.g., an octahedron, which Kekulé considered as a three-dimensional version of the Claus centric structure in a later section] are ruled out due to the great stability of the aromatic nucleus, the number of acceptable hypotheses is sharply reduced. If one further concludes, from the general behavior of aromatic substances, that the six usable affinities (Verwandschaften) are more or less equally distributed to the six carbon atoms and in addition are equally weighted (gleichwertig), then only a relatively small number of acceptable hypotheses remain."

Kekulé then devotes several pages to the detailed analysis of five structural possibilities, which had been proposed, for example, by Claus, Dewar, and Ladenburg. On the basis of experimental observations and chemical arguments, he eliminates all but cyclohexatriene. While this section is interesting reading in a historical context, it is not directly pertinent except for Kekulé's repeated emphasis on the need for "a regular arrangement of the six carbon atoms" and that "the six remaining affinities of the aromatic nucleus should be equally distributed over the six carbon atoms."

He then considers criticisms of his original cyclohexatriene formulation, principally that it predicts the existence of two ortho (1,2- and 1,6-disubstituted) benzenes. He mentions the view of others that differences between these two "ortho isomers" might be too small to matter but states "I would have abandoned my proposed benzene formula, if it could be saved only through such an assumption." Note that Kekulé does not mention the "oscillation" possibility as a simple way around this problem (the less stable "ortho" form would readily be converted into the more stable one), either here or later in the text. Kekulé then states that he has held the opinion for a long time that the criticism (that his proposal predicts two

ortho isomers) is derived from the overly literal interpretation of the cyclohexatriene formula irrespective of the possibility that the conventions employed (for this representation) may be somewhat incomplete or inaccurate.

"I think it is now appropriate to express my view of this opposition in somewhat more detail." Kekulé states that this involves a hypothesis he developed over the years about the "nature of the motion of atoms in molecules" and still would not publish, except that its application to benzene leads to a solution "that I think is important."

"The atoms in the systems we call molecules must be assumed to be in continuous motion. This view has long been discussed by physicists and chemists and was expressed several times in the first volume of my textbook. But no one, as far as I know, has discussed in detail the form of this intramolecular motion of atoms. ... the motion must, in any event, maintain the atoms in the same relative order, and must lead back to the middle equilibrium position." Kekulé then develops what he considers, among many imaginable possibilities, to be the most likely assumption.

"The individual atoms of the system collide with one another in an essentially straight-line motion and then, as elastic bodies, move apart again. What one describes in chemistry as valence, now takes on a more mechanical meaning: valence is the relative number of collisions an atom experiences in a given time interval with other atoms. In the same time interval that the monovalent atoms in a diatomic molecule collide with one another, at the same temperature, divalent atoms in a diatomic molecule collide twice. [The concept that double and single bonds have different force constants lay far in the future.] Under the same conditions and time interval, the number of collisions a molecule comprised of one divalent atom and two monovalent atoms undergoes =2 for the divalent atom, and =1 for each monovalent atom."

Kekulé then states that two tetravalent carbon atoms, connected by a single bond, collide together once in the same time interval that a monovalent hydrogen traverses its path. The carbons also collide with three other atoms. In the same time interval, carbon atoms with double bonds collide twice and experience collisions with two other [monovalent] atoms. Viewing benzene first as a cyclohexadiene with a C1=C2 double bond, every carbon (e.g., C1) collides twice with one carbon neighbor (e.g., C2) and once with the other (C6), as well as once with a hydrogen atom in the first time interval. "In the second time interval, the same carbon [C1] which just returned from [colliding with] C2 turns for the moment to carbon 6. Its [C1] collisions in the second time interval [are twice with C6, once with C2, and once with H]." This was represented by a second, equivalent cyclohexatriene formula, but with a C1=C6 double bond. "Therefore, the same carbon atom [C1] is doubly bonded to one of its neighbors [C2] in the first time interval, but in the second, to the other neighbor [C6]."

"The simplest mean of all the collisions of a carbon atom is determined by the sum of its collisions in the two first time intervals, which then repeat periodically. This mean is [based on the sum, three collisions with both C2 and C6, and two with H] and one sees as a consequence that every carbon atom has exactly the same relationship to its two [carbon] neighbors with which it collides equally often [our emphasis]. The usual benzene formula [a single cyclohexatriene] naturally only represents the collisions in one time interval, that is, only a single phase, so that one is led to the view that 1,2- and 1,6- disubstituted derivatives must necessarily be different. When the interpretation given above or a similar one is taken to be correct, it follows that this apparent difference is not real."

Comment. Kekulé's "time interval" is spectroscopic, that is, far shorter than that required by even a very rapid equilibration. He never proposes or discusses the "oscillation" model (OSC) so commonly attributed to him. Instead, his vibration hypothesis led him to the conclusion that benzene has a fully symmetrical structure, in which all carbons have the exactly the same relationship to one another (VIB).⁹

8. References

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