CHEMICAL REVIEWS

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Introduction: Aromaticity

Michael Faraday discovered benzene in 1825 (*Phil. Trans. R. Soc. London*, **1825**, 440). He isolated "bicarburet of hydrogen" (i.e., a 2:1 C:H ratio) by repeated fractionation of the "fluid obtained during compression of oil gas" furnished "through the kindness of Mr. Gordon" from "the Portable Gas Company". Faraday's descriptive name reflected the "C_6H_3" composition he deduced (based on the erroneous hydrogen equivalent weight of the day). He determined its melting and boiling points, as well as the density, with remarkable accuracy. Faraday noted its reactions, e.g., with chlorine when "placed in sun-light" and with sulfuric acid. "The odour of the substance with [nitric] acid was exceedingly like that of almonds." In contrast, "carburet of hydrogen" (probably *trans*-2-butene), which Faraday also isolated, was much more reactive.

Each succeeding generation of chemists, while taking advantage of the structural integrity of benzene and its analogs for synthetic and practical purposes, has grappled with the elusive origin and essence of "aromaticity". Of the many fine historical accounts, I mention only three here. J. P. Snyder (*Nonbenzenoid Aromatics*; Academic Press: New York, 1969; Vol. 1, Chapter 1) reviews the "preelectron events", i.e., from Faraday and Kekulé to Hückel. P. J. Garratt (*Aromaticity*; Wiley: New York, 1986) traces "the continuous thread" of development further, up to the present "ab initio era". J. Berson's recent account of the life of Erich Hückel and the "chilly reception [of his theory] from the experimentalists" [*Chemical Creativity*; Wiley-VCH: New York, 1999] is highly commendable.

Despite the very frequent use of aromatic and aromaticity in the current scientific literature (see Table 1 in the review by Krygowski and Cyrański, this issue), these designations, like many other useful and popular chemical terms, are nonreductive. They have no precise meaning and do not denote directly measurable quantities. Consequently, definitions, which continue to evolve since the 1865 Kekulé and the more general 1866 Erlenmeyer formulations, are now often based on experimental observables and, more recently, quantities obtained from theoretical computations. Aromatic compounds are more stable—often far more stable—and their geometries tend to be more regular than they "ought to be". The magnetic and spectroscopic properties have special characteristics. The electronic structures requiring "closed circuits of mobile electrons" are very sensitive to the symmetry of the wave functions and the number of electrons. Early restrictions—that aromatic compounds should be planar and confined to rings with $4n + 2$ π electrons—have long since vanished. The mobile electrons may circulate in the ring plane (note the "[*n*]trannulenes"), σ rather than π orbitals may be involved, pericyclic transition states are aromatic, ring CX_2 groups can participate effectively in π-electron delocalization hyperconjugatively, and $4n$ electron aromaticity has been demonstrated in Möbius as well as in triplet annulenes. A very large number of transition-metal sandwich (e.g., ferrocene, dibenzenechromium), half-sandwich, and other complexes are aromatic. It also has been apparent for some time that aromaticity in main-group element compounds can be manifested in three physical dimensions rather than just two. One can regard such systems as having ring currents in the three principal dimensions with no (or little) anisotropy. R. B. King reviews such three-dimensional aromaticity in diverse boron-based clusters authoritatively. M. Bühl and A. Hirsch point to the relationship between the buildup of electrons in atomic π-electron shells and the spherical aromaticity of icosohedral fullerenes.

The proliferation of "types" of aromaticity, going far beyond the conventional confines of benzenoid hydrocarbons and their related heteroarenes, will continue as the following examples show. Homoaromaticity, long since established in carbocation chemistry, now is considered by R. V. Williams to be "fully characterized" for anionic compounds. The same recognition for neutral homoaromaticity, after several withdrawn claims, can be anticipated. The metallabenzenes, where a transition-metal group replaces an arene CH, are reviewed by J. Bleeke, a major contributor to the area. L. Nyulászi focuses on the hitherto underappreciated ability of "normal valent" phosphorus to participate in cyclic electron delocalization, whereas V. I. Minkin and R. M. Minyaev review the critical participation of "hypervalent" phosphorus and other main-group elements in aromatic systems. The large polycyclic aromatic hydrocarbons synthesized in Mainz and described by M. D. Watson, A. Fechtenkötter, and K. Müllen indeed

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are “beautiful”. These “extended π systems create challenging problems for any discussions into π-structure”.

The 1994 book by Minkin, along with M. N. Glukhovtsev and B. Y. Simkin, *Aromaticity and Antiaromaticity. Electronic and Structural Aspects*, as well as the maturation of ab initio and density functional methods, served as stimuli for this special issue. It is now possible to examine, quite reliably and in far more detail than formerly, ever larger and structurally more complex systems. There are now too many topics to cover, but the 18 reviews published together here should help launch aromaticity into the new century. My thanks go to all the authors for their fine contributions and to John Gladysz and his staff at Erlangen for organizing and realizing this project so effectively. We regret that many other prospective contributors who expressed interest in the project could not meet the necessary deadline. I am sorry to be one of them.

Faraday also deserves his cover page recognition for his discovery that ordinary matter interacts with a magnetic field. This repulsion, a phenomenon he called “diamagnetism”, led eventually to the first physical method for characterizing aromatic compounds and much later to nuclear magnetic resonance. In 1910, Pascal devised the first increment system for relating the magnitude of diamagnetic repulsion—the magnetic susceptibility—to molecular structures. The repulsions of benzene compounds by the magnetic field were “exalted”, i.e., unusually large based on the increment-sum expectations.

In 1936, Linus Pauling (and, independently, Dame Kathleen Lonsdale) suggested that induced “ring currents” of the six benzene π electrons were responsible for this exaltation. Fritz London, a year later, employed Hückel theory to compute such exaltations, which often were referred to as “London diamagnetism” in the earlier literature. Hyp Dauben's impressive work in the late 1960s revived interest in magnetic susceptibility, and W. H. Flygare proposed magnetic susceptibility anisotropy as aromaticity criteria. However, this interest ended with their untimely deaths, the difficulty of the measurements, and the rapidly emerging importance of nuclear magnetic resonance. The latest edition of only one of the advanced organic chemistry textbooks mentions magnetic susceptibility.

Arguably, the special magnetic behavior associated with induced ring currents in aromatic compounds is most closely related to the cyclic electron delocalization which characterizes such species. Not surprisingly, there have been many proposed aromaticity definitions in terms of magnetic properties before my own (What is Aromaticity? Schleyer, P. v. R; Jiao, H. *Pure Appl. Chem*. **1996**, *68*, 209−218). Our NICS (nucleus-independent chemical shift) criterion, based on magnetic shieldings computed ab initio or with DFT at or above ring centers, is now widely applied. Its parameterization for MNDO by S. Patchkovskii and W. Thiel is described in a paper (*J. Mol. Model* **2000**, *6*, 67) which also summarizes published NICS results from my group and others.

In 1956, Pople applied ring current theory to explain the downfield chemical shift of benzene protons (relative to those of vinyl H’s). The shielding of protons structurally located above an aromatic ring or within the plane of the ring (as is possible with larger annulenes) also was accounted for. This is the basis of NICS and also of R. H. Mitchell’s ingenious method for assessing the aromaticity of rings fused to bridged [14]annulenes where the methyl derivatives act as NMR probes. In addition, Pople also applied his theory to the magnetic behavior of antiaromatic compounds. Appraised here in complementary reviews, this far more recent development stems from Willstätter’s synthesis of the olefin-like cyclooctatetraene (and his failure to prepare cyclobutadiene). The 4*n* electron annulenes were considered to be nonaromatic until R. Breslow demonstrated that they were destabilized. K. B. Wiberg analyzes, in his characteristically thorough manner, the 4*n* π-electron monocyclic annulenes employing his own ab initio and DFT data. From a more experimental /historical viewpoint, A. D. Allen and T. T. Tidwell consider, in addition, polycyclic and $4n + 1$ electron systems. Some of the latter exhibit aromatic but others antiaromatic characteristics.

In a rather dissenting opinion, J. A. N. F. Gomes and R. B. Mallion express fundamental misgivings concerning the relationship between ring currents and aromaticity (as does P. Lazzaretti in a notable related article Ring Currents. *Prog. Nucl. Magn. Reson. Spectrosc.* **2000**, *36*, 1−88) but recommend relating “the general topological analysis of the current-density field... to age-proven concepts like ring currents and aromaticity” and call for “more extended numerical comparisons of relative NICS values with relative ring-current intensities”.

Reviews are concerned with the quantification of various aromaticity criteria and their interrelationships. To what extent and under what circumstances do various measures of aromaticity agree (if at all)? T. M. Krygowski and M. K. Cyrański apply the HOMA index (based both on the degrees of bond length alternation and the average deviation from standard values) widely as a revealing measure not only of the aromaticity of a variety of individual rings but also of the global character of polycyclic systems. They conclude that “in most cases, HOMA correlates well with magnetic indexes, such as NICS and the magnetic susceptibility exaltation”. A. R. Katritzky, K. Jug, and D. C. Oniciu carry out statistical principal component analyses of a number of energetic, geometrical, and magnetic aromaticity criteria of heterocyclic five- and six-membered ring systems. While stressing that “approximate linear relationships between two or more aromaticity scales can be found” for “certain subsets of compounds”, “different physical properties described by corresponding aromaticity criteria will, in general, not lead to the same classification of compounds and that the notion of a single index to characterize the properties of aromatic compounds has to be abandoned.” In my view, this situation certainly emphasizes the inherent difficulties in reducing “different physical properties” of diverse systems to “corresponding aromaticity criteria” or indexes. For example, there is no agreement on the aromatic stabilization energy (ASE) even of benzene or the best way to evaluate such a quantity. At most, the ASE would only be 3−4% of the total binding (atomization) energy of benzene. With their charge topological stabilization effects and heteroatom−heteroatom interactions, Katritzky's heterocycles are far more complex to evaluate. This problem is general. What is the ASE of C_{60}? How can one unravel this from the strain energy reliably? The failure to find correlations between aromaticity criteria may only reflect deficiencies in the procedures currently used to devise and to evaluate such indexes. I am not convinced that the search for a global aromaticity index "has to be abandoned". This challenge may be met by the development of more highly refined methods to dissect aromaticity effects from other influences. I hope that some clever scientist will find a direct or indirect way to employ an easily determinable quantity, like HOMA or NICS in modified form, to deduce accurate stabilization energies due to cyclic electron delocalization in all kinds of complex systems.

Density functional theory not only facilitates quantum chemical computations of structures, energies, and spectroscopic properties of larger molecules, it provides, as emphasized by F. De Proft and P. Geerlings, new conceptual measures based on the electron density, "hardness", for example, proposed "to quantify the aromaticity of molecules".

L. J. Schaad and B. A. Hess, Jr. review the "early history of resonance energy" which applied improvements of Hückel "π-electron only" theory to evaluate, for example, the sets of planar fully conjugated systems compared in Figure 6 of this paper. There is some qualitative agreement among the sets, but an evaluation against ab initio data would confront the problem of separating "the various steric energy changes" from "the resonance energy changes". K. Jug, P. C. Hiberty, and S. Shaik also review related earlier history and then describe several methods to separate σ and π energies by means of all electron quantum chemistry procedures. Conclusions regarding the origin of the symmetric structures of the allyl radical and benzene as well as the classification of substituents and the determination of σ- and π-bond energies are presented. The related review by S. Shaik, A. Shurki, D. Danovich, and P. C. Hiberty emphasizes "the duality of the π-component of benzene... which characterizes all delocalized π-components". The distortivity "along the Kekulé mode" (which favors CC bond length alternation) is balanced against the stabilization energy (which decreases the bond length alternation in a linear polyene). The basis for the conclusion that the D_{6h} structure of benzene is due to the σ framework, now widely accepted, is applied instructively to interpret a number of related aromatic, antiaromatic, and strained systems.

S. W. Slayden and J. F. Liebman demonstrate that one can go quite far in using experimentally available energies to evaluate "homodesmotic resonance energies HSE". Again, strain effects, which are only roughly approximated, bedevil these estimates, e.g., "These numbers [the HSE values] suggest that neither C60 nor C70 is aromatic and indeed are better described as antiaromatic. This result is not so surprising because the fullerenes are nonplanar and strained."

Historically, aromaticity has been a time-dependent phenomenon. Aromatic implies various features, properties, or behaviors to chemists with different backgrounds. While "benzene-like" still suffices for some, the "cyclic delocalization of mobile electrons" description now seems paramount. Its general implication for energies and structures, both geometrical and electronic, as well as magnetic and other properties, necessarily results in an ever increasing widening of the 19th century aromaticity concept.

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