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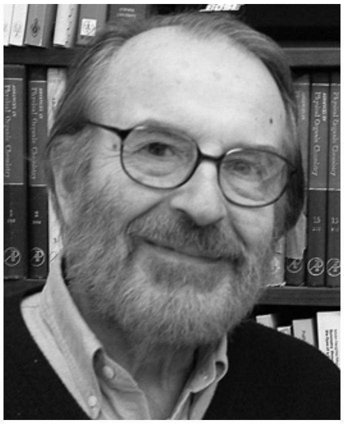

Paul von Ragué Schleyer was born in Cleveland, Ohio, in 1930. After education at Princeton and at Harvard (Ph.D. in physical organic chemistry with P. D. Bartlett), he returned to Princeton as Instructor in 1954 and was named Eugene Higgins Professor of Chemistry in 1969. Needing more computer time, 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, as well as 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.

Introduction: Delocalization—Pi and Sigma

The May 2001 thematic issue of *Chemical Reviews*, “Aromaticity”, was well received and won the Best Single Issue Prize of the Association of American Publishers, among the journals of the Professional and Scholarly Publishing Division. Thus encouraged, the Editors of *Chemical Reviews* agreed that the present thematic issue on related, but broader, topics was warranted. The title chosen reflects the increasing awareness that many molecules considered to be delocalized in the “aromatic sense” may involve “σ” as well as “π” electron delocalization, or even both together, either cooperatively or antagonistically. While it can be argued that electron delocalization is present in all molecules, the term is employed here in its more traditional usage. Although not being classified as “aromatic”, highly conjugated polyenes (discussed by Kertesz, Choi, and Yang) exemplify strongly delocalized acyclic systems. That all nanotubes with “zigzag” structures but only some of those of the “armchair” type are “metallic” illustrates the rather complex relationship among the local aromaticity of individual nanotube rings and the overall behavior of extended systems (discussed by Lu and Chen). Clearly, all aspects of the topic suggested by

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the title are far too broad to be included in a single issue. Selection was necessary, and electron delocalization in metals was not included. The reviews are international in origin; only two out of the 35 authors were born in the U.S.A.!

Johannes Thiele and Robert S. Mulliken, who invented the terms “conjugation” and “hyperconjugation”, respectively, are my choices as the intellectual pioneers of the theme of this issue of *Chemical Reviews*. Thiele, who discovered the unusual stability of the cyclopentadienyl anion, applied his ingenious “partial valence” concept (1899) broadly to rationalize the special chemical behavior of unsaturated compounds (now called “delocalized π systems”). Thiele attributed the greater reactivity of double bonds to “residual affinities” (equivalent to p orbitals), which could link across the central atoms of a “conjugated” diene (the term he invented), thus explaining 1,4-additions. Fully conjugated cyclic polyenes had no residual affinities; all are linked. This eliminated the distinction between single and double bonds in benzene and was responsible for both its relative inertness and high symmetry. Thiele’s theory was widely applied for over a decade until Willstätter synthesized cyclooctatetraene (1911, 1913) and found it to lack aromatic character completely, contrary to the prediction of Thiele’s theory. Geuenich, Hess, Köhler, and Herges briefly trace the development of the concept of double bonds, first represented by Loschmidt, from Thiele’s conjugation hypothesis to Hückel’s and later theoretical contributions.

Mulliken’s “fundamental work concerning chemical bonds and the electronic structure of molecules by the molecular orbital method” (the citation of his unshared 1966 Nobel Prize) arose from his involvement with molecular spectroscopy. Mulliken (with C. A. Riecke and W. G. Brown, *J. Am. Chem. Soc.* **1942**, *63*, 41) developed the concept of hyperconjugation to account for the shift in UV maxima of unsaturated systems and their stabilization by alkyl substitution. This type of delocalization involved the interaction of “σ” (meaning single) with “π” bonds. M. J. S. Dewar and M. L. McKee’s “σ aromaticity” (1980), explaining the lower-than-expected strain energy of cyclopropane, extended the σ delocalization concept further. “Double aromaticity”, involving in-plane σ as well as π delocalization, was recognized one year earlier (Chandrasekhar, J.; Jemmis, E. D.; Schleyer, P. v. R. *Tetrahedron Lett.* **1979**, 3707). Tables 1 and 2 in the paper by Chen, Wannere, Corminboeuf, Puchta, and Schleyer list selected contributions to the development of the aromaticity concept.

This thematic issue begins along such historical lines with a preface (by Balaban, Schleyer, and Rzepa) emphasizing some less well-known aspects of the development of this aromaticity concept. Notwithstanding the astonishing prescience of Loschmidt’s 1861 structural proposals and his nearly modern representations of molecules, including many with rings as well as several 1,3,5-triazabenzene derivatives with three double bonds, Kekulé was the first (1865) to suggest a cyclohexatriene formula for benzene itself (albeit with relatively crude depictions). However, Kekulé’s 1872 refinement proposed a fully six-fold symmetrical, but “vibrating”, benzene structure. *He did* ***not*** *intend the “oscillating” hypothesis others mistakenly ascribed to him later.* This almost universal misinterpretation should not be repeated in the literature and in textbooks.

Balaban et al. focus on the achievements of two “unsung heroes” in the further development of the aromaticity concept. A decade before Thiele, Armstrong was alone in extending the Claus−Meyer−Baeyer−Armstrong−Bamberger “centric” representation (with six affinities—which we would now equate with π electrons—pointing toward the center of benzene) correctly to polycyclic aromatic compounds in the same manner as Clar recommended many decades later. It is almost completely forgotten that Crocker was the first to recognize (in a 1922 *J. Am. Chem. Soc.* paper) that six electrons were responsible for the aromaticity of benzene, thiophene, and pyrrole, three years before the famous Armit−Robinson “atomatic sextet” publication (1925) with its “inscribed circle” notation. Unlike Armstrong, Robinson did not understand how to extend his notation satisfactorily to naphthalene and anthracene. We agree with others that *the indiscriminate practice of inscribing circles uncritically in every ring of a polycyclic aromatic hydrocarbon should be abandoned*. It would be far better to follow Clar’s recommendation to restrict the circle notation to the representation of six aromatic electrons.

The fourteen reviews that follow have been grouped loosely into three categories, but the themes often overlap. Thus, the “ACID” representations of the Herges group (unlike other visualization methods) can detect and display even weak delocalization due, for example, to conjugation, hyperconjugation, spiroconjugation, and homoaromaticity (as in 1,3,5-cycloheptatriene). Kertesz et al. discuss the relationship between extended conjugated polymers and the effect of the size of aromatic rings, particularly with regard to bond length alternation and the band gap. In higher dimensional systems, like single-wall nanotubes and graphene, this leads to zero band gaps. Krygowski and Stępień present a modern view of L. P. Hammett’s classical concerns, by analyzing substituent effects on the π-electron delocalization of benzene rings and related systems. Stability, bond lengths, and magnetic properties are affected, especially when quinoid canonical structures are important. Substituent effects on $4N + 1$ and $4N - 3$ π-electron systems can be pronounced.

Hydrogen bonds also are manifestations of electron delocalization, especially when single-well potentials are involved. Sobczyk, Grabowski, and Krygowski also consider the influence of H-bonding on the electron delocalization of associated aromatic systems (2-hydroxybenzaldehyde is an example), as indicated by changes in the electron density distribution, geometries, spectroscopic properties, and other properties. Tautomeric equilibria also are influenced by H-bonding, but as reviewed by Raczyńska, Kosińka, Ośmiałowski, and Gawinecki, other effects are more important in these highly biochemically relevant systems. Different tautomers have different degrees of delocalization, in acyclic as well as cyclic isomer pairs, such as α-hydroxypyridine and α-pyridone. The HOMA geometric index can be applied effectively to the analysis of acyclic tautomers.

The second group of reviews deals with the emerging frontier of three-dimensional delocalization, ranging from the most highly symmetrical "spherical" molecules (deltahedral boranes, fullerenes, and elemental clusters considered by Chen and King), to the extended nanotubes (Lu and Chen), and to the numerous half-twisted Möbius sytems described by Rzepa in his review. Rzepa is chiefly responsible for broadening Heilbronner's original Möbius concept even to rather small rings. Likewise, the fruitful theoretical−experimental collaboration of Boldyrev and Wang has demonstrated the extension of the aromaticity/antiaromaticity concept to clusters comprised solely of atoms of metallic elements.

Although very useful, "delocalization" and "aromaticity" are virtual concepts, which cannot be measured directly experimentally. Consequently, many evaluation and visualization methods have been devised, some of which, such as current density plots, are highly instructive but afford only qualitative information. Conversely, other methods provide quantitative estimates but are not well suited for visualization. Descriptions of different methods and assessments of their performance comprise the last set of reviews in this thematic issue. Herges's illuminating anisotropy of the induced current density (ACID) method has been mentioned above.

Nucleus-independent chemical shifts (NICS; see the paper by Chen, Wannere, Corminboeuf, Puchta, and Schleyer) have been widely employed since their introduction as a magnetic index of aromaticity a decade ago. Since then, the NICS method has been refined and extended considerably, facilitating more detailed analyses. These may now be based on the tensor component parallel to the applied magnetic field (perpendicular to the ring) as a more soundly based magnetic measure of the induced ring current and the cyclic electron delocalization.

Heine, Corminboeuf, and Seifert present in instructive detail the theoretical background and the basis of the relationship between π-electron delocalization and the shielding induced by an applied magnetic field, as exemplified by the ACID, the NICS, the aromatic ring current shielding (ARCS), and the gauge-independent magnetic induced currents (GIMIC) methods. Applications to four illustrative examples are analyzed. Each of these methods, along with current density maps, provide complementary insights.

Cyrański describes and assesses critically the energetic, geometric, magnetic, and reactivity criteria of aromaticity and analyzes the degree to which they agree. Conceding that pitfalls may be involved, e.g., in the selection of reference molecules (even the seemingly "best" choices are still arbitrary), the quantities given by different measures can agree either quite well (for sets of related molecules with widely ranging properties) or very poorly. An example is [18]annulene. The D_{3h} bond length-alternating and D_{6h} bond-equalized structures differ very little in energy but enormously in all their magnetic properties. In such cases, the various criteria of aromaticity do not respond to the same extent to the degree of delocalization. As many criteria as possible should be applied to analyze aromaticity.

Merino, Vela, and Heine's comprehensive review of descriptions of electron delocalization by the analysis of molecular fields stresses that different descriptors may be complementary. "The panoramic view gained by the application of different descriptors" is, "in many instances, mandatory for a better and coherent understanding of the underlying mechanisms of electron localization and delocalization that contribute to chemical bonding."

The atoms in molecules (AIM) and the visually appealing electron localization function (ELF) topological approaches are reviewed authoritatively by Poater, Duran, Solà, and Silvi. These methods provide quantitative information highly useful for more detailed interpretations of delocalization. After pointing out several discrepancies, these authors also conclude, "there is not a single measure of aromaticity that can be universally applied."

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