EDITORIAL

Aromaticity

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Aromaticity has been lately in the center of attention of chemists with books [1-3], journal special issues [4-10], reviews [11, 12], and publications (these are too numerous to cite). The discoveries of fullerenes, nanotubes, nanocones, and nanotori as well as the recent techniques for obtaining graphene sheets with monatomic thickness and astounding properties have enlarged our views about the power of electronic delocalization that occupies a prominent place in explaining the properties of aromatic systems. Although there is some disagreement on how to define and measure local and global aromaticity, there are no longer any voices asking for striking out the notion of aromaticity from the chemists' vocabulary. I like Gernot Frenking's metaphor [13] about

> "unicorns, mystical animals whose appearance is known to everybody although nobody has ever seen one: creatures that bring law and order, health and good fortune, fame and satisfaction in an otherwise chaotic and disordered world. In the world of chemical bonding models, there are many unicorns such as resonance, conjugation, hyperconjugation, frontier orbitals, covalent bonding, donor-acceptor bond, π-bonding, and a particularly fickle species–aromaticity."

Eric Clar's theory [14] has conferred a precise role to the Armit-Robinson + Crocker sextet [15], and Erich Hückel has shown that the sextet is a particular case of his now famous $4n+2$ π-electron rule. I remember the excitement of organic chemists when Michael J. S. Dewar [16] published his findings about stipitatic acid (a tropolone derivative) as experimental evidence for Hückel's prediction of aromaticity in tropylium rings, later brilliantly confirmed by the synthesis of tropylium salts and tropolone by Doering and Knox [17, 18]. Also it was amazing to find out that tropylium bromide had paradoxically been obtained much earlier [19], and that without the right theory it was impossible to understand why C_7H_7Br would be water-soluble. A similar paradox happened a little later, when pyrylium salts formed as by-products in the much-studied acylation of alkenes used to be discarded (being water-soluble) till chance observations led to the isolation of such salts in what is now recognized as the Balaban-Nenitzescu-Praill pyrylium salt synthesis by alkene diacylation [20].

Just as the Hückel "2(modulo 4)-π-electron Rule" governs planar conjugated aromatics, the circle notation for the aromatic sextet allows a simple representation of the "0(modulo 3)-Clar-sextet" congruence rules in three-dimensional molecules and macromolecules formed by folding graphene sheets, and their different electrical conductivities (metallic or semiconducting).

Going back a few decades, ever since the Kekulé centennial and its celebration in Belgium, Germany, England, and USA, it is evident that theoretical calculations continued to evolve gradually from the simple approaches of Erich Hückel and Eric Clar to resonance-VB or MO theories, semiempirical, and *ab initio* calculations. Still, there is a disagreement between local aromaticity indices determined on one hand by chemical reactivity, energetic or geometric

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(bond length) criteria and on the other hand by NMR or nucleus-independent chemical shift calculations: apparently aromaticity is a multidimensional phenomenon.

In the present issue, Milan Randić describes a new approach to aromaticity as a collection of local features, in a paper triggered by simple computations of ring currents based on conjugated circuits. Then Douglas J. Klein and the present author are reviewing the contributions concerning benzenoid hydrocarbons, their one-dimensional, two-dimensional and three-dimensional finite, semi-infinite, and infinite aggregates. The aromaticity of bipyramidal and sandwich complexes formed by *s*- and *d*-metals and the corresponding electron-count rules are discussed by T. N. Gribanova, R. M. Minyaev and V. I. Minkin. Fernandez and Frenking's article describes a method for estimating the aromaticity or antiaromaticity using a DFT approach for various structures including small rings and metallabenzenes. Fuji Zhang and his coworkers review graph-theoretical aspects of Clar's sextet theory and of Randić's conjugated circuit model. Finally, A. T. Balaban and K. P. C. Vollhardt survey known and anticipated features of helical phenylenes.

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