

IS AROMATICITY OUTMODED ?

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Abstract - A brief historical tabellar survey reveals two intensive research periods in aromaticity, closely following the two major theoretical breakthroughs : Kekule's formula, and Hückel's rule. The post-war upsurge of interest in the Hückel theory was triggered by Dewar's insight of the tropolone structure. The limitations of the Hückel method, made evident by the introduction of the Dewar resonance energy, led to pace slackening in the last decade and to severe criticisms towards the notion of aromaticity. In defense of this concept, the paper argues that a reasonable balance of generality makes the concept of aromaticity extremely useful qualitatively; however, for quantitative determinations, narrower, more precisely defined, areas of aromaticity are to be specified.

From the author's research areas, theoretical concepts are presented (graph-theoretical approach to predicting all possible monocyclic aromatic systems with heteroatoms, to enumerating cata-condensed polycyclic systems and valence isomers of annulenes) as well as experimental contributions (synthesis and reactions of pyrylium and boroxaropyrylium salts, measurements of relative ring currents using N-aryl-2,4,6-trimethylpyrylium salts, lack of aromaticity in 1,3-diketone chelates). By means of graph theory new and better definitions and nomenclature may be obtained for some categories like cata/peri/corona-condensation, mesoionic compounds, valence isomers.

The review closes with a few challenging problems in aromatic chemistry, physical chemistry and biochemistry.

1. INTRODUCTION

Tables 1 and 2 provide a convenient historical introduction by displaying a few landmarks in the pre-and post Hückel ideas on aromaticity. A personal bias in selecting the data as well as errors and omissions are inevitable. Apologies are offered for the latter and for omitting (owing to evident space limitations) the extensive lists of references to Tables 1 and 2; instead a few books are listed containing most of the literature data (refs. 1-13). Since the post-period only encompasses 30 years, no years are displayed in Table 2, but most advances occurred in the 1945-1965 period.

Table 1
Pre-Hückel facts and ideas on aromaticity

Year	Author(s)	R e s u l t s
1608	B. de Bignière	Obtains benzoic acid
1776	C. W. Scheele	Discovers uric acid, rediscovers benzoic acid
1825	M. Faraday	Discovers benzene in whale oil gas condensate
1832	J. Liebig, F. Wöhler	Recognize benzoyl radical ; benzaldehyde
1832	J. W. Döbereiner	Obtains furfural from vegetal products
1834	E. A. Mitscherlich	Decarboxylates benzoic acid to C_6H_6 ; analysis
1845	A. W. Hofmann, C. B. Mansfield	Discover benzene in coal tar
1849	Anderson	Discovers pyridine
1858	P. Griess	Discovers diazonium salts
1865	F. A. Kekule	Proposes benzene formula and term "aromatic"
1866	E. Erlenmeyer	Defines aromaticity by reactivity ; naphthalene
1867	J. Dewar	Proposes Dewar benzene formula
1868	C. Graebe	Proves Erlenmeyer's naphthalene formula
1869	W. Körner, J. Dewar	Propose pyridine formula
1869	A. Ladenburg	Objects Kekule formula, advocates prismane
1872	F. A. Kekule	Oscillating bond hypothesis
1881-5	E. Fischer	Synthesises purine bases (Nobel Prize 1902)
1882-8	A. Claus, H. E. Armstrong, A. Baeyer	Centric benzene formula
1883	V. Meyer	Discovers thiophene in coal tar benzene
1891	G. Merling	Obtains tropylium but fails to recognize it
1892	I. L. Kondakov	Fails to look for water-soluble pyrylium salts
1891-3	E. Bamberger	Centric formulas for 5-membered heterocycles
1894	V. Meyer	Discovers diaryliodonium salts
1898-9	J. Thiele	Partial valence hypothesis
1899	J. W. Collie, T. Tickle	Obtain crystalline pyrone methiodides
1901	J. Thiele	Observes acidity of C_5H_6 and lack of it for C_7H_8
1905	A. Baeyer	Nobel Prize
1911	R. Willstätter	Obtains C_8H_8 and disproves Thiele's hypothesis
1911-5	A. Baeyer	Prepares alkyl-substituted pyrylium salts
1915	R. Willstätter	Nobel Prize ; anthocyanine structures
1925	R. Robinson	Advocates aromatic sextet of electrons
1926	A. Stock	Prepares borazine
1928	O. Diels, K. Alder	Discover the diene reaction (Nobel Prize, 1950)
1925-9	A. Lapworth, C. K. Ingold	Mechanism of aromatic electrophilic substitutions
1930	H. Fischer	Nobel Prize for hemin and chlorophyll structures
1931-8	E. Hückel	HMO Theory, Hückel Rule for aromaticity
1931-9	R. Robinson	Anthocyanine syntheses (Nobel Prize, 1947)
1938	M. G. Evans	Proposes aromatic transition state in diene react.
1943	A. C. Byrns	Fails to recognize pyrylium chlorozincates

Author(s)	R e s u l t s
J. i. Aihara	Applies GT for calculating DRE
A. J. Ashe	As-, Sb-, Bi-heteroatoms in six-membered heterocycles
A. T. Balaban	Theor.:GT for heterocycles, polycyclics, valence-isomers Exp.: Pyrylium, pyridinium and boroxaropyrylium salts
E. D. Bergmann	Fulvenes
V. Boekelheide	[14] Annulenes with substituents in π -electron cavity
R. Breslow	Cyclopropenium salts
M. Calvin	Renews Robinson's hypothesis on arom. of metal chelates
E. Clar	Condensed benzenoid hydrocarbons ; local sextets
C. A. Coulson	MO Theories for aromaticity
D. P. Craig	Symmetry of ground state wave function as CFA
D. J. Cram	Cyclophanes, "bent and battered benzene rings"
F.H.C.Crick, J.D.Watson	Nobel Prize for double helix structure of DNA, based on pairing of complementary aromatic bases
R. Criegee	Tetramethylcyclobutadiene and its dimers
R.Daudel, B.Pullmann	MO Theories for carcinogenicity of polycyclic aromatic hydrocarbons
H. J. Dauben Jr.	Diamagnetic susceptibility exaltation as CFA
M. J. S. Dewar	Theor.: Tropolone structure ; DRE using new standard Exp.: Boroxaro- and borazaro-analogues of benzenoids
W. E. Doering	Tropylium salts ; predicts bullvalene
K. Dimroth	Pyrylium salts ; phosphorins
J. A. Elvidge, L. M. Jackman	Ring currents as CFA
E. O. Fischer, G.Wilkinson	Nobel Prize for metallocenes
M. J. Goldstein, R. Hoffmann	Spiroconjugation
I. Gutman GT	GT and topological properties of aromatics
K. Hafner	Azulene and pentalene derivatives
E. Heilbronner, G. Binsch	First and second-order bond fixation as CFA
B.A.Hess,L.J.Schaad	Obtain DRE on the basis of simple HMO and GT methods
R. Huisgen	New mesoionic compounds (münchnones), pentazoles
A. Julg	Bond distance equalization as CFA
C. Jutz	Borabenzene anion
A. R. Katritzky	Protonation of pyridones does not interfere with arom.
T. J. Katz	Dianions of cyclooctatetraene and other annulenes
J. Kruszewski, T.M.Krygowski	Harmonic oscillator index as CFA
J. F. Labarre	Faraday effects in aromatics ; strobilism as CFA
D. Lloyd	Meneidic character as CFA
H.C.Longuet-Higgins L. Salem	Alternating bond lengths calculated for large annulenes

Abbreviations : CFA = criterion for aromaticity ; DRE = Dewar resonance energy ; GT = graph theory . Table continues on next page

Table 2 (continued)

G. Maier	Tetrahedrane derivatives ; silabenzene
G. Märkl	Phosphorins
R. H. Martin	Large helices, their non-planarity and chirality
J. F. W. McOmie	Diphenylenes
V. I. Minkin	Fluctuating and static Meisenheimer complexes
J. I. Musher	Criticizes ring current as CFA
H. Musso	Measures ring currents, metal chelates are not aromatic
C.D.Nenitzescu,	Cyclobutadiene dimers ; first valence isomer of an
M. Avram	annulene, the Nenitzescu hydrocarbon (CH) ₁₀
T. Nozoe	Tropolones
G. A. Olah	Dications of (CH) ₄ , (CH) ₈ and other systems
W. D. Ollis	Mesoionic compounds : sydnones
P. L. Pauson	Ferrocene
R. Pettit	Homotropylium ; cyclobutadiene
J. R. Platt	Applies Hückel's Rule to periphery of polycyclics
O. E. Polansky	MO Methods for local sextets
M. Randić	GT Methods for local sextets
G. Schröder	Bullvalene ; large annulene ions
F. Sondheimer,	Large annulenes or dehydroannulenes and their ions
P. J. Garratt	
A. Streitwieser	Uranocene ; MO methods for aromatics
E. E. van Tamelen	Prepares Dewar-benzene and [10] annulene
N. Trinajstić	Topological resonance energies ; GT methods for arom.
I. Ugi	Pentazoles
E. Vogel	Bridged [10] annulene and larger ones, ions, ketones
M. E. Volpin	Equivalence of all seven tropylium atoms
G. W. Wheland	MO Studies of aromatic substitution intermediates
C.F.Wilcox,	Algebraic structure count of Kekule structures using
W.C.Herndon	GT methods
K.E.Wilzbach + L.Kaplan	: Benzvalene, photochemistry of benzene
S. Winstein	Homoaromaticity
R.B.Woodward + R.Hoffmann	: Their rules for aromatic transition states
H. Wynberg	Measurements of ring currents
R. Zahradnik	MO Calculations for non-alternant systems

It may be seen clearly that during the past 150 years the "temporal density" of discoveries and research in the field of aromaticity was far from uniform.

The two outbursts which may be noted followed closely the two theoretical breakthroughs, namely the Kekulé formula and the Hückel theory. Tables 1 and 2 will be discussed in more detail in the next section. Table 2 also displays the topics from the present author's research areas which will be discussed in a later section.

2. HISTORICAL BACKGROUND

After Faraday's discovery of benzene in 1825 in the condensate of an illuminating gas obtained from pyrolysis of whale oil, Mitscherlich obtained the same hydrocarbon by decarboxylating benzoic acid which had been known earlier, and established the benzene molecular formula as C₆H₆ in 1834. In 1845 A. W. Hofmann and C. B. Mansfield discovered benzene in coal tar, and proposed methods for isolating benzene from this source, though thiophene which accompanied benzene from coal tar was recognized by Victor Meyer only in 1883.

Immediately after 1865 when Kekulé proposed his famous formula for benzene, the first cyclic formula of a chemical substance, there followed a period of intensive research and development, both in advancing the limits of knowledge and in applying this knowledge for practical uses, mainly in the dyestuff industry.

Kekulé also introduced the words "aromatic" and "aromaticity" to describe structural characteristics of compounds related to benzene, i.e. the presence of cyclic conjugation in 6-membered rings. His treatise of organic chemistry is based on the dichotomy aromatic - aliphatic.

The objections raised by Ladenburg that one, not two, ortho-disubstituted isomers may be always isolated, were countered in 1872 by Kekulé through his oscillating bond hypothesis.

Erlenmeyer was the first proponent of a generalizing trend which was bound to continue afterwards, namely by proposing that the concept of aromaticity should be associated to similar reactivity rather than similar structure. This generalization which encompassed Erlenmeyer's naphthalene and Victor Meyer's thiophene, enabled Bamberger in 1891-3 to recognize the importance of the six free valencies by adapting to five-membered heterocycles the Armstrong-Baeyer centric formula, to which Claus, the proponent of an impossible diagonal formula, had also adhered.

A blind, yet fruitful, alley was Thiele's explanation (1899) of the apparent saturation of benzene through the "residual valency" hypothesis. In 1911 Willstätter, prompted by Thiele's ideas, prepared cyclooctatetraene and disproved thereby Thiele's hypothesis that all conjugated cyclopolyenes were aromatic; however, traces of Thiele's theory still linger in recent textbooks attributing mainly to steric strain the non-planarity of cyclooctatetraene and the instability of cyclobutadiene, instead of the principal factor, their anti-Hückel character ($4n \pi$ -electrons).

A clear filiation of ideas is traceable from (i) Armstrong-Baeyer's centric formula of benzene (1887), through (ii) Bamberger's recognition (1891-1893) that even five-membered heterocycles like thiophene or pyrrole could be written to display a hexacentric system through what we nowadays called an unshared electron pair, to (iii) Armit and Robinson's aromatic sextet of electrons (1925). However, it was Erik Hückel's merit to propose the first, crude, quantum-mechanical model for aromatic compounds and to obtain thereby the magic $4n+2 \pi$ -electron rule. Although its importance was not recognized immediately, Hückel's theoretical insight had opened the gates of discovery and applications in the dyestuff and pharmaceutical industry.

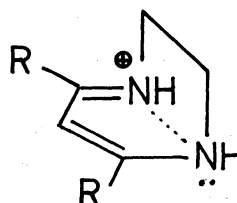
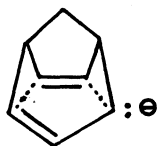
I consider that M. J. S. Dewar was instrumental in triggering the post-war revival of interest in aromaticity and in the Hückel theory both through his theoretical insight (elucidation of the tropolone structure in 1945 (ref. 14), restatement of Hückel's prediction that tropylium should be aromatic as was indeed proved later by Doering, and, last but not least, the formulation of a better standard than Hückel's for the conjugation energy in aromatics leading to the Dewar resonance energy (ref. 15)) as well as through experimental evidence for borazaro and boroxaroaromatics.

It is interesting that though earlier discoveries in organic chemistry were often serendipitous, the present-day state of art is such that unless one

knows what to look for, interesting products escape detection; such are the cases (mentioned in Table 1) of (i) tropylium bromide obtained earlier by Merling, and (ii) of pyrylium salts formed by Friedel Crafts diacylation of alkenes; the former product, when it was first obtained accidentally, had such unexpected properties (water solubility) that its structure could not be guessed; the latter salts escaped notice for a long time also because of the water solubility of the chloroaluminates; when zinc chloride was the Friedel-Crafts catalyst and crystalline pyrylium chlorozincates had been obtained, these were mistaken for $ZnCl_2$ - complexes of 1,3-diketones. A third case not mentioned in Table 1 is of pentazoles which had first been produced in 1893 by Noelting and Michel without being recognized; only the kinetic analysis of N_2 evolution induced Huisgen and Ugi to look for, and discover, pentazoles (ref. 16).

Following the upsurge of interest for novel types of aromaticity, exciting discoveries were made by Vogel for bridged 10-, 14- and 18- π -electron systems, by Boekelheide for 14- π -electron systems, by Sondheimer on large annulenes and dehydroannulenes, by Breslow for cyclopropenylium systems, by Katz for $(CH)_9^-$ and $(CH)_8^{2-}$, etc. The sydnones and münchnones are examples of mesoionic aromatic compounds (cf. the definition of mesoionic compounds in a subsequent section). The metallocenes obtained serendipitously were an exciting discovery (P. L. Pauson, R. B. Woodward, G. Wilkinson, E. O. Fischer, A. Streitwieser), so far the only one in post-war aromatic chemistry to be honoured with a Nobel prize. Table 2 also mentions Watson and Crick's insight of the double helix but aromaticity there, is a marginal, though important, aspect.

The Hückel rule operates not only in planar continuously conjugated systems, but also in homoaromatic systems where one or more out-of-plane CH_2 groups are intercalated. It should be noted that the name "homoaromatic" is sometimes misleading since one speaks of aromatic heterocycles as "heteroaromatics" and, by contrast, one would be tempted to associate aromaticity in rings consisting only of carbon atoms with "homoaromaticity". Moreover bishomoaromatic could mean either a system with two vicinal (cf. Lloyd's pseudoaromatic or mendeic compounds), or two unconnected CH_2 groups.



(hypothetical)

A notable trend is observed in Table 2 towards a third approach to the aromaticity problem, namely by means of physical properties such as induced ring current, Faraday effect, diamagnetic susceptibility exaltation, tendency towards bond equalization, first and second-order bond fixation, etc. All these properties have the advantage that they are easily measurable but unfortunately they seldom give consistent results among themselves. This contributed to the irritation among physical chemists and to their tendency of blaming it on the concept of aromaticity. Though understandable, this attitude is as

unexcusable as that of the irate mother who throws away bathtub, dirty water and her baby.

Though not mentioned explicitly in Table 2, a fourth type of approach to the aromaticity problem exists (in addition to that based on structure, reactivity, and physical properties): by combining chemical and physical measurements, aromaticity scales were proposed based on the ability of rings to act as transmitter of electronic effects, in conjugation with linear free energy relationships. Again, the scales were not consistent with the other ones. The final result is somewhat reminiscent of the tower of Babel; together with the disenchantment caused by the lack of exciting discoveries in the past ten years, this has led to severe criticisms against the notion and the term aromaticity.

3. CRITICISMS VOICED TOWARDS "AROMATICITY", A SUGGESTION AND AN ANALOGY

I should like to start by telling you a little story taking place in a mad-house.

A madman trails a boot tied with a string addressing the boot from time to time: '-Come on, you stubborn dog'. The physician arrives and to humour his patient says: '-A nice little dog you have here!' '-Are you crazy?', replies the madman, 'Don't you see it's a boot?' '-You're recovering finely', the physician says, 'to-morrow I'll allow you to return home'. After the physician is out of sight, the madman winks to the boot and says: '-You see, dog, I've told you we would fool him, haven't I ?'.

Sometimes the discussions about aromaticity take place in the same mood as above, replacing "dog" by "aromatic". The semantic elasticity of the notions "aromatic" and "aromaticity" has worried many chemists. In my talk I would like to give a personal view on this topic.

Critical views on the present use of the term "aromaticity" were expressed by several chemists during the last ten years:

Binsch in his paper "Aromaticity - An Exercise in Chemical Futility" (ref. 17) wrote: 'It is indeed suspicious how often magic rules had and have to serve as an alibi for creating an aura of intellectual respectability for chemical research which is on the verge of turning stale... For us in pure chemistry the embarrassing question arises with alarming frequency whether we are not simply contributing another tombstone to an already enormous data cemetery.'

Heilbronner in the discussions at the "Aromaticity, Pseudo-Aromaticity and Anti-Aromaticity" Symposium in Jerusalem stated: 'The amount of confusion caused by the term "aromaticity" in the student's mind is not compensated for by gain in the understanding of the chemistry and physics of the molecules so classified... Nobody can claim that the vague concept of "aromaticity" must be

introduced at any stage to make quantum chemical theories work... "Aromaticity", if to be used at all, should be a purely structural concept. "Aromaticity" cannot be measured, it is not a physical quantity, as shown by the well-known but elusive "resonance energy" which is a defined quantity and not an observed one. ' (ref. 18).

Lloyd in his books and in the lecture declared: 'The term aromatic was interpreted at different times in terms of molecular structure, of reactivity and of electronic structure, and, in consequence, there has been much confusion over its precise meaning and definition. We suggest that because of this confusion, it would be better if the use of the term "aromatic" were discontinued, save perhaps with its general and original connotation of "perfumed", and that it should pass with other technical terms which have outlived their precision and usefulness into the realm of the historian of chemistry.' (ref. 19). He also proposed to use only such terms as benzenoid for structural features, Hückel or anti-Hückel systems for ground state properties, or mendeic (regenerative) for chemical reactivity.

Labarre, at the same symposium and in his "Critique of notion of aromaticity" stated: 'The considerable number of prefixes joined to the term "aromaticity" (non-, anti-, quasi-, pseudo-, homo-, etc.) indicates sufficiently that this term is outdated. The solution to this problem is not as Coulson has remarked (private communication) to look for a new word to replace aromaticity. It is preferable to propose several (as meaningful as possible) new words, so that each one of them refers to one of the multiple chemical or physical properties that were intended to be expressed by the term "aromaticity". We have considered introducing the concept of potential strobilism to describe the phenomenon measured by the Faraday effect and by NMR in the case of cyclic molecules that are the seat of a pi-electronic delocalization, that is, of a ring current.' (refs. 20, 21).

I wish to stand up and testify in favour of retaining this term whose usefulness resides namely in its generality; it is because of this generality that it cannot be conveniently and simply measured, just as other useful and widely-used chemical concepts such as unsaturation, stability, orbital or hybridization. My proposal is to retain the notion of aromaticity and to allow its use as a general qualitative structural feature. Whenever we try to measure the aromaticity we should define strictly which particular aspect of aromaticity is being measured, be it strobilism, relative ring current, ground state-energy or bond lengths. In other words, if the term "aromaticity" is to survive, then it has most chances to do so for its generality rather than for the particular aspects which can be clearly defined and are apt to be measured quantitatively. These particular aspects could and should have separate names in accordance with Lloyd's and Labarre's ideas. The aromatic character for a given class of compounds encompasses to a higher or lesser degree each of these particular aspects.

Tradition is strong, yet science knows many obsolete terms which are no longer in use nowadays. It does not seem probable that "aromaticity" is soon going to

be one of them if one looks at headings of surveys such as Annual Reports, Chem. Abstr., at titles of papers, at contents of textbooks. So instead of trying to turn our thumbs down on a frequently used term, we should better make the best use of it.

The prefixed aromaticities thus could be replaced by other names: non- or anti-aromatic by non- or anti-Hückel, respectively; quasi-aromatic by mendeidic; pseudoaromatic by non-benzenoid aromatic. Homo, bishomo and trishomo-aromatic seem difficult to replace, but through-space conjugation could occasionally be preferred. However, other "prefixed aromaticities" cannot be replaced by other words, so they are bound to survive as long as "aromaticity" will survive: heteroaromatics, perfluoroaromatics, etc.

On the other hand, one can recently observe the tendency to extend the concept of aromaticity to polyhedral (deltahedral) structures such as the icosahedral carboranes (ref. 22). Both sophisticated theoretical treatments and simple graph-theoretical approaches reveal in such compounds the presence of a closed electronic shell, i.e. absence of non-bonding MO's, all bonding MO's doubly occupied and all anti-bonding MO's empty. An analogous graph-theoretical treatment also explains the pyramidal structures of $(\text{CH})_5^+$ and $(\text{CH})_6^{2+}$ (ref. 23). The temptation to call such tridimensional structures aromatic is motivated by (i) the exceptional stability, (ii) the tendency to retain the type and (iii) the presence of closed electronic shells which explains the preceding features.

Interestingly, the same three features are present in triple-bond compounds such as the homodiatom molecule N_2 , ions C_2^{2-} , O_2^{2+} (refs. 24, 25), and heteroatomic congeners (CO , NO^+ etc.). One could argue that such systems possess "unidimensional aromaticity"; one would be gradually falling into the previously mentioned "dog" trap because it would be difficult to stop. Undoubtedly there are many other systems with closed electronic shells, both molecules (ethylene, the polyenes) or atoms (the rare gases) and it would be preposterous to call these aromatic.

Therefore despite the temptation to use the term aromaticity in its maximal generality, caution must be exercised and the best suggestion is to reserve the term aromaticity for the bidimensional case with its ring-current counterpart. Indeed, the drawback of the present situation is that definitions of aromaticity cannot be converted into measurable data, and that these definitions do not lead to sharp contours but to blurred, fuzzy limits of the image. On the other hand, it is convenient to have the means of classification provided by the notion of aromaticity even though marginal cases are imprecise (after all if mathematicians are working with fuzzy functions, why chemists could not?). This classification is useful for teaching purposes, for titles of books and of symposia like that organized at Sheffield, Jerusalem or the present one.

The best analogy I can find is with the notion of organic chemistry. There is no fully satisfactory and generally accepted definition of organic chemistry delineating sharply all borderline cases, yet we have learnt to live with this

situation or, if you like, with this necessary evil. Then, why not try and do the same with aromaticity? The necessity arises from the sheer numbers of compounds: from the four odd million of known compounds, more than nine tenths are (at least partly) organic, and from the latter, three quarters are aromatic.

By implication and contrast discussions on aromatics also include frequently antiaromatics. It would be useful to have a general term describing cyclic conjugation, i.e. the logical union between aromatic, anti-aromatic and non-aromatic systems. Such a term may be "strobilic" as proposed by Labarre.

4. CONTRIBUTIONS TO THE PROBLEM OF AROMATICITY

I would like now to present or to reiterate some contributions of my coworkers and myself to the problem of aromaticity, discussing separately theoretical and experimental data.

4.1. Theoretical Data

4.1.1. Systematization of heterocyclic aromatics

In 1959 I published in Roumanian (ref. 26) an attempt towards a systematic graph-theoretical combinatorial approach to monocyclic aromatic systems. According to Pauli's exclusion principle, the non-hybridized p_z orbital of an sp^2 -hybridized atom belonging to an aromatic ring can contain 0, 1, or 2 π -electrons which contribute to the delocalized aromatic electronic cloud. Accordingly, we can have three types of ring atoms, namely Z, \dot{Y} , and \ddot{X} , respectively, forming the aromatic compound $X_x Y_y Z_z$. Table 3 presents these atom types, indicating by dots the electrons in the p_z orbital and by dashes shared (a-type atoms), or unshared electrons (b-type atoms). Only First-Row atoms, with at most one \pm electrical charge are included,

Type	3b	4a	4b	5a	5b	6a
\ddot{X}			$\begin{array}{c} \ddot{C}- \\ \\ R \end{array} \ominus$	$\begin{array}{c} \ddot{N}- \\ \\ R \end{array} \ominus$	$\begin{array}{c} \ddot{N}- \\ \\ R \end{array}$	$\begin{array}{c} \ddot{O}- \\ \\ R \end{array}$
			- 100	-77	- 26	- 3
\dot{Y}	$\begin{array}{c} \dot{B}- \\ \\ R \end{array} \ominus$	$\begin{array}{c} \dot{C}- \\ \\ R \end{array} \ominus$	$\begin{array}{c} \dot{C}- \\ \\ R \end{array}$	$\begin{array}{c} \dot{N}- \\ \\ R \end{array}$	$\begin{array}{c} \dot{N}- \\ \\ R \end{array} \oplus$	$\begin{array}{c} \dot{O}- \\ \\ R \end{array} \oplus$
	- 72	- 50	0	+ 23	+ 74	+ 97
Z	$\begin{array}{c} -B- \\ \\ R \end{array}$	$\begin{array}{c} -C- \\ \\ R \end{array}$	$\begin{array}{c} -C- \\ \\ R \end{array} \oplus$	$\begin{array}{c} -N- \\ \\ R \end{array} \oplus$		
	+ 28	+ 50	+ 100	+ 123		

Table 3

First-Row atom types which may form aromatic rings, and associated aromatic electronegativity constants k_H (assuming for b-type atoms that $R=H$).

If the ring is m -membered and if the Hückel rule is assumed to be valid (i.e. for monocyclic systems formed from First-Row atoms) then we have a system of

two linear equations with three unknowns, x , y , z , i.e. the numbers of \ddot{X} -, \dot{Y} - and Z - type atoms, respectively:

$$\begin{aligned}x + y + z &= m \\2x + y &= 4n + 2\end{aligned}$$

For given integer values of $m \geq 3$ and $n \geq 0$ we may find all possible solutions of the above two equations. The algebraic solutions then can be arranged in a ring by combinatorial, or graph-theoretical techniques (in the latter case Polya's theorem was employed). As a result, all theoretically possible aromatic systems fulfilling the initial conditions can be found. Thus a structural approach to the aromaticity of carbocyclics and heterocyclics was proposed, in which "aromatic" was the answer to the question "how?", and not "how much?". However, not all of them are able of existence because of electronegativity and other factors. A formula for a semiempirical "aromatic electronegativity constant", k , i.e. an increment or decrement relative to a carbon atom in benzene was proposed (ref. 27) taking as standard values for tricoordinated carbon atoms $k[X4b] = -100$ for the cyclopentadienide anion, $k[Y4b] = 0$ for benzene, and $k[Z4b] = +100$ for the tropylium cation.

$$k_H = 100(0.478Z^*/r - 1.01 - n_\pi), \quad \text{with } n_\pi = 0, 1 \text{ or } 2 \text{ for } Z, Y$$

or X -type atoms; where:

$$Z^* = Z_n - 0.85n_K - 0.525n_{L,n} - 0.175n_{L,b} \quad \text{with } Z_n = \text{atomic number, } r = \text{covalent radius (}\text{\AA}\text{), } n_K, n_{L,n}, n_{L,b} \text{ are the numbers of electrons in the K-shell, nonbonding and bonding L-electrons.}$$

For any carbocyclic or heterocyclic ring, the overall "aromaticity constant" K is obtained additively:

$$K = \sum_i k_i \quad \text{where index } i \text{ extends over all ring atoms;}$$

all known systems which have so far been isolated or identified have this "aromaticity constant" within the range -200 to $+200$.

For atoms bonded to other groups R than hydrogen (cf. Table 3), the "aromatic electronegativity" increment can be calculated using the Hammett σ_{p-R} value:

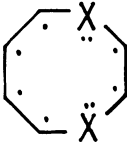
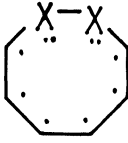
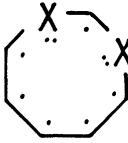
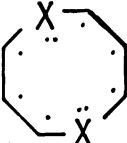
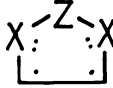
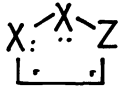
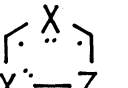
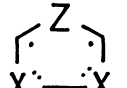
$$k_R = k_H + 20 \sigma_{p-R}$$

The above approach was able to afford a simple definition of mesoionic aromatics as systems possessing odd-numbered strings of Y -type atoms between X - or Z -type atoms. So far only mesoionic aromatics with five-membered rings are known.

Further extensions of the above approach are possible: (i) For polycyclic systems like naphthalene, any b -type atom (ignoring the R group) can function as bridgehead atom. However for non-alternant systems additional electronegativity factors must be taken into account if Z -type atoms are present in positions of low electronic density or X -type atoms in positions of high electronic density.

(ii) The combinatorial problem was initially solved without adjacency restrictions between various atom types. It is clear from the free electron model, however, that strings of several X-type, or of several Z-type atoms, destabilize the molecule, while alternation $-X-Z-X-Z-$ is much more favourable. Thus borazene is known, but none of its isomers with B-B or N-N bonds are known. This is reflected in the HMO energy per π -electron in a few selected examples presented in the first part of Table 4 (ref. 28).

Table 4. Binding energy per π -electron calculated in β units by the HMO method

Non-mesoionic		Mesoionic	
			
8.522	8.484 (adjacent X's)	8.466	8.456
			
4.456	4.340 (adjacent X's)	4.302	4.172 (adjacent X's)

In the initial enumeration of all possible monocyclic aromatic systems, we also considered combinatorial arrangements avoiding adjacent X-type or Z-type atoms. The complete mathematical solution to this combinatorial problem was provided recently (ref.28a). Now one should find a numerical increment for a Z-Z bond or decrement for an X-X bond in order to take into account the lower stability of compounds with adjacent X- or adjacent Z-type atoms.

(iii) As mentioned before, so far no mesoionic compound is known unless it has a five-membered ring. From five-membered aromatic heterocyclic compounds, the mesoionic ones have the lowest stability as reflected in the second part of Table 4 (ref. 28). Hence one should find a numerical value to be taken into account in the overall "aromaticity constant" K for a pair of odd strings of Y-type atoms.

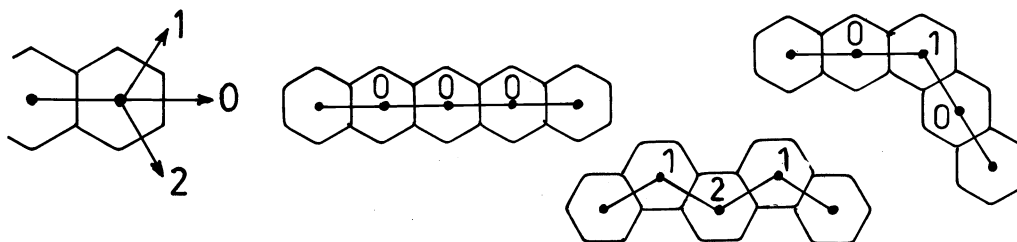
In concluding this paragraph, it should be emphasized that the overall "aromaticity constant" K is merely a semiempirical measure of the overall electronegativity of the whole ring and it serves as a rough guide whether under normal conditions an imagined system is, or is not, able to exist. Aromaticity being a structural property is not measured by this "aromaticity constant".

However, this aromaticity constant is a fairly reliable measure of the " π -deficient" or the " π -excessive character". There exists some confusion in the literature caused by this dichotomy exemplified by pyridine (π -deficient) and pyrrole (π -excessive) so that some authors (ref. 9) consider that there are correspondingly two types of aromatic heterocycles. Actually there exist three types: starting from benzene, one could add a Z-type atom, one can replace a CH group by another Y-type atom, or one can replace a CH=CH group by an X-type atom.

Before leaving this topic I would like to remark that pairwise combination of Y-type atoms in Table 1 affords all possible triple-bond compounds; not all combinations are yet known especially those involving boron [Y3b] where the large electronegativity differences in combinations with [Y5b] and [Y6a] tend to decrease the bond order. I had predicted in 1961 on this basis that O_2^{2+} (isoelectronic with dinitrogen), would be a bonded molecule, and had indicated a means of identifying it (ref. 24) by mass spectrometry of $[^{16}O \equiv ^{17}O]^{2+}$; this prediction was verified (ref. 25). The Y-type atoms also lie at the basis of a systematic classification and discussion of persistent free radicals, especially the nitrogen free radicals derived from [Y5b] by combination with neutral or anionic groups like O^- .

4.1.2. Graph-theoretical considerations on polycyclic aromatics

In the field of polycyclic aromatics, the application of graph theory allowed new definitions, enumerations, systematizations, nomenclature, and correlations (refs. 29, 30). The dualist graph of a condensed polycyclic aromatic system has as its vertices the centres of each ring; two vertices are adjacent (i.e. are joined by an edge) whenever the corresponding rings are condensed, i.e. ortho-fused. Unlike dual graphs known in graph theory, in dualist graphs angles are fixed and there is no vertex corresponding to the outer region of the polycyclic system. Dualist graphs afford a simple new definition and classification of polycyclic aromatics (ref. 31): whenever the dualist graph is acyclic, the system is cata-condensed; when the dualist graph has three-membered rings, the system is peri-condensed, and when the dualist graph has larger rings, the system is corona-condensed. For benzenoid polycyclic systems, according to the new definition, all cata-condensed systems with the same number of benzenoid rings are isomeric. A simple formula for the enumeration of non-branched cata-condensed systems was found (ref. 31) and a more complicated one for branched systems (ref. 32). Taking into account that annulation can take place in certain directions only (at the endpoint of a benzenoid system in three directions), a simple codification can be devised, which may be used for nomenclature purposes (refs. 32, 33): a straight annulation is deno-



ted by 0, a left-turn by 1, and a right-turn by 2. Thus pentacene has code 000, picene 121 and pentaphene 010 because we adopt the convention that from all possible codes compatible with the above rules the lowest number is selected. This coding system was extended to branched cata-condensed benzenoid systems, using brackets for indicating branching (ref. 33), and to non-benzenoid systems (ref. 34). Interestingly, the number of zeroes in the code, and the number of benzenoid rings in cata-condensed systems, afford a good linear two-parametric correlation with the resonance energy and other properties (ref. 35) rationalizing graph-theoretically a more complicated type of correlation proposed earlier by Sahini (ref. 36).

However, peri-condensed systems are much more complicated and so far their enumeration even for benzenoid systems, was only possible using computer algorithms. A new approach, in collaboration with Dr. Bonchev, seems promising in this area, based on the generalized concept of topological centre of the dualist graph (ref. 37). Before closing this section, I should mention that dualist graphs may be imagined not only for condensed benzenoid aromatics which are portions of the planar graphite lattice, but also for portions of the tridimensional diamond lattice. The latter dualist graphs which may represent carbon skeletons of staggered alkane or cycloalkane rotamers, may be used for definitions, enumerations, codifications and nomenclature of diamondoid hydrocarbons such as the polymantanes (ref. 38).

4.1.3. Aromatic transition states

In reactions with cyclic six-membered transition states which are allowed according to the Woodward-Hoffmann rules, a different kind of graphs may be used for a complete analysis of all possible cases, based on bonds which are common to the initial and final states (ref. 39). This approach was subsequently developed by Hendrickson (ref. 40) and by Hass and Plath (ref. 41).

4.2. Experimental Data

4.2.1. Pyrylium salts

Pyrylium salts are the six-membered aromatic heterocycles with the highest possible perturbation caused by one heteroatom (ref. 42). Their stability relative to oxonium salts and their structure (confirmed by X-ray diffraction) leaves no doubt that they are aromatic. Having discovered a simple synthesis of pyrylium salts by diacylation of alkenes (ref. 43), we embarked on a thorough study of their physical and chemical properties. All spectral data: electronic (ref. 44), vibrational (ref. 45), $^1\text{H-NMR}$ (ref. 46), $^{13}\text{C-NMR}$ (ref. 47) and half-wave reduction potentials (ref. 48) indicate close similarity to the corresponding properties of benzene and the related heterocycles pyridine or pyridinium salts. However, the reactivity of pyrylium salts is quite different from the normal aromatic reactivity: pyrylium salts give no electrophilic substitutions; their nucleophilic additions which occur most easily in α are accompanied by ring opening (with possible reclosure to other 5-, 6-, or 7-membered heterocycles). While this is understandable owing to the high electronegativity of the oxygen heteroatom, the study of pyrylium salts is

another proof that aromaticity cannot be connected with tendency towards electrophilic substitution, or even towards retention of type (meneidic character).

4.2.2. Measurement of ring currents

As mentioned before, I am in favour of retaining the term "aromatic" in its present qualitative general usage indicating cyclic delocalization in a quasi-planar conjugated system.

For quantitative determinations, we can always measure only certain facets or manifestations of the aromatic character so that it should always be clearly stated that we establish scales of electrophilic reactivity or a diamagnetic susceptibility exaltation, etc., and not of aromaticity. The ready conversion of 2,4,6-trimethylpyrylium salts into pyridinium salts on treatment with primary amines RNH_2 affords a simple means of measuring relative ring currents RRC in the group R by measuring the $^1\text{HNMR}$ chemical shifts of α - and β -methyl groups. Whereas in 2,4,6-trimethylpyrylium or in 2,4,6-trimethyl-N-alkylpyridinium salts the α -methyl groups appear at lower field than the β -methyl, in 2,4,6-trimethyl-N-arylpyridinium salts the reverse is true owing to the ring current in the N-aryl group. The relative ring current is measurable with the formula:

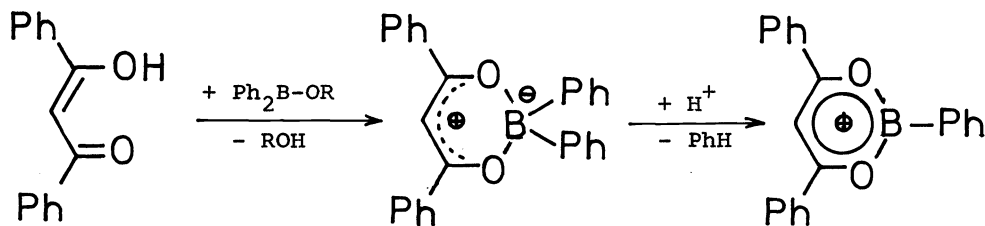
$$\text{RRC} = 200 \left[\delta(\text{Me}_\beta) - \delta(\text{Me}_\alpha) + 0.25 \right] - 71.7x / (1 + 2.26x)$$

where x is the number of ortho-standing groups. The value of RRC for phenyl is taken as 100 by this formula (ref. 49).

This method is simpler synthetically than similar approaches proposed by Musso and coworkers (who employed mesityl groups instead of 2,4,6-trimethylpyridinium) or by de Jongh and Wynberg (who employed spiranic ketones), cf. refs. 50 and 51, respectively.

4.2.3. Boroxaropyrylium salts and boron chelates

Table 3 reveals that boron is potentially able to afford a host of aromatic rings, from which very few have so far been obtained experimentally. Protodeboronation of the chelates formed from dibenzoylmethane with diphenylborinic esters affords 2,4,6-triphenyl-1,3,2-dioxaborinium salts, or in Dewar's terminology, boroxaropyrylium salts (ref. 52,53).



$^1\text{H-NMR}$ studies of boron chelates similar to the preceding ones (ref. 54) helped to rule out Robinson's and Calvin's hypothesis (ref. 55) that metal chelates with 1,3-diketones might possess aromatic character, which had also been invoked in compounds possessing silicon instead of a metallic atom. In the boron chelates, which possess similar NMR spectra, no aromaticity can be imagined because the boron atom has sp^3 hybridization. On the contrary, in boroxaropyrylium salts, despite their high reactivity and ease of decomposition, there is aromatic character.

5. FUTURE PROSPECTS AND CHALLENGES

It is probable that some of the criticisms levelled at the concept of aromaticity are due to the slower pace of spectacular developments in this field during the past decade. Once it was recognized that resonance energies calculated by the simple HMO method do not reflect intrinsic stabilities, and that Dewar resonance energies (or some modified form of these energies) must be used instead, it became clear why a host of interesting molecules (cyclobutadiene, pentalene, octalene, etc.) were out of reach of the normal chemist who wishes to manipulate stable compounds; that some of these molecules, or substituted derivatives thereof, have been nevertheless prepared, is even more commendable.

I believe, however, that aromaticity still poses interesting and challenging problems both to the theoretical and to experimental chemists, and I would like to enumerate some of these problems.

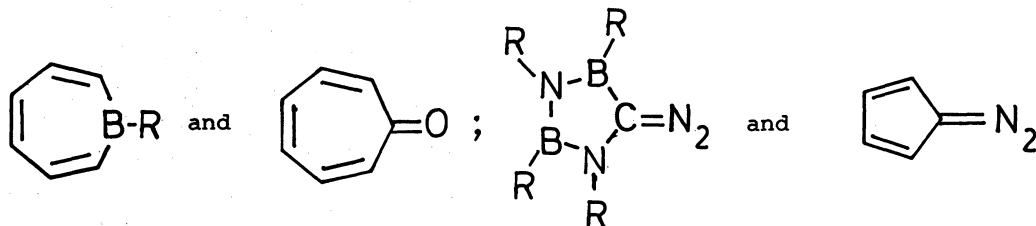
5.1 Chemical problems

5.1.1. Borepine

Since it was shown that tropone has little or no aromatic character it would be interesting to prepare and examine its heteroatom analogue, borepine (boracycloheptatriene), which is still unknown; only benzoderivatives have so far been prepared.

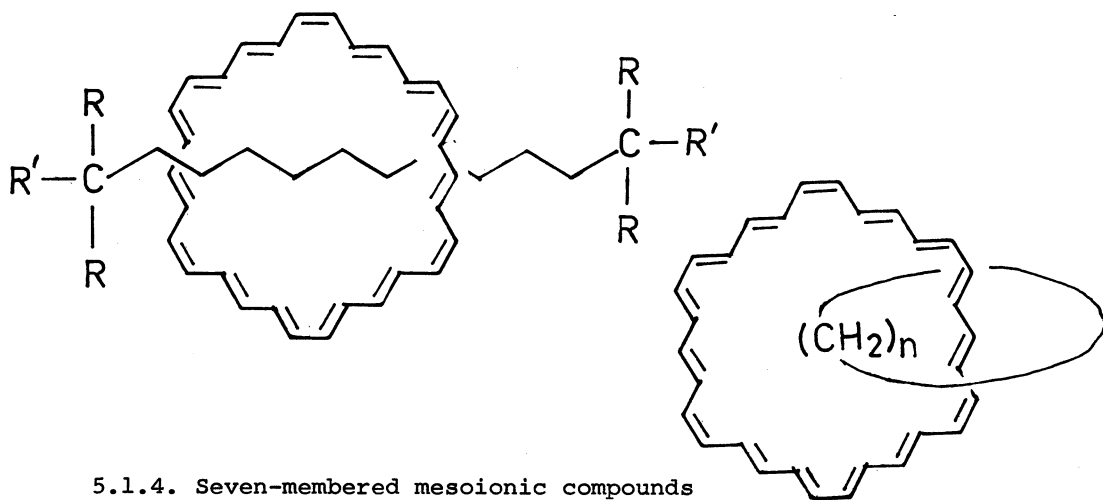
5.1.2. Borazaro- and boroxaro-aromatics; polyaza-aromatics

In line with the previous challenge, many borazaro- or boroxaro-aromatics are interesting, for instance those related to diazocyclopentadiene, cf. formulas below relating unknown compounds on the left-hand side to known aromatics on the right-hand side. The tetra-aza-diazocyclopentadiene with a tetrazole ring, and molecular formula CN_6 , would be an almost inorganic compound, and would deserve together with pentazole Huisgen's denomination as a "honorary organic compound".



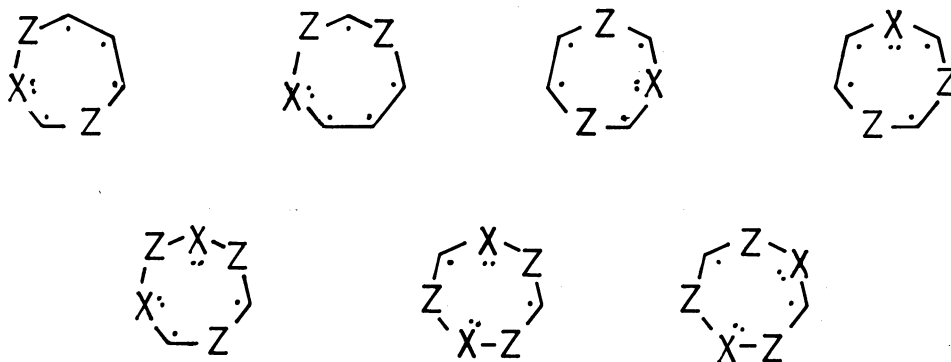
5.1.3. Aromatic catenanes and rotaxanes

So far the only catenanes and rotaxanes which have been prepared, are not aromatic. It would be extremely interesting to prepare and study the NMR spectra (especially at variable temperatures) of the analogues derived from higher annulene rings.



5.1.4. Seven-membered mesoionic compounds

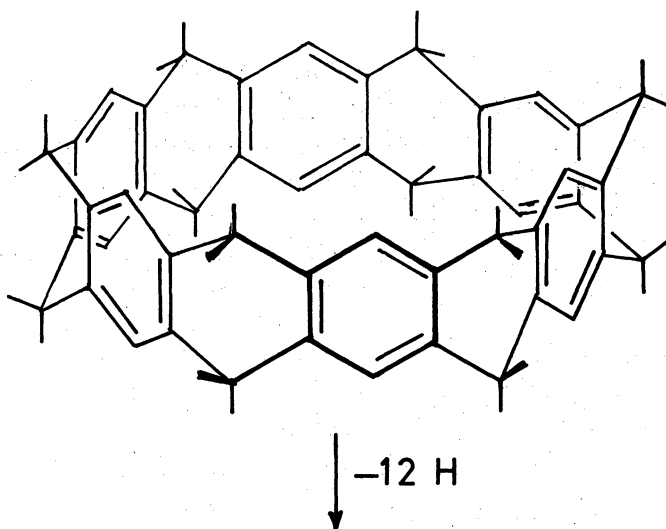
So far the only known mesoionic compounds have five-membered rings. Attractive structures may be imagined with seven-membered rings, devoid of Z-Z or of X-X adjacencies which would lower the stability.



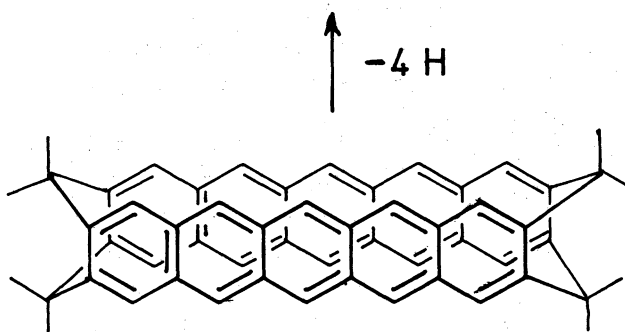
5.1.5 Cycloacenes and their Möbius counterparts

Since the interesting work of Cram and of Vögtle with cyclophanes, or that of Martin with helicenes, has shown that deviation from planarity does not depress markedly the stability of benzenoid rings, it would be interesting to calculate, and then attempt to synthesize, "cycloacenes". Taking into account the dihedral angle in 9,10-dihydroanthracene, a hexadeca-hydro-cyclohexadecaacene should be strain-free and stable. With a smaller number of rings, as in the following illustration, compounds would be strained. Alternatively, very strained acenes with parallel orientation and bridging atoms may be imagined, as in the following illustration. By dehydrogenation, the

highly strained "cycloacenes" should be obtained. It would be interesting to calculate the strain energy in such $[n]$ -cycloacenes as a function of n .

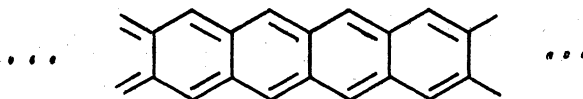


[12] CYCLOACENE

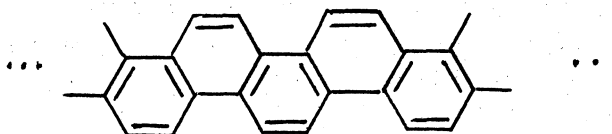


Molecules or metal atoms inside the cavity of such cycloacenes would perceive interesting steric and magnetic effects. It is also conceivable that a Möbius-type molecule could be formed analogously from longer acenes.

It is well-known that acenes are less stable than isomeric condensed hydrocarbons which do not have a linear, but a ziz-zag kind of condensation.



An acene is less stable than



Therefore the preceding problem could be reformulated in terms of cyclic or "tubular" arrangements of such condensed systems in place of acenes.

5.1.6. Other problems

The problem of taking numerically into account the influence of adjacency for two or more X-type or Z-type atoms, or the influence of mesoionic structures, was mentioned earlier. Another problem would be to calculate the size of a stable large-membered cyclic polyacetylene, which would be a truly elemental carbon because unlike diamond, graphite, or linear carbyne, it would have no end-groups. Of course, in larger annulenes the resonance energy per -electron decreases so that the difference between Hückel and anti-Hückel gradually disappears with increasing ring-size ; the problem is to calculate the optimum compromise between this tendency and the strain in cyclopolyyne.

5.2. Biochemical and physical problems

5.2.1. It is fairly certain that natural selection has not picked at random the two purinic and three pyrimidinic bases which lie at the basis of DNA and RNA, forming the genetic fundamentals of life. The common features of the metal porphyrins with Mg, Fe and Co atoms also indicate selective advantages of such aromatic molecules. Picket-fence porphyrins and other cleverly designed molecules can help unravel the role of these compounds, and perhaps lead to better ways of solar energy utilization. Since fluorouracil is known to be a good anticancer agent, variations on the aromaticity theme of the five bases A, C, G, T, U might produce other remedies for cancer.

5.2.2. So far, physical effects associated with aromaticity have been studied mainly by spectroscopic, magnetic, or electrochemical methods, by X-ray diffraction and electron impact. With the advent of (polarized) proton, neutron, electron, and molecular beams, it should be possible to study electromagnetic inductive and mechanical effects using these beams as linear conductors, and aromatic rings oriented magnetically or in single crystals as circular currents.

5.2.3. Low-dimensional (semi)-conducting materials such as the charge-transfer complex of TCNQ with TTF are now intensely studied. Structural variation of the two components will possibly lead to organic conductors or superconductors, in which aromaticity is involved.

CONCLUSION

Far from being dangerous, antipedagogical and non-scientific, the notion of aromaticity will continue to serve a useful purpose, because I think that it reflects a real phenomenon, associated with the presence of an odd number of electron pairs interacting in an approximately planar ring with continuous conjugation. The structural, chemical and physical manifestations of this phenomenon are combined into the notion of aromaticity. Names such as Kekule-Armstrong-Baeyer-Bamberger-Robinson-Ingold-Evans-Hückel-Dewar-Woodward-Hoffmann and other distinguished chemists revealed new facets of this phenomenon. It is my belief that novel interesting and useful facts are still awaiting discovery in this field of aromaticity.

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