Translated from *Uspekhi Khimii* **59** 197–228 (1990) U.D.C. 547.173 + 539.194

Current state of the problem of aromaticity

M V Gorelik
Scientific-Research Institute of Organic Intermediates and Dyes, Moscow

ABSTRACT. The different aspects of the current concept of aromaticity, which is based on the advances in the synthesis of aromatic systems and a study of their properties by experimental physical techniques and theoretical quantum-mechanical methods, are examined. Magnetic, structural, and energy properties, but not reactivity, can serve as criteria of aromaticity as characteristics of the electronic structure of cyclic conjugated systems, stabilisation of which is due to a cyclic delocalisation of electrons. A wider interpretation on which ideas about multiple types of aromaticity are based is unjustified and unsuitable.

Contents

I.	Introduction	116
II.	Progress in the synthesis of aromatic systems	116
III.	Criteria of aromaticity	119
IV.	Aromaticity and reactivity	125
V.	The concept of aromaticity	126
VI.	Types of aromaticity	127

I. Introduction

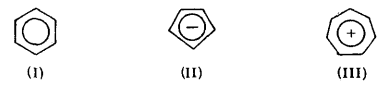
The problem of aromaticity is one of the principal problems in organic chemistry. More than 130 years since the Kekulé structure of benzene was established, it is undergoing a fruitful development through the close interaction between experiment and theory.[1–10] In the area of aromatic compounds, to which about 30% of all known organic products belong,[11] many fundamental rules of structure and reactivity have been established for the first time. During the time that the problem of aromaticity has been studied, theoretical organic chemistry has attained its most important achievements, such as the well-known Hückel rule, and at this point it has confronted a crisis, which has arisen from the proposal that the concept of aromaticity should be rejected altogether.[12–15]

The current state of the problem of aromaticity is very ambiguous. On the one hand, running in parallel to the development of the practical chemistry of aromatic compounds, the experimental and theoretical principles of aromaticity continue to be improved and extended. On the other hand, objections to aromaticity are discussed as before and all the time new types and variants of aromaticity are proposed, as a rule not being compatible with this concept. The main objects to aromaticity, which were put forward in the 1970s, are that aromaticity is not a physical quantity that could be measured directly[12] and the concept of aromaticity does not have a single meaning, as it comprises a number of postulates and theories.[13,14] The questions: "Aromaticity—myth or reality?",[14] "Aromaticity—an exercise in chemical nonsense?",[15] "Aromaticity not in fashion?",[16] "Aromaticity—theory or myth?",[17] became the titles or topics of publications, and the abundant forms of aromaticity became the subject of jokes ("schizoaromaticity"[12]). Even in studies that defended the usefulness of the concept of aromaticity,[6,10,16] together with wideness and universality, its diffuseness, physical heterogeneity, and the impossibility of a more or less rigorous determination are emphasised.

The erosion of the concept, the multiplicity of the types of aromaticity, the lack of a common view of the criteria for aromaticity, in particular the possibility of using reactivity as a criterion, have created certain complications in the chemistry of aromatic compounds. The present review aims to analyse the recent advances in the experimental and theoretical principles of aromaticity, to discuss the resulting concept of aromaticity, and to consider the ideas about the different types of aromaticity in this context.

II. Progress in the synthesis of aromatic systems

An accumulation of data from physical methods that constitute the foundation on which the concept of aromaticity is based has proved possible mainly as a result of the synthesis of different aromatic systems. During the early period of development of ideas about aromaticity[18] chemists did not even suspect that these systems existed. The modern era of the problem of aromaticity was started in 1931–1938 when Hückel developed the molecular orbital (MO) method to represent the electronic structure of unsaturated hydrocarbons, which led to the Hückel rule ($4n + 2$, $n = 0, 1, 2$, etc.) for determining the number of π-electrons with which a monocyclic, conjugated, planar carbopolyene is aromatic. Up to that time, benzene (I) and the cyclopentadienyl anion (II) as well as their heteroanalogues (pyridine, pyrrole, thiophene, etc.) were known as aromatic systems. Hückel attributed the aromaticity of benzene and the cyclopentadienyl anion to the completeness of the electron shell, in which six π-electrons completely occupied all three bonding orbitals, and he predicted the aromaticity of the cycloheptatrienyl cation (III). The synthesis of cycloheptatrienyl (tropylium) bromide in 1954[19] was the first step in a series of significant advances confirming the predictive power of the Hückel rule.



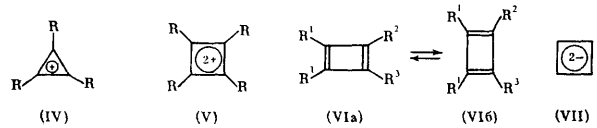
(I) (II) (III)

During the following years monocyclic, conjugated, neutral and charged polyenes were synthesised with the number of atoms (N) in the ring ranging from 3 to 30 ([N]annulenes); out of these the planar systems containing $4n + 2$ π-electrons were classed as aromatic,

while those containing $4n$ π-electrons were classed as antiaromatic. Many new polycyclic and heterocyclic aromatic systems were also obtained. It is useful within the scope of the present review to describe briefly a selection of the main products, studies on which led to elaboration of criteria and the development of the theory of aromaticity.

Systems containing 2π-electrons are known—the cyclopropenium cation (IV) and cyclobutadienyl dication (V). Salts of cyclopropenium[20] and its trialkyl-, triaryl-, and tricyclopropyl-substituted derivatives are stable, so they can be isolated in a crystalline state. Tetramethyl and tetraphenyl derivatives of dication (V) have been synthesised in a superacid medium at a low temperature and have been characterised from their NMR spectra.[21]

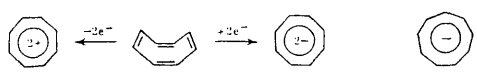
Cyclobutadiene (VI)[22] is the simplest antiaromatic system;[23] it has only been detected in an argon matrix during low-temperature photolysis (20 K). Cyclobutadiene derivatives stabilised by substituents such as t-butyl groups have been isolated in a pure form. A study of tri-t-butylcyclobutadiene using NMR spectroscopy[24] and generation of 1,2-dideuterocyclobutadiene with trapping of the isomers by dienophile[25] suggest that there is an equilibrium between the valence isomers (VIa) and (VIb), which, according to the NMR data, cannot be "frozen out" even at −185 °C.



(IV) (V) (VIa) (VIb) (VII)

Despite the presence of 6π-electrons, the dicyclobutadienyl dianion (VII) does not possess aromaticity because of destabilisation resulting from interelectron repulsion in the small ring.[26,27]

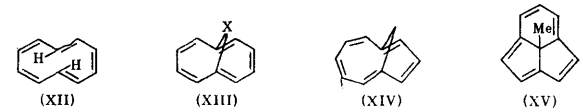
Apart from benzene (I), the cyclopentadienyl anion (II), and the tropylium cation (III), the cyclooctatetraenyl dication (VIII) also belongs to the group of 6π-electron aromatic systems. The 1,3,5,7-tetramethyl-, tetraphenyl-, and 1,4-dimethyl-substituted derivatives of the latter are obtained when cyclooctatetraene (IX) is treated with SbF_5 at −78 °C.[28,29] When cyclooctatetraene (IX) is reduced with an alkali metal, it is converted to the cyclooctatetraenyl dianion (X)—a 10π-electron aromatic system.[30] The aromatic cyclononatetraenyl anion (XI) also has a 10π-electron shell.[31,32] In contrast to ions (VIII) and (X), cyclooctatetraene itself[33] is a typical cycloolefin; its non-planar molecule with $4n$ π-electrons ($n = 2$) has a boat conformation



(VIII) (IX) (X) (XI)

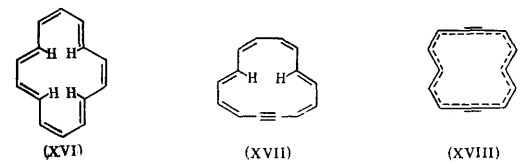
Neutral monocyclic [10]annulenes[34] do not exhibit aromatic properties because of steric hindrance. Completely *cis*- and mono-*trans*-stereoisomers of [10]annulene have been isolated in a crystalline state at −80 °C, but they decompose when the temperature is increased. Despite the attempts undertaken, stereoisomer (XII) has not been prepared, since it is destabilised by the mutual repulsion of the hydrogen atoms at the 1- and 6-positions. Replacement of these hydrogen atoms by a bridging group (X = CH_2, CO, O, NH) leads to stable aromatic bridged 1,6-X-[10]annulenes (XIII) with a periphery as in naphthalene.[35–37] 1,5-Methano[10]annulene (XIV), with a periphery as in azulene, has also been synthesised.[38,39]

Another type of bridged [10]annulene is the methano[10]annulene (XV) (7*b*-methyl-7*bH*-cyclopent[*cd*]indene).[40]



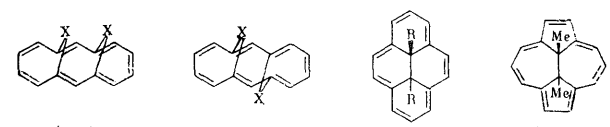
(XII) (XIII) (XIV) (XV)

In [14]annulene (XVI), just as in [10]annulene (XII) but to a lesser degree, there is overlap of the inner hydrogen atoms, and so compound (XVI) has comparatively low stability.[41] The overlap can be eliminated by the introduction of one (XVII) or two (XVIII) triple bonds with a change to dehydroannulenes.[42]



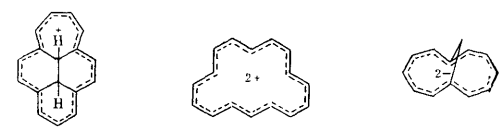
(XVI) (XVII) (XVIII)

Many bridged *syn*-1,6:8,13-bis-X-[14]annulenes (XIX) with a periphery as in anthracene, where X = CH_3, CO, CF_2, O, NH or X,X = $CH(CH_2)_nCH$ when $n = 0-3$, i.e. the bridges are joined together, have been synthesised. In contrast to the aromatic *syn*-isomers (XIX), the *anti*-isomers (XX) are extremely labile, reactive olefins. While *syn*-dioxo[14]annulene (XIX), X = CO, withstands flash pyrolysis at 500 °C, the corresponding *anti*-isomer (XX) must be kept in an atmosphere of argon at −40 °C. Another widely investigated group of bridged [14]annulenes is made up by 15,16-dihydropyrene compounds (XXI),[43] to which the bridged [14]annulene (XXII) (dicyclopenta[*ef*,*kl*]heptalene) is related.[44]



(XIX) (XX) (XXI) (XXII)

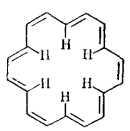
Aromatic ions containing 14π-electrons in the ring are known.[4,5] These are the bridge [15]annulenyl cation (XXIII), the [16]annulenyl dication (XXIV), the bridged 1,7-methano[12]annulenyl dianion (XXV), and others.



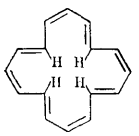
(XXIII) (XXIV) (XXV)

[18]Annulene (XXVI)—an example of aromatic systems with 18π-electrons—was historically the first macrocyclic annulene to be synthesised.[41] With its large ring size, the inner protons do not shield each other. The compound is relatively stable, it withstands distillation under reduced pressure, and can undergo aromatic substitution. Examples of bridged [18]annulenes are hexahydrocoronene which contains a central hydrogenated ring[45] and [18]annulene oxides, which contain the bonds of furan rings as a macrocycle.[46] Ions with 18π-electrons—the [17]annulenyl anion and [16]annulenyl dianion—have been reported. From among the higher annulenes with $4n + 2$ π-electrons, [22]annulene, a

[30]annulene derivative, and bisdehydro[22]-, bisdehydro[26]-, and bisdehydro[30]-annulenes have been synthesised. From among macrocyclic systems with $4n$ π-electrons, the extremely unstable [12]annulene and bridged [12]annulenes are known. [16]Annulene (XXVII), [20]annulene, and [24]annulene have been isolated in a crystalline state as have the corresponding bisdehydroannulenes. The monocations of the bridged [13]annulene and [15]annulene, the dianion of [18]annulene, and some others[4,5] have been detected spectroscopically.



(XXVI)



(XXVII)

The Hückel rule, strictly applicably only to monocyclic conjugated polyenes, has been extended to polycyclic compounds with the assumption, which has no theoretical basis, that the π system is determined by the periphery while the "inner" bonds and atoms do not introduce any significant perturbations (see, for example, the study of Rabinovich et al.[47]). Naphthalene (XXVIII) and azulene (XXIX) are aromatic bicyclic systems with 10π-electrons that have been thoroughly studied. The pentalene dianion (XXX) and bicyclo[6.2.0]-decapentaene (XXXI) [48] belong to the same group of 10π-electron systems. Bicyclic aromatic annulenoannulenes with one and three common bonds between the macrocycles,[49] such as a structure consisting of two rings of bisdehydro[14]annulene (XVIII), have been synthesised.



(XXVIII)



(XXIX)



(XXX)



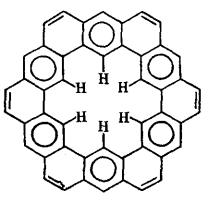
(XXXI)

The variety of polycyclic aromatic hydrocarbons is created through linear, angular, and peri-annelation to bicyclic structures. Linear benzannelation leads from naphthalene to anthracene, tetracene, pentacene, etc; angular benzannelation leads to phenanthrene and then to helicenes, which are hydrocarbons with their molecules in the form of cylindrical spirals, such as in octahelicene (XXXVI), since the spatial overlap of the rings makes a planar structure impossible. They have spiral asymmetry which is a special case of chirality. Helicenes containing 13 and 14 rings twisted into three coils of a single spiral have been synthesised.[50]

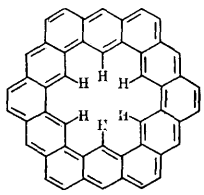
Polycyclic hydrocarbons that are built up from annelated benzene rings forming a closed loop have the group name of corannulenes.[51] The simplest example of a corannulene, for which the name was originally proposed, is the sterically strained hydrocarbon composed of five benzene rings with a pentahedron in the centre. Coronene and kekulene (XXXIII) which on the inside have a periphery of [6]- and [18]-annulene and on the outside have a periphery of [18]- and [30]-annulene respectively, belong to this group. The synthesis and study of the properties of kekulene (XXXIII) [52] and a theoretical analysis[51,53] have led to the conclusion that the electronic system of corannulenes consists of benzenoid rings with a sextet of π-electrons (XXXIIIa) rather than two electronic systems of annulenes (XXXIIIb).



(XXXII)



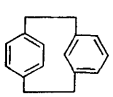
(XXXIIIa)



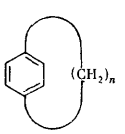
(XXXIIIb)

The Hückel rule is not applicable to polycyclic peri-annelated structures that have atoms common to the three rings if all of the π-electrons are taken into account. The phenalenium cation, pyrene, and perylene are examples of peri-annelated aromatic systems with the total number of electrons being $4n$ but with $4n + 2$ π-electrons around the periphery.

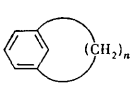
Polycyclic non-condensed hydrocarbons in which the benzene rings are joined together by polymethylene chains in a ring are classed as cyclophanes.[54] For two benzene rings, three series of [m,n]cyclophanes are possible: para–para, meta–meta, and meta–para, when $m,n \geqslant 2$, for example, [2,2]metaparacyclophane (XXXIV). The benzene rings can be joined by three chains at the 1-, 3- and 5-positions, and also arranged in several layers when one ring simultaneously forms two loops. [n]Cyclophanes in which the polymethylene chain links the para- (XXXV) or meta- (XXXVI) positions of a single ring are also known. Cyclophanes with the shortest chain, in which the benzene ring is substantially bent, are of interest for studying the relationship between aromaticity and coplanarity (Section III).



(XXXIV)



(XXXV)



(XXXVI)

A whole series of heteroaromatic compounds can formally be derived from carbocyclic compounds by replacing a single CH group with a heteroatom Y that can supply one electron to the aromatic π-system or by replacing two adjacent CH groups with a heteroatom X that can supply a pair of electrons. The replacement of one or more CH groups in benzene by a heteroatom Y results in a six-membered aromatic heterocycle, and replacement of two adjacent CH groups in benzene or, from another viewpoint, replacement of a CH^- group in the cyclopentadienyl anion by a heteroatom X leads to five-membered aromatic heterocycles. Replacement of a CH^+ group in a cationic aromatic system by a heteroatom from Group III can result in the conversion to a neutral heteroaromatic molecule, for example, going from the tropylium cation to borepine.

A similar conversion is possible in other [$4n + 2$]annulenes and in polycyclic compounds. Among 10π-electron heteroaromatic systems, there have been reports on heteronines (XXXVII),[55] which are isoelectronic to the cyclononatetraenyl anion (XI) and from amongst which azonine (X = NH) is thermally stable to 50 °C and oxanine (X = O) is unstable, and on diheteronines (XXXVIII),[56] which are isoelectronic to the cyclooctatetraene dianion (X). Stable bridged aza analogues of 1,6-methano[10]annulene (XIII) with a quinoline and isoquinoline periphery and monoazoanalogues of [14]annulene (XVI) and [18]annulene (XXVI) [36,57] have been synthesised.

Dihydroporphins (around a ring that contains pyridine nitrogen atoms and excludes pyrrole nitrogen atoms) are regarded as 1,10-diaza[18]annulenes.[58]


(XXXVII)


(XXXVIII)


(XXXIX)


(XL)

In polycyclic heteroaromatic compounds, heteroatoms can simultaneously form part of two rings as in indolizine or the quinolizinium cation and in specific cases they can belong to three rings at the same time. Cyclazines,[57] which in view of the insignificant electronic interaction through the central atom can be regarded as analogues of bridged methenoannulenes, have a similar structure. Thus, [2.2.3]cyclazine (XXXIX) is analogous to the aromatic methenoannulene (XV), while [3.3.3]cyclazine (XL) is analogous to the antiaromatic [12]annulene. since in polycyclic compounds carbon atoms in different rings and different combinations can be replaced by heteroatoms, the number of known heterocyclic aromatic systems many times exceeds the number of carbocyclic systems.

III. Criteria of aromaticity

Of crucial significance is the question of choosing criteria which would make it possible to judge whether a given compound is aromatic and if possible to measure the degree of aromaticity. Properties of molecules that can be measured by experimental physical methods are used as criteria. These constitute magnetic and structural methods and data on the thermodynamic stability obtained mainly by calculation

1. Magnetic criteria

As the electronic system of organic compounds in the vast majority of cases does not have spherical symmetry, their magnetic susceptibility is anisotropic. In aromatic compounds this is reflected particularly clearly, since apart from the effect of local anisotropy caused by the electron shells of individual atoms, non-local anisotropy occurs, due to the combined system of π-electrons in the molecule, the so-called "ring current". The concept of the ring current is given by a postulated model,[59] the veracity of which has been confirmed by the agreement of the properties calculated using it and those measured experimentally. The use of magnetic criteria essentially consists of detecting magnetic properties non-local components, which would indicate the presence of a ring current.

The magnetic susceptibility on right-angled coordinates is expressed as the sum $\chi_M = 1/3(\chi_x + \chi_y + \chi_z)$. The essence of anisotropy of diamagnetic susceptibility is that the component along the axis perpendicular to the plane of the aromatic ring is always greater than that measured in the plane of the ring: $\chi_z \gg \chi_x \approx \chi_y$.

The difference between the components is a measure of the anisotropy:

$$\Delta\chi_M = \chi_z - 1/2(\chi_x + \chi_y).$$

Direct measurement of the anisotropy of molar diamagnetic susceptibility $\Delta\chi_M$ requires the growth of a monocrystal and an initial determination of the molecular orientation. Other methods are based on the Zeeman effect in microwave rotational spectra[60] and on a determination of deuteriated compounds in high-resolution ^{2}H NMR spectra.[61] Analysis shows[60,62] that only a fraction of $\Delta\chi_M$ (Table 1) for aromatic compounds, about a half for benzene,[60] can be attributed to the ring current, whereas the other fraction is due to local anisotropy. The experimental difficulties and the need to separate the contributions of the local and non-local components limit the widespread use of the anisotropy of diamagnetic susceptibility as a criterion of aromaticity.

Table 1. Anisotropy and exaltation of diamagnetic susceptibility (-10^{-6} cm^3 mol^{-1}).

Compound	$\Delta\chi_M$ (Ref.60)	χ_M (Ref.63)	$\chi_M - \chi_M^{loc}$	
			Λ **	χ_M^{nonloc}***
Benzene	59.7*; 62.7	54.8	13.7 (18.0)	12.5
Naphthalene	119.8*	91.9	30.5 (36)	—
Anthracene	182.4*	130.3	48.6 (55)	—
Phenanthrene	165.5*	127.9	46.2 (53.5)	—
Pyrene	222.4*	155	57	—
Azulene	—	91.0	29.6 (35.5)	—
Pyridine	57.2	49.2	13.4 (18.3)	9.1
Pyrrole	42.4	47.6	10.2 (14.5)	12.7
Furan	38.7	43.1	8.9 (13.9)	9.9
Thiophene	50.1	57.4	13.0 (17.8)	13.0
1,3-Cyclohexadiene	—	48.6	—0.7	—
[16]Annulene	—	105	—5	—

* Determination using the monocrystal orientation method; the remaining figures were obtained using microwave spectroscopy.

** Using the Haberditzl increments[63] to calculate χ_M^{loc}; in brackets — using Pascal constants, taken from Ingold[64] for hydrocarbons and from Pozharskii[9] for heterocycles.

*** Using Hameka parameters[65] to calculate χ_M^{loc}.

A property which is simpler to determine is the difference between the total molar magnetic susceptibility of an aromatic compound and that of an analogous hypothetical compound with localised bonds $\chi_M - \chi_M^{loc}$, known as the exaltation of diamagnetic susceptibility (Λ) [63] or non-local magnetic susceptibility (χ_M^{nonloc}).[65] The total magnetic susceptibility χ_M of the compound under study is measured experimentally by determining the force at which the sample of the substance is repelled by a magnetic field of given strength. The magnetic susceptibility of the hypothetical compound with localised bonds χ_M^{loc} is calculated as the sum of the contributions of the separate structural elements of the molecule. It is clear from the examples in Table 1 that the exaltation of diamagnetic susceptibility Λ is negative and considerable in absolute value, for the non-aromatic 1,3-cyclohexadiene it is equal to zero, and for the antiaromatic [16]annulene (XXVII) it is opposite in magnitude. It should be mentioned that, based on some of the same experimental values of χ_M, different values of Λ or χ_M^{nonloc} are given in the literature depending on which parameters are used in the calculation of χ_M^{loc} (see Table 1). A relationship between the non-local components of the diamagnetic susceptibility, its axial component, and the anisotropy has been deduced: $3\chi^{nonloc} = \chi_z^{nonloc} = \Delta\chi^{nonloc}$.[65] The index based on the anisotropy of optical polarisability[66] is similar to the exaltation of diamagnetic

susceptibility. The index based on the Faraday effect—the enhancement of the rotation of the plane of polarised light by a sample of an aromatic compound placed in a magnetic field compared to the rotation for the hypothetical model with localised bonds calculated from increments[14]—is also related to the magnetic susceptibility.

The comparative simplicity of determination and the applicability to different classes of compounds make the enhancement of diamagnetic susceptibility a practicable index for aromaticity. Its weak point lies in the need to calculate the diamagnetic susceptibility of hypothetical compounds by an additive scheme, which always holds the chance of errors, especially since anomalies are found for real compounds. Thus, for cycloheptatriene and cyclopentadiene values are obtained which would class them as aromatic compounds (Λ = 8.1 and 6.5 respectively).[63,65]

The simplest method to use in the study of aromaticity, requiring moreover a minimal quantity of substance, is the determination of chemical shifts of the protons in an aromatic ring in ^{1}H NMR spectra. As a result of the ring currents which generate an anisotropic diamagnetic field in aromatic compounds, inside the ring directed against the external magnetic field and outside the ring lying along the line of the external magnetic field, the signals from protons positioned inside the ring or above it are displaced upfield, while the signals from protons lying in the plane of the ring on the outer side are displaced downfield (diatropy). In antiaromatic compounds a paramagnetic field occurs, so that the signals from the inner protons are displaced downfield and the signals from the outer protons are displaced upfield (paratropy).

The difference between diatropic aromatic and paratropic antiaromatic systems is shown most clearly in a series of annulenes, where the recording of the chemicals shifts of protons has served as an important instrument in the classification of aromaticity, confirming the validity of the Hückel rule. The difference between the chemical shifts of the outer and inner protons in the ^{1}H NMR spectra of neutral aromatic [4n + 2]annulenes is 7–12 p.p.m., in the spectrum of the aromatic [16]annulenyl dianion it is about 16 p.p.m.[4] For antiaromatic annulenes this difference has a reverse sign and amounts to 2–7 p.p.m., while for the antiaromatic [18]annulenyl dianion it is about 30 p.p.m. The greater difference for the anions reflects the phenomenon, which has a theoretical basis,[67] that in charged aromatic–antiaromatic systems the ring current is greater than in neutral systems. In a series of diatropic tetra-t-butyl-substituted bisdehydro[N]annulenes containing t-butyl groups at the α-positions relative to the triple bonds, the difference between the chemical shifts of the outer and inner protons, taken as a measure of the ring current, decreases from 13.8 p.p.m. when N = 14 (XVI) to 4.0 p.p.m. when N = 30.[42] The fact that in the ^{1}H NMR spectrum of kekulene (XXXIII) the signal from the six inner protons occurs downfield at 8.37 p.p.m. and not far upfield as in [18]annulene has served as evidence for the benzenoid structure of (XXXIIIa) [52] (see Section II).

In bridged [4n + 2]annulenes the chemical shifts of the protons situated above the plane of the ring are strongly displaced upfield. For example, in 1,6-methanol[10]annulene (XIII), X = CH_2, the protons of the CH_2 group resonate at −0.51 p.p.m. while the ring protons resonate at 6.95–7.27 p.p.m.[41] Reduction of *trans*-15,16-dimethyl-15,16-dihydropyrene (XXI), R = Me, to the dianion, with a change from a 14π-electron aromatic system to a 16π-electron antiaromatic system causes the chemical shifts of the protons of the methyl group to change from −4.25 to 21.0 p.p.m. and the ring protons to change from 8.14–8.65 to −3.2 to −4.0 p.p.m.[41]

The vast majority of aromatic compounds contain medium or small rings which have only outer electrons. Their chemical shifts have to be compared with the chemical shifts of protons in model compounds rather than those of inner protons. In the case of benzene, for example, the signal in its spectrum is displaced 1.5 p.p.m. downfield relative to the signals from the olefinic protons of 1,3-cyclohexadiene, which can be selected as a model. It would appear to be possible to estimate the strength of the ring current from the degree of displacement of the signals, and hence estimate the degree of aromaticity. The ready availability of ^{1}H NMR spectra and the apparent simplicity in interpretation have given rise to many attempts of this type. Their failure has generally been because only a part of the chemical shift can correctly be related to the ring current. It is also necessary to take into account the contribution of the effect of local anisotropy and the influence of the distribution of electron density. An analysis applied to polycyclic benzenoid hydrocarbons[68] shows that only 50% or less of the total magnitude of the chemical shift can be attributed to the delocalisation effect, while the remaining proportion is defined as the contribution from local anisotropy. A simple comparison of the values of the chemical shifts of protons cannot give a true picture of the ratio of ring currents and is more suitable for establishing aromaticity than quantifying it.

The displacement of the signals in ^{13}C NMR spectra when a ring current occurs are approximately the same in absolute magnitude as in proton spectra, but since the range of chemical shifts of ^{13}C NMR is an order higher than for ^{1}H nuclei, the relative changes in chemical shifts in ^{13}C NMR spectra are small and are readily masked by other effects.[69]

From among the indices of aromaticity in use that are based on the measurements of chemical shifts, mention should also be made of "displacement by dilution" and "displacement from the solvent". The first of these is the displacement of a signal in the ^{1}H NMR spectrum when a liquid aromatic compound is diluted with an inert non-polar solvent multiplied by the molar volume: $\Delta\delta.V_M$. Referral of this value to the analogous one for benzene gives an index expressed in percent.[8] "Displacement from the solvent" is the difference between the chemical shifts of a polar molecule (acetonitrile) and a non-polar molecule (cyclohexane) in the liquid aromatic compound under study. It has been shown[70] that this parameter does not measure the ring current or aromaticity.

2. Structural criteria

A geometric characteristic of the molecules of aromatic compounds is their tendency to form a coplanar configuration of the atoms and bonds of equal length in the aromatic ring. Current methods for establishing the molecular structure—X-ray and neutron diffraction analysis, gas-phase electron diffraction analysis and microwave spectroscopy of free molecules—make the geometric parameters of almost all aromatic systems possible to determine.

The tendency towards coplanarity is due to the advantage of colinearity of the axes of the p orbitals for their effective overlap. An important question concerns what deviation from a planar configuration is admissible without a loss of aromaticity. A study of sterically strained aromatic compounds such as helicenes, corannulenes, and particularly cyclophanes with short bridges, provides data about this. The benzene ring in [n]paracyclophanes (XXXV) is distorted into the form of a boat with a deviation of 15–17° from planarity when n = 7,[54] 20–21° when n = 6 [71] (X-ray diffraction data), 22–24° when n = 5 (data from calculations).[72] In one derivative[5] of metacyclophane (XXXVI),

n = 5, one side of the boat is deflected by 27° and the other by 12°.[73] Despite this, the bonds in the benzene ring of these compounds are of equal length, and the values of the bond lengths and chemical shifts in the ^{1}H NMR spectra lie in the usual region for aromatic compounds. A determination of the anisotropy of diamagnetic susceptibility using high-resolution ^{2}H NMR for 8,11-dideutero[5]metacyclophane confirms that the ring is aromatic.[74] Calculations on the molecules of [5]paracyclophane [72] and [6]paracyclophane [75] using non-empirical quantum-chemical methods suggest that there is considerable destabilisation due to strain in the distorted benzene ring.

In unstrained aromatic systems the deviations from planarity that occur are usually small. From the data for strained structures and quantum-chemical calculations the view was expressed that even unstrained aromatic rings are flexible in the ground state when the deviations from planarity range from 5–20°.[76] An analysis of the vectors of the π-orbital axes in the case of bridged [10]annulenes (XIII)–(XV) shows that the molecule has a tendency to bend in order that the overlap of the π-orbitals should be at a maximum.[77]

The stability of a planar geometry of the system as determined by calculating the change in energy on bending about one of the axes has been proposed as a theoretical conformational criterion of aromaticity or antiaromaticity.[78] Systems in which the change to a non-planar conformation gives rise to a large endothermic change, a large exothermic change, or a small change in energy are classed as aromatic, antiaromatic, or non-aromatic respectively. It was found using a non-empirical MO method (6–21 G basis) that for aromatic benzene, pyridine, and pyrazine bending along the 1–4 axis by 20° requires energies of 62.8, 37.7, and 33.5 kJ mol^{-1}, while for the non-aromatic 1,4-dihydropyrazine the energy required is −9.2 kJ mol^{-1}. According to this criterion the system of the cyclobutadienyl dication (V), R = H, Me, for which non-empirical calculations[27,29] show that a non-planar conformation folded along a diagonal by about 35°, for example, when R = H, with an energy barrier of 19 kJ mol^{-1} (4–31 G basis) should be classed as non-aromatic. From the data on the distortion of a planar structure of the ring in strained aromatic molecules and the absence of a direct relationship between acoplanarity and antiaromaticity[10] it follows that the degree of planarity is not in itself sufficient as a criterion.

The carbon–carbon bond lengths in aromatic compounds have values that are intermediate between the length of a single C_{sp^2}–C_{sp^2} bond [(1.465 Å in butadiene)[80]] and a C=C double bond (1.337 Å in ethylene[80]). There is a clear difference between aromatic and antiaromatic compounds in the distribution of bonds. Thus, in the planar molecule of the aromatic [18]annulene (XXVI) there is no alternation in bonds: the 12 inner bonds have a length of 1.38 Å and the 6 outer bonds have a length of 1.42 Å, whereas in the conformationally mobile molecule of the antiaromatic [16]annulene (XXVII) single (1.44–1.47 Å) and double (1.31–1.35 Å) bonds alternate.[4]

According to the data from all known methods the benzene molecule has D_{6h} symmetry with equal bonds (1.397 Å). Despite this, the view has recently been expressed that even in this case a structure with D_{3h} symmetry and alternating bonds cannot be excluded because of the possibility of a molecular configuration with a 30° bend in crystals and the averaging out when gas-phase methods are used.[81] This point of view raises objections, particularly on the grounds that according to quantum-chemical calculations using a non-empirical method (3–21 G* basis) a structure with D_{3h} symmetry does not correspond to a minimum on the potential energy surface and has appreciably inferior stability compared to a D_{6h} structure.[82]

In a few other aromatic systems the bond lengths are also equal, according to X-ray diffraction data. For example, in the triphenylcyclopropenium cation (IV), R = Ph, they are 1.373 Å,[83] and in the cyclooctatetraenyl dianion (X) they are 1.407 Å.[84] However, a complete uniformity of bonds is rather more than the exception. In the vast majority of carbocyclic aromatic compounds, not to mention heterocyclic compounds, the C–C bond lengths are not fully equivalent. Introduction of substituents or annelation into the benzene ring disrupts the complete uniformity of the bonds. In napthalene (XXVIII) the C_α–C_β bonds are reduced to 1.371 Å, and the remaining bonds are increased to 1.412–1.422 Å;[80] in phenanthrene the C(9)–C(10) bond length is only 1.350 Å while the C(10)–C(10a) bond is elongated to 1.453 Å.[85]

The lengths of the bonds involving heteroatoms in heteroaromatic compounds vary over a wide range. Structural studies of the hetero analogues of benzene with Group V elements indicate that as its number in the Periodic Table increases, the angle in the ring at the heteroatom decreases while the length of the carbon–heteroatom bond increases, constituting 117° and 1.37 Å in pyridine, 101° and 1.73 Å in phosphabenzene (phosphorine), 97° and 1.85 Å in arsabenzene, and 93° and 2.04 Å in stibabenzene.[86] The stability of the compounds decrease in the same series. However, all molecules remain planar with C–C bond lengths equalled out to 1.38–1.41 Å, which suggests that there is a retention of aromaticity, which is weakened by an unfavourable geometry.

It has been proposed through the introduction of special indices that the degree of equivalence of the bond lengths in the ring should be used as a quantitative characteristic of aromaticity. The index of Julg[87] constitutes the product of two factors:

$$A = A_1 \cdot A_2 = [1 - 225/n\Sigma (1 - d_{rs}/\bar{d})^2] \cdot \Pi [1 - (\Delta q_{ij}/d_{ij})^2].$$

The first term strictly represents the degree of equivalence of n C–C bonds in the ring, having length d between atoms r and s with average length $\bar{d}$. This factor is not very sensitive to the variation in bond lengths: benzene 1.00, naphthalene 0.90, azulene 1.00, pyrrole 0.91. Therefore a second factor is introduced, taking into account the difference in the π-charges Δq_{ij} on the neighbouring atoms. The introduction of a corrective factor which operates with the magnitudes of charges calculated by a quantum-chemical method has the result that index A loses its purely experimental basis. Critical comments have been made and the opinion has been expressed that the Julg index is unsatisfactory.[9,88,89]

An index has been built up from an analysis of the bond lengths obtained experimentally or calculated by a quantum-chemical method. This index is based on the so-called "harmonic oscillator model of aromatic stabilisation" (HOMAS):[90]

$$I(\mathrm{HOMAS}) = 1 - \frac{98,89}{n} \sum_{r=1}^{n} (d_{\mathrm{opt}} - d_r)^2.$$

Calculation and summation of the squares of the differences are carried out separately for each type of bond using the optimum value of the length (d_{opt}): C–C 1.397, C–N 1.338, N–N 1.308, C–O 1.300 Å. When applied to polycyclic compounds, this index is more convenient for characterising the aromaticity of individual rings.[90]

Since a direct comparison of the lengths of bonds involving different atoms is impossible, a conversion from the experimental values of the bond lengths (d) to their orders (N) is used by calculation from the correlative equation: $N = ad^{-2} - b$, where a and b are empirical constants (for values, see the studies of Pozharskii[9] and Bird[91]). The problem then essentially consists of developing an index which reflects the variation in the bond orders. Pozharskii[9] proposed the index $\Delta\overline{N}$, which is the average value of the variations of the orders of n bonds, including single bonds, calculated as the sum of all the differences ΔN divided by their quantity, which is equal to the number of sets of n to the power 2: $\Delta\overline{N} = \Sigma\Delta N/C_n^2$. In order to express the aromaticity in percent, the aromaticity of benzene ($\Delta\overline{N} = 0$) is taken as 100% and that of cyclopentadiene ($\Delta\overline{N} = 0.49$) is taken as 0%, which gives a scale relative to the factor $I = 100(1 - \Delta\overline{N}/0.49)\%$.

On the same basis, Bird[91-93] introduced a similar scale, in which the variation of the bond orders is given by the ratio of the mean square deviation to the arithmetic mean of the bond orders:

$$V = \frac{100}{N}\sqrt{\Sigma(N - \overline{N})^2/n}.$$

For the aromaticity scale, the aromaticity of a completely delocalised system ($V = 0$) was taken as 100% and the index of the corresponding Kekulé structure with completely localised bonds ($V_K = 35$ for five-membered rings, $V_K = 33.5$ for six-membered rings) was taken as 0%; $I = 100(1 - V/V_K)\%$ (Table 2).

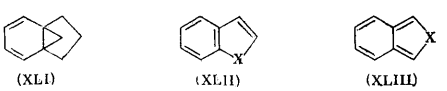
Table 2. Structural indices of aromaticity.

Compound	Aromaticity, %		Compound	Aromaticity, %	
	(Ref.9)	(Refs.91, 92)		(Ref.9)	(Refs.91, 92)
Benzene	100	100	Pyridine	82	85.7
Naphthalene	63	—	Pyridazine	65	78.9
Thiophene	45	66	Pyrimidine	67	84.3
Pyrrole	37	59	Pyrazine	75	88.8
Selenophene	37	59	1,2,3-Triazine	65	76.9
Tellurophene	20	48	1,2,4-Triazine	71	86.1
Furan	12	43	1,3,5-Triazine	100	100
Phosphole	8	35	1,2,4,5-Tetrazine	88	97.8
Tetrazole	80	72	Pyridinium	54	66.7
1,2,4-Triazole	71	81	Pyrilium	28	65.8
Pyrazole	61	73	Phosphorine	61	74.1
Imidazole	43	64	Sydnone	17	42
Thiazole	43	64	2-Pyridone	22	59

The structural indices are based on experimental results, they effectively differentiate the aromaticity of compounds, they provide a single continuous scale, and in the case of polycyclic compounds they can be used to determine both the system as a whole and its separate cyclic fragments. Inapplicability to symmetric systems is among their limitations. In comparing the two variants of structural index it is clear that the distribution of compounds in terms of aromaticity is on the whole similar, although the ratios of aromaticities in a number of cases do not agree, sometimes by a substantial amount. Thus, according to the Pozharskii index, furan is 8 times and phosphole is 12 times less aromatic than benzene, whereas according to the Bird index they are only respectively 2.3 and 2.8 times less aromatic. On the first scale 1,2,4-triazole is less aromatic than tetrazole, on the second scale it is the reverse. Since both indices are based on the same collection of data and only differ according to the way these are treated mathematically, qualitative discrepancies cannot be justified. The development of a common approach is required.

Jug[94] has proposed that the least of the complete ($\pi + \sigma$) bond orders of the system, calculated by one of the semiempirical MO methods (SINDOl) with optimisation of geometry, should be taken as a criterion of aromaticity and called the ring current index. Examination of the values given reveals a number of discrepancies with the results of experimental criteria. Thus, pyrazole proves to be a non-aromatic compound and furan is more aromatic than pyrazole as well as imidazole (cf. Table 2).

Information about the degree of fixation of the bonds in an aromatic ring can be obtained from the values of spin-spin coupling constants of vicinal protons ($^3J_{HH}$) in ^{1}H NMR spectra. The $^3J_{HH}$ constants when other conditions are equal show a linear dependence on the length (order) of the C–C bond and are larger the shorter the length (higher order) of the bond.[69] When the bonds are exactly the same length as in benzene, the ratio of constants of the neighbouring bonds $J_{rel} = 1$, when there is complete localisation of single and double bonds as in 1,3-cyclohexadiene or compound (XLI) $J_{rel} \approx 0.5$. In bicyclic aromatic compounds J_{rel} has intermediate values; in naphthalene, for example, $J_{12}/J_{23} = 0.82$.[95] As the vicinal spin-spin coupling constants depend not only on the length of the C–C bond but also on the C–C–H bond angles in planar systems, which are different in five- and six-membered systems, and on the electronegativity of the heteroatoms and substituents present in a molecule, this index has limited use. It is only suitable when comparing compounds that are similar in structure, such as the benzoheterocycles (XLII) and (XLIII), which formally have a benzenoid and orthoquinoid structure, and the values of the constants $J_{rel} = J_{45}/J_{56}$ vary from 0.89 to 0.93 and 0.70 to 0.74 respectively.



(XLI) (XLII) (XLIII)

X = NR, O, S

3. Energy criteria

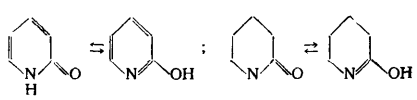
The opportunity for aromatic systems to exist arises because cyclic declocalisation of the π-electrons leads to an increase in thermodynamic stability of the molecule, namely, to a decrease in the level of its internal energy. A gain in energy is a necessary condition of aromaticity and could serve as a sufficient criterion if there were reliable methods of determining it. The difficulty in using energy criteria occurs precisely because of the inadequacy of these methods. The principal difficulty is that the energy of a real aromatic molecule has to be compared with the energy of a hypothetical molecule with non-interacting localised double and single bonds. The difference between the energies of these structures, which is known as the resonance energy (RE), cannot be completely determined on an experimental basis since the reference structure does not exist in reality. Therefore the resonance energy as the principal energy criterion of aromaticity is either determined by combining experiment with calculation (empirical RE) or calculated theoretically using quantum-mechanical methods.

The empirical resonance energy (ERE) is determined as the difference between the heat of combustion or heat of hydrogenation of an aromatic compound determined experimentally and the corresponding value for a model structure calculated by an additive scheme as the sum of the contributions of individual bonds.

$$E(\text{ERE}) = -(\Delta H^{\text{exp}} - \Delta H^{\text{addit}})$$

(The minus sign indicates that the resonance energies of aromatic systems are defined as positive). A determination of the ERE from the heat of hydrogenation is preferred if hydrogenation is practicable, as it constitutes the difference between not such large numbers as in a determination from the heat of atomisation. The main source of uncertainty arises not because of errors in the thermodynamic experiment but in the complexity of including all the factors in calculating the heats of atomisation or hydrogenation of the model compound. In particular, there is no single method for determining the energy of a single $C_{sp^2}-C_{sp^2}$ bond in structures without conjugation. Depending on whether averaged bond contributions or bond contributions that take into account the environment are used in the calculation of the heat of combustion of 1,3,5-cyclohexatriene, the ERE value of benzene varies from 0.5 to 3 eV (see Ref. 3, p. 19). The ERE values of some compounds, determined from heats of combustion, are given below in Table 3. Attempts to deduce rational numerical values of the bond contributions based on a critical analysis of thermochemical data by compromises and assumptions do not improve the situation very much.[96]

An experimental study of reversible chemical reactions—acid–base, tautomeric, and redox reactions—can give some idea of the magnitude of the stabilisation energy. Thus, the equilibrium constants that corresponds to formation of aromatic ions clearly indicate their stabilisation. This is suggested by the high acidity of cyclopentadiene, which is deprotonated to the aromatic cyclopentadienyl anion (II) (pK_a = 15 [5]) compared to the acidity of alkanes, for example (pK_a = 68–70 [97]); the high basicity of the ketones—cyclopropenone, tropone, and phenalenone (pK_a = −3.1, −0.6, −1.4 respectively[98])—protonation of which leads to the formation of the hydroxy derivatives of the aromatic cyclopropenium (IV), tropylium (III), and phenalenium cations, compared to the basicity of acetone, for example (pK_a = −7.2); and the values of the equilibrium constants (pK_{R^+}) of the reaction: $R^+ + H_2O \leftrightarrows ROH + H^+$, for aromatic cations such as tricyclopropylcyclopropenium (IV), R = C_3H_5, (pK_{R^+} = 10.0)[99] one of the most stable carbocations, tropylium (III) (pK_{R^+} = 4.7),[100] the bridged cation of [15]annulene (XXIII) (pK_{R^+} > 8.7),[5] etc. compared to a stabilised conjugated cation such as Ph_3C^+ (pK_{R^+} = −6.4).[100] From a comparison of two reversible reactions, one of which involves aromatic compounds and the other involves non-aromatic compounds, these being similar in structure, the ERE difference between the aromatic tautomers can be determined. Thus, a comparison of the constants of the tautomeric equilibrium of the aromatic compounds 2-pyridone (XLIVa) ⇆ 2-hydroxypyridine (XLIVb) with the corresponding hydrogenated models (XLVa) ⇆ (XLVb) shows that the ERE of 2-hydroxypyridine is 0.32 ± 0.04 eV greater than that of 2-pyridone.[8]



(XLIVa) (XLIVb) (XLVa) (XLVb)

In determining the empirical resonance energy, the reference structure, the energy of which is calculated by summation of the bond contributions derived from data for alkanes and alkenes, is a model with alternating bonds, namely, with a geometry that differs from the geometry of the aromatic molecule which has equalised bonds. The resonance energy relative to the reference structure with the same geometry is known as the vertical resonance energy. It is greater than the ERE by an amount equal to the distortion energy that is necessary to stretch the double bonds and compress the single bonds. The deformation energy on going from cyclohexatriene to benzene is estimated at 1.17–1.60 eV while the vertical resonance energy is estimated at 2.73–4.83 eV.[101]

Since the total stabilisation energy of the system depends on its size, in order to compare different systems resonance energy values calculated for one π-electron are used. Standardisation of the resonance energy on the basis of one atom [102] and one bond [103] and the ratio of the resonance energy to the complete π-electron energy of the reference structure (% RE) have also been proposed.[104]

In the Hückel approximation the quantity which should correspond to the vertical resonance energy is the delocalisation energy (DE). It constitutes the difference between the π energy of the system calculated by the Hückel MO method and the π energy of double bonds represented as a Kekulé structure. The contribution of each of the latter is equated with the π-energy of an ethylene molecule (2β). Since benzene has a π-energy equal to 8β as calculated by the Hückel MO method while cyclohexatriene has a π-energy of three ethylene molecules, equal to 6β, the delocalisation energy of benzene is 2β. The delocalisation energy values of certain other hydrocarbons are given in Table 3. It is to be expected from the delocalisation energy values that all the annulenes except for cyclobutadiene, not only those that satisfy the Hückel rule but also benzocyclobutadiene or pentalene, which do not exist in a free state, should be aromatic. With respect to its resonance energy value per π-electron (Table 3) benzene is below the polycyclic hydrocarbons, and the lower polyacenes fall below the higher members, which is at variance with the actual data on the stability and properties of these compounds.

By taking into account the unsuitability of the resonance energy as a criterion of aromaticity and the rought approximation that have to be resorted to in calculating the energies of hypothetical cyclic polyenes as reference compounds, Dewar proposed that they should be replaced by acyclic polyenes with an open chain.[105] This introduced a fundamental improvement in the calculation of resonance energy. In a determination of the Dewar resonance energy (DRE), the Pariser–Parr–Pople SCF MO method is used to calculate the heats of atomisation of the cyclic compound under study, and in order to calculate the heat of atomisation of the reference structure the energies of the double and single bonds, which in a series of polyenes are given by the constants:

$$E(\text{DRE}) = -(\Delta H^{\text{cycl}} - \Delta H^{\text{acyl}}).$$

are added up. Relating this to the number of π-electrons in the system gives the Dewar resonance energy per π-electron, denoted by the acronym REPE (resonance energy per electron). This parameter (Table 3) is in much better agreement with the actual material. Its value is highest for benzene, it decreases on going from lower polyenes to higher polyenes, it is close to zero for pentalene, and for cyclobutadiene it acquires a negative value. When thermochemical data are available for acyclic polyenes, the Dewar resonance energy can be calculated from them with the same results reached as in the

calculation of the heats of atomisation of acyclic polyenes by summation of the bond energies.[106] The Dewar resonance energy (DRE) is less than the empirical resonance energy (ERE) by an amount equal to the conjugation energy in the acyclic polyene, which may be expressed in terms of the conjugation energy (CE) of butadiene:[107]

$$E(\text{DRE}) = E(\text{ERE}) - nE(\text{CE}) \text{ (butadiene)},$$

where n is the number of single bonds in the reference structure.

With the development of quantum chemistry it became possible to calculate the resonance energy on an entirely theoretical basis using a non-empirical method. The quantum-mechanical vertical resonance energy for benzene, obtained by a non-empirical MO method (DZ basis) which takes into account electron correlation, is 3.34 eV; the distortion energy is 1.30 eV; the adiabatic resonance energy, which is equivalent to the empirical resonance energy, is 2.17 eV; and the standardised energy, which is equivalent to the Dewar resonance energy calculated from the equation above, is 1.00 eV when the conjugation energy of butadiene is 0.39 eV.[107]

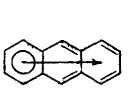
By formulating a new theoretical criterion of aromaticity, Dewar rejected at the same time hypothetic cyclopolyenes as reference models and the Hückel MO method for the calculation of energies, having expressed the view that it was unsuitable for further use in organic chemistry.[105] It transpired, however, that the main point was not the change in method of calculation but the exchange of models. Hess and Schaad showed[106,107] that in a correlation of the π-energy of a conjugated cyclic system calculated by the Hückel MO method with the π-energy of the corresponding acyclic polyene obtained by an additive method, agreement with the actual data is just as satisfactory as when using a SCF MO method (Table 3). In order to calculate the energy of an acyclic polyene in a determination of the resonance energy by the Hess–Schaad method (HSRE), the empirical parameters required for the bond energies are not of two types but eight types, depending not only on the multiplicity of the bond but also the number and position of the hydrogen atoms.[112,116]

A way of calculating the resonance energy within the scope of the Hückel MO method has been developed[114,115] with the use of graph theory techniques. In the Hückel MO method the complete π-energy of the molecule is expressed as the sum of the molecular orbital energies, taking into account how they are filled. The problem essentially consists of determining the coefficients of the characteristic polynomial, the roots of which constitute the orbital energies (in β units). By using a topological scheme based on the graph-theory theorem of Sachs, it is possible to calculate the polynomial coefficients directly from the molecular structural formula (molecular graph). The coefficients are calculated by summation of the total number of components of the molecular graph, taking into account the cyclic component. If the contribution of the cyclic component in the coefficients is omitted, a polynomial that corresponds as if to the same system but without the ring will be obtained. Summation of the roots of this polynomial, known as acyclic, gives the reference energy, which is subtracted from the π-energy of the conjugated system to give the topological resonance energy (TRE):[114,115]

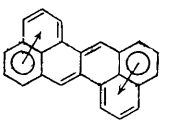
$$E(\text{TRE}) = \sum_{i=1}^{n} g_i(x_i - x_i^{\text{ac}}),$$

where x_i and x_i^{ac} are the roots of the cyclic and acyclic polynomial and g_i is the degree of occupation of the π-orbitals by electrons (Table 3). While in a determination of the Dewar resonance energy and Hess–Schaad resonance energy the reference energy belongs to an acyclic polyene represented by a structural formula, in the determination of the topological resonance energy it has only a mathematical representation as an acyclic polynomial. Because of this, the topological resonance energy is applicable not only to neutral carbocyclic and heterocyclic molecules for which Kekulé structures can be drawn but also to ions, radicals, excited states, and unusual combinations of atoms.

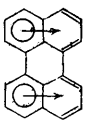
In addition to calculations of the resonance energy based on SCF MO and Hückel MO methods, several methods have been proposed for calculating the resonance energy of carbocyclic benzenoid systems with empirical parametrisation, having similar features to the valence method and based on the sextet structures of Clar,[117] Kekulé structures,[108] or "conjugated" rings,[118] revealed in the molecular structure. Clar introduced a circle as a distinctive symbol of a sextet of π-electrons for those rings in polycyclic hydrocarbons which, as in the Kekulé structure of benzene, have three double bonds; this made it possible to make a qualitative interpretation of many properties.[119,120] Apart from sextets in the molecule there are rings which are capable of "diluting" the sextet through transfer of two π-electrons to them, which is shown by an arrow as in anthracene (XLIV), rings with fixed double bonds as in cetrene (XLV), or "empty" rings like the central ring in perylene (XLVI). It is assumed that the more aromatic a compound is, the more sextets there are in its structure and the less the sextets are "diluted" through the participation of neighbouring rings.



(XLIV)



(XLV)



(XLVI)

In order to make a quantitative determination of the resonance energy of a polycyclic benzenoid hydrocarbon, all of the Clar structures are written out and the number of sextets, isolated double bonds, and rings "diluting" an adjacent sextet are determined in each, the numbers are added up, and after that, by using numerical values of these parameters (in eV), the resonance energy is calculated from a linear equation.[117] The values of the parameters are defined from an empirical correlation with the Dewar resonance energy. This method is also suitable for characterising the local aromaticity of individual rings. In a similar manner, a calculation is carried out on the basis of Kekulé structures[108] or conjugated rings,[118] when each ring in each Kekulé structure is examined and evaluated by type. Theoretical analysis suggests that there is an inherent similarity between the different methods for calculating the resonance energy.[116]

All variants of the resonance energy which are calculated using an acyclic polyene as the reference structure are resonance energies in the Dewar sense. By using this theoretical index of aromaticity it is possible to trace the border between aromatic, antiaromatic, and non-aromatic compounds, depending on whether the resonance energy is positive, negative, or close to zero, and also to develop a continuous scale of aromaticity as the resonance energy per π-electron increases. Comparison of the three variants of the scale—DRE, HSRE, and TRE (Table 3)—shows that on the whole they agree non-linearly, although they have particular differences or

discrepancies. Thus, according to the value of the Dewar resonance energy, benzocyclobutadiene is aromatic, to a greater degree that azulene and furan, while pentalene is non-aromatic. On the other hand, according to the values of the Hess–Schaad and topological resonance energies, benzocyclobutadiene and pentalene are anti-aromatic. Attention is drawn to the fact that on the latter two scales, where the resonance energies of ions are calculated, it is not benzene that occupies the first place with respect to aromaticity, but separated by a large amount is the cyclopropenium cation, followed by the cyclopentadienyl anion and the tropylium cation. According to its Hass–Schaad resonance energy value per π-electron (-0.002β),[102] the cyclobutadienyl dication is classed as a non-aromatic system, which is consistent with the data of the conformational criterion (see Section III). The relative positions on the different scales for compounds that are similar in structure do not always coincide. For example, on the DRE and TRE scales pyrimidine is more aromatic than pyrazine while on the HSRE scale their aromaticity is the same, whereas according to the data of structural criteria (Table 2) pyrazine is more aromatic than pyrimidine.

Table 3. Resonance energy values.

Compound	*E*(ERE), eV (Refs.8, 101)	calculated per π-electron			
		E(RE), β (Refs.99,108)	*E*(DRE), eV (Refs.105, 109–111)	*E*(HSRE), β (Refs.102, 112, 113)	*E*(TRE), β (Refs.114, 115)
Benzene	1.56	0.333	0.145	0.065	0.046
Naphthalene	2.64	0.368	0.132	0.055	0.039
Anthracene	3.62	0.380	0.114	0.047	0.034
Phenanthrene	3.96	0.389	0.138	0.055	0.039
Tetracene	4.77	0.385	0.101	0.042	0.031
Pentacene	—	0.388	0.091	0.038	0.029
Pyrene	4.72	0.407	0.131	0.051	0.037
Perylene	5.48	0.412	0.131	0.048	0.037
Azulene	1.30	0.336	0.017	0.023	0.015
Cyclobutadiene	—	0.000	−0.193	−0.268	−0.307
Benzocyclobutadiene	—	0.298	0.054	−0.027	−0.049
Pentalene	—	0.307	0.001	−0.018	−0.026
Cyclopropenium cation	—	—	—	0.365	0.268
Cyclopentadienyl anion	—	—	—	0.111	0.094
Tropylium cation	—	—	—	0.108	0.032
Pyridine	1.00	—	0.151	0.058	0.038
Pyrimidine	—	—	0.146	0.049	0.032
Pyrazine	—	—	0.106	0.049	0.022
Pyrrole	0.92	—	0.038	0.039	0.040
Furan	0.68	—	0.031	0.007	0.007
Thiophene	1.24	—	0.047	0.032	0.033
Quinoline	2.05	—	0.142	0.052	0.036
Isoquinoline	—	—	0.142	0.051	0.033
Indole	2.04	—	0.103	0.047	0.038
Isoindole	—	—	0.050	0.029	0.032
Carbazole	3.21	—	0.127	0.051	—

It should be noted that the conclusions about aromaticity that are based on the value of the resonance energy depend to a considerable extent on the quantum-chemical calculation method being used, particularly in borderline cases. An obvious example of this is the controversy over the nature of the electronic system of bicyclo[6.2.0]decapentaene (XXXI).[48] The system was predicted to be antiaromatic using the simple Hückel MO method and other methods, and at the same time from graph theory it was concluded to be diatropic,[121] which could have fundamental importance as a refutation of the obligatory interrelationship between diatropy and aromaticity. On the other hand, a non-empirical method gave an indication that it was weakly aromatic $E(\mathrm{RE}) = 0.17$ eV,[122] which is in better agreement with the conclusions from the experimental data (NMR, X-ray diffraction, thermochemical).[48] In order to avoid similar situations, it is advisable on the basis of calculations that only those systems with a large absolute value of the resonance energy should be termed aromatic (antiaromatic).[123]

The essential significance of the theoretical methods lies in their identification of the nature of aromatic stabilisation and establishing its relationship with magnetic and structural properties used as experimental criteria. The determination of a quantitative relationship between the resonance energy and the magnetic parameters of a molecule is regarded[59] as a considerable success. A simple ratio has been derived, relating the resonance energy to the ring current (K) and the non-local diamagnetic susceptibility resulting from it for [N]annulenes with $4n + 2$ π-electrons:[124,125]

$$E(\mathrm{RE}) = -\frac{\pi^2}{mS}K, \tag{1}$$

$$E(\mathrm{RE}) = -\mathrm{const}\,\frac{\chi^{\mathrm{nonloc}}}{S^2}, \tag{1'}$$

where S is the area of the ring (for benzene S is assumed to be 1), $m = 3$ [125] or $m = 4$,[126] $\mathrm{const} = -\frac{1}{8m}\left(\frac{hc}{e}\right)^2$. . The sign of the ring current indicating its direction, which is opposite in sign to the resonance energy, denotes that diatropy is a necessary attribute of aromaticity.[104] From equation (1) it is possible to develop a linear correlation between the ratio of the difference in chemical shifts ($\Delta\delta$) of the outer and inner protons in neutral aromatic [N]annulenes (see Table 2) to the area of the ring and the value of E(RE) per π-electron:[126]

$$\Delta\delta/S = k.E(\mathrm{RE})/\mathrm{N}, \tag{2}$$

where k is a proportionality coefficient. The relationship established between the resonance energy and the ring current, which shows that delocalisation of the bonding π-electrons in the ring serves as a common origin of both aromatic stabilisation and diamagnetic exaltation, provides a theoretical basis for using experimental magnetic criteria.

It was concluded from statistical treatment of the numerical values of 12 different indices of aromaticity for 15 heterocycles and benzene using the main characteristics that the structural criteria I and ΔN and the energy criterion DRE on the one hand and the magnetic criteria χ_M and Λ on the other hand are mutually orthogonal, constituting the scales of two types of aromaticity—"classical" and "magnetic".[89] The remaining indices occupy an intermediate position. No opinions are put forward about the physical nature of the orthogonality, even though this conclusion clearly contradicts the relationships in equations (1) and (2). It cannot be excluded that this is not related to the fundamental difference between the scales but to a deficiency in determining the numerical values of the magnetic characteristics χ_M and Λ, especially for heterocycles (see Section III).

IV. Aromaticity and reactivity

For a long time reactivity was the main criterion of aromaticity. A year after the publication by Kekulé on the structure of benzene and about aromatic compounds being structurally similar to

benzene, the idea was put forward by Eilenmeyer about the chemical similarity of aromatic compounds.[18] Since electrophilic substitution reactions are typical for benzene, it was the capacity for these reactions that was considered, and in a number of studies up to the present time has been considered, to be a sign of aromaticity. The tendency of aromatic compounds to undergo substitution rather than addition reactions, the tendency to "retain their form" is due to their increased thermodynamic stability, namely, to a reduced level of free energy. However, the reactivity depends not only on the level of the free energy of the ground state of the substrate but is determined by the difference between the levels of the ground and transition states—the free energy of activation. The energy of the transition state varies in general over such a wide range that the variation of the upper limit of the activation barrier can completely mask the effect of a change in the lower limit, which depends on the degree of aromaticity.

This is clearly illustrated by an examination of the following series of aromatic compounds: sodium cyclopentadienide, pyrrole, benzene, pyridine, tropylium bromide. The cyclopentadienyl anion undergoes electrophilic substitution extremely readily; on going to pyrrole and then benzene and pyridine the ease of electrophilic substitution is decreased, and up to now it has not been possible to involve the tropylium cation in any electrophilic reaction. On the other hand, tropylium salts react very readily with various nucleophilic reagents, pyridine undergoes these reactions with more difficulty, benzene reacts with great difficulty, and sodium cyclopentadienide does not react at all. In this series the reactivity towards electrophilic reagents decreases on going from the cyclopentadienyl anion. The same applies to the ease of nucleophilic nucleophilic reagents it is in the reverse order without any apparent relationship to the degree of aromaticity. The reason for the lack of correlation between the reactivity and aromaticity in this case is precisely because the energy of activation changes mainly as a result of the reduction or increase in the energy level of the transition state. The nature of this change is clear in terms of the collision theory. It is obvious that the repulsion forces which the converging particles have to overcome are incomparably greater when the particles have the same charge as in electrophilic attack on a tropylium cation that when they have different charges as in electrophilic attack on a cyclopentadienyl anion. The same applies to the ease of nucleophilic attack on a tropylium cation and its difficulty in the case of a cyclopentadienyl anion. The same applies to the ease of nucleophilic the π-deficient heterocycle of pyridine occupy respective intermediate positions between ions and benzene.

Even under ideal conditions for comparing compounds—with the reagent standardised, a common mechanism, the absence or levelling out of solvation, catalytic, and other effects—the reactivity depends directly on the degree of aromaticity only when the energy level of the transition state remains constant. In practice, these conditions cannot usually be achieved. Therefore reactivity cannot in general serve as a criterion of aromaticity. Only in a series of compounds that are similar in structure, when the changes in energy of the transition state and ground state are proportionate, there is a linear correlation between the changes in resonance energy and the free energy of activation, as for example in the case of the Diels–Alder reaction of aromatic hydrocarbons with maleic anhydride.[127] Moreover, the tendency for "preservation of form" is typical not only for aromatic but also for certain non-aromatic conjugated systems. On the strength of this, Lloyd and Marshall[13,128] proposed that aromatic and non-aromatic compounds that exhibit this tendency should be combined into the same group, having given them the new name "meneidic", and the term "aromatic" should be rejected, but they did not meet with support.

There is a fundamental and complex interdependence between reactivity and aromaticity rather than a simple relationship. The electronic structure of the substrate not only determines the lower level of the activation barrier but also has an effect on the structure of the transition state and intermediates. Information about aromaticity is not sufficient but entirely necessary for an understanding of reactivity. However paradoxical are the general features of reactivity, which cannot serve as a criterion of aromaticity but are extremely important in the practical sense, the main concern is what binds together the chemistry of aromatic compounds and prompts its separation into an independent branch of organic chemistry.

V. The concept of aromaticity

The accumulated facts and interrelationships suggest that cyclic conjugated molecules or ions have common structural features which are responsible for their stabilisation, and they are known as aromatic. The means of representing the electronic structure depends on the chosen method. When applying the MO method, which is that most widely used at the present time, the movement of electrons in delocalised orbitals is the topic under discussion, for the model with localised orbitals, their overlap (spin interaction) is being considered.[129]

Thus, the concept of aromaticity applies to molecules whose structural features serve to combine atoms into a ring and conjugation in the ring is "an alternating sequence (in the structural formula) of single and double bonds."[130] In ions this sequence is augmented with a cation or anion site. The physical scope of aromaticity in terms of the MO method is cyclic delocalisation of electrons causing a gain in energy, which stabilises the system.

Aromaticity is a special property of electron shells, and the latter cannot be observed directly. Therefore the objection to aromaticity on the grounds that it cannot be measured directly is unjust.[12] In reality aromaticity is exhibited in magnetic, structural, energy, and magnetic properties. If the phenomenon is not confused with its effect on properties, another objection to aromaticity, namely, that aromaticity is a combination of different ideas[13,14] is eliminated.

The present concept of aromaticity does not leave room for the ideas about different types of aromaticity that appear in the literature. In the vast majority of cases these ideas are based on a different, wider interpretation of aromaticity, where all distinguishing features apart from stabilisation of the system, including the occurrence of cyclic delocalisation or electrons and the ring itself, may be omitted as non-essential, and conjugation is taken to mean "overlap of the atomic *p* orbitals of three or more neighbouring atoms"[130] rather than an alternating sequence of bonds. The variety of types of aromaticity strengthens the position of critics of the concept, since if there are many "aromaticities", it may not as such exist. It is useful to examine the terms that have been introduced to denote the types of aromaticity, responding to two questions in each case: whether the type of stabilisation which is implied by the term introduced has been demonstrated, and if so, to what extent can it be justified to call this type of stabilisation aromatic.

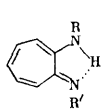
VI. Types of aromaticity

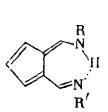
In the literature there are about 20 terms that are formed by adding a prefix or adjective to the word "aromaticity". Some of them only stress the degree of aromaticity (arch-, super-aromaticity)[14,53] or constitute abbreviations (heteroaromaticity,[9] perfluoroaromaticity[16]). Antiaromaticity (non-aromaticity) is the opposite of aromaticity and is an inherent part of the concept. Conjugated cyclic systems in which cyclic delocalisation of electrons leads to destabilisation are considered to be antiaromatic.[23] The remaining terms put forward to denote the types of aromaticity can be divided into three categories: those arising from the basic concept of aromaticity given above; those based on a wider interpretation of it; those related to an extension of the concept of aromaticity.

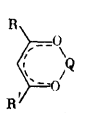
1. Ideas arising from the basic concept of aromaticity (pseudo-, non-classical, quasi-, homo-aromaticity)

Pseudoaromaticity. This term arose from the empirical rule of Craig for dividing conjugated mono- and poly-cyclic structures into aromatic and pseudoaromatic according to their formal symmetry sign in valency schemes.[131] The latter category contained those structures from which stabilisation could not be expected as a result of cyclic delocalisation of π-electrons, including all monocyclic molecules with $4n$ π-electrons starting with cyclobutadiene. Thus the concept of pseudoaromaticity in this sense completely duplicates the more contemporary concept of antiaromaticity. Moreover, single attempts were made to use the term pseudoaromaticity (and pseudoantiaromaticity) in a discussion of the *p*-orbital interactions in non-aromatic species—the cyclopropyl cation and anion,[132] and unsaturated diradicals.[133]

Non-classical aromaticity and quasiaromaticity. The terms non-classical aromaticity[134] and quasiaromaticity[135] have been put forward to represent the aromaticity of conjugated compounds with intramolecular hydrogen bonding (IHB), while quasiaromaticity has also been proposed for the aromaticity of metal chelates.[136] In these structures cyclic delocalisation of the π-electrons in a chelate ring involving vacant $2p$ orbitals of the hydrogen atom or *d* orbitals of the metal atom was proposed. For example, in compounds (XLVII) and (XLVIII) an aromatic 10π-electron system as in azulene has been proposed, with a symmetrical configuration of the hydrogen atom equidistant from the heteroatoms (when R = R′ = Ph), which would appear to be confirmed by the nature of the NMR spectra and the X-ray diffraction data. However, subsequent studies showed that this was an illusion created by the rapid prototropic tautomerism and the statistical distribution of tautomers in crystals. The asymmetric configuration of the hydrogen atom in IHB in compounds (XLVII) was demonstrated by spin-lattice relaxation,[137] and low-temperature ^{1}H NMR spectroscopy was used to demonstrate the existence of tautomers in compounds (XLVIII),[138] which excludes delocalisation via IHB, which would cause the stabilisation of a single form with equivalent bonds.


(XLVII)


(XLVIII)

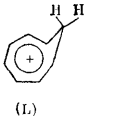

(XLIX)

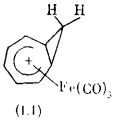
The ^{1}H NMR spectra of acetylacetonates (XLIX) do not provide any evidence of a ring current.[139,140] The displacement of the signals downfield is satisfactorily shown to be due to a redistribution of positive charge of both metal chelates and borochelates, although in the latter cyclic delocalisation is impossible since the tetrahedral boron atom does not have any vacant low-lying orbitals for the formation of π-bonds.[139] Hence the π-electron system in conjugated compounds with IHB and metal chelates is acyclic in nature. Lloyd and Marshall[141] suggested that the scope of the term "quasi-aromatic" should be changed and applied to non-aromatic compounds that are similar to aromatic compounds in the tendency to "retain their form", but shortly afterwards they rejected their proposal.[13] Recently this recommendation was put foward again.[123]

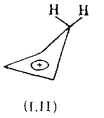
Homoaromaticity. The concept of homoaromaticity was put forward by Winstein in 1959 in relation to cyclic structures in which the sequence of conjugated bonds is interrupted one or more times by a methylene group with an sp^3-hybridised carbon atom. It was suggested that cyclic delocalisation of electrons may be preserved in this case because of overlap of the atomic *p* orbitals of non-bonded carbon atoms of a type intermediate between π- and σ-overlap. Mono-, bis-, and tris-homoaromaticity has been proposed in a very large number of structures, both neutral and charged (see reviews[142–144]), but homoaromaticity can only be regarded as firmly established in certain cations.

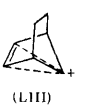
The clearest example of monohomoaromaticity is the homotropylium cation (L), which is formed by the action of strong acids on cyclooctatetraene. Arguments in favour of the homo-aromaticity of cation (L) were obtained from ^{1}H NMR spectra and X-ray diffraction data.[144] In the NMR spectra the signals from the protons of the methylene group differ markedly; the signal from the exocyclic proton occurs at 5.86 p.p.m. and that from the endocyclic proton is at −0.73 p.p.m. Such an unusual upfield shift of the latter signal for carbocations has been attributed to the effect of a ring current in the seven-membered residue, having a sextet of π-electrons. X-Ray diffraction analysis of 2-hydroxyhomotropylium hexachloroantimonate shows that the seven-membered residue has the conformation of a shallow boat, and the methylene group deviates from the average plane of this by approximately 90 degrees. The C(1)–C(7) distance of 1.626 Å suggests that there is a bonding interaction and at the same time excludes the alternative structure of a bicyclo[5.1.0]octadienyl cation. This type of bicyclic structure is exhibited by the ligand in a complex with iron tricarbonyl (LI), where the chemical shifts of the protons of the CH_2 group are almost the same (1.53 and 1.35 p.p.m.) while the C(1)–C(7) bond length in the fluoroborate is 1.474 Å.[144] A theoretical study of the structure of cation (L) reveals a minimum on the potential energy surface when the C(1)–C(7) bond length is 1.7–2.0 Å and the occurrence of a ring current.[145]

From among the other well studied homoaromatic cations, the cyclobutenyl (homocyclopropenium) (LII), 7-norbornenyl (bishomocyclopropenium) (LIII), and cyclohexenyl (trihomocyclopropenium) cations (LIV) may be mentioned.[143]


(L)


(LI)

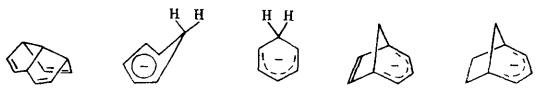

(LII)


(LIII)


(LIV)

In neutral molecules, as was recognised in the result of detailed experimental and quantum-chemical studies, homoaromatic stabilisation is absent,[146,147] and the corresponding structures are even destabilised through repulsion between the filled orbitals. However, for the bridged trishomobenzene — triquinacene (LV) — by determining the heat of hydrogenation compared to the corresponding monoolefin, the stabilisation energy was found[148] to be E(ERE) = 0.19 eV, which would appear to require the question to be raised again.

Even more controversial is the question of homoaromaticity in anions. It was shown by means of NMR spectroscopy that the anions formed by deprotonation of 1,3- and 1,4-cyclohexadienes have the planar structure of the cyclohexadienyl anion (LVII) [149] rather than the structure of the homocyclopentadienyl anion (LVI). The main debate has revolved around the homoaromaticity of the bicyclo[3.2.1]octadienyl anion (LVIII). Deuterium exchange (DMSO/t-BuOK) in a hydrocarbon corresponding to anion (LVIII) occurs $10^{4.5}$ time faster than in its analogue without a double bond, corresponding to anion (LIX).[150] A determination of the acidity of the hydrocarbons in cyclohexylamine by treatment with caesium cyclohexylamide[151] and in the gas phase[152] shows that anion (LVIII) is more stable than anion (LIX) by 51 and 44 kJ mol^{-1} respectively. In the ^{1}H and ^{13}C NMR spectra of the anion the signals from the nuclei at the double bond in the 6- and 7-positions are displaced 2.3 p.p.m. (^{1}H) downfield and 43.8 p.p.m. (^{13}C) upfield compared to the spectrum of the conjugated acid, which suggests the delocalisation of negative charge involving the double bond.[153] The authors of the experimental studies regard these findings as proof of the bishomoaromaticity of anion (LVIII). However, it was concluded from quantum-chemical calculations carried out using semiempirical and non-empirical methods[154,155] that homoaromaticity does not play a substantial role in the stabilisation of anion (LVIII), which is attributed to the inductive effect of the double bond. Calculations by Brown et al.[156] led to the opposite conclusion, but a non-empirical calculation at a higher level[157] confirmed the absence of homoaromaticity. In order to account for the delocalisation of charge, the suggestion was made concerning salts of anion (LVIII) existing in solution as a contact ion pair in which the metal atom serves as a charge relay between the double bond and the anion site.[157] This hypothesis is supported by the agreement between the results of calculating the ion pair between the bicyclooctadienyl anion (LVIII) and lithium cation[158] and the X-ray diffraction data for the complex between lithium bicyclooctadienide and tetramethylethylenediamine.[159]



(LV) (LVI) (LVII) (LVIII) (LIX)

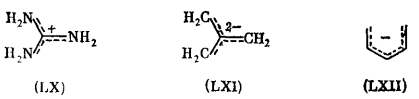
Thus in this group of examples only homoaromaticity relates to a proven structural form of aromaticity, characteristic of only a fairly limited group of carbocations.

2. Ideas arising from a wider interpretation of the concept of aromaticity (*Y*-, *U*-, bicyclic, spiro-, in-plane, double, trefoil, cruciform, metallo-, three-dimensional, and spherical aromaticity)

In accordance with a wider interpretation, the concept of aromaticity can be applied to various systems where there is stabilisation through orbital interactions. The forms of aromaticity differ from each other according to the manner of overlap of the atomic orbitals in the respective structures.

Y-Aromaticity. This is an application of the concept of aromaticity to a non-cyclic system. The term was introduced[160] to interpret the remarkable stability of the acyclic guanidinium cation (LX), as a result of which the basicity of guanidine (pK_a = 13.6) approaches that of the hydroxide anion. The stability of cation (LX) has been related to the completeness of its electron shell, which is formed by π-overlap of atomic p orbitals in which 6 electrons, as in the benzene molecule, are located in three bonding MOs, which gives rise to the analogy. This type of stabilisation has been proposed in other species with a *Y*-configuration,[160] in particular in the trimethylenemethane dianion (LXI).[161] However, dimetallation of 2-methyl-1,5-hexadiene does not give a substituted trimethylenemethane dianion.[162] Quantum-chemical calculations of the isolated dianion (LXI) and its derivatives indicate that D_{3h} symmetry is energetically preferred,[163,164] but in the crystalline state of the dilithium salt of the tribenzylidenemethane dianion an asymmetric structure occurs, with a geometry that is determined by the interaction with the counterions.[164] The stability of the guanidinium cation (LX) and similar heteroatomic structures is accounted for by the rule of topological stabilisation of charge[165] — the advantage in replacing carbon atoms by a more electronegative heteroatom at those positions where there is the highest electron density in the isoelectronic hydrocarbon. Stable ions with a *Y*-configuration are classified as quasiaromatic (see above), namely, they do not possess aromaticity but display a tendency to preserve their system of conjugation.[123]

U-Aromaticity. This term is used in relation to stabilisation of the *U*-conformation of 6π-electron anions of acyclic conjugated polyolefins — the 1,3-butadienyl dianion, 1,3,5-hextrienyl dianion, and pentadienyl anion (LXII) — through orbital interactions.[161]



(LX) (LXI) (LXII)

Bicycloaromaticity. The concept of bicycloaromaticity was introduced[166,167] in relation to bicyclic ions in which the charged site is formally included simultaneously in two bishomoaromatic rings with $4n + 2$ π-electrons, as in the 7-norbornadienyl cation (LXIII) or bicyclo[3.2.2]nonatrienyl anion (LXIV). It has been suggested that the orbital interaction between the two bishomoaromatic rings results in additional stabilisation through the formation of a single bicycloaromatic system. The fact that cation (LXIII) is stabilised relative to its saturated analogue (LXV) is not in doubt. Solvolysis of 7-X-norbornadiene (X = Cl, OTs), giving cation (LXIII), occurs 10^{14} times faster than the solvolysis of 7-X-norbornane, which is regarded as the "world record" for anchimeric assistance.[142] The question arises as to what proportion of the stabilisation energy is due to bishomoaromaticity and how much can be attributed to bicycloaromaticity. Comparison with the solvolysis of 7-*anti*-X-norbornene, which gives the bishomocyclopropenium cation (LIII), shows that introduction of one double bond increases the rate of solvolysis by a factor of 10^{11} while introduction of the second double bond with a conversion to cation (LXIII) increases it by a factor of 10^3.[168] Hence, the main role is played by bishomoaromaticity. Since in the 7-norbornadienyl cation (LXIII), where the

conditions for bicycloaromaticity are most favourable, the effect is small, there is no serious basis for expecting bicycloaromaticity in other cationic structures.[154,168] In order to interpret the effect of the bridging double bond in cations of the type (LXIII), which is one of a large number of cases of neighbouring group participation, it is quite unnecessary to resort to ideas of a special type of aromaticity. As far as anions of the type (LXIV) are concerned, the probable absence of homoaromatic stabilisation in anions (see above) eliminates the question of their bicycloaromaticity.



(LXIII) (LXIV) (LXV)

Spiroaromaticity. This has been suggested[169,170] in relation to the concept of spiroconjugation,[171] which is the stabilisation in unsaturated spiro compounds, such as in *spiro*-[4,4]nonatetraene (LXVI), through overlap of orthogonal *p* orbitals of the atoms of the double bonds adjacent to the nodal carbon atom. The consequence of spiroconjugation is a relative change in the HOMO and LUMO levels, so that experimental confirmation of the effect can be seen mainly in displacement of maxima in the electronic and photoelectronic spectra.[171] However, theoretical analysis using perturbational molecular orbital theory[172] leads to the conclusion that the total stabilisation due to spiroconjugation, called spiroaromaticity, is not significant in the molecule of (LXVI), and on increasing or decreasing the size of the rings becomes even less likely. The only case of appreciable stabilisation was predicted in *spiro*-[3.3]heptadienyl (LXVII) as a hypothetical non-classical species.[172]



(LXVI) (LXVII)

In-plane (radial), double, and trefoil aromaticity. All these variants of aromaticity assume that a cyclopolyene is stabilised through overlap of the radially positioned *p* orbitals lying in the plane of the ring. A group of compounds in which in-plane (radial) aromaticity[147] can be visualised is made up by [*n*]pericyclynes, which are cyclic hydrocarbons with a skeleton made up of *n* acetylene residues alternating with CH_2 groups. In pericyclynes the interaction between *p* orbitals lying in orthogonal planes has been studied theoretically.[173,174] The best conditions for in-plane orbital interaction exist in the first member of the series—the so far unknown [3]pericyclyne (LXVIII). Overlap of the orbitals in its molecule could be expected to lead to the formation of two 6π-electron systems—trishomoaromatic and in-plane. However, a quantum-chemical calculation (MNDO method) shows that [3]pericyclyne (LXVIII) is less stable by 2.63 eV than its valence isomer, tricyclopropanebenzene (LXIX).[174] In decamethyl-[5]pericyclyne the empirical resonance energy has been determined thermochemically as being of the order of 0.34 eV, attributed to homoconjugation[175] rather than in-plane conjugation. As a result of the calculation (MNDO) of about 100 different three-dimensional structures in which radial overlap could be expected, only in one of the isomers of dodecahedropentaene was a stabilisation energy of the order of 0.35 eV recorded.[147]



(LXVIII) (LXIX) (LXX)

The term "double aromaticity" was applied[176] to the 3,5-dehydrophenyl cation (LXX), the structure of which is assigned to the $C_6H_3^+$ ion in the mass spectrum. In cation (LXX), in addition to a sextet of π-electrons, a three-centre, two-electron bond inside the ring has been postulated, which provided a basis for suggesting aromaticity in orthogonal planes or double aromaticity.

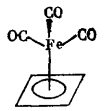
The idea of such a three-centre, two-electron bond in annulenes with $4n + 2$ π-electrons on the periphery has been put forward as a new type of aromaticity—trefoil aromaticity—and the respective structures as a potentially new class of aromatic molecules for which a new name has been proposed—trefoilenes, for example, [5.5.5]trefoilene (LXXI).[177] However, calculations have so far not confirmed the energy preference of the trefoilene configuration in any single model.[147] In all cases the valence isomers have proved much more stable; for example, the so far unknown trisallene (LXXII) is more stable by 4.3 eV than the hypothetical [5.5.5]trefoilene (LXXI).[178] According to calculations,[179] structure (LXXI) is only possible as a transition state of the degenerate isomerisation of a bicyclic carbene.



(LXXI) (LXXII) (LXXIII)

Cruciaromaticity. This has been put forward[180] to denote the orbital interaction in planar complexes of unsaturated ligands with transition metals such as iron in (LXXIII), where intersection of two π-systems occurs as a result of the participation in them of d_{xz} and d_{yz} metal orbitals, the plane of which form a cross on the surface.

Metallo- and three-dimensional aromaticity. A considerable advance in organometallic chemistry was the synthesis of a complex between the antiaromatic cyclobutadiene molecule and iron tricarbonyl $C_4H_4Fe(CO)_3$, which proved to be a stable compound that underwent electrophilic substitution without decomposition. A large number of complexes of cyclobutadiene with other metals have been prepared (see reviews[181,182]). According to X-ray diffraction data the $C_4H_4Fe(CO)_3$ complex is in the form of a bipyramid (LXXIV), at the base of which is a square with a side of 1.44 Å and at the apex is an iron atom with an Fe–C distance of 2.05 Å. Quantum-chemical calculation using a non-empirical method[183] shows that the C_4H_4Fe residue has 6 electrons in three bonding orbitals which are formed by effective overlap of the cyclobutadiene orbitals (e_g) with d_π orbitals of iron that have a similar level of energy. The C_4H_4–Fe bond is largely covalent. On the whole the molecule can be represented as the C_4H_4Fe metalloaromatic fragment perturbed as bonding with carbonyls. In contrast to compounds (LXXIV), complexes of transition metals with benzene and the cyclopentadienyl anion having the general formula (LXXV) should more accurately be regarded as systems of benzene and the cyclopentadienyl anion perturbed by bonding with the metal[183] rather than metalloaromatic systems.



(LXXIV)



(LXXV)



(LXXVI)

Complexes with the general formula (LXXV), where X above the annulene ring at the apex of the pyramid is not necessarily a transition metal atom but may also be an atom of an element from the first period (Li, Be, B, C, N), have been assigned[184] to a special type of three-dimensional aromatic system where there is a complete electron shell with $4n + 2$ π-electrons, regardless of whether the bonding of the X-link is a decisive factor. In this case, for example, the unstable complex π-complex of benzene with the Li^+ cation (LXXVI) is classed as an example of three-dimensional aromaticity on a level with the cyclobutadiene complex (LXXIV). More justified is the approach[183] in which the weak interactions are regarded as an excitation of the planar aromatic system. Pyramidal structures of the type (LXXV) and other three-dimensional non-classical structures have been successfully represented without involving the concept of aromaticity.

Spherical aromaticity. When the surface of a graphite disk is evaporated using a laser beam, among the products is detected a stable C_{60} cluster,[186] for which the structure of a truncated icosahedron having 12 five-membered and 20 six-membered rings on the surface of a sphere has been proposed. The structure, which has been called buckminsterfullerene or footballene, has so far not been substantiated, but has attracted the attention of theoretical chemists as an example of a compound with possible spherical aromaticity.[187,188] According to the value of the resonance energy per π-electron this structure can be classed as aromatic, but judging by the ratio of the resonance energy to the total π-electron energy of the reference structure (% RE), the stabilisation energy is insufficient to isolate buckminsterfullerene in macroscopic quantities.[187] A theoretical analysis of the magnetic properties led to the conclusion that this compound should be very slightly diamagnetic.[189]

Thus, the types of stabilisation of molecules or ions that are described by forms of aromaticity constitute in the majority of cases unproven or rejected ideas. In the individual cases where the stabilisation effect has been established, it can be interpreted without difficulty independently of the concept of aromaticity. A wider interpretation of the concept of aromaticity is not appropriate since, not having a proper basis or being created through necessity, it has a destructive effect on the concept of aromaticity as a whole. The acceptance of a wider interpretation would signify a rejection of the elaborated experimental criteria of aromaticity, both magnetic, related to the ring current, and structural, which are inapplicable to non-planar or acyclic structures, and also ideas about the common nature of aromatic reactivity.

3. Extension of the concept of aromaticity. σ-Aromaticity.

The generally accepted ideas about the electronic structure of organic compounds are based on models, according to which π-electrons are distinct from the electrons of σ-bonds. It is assumed in this case that the σ-system consists of effectively localised two-centre, two-electron bonds, and that all deviations from additivity, including those related to aromaticity, are due to delocalisation of the π-system. However, both types of bond, both π and σ, can exhibit "localisation" and "delocalisation" to comparable degrees.[190] Additivity of the properties of σ-bonds is not due to the absence of σ-delocalisation but occurs because the interaction between neighbouring σ-bonds is approximately constant, does not depend on the environment, and in calculations is included in the empirical bond constants. As the individual sp^3-hybridised orbitals of a carbon atom interact effectively with each other, each CH_2 group in an alkane can be regarded as an equivalent valence group in a polyene. The system of hybrid orbitals of the C–C bonds in cyclopropane is topologically similar to the π-orbital system of benzene, while the cyclobutane system is topologically similar to the system of planar cyclooctatetraene. Therefore, by analogy with π-aromaticity and π-antiaromaticity, the question of the σ-aromaticity of cyclopropane and the σ-antiaromaticity of cyclobutane can be raised.[179,190] The concept of σ-aromaticity for cyclopropane can be used to explain its outstanding stability and other properties.[190,191] The same criteria of aromaticity as those for π-aromatic systems are applied to cyclopropane, including the cyclic delocalisation of electrons found in the magnetic properties from NMR spectroscopic data and the Dewar resonance energy, which constitutes 0.694 eV.[192] From an analysis of orbital interactions, electronic calculation rules for the determination of σ-aromaticity in cyclic structures have been formulated.[193,194] With an increase in size of the ring the degree of aromaticity decreases so rapidly that even in cyclopentane it is extremely small and cannot have any appreciable effect on its properties. Only π,σ-aromatic compounds, from which the greatest contribution is provided by σ-aromaticity in the cyclopropenium cation ($2\pi 6\sigma$), have a high stabilisation energy. In an article by Cremer[192] entitled "For and against σ-aromaticity", it is observed that the characteristics of cyclopropane may adequately be represented using the concept of "surface" overlap of the σ-orbitals instead of σ-aromaticity, while the characteristics of a tetrahedron[195] can be represented by "three-dimensional" overlap instead of three-dimensional σ-aromaticity.

It was important to determine how the inclusion of electrons from σ-bonds would effect the basic conclusions of the aromaticity concept that were derived from a model that took only π-electron delocalisation into consideration. It was shown by non-empirical calculations of the benzene molecule[196] that on going from a structure with D_{6h} symmetry to a Kekulé structure with D_{3h} symmetry and alternating bonds the π-electron energy decreases but the σ-electron energy increases to a greater degree, in other words, equalising the bonds is determined by the σ-skeleton. The question arises as to the legitimacy of using the equalising the bonds as a structural criterion of aromaticity related to the cyclic delocalisation of π-electrons. Calculation of the topological resonance energy (see Section III)[197] led to the separation of a component resulting from the cyclic π-electron delocalisation and having, as it transpired, the opposite sign to the change in total π-electron energy of the system. The decrease in the latter on distorting the symmetrical structure of benzene to a Kekulé structure occurs at the same time as an increase in energy of the cyclic π-electron delocalisation, as a result of which it is possible to balance the increase in σ-electron energy. On the other hand, in the case of the antiaromatic cyclobutadiene the change from a square structure to the structure of a rectangle with alternating bonds causes a decrease in both the total π-electron energy and the energy of the cyclic π-electron delocalisation, as a result of which the decrease in π-electron energy is not balanced by the increase in σ-electron energy and the structure with alternating bonds proves to be more stable. Thus, equivalence of bond lengths is in fact related to cyclic delocalisation of the π-electrons and can be

justified as a criterion of aromaticity. The concept of σ-aromaticity does not contradict the concept of π-aromaticity but complements it, as ideas about σ-conjugation complement the generally accepted theory of the structure of organic compounds.

- - - o 0 o - - -

The current concept of aromaticity which is based on the progress in the synthesis of aromatic systems and their study using experimental physical techniques and theoretical quantum-chemical methods relates to conjugated cyclic systems that have cyclic delocalisation of electrons. As a special property of the electron shell, aromaticity is exhibited in their properties, from which magnetic, structural, and energy characteristics can serve as criteria of aromaticity, but reactivity cannot since it depends not only on the ground state but also on the transition state. The extension of the concept of aromaticity to systems that are devoid of cyclic declocalisation of electrons, resulting in ideas about multiple types of aromaticity, is unjustified and inappropriate. The common nature of the electronic structure and properties is responsible for the chemistry of aromatic compounds being formed as a separate branch of organic chemistry.

References

1. M E Vol'pin *Usp. Khim.*, 1960, **29**(3) 298 [English translation in *Russ. Chem. Rev.*, 1960(3)]
2. G M Badger *Aromatic Character and Aromaticity*, Cambridge University Press, Cambridge, 1969
3. D Lewis, D Peters *Facts and Theories of Aromaticity*, Macmillan Press, London, 1975
4. D Lloyd *Non-benzenoid Conjugated Carbocyclic Compounds*, Elsevier, Amsterdam, 1984
5. P J Garratt *Comprehensive Organic Chemistry*, Vol. 1 (Edited by D Barton, W D Ollis) (Translated into Russian from English), 1981, pp 218, 455
6. P J Garratt *Aromaticity*, Wiley, New York, 1986
7. L S Efros, M V Gorelik *Khimiya i Tekhnologiya Promezhutochnykh Produktov* (The Chemistry and Technology of Intermediates), Izd. Khimiya, Leningrad, 1980, p. 8
8. M J Cook, A R Katritzky, P Linda *Adv. Heterocycl. Chem.*, 1974, **17** 257
9. A F Pozharskii *Khim. Geterotsikl. Soedin.*, 1985, 867
10. M N Glukhovtsev, B Ya Simkin, V I Minkin *Usp. Khim.*, 1985, **54**(1) 86 [English translation in *Russ. Chem. Rev.*, 1985(1)]
11. H-G Frank, J W Stadelhofer *Industrial Aromatic Chemistry*, Springer, Berlin, 1988
12. E Heilbronner *Aromaticity, Pseudo-Aromaticity, Anti-Aromaticity* (Edited by E D Bergmann, B Pullman), Israel Acad. Sci. Humanities, Jerusalem, 1971, p. 21
13. D Lloyd, D R Marshall *Aromaticity, Pseudo-Aromaticity, Anti-Aromaticity* (Edited by E D Bergmann, B Pullman), Israel Acad. Sci. Humanities, Jerusalem, 1971, p. 85
14. J-F Labarre, F Crasnier *Top. Curr. Chem.*, 1971, **38** 33
15. G Binsch *Naturwissenschaften*, 1973, **60** 369
16. A T Balaban *Pure Appl. Chem.*, 1980, **52** 1409
17. B Ya Simkin, M N Glukhovtsev *Khim. i Zhizn'*, 1984, (9) 16
18. J P Snyder *Nonbenzenoid Aromatics*, Academic Press, New York, 1969, p. 1
19. W Doering, L H Knox *J. Am. Chem. Soc.*, 1954, **76** 3203
20. R Breslow, J T Groves *J. Am. Chem. Soc.*, 1970, **92** 984
21. G A Olah, J S Staral *J. Am. Chem. Soc.*, 1976, **98** 6290
22. T Bally, S Masamune *Tetrahedron*, 1980, **36** 343
23. R Breslow *Acc. Chem. Res.*, 1973, **6** 393
24. G Maier, H-O Kalinowski, K Euler *Angew. Chem.*, 1982, **94** 706
25. D W Whitman, B K Carpenter *J. Am. Chem. Soc.*, 1982, **104** 6473
26. P J Garratt, R Zahler, *J. Am. Chem. Soc.*, 1978, **100** 7753
27. B A Hess, C S Ewig, L J Schaad *J. Org. Chem.*, 1985, **50** 5869
28. G A Olah, J S Staral, G Liano, et al. *J. Am. Chem. Soc.*, 1977, **99** 3349
29. G K Prakash, T N Rawdah, G A Olah *Angew. Chem.*, 1983, **95** 356
30. T J Katz *J. Am. Chem. Soc.*, 1960, **82** 3784
31. T J Katz, P J Garratt *J. Am. Chem. Soc.*, 1964, **86** 5194
32. E A LaLancette, R E Benson *J. Am. Chem. Soc.*, 1965, **87** 1941
33. G I Fray, R G Saxton *Chemistry of Cyclooctatetraene and its Derivatives*, Cambridge University Press, Cambridge, 1978
34. S Masumune *Acc. Chem. Res.*, 1972, **5** 272
35. E Vogel *Chimia*, 1968, **22** 21
36. E Vogel *Pure Appl. Chem.*, 1982, **54** 1015
37. M Simonetta *Pure Appl. Chem.*, 1980, **52** 1597
38. S Masamune, D W Brooks *Tetrahedron Lett.*, 1977, **18** 3239
39. L T Scott, W R Brunsvold, M A Kirms, I Erden *Angew. Chem.*, 1981, **93** 282
40. R McCague, C J Moody, C W Rees *J. Chem. Soc., Perkin Trans. 1*, 1984, 165
41. F Sondheimer *Acc. Chem. Res.*, 1972, **6** 81
42. M Nakagawa *Pure Appl. Chem.*, 1975, **44** 885
43. V Boekelheide *Pure Appl. Chem.*, 1975, **44** 751
44. W Huber, J Lex, T Meul, K Müllen *Angew. Chem.*, 1981, **93** 401
45. T Otsubo, R Gray, V Boekelheide *J. Am. Chem. Soc.*, 1978, **100** 2449
46. H Ogawa, N Sadaraki, T Imoto, et al. *Angew. Chem.*, 1983, **95** 412
47. M Rabinovich, I Willner, A Minsky *Acc. Chem. Res.*, 1983, **16** 298
48. M Oda *Pure Appl. Chem.*, 1986, **58** 7
49. N Nakagawa *Angew. Chem.*, 1979, **91** 215
50. H Heaney *Comprehensive Organic Chemistry*, Vol. 1 (Edited by D Barton, W D Ollis) (Translated into Russian from English), Izd. Khimiya, Moscow, 1981, p. 433
51. I Agranat, B A Hess, L J Schaad *Pure Appl. Chem.*, 1980, **52** 1399
52. H A Staab, F Diederich, C Krieger, D Schmitzer *Chem. Ber.*, 1983, **116** 3504
53. P M Lahti *J. Org. Chem.*, 1988, **53** 4590
54. P M Keehn, S M Rosenfeld (Editors) *Cyclophanes*, Vol. 1, Academic Press, New York, 1983, p. 2
55. A G Annastassiou *Pure Appl. Chem.*, 1975, **44** 751
56. A G Annastassiou, H S Kasmai *Adv. Heterocycl. Chem.*, 1978, **23** 55
57. D Leaver *Pure Appl. Chem.*, 1986, **58** 143
58. W Flitsch *Pure Appl. Chem.*, 1986, **58** 153
59. R B Mallion *Pure Appl. Chem.*, 1980, **52** 1544
60. W H Flygare *Chem. Rev.*, 1974, **74** 653
61. P C M Zijl, B H Ruessink, J Bulthus, C MacLean *Acc. Chem. Res.*, 1984, **17** 172

62. Yu B Vysotskii *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, 1980, (2) 3
63. H J Dauben, J D Wilson, J L Laity *Nonbenzenoid Aromatics*, Vol. 2 (Edited by J P Snyder), Academic Press, New York–London, 1971, p. 167
64. C K Ingold *Theoretical Principles of Organic Chemistry* (Translated into Russian from English), Izd. Mir, Moscow, 1973, p. 191
65. A K Burnham, J Lee, T G Schmalz, et al. *J. Am. Chem. Soc.*, 1977, **99** 1836
66. S V Bulgarevich, T A Yusman, O A Osipov *Zh. Obshch. Khim.*, 1984, **54** 1603
67. S Kawajima, Z G Soos *J. Am. Chem. Soc.*, 1987, **109** 107
68. M Barfield, D M Grant, D Ikenberry *J. Am. Chem. Soc.*, 1975, **97** 6956
69. H Günther *Introductory Course on NMR Spectroscopy* (Translated into Russian), Izd. Mir, Moscow, 1984, pp 121, 403
70. F M Dean, R S Varma *Tetrahedron*, 1982, **38** 2069
71. J Liebe, C Wolff, C Krieger, et al. *Chem. Ber.*, 1985, **118** 4144
72. J E Rice, T L Lee, R B Remington, et al. *J. Am. Chem. Soc.*, 1987, **109** 2902
73. L W Jenneskens, J C Klamer, H J R De Boer, et al. *Angew Chem.*, 1984, **96** 236
74. P C M Zijl, L W Jenneskens, E W Bastian, et al. *J. Am. Chem. Soc.*, 1986, **108** 1415
75. T J Lee, J E Rice, W D Allen, et al. *Chem. Phys.*, 1988, **123** 1
76. H Wynberg, W C Nieuwpoort, H T Jonkman *Tetrahedron Lett.*, 1973, 4623
77. R C Haddon *Acc. Chem. Res.*, 1988, **21** 243
78. B L Podlogar, W A Glauser, W R Rodriguez, D J Raber *J. Org. Chem.*, 1988, **53** 2129
79. M Bremer, P R Schleyer *J. Am. Chem. Soc.*, 1989, **111** 1147
80. L V Vilkov, V S Mastryukov, N I Sadova *Opredelenie Geometricheskogo Stroeniya Svobodnykh Molekul* (Determination of the Geometric Structure of Free Molecules), Izd. Khimiya, Leningrad, 1978
81. O Ermer *Angew. Chem.*, 1987, **99** 791
82. R Janoschek *Angew. Chem.*, 1987, **99** 1312
83. M Sundaralingam, L H Jensen *J. Am. Chem. Soc.*, 1966, **88** 198
84. S Z Goldberg, K N Raymond, C A Harmon, D H Templeton *J. Am. Chem. Soc.*, 1974, **96** 1348
85. W C Herndon *J. Am. Chem. Soc.*, 1974, **96** 7605
86. J Ashe *Acc. Chem. Res.*, 1978, **11** 153
87. A Julg *Aromaticity, Pseudo-aromaticity, Anti-aromaticity* (Edited by E D Bergman, B Pullman), Israel Acad. Sci. Humanities, Jerusalem, 1971, p. 383
88. J P Gastmans, D F Gastmans, P da Camara *Eclectica Quim.*, 1981, **6** 43; *Chem. Abs.*, 1983, **98** 33937
89. A R Katritzky, P Barczynsky, G Musumara, et al. *J. Am. Chem. Soc.*, 1989, **111** 7
90. J Kruszewski, T M Krygowski *Can. J. Chem.*, 1975, **53** 945
91. C W Bird *Tetrahedron*, 1985, **41** 1409
92. C W Bird *Tetrahedron*, 1986, **42** 89
93. C W Bird *Tetrahedron*, 1987, **43** 4725
94. K Jug *J. Org. Chem.*, 1983, **48** 1344
95. M H Palmer, S M F Kennedy *J. Chem. Soc., Perkin Trans. 2*, 1976, 81
96. P George *Chem. Rev.*, 1975, **75** 85
97. R Breslow, J L Grant *J. Am. Chem. Soc.*, 1977, **99** 7745
98. A Kende *Adv. Chem. Phys.*, 1965, **8** 133
99. K Komatsu, I Tomioka, K Okamoto *Tetrahedron Lett.*, 1980, 947
100. D Bethell, R Gold *Carbonium Ions* (Translated into Russian), Izd. Mir, Moscow, 1970, p. 144
101. A Streitwieser *The Theory of Molecular Orbitals for Organic Chemists* (Translated into Russian from English), Izd. Mir, Moscow, 1965
102. B A Hess, L J Schaad *Pure Appl. Chem.*, 1980, **52** 1471
103. J Aihara *Bull. Chem. Soc. Jpn.*, 1977, **50** 3057
104. J Aihara *Pure Appl. Chem.*, 1982, **54** 1115
105. M J S Dewar, C de Liano *J. Am. Chem. Soc.*, 1969, **91** 789
106. N C Baird *J. Chem. Educ.*, 1971, **48** 509
107. H Kollmar *J. Am. Chem. Soc.*, 1979, **101** 4832
108. W C Herndon, M L Ellzey *J. Am. Chem. Soc.*, 1974, **96** 6631
109. M J S Dewar, A J Harget, N Trinajstic *J. Am. Chem. Soc.*, 1969, **91** 6321
110. M J S Dewar, N Trinajstic *J. Am. Chem. Soc.*, 1970, **92** 1455
111. M J S Dewar, A J Harget, N Trinajstic, S D Worley *Tetrahedron*, 1970, **26** 4505
112. B A Hess, L J Schaad *J. Am. Chem. Soc.*, 1971, **93** 305
113. B A Hess, L J Schaad, C W Holyoke *Tetrahedron*, 1972, **28** 3657
114. J Aihara *J. Am. Chem. Soc.*, 1977, **99** 2048
115. I Gutman, M Milun, N Trinajistic *J. Am. Chem. Soc.*, 1977, **99** 1692
116. L J Schaad, B A Hess *Pure Appl. Chem.*, 1982, **54** 1097
117. W C Herndon, H Hosoya *Tetrahedron*, 1984, **40** 3987
118. M Randic, *Tetrahedron*, 1977, **33** 1905
119. E Clar *Polycyclic Hydrocarbons*, Vol. 1 (Translated into Russian from English), Izd. Khimiya, Moscow, 1971, p. 41
120. E Clar *The Aromatic Sextet*, Wiley, London, 1972
121. J Aihara *Bull. Chem. Soc. Jpn.*, 1981, **54** 1245
122. D Cremer, T Schmidt, C W Bock *J. Org. Chem.*, 1985, **50** 2684
123. J Aihara *Bull. Chem. Soc. Jpn.*, 1987, **60** 2268
124. R C Haddon *J. Am. Chem. Soc.*, 1979, **101** 1722
125. J Aihara *Bull. Chem. Soc. Jpn.*, 1980, **53** 1163
126. A Verbruggen *Bull. Soc. Chim. Belg.*, 1982, **91** 865
127. W C Herndon *Chem. Commun.*, 1977, 817
128. D Lloyd, D R Marshall *Angew Chem.*, 1972, **84** 447
129. D L Cooper, S C Wright, J Gerratt, M Raimondi *J. Chem. Soc., Perkin Trans. 2*, 1989, 255
130. *Nomenklaturnye Pravila IYuPAK po Khimii* (IUPAC Nomenclature Rules for Chemistry), Vol. 5, Izd. VINITI (All-Union Institute of Scientific and Technical Information), Moscow, 1985, pp. 147 235
131. D P Craig *Theoretical Organic Chemistry* (Translated into Russian from English), Izd. Inostr. Lit., Moscow, 1963, p. 31
132. D T Clark, D R Armstrong *Chem. Commun.*, 1969, 850
133. L A Paquette, M R Short, J F Kelly *J. Am. Chem. Soc.*, 1971, **93** 7179
134. W R Brasen, H E Holmquist, R E Benson *J. Am. Chem. Soc.*, 1961, **83** 3125
135. D N Shigorin *Vodorodnaya Svyaz'* (Hydrogen Bonding) (Edited by N D Sokolov, V M Chulanovskii), Izd. Nauka, Moscow, 1964, p. 195
136. J P Collman, R L Marshall, W L Young *Chem. Ind. (London)*, 1962, 1380
137. L M Jackman, J C Trewella *J. Am. Chem. Soc.*, 1979, **101** 6428
138. U Müller-Westerhoff *J. Am. Chem. Soc.*, 1970, **92** 4849
139. R C Fay, N Serpone *J. Am. Chem. Soc.*, 1968, **90** 5701
140. M Kuhr, H Musso *Angew. Chem.*, 1969, **81** 150

141. D Lloyd, D R Marshall *Chem. Ind.*, 1964, 1760
142. S Winstein *Carbonium Ions* (Translated into Russian from English), Izd. Mir, Moscow, 1976, p. 9
143. L A Paquette *Angew. Chem.*, 1978, **90** 114
144. R F Childs *Acc. Chem. Res.*, 1984, **17** 347
145. R C Haddon *J Am. Chem. Soc.*, 1988, **110** 1108
146. K N Houk, R W Gandour, R W Strozier, et al. *J. Am. Chem. Soc.*, 1979, **101** 6797
147. A B McEwen, P R Schleyer *J. Org. Chem.*, 1986, **51** 4357
148. J F Liebman, L A Paquette, J R Peterson, D W Roger *J. Am. Chem. Soc.*, 1986, **108** 8267
149. G A Olah, G Arsenio, H Mayr, P R Schleyer *J. Am. Chem. Soc.*, 1978, **100** 4347
150. J M Brown, J L Occolowitz *J. Chem. Soc. B*, 1968, 411
151. W N Washburn *J. Org. Chem.*, 1983, **48** 4287
152. R E Lee, R R Squires *J. Am. Chem. Soc.*, 1986, **108** 5078
153. M Christl, H Leininger, D Brückner *J. Am. Chem. Soc.*, 1983, **105** 4843
154. J B Grutzner, W L Jorgensen *J. Am. Chem. Soc.*, 1981, **103** 1372
155. E Kaufmann, H Mayr, J Chandrasekhar, P R Schleyer *J. Am. Chem. Soc.*, 1981, **103** 1375
156. J M Brown, R J Elliott, W G Richards *J. Chem. Soc., Perkin Trans. 2*, 1982, 485
157. R Lindh, B O Roos, G Jonsäll, P Ahlberg *J. Am. Chem. Soc.*, 1986, **108** 6554
158. P R Schleyer, E Kaufmann, A J Kos, et al. *Chem. Commun.*, 1986, 1583
159. N Hertkorn, F H Köhler, G Müller, G Reber *Angew. Chem.*, 1986, **98** 462
160. P Gund *J. Chem. Educ.*, 1972, **49** 100
161. J Klein *Tetrahedron*, 1983, **39** 2733
162. N S Mills *J. Am. Chem. Soc.*, 1982, **104** 5689
163. S Inagaki, K Iwase, N Goto *J. Org. Chem.*, 1986, **51** 362
164. W Dieter, H Dietrich, T Clark, et al. *J. Am. Chem. Soc.*, 1984, **106** 7279
165. B M Gimarc *J. Am. Chem. Soc.*, 1983, **105** 1979
166. M J Goldstein *J. Am. Chem. Soc.*, 1967, **89** 6357
167. M J Goldstein, R Hoffmann *J. Am. Chem. Soc.*, 1971, **93** 6193
168. J B Grutzner, S Winstein *J. Am. Chem. Soc.*, 1972, **94** 2200
169. H E Simmons, T Fukunaga *J. Am. Chem. Soc.*, 1967, **89** 5208
170. R Hoffmann, A Imamura, G D Zeiss *J. Am. Chem. Soc.*, 1967, **89** 5215
171. J Dürr, R Gleiter *Angew. Chem.*, 1978, **90** 591
172. M J S Dewar, M L McKee *Pure Appl. Chem.*, 1980, **52** 1341
173. M J S Dewar, M K Holloway *Chem. Commun.*, 1984, 1188
174. K N Houk, L T Scott, N G Rondan, et al. *J. Am. Chem. Soc.*, 1985, **107** 6556
175. L T Scott, M J Cooney, D W Rogers, K Dejroongruang, 1988, **110** 7244
176. J Chandrasekhar, E D Jemmis, R Schleyer *Tetrahedron Lett.*, 1979, 3707
177. T Fukunaga, H E Simmons, J J Wendoloski, M D Gordon *J. Am. Chem. Soc.*, 1983, **105**, 2729
178. R W Alder, J C Petts, T Clark *Tetrahedron Lett.*, 1985, 1585
179. M N Glukhovtsev, B Ya Simkin, V I Minkin *Zh. Org. Khim.*, 1986, **22** 3
180. M J S Dewar, E F Healy, J Ruiz *Pure Appl. Chem.*, 1986, **58** 67
181. R Pettit *J. Organomet. Chem.*, 1975, **100** 205
182. A Efraty *Chem Rev.*, 1977, **77** 691
183. B E Burstein, R F Fenske *Inorg. Chem.*, 1979, **18** 1760
184. E D Jemmis, P R Schleyer *J. Am. Chem. Soc.*, 1982, **104** 4781
185. V I Minkin, R M Minyaev *Neklassicheskie Struktury Organicheskikh Soedinenii* (Nonclassical Structures of Organic Compounds), Izd. Rostov. Univ., Rostov-on-Don, 1985, 164 pp
186. H W Kroto, J R Heath, S C O'Brien, et al. *Nature (London)*, 1985, **318** 162
187. J Aihara, H Hosoya *Bull. Chem. Soc. Jpn.*, 1988, **61** 2657
188. M Randic, S Nikolic, N Trinajstic *Croat. Chem. Acta*, 1987, **60** 595
189. V Elser, R C Haddon *Nature (London)*, 1987, **325** 792
190. M J S Dewar *J. Am. Chem. Soc.*, 1984, **106** 669
191. D Cremer, J Gauss *J. Am. Chem. Soc.*, 1986, **108** 7467
192. D Cremer *Tetrahedron*, 1988, **44** 7427
193. V I Minkin, M N Glukhovtsev, B Ya Simkin *Zh. Org. Khim.*, 1988, **24** 3
194. V I Minkin, M N Glukhovtsev, B Ya Simkin *J. Mol. Struct. (Theochem.)*, 1988, **181** 93
195. M N Glukhovtsev, B Ya Simkin, V I Minkin *Dokl. Akad. Nauk SSSR*, 1988, **300** 144
196. S Shaik, P C Hiberty, J-M Lefour, G Ohanessian *J. Am. Chem. Soc.*, 1987, **107** 363
197. M N Glukhovtsev, B Ya Simkin, V I Minkin *Zh. Org. Khim.*, 1989, **25** 673