NON-BENZENOID AROMATIC COMPOUNDS AND THE CONCEPT OF AROMATICITY

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INTRODUCTION

The structure of aromatic compounds and the causes of their special aromatic properties became one of the fundamental problems of theoretical organic chemistry almost from the moment that A. M. Butlerov put forward his theory of chemical structure.

The cyclic structural formula for benzene proposed by Kekulé and advances in synthetic organic chemistry enabled a vast range of benzene derivatives, termed "aromatic compounds", to be isolated. The concept of "aromatic compounds" was very soon extended to derivatives of naphthalene, anthracene, and other fused-ring systems. It was subsequently found that numerous heterocyclic compounds – derivatives of furan, pyrrole, thiophen, pyridine, etc. – also possess a number of properties in common with benzene derivatives and distinguishing these compounds from other heterocyclic systems.

A number of properties appeared by that time to be common to aromatic compounds:

1) Ease of formation of aromatic rings in the most varied reactions.
2) Stability of aromatic systems, and in particular the difficulty of effecting addition reactions at the multiple bonds.
3) Ease of replacement of hydrogen by various groups in electrophilic-substitution reactions (nitration, sulphonation, halogenation, acetylation, alkylation, mercuration, etc.)
4) Characteristic properties of certain substituents in aromatic systems (acidic properties of aromatic hydroxyl, weakened basicity of amino group, stability of diazo compounds, ability to undergo azo coupling, lack of reactivity of halogen, etc.).

These properties taken together, were often denoted as "aromatic properties" or "indications of aromatic character", and were also the chemical criterion of aromaticity, on the basis of which it was determined whether substances of a given class were to be included among aromatic compounds.

In reality, however, only benzene itself is characterised by all these properties. On passing from benzene to its substituted derivatives, or still more to other aromatic systems, some of the aromatic properties become weaker or even disappear, while others are appreciably strengthened and come to the fore. Thus pyrrole and furan undergo electrophilic substitution considerably more readily than does benzene, and therefore are usually regarded as "superaromatic" systems. However, they are not very stable; they readily decompose under the action of strong acids and oxidising agents, and form addition products more readily than benzene (furan even enters into a diene synthesis reaction); from this point of view they are feebly aromatic. Naphthalene, anthracene, and other polycyclic systems are also less stable than benzene, but undergo electrophilic substitution more readily.

On the other hand, the pyridine and pyrazole systems are chemically more stable than the benzene system, and more easily give substitution products under the action of nucleophilic reagents (Chichibabin amination, hydroxylation), but undergo electrophilic aromatic substitution with considerably greater difficulty than does benzene.

Thus, even with the "classical" aromatic systems no single one of the chemical properties can serve as a strict criterion of aromaticity, the more so as many olefins and especially conjugated dienes are also capable of undergoing electrophilic substitution (sulphonation, acylation, azo coupling, etc.).

Besides the chemical properties, a number of physical properties and structural peculiarities of aromatic compounds may be noted, among which are: (1) the character of the C–C bonds, which are intermediate between single and double bonds (as is shown in particular by the values of the interatomic distances); (2) the equivalence of all carbon–carbon bonds in unsubstituted monocyclic carbocyclic systems and the equivalence of all the carbon atoms; (3) the planar or almost planar structure of the ring (it has now been shown theoretically and experimentally that the atoms forming an aromatic ring may not lie strictly in a single plane, and that slight deviations from coplanarity have little effect on the total energy of the aromatic system); (4) absorption of light at comparatively long wavelengths; (5) ready polarisability; and (6) anisotropy of diamagnetic susceptibility.

As will be shown, these physical properties and structural features are characteristic in lesser or greater degree of a wide variety of aromatic systems.

The development of quantum-mechanical ideas of the nature of the chemical bond and the progress of organic synthesis during the past two decades have produced not only a considerable change in our ideas as to the nature of aromaticity and its peculiarities, but also a considerable extension of the range of systems which can be regarded as

aromatic. Compounds which are quite different in composition and properties from the "traditional" aromatic derivatives of the benzene series can be included among aromatic compounds, such as organic anions (cyclopentadienyl anion), organic cations (tropylium, cyclopropenylium, phenalenylium), dipolar compounds (azulenes, sydnones), organometallic compounds (ferrocene and other "cenes"), and finally even some inorganic compounds (borazoles, phosphoronitrile halides). Further, progress in theoretical organic chemistry has enabled the possible existence of a number of other, as yet unknown, aromatic systems to be predicted. The characteristic properties and structure of various non-benzenoid aromatic systems will be considered below, starting with carbocyclic systems.

Work on systems which are formally analogous to benzene, and in which aromatic properties are therefore to be expected, has been especially significant in the development of the structural theory of aromatic compounds. These researches are considered in the sections concerned with the so-called pseudoaromatic compounds – cyclobutadiene, cyclooctatetraene, pentalene, heptalene.

Fourteen years have elapsed since the publication in "Uspekhi Khimii" of a review on non-benzenoid aromatic systems[1]. Since that time this field of organic chemistry has undergone such an intensive development that a revision of its fundamental theoretical principles has been required. Later foreign reviews[2,3] are far from complete; furthermore, in the few years which have elapsed since their publication much new material has appeared which is of fundamental importance.

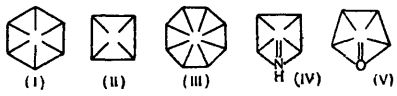
STRUCTURE OF AROMATIC COMPOUNDS AND NATURE OF AROMATICITY

The vigorous development of the chemistry of aromatic compounds at the end of the nineteenth and the beginning of the twentieth centuries led to a large number of hypotheses as to the structure of benzene and multinuclear aromatic compounds. The majority of them are now only of historic interest, and will not be considered further here (they were reviewed, for example, in 1934 [4]).

It appeared at first that the dynamic hypothesis of Kekulé[5-7] and Thiele's hypothesis of partial valencies[8,9] might form the basis of a theory of the structure of aromatic compounds. Further, the hypothesis of partial valencies enabled both unsaturated compounds, conjugated and unconjugated, and also aromatic systems, including polycyclic systems, to be considered from a single point of view.

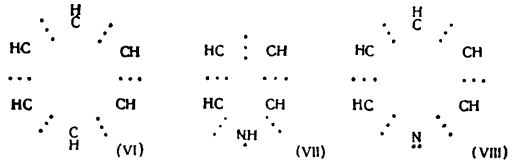
This hypothesis could not be seriously shaken even by the many cases of 1,2-addition in conjugated systems, in contradiction to Thiele's fundamental postulates. However, it received its most serious blow from the failure of Willstätter's attempt to synthesise cyclobutadiene and from the absence of aromatic properties in the cyclooctatetraene prepared by him, since it follows from the fundamental principles of this hypothesis that a simple alternation of single and double bonds in a cyclic system is the necessary and sufficient condition for its aromaticity. When this prediction of the hypothesis of partial valencies was not confirmed, a number of its supporters were compelled to accept a centric formula (I) for the structure of benzene[10].

However, acceptance of the Meyer[11] or Armstrong–Baeyer[12-14] centric formulae in fact meant only a recognition of the peculiar character of aromatic bonds, but in itself had no clear physical significance. The inadequacy of these formulae was aggravated by the fact that, like those of Kekule and Thiele, they were unable to explain why cyclobutadiene (II) and cyclooctatetraene (III) should differ from benzene (I).



As Bamberger correctly remarked[15-17], after having put much effort into defending and developing the idea of centric formulae, they can be appropriate and useful only if it is accepted as an axiom that a centric system can be stable only if it is "hexacentric", i.e. if the occurrence of the aromatic state requires six "potential valencies". In such a case, as Bamberger showed[15,16], cyclic formulae can easily be constructed also for various aromatic heterocyclic systems (cf. IV and V).

On the basis of the electronic theory of valency, Thomson, and then Kermack and Robinson, suggested for benzene and other aromatic systems formulae of the type (VI)–(VIII) containing three-electron bonds, regarding such bonds as specially stable and as engendering aromaticity[18].



However, Robinson[19] soon rejected this point of view, and came to the conclusion that "six electrons of the benzene molecule form a stable system, responsible for the aromatic character of the substance".

In spite of the apparently purely formal character of the hypothesis that six π electrons have a peculiar "magic" effect and in spite of the absence of any physical explanation, this idea proved to be very fertile. Not only did it enable a common factor to be found in the structure of benzene and aromatic heterocycles, and the absence of aromaticity in cyclobutadiene and cyclooctatetraene to be explained (although still purely formally), but it also allowed Armit and Robinson[19] to foretell the stability of systems containing the cyclopentadienyl anion. It was only considerably later, with the development of modern ideas of the quantum theory of the chemical bond, that the hypothesis of the special character of a sextet of π electrons received a physical basis.

In the 1930's a revision of valence theory from the standpoint of quantum mechanics was begun. It was natural that special attention should be paid to the quantum-mechanical examination of aromatic systems. For this purpose both of the main methods of calculation of quantum chemistry were widely used – the molecular-orbital method and the valence-bond method.

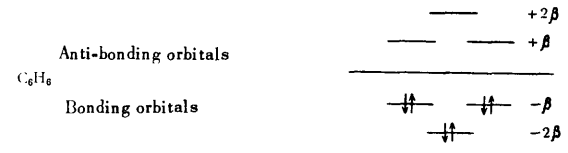
An important part in the foundation of the modern theory of aromaticity was played by Hückel[20,21], who was the first to apply the molecular-orbital method to aromatic systems. In this method the π electrons of a conjugated system are regarded as common to all the carbon atoms of the system and occur in common molecular orbitals. The number of such orbitals is equal to the number of atoms taking part in the formation of the conjugated system.

The following three types of molecular orbitals are possible: (*a*) bonding orbitals (the energy of electrons is less than their energy in the atomic orbitals, and consequently their occurrence in these orbitals makes the system more stable); (*b*) non-bonding orbitals (the energy of electrons occupying these orbitals is equal to the energy of the electrons in atomic orbitals); and (*c*) anti-bonding orbitals (the energy of electrons is greater than that in atomic orbitals, so that the occurrence of electrons in these orbitals is energetically disadvantageous).

The energy of the π electrons is often expressed in terms of so-called "resonance integrals" β, whose value is determined empirically and is usually taken to be 17–20 kcal/mole.

The numbers of bonding, non-bonding, and anti-bonding orbitals and their energies depend on the number of atoms in the system and its symmetry, and are determined by the solution of the wave equation. In conformity with the Pauli principle, not more than two electrons can be allocated to each such molecular orbital.

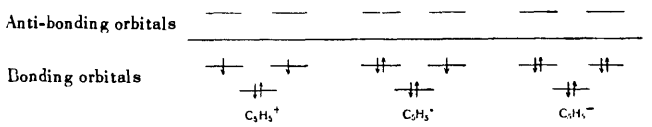
Calculation by the molecular-orbital method shows that benzene contains three bonding and three anti-bonding molecular orbitals. The energy levels are -2β, $-\beta$, and $-\beta$ for the former, and $+2\beta$, $+\beta$, and $+\beta$ for the latter (see diagram)*.



In the ground state the six π electrons of benzene occupy the most favourable, lowest energy levels, i.e. the three bonding orbitals. The energy of the π electrons consequently amounts to $2(-2\beta) + 4(-\beta) = -8\beta$. It can be shown by an analogous calculation that, in the case of three isolated double bonds, the energy of the π electrons amounts to only -6β; thus the energy of conjugation, associated with the transition of six π electrons to the common molecular orbitals, amounts to 2β.

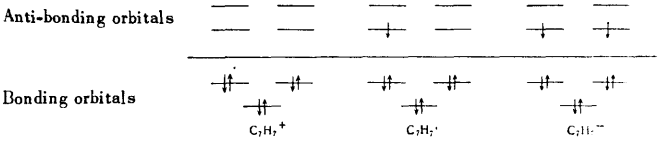
It follows even from such an elementary treatment that benzene (in the ground state) contains a stable system of six π electrons. Peculiarities of such a "closed" system of π electrons are (*a*) the absence of unoccupied positions in the bonding orbitals (i.e. entry of a new electron requires the expenditure of energy), and (*b*) all the π electrons are in bonding orbitals (i.e. the removal of any electron requires the expenditure of energy). In this respect the "closed" system of six π electrons of benzene may be compared with the specially stable electron shell of the inert gases.

The concept of a closed π-electron shell in aromatic systems was successfully applied by Hückel also to five- and seven-membered conjugated ring systems. Calculation shows that the five-membered ring C_5H_5 contains three bonding and two anti-bonding molecular orbitals. Thus the radical $C_5H_5^{\cdot}$ contains one vacancy and the cation $C_5H_5^+$ two vacancies in their bonding orbitals.



It is only in the $C_5H_5^-$ anion that all the bonding orbitals are occupied, and the six π electrons form a closed shell. Consequently, the anion should be the most stable.

Analogous considerations show that, for a seven-membered ring, possessing three bonding and four anti-bonding orbitals, the radical $C_7H_7^{\cdot}$ and the anion $C_7H_7^-$ contain respectively one and two electrons in anti-bonding orbitals, and these can therefore be easily split off; it is only in the cation $C_7H_7^+$ that all the π electrons are arranged in bonding molecular orbitals, and form a closed electron shell.



Appropriate calculation gives the conjugation energy as 2.99β for the cation $C_7H_7^+$, 2.54β for the radical $C_7H_7^{\cdot}$, and only 2.10β for the anion $C_7H_7^-$, and this anion, as the diagram shows, should occur in a triplet ground state[22].

Thus as early as 1931 Hückel had shown theoretically that not only the benzene system but also five- and seven-membered rings, possessing conjugated systems of six π electrons and bearing a negative and a positive charge respectively – the $C_5H_5^-$ anion and the $C_7H_7^+$ cation – could be aromatic and energetically stable. "It may be expected", wrote Hückel, "that a seven-membered ring will tend to lose its unpaired electron with the formation of a positively charged ion; so that a seven-membered system will behave in relation to benzene in the same way as an atom of an alkali metal in relation to an atom of the neighbouring inert gas". This bold conclusion had to wait twenty-three years for experimental confirmation by the synthesis of the cycloheptatrienylium (tropylium) cation.

The approach described frequently allows the question of the aromaticity of a wide variety of cyclic systems to be elucidated even without numerical calculations. It is found that a closed electron shell is possible in rings not only with 6 but also with 2, 10, 14, etc. π electrons. In its general form the rule derived by Hückel states that *monocyclic conjugated polyolefins having the symmetry of a regular polygon possess a closed electron shell, and consequently aromatic stability, if the number of π electrons is $4n + 2$ (where n is any integer).*

The molecular-orbital approach to the problem of aromaticity, and in particular Hückel's rule, enabled a number of deductions of importance to organic chemistry to be made:

1) For the first time a definition having physical significance was given to the concept of an "aromatic system", as a cyclic system in which all the π electrons form a single chain of conjugation and occur in bonding molecular orbitals, each of which contains two electrons.

2) The peculiar stability of the aromatic sextet of π electrons, which had been noted but not explained by classical theory, was explained as a particular case of the general rule $4n + 2$ with $n = 1$.

* Here and in subsequent calculations the energy of the π electrons in the atomic orbitals (α) is arbitrarily taken to be zero; the energy of anti-bonding orbitals is denoted by a + sign (energy of system increases when these orbitals are filled with electrons); and the energy of bonding orbitals is denoted by a − sign (energy of system diminished when electrons occupy these orbitals).

3) The aromatic character of five-membered heterocycles was explained, as these, like benzene, contain six π electrons (four electrons from double bonds and two unshared electrons of the hetero atoms) in three bonding molecular orbitals.

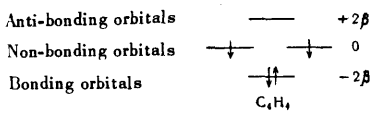
4) The aromatic character of the $C_5H_5^-$ anion and the $C_7H_7^+$ cation was predicted, which could not be done on the basis of classical structural theory.

5) Indications were obtained of the possible existence of a number of new aromatic systems. Thus, in conformity with Hückel's rule, the existence of an aromatic cyclopropenylium system could be expected with two π electrons ($4n + 2$ with $n = 0$). Comparatively simple assumptions enable the Hückel method to be applied also to elucidate the problem of new heterocyclic aromatic systems (see below). Finally, this method can be extremely fruitful when applied to various non-benzenoid polycyclic aromatic systems[22,23].

6) The molecular-orbital method enabled calculations to be made of the energies of the ground and excited states, the bond order, free valence, and the charges on atoms in aromatic systems, and thus their stability and reactivity to be characterised.

7) The molecular-orbital approach showed that cyclobutadiene and cyclooctatetraene would not be aromatic, in spite of the presence in their molecules of alternating single and double bonds[22,24-31]. Systems of this type – cyclobutadiene, cyclooctatetraene, pentalene, heptalene, etc. – have been termed, at Craig's suggestion[25], "pseudoaromatic".

The cyclobutadiene system contains four π electrons, a number which does not fit the Hückel formula $4n + 2$. Of these electrons, two are in a bonding orbital (with energy 2β), and two in two non-bonding orbitals, i.e. they have unpaired spins.



Thus the molecule would not possess a closed electron shell in Hückel's sense, and may be a diradical. The total energy of the π electrons of cyclobutadiene proves to be 4β, i.e. the same as for two unconjugated double bonds; hence the conjugation energy is zero[22,27]. In contrast to benzene, the C–C bonds should not be equivalent: calculation by the molecular-orbital method shows that the molecule should not be a square but a rectangle having sides of 1.33 Å (C=C bond) and 1.54 Å (C–C bond)[27,29,31].

In the same way, the total number of π electrons in cyclooctatetraene does not conform to Hückel's rule, and the calculated energy of conjugation (even without taking into account the lack of planarity of the eight-membered ring) does not exceed that in open-chain systems. In the eight-membered system, as in the four-membered one, an alternation of normal single and double bonds is to be expected[25,27,32].

Hence from the standpoint of the molecular-orbital method and the Hückel rule neither cyclobutadiene nor cyclooctatetraene should possess aromatic stability. This conclusion could not be derived from classical theory.

Another method of calculation used in quantum chemistry, the valence-bond (bond diagrams, localised pairs) method, has also been extremely widely applied to various aromatic systems. Further, during the first 10–15 years of existence of the two methods, the valence-bond method has been considerably more widely employed in the solution of structural problems in organic chemistry. This was due to a number of causes, including the greater descriptiveness of this method, the satisfactory results obtained for benzene and polycyclic benzenoid systems, and also the widespread use of corresponding bond diagrams by the then prevalent theory of resonance.

Applied to non-benzenoid systems, however, this method, and also the theory of resonance, yielded conclusions which were directly opposed to those resulting from the molecular-orbital method, and, as the subsequent development of organic chemistry showed, these conclusions were erroneous.

Thus the valence-bond method cannot explain the peculiar nature of a ring containing six π electrons. It is incomprehensible, why such five-membered heterocycles as pyrrole, thiophen, etc., in contrast to seven-membered heterocycles, posses an aromatic character. Finally, it is impossible to explain the aromaticity and stability of the five-membered anion $C_5H_5^-$ and the seven-membered cation $C_7H_7^+$.

Thus, for example, the explanation suggested by Wheland[33] for the acidity of cyclopentadiene (and the stability of the $C_5H_5^-$ anion) in terms of resonance theory could be equally well applied to cycloheptatriene, but the latter is known to differ markedly in this respect from cyclopentadiene, and the $C_7H_7^-$ anion is not stable.

According to the valence-bond method and the theory of resonance, cyclobutadiene is a four-membered analogue of benzene, and should possess aromatic stability[26,34-38]. Its conjugation energy should amount to 1.0 α (the value of α is approx. 32 kcal/mole), whereas that for benzene is 1.11 α: i.e. for a single π electron it should be even greater in cyclobutadiene than in benzene[35]. Cyclooctatetraene should also be aromatic according to this method and resonance theory[25], with a conjugation energy of 1.17 α, if it were planar, i.e. greater than that of benzene. Thus in 1945 Pauling wrote: "For cyclobutadiene and cyclooctatetraene the plane configuration should be stabilised as a result of resonance, but the valence angles in such plane molecules, 90° and 135°, are so far removed from the normal value that considerable strain arises; the molecules prove to be less stable and in part lose their aromatic properties"[39].

As will be shown, both these and some other conclusions regarding non-benzenoid aromatic systems made on the basis of the valence-bond method have been disproved by experimental investigations.

Thus, of the two main methods of calculation of quantum chemistry, only the molecular-orbital method gives a correct idea of the nature of aromaticity. Not only does this method enable the energy and other parameters of aromatic systems to be calculated, but also, what is especially important for the organic chemist, it often makes it possible to determine qualitatively whether a given class of compound will be aromatic.

THE CYCLOPENTADIENIDE ANION*

The five-membered ring C_5H_5 should possess a closed electron shell in the way described and should be stable in

* The suffix "ide" is widely employed at the present time to denote organic anions.

the form of the anion, which has a system of six π electrons. Calculation by the molecular-orbital method gives conjugation energies of 2.47 β for the cyclopentadienide anion $C_5H_5^-$, 1.85 β for the radical C_5H_5, and only 1.24 β for the cation $C_5H_5^+$, the last of which would occur in a diradical triplet ground state[22].

The cyclopentadienide anion forms salts with cations of the alkali and alkaline-earth metals, manganese, and the rare-earth elements. There is every reason to suppose that the bond with the metal in these compounds is ionic. Thus the close agreement between the magnetic moments found for $(C_5H_5)_2Mn$, $(C_5H_5)_3Pr$, $(C_5H_5)_3Nd$, $(C_5H_5)_3Sm$, $(C_5H_5)_3Gd$, $(C_5H_5)_3Dy$, $(C_5H_5)_3Er$, and $(C_5H_5)_3Yb$ and those calculated for the corresponding ions Mn^{2+}, Pr^{3+}, Nd^{3+}, etc. demonstrate convincingly the ionic character of the bond in these compounds[40,41]. This is confirmed also by the appreciable electrical conductivity of solutions of C_5H_5Na, $(C_5H_5)_2Mg$, and $(C_5H_5)_2Mn$ in liquid ammonia[40]. X-ray data show the salts $(C_5H_5)_2Mg$ [42] and $(C_5H_5)_2Mn$ [43] to have a pentagonal antiprism structure (like that of ferrocene).

It is impossible, in view of these results, to agree with Fritz[44], who, on the basis of a study of frequencies in the infra-red spectra of the cyclopentadienides of potassium, magnesium, beryllium, thallium, and other metals concludes that the five-membered rings in these compounds are not fully aromatic in character and that the double bonds are to a considerable extent fixed. Fritz's conclusions seem still more dubious since the spectra of these compounds do not contain any metal-carbon bond frequencies, and hence he is forced to admit that the link between the cyclopentadienyl ring and the metal is ionic. Thus, following Fritz, we would be compelled to accept the existence of a $C_5H_5^-$ ion with a charge which is to a considerable degree fixed on one of the carbon atoms in the ring, in obvious contradiction to the X-ray data (e.g. for dicyclopentadienylmagnesium, which has a sandwich structure with the magnesium atom equidistant from all the carbon atoms).

A characteristic property of the cyclopentadienide anion is its extremely high reactivity towards electrophilic reagents. Thus its salts are decomposed by water and alcohol, are carboxylated by CO_2,[45] and alkylated and arylated by alkyl and aryl halides[46]. When an alkali and chlorine (or bromine) react with cyclopentadiene all the hydrogen atoms are replaced by halogen atoms[47]: this is evidently the result of the extremely ready halogenation of the cyclopentadienide anion formed under these conditions.

The cyclopentadienide system is thus still more "superaromatic" in its reactivity than the five-membered heterocyclic systems. This conclusion is confirmed by a study of deuterium exchange in the cyclopentadienide anion, which rapidly exchanges all its hydrogen atoms for deuterium in alkaline medium, i.e. at very low D^+ concentrations[48]. Pyrrole undergoes deuterium exchange only in aqueous solutions of mineral acids (at pH $\leq$ 1)[49], and benzene slowly exchanges its hydrogen only under the action of concentrated D_2SO_4.[50] Thus the ease of deuterium exchange, the simplest electrophilic substitution, increases very markedly on passing from benzene and pyrrole to the cyclopentadienide anion.

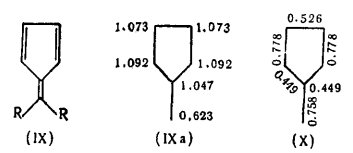
The aromatic character of the $C_5H_5^-$ anion is shown in the fact that, in spite of its high reactivity, it is nevertheless far more stable than other carbanions. As a result, cyclopentadiene and its benzo-derivatives are considerably stronger acids than other hydrocarbons (with the exception of acetylenic hydrocarbons). Whereas pK_a for diphenylmethane is 35, and for triphenylmethane 33 (in spite of the comparative stability of the triphenylmethyl anion) for fluorene it is 25, for indene 21,[51] and for cyclopentadiene not greater than 19. This value follows from the fact that potassium t-butoxide quantitatively converts cyclopentadiene into potassium cyclopentadienide[52], the value of pK_a for t-butyl alcohol being 19.

The stable cyclopentadienide anion is formed from cyclopentadiene not only by the action of alkali metals[53-55], but also in the presence of bases of moderate strength, e.g. pyridoneimine[48].

Finally, a consequence of the tendency to form the $C_5H_5^-$ anion and of the lability of the hydrogen atoms is the well known ability of cyclopentadiene to form fulvenes under the action of ketones and aldehydes in alkaline medium[56,57], to be readily mercurated with mercuric chloride in methyl alcohol[58], to undergo azo coupling[59], and to be cyanoethylated in the presence of bases (with the formation of a hexakiscyanoethyl derivative)[60].

Heterolysis of a σ C–H bond is necessary to obtain the cyclopentadienide anion from cyclopentadiene: in the fulvenes (IX), however, it is only necessary to break the more labile π bond (which requires less energy). Hence the tendency to form the cyclopentadienide system has an appreciable effect on the structure of the fulvenes and on the distribution of electron density in the ground state. This is shown primarily in the magnitude of the dipole moments of the fulvenes, which is 1.48 ± 0.03 D for dimethylfulvene, 1.34 ± 0.03 D for diphenylfulvene, etc.[61].

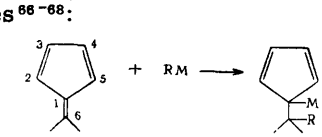
The diagram (IXa) showing the distribution of electron density, obtained by the molecular-orbital method, is also in full agreement with these experimental results (values $>>$ 1 indicate a negative charge, and those $<$ 1 a positive charge)[62]



(IX) (IXa) (X)

It can be seen from the diagram that the five-membered ring acquires a partial negative charge, and consequently some of the aromaticity of the cyclopentadienide anion. Consequently, there are no "purely" double and single bonds in the fulvenes, as is readily seen from the diagram of the π-bond indices (X) (for a double bond the index is 1, and for a single bond 0)* [63].

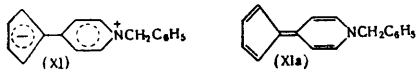
The polarity of the carbon–carbon bonds in fulvenes is shown by their ready reducibility with lithium tetrahydroaluminate[64], which distinguishes them from other hydrocarbons; this reaction involves the intermediate addition of Li^+ and H^- at the semicyclic double bond. In exactly the same way fulvenes can add on at the polar 1,6-bond organometallic compounds, e.g. phenyllithium[65] and alkylmagnesium bromides[66-68]:



The polarity of the bonds is revealed also by some other properties of the fulvenes (see, for example, the review by Bergmann[57]).

* This is equivalent to Coulson's mobile bond order, c.f. Proc. Roy. Soc., A 169, 413 (1939) (Ed. of Translation).

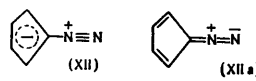
Introduction of electron-donor substituents into position 6 appreciably strengthens the aromatic character of the five-membered ring and the polarity of the fulvene molecule. This has a marked effect on the spectra, dipole moments, and reactivity[69]. Thus the dipole moment of diphenyldibenzofulvene is 1.20 D,[70] and that of bis(*p*-dimethylaminophenyl)dibenzofulvene is 3.90 D.[71] The compound obtained by Kursanov et al.[72] by the reaction of benzylpyridinium chloride with cyclopentadienyllithium is of great interest in this connection.



(XI) (XIa)

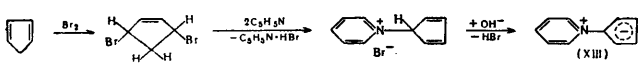
This compound can be represented by the ionic (XI) and the covalent (XIa) fulvene structures. Electrostatic forces hinder the formation of the dipolar structure (XI), but the considerable stabilisation energy of the cyclopentadienide and pyridine aromatic systems favour it. As a result, the structure of this compound is represented to an appreciable extent by formula (XI), as shown by its extremely high dipole moment of 9.7 D.[73].

The aromatic cyclopentadienide system is still more strongly stabilised when the five-membered ring is directly linked with a positively charged hetero-atom. The first example of compounds of this type (the so-called cyclopentadienylides) was obtained in 1953, when Doering and De Puy[74] prepared diazocyclopentadienylide, whose structure is more accurately represented by formula (XII) than by (XIIa).



(XII) (XIIa)

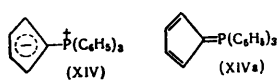
In 1955 Lloyd and Sneezum[75,76] obtained pyridinium cyclopentadienylide (XIII) by the action of pyridine on dibromocyclopentadiene followed by treatment with alkali:



(XIII)

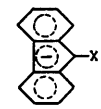
In a similar manner 4-benzylpyridinium cyclopentadienylide[77], 4-carbamoylpyridinium cyclopentadienylide, and pyridinium 2,3,4,5-tetraphenylcyclopentadienylide[76] were obtained subsequently. The distinguishing structural feature of these cyclopentadienylides is that their nitrogen atom cannot form a fifth covalent bond, and consequently the covalent fulvene structure is impossibe for them; they therefore possess an extremely high dipole moment (e.g. XIII has a dipole moment of 13.5 D)[73]. There is also a brief account of the synthesis of trimethylammonium cyclopentadienylide[79].

Triphenylphosphonium cyclopentadienylide (XIV) is also known[80]. Its dipole moment (6.99 D),[73] however, is considerably lower than that calculated for a dipolar structure (14 D); this discrepancy is associated with the fact that phosphorus, in contrast to nitrogen, can form a fifth covalent bond, owing to a vacant *d* orbital, and the substance obtained may have a structure intermediate between the "ylide" (XIV) and fulvene (XIVa) structures:



(XIV) (XIVa)

A number of analogous dipolar derivatives of the fluorenide anion (XV) are also known – the trimethylammonium (XVa), dimethylsulphonium (XVb), trimethylphosphonium (XVc), and pyridinium (XVd) derivatives[82-84].

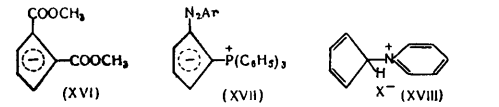


(XVa) X = $\overset{+}{N}(CH_3)_3$ (XVc) X = $\overset{+}{P}(CH_3)_3$

(XVb) X = $\overset{+}{S}(CH_3)_2$ (XVd) X = –$\overset{+}{N}$

The stability of the cyclopentadienide anion can be increased not only by introducing positively charged "onium" substituents but also by means of other electron-acceptor groups. Thus the 1,2-dimethoxycarbonylcyclopentadienide anion (XVI) is extremely stable. Its sodium salt is stable not only in alkaline but also in neutral solution[85].

The cyclopentadienylides are good subjects for the study of the properties of the cyclopentadienide aromatic system because of their stability. It has now been shown in a number of cases that cyclopentadienylides undergo aromatic substitution extraordinarily readily. Thus according to Kursanov and Parnes the cyclopentadienylides (XI) and (XIII) undergo deuterium exchange with enriched alcohol in alkaline, neutral, and feebly acid solutions[73]. Ramirez and Levy[86] have shown that triphenylphosphonium cyclopentadienylide (XIV) readily undergoes azo coupling with arenediazonium salts to form arylazo-derivatives (XVII).



(XVI) (XVII) (XVIII)

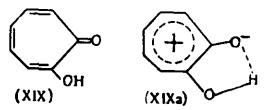
It is difficult, however, to investigate electrophilic substitutions in the cyclopentadienylides because of their high reactivity, and in particular because of the rapid entry of, not one, but several substituents with the formation of poly-substituted derivatives.

Interesting results confirming the aromatic character of five-membered rings in cyclopentadienylides have been obtained by Baranetskaya[87] and Balandin and Khidekel'[88] during the investigation of the catalytic hydrogenation of pyridinium cyclopentadienylide (XIII). Thus the velocity constant for the hydrogenation of (XIII) on a rhodium catalyst in alcoholic medium is k = 7.8 ml/min. In acetic acid, however, where as a result of addition of a proton the pyridinium cyclopentadienylide (XIII) is converted into the cyclopentadiene derivative (XVIII), the velocity of the reaction is markedly increased and k = 24.0 ml/min. These results are consistent with the general rule that the diminution in conjugation energy on passing from the aromatic to the corresponding unsaturated structure increases the rate constant for hydrogenation[88].

THE TROPYLIUM CATION

The conclusion reached by Huckel on the basis of the molecular-orbital method that the $C_7H_7^+$ cation should be stable remained for a long time without experimental confirmation. Only in 1945 was the idea of a stable seven-membered aromatic system successfully employed by Dewar[89] to explain the properties and structure of a new class of natural products, the tropolones. The properties of tropolone (XIX) and its derivatives can be explained in

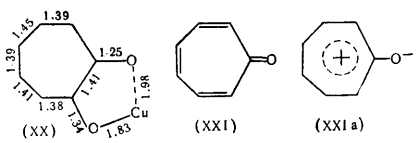
terms of a structure based on a seven-membered aromatic system (XIXa).



(XIX) (XIXa)

The chemistry of the tropolones has now grown into a vast self-contained field of organic chemistry, the number of papers on which exceeds 600. We shall not, therefore, consider the chemistry of tropones and tropolones in the present review, especially as a number of good reviews on this subject have appeared in recent years [90-94]. It will be useful, however, to describe briefly the main chemical and physical properties of these compounds which point to their aromatic character.

Like the benzene ring, the seven-membered ring in the tropolones is a planar almost regular polygon, the lengths of the carbon–carbon bonds averaging 1.40 Å. This result was obtained by Robertson [95] in an X-ray study of the copper salt of tropolone; the values found for the interatomic distances are indicated in diagram (XX).



(XX) (XXI) (XXIa)

Similar results have been obtained in an X-ray investigation of the hydrochloride and the sodium salt of tropolone [96].

Electron diffraction measurements led to the same conclusions [97], yielding the bond lengths C–C 1.39, C–H 1.10, C–O 1.34, and C=O 1.26 Å. In the tropone molecule (XXI), whose structure approximates to the dipolar structure (XXIa) with an aromatic seven-membered ring, the length of the C–C bonds is 1.41 Å.[98] Thus the values for the interatomic C–C distances in the tropolones and tropone correspond to a bond order intermediate between that of a single and a double bond, which confirms the aromatic character of these rings.

A number of physical properties of tropones and tropolones indicate the polarity of their structures, which is associated with the formation of positively charged aromatic seven-membered ring (XXIa) and (XIXa). Thus the dipole moment of tropone is 4.30 D, [99,100] whereas that of cycloheptanone is only 3.04 D.[101] Derivatives of benzotropone also have high dipole moments [102].

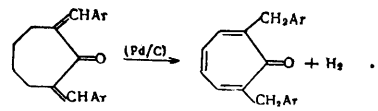
The distinguishing feature of the tropolones is the acidic character of the hydroxyl group (p*K* 7.0), which exceeds that of phenolic hydroxyl (p*K* 10.0) in acidity.

The reactivity of the tropolones also resembles in many respects that of the phenols. Tropolones readily undergo various electrophilic substitution reactions: they couple with arenediazonium salts, are nitrated by nitric acid in glacial acetic acid, sulphonated by sulphamic acid, nitrosated by nitrous acid, are readily halogenated, undergo hydroxymethylation with formaldehye in alkaline medium, and undergo the Reimer–Tiemann reaction. These reactions show the effect of the hydroxyl group and the polarised keto-group on the reactivity of the seven-membered ring. It was not possible, however, to carry out a Friedel–Crafts acylation of tropolone (possibly because of the formation of complexes with the catalyst), or to carry out its chloromethylation or its carboxylation by Kolbe's method.

On the other hand, tropolones and substituted tropones readily undergo nucleophilic substitution. Thus the methoxy group in the methyl ether of tropolone can be replaced by the radicals NHR (by the action of amines), C_6H_5 (with C_6H_5MgBr), RS (by means of RSNa), etc.

Finally, the aromatic properties of the tropones and tropolones are revealed by the ease with which they are formed from cycloheptane derivatives in the most varied reactions: bromination and dehydrobromination, dehydrogenation by means of selenium dioxide [103], oxidation with potassium permanganate [104], etc.

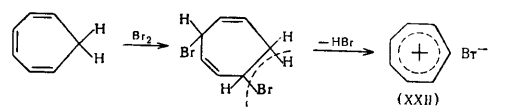
It is very interesting that palladium-on-charcoal, a highly active catalyst for the dehydrogenation of six-membered cycloalkanes, can also cause the dehydrogenation of a seven-membered ring with the formation of the aromatic tropone system [105]:



Here migration of the semicyclic double bonds into the ring and dehydrogenation occur simultaneously. As we shall see, attempts to obtain conjugated pseudoaromatic systems (cyclobutadiene, pentalene, heptalene, etc.) by the same methods were not successful.

The ease of formation of the tropolone system is consistent also with thermochemical data, according to which the conjugation energy in this aromatic system amounts to 33–36 kcal/mole.[106]

Only in 1954, some 23 years after Hückel's prediction, did Doering and Knox [52] describe the preparation of the unsubstituted tropylium cation. Tropylium bromide (XXII) was obtained by thermal elimination of hydrogen bromide from dibromocycloheptadiene according to the scheme

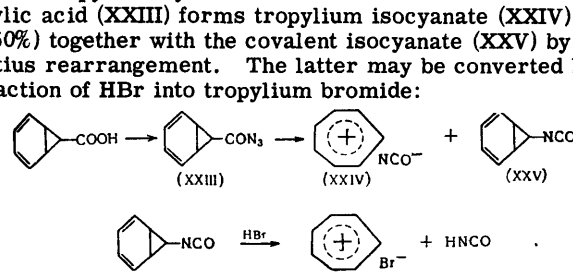


(XXII)

As early as 1891 Merling [107] had carried out the same reaction and had apparently obtained tropylium bromide. He was, however, unable to identify the compound and regarded it as a solid isomer of dibromocycloheptatriene.

Doering's method was later used to obtain salts of tropylium derivatives containing a substituent in the seven-membered ring — the bromides of carboxytropylium [108], bromotropylium, phenyltropylium, and t-butyltropylium [109].

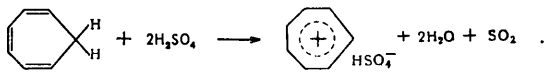
A different method, devised later by Dewar and Pettit [110,111], was based on the ready isomerisation of the norcaradiene into the tropylium system. The azide of norcaradienecarboxylic acid (XXIII) forms tropylium isocyanate (XXIV) (0–50%) together with the covalent isocyanate (XXV) by a Curtius rearrangement. The latter may be converted by the action of HBr into tropylium bromide:



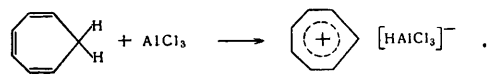
(XXIII) (XXIV) (XXV)

Methyltropylium salts are obtained similarly from the azide of methylnorcaradienecarboxylic acid.

It might be expected that tropylium, as a stable aromatic system, would be readily formed directly from cycloheptatriene (tropylidene) by fission of a hydride ion from the CH_2 group accompanied by transition of the carbon atom from an sp^3 into an sp^2 state of hybridisation. Kursanov and Vol'pin have indeed shown[112] that tropylium salts are formed by the action of a wide variety of electrophilic reagents on cycloheptatriene, in spite of the fact that many of these substances react vigorously with the double bonds of the cycloheptatriene. Thus concentrated sulphuric acid converts up to 18% of the cycloheptatriene into a tropylium salt according to the scheme



The formation of tropylium in this reaction is similar to the formation of aliphatic carbonium ions by the action of concentrated sulphuric acid on saturated hydrocarbons containing a tertiary carbon atom[113]. The oxidation of tropylidene in acid medium with other oxidising agents (CrO_3, SeO_2) converts it also to a greater or lesser extent into tropylium. Although such strong Lewis acids as BF_3 and $AlCl_3$ react vigorously with the ethylenic bonds in tropylidene, in this case too the hydride ion is split off with formation of a tropylium salt:



Halides of elements of variable valency are especially effective for the conversion of cycloheptatriene into tropylium salts. Thus phosphorus pentachloride reacts extraordinarily readily with cycloheptatriene to form tropylium chloride, undergoing reduction to the trichloride in the process:



The reaction goes with an almost quantitative yield at room temperature, and can serve as a convenient method for the preparation of tropylium salts[112]. This method has been used also to obtain methyltropylium[113] and bromotropylium[114] salts.

Cycloheptatriene reacts in a similar manner with sulphuryl chloride, titanium tetrachloride, and ferric chloride[73]:

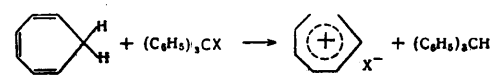
$$C_7H_8 + SO_2Cl_2 \rightarrow C_7H_7^+Cl^- + SO_2 + HCl \quad ,$$

$$C_7H_8 + TiCl_4 \rightarrow C_7H_7^+Cl^- + TiCl_3 + HCl \quad ,$$

$$C_7H_8 + 2FeCl_3 \rightarrow C_7H_7^+Cl^- + 2FeCl_3 + HCl \quad .$$

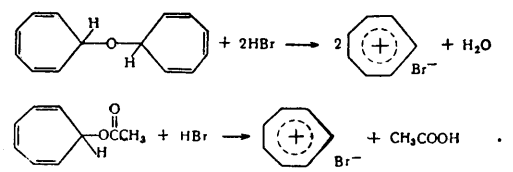
Thus, just as the action of alkali metals and strong bases on cyclopentadiene causes a proton to be split off with formation of the cyclopentadienide anion, strong Lewis acids act on cycloheptatriene to split off a hydride ion and form a tropylium cation. In both cases a non-benzenoid aromatic system containing six π electrons is formed.

Recently Dauben et al.[115] have employed yet another reaction to obtain tropylium salts by fission of a hydride ion from cycloheptatriene. They have shown that triphenylmethyl halides act on cycloheptatriene in solvents of high dissociating power to form tropylium salts:

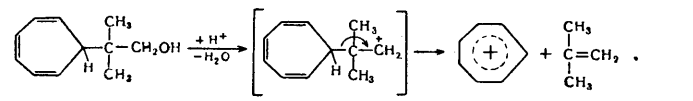


This method has given high yields (60–90%) of tropylium salts with $X^- = Cl^-$, Br^-, I^-, BF_4^-, and ClO_4^-, as well as methyltropylium, bromotropylium, and methoxytropylium salts.

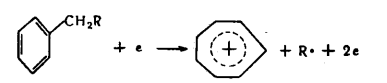
The great stability of the tropylium system is shown also by the fact that cycloheptatrienyl ethers and esters — — methoxycycloheptatriene, dicycloheptatrienyl ether[26], cycloheptatrienyl acetate, and cycloheptatrienyl benzoate[116,117] — are unusually easily cleaved by mineral acids with formation of tropylium salts, e.g.:



Vol'pin and Kursanov have recently shown that formation of tropylium may occur as a result of the rupture of carbon–carbon bonds. 2-Cycloheptatrienyl-2,2-dimethylethanol is extremely readily decomposed, even at room temperature, in the presence of acids (acetic, formic, hydrochloric, hydrobromic) or under the influence of thionyl chloride, with formation of a tropylium salt*:



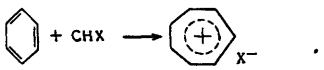
Of special interest are the few examples of direct transition from the benzene aromatic system to the tropylium system. Thus Rylander et al.[118] studied the reactions of various deuterium-labelled alkylbenzenes in the gas phase on collision with electrons in the mass spectrometer. From the distribution of deuterium in the mass spectrum of the reaction products they concluded that in all cases it is not the benzyl but the isomeric tropylium cation which is formed:



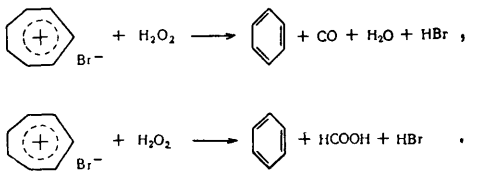
Evaluation of the energy changes in this process shows that the transition of a benzyl cation into a tropylium cation is thermodynamically probable. Such a rearrangement has not yet been observed in solution apparently because the benzyl cation (owing to the less disperse character of its charge) is stabilised by solvation to a considerably greater extent than is the tropylium cation.

* The occurrence of this type of rupture of a carbon—carbon bond has also recently been reported by Conrow [J. Amer. Chem. Soc., 81, 5461 (1959)].

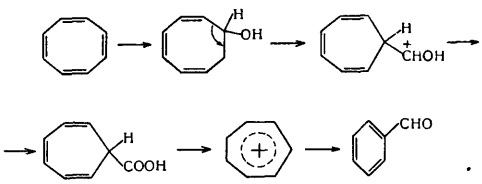
Recently Vol'pin et al.[119] have shown that benzene can be directly converted into tropylium by the action of monohalogenocarbenes, which are formed in small amounts during the reaction of CH_2Cl_2, CH_2Br_2, or CH_2I_2 with potassium t-butoxide:



Vol'pin and Kursanov[120] have discovered also the reverse reaction of the direct conversion of tropylium salts to benzene, which occurs rapidly under the influence of aqueous hydrogen peroxide and is accompanied by the formation of carbon monoxide and formic acid:



Finally, the tropylium system can be formed also by the contraction of an eight-membered ring. Thus Ganellin and Pettit[121,122] have shown that the oxidation of cyclooctatetraene to benzaldehyde occurs via the intermediate formation of a tropylium ion:



The properties and the structure of tropylium salts have attracted the continued attention of chemists[73,109].

Salts of the tropylium cation are now known with a wide variety of anions. They are solids melting at high temperatures. The majority of them (with the anions Cl^-, Br^-, I^-, BF_4^-, SiF_6^-) are readily soluble in water and are insoluble in organic solvents of low polarity; their aqueous solutions give an instantaneous reaction for the corresponding anion; tropylium chloride and bromide are extremely hygroscopic. These properties alone of the tropylium salts are sufficient to indicate the great difference between them and the alkyl halides and other organic compounds having a covalent C–X bond; in a number of their properties they resemble the salts of the alkali metals. Thus, like the K^+ cation, the tropylium ion forms a difficultly soluble (in water) perchlorate $C_7H_7ClO_4$ and a very insoluble chloroplatinate $(C_7H_7)_2PtCl_6$ and tetraphenylborate $C_7H_7B(C_6H_5)_4$. These last two salts can be employed for the analytical determination of tropylium salts in solution[123].

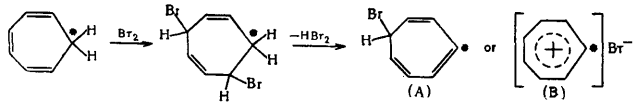
Polarographic studies have shown[123,124] that reduction of the tropylium ion begins at a very low potential (0.2 V), the character of the reduction curves being independent of the anion. A quite remarkable fact is the adsorption of the tropylium cation on the positively charged mercury surface, in spite of electrostatic repulsion. This phenomenon points to the polarisability of the π-electron cloud in the tropylium ion and indicates a similarity to benzene and other aromatic substances: these also are adsorbed on a positively charged mercury surface[125].

The existing physicochemical data for tropylium salts are in full agreement with the ionic character of the link between C_7H_7 and X and with the aromatic nature of the tropylium cation. As expected for a completely symmetrical plane seven-membered ring (D_{7h}), the infra-red spectrum of the tropylium ion contains only four strong lines, and the Raman spectrum seven, which do not coincide with the first lines. The character of these lines is similar to those of benzene and confirms the planar aromatic structure of the tropylium ion[126–138].

Theoretical examination of the electronic spectra of tropylium salts shows that they should have a weak absorption band at 4.33 eV and an intense band at 6.36 eV.[129] In close agreement with this, λ_{max} is observed at 4.51 eV ($\log\epsilon$ = = 3.64) in aqueous solutions of tropylium salts; no measurements were made at wavelengths corresponding to the second possible maximum.

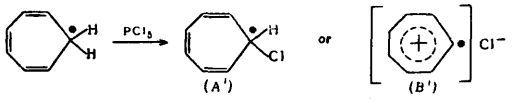
At present there are no X-ray or electron diffraction data confirming directly whether the tropylium ring is a regular heptagon. An attempt at an X-ray investigation of crystals of tropylium chloride was unsuccessful[130]; only the dimensions of the unit cell were determined. X-ray studies of the structure of tropylium perchlorate and iodide[131,132] revealed an interesting peculiarity: the tropylium ion is not completely fixed in the crystal lattice, but rotates freely in the plane of the ring (or is distributed at random about an axis perpendicular to this plane). Unfortunately this fact prevented the determination of the interatomic distances in the tropylium ring. However, a necessary consequence of its aromatic character should be the equivalence of all the carbon–carbon bonds and of all the carbon atoms in tropylium (just as in benzene).

The first direct experimental proof of the equivalence of all the carbon atoms in the tropylium ion has recently been obtained by means of labelled carbon[133]. Cycloheptatriene labelled with ^{14}C in the methylene group was converted via [^{14}C]dibromotropylidene into [^{14}C]tropylium bromide. Treatment of the product with phenylmagnesium bromide yielded [^{14}C]phenylcycloheptatriene, which was oxidised to benzoic acid.

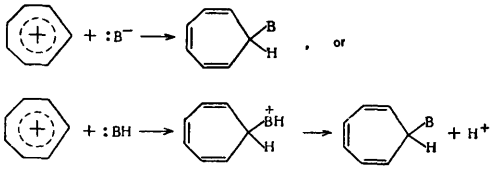


If the carbon–carbon bonds in [^{14}C]tropylium bromide were not equivalent, and if, consequently, the bromine atom were linked to one particular carbon atom (as in structure A), substitution of the bromine atom by the C_6H_5 group followed by oxidation should yield a non-radioactive benzoic acid. However, the benzoic acid was found to have a radioactivity of about one-seventh of the activity of the initial tropylium bromide. This is a consequence of the identity of all the carbon atoms (structure B) and the equal probability of attack by the phenyl group at any one of them. In another series of experiments labelled cycloheptatriene was treated with PCl_5, and the resulting tropylium salt also converted by treatment with C_6H_5MgBr into [^{14}C]phenylcycloheptatriene. Oxidation of the latter yielded a benzoic acid having the same activity (one-seventh) as in the previous case. These results also indicate the equivalence of all the carbon atoms (structure B'), since if this were not so (structure A')

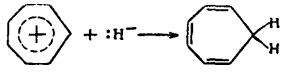
replacement of Cl by C_6H_5 should have led to the formation of a benzoic acid containing 100% ^{14}C.



The most characteristic chemical property of the tropylium salts is their ability to react with a wide variety of nucleophilic reagents according to the general scheme

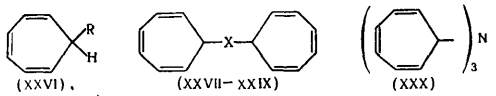


The simplest of these reactions is clearly that between tropylium and a hydride ion:



Thus cycloheptatriene is formed by the action of lithium tetrahydroaluminate or sodium tetrahydroborate (as donors of the hydride ion) on tropylium bromide. This reaction is the reverse of that described for the conversion of cycloheptatriene into tropylium salts upon reaction with electrophilic reagents.

According to Doering and Knox[52,134] tropylium salts react with CH_3O^- to form 7-methoxycycloheptatriene (XXVI), and with aqueous $NaHCO_3$ to yield ditropyl ether (XXVII). Similarly, hydrogen sulphide reacts with tropylium salts to give ditropyl sulphide (XXVIII). Aqueous ammonia forms ditropylamine (XXIX), and an ethereal solution of ammonia yields tritropylamine (XXX). Amines and acid amides react with tropylium salts in the same way: dimethylamine forms tropyldimethylamine (XXXI), acetamide gives *N*-tropylacetamide (XXXII), and succinimide yields *N*-tropylsuccinimide (XXXIII); this last compound is obtained also by the action of *N*-bromosuccinimide on cycloheptatriene[135]. The reaction of tropylium salts with potassium cyanide occurs in a similar manner and leads to the formation of 7-cyanocycloheptatriene (XXXIV).[110,111,116,134]

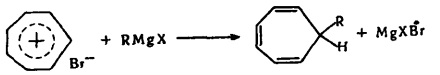


(XXVI), (XXXI – XXXIV) (XXVII – XXIX) (XXX)

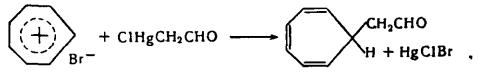
(XXVI) R=OCH_3; (XXVII) X=O; (XXVIII) X=S; (XXIX) X=NH; (XXXI) R=$N(CH_3)_2$;

(XXXII) R=$NHCOCH_3$; (XXXIII) R=; (XXXIV) R=CN.

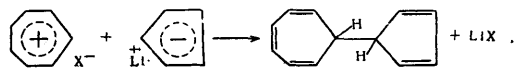
The electrophilic character of the tropylium ion is shown also in its ability to react readily with organometallic compounds. Phenyllithium or phenylmagnesium bromide reacts with tropylium bromide to yield phenyltropylidene[134], and the appropriate alkylmagnesium halides yield methyl-, isopropyl-, and t-butyltropylidenes[109].



Tropylium salts react readily with certain organomercury compounds[136], e.g.



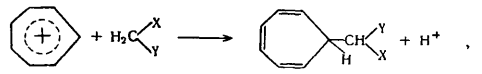
An interesting reaction occurs between tropylium salts and cyclopentadienylsodium or cyclopentadienyllithium[109, 116,117]: the salt $C_5H_5^-\ C_7H_7^+$ is not formed; a covalent compound, cyclopentadienylcycloheptatriene, is obtained, with a dipole moment of 0.6:



The formation of a covalent instead of an ionic link is intelligible if it is remembered that cyclopentadiene is an extremely weak acid.

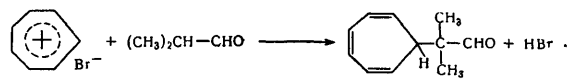
The unusually high activity of tropylium salts discovered by Vol'pin et al.[137] in alkylation reactions is associated with the "carbonium" electrophilic properties of the tropylium ion. Whereas the alkylation of compounds containing a reactive hydrogen atom with alkyl halides requires additional activation (catalysts, bases), tropylium salts react in acid medium without any activators, frequently in the cold and even with evolution of heat.

Thus tropylium salts react very readily in the cold with substances containing an active methylene group: with esters of β-keto acids (acetoacetic, diacetoacetic), β-diketones (acetylacetone, dimedone), β-dicarboxylic acids and their derivatives (malonic acid, malonic ester, cyanoacetic ester). The active hydrogen atom in the cycloheptatrienyl radical is replaced in these reactions according to the general scheme



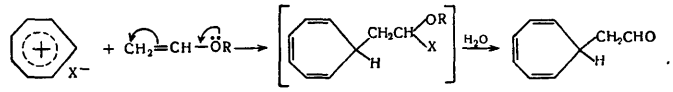
where X and Y = COOH, $COOC_2H_5$, $COCH_3$, NO_2, CN, etc.

Tropylium salts react in a similar manner with aliphatic aldehydes (acetaldehyde, propionaldehyde, isobutyraldehyde, etc.)[138], e.g.:



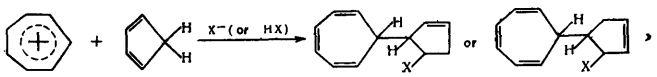
Aliphatic and alkyl aryl ketones also react with tropylium salts, but only on heating. A few aromatic compounds also react with tropylium salts — phenol, quinol, phloroglucinol, resorcinol, and α- and β-naphthols[137].

The highly electrophilic character of the tropylium ion is shown also by the fact that it readily attacks several compounds having activated double bonds[136,137]. Here activation of the multiple bond for reaction with the tropylium ion cannot be achieved solely by its conjugation with other bonds: conjugated compounds having electron-acceptor groups acrylonitrile, cinnamic acid, acrylic acid) do not react on being heated with tropylium salts. Vinyl ethers, however, readily react even in the cold[136]:



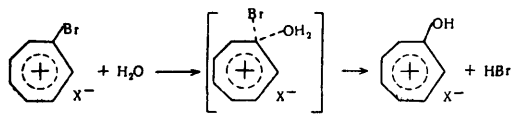
The high reactivity of the vinyl ethers is obviously connected with the supply of electrons by the oxygen and the appearance of an increased electron density at the terminal carbon atom, which is readily attacked by the tropylium cation.

An analogous phenomenon occurs in cyclopentadiene, in which the increased electron density on the C atoms is a result of the tendency to form the stable cyclopentadienyl anion. Cyclopentadiene, in contrast with other dienes, reacts readily with tropylium salts[73,137]:



where X = Br, OC_2H_5, OH, $OCOCH_3$.

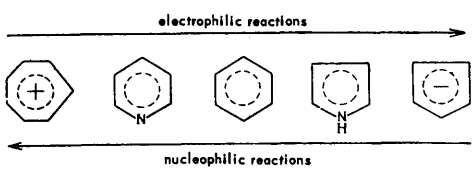
These examples show that attack of the tropylium ion by nucleophilic reagents is greatly facilitated. In the majority of cases it leads to addition of the attacking agent, but examples are also known now of nucleophilic substitution in the tropylium nucleus. Thus halogen-substituted tropylium (chlorotropylium or bromotropylium) salts on treatment with water extremely readily exchange the halogen atom for a hydroxyl group[109,114]. The mechanism of this reaction evidently involves nucleophilic attack on the tropylium nucleus by the H_2O molecule (or OH^- ion) with elimination of HBr (or the Br^- ion)[114]:



On the other hand, the tropylium system is extremely inert towards electrophilic reagents. It has not yet been possible to induce in tropylium salts any of the electrophilic reactions which are normally characteristic of aromatic systems of the benzene series — nitration, sulphonation, acylation, alkylation, etc. The ability of the tropylium system to exchange hydrogen for deuterium atoms under the influence of strong acids may be taken as a measure of the activity of the system in electrophilic substitution. Even on prolonged treatment with concentrated D_2SO_4, however, the tropylium cation does not undergo deuterium exchange[139]. Furthermore, tropylium salts do not undergo deuterium exchange even with a solution of $AlBr_3$ in liquid DBr, which is one of the strongest deutero acids[139]. Under the same conditions benzene exchanges hydrogen for deuterium almost instantaneously, and even saturated hydrocarbons undergo rapid deuterium exchange[140].

Thus, the "typical" reactions of aromatic electrophilic substitution are far from characteristic of all aromatic systems, and the tropylium system is in this respect one of the most inert.

If five-, six-, and seven-membered aromatic carbo- and heterocyclic systems are arranged in order of increasing susceptibility to electrophilic reactions (to attack by electrophilic reagents), then the series begins with the tropylium ion and ends with the cyclopentadienide anion.

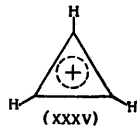


The reactivity towards nucleophilic reagents increases in the reverse order. Hence, by itself, the type of reactivity of aromatic compounds cannot serve as any strict criterion of their aromatic character.

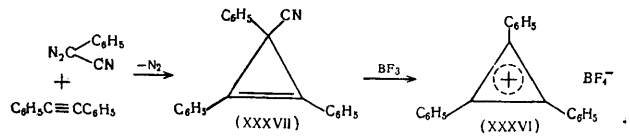
THE CYCLOPROPENYLIUM CATION

The simplest aromatic system should be the cyclopropenylium cation (XXXV) with two π electrons in the field of three nuclei. This number of π electrons conforms to the Hückel rule $4n + 2$ with $n = 0$.

Calculation by the molecular-orbital method[22] shows that the energy of conjugation is 2β for the $C_3H_3^+$ cation, β for the C_3H_3 radical, and 0 for the $C_3H_3^-$ anion.

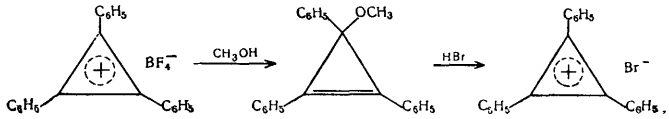

(XXXV)

No salts of the unsubstituted cyclopropenylium cation are yet known. Recently, however, the first derivatives of this new aromatic system have been obtained. Breslow[141,142] in 1957 was able to synthesise triphenylcyclopropenylium tetrafluoroborate (XXXVI) by the series of reactions

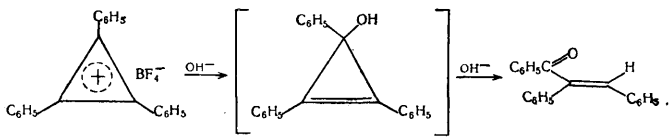

(XXXVII) (XXXVI)

The covalent 1,2,3-triphenylcyclopropenyl cyanide (XXXVII) on treatment with moist BF_3 etherate is converted into the ionic salt (XXXVI), insoluble in benzene and ether but soluble in warm acetone, methanol, and acetonitrile. The nuclear-magnetic-resonance spectrum shows all the hydrogen atoms in this compound to be equivalent, and hence that all the carbon atoms in the three-membered ring are equivalent.

Triphenylcyclopropenylium tetrafluoroborate reacts with methanol in the presence of alkali to form a covalent cyclopropenyl methyl ether, which on treatment with gaseous HBr is converted into the ionic triphenylcyclopropenylium bromide:

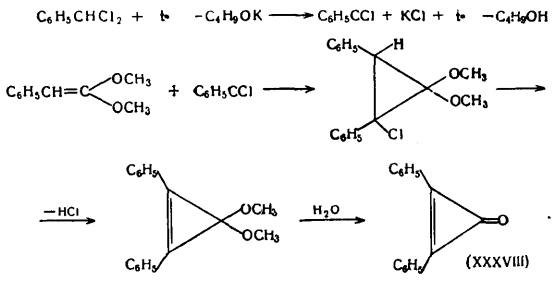


The three-membered ring of triphenylcyclopropenylium salts is opened up by reaction with aqueous alkali:

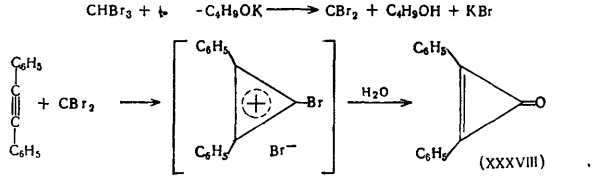


According to calculations by Bochvar at al.[143] the total conjugation energy in the triphenylcyclopropenylium cation amounts to 9.16 β; this exceeds the sum of the conjugation energies in the three phenyl groups and in the cyclopropenylium cation by 1.16 β.

A second derivative of the cyclopropenylium system obtained recently is diphenylcyclopropenone (XXXVIII). Breslow et al.[144] synthesised it starting from the acetal of phenylketen by the series of reactions



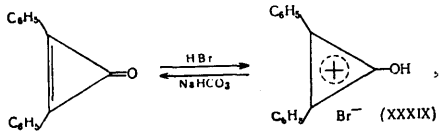
Vol'pin et al.[145] obtained this compound by addition of dichlorocarbene or dibromocarbene to diphenylacetylene:



Diphenylcyclopropenone which has a tendency to form the aromatic cyclopropenylium system is a three-membered analogue of tropone judging by its properties.

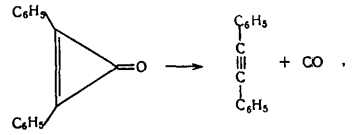
The high dipole moment of this ketone is remarkable, amounting to 5.08 D according to Syrkin and Shidlovskaya[145]. The dipole moment of benzophenone by comparison is only 2.95 D, and that of tropone itself 4.30 D.

Like tropone, diphenylcyclopropenone reacts with gaseous hydrogen chloride and hydrogen bromide to form salts[145]:

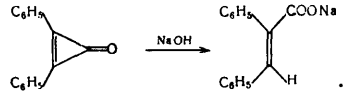


The derivative of the aromatic cyclopropenylium cation thus obtained, hydroxydiphenylcyclopropenylium bromide (XXXIX), is insoluble in non-polar solvents, but soluble in alcohol, acetone, and acetonitrile. The ionic structure of the bromide is indicated by the immediate precipitation of AgBr on addition of an alcoholic solution of $AgNO_3$, and also by the evolution of HBr by the action of concentrated sulphuric acid. On treatment of the bromide with aqueous $NaHCO_3$ it is quantitatively converted into diphenylcyclopropenone.

The stability of this ketone and the bromide is remarkable in view of the considerable angular strain, amounting in all to 180°. Only at temperatures above 130° does the ketone decompose according to the equation[144]



The three-membered ring can be opened also by heating with a solution of alkali[145]:



Even at -70° lithium tetrahydroaluminate reduces not only the carbonyl group but also the double bond of the diphenylcyclopropenone, and this is evidently also connected with the high polarity of its molecule[145].

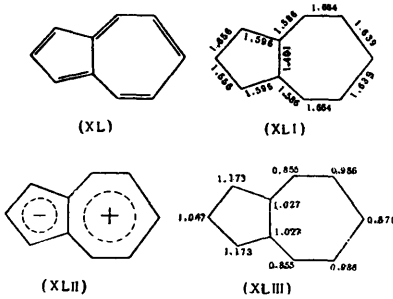
The stability of diphenylcyclopropenone, its unusually high dipole moment, and its ability to form salts with acids can be explained only by the existence of the aromatic cyclopropenylium system.

The chemistry of the aromatic cyclopropenylium system is now at the beginning of its development. The immediate task in this field should be the synthesis of salts of the unsubstituted cyclopropenylium cation and study of its properties.

AZULENES

An interesting class of non-benzenoid aromatic compounds is formed by the azulenes, which contain a fused system consisting of a five- and a seven-membered ring (they have already been reviewed[146-148]).

Pfau and Plattner[149] in 1936 established the structure of azulene as a bicyclic hydrocarbon (XL) with alternating single and double bonds. The number of π electrons in azulene (ten) is the same as in naphthalene, and obeys the Hückel rule ($4n+2$ with $n=2$), and there is therefore every reason to expect the azulene system to be aromatic in character.

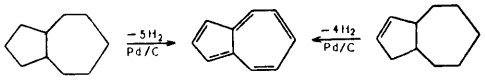


The aromatic character of the azulenes is confirmed by measurement of their heats of combustion. It was found experimentally[150] that the energy of conjugation in the azulene system is 45 kcal/mole. The value found by calculation amounts to 3.0154 β.[151] Hence the order of all the bonds in azulene is intermediate between double and single bonds (see diagram XLI).[152]

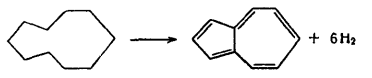
The ease of formation of the azulene system is associated with its aromatic stability. A large number of the most

varied reactions are now known in the course of which azulenes are obtained. Hydrogenated derivatives containing the azulene skeleton are readily dehydrogenated to azulene by the action of chloranil or SeO_2.

It is particularly interesting that azulenes may be successfully obtained by dehydrogenation over catalysts of the platinum group, which are so effective in the dehydrogenation of cyclohexane derivatives to substituted benzenes. Thus with palladised charcoal at 320°–335°, in conditions under which decalin is dehydrogenated to naphthalene, bicyclo[0,3,5]decane and various bicyclo[0,3,5]decenes are dehydrogenated to form azulene[153,154].



The dehydrogenation of macrocyclic hydrocarbons to form aromatic derivatives having fused six-membered rings is accompanied by the production of appreciable quantities of azulene. According to the data of Prelog[155,156], cyclodecane dehydrogenated over palladised charcoal at 350° gives a 19% yield of azulene, and cyclodecene gives a 20.8% yield.



Over activated charcoal at 420°–480° cyclodecene yields up to 60% of azulene.

Azulenes are formed also by the high-temperature (500°–600°) dehydrogenation of tetrahydrodicyclopentadiene, decalin, and perhydroacenaphthene over mixed oxide catalysts[157].

All these results confirm the aromatic character of the azulene system and its stability, which is quite comparable with that of naphthalene under the same conditions.

The π-electron cloud in the azulene molecule, however, is not symmetrical. This is a reflection of the tendency considered above for the five-membered ring to be converted into a cyclopentadienide anion, and for the seven-membered ring to change into a tropylium cation. Although such a separation of charges, represented by formula (XLII), occurs to only a slight extent (the dipole moment of azulene is 1.0 D)[61], it has a very marked effect on the physical and chemical properties of the azulenes.

Quantum-mechanical calculation of the distribution of electron density in azulene[152] confirms its dipolar structure, the charge distribution being as shown in the diagram (XLIII) (a π-electron density greater than unity indicates a negative charge on the atom, while a density less than unity indicates a positive charge). Thus all the carbon atoms in the five-membered ring carry a negative charge, while those in the seven-membered ring (apart from the atoms common to the two rings) are positively charged. From the magnitudes of the charges and taking into account the polarisability of the azulene molecule, Brown[152] concluded that electrophilic substitution will occur at position 1 in the azulenes, whereas nucleophilic and radical substitution will occur at position 4.

The "cyclopentadienide" character of the azulenes appears in the great readiness with which electrophilic substitution occurs in the five-membered ring. Azulene is considerably more reactive in such reactions than is the isomeric naphthalene. The first substituent always enters azulene in position 1, and the second in position 3.

When azulenes are nitrated with such mild reagents as copper nitrate in acetic anhydride or in tetranitromethane, 1-nitroazulene is obtained in good yield[158,159]. Nitric acid in acetic anhydride yields a mixture of 1-nitro- and 1,3-dinitroazulene[160]. Azulenes are readily sulphonated by dioxan–sulphur trioxide forming 1-monosubstituted derivatives[161]. Azulene undergoes electrophilic substitution also with *N*-bromo- or *N*-chlorosuccinimide (action of Cl^+ or Br^+), the products being 1-chloro- or 1-bromo- or else 1,3-dichloro- or 1,3-dibromoazulene[159].

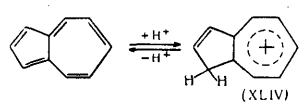
Friedel–Crafts acetylation of azulene leads to the 1,3-diacetyl derivative, but under milder conditions (acetic anhydride and $SiCl_4$ in CH_2Cl_2) it is possible to obtain 1-acetylazulene[159,160]. It is interesting that the acetyl group in 1,3-diacetylazulene readily undergoes electrophilic substitution by Cl^+ (by the action of NaOCl)[160]. Acylation of azulene with carbonyl chloride occurs under still milder conditions, in the cold and in absence of catalysts[162], the COCl group entering positions 1 and 3. 1-Acylazulenes can also be obtained by direct interaction between azulenes and carboxylic acids in the absence of catalysts[163].

The formylation of azulene occurs readily with dimethylformamide and phosphorus oxychloride (with formation of azulene-1-aldehydes)[164–166]. The halides CH_3I and CH_3Cl, methylate azulene also in position 1.[158]. The aminomethylation of azulenes, which occurs in positions 1 and 3, has also been described[167].

Azulenes also readily undergo azo coupling with arenediazonium salts with formation of 1-arylazoazulenes[168,169]. Mercuric chloride in alcohol at once precipitates a mercuration product, this reaction occurring considerably more readily than with thiophen[159].

Finally, the readiness with which electrophilic substitution occurs with azulene can be demonstrated also in the case of the simplest of such reactions, deuterium exchange. It has recently been shown[170] that azulene, like cyclopentadienylides, undergoes rapid deuterium exchange in neutral medium, only the two H atoms in positions 1 and 3 being replaced by D.

The properties of azulene as a derivative of the cyclopentadienide anion are exhibited also in the readiness with which it adds on a proton on dissolution in mineral acids to form the azulenium cation (XLIV):

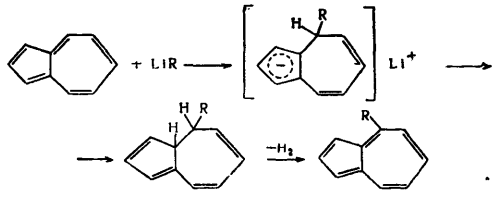


(XLIV)

In basic strength azulene approaches *o*-nitroaniline[171] (pK = 0.55 in HCOOH). On salt formation the chromophoric system of azulene breaks down, the colour changing from blue to yellow; the resulting azulenium ion is essentially a substituted tropylium ion and has an absorption maximum in the ultra-violet (λ_{max} 352 mμ), which differs markedly from the absorption maximum of the original azulene (λ_{max} 580 mμ).

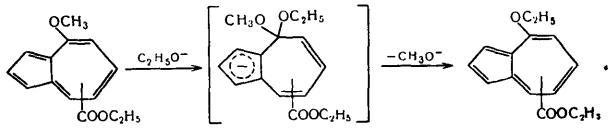
The nucleophilic reactions characteristic of tropylium salts have been considerably less studied in the azulene system. Hafner and Weldes[172,173] have shown that organometallic compounds are able to add on to the azulene molecule, the first alkyl or aryl group entering position 4, and

the second entering position 8 (i.e. the positions having the greatest positive charge):



This reaction is analogous to the addition of organometallic compounds to the semicyclic double bond in fulvenes (see above).

According to Reid et al.[174] the action of sodamide on azulene leads to nucleophilic substitution with entry of the amino group into the seven-membered ring (in position 4). However, only small amounts of the reaction product were formed, and its structure cannot strictly be regarded as proved. The occurrence of nucleophilic reactions in the azulene system is evidently complicated by its lack of stability towards bases. Thus azulene is rapidly decomposed on heating with alcoholic alkali. In the case of the more stable azulenecarboxylic acid it was possible to show that the 4-methoxy group readily undergoes nucleophilic substitution by the ethoxy group with alcoholic alkali[174]:



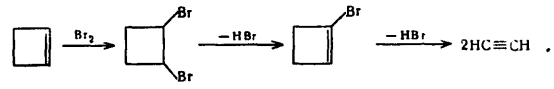
It may be expected to be possible to cause azulene and its salts to undergo many of the nucleophilic reactions studied with tropylium salts which occur in weakly alkaline, neutral, and acid media.

Thus numerous physical and chemical results confirm the aromatic character of the azulenes, which can be regarded as "tropylium cyclopentadienylides" combining the properties of the aromatic cyclopentadienide anion with those of the aromatic tropylium cation.

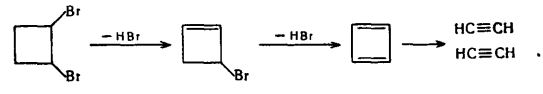
CYCLOBUTADIENE

Investigations of the pseudoaromatic systems cyclobutadiene, cyclooctatetraene, pentalene, and heptalene, which would be expected to be similar to benzene and to possess aromatic properties, serve as an especially clear example of the attempts made to verify experimentally theoretical ideas about aromaticity.

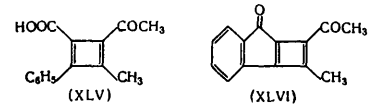
Starting from the idea of partial valencies, Willstätter and Schmädel[175] undertook in 1905 the first attempt to synthesise cyclobutadiene as a possible four-membered aromatic system. They obtained 1,2-dibromocyclobutane on adding bromine to cyclobutene, but elimination of hydrogen bromide from this material proved to be considerably more difficult than with the ordinary aliphatic dibromides. The action of quinoline on dibromocyclobutane yields a coloured polymer and small amounts of butadiene. When the dibromide is heated with alkali at 100°–105° only one molecule of hydrogen bromide is eliminated to form 1-bromocyclobutene. Elimination of the second molecule of hydrogen bromide requires heating with caustic potash to 210°, but acetylene is then formed instead of cyclobutadiene:



Discussing these results, Favorskii and Favorskaya[176] concluded that Willstätter had represented the structure of the unsaturated bromide incorrectly, and that the reaction very probably occurs with the formation of an allyl type of bromide and its conversion into cyclobutadiene, which breaks down further to acetylene:

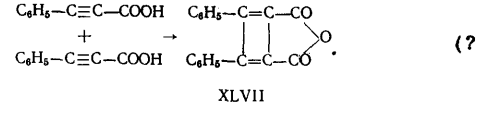


The failure of the first attempt to synthesise cyclobutadiene dissuaded chemists for a long time from studying this question afresh. Though from time to time attempts were made to ascribe the structure of a cyclobutadiene derivative to some organic compound or other, these were never based on any adequate grounds. Thus Ruhemann and Merriman[177], completely without proof, assigned the structure (XLV) to one of the reaction products formed by reaction of C_6H_5C : : C.COCl with the sodium derivative of acetonylacetone, and the structure (XLVI) to the compound derived from it.



A recent check of these results has shown that the first substance is actually 5-methyl-6-phenylsalicylic acid, and the second 2-hydroxy-4-methyl-9-fluorenone[178].

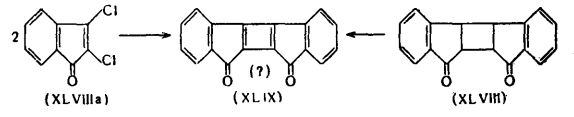
Manthey[179] and Lanser[180] suggested a substituted cyclobutadiene structure (XLVII) for triphenyltrimesic acid and its anhydride (formed from phenyltetrolic acid):



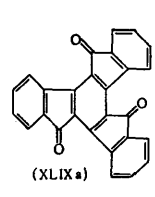
XLVII

However, it was soon established that this acid is definitely 1-phenylnaphthalene-2,3-dicarboxylic acid[181,182].

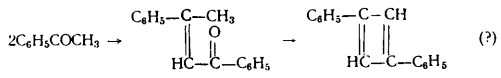
Similarly, truxinquinone, formed by the oxidation of truxone (XLVIII) or by treating dichloroindone (XLVIIIa) with copper[183],



for which the above cyclobutadiene structure (XLIX) had been proposed[180,183-185], actually proved to be a trimer of the indenylene radical s-tris(1-oxo-2,3-indenylene)benzene (XLIXa)[186-188]:



Equally unfounded was the cyclobutadiene structure assigned to one of the condensation products of acetophenone or phenylacetaldehyde in the presence of sodium ethoxide or alcoholic alkali[189,190].

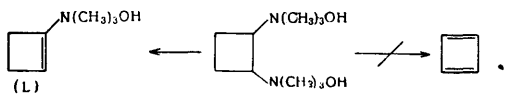


This proved to be 3,5-diphenyltoluene[191].

These examples suffice to show that special caution is necessary when authors assume, solely on the basis of their methods of synthesis and their elementary analysis, that any particular compound has a structure which includes a cyclobutadiene residue. Hitherto it has proved on checking the results only that either isomerisation or else tri(poly)--merisation has occurred in these cases, but it has never been possible to confirm the presence of a cyclobutadiene ring.

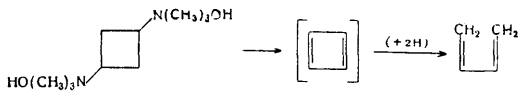
Recently, however, fresh attempts have been made to synthesise cyclobutadiene and its derivatives.

Buchman et al.[192] tried to use for this purpose the decomposition of *trans*-cyclobutane-1,2-bistrimethylammonium hydroxide:



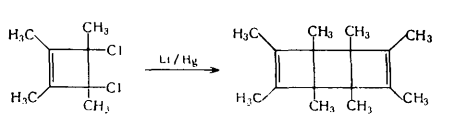
Among the reaction products were found dimethylamine, trimethylamine, *trans*-1,2-bisdimethylaminocyclobutane, and cyclobutanone, but it was not possible to detect cyclobutadiene. These workers consider that their failure is explained by the occurrence of *cis*-1,2-elimination with the intermediate formation of cyclobutene-1-trimethylammonium hydroxide (L).

To avoid 1,2-elimination, Nenitzescu et al.[193] have recently tried to obtain cyclobutadiene by the decomposition of cyclobutane-1,3-bistrimethylammonium hydroxide. They found surprisingly that, instead of cyclobutadiene, the main product was buta-1,3-diene:

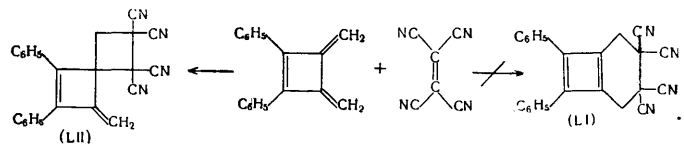


Nenitzescu considers that cyclobutadiene is first formed in the course of the reaction, and is then converted into butadiene by hydrogen abstraction from other substances present in the reaction mixture.

Similarly, the attempt of Criegee and Louis[194] to convert 3,4-dichloro-1,2,3,4-tetramethylcyclobutene[195] into tetramethylcyclobutadiene was also unsuccessful. Dehalogenation could be achieved only by the action of lithium amalgam, but then, instead of the cyclobutadiene derivative, its dimer was formed:

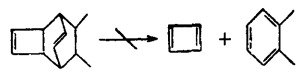


The reaction of 3,4-dimethylene-1,2-diphenylcyclobutene with tetracyanoethylene should form the cyclobutadiene derivative (LI) according to the usual pattern of diene synthesis, but unexpectedly its spirocyclic isomer (LII) is obtained instead[196]:



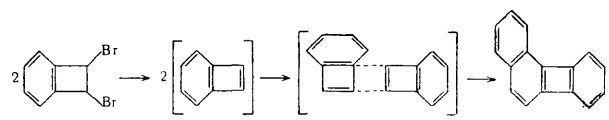
In no case in which isomerisation of some compound into a cyclobutadiene derivative could be expected (by analogy with the isomerisation of numerous compounds into benzene derivatives) did such a change occur. Thus 1,3-dimethylenecyclobutane does not pass into 1,3-dimethylcyclobutadiene. 1-Methyl-3-methylenecyclobut-2-ene readily isomerises to 1,3-dimethylenecyclobutane, but does not give a cyclobutadiene derivative[197]. Similarly, among the derivatives of cyclobutenone and cyclobutanedione no enols or enol acetates are formed corresponding to the cyclobutadiene structure[196,199].

It might be expected that the cyclobutene bridge would break away with the formation of cyclobutadiene in the pyrolysis of various adducts of cyclooctatetraene, e.g.:

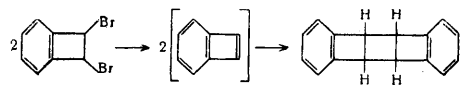


In all such cases, however, buta-1,3-diene is formed instead[193,200].

Finally, reference may be made to attempts to obtain benzocyclobutadiene, which should be more stable than cyclobutadiene itself. Treatment of 1,2-dibromobenzocyclobutene with zinc dust gave not benzocyclobutadiene but its dimer[201]:

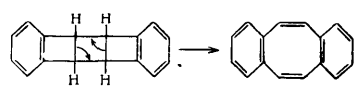


Similarly, in the dehydrobromination of 1,2-dibromobenzocyclobutene, instead of the bromobenzocyclobutadiene its dimer is formed[201]. Debromination occurs in an analogous manner even with lithium amalgam[202]. Curiously, if the same reaction is carried out in the presence of tetracarbonylnickel, a dimer with a different structure is formed[203]:



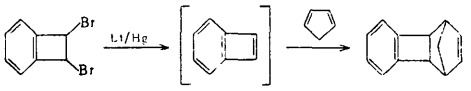
The role of the tetracarbonylnickel is apparently to form an unstable π complex with the benzocyclobutadiene formed as an intermediate, which on thermal decomposition gives the dimer.

It might be expected that pyrolysis of this dimer would lead to the formation of the monomeric benzocyclobutadiene, but it was found that at 150°–155° the dimer is converted into dibenzocyclooctatetraene[203]:

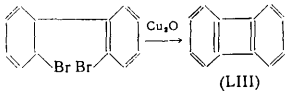


Nenitzescu et al.[202] demonstrated the formation of an unstable benzocyclobutadiene intermediate in reactions of

this type by an ingenious method. They carried out the reaction of 1,2-dibromobenzocyclobutene with lithium amalgam in the presence of cyclopentadiene (as diene component in a Diels–Alder reaction), and separated the adduct of cyclopentadiene with benzocyclobutene:



It is to be specially noted that dibenzocyclobutadiene (biphenylene) (LIII), in contrast to cyclobutadiene and benzocyclobutadiene, is a quite stable substance. After numerous unsuccessful attempts, it was obtained in 1941 by Lothrop[204] by distilling 2,2'-dibromobiphenyl or 9-iodoniofluorene iodide over cuprous oxide:



(LIII)

Subsequently biphenylene was synthesised also by the reaction of 2,2'-biphenyldimagnesium bromide with cupric chloride[205,206] and by heating *o,o'*-biphenylylenemercury with silver[207]. Substituted biphenylenes[206,208], 1,2-binaphthylene[209], and 2,3-binaphthylene[210] were obtained by an analogous method. The structure of biphenylene was confirmed by electron-diffraction[211] and X-ray[212] measurements.

The difference between cyclobutadiene and its dibenzo derivative is obviously explained by the fact that the latter is not really a cyclobutadiene derivative. It contains two benzene rings linked by sp^2-hybridised σ-bonds, as a result of which the distance between the rings is 1.46 A. The ultra-violet spectra of biphenylene[213,214] apparently indicate some interaction between the aromatic rings through the four-membered ring.

Consideration of the attempts to synthesise cyclobutadiene and its derivatives shows that it is an extremely unstable compound. The formation of cyclobutadiene is extraordinarily difficult to accomplish. Even if it is formed, it very rapidly undergoes secondary reactions. In this respect cyclobutadiene may be regarded as one of the most reactive olefines, but not as an aromatic system.

The instability of cyclobutadiene and the difference between it and benzene are most often explained by the considerable angular strain in a four-membered ring containing two double bonds. Indeed, the strain at each corner of the cyclobutadiene ring amounts to 120–90 = 30°, and that for the whole molecule to 30° × 4 = 120°. This explanation has been given by many authors hitherto both in papers on aromatic systems[1,215] and in general textbooks[216]. However, it does not stand up to serious criticism. Why, then, are biphenylene (with a total angular strain also of 120°), diphenyldimethylenecyclobutene (strain 120°), and cyclopropene (strain 169°) stable? Furthermore, the recently prepared derivatives of cyclopropenone and cyclopropenylium, with an angular strain of ~180°, have proved to be quite stable.

Knunyants et al.[217] have recently shown convincingly from an examination of published evidence that this generally accepted idea as to the difficulty of formation of four-membered rings and the instability of compounds of this type has, in fact, no sound basis. It may be concluded that the marked difference in properties between cyclobutadiene and benzene is due, not to any tension in the former system[32], but to the difference in the character of the π-electron systems of these compounds predicted by the molecular-orbital method.

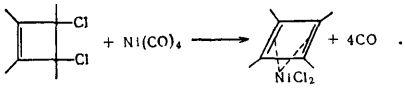
The experimental results cited show also the error of conclusions as to the aromatic character of cyclobutadiene based on the valence-bond method.

On the basis of results obtained by the molecular-orbital method for the instability of the π-electron system in cyclobutadiene and the presence in its molecule of two unpaired electrons, Longuet–Higgins and Orgel[218] suggested that cyclobutadiene should form stable complexes with the transition metals. From an examination of the symmetry of the molecular orbitals of cyclobutadiene they concluded that the two unpaired electrons, occurring in the doubly degenerate non-bonding orbital e_{1g}, could form two covalent π bonds with the metal atom. In addition, a weak coordinate σ bond between the metal and the bonding a_{1u} ring orbital and a weak σ bond with the anti-bonding a_{2u} ring orbital are possible. It follows from this that the cyclobutadiene complex will be even more stable than the cyclopentadienyl complex.

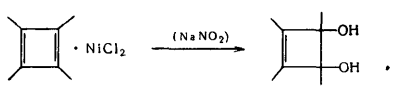
Considering the possible electronic structure of cyclobutadienyl complexes of this type, Longuet–Higgins and Orgel conclude that the formation of complexes of the type $(C_4H_4)MX_4$ is possible, with an outer shell containing 18 or 16 electrons (with complexes of neutral atoms or cations respectively), e.g. $[(C_4H_4)AuCl_2]^+$, $(C_4H_4)Ni(CN)_2$, $[(C_4H_4)\cdot Ni(CO)_2]^+$, $[(C_4H_4)Co(CO)_2]^+$, etc.

The suggestion of the possible existence of stable cyclobutadiene complexes of this kind proved to be extremely fruitful. Thus it is possible that the compound obtained as early as 1908 by Makowka[219] by passing acetylene into an aqueous solution of $PdCl_2$, which has the composition $(C_4H_4)PdCl(OH)$, is actually a cyclobutadiene complex. It is quite probable that the polymerisation of acetylene to cyclooctatetraene in the presence of $Ni(CN)_2$ occurs via the intermediate formation of the cyclobutadiene complex $(C_4H_4)Ni(CN)_2$. Such complexes may form intermediate stages in a number of other reactions of acetylene[220].

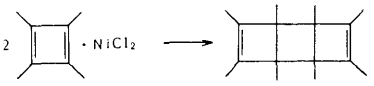
The correctness of the prediction that cyclobutadiene would form stable complexes with transition metals is provided by recent syntheses of such compounds. Criegee and Schroder[221] obtained in good yield a tetramethylcyclobutadiene complex of composition $C_8H_{12}NiCl_2$ by the action of nickel carbonyl on tetramethyldichlorocyclobutene in boiling benzene:



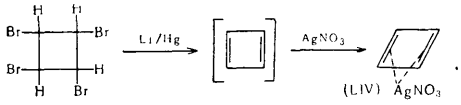
This substance forms reddish-violet crystals, soluble in water to yield a blood-red solution, and in chloroform with a violet coloration. The nuclear-magnetic-resonance spectrum of this material indicates the presence of twelve equivalent hydrogen atoms. The fact that the tetramethylcyclobutadiene is monomeric in this complex is shown by its reaction with sodium nitrite, in which a tetramethyl-*cis*-cyclobutenediol is formed which had been obtained earlier by hydrolysis of tetramethyldichlorocyclobutene:



The complex is so stable that it decomposes only at 250°, forming the dimer of tetramethylcyclobutadiene:



Avram et al.[222] treated 1,2,3,4-tetrabromocyclobutane with lithium amalgam, and separated the resulting unstable cyclobutadiene in the form of its complex with silver nitrate, which apparently has the structure (LIV):



(LIV)

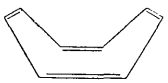
This complex is decomposed on heating with water, and the extremely unstable gas which is then evolved can again be absorbed in silver nitrate solution.

CYCLOOCTATETRAENE

The absence of aromatic properties in cyclooctatetraene is now well known and has been so widely demonstrated experimentally that we shall confine ourselves here to a brief consideration of the main results.

The chemical properties of cyclooctatetraene indicate the presence of typical double bonds in its molecule. Thus it is readily oxidised by potassium permanganate or mercuric sulphate solution, it adds on chlorine, bromine and hydrogen bromide, and also lithium and sodium, it is reduced by hydrogen on nickel, palladium, and platinum catalysts, and undergoes the Diels–Alder reaction with dienophiles (see, for example, Craig's review[223]).

Electron-diffraction and X-ray study of the structure of the cyclooctatetraene molecule also indicates the presence of alternating single and double bonds[224,225]. This agrees with the results of many spectral investigations. The spatial structure of the cyclooctatetraene molecule evidently corresponds to the symmetry D_{2d} in conformity with the "tub" or "boat" form (LV)[226–228].



(LV)

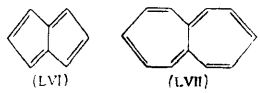
Thermochemical studies indicate the absence of appreciable conjugation in cyclooctatetraene; its heat of formation from the elements at 25° amounts to 59.07 ± 0.29 kcal/mole, and it is 34 kcal/mole less stable than the isomeric styrene[229].

Thus both the physical and chemical results are in agreement with molecular-orbital calculations, according to which the cyclooctatetraene molecule should not be aromatic[25,27,32,230], its conjugation energy should be low (not above 18.8 kcal/mole), and the molecule should contain alternating single and double carbon–carbon bonds of different lengths[27].

Cyclooctatetraene forms a dilithium derivative $Li_2C_8H_8$. According to a communication of Ubbelohde[231], not yet corroborated, the magnetic susceptibility of this compound indicates that it has the structure $(Li^+)_2(C_8H_8)^{2-}$ and is a derivative of the $C_8H_8^{2-}$ system containing ten π electrons and possessing aromatic character. In contrast to the dilithium derivative, dibromocyclooctatetraene is not a salt of the $C_8H_8^{2+}$ cation and is not aromatic.

PENTALENE AND HEPTALENE

If the nearest bicyclic analogues of azulene and naphthalene – pentalene (LVI) and heptalene (LVII) – are examined on the basis of the theoretical considerations described, it is readily concluded that, in spite of the presence of alternating single and double bonds, they should not possess aromatic properties.



(LVI) (LVII)

Pentalene contains a system of eight π electrons, and heptalene one of twelve π electrons; i.e. in neither case are conditions satisfied for the formation of a closed shell (in Hückel's sense) containing $(4n + 2)$ π electrons.

Quantum-mechanical calculations for pentalene and heptalene by the valence-bond method give quite different results. For pentalene they give a conjugation energy of 1.10 α (where $\alpha \cong 32$ kcal),[232–236] i.e. the same as for benzene; for a single π electron, however, calculation gives the same conjugation energy as in azulene.

The difference consists in the fact that, according to the valence-bond method, the wave function representing the ground state of pentalene and heptalene (and also of cyclobutadiene) is unsymmetrical relative to the symmetry axes of the molecule (it changes sign under certain symmetry operations)[25,233,234], whereas the wave functions of azulene, naphthalene, and anthracene are completely symmetrical. Craig[25] therefore suggested that cyclic molecules having a completely symmetrical ground state should be classed as normal aromatic molecules, and those having an incompletely symmetrical ground state (pentalene, heptalene, cyclobutadiene, cyclooctatetraene) as pseudoaromatic. However, Craig admits that there is no direct connection between this difference in symmetry of the wave function and the possible instability of such pseudoaromatic systems, since the valence-bond method predicts a high conjugation energy for them.

Calculations by the molecular-orbital method also indicate a considerable conjugation energy, 2.486 β (or 1.087 γ) in pentalene[232–236] and 3.61 β in heptalene[235]. A number of authors have concluded from this that these systems are stable[235,237].

Such a conclusion is, however, premature, and the above quantum-mechanical criteria of aromaticity permit different conclusions to be reached. Calculation by the molecular-orbital method gives the following energy levels for the molecular orbitals in pentalene, heptalene, and for comparison azulene (in γ units, where γ is about 42 kcal/mole)[238].

	Pentalene	Azulene	Heptalene
Anti-bonding levels		+4.4003	+4.7436
		+3.5089	+3.5873
	+4.000	+2.5566	+3.0548
	+3.3180	+0.9045	+1.3333
	+2.1876	+0.4449	+0.7985
			+0.3373
Non-bonding levels	0	—	0
Bonding levels	−0.4221	−0.4264	−0.8000
	−0.8000	−0.7260	−0.9910
	−1.0448	−1.0125	−1.0809
	−1.4775	−1.1689	−1.2087
		−1.4645	−1.4516

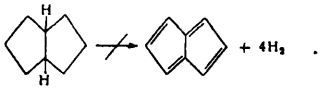
These data show that the eight π electrons in pentalene can occupy four bonding orbitals, and the ten π electrons in azulene five bonding orbitals. The nearest unoccupied level in pentalene proves to be one of zero energy, whereas in azulene, benzene, naphthalene, and all other fused benzene derivatives the nearest unoccupied level is always anti--bonding. The difference between the highest occupied and the lowest unoccupied levels is therefore comparatively low (0.4221 γ) in the case of pentalene, whereas it amounts to 0.8713 γ with azulene, 2.1333 γ with benzene, 1.2662 γ with naphthalene, 1.2388 γ with phenanthrene, etc.[238]. Since an unoccupied level of zero energy is present in pentalene, its molecule should be comparatively readily converted from the ground singlet state to an excited triplet (diradical) state, and consequently should be extremely reactive. On the other hand, the high reactivity of pentalene is due also to the fact that its molecule can accept a pair of electrons into an unoccupied non-bonding level and can therefore react readily with various nucleophilic reagents.

In heptalene ten of the twelve π electrons are in bonding levels, and two in a non-bonding level of zero energy. Consequently, it may be expected that the heptalene molecule will readily give up its electron pair under the influence of even weak nucleophilic reagents.

It may be concluded that the π-electron systems of pentalene and heptalene are not "closed", since they can readily either acquire (pentalene) or give up (heptalene) π electrons without appreciable consumption of energy. The case of pentalene and heptalene shows very clearly that the stability of an aromatic system is determined not only by a high conjugation energy of the π electrons but also by the way in which its molecular orbitals are filled (the "degree of completion" of the electron shell). Other examples supporting this thesis are the cation $C_5H_5^+$, for which the energy of conjugation is 1.24 β, and the anion $C_7H_7^-$ with a conjugation energy of 2.83 β. However, the former has one unoccupied bonding electronic level, and the latter contains two electrons in anti-bonding levels. Both these systems, therefore, in spite of their high conjugation energy, are unstable and are not aromatic. The abundant experimental data resulting from the numerous attempts to synthesise the pentalene and heptalene systems confirm the above conclusion as to their non-aromatic character.

The question of the existence of pentalene as a possible aromatic system was first raised by Armit and Robinson[239]. Subsequently, based on Robinson's idea of the necessity of a sextet of π electrons in aromatic systems, they expressed doubt about the possible aromaticity of pentalene[19].

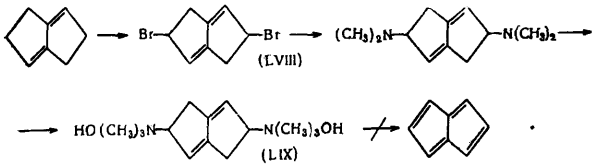
The formal analogy between pentalene and naphthalene, led Barrett and Linstead[240] to suggest that pentalene might be obtained by the dehydrogenation of *cis*-bicyclo[0,3,3]octane, since naphthalene is readily obtained by the dehydrogenation of decalin:



However, *cis*-bicyclo[0,3,3]octane remained unchanged at 300°–320° over platinised asbestos. Similarly, 2-benzylidene-*cis*-bicyclo[0,3,3]octane could not be dehydrogenated in the liquid phase by means of selenium[241].

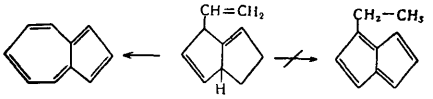
The attempted catalytic dehydrogenation of tetrahydropentalenes also failed[242]. When a mixture of them was passed over platinised asbestos at 360°–380° or over platinised charcoal at 320°–340° they remained practically unchanged, although under the same conditions tetralin is almost quantitatively converted to naphthalene. Attempts to convert tetrahydropentalene to pentalene by successive halogenation and dehydrohalogenation also proved unsuccessful[242].

Blood and Linstead[241] studied various routes to pentalene or its derivatives. Thus by the action of *N*-bromosuccinimide on tetrahydropentalene the dibromide (LVIII) was obtained, and was converted further into the bisquaternary ammonium base (LIX). Cleavage of this by Hofmann's method, however, yielded only a resin instead of pentalene:

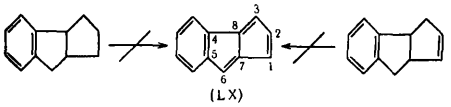


Finally, attempts by the same workers to dehydrogenate tetrahydro-1,4-dimethylpentalene to 1,4-dimethylpentalene over palladium black or palladised charcoal also ended in failure.

Vinyltetrahydropentalene when passed over palladised asbestos likewise is not converted into the substituted pentalene, small quantities of azulene only are formed[243]:

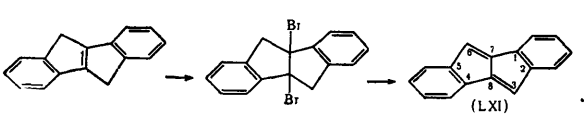


The attempted catalytic dehydrogenation of the hexahydro or the tetrahydro derivative to obtain benzopentalene (LX) was just as unsuccessful[244,245]:



Nor was it possible to dehydrogenate 4,5-dihydro-3,6--diphenylbenzopentalene, although the most varied methods were used (catalytic dehydrogenation, action of chloranil, dehydroindigo, sulphuryl chloride, lead tetraacetate, selenium dioxide, bromination with *N*-bromosuccinimide followed by dehydrobromination, etc.)[246]. An analogous attempt to obtain 4-methyl-6-isopropylbenzopentalene also ended in failure[247].

In 1952 Blood and Linstead[248] prepared 1,2:4,5-dibenzopentalene (LXI), in which the pentalene system is stabilised by two benzene rings; they obtained it by heating the bromination product of 3,6-dihydrodibenzopentalene with silver acetate:

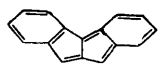


The properties of this compound clearly point to the absence of aromatic character in the pentalene system. Dibenzopentalene is rapidly hydrogenated at room temperature in the presence of palladised charcoal with the formation of

tetrahydrodibenzopentalene, it is reduced by sodium amalgam in alcohol to 3,6-dihydrodibenzopentalene, it is readily polymerised in solution in the presence of catalytic amounts of acid, it vigorously adds on a molecule of bromine, and very readily undergoes ozonisation at the 6,7 and 3,8 bonds. Thus the chemical behaviour of dibenzopentalene is like that of conjugated dienes.

In contrast to pentalene (LVI), the stabilised 1,2 : 4,5--dibenzopentalene system (LXI) is formed comparatively easily, and its numerous 3,6-derivatives have been known for a comparatively long time[249-260], having been obtained mainly by Brand and his collaborators[250-260]. All these compounds, like the unsubstituted dibenzopentalene, display the properties of typical olefins.

Attempts to synthesise 1,2 : 5,6-dibenzopentalene (LXII) have been unsuccessful[261], although calculation suggests that its conjugation energy should have almost the same value (110 kcal/mole) as the 1,2 : 4,5-isomer (120 kcal/mole)[236].



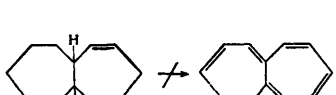
(LXII)

The following conclusions can be drawn from synthetic studies in the chemistry of pentalene:

1. Pentalene and its benzo and dibenzo derivatives, in contrast to naphthalene and azulene, are not obtained by the catalytic dehydrogenation of the corresponding di-, tetra-, hexa-, or octahydro derivatives.
2. In a wide variety of attempts to synthesise pentalene and benzopentalene by successive introduction of double bonds into the ring only polymerisation products were formed.
3. In cases in which bicyclic ketones could form the pentalene double-bond system by enolisation, such enolisation does not take place.
4. The central double bonds in dibenzopentalene display the properties of conjugated double bonds, not those of aromatic bonds.
5. In contrast to azulene, neither pentalene nor its derivatives are encountered among natural products.

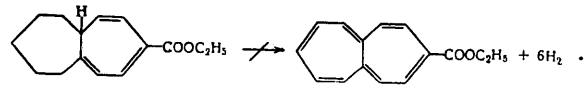
In conclusion, we may briefly consider the attempted synthesis of heptalene. The possibility that heptalene was an aromatic system was first raised by Baker[1], who in 1945 concluded, on the basis of incorrect views as to the nature of aromaticity, that the heptalene system should possess aromatic stability. The error of this conclusion is evident both from the preceding theoretical discussion and from the results of attempts to synthesise heptalene and its derivatives experimentally.

Thus an attempt at the catalytic dehydrogenation of decahydroheptalene (LXIII) over palladised charcoal at 310°--330° (in a vacuum, at 4 mm Hg) was unsuccessful[262]:

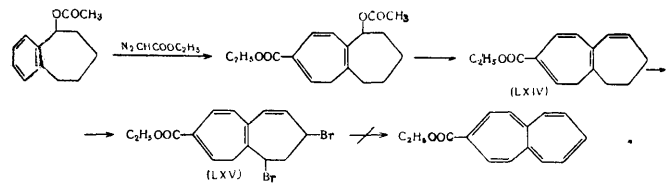


(LXIII)

Similarly, it proved impossible to obtain a substituted heptalene from the ethyl ester of bicyclo[5,5,0]dodeca-1,3,5--triene-3-carboxylic acid by liquid-phase dehydrogenation or by passing it over palladised charcoal in the vapour phase[263]:



The possibility of obtaining the heptalene system by successive introduction of double bonds was investigated[262], the following reactions being carried out:



The tetrahydroheptalene derivative (LXIV) yielded the dibromide (LXV) by the action of two molecules of *N*-bromosuccinimide, but on dehydrobromination of (LXV) with the most varied agents, rearrangement occurred with formation of substances containing a benzene ring.

Thus it has never been possible to synthesise heptalene or its derivatives, which indicates their instability and the absence of aromatic character in the heptalene system.

POLYCYCLIC SYSTEMS. GENERALISED HÜCKEL RULE

In the discussion of the azulene, pentalene, and heptalene systems, it is useful to consider the general question of the applicability of Hückel's rule to bicyclic and polycyclic systems.

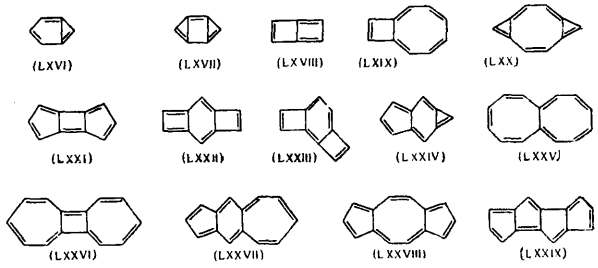
The criterion of a closed electron shell as a necessary condition for aromatic behaviour is applicable to any cyclic system. The rule for the stability of a system of $(4n + 2)$ π electrons, however, was derived by Hückel only for monocyclic molecules. Examination of numerous experimental results shows it to be applicable also to bicyclic fused systems. This is readily understood if it is assumed that the central, bridging bond introduces no appreciable change in the aromatic character of the system and is necessary only to maintain coplanarity. Such a simplification is the more admissible in that, as calculation shows, the "perturbation" caused by the central bond in naphthalene and azulene is in fact not too great and cannot affect the general aromatic character of the system.

If the bridge bond is neglected, naphthalene and azulene are derivatives of a ten-membered cyclic hydrocarbon, cyclodecapentaene, containing ten π electrons (i.e. $n = 2$ in the Hückel formula $4n + 2$) and therefore aromatic. Pentalene can be regarded as a derivative of cyclococtatetraene having eight π electrons, and heptalene as a derivative of dodecahexaene having twelve π electrons, and therefore aromatic properties can be expected to be absent from them. This rule can be extended also to a number of polycyclic systems. Thus anthracene and phenanthrene have fourteen π electrons, and as derivatives of a fourteen--membered ring they should be aromatic according to the Hückel rule (with $n = 3$), etc.

In its general form the rule can be stated as *any plane (or nearly plane) fused system containing no atoms common to more than two rings will be aromatic if the number of* π

*electrons in it is equal to 4n + 2 (where n is a whole number)**.

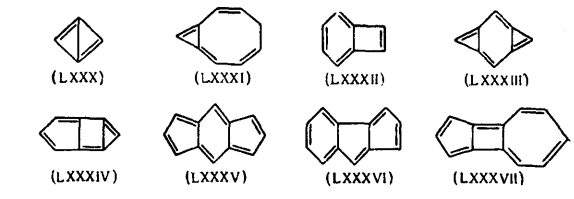
According to this generalised rule, aromaticity may be expected in the following as yet unknown systems: (LXVI)–(LXVIII), in which $n = 1$; (LXIX)–(LXXIV), where $n = 2$; and (LXXV)–(LXXIX), where $n = 3$:



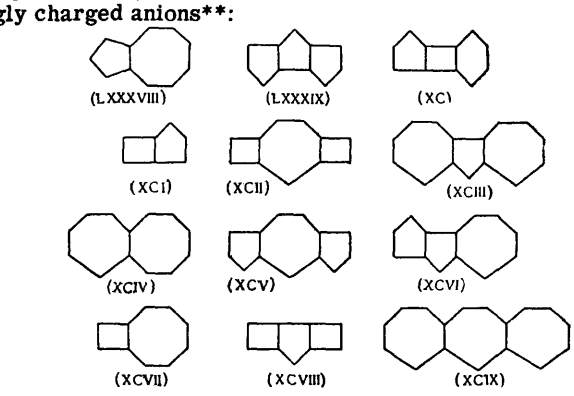
In each individual case, of course, the possibility must be taken into account of a reduction in stability due to the considerable angular strain, e.g. in (LXVII), and due to the possible non-coplanarity of eight-membered rings, e.g. in (LXXV).

Calculations have been made for the systems (LXVI), (LXVIII), and (LXXVI) which confirm the above qualitative conclusion; the conjugation energy for these systems is 2.39 β, 1.66 β, and 4.51 β respectively[22]. It is remarkable that aromaticity may be expected in fused systems composed of two cyclobutadiene (LXVIII), two cyclooctatetraene (LXXV), and two pentalene (LXXIX) residues.

From the same generalised rule, aromatic stability may be expected to be absent from the as yet unknown systems (LXXX)–(LXXXVII):



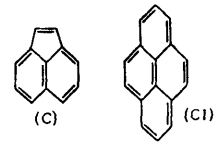
Finally, it follows from the generalised rule that the systems (LXXXVIII)–(XCIII) will be stable in the form of singly charged cations, and systems (XCIV)–(XCIX) in the form of singly charged anions**:



* This rule obviously relates only to systems in which the bridge contains no additional atoms (in the Baeyer nomenclature, to systems containing a zero-atom bridge).

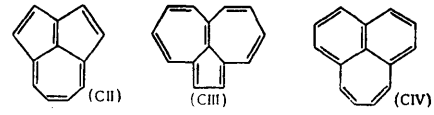
** Here and in formulae (CV)–(CVIII), for the sake of simplicity, only the carbon skeletons of the aromatic systems are indicated.

Matters are more complicated with tri- and polycyclic systems having atoms which are common to three rings. The rule of $(4n + 2)$ π electrons no longer operates with such systems. Thus, for example, the acenaphthylene (C) and pyrene (CI) systems have twelve and sixteen π electrons respectively, i.e. they do not conform to the formula $4n + 2$, although they are aromatic.

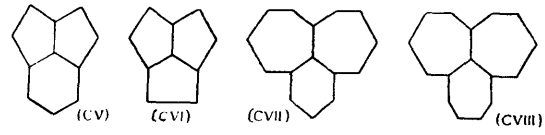


It is obviously necessary to carry out a calculation by the molecular-orbital method for each system to determine the numbers of bonding, non-bonding, and anti-bonding levels and thus to learn whether the molecule contains a closed π-electron system.

This type of calculation was carried out by Dyatkina and Shustorovich[23,264] for a number of tricyclic fused systems composed of five-, six-, and seven-membered rings, including some containing the pentalene and heptalene systems.



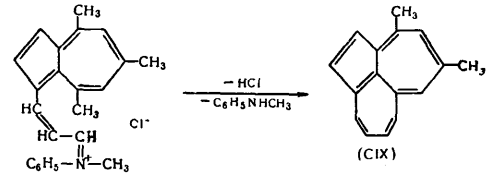
It was found that systems (CII)–(CIV) should possess aromatic stability, since the first has six bonding orbitals with a total of twelve π electrons, while the second and third have seven bonding orbitals and fourteen π electrons. Systems (CV) and (CVI) each have six bonding orbitals and eleven and ten π electrons respectively:



They should be stable in the form of the respective singly and doubly charged anions containing twelve π electrons.

Similar reasoning leads to the conclusion that the system (CVII) (seven bonding orbitals and fifteen π electrons) will have a tendency to change into the singly charged cation, whereas system (CVIII) (seven bonding orbitals and sixteen π electrons) will change into the doubly charged cation.

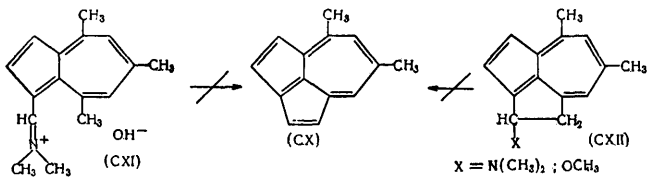
The results of this calculation by the molecular-orbital method have recently been confirmed experimentally. Hafner and Schneider[265] have synthesised the derivative (CIX) of one of the systems (CIII) calculated by Dyatkina and Shustorovich[23]:



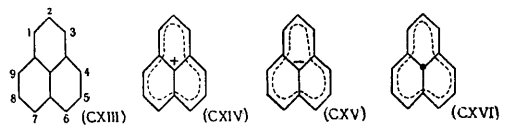
This compound proved to be quite stable. Like azulene, it dissolves in 50% sulphuric acid (with a red coloration) and is precipitated from these solutions with water, it readily

undergoes electrophilic substitution (Friedel–Crafts acetylation, and formylation), and its spectrum is similar to that of azulene. None of these results is consistent with Hafner and Schneider's view that the substance they have obtained is a heptalene derivative. Judging from its properties, it is rather an azulene derivative, in which the positive charge occurs in both seven-membered rings.

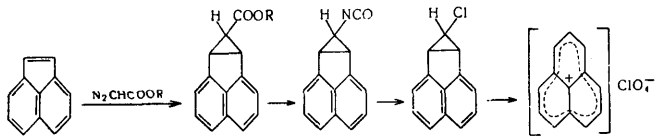
The analogous azulene derivative containing two five-membered rings (CX) should also be stable according to calculation[23], but it has not yet been possible to obtain it by cyclisation of the corresponding ammonium salts (CXI) or by introducing a double bond into 1,8-cyclopentenoazulene (CXII)[266]:



Finally, yet another interesting tricyclic system should be considered, the phenalenyl system (CXIII), which is remarkable in that it can exist in the form of the comparatively stable cation (CXIV), the anion (CXV), and the free radical (CXVI):



The phenalenyl cation (CXIV) was obtained by Pettit[267] by a method developed previously for the synthesis of tropylium salts. The action of diazoacetic ester on acenaphthylene yielded an acid, which was then converted, after a Curtius rearrangement, into a covalent isocyanate and then into a covalent chloride. The latter was converted into phenalenylium perchlorate on treatment with silver perchlorate:

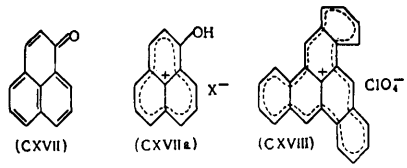


This salt is insoluble in non-polar solvents and soluble in strong acids, but it is readily hydrolysed and is not stable in air. The same salt can be obtained by interaction of silver perchlorate with the phenalenyl radical[268]:

$$C_{13}H_9^{\cdot} + AgClO_4 \rightarrow C_{13}H_9^{+}\,ClO_4^{-} + Ag.$$

The properties of phenalenylium iodide $C_{13}H_9I$ also indicate the ionic character of the link between the iodine and the organic residue[268].

The phenalenylium cation, although less stable than the tropylium cation, is, however, far more stable than the triphenylmethyl cation. The ability of the phenalenyl system to form a cation is shown also in the properties of the corresponding ketone, phenalenone (CXVII), which in many respects resembles tropone. Thus, phenalenone is soluble in acids and yields comparatively stable salts of the type (CXVIIa)[269, 270].

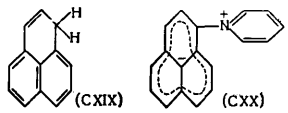


A close analogy with tropone is indicated also by the comparatively high dipole moment of phenalenone, which according to Zhdanov et al.[271] is 3.99 D (in dioxan). The complex formed by the ketone with $SbCl_5$ has a still higher dipole moment (8.49 D).[271] The ultra-violet spectrum of phenalenone perchlorate is very similar to that of the perchlorate of the phenalenyl cation[272]. The lower frequency of the CO bond in the ketone (1637 cm^{-1}) also points to considerable polarisation of the carbonyl group. The tribenzophenalenyl cation (CXVIII) also possesses similar stability. and also gives a quite stable perchlorate[273].

On the other hand, the properties of the original hydrocarbon, phenalene (CXIX), indicate that, like cyclopentadiene, indene, and fluorene, it is readily converted into the corresponding anion (CXV) by strong bases (phenyllithium, potassium methoxide)[272]:

$$C_{13}H_{10} + CH_3O^- \rightarrow C_{13}H_9^- + CH_3OH.$$

This anion is coloured an intense red; on treatment with methyl iodide it is alkylated forming methylphenalene. The ready formation of an anion is shown also by the fact that, like cyclopentadiene, phenalene readily condenses with benzaldehyde in the presence of bases. The hydrogen of the methylene group of phenalene is considerably more acidic than that in triphenylmethane, although less so than that in cyclopentadiene. Phenalene may be expected, like cyclopentadiene, to form stable "ylides" of the type (CXX).



The stable phenalenyl radical (CXVI) is also formed unusually readily[268,272,274]. Thus the phenalenide anion (obtained from phenalene by the action of potassium methoxide) on shaking in air is oxidised by molecular oxygen to the free radical:

$$C_{13}H_{10} \xrightarrow{OR^-} (C_{13}H_9:)^- \xrightarrow{+O_2} C_{13}H_9^{\cdot} + O_2 .$$

Phenalene reacts with triphenylmethyl to form triphenylmethane and the phenalenyl radical[272]:

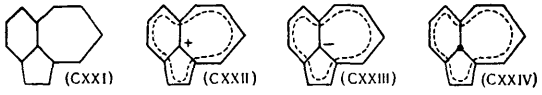
$$C_{13}H_{10} + (C_6H_5)_3C^{\cdot} \rightarrow C_{13}H_9^{\cdot} + (C_6H_5)_3CH.$$

Finally, phenalenyl is formed by treating phenalene with *N*-bromosuccinimide, by the action of organic bases on phenalene 2,3-dibromide[272], and also by the oxidation of phenalene with osmium tetroxide in the presence of pyridine[268]. This free radical can be isolated in the solid form. It has a green colour, does not react with nitric oxide, and adds on oxygen forming a peroxide.

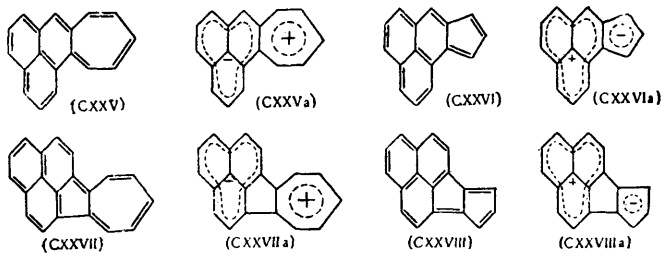
Apart from the unsubstituted phenalenyl radical, the following derivatives have now been obtained as stable radicals: 1,4,7-trimethyl, 1-hydroxy-3-phenyl, 1-methoxy, 1-acetoxy, and 1-benzoyloxy derivatives[275].

Thus the phenalenyl system can form a stable cation, anion, and free radical, which are appreciably more stable than the corresponding triphenylmethyl forms. This feature of the system can be explained by the character of its molecular orbitals. Calculation[23] shows the phenalenyl system to have molecular orbitals with the following energy values (in β units): six bonding (-2.45, -1.73, -1.73, -1.00, -1.00, and -1.00), one non-bonding (0), and six anti-bonding orbitals. The twelve π electrons of the cation can be arranged in six bonding orbitals, which explains its stability. On the other hand, the non-bonding orbitals can take up, without any gain or loss in energy, either one or two electrons with the formation of a radical or an anion respectively. The energy of the cation, radical, and anion proves to be the same (15.82 β). Thus, although the phenalenyl system does not possess a closed electron shell, it will be stable, depending on the conditions, in strongly acid media in the form of a cation, in strongly alkaline media in the form of an anion, and in the presence of free-radical reagents or when acted upon by oxidising agents in alkaline media or reducing agents in acid media in the form of a free radical. The triphenylmethyl system, which possesses analogous properties (although less strongly marked), also has one non-bonding level of zero energy.

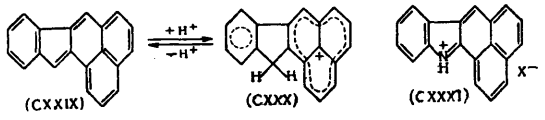
There is every reason to suppose that other cyclic systems containing an odd number of atoms and possessing non-bonding orbitals should also exhibit their own kind of "amphoteric" properties, like the phenalenyl system. Thus, for example, the system (CXXI), which is isoelectronic with the phenalenyl system and has six bonding, one non-bonding, and six anti-bonding orbitals[23], should apparently form the stable cation (CXXII), anion (CXXIII), and free radical (CXXIV).



On the basis of the "amphoteric" properties of the phenalenyl system described above, Reid[268] suggested that it will be able to form dipolar compounds of the azulene type, in which either the five-membered or the seven-membered ring may be replaced. Such are the aromatic systems (CXXV)–(CXXVIII), which like azulene should show a tendency to be polarised to (CXXVa)–(CXXVIIIa).



Reid was able to obtain a benzo derivative of one of these systems, indeno[2,1-*a*]phenalene (CXXIX)[274]:



This hydrocarbon, like azulene, possesses basic properties and dissolves in strong acids forming the corresponding cation (CXXX) (green colour). The basic strength of (CXXIX) is equal to that of azulene. It readily undergoes electrophilic substitution, being acetylated (even in the absence of catalysts) and nitrated. Reid also obtained heterocyclic nitrogen-containing analogues (CXXXI) of this dipolar system.

However, it was not possible to synthesise the unsubstituted cyclopenta[*a*]phenalene (CXXVI) by dehydrogenation of the corresponding tetrahydro derivative (either catalytically or with sulphur), or by bromination and dehydrobromination.

MACROCYCLIC AROMATIC SYSTEMS

It is theoretically possible on the basis of Hückel's rule that aromatic systems containing not only six but also a large number of π electrons can exist. Aromaticity could apparently be expected in conjugated cyclic polyolefins C_mH_m having m = 10, 14, 18, 22, etc. (corresponding to values of n = 2, 3, 4, 5, etc. in the Hückel formula $4n + 2$).

However, the existence of such macrocyclic systems in the form of plane regular polygons is unlikely owing to the great angular strain, and the transition of the molecules into a non-planar form would considerably diminish the conjugation energy.

A second possibility consists in the formation of a hydrocarbon skeleton of unstrained plane equilateral polygons having internal angles not only of 120° but also of 240°. It is easy to show from general geometrical considerations that, if the number of 120° angles is denoted by x, and that of 240° angles by y, any polygons having both 120° and 240° angles and a total of $2k$ angles (where k is an integer $\geqslant 3$) will conform to the relationship $x = k + 3$ and $y = k - 3$*. The Table gives numerical values of x and y calculated from these relationships for cyclopolyolefins.

Numbers of 120° angles (x) and 240° angles (y) in unstrained plane cyclopolyolefins.

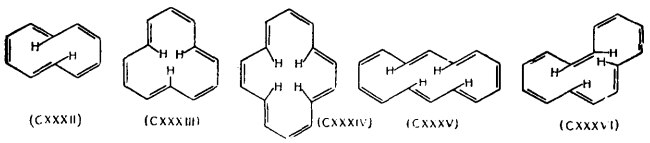
k	$C_{2k}H_{2k}$	x	y
3	C_6H_6*	6	0
4	C_8H_8	7	1
5	$C_{10}H_{10}$	8	2
6	$C_{12}H_{12}$	9	3
7	$C_{14}H_{14}$	10	4
8	$C_{16}H_{16}$	11	5
9	$C_{18}H_{18}$	12	6
15	$C_{30}H_{30}$	18	12

* Only a regular hexagonal structure is possible.

The values of x and y given correspond formally to the unstrained systems cyclodecapentaene (CXXXII) (x = 8, y = 2), cyclododecahexaene (CXXXIII) (x = 9, y = 3), and

* The total number of angles $2k = x + y$; the sum of all the angles is $120x + 240y = 180 \times 2k - 360°$; values of x and y are deduced from these two equations.

cyclotetradecaheptaene (CXXXIV)–(CXXXVI) ($x = 10$, $y = 4$):



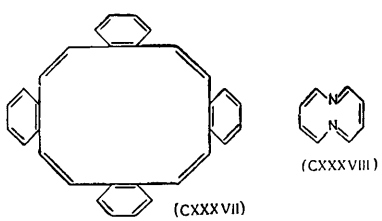
(CXXXII) (CXXXIII) (CXXXIV) (CXXXV) (CXXXVI)

Among these, systems having odd values of k ($C_{10}H_{10}$, $C_{14}H_{14}$, $C_{18}H_{18}$, etc.) should be aromatic according to the Hückel rule. As Mislow[276] showed in 1952, however, if the C–C distance is taken as 1.40 Å, C–H as 1.10 Å, and the van der Waals radius of hydrogen as 1.10 Å, a very marked repulsion between the central hydrogen atoms is to be expected in all such molecules. This repulsion would produce a considerable distortion of the system and force it out of planarity. It is only when the ring has grown considerably, to $C_{30}H_{30}$, that the interaction between the central hydrogen atoms can be neglected. Mislow pointed out that the conjugation energy calculated for cyclotriacontapentadecaene, $C_{30}H_{30}$, is 140 kcal/mole, and the compound may be expected to be aromatic.

Until recently no experimental results were available on the properties of macrocyclic polyenes of this type. The hydrocarbon $C_{10}H_{10}$, obtained by Reppe together with cyclooctatetraene in the polymerisation of acetylene[277], proved to be not cyclodecapentaene, as was supposed at first, but a mixture of vinylcyclooctatetraene and 1-phenylbuta-*cis*-1,3-diene[278,279]. The hydrocarbon $C_{12}H_{12}$, formed under the same conditions, is evidently not cyclododecahexaene, although there is as yet no reliable information on its structure.

In the dehydrogenation of various cycloalkanes on palladised charcoal Prelog et al.[280] failed to obtain monocyclic polyenes. Intracyclic formation of new carbon–carbon bonds with the production of polycyclic structures always occurred. Thus cyclodecane changed into azulene and naphthalene, cyclododecane into acenaphthene and acenaphthylene, cyclotetradecane into phenanthrene and anthracene, and cyclohexadecane into fluoranthene. However, the small amounts of the initial cycloalkanes (1–2 g) and the low yields of dehydrogenation products (20–30%) in Prelog's experiments make it possible to ascertain only the main direction of the reaction, and do not exclude the possibility of the formation of comparatively small quantities of cyclopolyenes. Further, as a result of the high temperature (400°), any cyclopolyenes which are formed may undergo secondary conversion into polycyclic systems. This question obviously requires further experimental investigation.

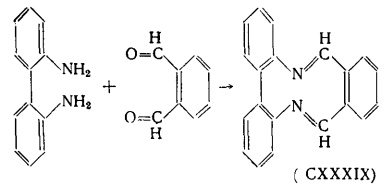
Few data exist on the tetrabenzo derivative of cyclohexadecaoctaene (CXXXVII), which is non-planar and contains olefinic double bonds in the *trans*-configuration according to its infra-red spectrum[281]; this ring with sixteen π electrons could not be expected to be aromatic in character according to the Huckel rule:



(CXXXVII)

(CXXXVIII)

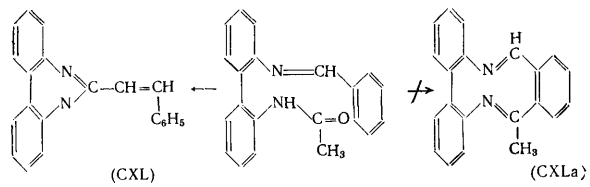
Recently several new approaches to the synthesis of aromatic macrocycles have been proposed. Blood and Noller[282] suggested that the repulsion between the central hydrogen atoms in the cyclodecapentaene system could be avoided by replacing the appropriate CH groups by N. They considered that the nitrogen analogue, 1,6-diazacyclodecapentaene (CXXXVIII) should (1) be unstrained, (2) be planar, (3) have no central H atoms, and (4) possess ten π electrons and be aromatic in conformity with the Hückel rule. However, no success was obtained in an attempt to synthesise the tribenzo derivative (CXXXIX) of such a system by the reaction



(CXXXIX)

only products of high molecular weight were formed. Evidently only linear polycondensation occurs in the course of the reaction.

Moreover, this system could not be obtained by intramolecular cyclisation of *N*-benzylidene-*N'*-acetyl-2,2'-diaminobiphenyl, the seven-membered ring closing (CXL), but not the ten-membered ring (CXLa):

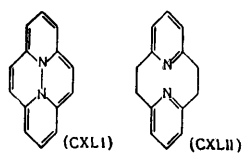


(CXL) (CXLa)

The reason for the failure of this work is obviously the omission by the authors from their theoretical premises of the considerable repulsion between the neighbouring nitrogen atoms in the 1,6-diazacyclodecapentaene system, although the distance between them (~ 1.4 Å) is only half the sum of the van der Waals radii of the two nitrogen atoms (~ 3 Å).

Nevertheless, this idea of Blood and Noller's must be regarded as useful, but it can be applied only to larger rings, in which the distances between the central atoms are considerably greater.

Another similar approach to the formation of macrocyclic aromatic systems was suggested by Baker[283]. Thus, for example, the system (CXLI) in Baker's opinion possesses the peripheral conjugated cyclotetradecaheptaene system with fourteen π electrons. This system should be almost unstrained, though it is possible that one nitrogen atom is above the plane and the other beneath it. So far Baker et al. have described only the tetrahydro derivative (CXLII), and there is some indication that its dehydrogenation leads to (CXLI)[283]:

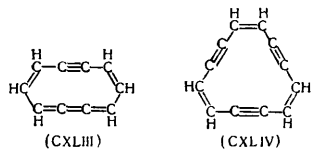


(CXLI) (CXLII)

However, one substantial defect is inherent in this interesting approach to the stabilisation of macrocyclic polyenes: there are no grounds for assuming that the lone pairs of p electrons of the nitrogen atoms will be isolated from the π electrons of the aromatic system. It is highly probable

that these p electrons will form a new system, different from the cyclotetradecaheptaene system and with different energies of the ground and excited states, in which the nitrogen bridge will form part not only of the framework but also of the aromatic system.

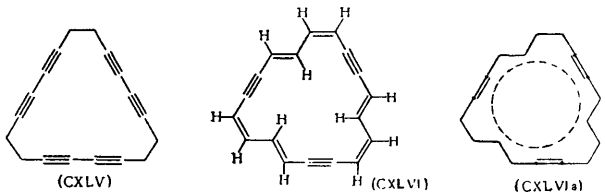
Yet another path to aromatic macrocycles, suggested by Sworski[284], consists in introducing linear acetylenic or cumulene groups into the benzene ring. Such are the systems (CXLIII) and (CXLIV), which can be written in the form of Kekulé structures having unstrained angles and are planar; every carbon atom in them has a p-orbital perpendicular to the ring:



(CXLIII) (CXLIV)

Sworski concludes that both these systems should be aromatic. The first contains fourteen π electrons, of which ten form a conjugated system, so that it obeys the Hückel rule. In the second, however, only twelve of the eighteen π electrons can take part in the conjugation, so that according to this rule the system should not be aromatic.

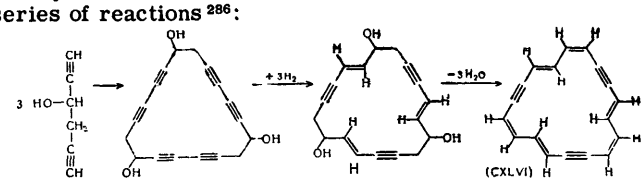
Sondheimer and Wolovsky[285] in 1959 published a paper on the synthesis of the first such macrocycle containing, in conformity with Sworski's hypothesis, triple bonds. Oxidation of hexa-1,5-diyne with copper acetate in pyridine yields the trimer, cyclooctadeca-1,3,7,9,13,15-hexayne (CXLV). This on treatment with potassium t-butoxide in t-butyl alcohol (at 90°) undergoes rearrangement to a substance which has been given the structure cyclooctadeca-*cis*-1,7,13:*trans*--3,9,15-hexaene-5,11,17-triyne (CXLVI). As can be seen from the structural formula, the ring in (CXLVI) has the form of a plane polygon, the distance between the internal hydrogen atoms being sufficiently great for their mutual repulsion to be low. This molecule contains twenty-four π electrons, of which eighteen form a conjugated system obeying the Hückel rule ($4n + 2$ with $n = 4$). A closed electron shell is thus formed, and this system is aromatic (cf. CXLVIa).



(CXLV) (CXLVI) (CXLVIa)

Too few results are yet available to confirm whether the substance obtained by Sondheimer and Wolovsky actually has the structure indicated. In their opinion this is supported by the ease of formation of the compound, its comparative stability (it decomposes only at 200°, and is stable to the action of light and air), and, confirming a monocyclic structure, its catalytic hydrogenation to cyclooctadecane.

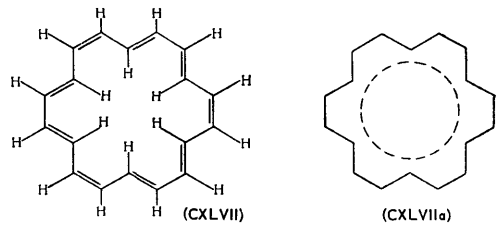
In order to prove the structure (CXLVI), the compound was synthesised from hexa-1,5-diyn-3-ol by the following series of reactions[286]:



It cannot be agreed, however, that this synthetic path proves the structure (CXLVI), since it was not possible to isolate any of the intermediate compounds in a pure form or to identify them.

This macrocyclic aromatic compound is of such great theoretical interest that a more rigorous determination of its structure will undoubtedly be made shortly. If the structure (CXLVI) is confirmed, it will be the first monocyclic aromatic compound to contain more than six π electrons. It will be interesting also as the first stable aromatic compound containing triple bonds in the ring, thus being an analogue of dehydrobenzene, whose transient formation has been established in a number of cases[287].

Especially interesting results were obtained by Sondheimer and Wolovsky[288] by the selective hydrogenation of (CXLVI) on a palladium catalyst, when *trans* addition of six hydrogen atoms to the triple bonds occurred with formation of cyclooctadecanonaene (CXLVII):



(CXLVII) (CXLVIIa)

This hydrocarbon contains a conjugated system of eighteen π electrons and thus conforms to the Hückel rule; its molecule can be planar or almost planar and relatively unstrained. Consequently, according to the criteria of aromaticity discussed above, cyclooctadecanonaene should exhibit aromatic properties. It was actually found to have a centrosymmetric, almost planar structure and to be considerably more stable than its acyclic analogue $CH_3.[CH:CH]_9.CH_3$. It is stable on heating even to 230°, although it gradually decomposes on prolonged standing in the light and in air. This substance is the first macrocyclic aromatic compound known, and can be represented by formula (CXLVIIa). It must be assumed that non-benzenoid aromatic macrocycles of this type will be the object of intense research in the immediate future.

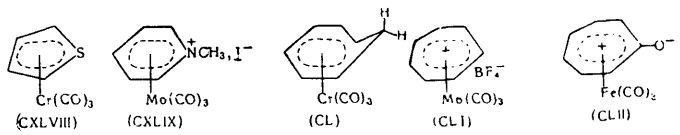
AROMATIC COMPLEXES OF METALS

During the past seven or eight years a completely new field of organic chemistry, the chemistry of aromatic complexes of metals, has arisen and has been vigorously developed.

The detailed reviews by Nesmeyanov and Perevalova on the cyclopentadienyl derivatives of metals and related systems[289] and by Dyatkina on the structure and nature of the bonds in these compounds[290] make it unnecessary to dwell on this question.

Recently the range of aromatic and unsaturated systems which form complexes with transition metals has been considerably extended. Among complexes which have been obtained are tricarbonylthiophenchromium (CXLVIII)[291], dicarbonylthiopheniron[292,293], tricarbonyl-1-methylpyridiniummolybdenum iodide (CXLIX)[292,293], tricarbonylcycloheptatrienechromium (and -molybdenum) (CL)[294], and finally

tricarbonyltropyliummolybdenum fluoroborate (CLI) and tricarbonyltroponeiron (CLII)[295,296]:



(CXLVIII) (CXLIX) (CL) (CLI) (CLII)

Diamagnetic complexes of cycloheptatriene and tropylium with salts of platinum, $(C_7H_8PtBr_2)_2$ and $(C_7H_7PtBr_2)_2$,[297] have also been obtained, as well as complexes of carbonyls of the transition metals with azulene, $C_{10}H_8Fe_2(CO)_5$ [292,293] and $C_{10}H_8Mo_2(CO)_6$,[298] in which one azulene molecule is associated with two atoms of the metal.

These results suggest that all aromatic systems are able through their π electrons, to form compounds with transition metals (or their carbonyls). This property, however, is characteristic not only of aromatic rings. Thus we have the complexes formed by cyclobutadiene with $AgNO_3$ and by tetramethylbutadiene with $NiCl_2$ which have already been considered, as well as cycloheptatriene complexes. An analogous complex of cyclooctatetraene has recently been obtained[299,300]. Complexes with carbonyls are formed even by bicycloheptadiene, whose system of multiple bonds is not conjugated[292,301].

The important question still remains open as to whether the cyclobutadiene and cyclooctatetraene systems become aromatic after they have formed complexes with transition metals. Interaction of the ring with the metal produces a new system of molecular orbitals, and there is every ground for supposing that the electron system in such complexes will be closed and stable in spite of the π-electron system in the original hydrocarbons being "unclosed".

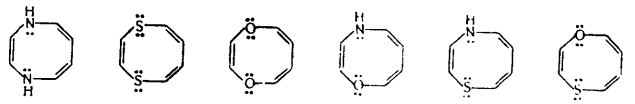
AROMATIC HETEROCYCLES

A large number of five- and six-membered heterocycles possessing an aromatic sextet of π electrons are now known. Owing to lack of space, only certain general aspects of aromatic heterocyclic systems will be considered here.

As Baker[2] points out, any systems of these types can be derived by replacing one or several =CH– groups in the Kekulé formula for benzene by =N– (e.g. pyridine), $=\overset{+}{N}R-$ (pyridinium derivatives), $=\overset{+}{O}-$ (pyrylium salts); or a –CH: :CH– group by hetero atoms having a lone pair of p electrons: –NH– (pyrrole), –NR– (*N*-substituted pyrroles), –O– (furan), –S– (thiophen). The "perturbation" caused by introduction of hetero atoms is not very great, and has no effect on whether or not the electron shell of the molecule is closed[20].

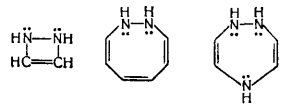
Baker establishes the following limitations to the formation of aromatic heterocycles: (1) for the heterocycle to retain its aromatic character it should be a five-, six-, or seven-membered ring; (2) formation of the heterocycle may be impeded by certain chemical restrictions, e.g. the instability of the –O–O– link.

The first of Baker's limitations is hardly correct. There are no grounds for supposing that eight-membered heterocycles should, like cyclooctatetraene, completely lose their aromatic character. Moreover, aromaticity can evidently be expected in the hypothetical eight-membered systems



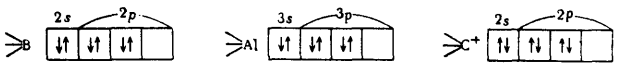
They form a closed system of ten π electrons, and thus conform to Hückel's rule (although they may not be completely planar). Just as five-membered heterocycles are "element-homologues" of the cyclopentadienyl anion, the eight-membered rings may be regarded as analogues of the $C_8H_8^{2-}$ anion. Synthesis of systems of this type could be of great theoretical interest.

On the other hand, a further restriction must be placed on the "construction" of heterocyclic aromatic systems. A single conjugated system of π electrons cannot be formed if a –CH:CH– group is replaced by two neighbouring hetero atoms; i.e. if the heterocycle contains side by side two atoms which are donors of p electrons and are linked by single bonds*. For example, aromaticity cannot be expected in the following heterocyclic systems, in spite of the presence in them of six or ten π electrons:

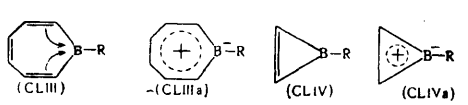


Besides the two methods of formation of aromatic heterocycles formulated by Baker (replacement of –CH= and –CH:CH– groups), there is another possibility which he did not consider: heterocyclic systems which are analogues of tropylium can be formed from the benzene system by addition of a hetero atom with a free orbital.

Whereas the characteristic aromatic heterocyclic analogues of the cyclopentadienyl anion are five-membered rings containing hetero atoms possessing a lone pair of electrons, the tropylium system may be expected to have seven-membered analogues containing hetero atoms possessing a vacant p-orbital, primarily boron and aluminium:



The electronic configuration of tervalent boron very closely resembles that of the carbon atom. Replacement of one C atom in the tropylium ion by a boron atom should lead to an uncharged molecule which is a seven-membered heterocyclic system having aromatic properties. Thus, the hitherto unknown 7-boratropylidene ("borepin") (CLIII) may be expected to form a stable aromatic system having six π electrons:



(CLIII) (CLIIIa) (CLIV) (CLIVa)

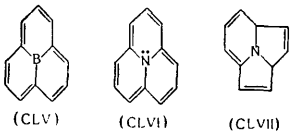
* This is because the number of bonding molecular orbitals is insufficient to contain all the p electrons in such cases.

As a result of the filling of the vacant orbital of the boron atom, the latter should become to a considerable extent quadricovalent and negatively charged, and the carbon atoms should acquire some positive charge: the molecule as a whole should possess an appreciable dipole moment (see CLIIIa).

Similar arguments lead to the conclusion that the existence of a three-membered aromatic system containing boron as hetero atom (CLIV or CLIVa) is possible.

This qualitative picture and the prediction of the existence of the new aromatic system borepin[73] have recently been supported by quantum-mechanical calculations made by Bochvar et al.[302]. It was found that the "perturbation" produced by replacing a $-CH=$ group by a less electronegative hetero atom does not affect the closed character of the electron shell, and borepin like tropylium should possess three bonding and four non-bonding orbitals with six π electrons; i.e. it should be aromatic.

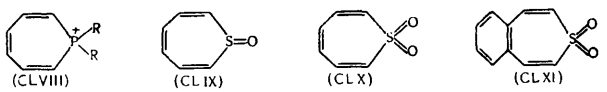
Interesting heterocyclic analogues may be suggested also for the phenalenyl system, which, as has been seen, exists both as a stable cation and as a stable anion (CXIV and CXV). When the central C^+ atom in the cation is replaced by the isoelectronic boron atom[268], and the C^- atom in the anion by the isoelectronic nitrogen atom, the uncharged systems (CLV) and (CLVI) are obtained, and these should evidently possess aromatic stability (although their peripheral hydrocarbon system possesses twelve π electrons).



(CLV) (CLVI) (CLVII)

The name "cyclazines" has recently been suggested for nitrogen-containing compounds of this type, and the first representative of these heterocycles, cycl[3,2,2]azine (CLVII), has been synthesised[303]. This compound, in contrast to pyrrolidine, does not possess basic properties. This means that the lone pair of electrons of the nitrogen atom takes part in the formation of an aromatic system, which is isoelectronic with the hypothetical anion (CXV) considered above. Cycl[3,2,2]azine is extremely stable and readily undergoes aromatic electrophilic substitution.

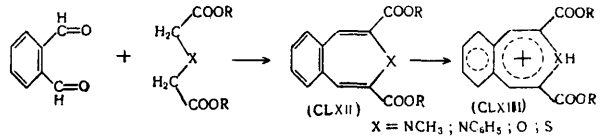
It may be expected that elements not only of Group III but also of other groups of the Periodic System which have vacant *p* or *d* orbitals (e.g. quadricovalent phosphorus) will be able to form aromatic systems analogous to those considered above, e.g. (CLVIII)–(CLXI):



(CLVIII) (CLIX) (CLX) (CLXI)

The arguments of Truce and Lotspeich[304] in support of the absence of aromatic properties in benzo-3-thiepin 3-dioxide (CLXI) are not convincing, since they did not investigate the behaviour of this compound towards acids, and it is in acid solutions that, like tropone, it should exhibit aromatic stability. Further, the fact that this sulphone is nitrated by concentrated nitric acid[304] may be regarded as a direct indication both of its aromatic character and of its stability towards acids.

It is interesting that Dimroth et al.[305-307] have found that derivatives of 7-aza-, 7-oxa-, and 7-thiabenzotropylidene (CLXII) in acid solution form stable salts of the type (CLXIII), which are heterocyclic analogues of the benzotropylium cation:



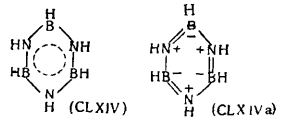
(CLXII) (CLXIII)

X = NCH_3 ; NC_6H_5 ; O ; S

INORGANIC AROMATIC COMPOUNDS

Successive replacement of all the carbon atoms in benzene or other aromatic systems by appropriate hetero atoms will yield compounds containing no carbon but retaining their aromatic properties.

The first example of this type was borazole ("inorganic benzene") (CLXIV), obtained by Stock and Pohland[308] in 1926 and now well investigated. In the six-membered borazole ring the boron atoms contain vacant *p*-orbitals, and the nitrogen atoms unshared pairs of *p*-electrons:



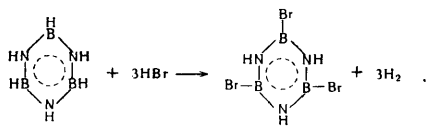
(CLXIV) (CLXIVa)

Conditions are thus created for the formation of molecular orbitals of the same type as in benzene, in which six π electrons are distributed. As a result, the boron atom becomes quadricovalent and negatively charged, while the nitrogen atom becomes quadricovalent and positively charged (cf. the "Kekulé" structure CLXIVa). The aromaticity to be expected in such a system is confirmed by electron diffraction data[309,310], according to which the borazole molecule is a planar equilateral hexagon with D_{3h} symmetry and NBN and BNB angles of 120°. The B–N interatomic distances are 1.44 Å, very close to the C–C bond lengths in benzene (1.42 Å); the experimental value lies between those calculated for single B–N bonds (1.50 Å) and for double B=N bonds (1.35 Å). Similar results were obtained for substituted borazoles[311].

Among the chemical properties of borazole its high thermal stability is remarkable. Thus it remains completely undecomposed even after being heated at 500° for 12 h.

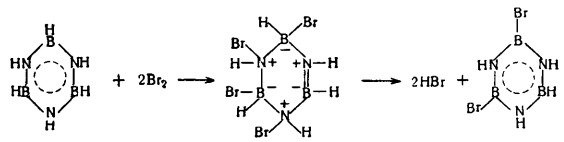
Borazole proves to be less stable than benzene towards chemical reagents (see Wiberg's review[312]). Even at room temperature it adds on hydrogen halides, water, alcohols, bromine, and chlorine, excess of the reagents frequently disrupting the borazole ring.

However, it is possible by heating with HBr at 100° or with HCl at 450° to replace hydrogen by halogen with the formation of substituted borazoles[313,314]:



This reaction is analogous to nucleophilic substitution in benzene derivatives.

Substitution products are formed also by the action of elementary bromine on borazole, this reaction occurring via intermediate addition of bromine and thermal decomposition of the adduct (slowly at room temperature, rapidly at 60°–70°)[313]:



All these results confirm the aromatic character of the borazole system.

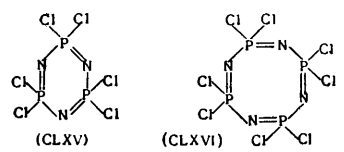
A further interesting class of inorganic aromatic compounds is formed by the cyclic phosphoronitrile halides $(PNX_2)_n$.[315]

The most accessible of them, the chlorides, can be readily synthesised by heating phosphorus pentachloride with ammonium chloride[316,317]:

$$n\,PCl_5 + n\,NH_4Cl \rightarrow (PNCl_2)_n + 4n\,HCl.$$

Phosphoronitrile chlorides are obtained with n = 2, 3, 4, 5, 6, and 7;[318] a linear polymer $(N:PCl_2)_n$ is also known.

The most thoroughly studied of these compounds are the trimer $P_3N_3Cl_6$ and the tetramer $P_4N_4Cl_8$, for which a monocyclic structure has been firmly established. By analogy with organic compounds, the formulae (CLXV) and (CLXVI), with alternating single and double bonds, can be written for the trimer and the tetramer:



(CLXV) (CLXVI)

Brockway and Bright[319] have shown by means of electron diffraction that the six-membered ring of the trimer is planar: all the PN bonds are equal with the chlorine atoms linked to phosphorus and situated below and above the ring. The interatomic PN distances are 1.65 Å; i.e. they lie between the values calculated for single and double bonds between phosphorus and nitrogen (P–N 1.80, P=N 1.61 Å). The PCl distances are 1.97 Å (calculated for P–Cl 2.09, for P=Cl 1.89 Å). The Cl–P–Cl angles are 107°–110°, and the N–P–N and P–N–P angles are 120°.

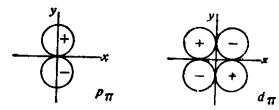
X-ray data show that, although the eight-membered ring of the tetramer is not planar, all the P–N distances are the same[320], like those in the six-membered ring. This result appears at first sight unexpected in view of the non-equivalence of the carbon–carbon bonds in the corresponding organic analogue, cyclooctatetraene.

The reactivities of the six- and eight-membered cyclic phosphoronitrile chlorides also proved to be similar. They are characterised by the comparative stability of the cyclic part of the molecule and the ready substitution of the chlorine atoms by other groups (OH, NR_2, C_6H_5) by the action of nucleophilic reagents such as water, amines, and phenylmagnesium bromide[321–325]. The chlorine atoms can be readily replaced by the phenyl group by condensation with benzene in the presence of aluminium chloride[326].

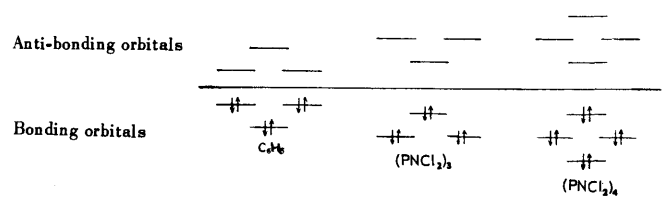
Particularly interesting results have been obtained in a quantum-mechanical examination of the cyclic phosphoronitrile chlorides carried out by Craig and Paddock[327–329].

Formation of the aromatic systems of benzene and other organic compounds involves the p-orbitals of the carbon atoms (p_π orbitals), and as a result of their interaction common molecular orbitals are produced. In the phosphoronitrile chlorides the nitrogen, like the carbon in benzene, can use its p_π orbital for the formation of an aromatic bond. The phosphorus atom, however, already linked to four other atoms by single bonds formed by one s and three p orbitals (sp^3 hybridisation), has only the nearest d_π orbital unoccupied. Thus the molecular orbitals in the cyclic phosphoronitrile chlorides are formed from alternating p_π and d_π atomic orbitals.

The six-membered ring of the trimer $(PNCl_2)_3$, like that of benzene, has three bonding molecular orbitals, among which are distributed six π electrons. However, as a result of p_π–d_π interaction, these molecular orbitals differ appreciably from those in benzene, the essential point being that the d_π orbitals have a different symmetry of the electron cloud from the p_π orbitals, as well as different energy levels:



This difference is shown in the phosphoronitrile chlorides by an exchange of positions between the degenerate and the non-degenerate level (see scheme below). Besides this, the highest bonding level now lies somewhat above that in benzene and is closer to the lowest non-bonding level, resulting in a lower excitation energy of the molecule.



The effect of the symmetry of the d orbitals of phosphorus becomes still more evident on passing from the six-membered trimer to the eight-membered ring of the tetramer. A new bonding orbital appears, in which two new π electrons are distributed. Thus, in contrast to cyclooctatetraene, a closed electron shell is formed in the eight-membered phosphoronitrile chloride, and the latter molecule should exhibit aromatic stability. The aromatic character of the tetramer is confirmed by the equality between the interatomic distances in the ring, and also by its chemical properties.

A similar result is obtained by the application of quantum-mechanics to rings containing ten, twelve, etc. atoms. The Hückel rule of $(4n + 2)$ π electrons in aromatic systems is confined solely to p-orbital interaction. In the case of p_π–d_π interactions, however, a closed system is formed with any even number of π electrons (formula $2n$ where n is an integer).

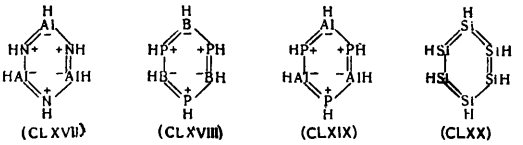
Craig and Paddock[327] have calculated the following energy values for a single π electron in cyclic phosphoronitrile chlorides (in appropriate δ units) and in cyclic hydrocarbons (in β units) (for plane systems):

Compound	Number of electrons (n)				
	4	6	8	10	12
$C_n H_n$	1.0	1.33	1.20	1.30	1.243
$(PNCl_2)_{n/2}$	1.78	1.87	1.89	1.90	1.908

The Table shows that, whereas in the hydrocarbons there is an alternation in stability, in the phosphoronitrile halides the energy increases steadily up to n = 8–10, and then remains constant. It is possible, however, that the absence of planarity in the higher rings will cause a diminution in the stability of the molecules.

The quantum-mechanical examination of the phosphoronitrile halides as an aromatic system provides yet another way of applying to inorganic compounds the laws and concepts of organic chemistry. These compounds may be supposed to form the first but by no means the only example of p_π–d_π aromatic systems.

Similarly, a number of new inorganic systems having p_π interaction may be expected to possess an aromatic character. Thus Wiberg[312] suggests the possibility of the existence of such "element homologues" of borazole as "alazole" $Al_3N_3H_6$ (CLXVII), "boraphosphole" $B_3P_3H_6$ (CLXVIII), and "aluphosphole" $Al_3P_3H_6$ (CLXIX), in which, as in borazole, atoms having vacant p orbitals alternate with atoms possessing free pairs of p electrons.



(CLXVII) (CLXVIII) (CLXIX) (CLXX)

Of interest in this connection is the preparation of a silicon analogue of benzene described by Urry[330]:

$$SiCl_4 \xrightarrow{Si} Si_6Cl_6 \xrightarrow{LiBH_4} Si_6H_6.$$

The reaction of the hexachloro derivative Si_6Cl_6 with dimethylmercury also yields a hexamethyl derivative $Si_6(CH_3)_6$. These compounds are apparently the first homocyclic analogues of benzene.

The chemistry of inorganic aromatic compounds has only just begun to develop, but it is clear from the examples already given that the concept of aromaticity can be successfully applied also to inorganic substances.

CONCLUSION

The concept of aromaticity arose nearly a hundred years ago as a purely qualitative idea without any physical basis. Since that time the range of aromatic systems has considerably expanded and has embraced compounds of the most varied classes. The quantum-mechanical approach to the structure of organic compounds has enabled a great stride forward to be made in the development of the chemistry of aromatic compounds. A particularly important part in this has been played by the molecular-orbital method, by means of which fundamental criteria of aromaticity have been formulated.

Progress in theoretical and synthetic organic chemistry in this field now enables us to determine afresh and more rigorously what compounds should be regarded as aromatic.

Baker[1], in 1945, wrote in his review on non-benzenoid aromatic compounds that " a molecule may be said to be of aromatic type if it is a cyclic unsaturated compound containing at least two conjugated double bonds in the ring, when represented by the conventional symbols, and in which these bonds interact to a greater or lesser extent [with one another]..."

It follows from the above account that this definition cannot now be regarded as in any way satisfactory. On the one hand aromatic compounds with a single pair of π electrons (one formally "double" bond) — cyclopropenylium derivatives — are known; on the other hand, such compounds as cyclobutadiene, pentalene, and heptalene, and many others are not aromatic, in spite of the formal presence of conjugated double bonds and of interaction between them.

A more rigorous definition, which in recent times has been widely quoted in a number of papers, was given in 1949 by Dewar[331], who regarded as aromatic those cyclic compounds having a large conjugation energy, and in which all the atoms in the ring take part in the formation of a single conjugated system.

It can be shown, however, that this definition, too, is inadequate. Thus, for example, in the cycloheptatrienyl anion all the ring atoms take part in the formation of a single conjugated system, and calculations show the anion to possess a considerable conjugation energy (2.83 β), but it occurs in a diradical ground state and is not aromatic. Nor are pentalene and heptalene aromatic, in spite of their considerable conjugation energies (2.49 and 3.61 β). Thus even Dewar's definition cannot be regarded as correct: it includes all the necessary, but not the sufficient, conditions for aromaticity, since no account is taken of the closed character of the electron shell in aromatic systems.

In conformity with the above remarks, the following definition of aromatic compounds may be given: *aromatic compounds are those unsaturated cyclic compounds in which all the ring atoms take part in the formation of a single conjugated system, and the π electrons of this system form a closed electron shell.*

By a "closed electron shell" is understood a system of π electrons such that both removal of electrons from it, and addition of further electrons to it, increase the total energy of the system, and consequently diminish its stability. In terms of the molecular-orbital method this means that all the π electrons occur only in bonding molecular orbitals, to each of which are allocated two electrons.

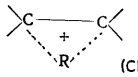
The formation of a closed electron shell determines the fundamental physical and chemical properties common to all aromatic systems: high energetic stability, with comparative ease of formation; predominance of substitution reactions, instead of addition at the multiple bonds; bond order intermediate between single and double bonds; planar or nearly planar structure of the molecule; and equivalence of carbon–carbon bonds in unsubstituted monocyclic carbocycles.

The past decade has been marked by great progress in the synthesis and investigation of non-benzenoid aromatic systems. This new field of organic chemistry is characterised by a mutual exchange of ideas and close collaboration between quantum-mechanical and synthetic methods of research. The fertility of the idea of aromaticity has been clearly demonstrated by the prediction and discovery of tropylium salts, π complexes of metal salts with cyclobutadiene, and new types of inorganic systems.

The concept of the special stability of an aromatic system of six electrons has been successfully applied by Syrkin[332] to the interpretation of the mechanisms of a large number of organic reactions. The activation energy is appreciably reduced when a conjugated system of six electrons is formed in the transition state, and therefore many reactions occur via the formation of five-, six-, and seven-membered transition states, which are in a way electronic analogues of the

cyclopentadienide, benzene, and tropylium aromatic systems.

Similarly, the occurrence of 1,2-migration during many rearrangements may be explained by the ease of formation of a system consisting of two electrons in the field produced by three nuclei. Among such electronic analogues of the cyclopropenylium aromatic system are also the so-called π complexes and "non-classical" ions of the carbonium type (CLXXI).



(CLXXI)

During the next few years a further intense development in the chemistry of non-benzenoid aromatic compounds may be expected, and in particular the synthesis of new aromatic macrocycles, the cyclopropenylium cation, and of new heterocyclic (e.g. containing boron), polycyclic, and inorganic aromatic systems.

On the other hand, the use of non-benzenoid aromatic compounds in organic synthesis provides new ways of preparing various compounds having new, previously unattainable properties, and will undoubtedly lead to valuable practical results.

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