MNDO STUDY OF BOND ORDERS IN SOME CONJUGATED
BI- AND TRI-CYCLIC HYDROCARBONS

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Abstract - MNDO calculations have been carried out on a number of conjugated bicyclic and tricyclic hydrocarbons. For reference purposes some acenes and monocyclic non-benzenoid hydrocarbons are also mentioned. While the influence of 2 or 6 π-electron systems in stabilising, and of 4 π-electron systems in destabilising, structures is readily evident, it is clear that arrays of 10 or more π-electrons have markedly less effect, and the balance between fixation of bonds and delocalisation in many compounds possessing such systems is subtle.

It has been recognised for a long time that biphenylene is best represented as in formula (1) with long interannular bonds connecting two 6-π-electron systems, thereby diminishing both cyclobutadienoid character in the four-membered ring and establishment of a peripheral 12-π-electron system, both of which would be destabilising; measurements of bond lengths by electron-diffraction[1] or X--ray crystallography[2] tally with this interpretation.
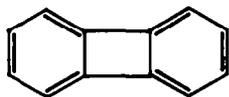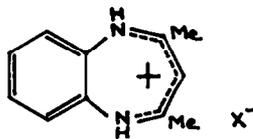
(1)   (2)

We recently reported[3] MNDO calculations[4] on the bond orders of biphenylene which accord with structure (1). We also pointed to a similar situation in the benzodiazepinium cation (2) wherein the two π-electron systems attempt to stay at arms' length in order to minimise destabilising electron interaction between them. The bond lengths[5] and bond orders[3] of the bonds linking the six-membered ring to the terminal nitrogens of the vinamidinium system[6] again support this interpretation of the structure of this cation.

This work provoked us into a general assessment of the interactions of π-electron systems within molecules. In some cases, *e.g.* (1) and (2), π-electron systems might prefer to be as separate as possible, but in others they might interact generously, while in yet other cases it was difficult to decide empirically what interactions might prevail.

Different compounds of this type are now considered severally by the MNDO method[4]. Despite the proliferation of calculations on them, we start by describing common molecules containing only benzenoid rings and simple non-benzenoid monocycles, in order that we may provide reference points for the later consideration of other polycyclic molecules which contain non-benzenoid rings in their make-up.

The calculated bond orders in benzene, = 1·412, ethane, = 0·991 and ethylene, = 1·986 are taken

as bench marks throughout this study. In diagrams indicating calculated bond orders only the σ-
-frameworks are drawn.

Species containing benzenoid rings only

In both naphthalene (3) and anthracene (4) calculations suggest extensive bond fixation. In
each case four bonds are of much higher order than all the remainder

a, 1·227;   b, 1·608;
c, 1·199;   d, 1·343

(3)

a, 1·160;   b, 1·686;
c, 1·130;   d. 1·350;   e, 1·368

(4)
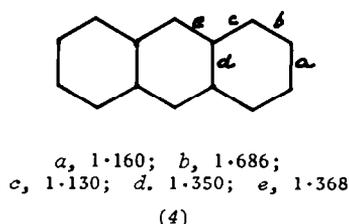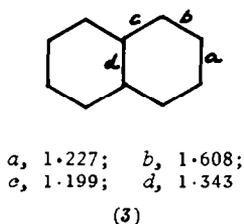
In naphthalene neither ring can reasonably be regarded as containing a delocalised 6 π-electron
system. In keeping with crystallographic data[7] the 1,2-bonds are of highest order. In anthracene,
the 1,2- and 2,3-bonds resemble those of naphthalene, although the difference in bond order is
exaggerated, but interestingly the central ring shows far less bond fixation than the other rings,
indicating that the most appropriate single representation for it is (4a).

(4a)
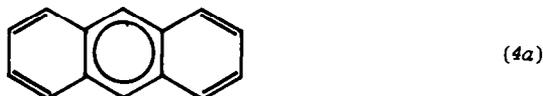
Inevitably anthracene can have only one complete sextet of π-electrons and the present work thus
suggests that this is primarily associated with the central ring. This does not conflict with
crystallographic results which indicate bond lengths of 1·399 Å and 1·428 Å for the bonds labelled
e and d respectively in (4)[7]. The fact that anthracene undergoes many reactions across its 9,10-
-positions is not indicative of its ground-state structure, but reflects that by so doing two 6-π-
-electron systems are set up, which would not be the case at other sites. This in turn implies
product-like character in the transition state. The influence of the frontier orbitals also
favours reactions at these sites[8]. It has been pointed out by other workers recently that although
a biradicaloid structure (4b) has two benzenoid rings there is little evidence for this in the
ground state, but an excited state of this form can often be adopted as a model in rationalising
its chemistry[9].

(4b)

The geometry of tetracene (5) when fully optimised, yields a structure of D_{2h} symmetry with the
bond orders shown.

a, 1·121;   b, 1·734;   c, 1·092;   d, 1·487;
e, 1·246;   f, 1·186;   g, 1·253

(5)

(5a)
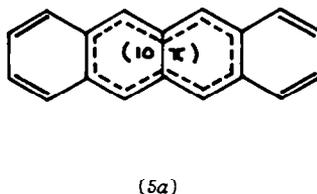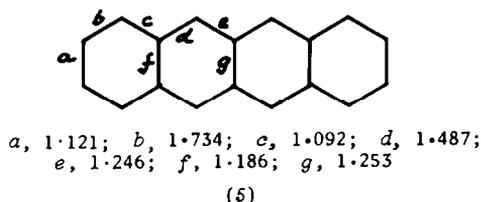
There is extensive bond fixation in the two end rings; in particular bonds b are of very high
order and bonds c of very low order. The two inner rings show less bond fixation and resemble
rather the rings in naphthalene. Although the bonds f and g are of low order, there is no indica-
tion of electron delocalisation around the formal 18-π-electron periphery. The best single
representation is as a bis-annelated naphthalene as in (5a). Crystallographic results provide a
generally similar picture[10].

Monocyclic non-benzenoid species

Calculations were made on a range of planar monocyclic molecules $(CH)_m$ and $(CH)_m^{\pm x}$ containing between 3 and 8 CH groups, with overall charges adjusted to provide 2, 4, 6 or 8 π-electrons. For each species calculations were made for both S_0 and S_1 states.

For all species except C_8H_8 the planar configuration represented an energy minimum; the configuration of C_8H_8 will be discussed below, along with C_8H_4 and C_8H_6.

The S_0 state of all molecules and ions having $4n + 2$ π-electrons optimised to D_{mh} symmetry, where m is the number of carbon atoms. In their S_1 states the symmetry is reduced to C_{2v} where m is odd and to D_{2h} where m is even. Molecules and ions with $4n$ π-electrons show the reverse behaviour. In these cases the S_1 states have D_{mh} symmetry while the S_0 states have C_{2v} symmetry when m is odd, D_{2h} when $m = 4$ or 6 and D_{4h} when $m = 8$.

A second important general distinction between the $4n$ and $(4n + 2)$ π-electron systems is the magnitude of the $S_0 - S_1$ energy gap. (See Table 1.) For $(4n + 2)$ π-electron systems this is generally calculated to be in the range 300 - 450 kJ. mol^{-1} but for $4n$ π-electron species it rarely exceeds 100 kJ. mol^{-1}.

Table 1. $\Delta H_f^{\ominus}$ values, and bond orders in non-benzenoid monocyclic molecules and ions

	$\Delta H_f^{\ominus}$ / kJ. mol^{-1}			Bond orders	
	S_0	S_1	Δ	S_0	S_1
(a) 2 π-electrons					
$C_3H_3^+$	1140.0	1478.0	338.0	1.414(×3)	1.456(×2), 0.358(×1)
$C_4H_4^{+2}$	2603.4	3076.5	473.1	1.204(×4)	1.197(×2), 0.944(×2)
(b) 4 π-electrons					
$C_3H_3^-$	551.1	575.9	24.8	see text	1.070(×3)
C_4H_4	379.6	507.1	127.5	1.968(×2), 0.956(×2)	1.212(×4)
$C_5H_5^+$	1074.6	1097.4	22.8	1.126(×2), 1.754(×2), 0.944(×1)	1.235(×5)
$C_6H_6^{+2}$	2417.8	2443.3	25.5	1.448(×4), 0.950(×2)	1.205(×6)
(c) 6 π-electrons					
$C_4H_4^{-2}$	1011.6	1408.3	296.7	1.202(×4)	1.208(×2), 0.934(×2)
$C_5H_5^-$	78.8	499.0	420.2	1.382(×5)	1.270(×2), 1.249(×2), 0.958(×1)
C_6H_6	88.7	536.3	447.6	1.412(×6)	1.447(×4), 0.966(×2)
$C_7H_7^+$	868.4	1285.7	417.3	1.376(×7)	1.196(×2), 1.308(×2), 1.456(×2), 0.956(×1)
(d) 8 π-electrons					
$C_6H_6^{-2}$	713.8	719.7	5.9	1.442(×4), 0.965(×2)	1.208(×6)
$C_7H_7^-$	126.0	149.7	23.7	see text	1.299(×7)
C_8H_8	268.8	373.3	104.5	1.859(×4), 1.014(×4)^a	1.331(×8)

^{a} For planar skeleton: 1.896 and 1.001 calculated for tub conformation.

Cyclopropenide and Cycloheptatrienide Anions

For both the 4 π-electron anion $[C_3H_3]^-$ and the 8-π-electron anion $[C_7H_7]^-$ the potential energy surface of their S_0 states is complex and probably involves a pseudo-rotational motion between minima of rather similar energies but different electronic and molecular structures. Thus other recent MINDO/3 and MNDO calculations[11] on $[C_7H_7]^-$ found two distinct minima, of virtually identical energies, for which the calculated geometries suggested the electronic structures (6a) and (6b).
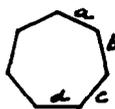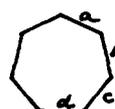
a, 1.415; b, 1.078; c, 1.714; a, 1.218; b, 1.623; c, 1.005; d, 0.984. $\Delta H_f^{\ominus}$, +126.0 kJ.mol^{-1} d, 1.861. $\Delta H_f^{\ominus}$, +126.5 kJ.mol^{-1}

(6a)	(6b)	(6c)	(6d)

Our calculations entirely concur and furthermore indicate the bond orders shown in (6c) and (6d), which are entirely consistent with the earlier formulations[11].

Similarly for $[C_3H_3]^-$ we find two C_{2v} minima for the S_0 state (7a) and (7b).

a, 1.952; b, 0.926
$\Delta H_f^{\ominus}$, +551.1 kJ. mol^{-1}

(7a)

a, 1.152; b, 1.462
$\Delta H_f^{\ominus}$, +564.9 kJ. mol^{-1}

(7b)
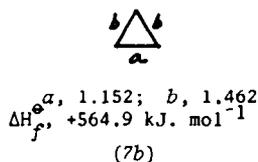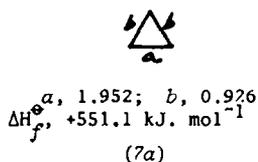
In (7a) the calculated bond lengths are 1.329 Å (×1) and 1.518 Å (×2) and in (7b) the values are 1.562 Å (×1) and 1.364 Å (×2). These structures may be pictorially represented as in (7c) and (7d) respectively. The pseudo-rotational behaviour of this anion has been discussed[12] in terms of ab-

(7c)   (7d)

-initio calculations and the energy calculated as a function of a single pseudo-rotation parameter.

Cyclooctatetraene and Dehydrocyclooctatetraenes. For cyclooctatetraene, C_8H_8, full geometry optimisation led to a tub-shaped structure of D_{2d} symmetry whose detailed geometry parameters are in excellent agreement with those determined experimentally[13] for isolated gas-phase molecules. The calculated bond orders for the long and short C-C bonds are 1.001 and 1.896 respectively, little different from those in ethane and ethylene, or those in trans-buta-1,3-diene (≈ 1.019 and 1.918).

When the C_8 skeleton is constrained to be planar, the resulting molecular geometry is D_{4h} and the calculated bond orders for the long and short bonds become 1.014 and 1.859. There is no significant delocalisation to form an 8-π-electron cycle.

The factors involved in determining the conformation of cyclooctatetraene have been discussed[14-16]. The main conclusion appears to be that the π-electron system, despite its anti-aromatic character, is of lowest energy in the planar conformation, but that the σ-system is dominant in the neutral cyclooctatetraene ring and suffers less strain in the tub conformation. As the number of π-electrons increases, the influence of the π-system, and the degree of delocalisation, both increase. For the 9-π-electron mono-anion $[C_8H_8]^-$ we calculate a planar structure of D_{4h} symmetry while the 10-π-electron dianion $[C_8H_8]^{2-}$ has full D_{8h} symmetry. This is consistent with the structure found experimentally for $[C_8H_4Me_4]^{2-}$.[17]

The structure of monodehydrocyclooctatetraene, C_8H_6, has been studied using the MINDO/3 method[18]. It was found that the structure should be represented as in (8a); no minimum corresponding to the valence isomer (8b) could be detected.

In contrast we have found minima corresponding to both of these valence isomers. The more stable isomer is (8a), the energy difference between this and (8b) being calculated as 228.4 kJ. mol^{-1} by the MNDO method and 215.7 kJ. mol^{-1} using the MINDO/3 technique. The trienyne isomer (8a) has C_{2v} molecular symmetry with bond orders as shown below.

a, 2.796; b, 1.019; c, 1.849; d, 1.006;
e, 1.864. $\Delta H_f^{\ominus}$, + 505.4 kJ. mol^{-1}

(8a)

a, 1.282; b, 1.339; c, 1.472; d, 1.363;
e, 1.484. $\Delta H_f^{\ominus}$, + 733.8 kJ. mol^{-1}

(8b)
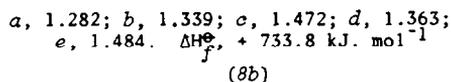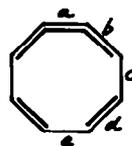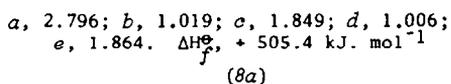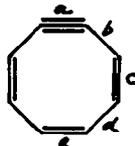
Although there are 10 π-electrons in all, 8 occur in non-delocalised orbitals perpendicular to the ring with the remaining two in an orbital in the plane of the ring. The cumulene isomer (8b) is non-planar with C_2 molecular symmetry and the calculated bond orders as shown.

In addition to the 1,2-dehydro isomer we have also investigated the 1,3-, 1,4- and 1,5- dehydro

isomers for which the calculated bond orders are as shown in (9 - 11).
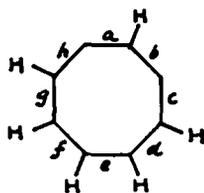
a, 1.822; b, 1.075; c, 1.143;
d, 1.710; e, 1.058; f, 1.818;
g, 1.000; h, 1,888
$\Delta H_f^{\ominus}$, + 719.6 kJ. mol^{-1}

(9)
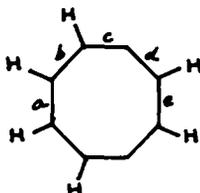
a, 1.823; b, 1.026; c, 1.863;
d, 1.919; e, 0.944
$\Delta H_f^{\ominus}$, +532.18 kJ. mol^{-1}

(10)
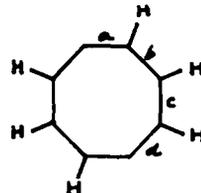
a, 1.225; b, 1.649; c, 1.023;
d, 1.869
$\Delta H_f^{\ominus}$, +680.6 kJ. mol^{-1}

(11)

Detailed examination of the molecular and electronic structures of these three isomers indicates that (9) is best represented as an allenic carbene (9a), (10) as a bis-allene (10a), and (11) as an allene containing also a 6-π-electron system delocalised over five centres (11a). In none of these isomers is there evidence of a delocalised 10-π-electron system.
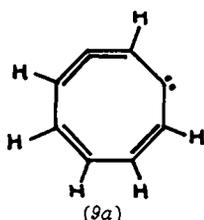
(9a)
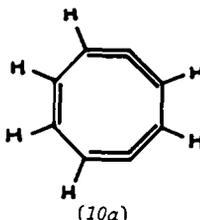
(10a)
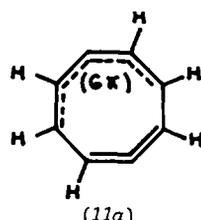
(11a)

Bicyclic non-benzenoid species

Butalene (12). Experimental evidence has indicated that butalene is formed as a transient inter-mediate[19,20]. Butalene is a valence isomer of 1,4-benzyne (13) and MINDO/3 calculations predict that singlet (13) is more stable than (12) by some 79 kJ. mol^{-1} .[21]

(12)
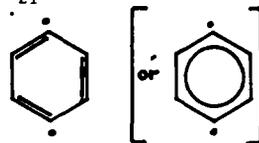
(13)

Calculations using the MNDO method predict (12) to be the more stable [$\Delta H_f^{\ominus}$ values calculated for (12) and (13) are, respectively, 698.7 and 726.4 kJ. mol^{-1}], but the MNDO geometries are similar to those found by MINDO/3[21].

In (12) (of D_{2h} symmetry) the HOMO is a σ-orbital, localised mainly in the cross-ring bond and strongly bonding between carbon atoms 1 and 4. In (13) (also of D_{2h} symmetry) the HOMO is again σ and localised on carbon atoms 1 and 4, but in this case is strongly anti-bonding in character.

The π-orbitals in (12) contain 6 electrons and resemble those of benzene. The bond orders (12a) indicate little bond fixation around the periphery.

a, 1.022; b, 1.427; c, 1.323

(12a)

a, 0.573; b, 1.600; c, 1.169

(13a)

This system provides an interesting discrepancy between molecular orbital and graph theoretical predictions. The molecular orbital results clearly indicate 6-π-electron delocalisation, so that butalene may be regarded simply as benzene perturbed somewhat by a cross-ring bond. However, according to graph theoretical predictions[22], butalene is strongly antiaromatic.

An obvious criticism of the graph theoretical approach to the question of 'aromaticity' is that it is based upon classical Kekulé-type structures, all of which are assigned equal weights in assessing the overall structure, thereby begging the whole question of the electronic structure which the method is presumably attempting to determine.

In 1,4-benzyne there is much more extensive bond fixation in the periphery (*13a*). However there are still 6 π-electrons in a framework of overall D_{2h} symmetry, and the overall electronic structure might be likened to the back-to-back combination of two π-allyl radicals such as to yield a singlet ground state.

Irrespective of whether (*12*) or (*13*) represents the energetically preferred structure, valence tautomerism between them may take place readily, and chemical evidence implicates the possible presence of a biradical structure in reactions which may generate butalene[19].

Benzocyclobutadiene *(14)* and bicyclodeca[6.2.0]pentaene *(15)*

Closely related to the classical valence bond structure of butalene (*12*) are the bicyclic species (*14*) and (*15*).
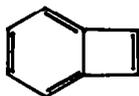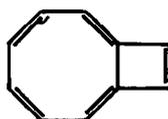
(*14*)   (*15*)

If, like butalene, these compounds were to behave as single π-electron loops with a cross-ring bond, their peripheries would contain 8 and 10 π-electrons respectively. Both structures optimise to C_{2v} symmetry, with calculated bond orders as shown in (*14a*) and (*15a*); these bond orders should be compared with those in the monocyclic 3,4-dimethylenecyclobutene (*16*).
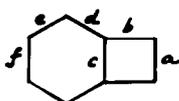
a, 1.901; *b*, 0.970; *c*, 1.135
d, 1.677; *e*, 1.159; *f*, 1.669

(*14a*)
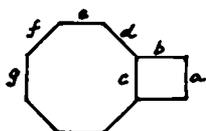
a, 1.815; *b*, 1.020; *c*, 0.962;
d, 1.822; *e*, 1.033; *f*, 1.825;
g, 1.036.

(*15a*)

a, 1.859; *b*, 0.998; *c*, 0.977;
d, 1.900

(*16*)

The bond-orders *b* and *c* in particular suggest that (*15*) behaves as a peripheral 10-π-electron system in which rather little electron delocalisation occurs and in which bond *c* acts merely as a cross-ring σ-bond. On the other hand (*14*) has bond *c* stronger and bond *b* weaker than in (*15*), and its structure should perhaps be regarded more as having a 6-π-electron system and a 2-π-electron system which are mutually repulsive. Such repulsive behaviour between two connected 6-π-electron systems is well established in the example of biphenylene[3].
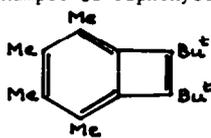
(*17*)

These results are in good accord with evidence available from X-ray structures. In compound (*17*) the bond linking the C-Bu[t] atoms is the shortest in the molecule, despite crowding between the two t-butyl groups, and can be interpreted as an isolated double bond, hardly influenced by the π-electrons of the six-membered ring[23]. The bonds linking this double-bond to the six--membered ring are somewhat longer than is usual for sp^2C - sp^2C single bonds. There is some delocalisation of electrons in the six-membered ring but there is some bond localisation in the sense indicated in (*14a*).

The most striking feature of an X-ray structure of the 9,10-diphenyl derivative of (*15*) is the length of the bridging bond (1.53 - 1.54 Å)[24] which is longer, for example, than the bridging bond in azulene. The molecule is effectively planar. There is some small alternation in bond lengths, suggesting some peripheral delocalisation of π-electrons, but with longer and shorter bonds arranged in accord with (*15a*). Comment is made[24] that delocalisation is appreciable enough to provide sufficient delocalisation energy to compensate for the strain energy involved in a planar conformation.

Azulene (*18*). Present calculations on azulene provide bond orders as shown (*18a*), indicating

considerable bond fixation.
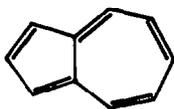
(18)
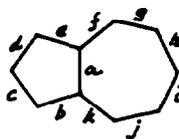
(18a)

a, 1.004; b, 1.657; c, 1.129; d, 1.720;
e, 1.081; f, 1.670; g, 1.120; h, 1.706;
i, 1.117; j, 1.716; k, 1.094.

The question of bond localisation in azulene has been investigated recently in great detail[25]. Geometry was optimised both without constraints (C_s symmetry), and with C_{2v} symmetry imposed. Geometries were calculated using both the semi-empirical MINDO/3 method and by *ab initio* calculations with an STO-3G basis set[25]. For each pair of geometries the energies were calculated with a range of *ab initio* basis sets, and, in general, the C_s structure with localised peripheral bonds was favoured in single configuration (HF) calculations, but, when electron correlation was introduced at the MP2 level, the C_{2v} valence isomer with a delocalised periphery became the lowest energy isomer. All calculations concur about the nature of the bridging bond. It is also interesting to note that introduction of electron correlation is necessary to explain the difference between the electronic spectra of azulene and naphthalene[26].

X-ray data are inconclusive. The crystal structure of azulene itself is disordered and bond lengths have not been determined with complete accuracy. However the transannular carbon-carbon bond is distinctly longer (1.482 Å) than the other carbon-carbon bonds, which lie in the range 1.38 - 1.42 Å[27]. The bond lengths of the azulene derivative (19)[28] also indicate a long transannular bond but provide a rather inconclusive comment on peripheral bonding.
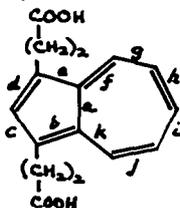
a, 1.490; b, 1.394; c, 1.412; d, 1.395;
e, 1.413; f, 1.373; g, 1.402; h, 1.382; (19)
i, 1.387; j, 1.384; k, 1.386.

It has been noted that crystal effects appear to be influencing the results and that the third decimal place is meaningless here[29]. In view of the apparent small difference in energy between localised and delocalised valence isomers of azulene it is possible that the disorder in the crystals is dynamic rather than, or in addition to, static.

The ready disruption of the delocalised system in azulene is shown in that annelation of a benzene or thiophene ring onto the five-membered ring of azulene causes some alternation of bond lengths in the seven-membered ring, as indicated by coupling constants in their ¹H-n.m.r. spectra[30,31].

Some general comments arising from the calculations on azulene. Similar conclusions concerning localised and delocalised valence isomers of similar energies have been reached for [10]annulene[25,29] and for the metheno[10]annulene (20)[32].

(20)

It is possible that similar conclusions may apply to a wide range of peripheral (4n + 2) π-electron systems. Where there are two possible valence isomeric forms for a system, one with a localised and the other with a delocalised periphery, and the difference in energy between them, calculated at the single configuration SCF level is small, in favour of the bond-fixed isomer, then the inclusion of electron correlation, although not changing the absolute $\Delta H_f^\ominus$ values very much,

will nevertheless reverse the stability order in favour of the delocalised isomer.

In certain cases, with particular patterns of substituents, it may happen that the two valence isomers will have virtually identical energies. In such cases the geometries observed experiment-ally by X-ray diffraction will be more dependent on inter-molecular forces than on intra-molecular forces, and the pattern of bonds deduced may be misleading. This could be the case for the azulene derivatives discussed in the preceding section.

Because of the constraints of computational economy, we have not performed any MNDO calculations involving CI. In several examples discussed in succeeding sections, two valence isomers of closely similar energy were found, one usually arising from a free optimisation, the other from the imposi-tion of a single symmetry element. It is possible that the inclusion in the calculations of electron correlation, whether using semi-empirical or *ab initio* methods, will reverse the order of stability of the localised and delocalised isomers, even though no significant changes to the geometry are likely. This proviso should be borne in mind throughout the subsequent discussion.

Pentalene and Heptalene. In pentalene *(21)* and heptalene *(22)* there is considerable bond-fixation, as shown by the calculated bond orders.

a, 1.008; b, 1.787; c, 1.020;
d, 1.844; e, 1.009

(21)
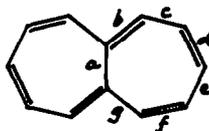
a, 1.015; b, 1.749; c, 1.060; d, 1.797;
e, 1.053; f, 1.823; g, 1.014

(22)

In both molecules the freely optimised structure has C_{2h} molecular symmetry. Bond fixation in their peripheries is almost complete. The cross-ring bond a, although of similar bond order to the bonds c, e and g is marginally the longest of the "single" bonds. In heptalene it is longer than the longest peripheral "single" bond by 0.002 Å, in pentalene by 0.026 Å, while in azulene it is 0.027 Å longer than the longer "single" bond in the five-membered ring and 0.059 Å longer than the longest "single" bond in the seven-membered ring. The range spanned by the 12-π-electron heptalene, 10-π-electron azulene and 8-π-electron pentalene may be due in part both to the greater ring strain when five-membered rings are present, and to the greater degree of π-electron delocal-isation in azulene, as compared with both pentalene and heptalene.

Benzocycloheptatrienium and benzocycloheptatrienide ions. The bicyclic benzocycloheptatrienium cation *(23)* is closely analogous to, and isoelectronic with, naphthalene.
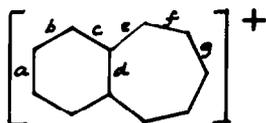
a, 1.239; b, 1.564; c, 1.225;
d, 1.233; e, 1.239; f, 1.458;   *(23)*
g, 1.350

This is a ten π-electron system whose structure optimises to C_{2v} symmetry. The bond orders calcul-ated for the benzenoid ring are very similar to those calculated for naphthalene, and the delocal-isation of the π-electrons appears to be somewhat similar overall to that in naphthalene.

The corresponding anion is the benzo-annelated derivative of the cycloheptatrienide anion, discussed earlier and for which two minima of essentially identical energy, corresponding to *(6a)* and *(6b)* occur.

(6a)   *(6b)*

Free optimisation of the structure of the benzocycloheptatrienide anion, without constraints, led to a structure *(24)* having only C_s symmetry, with $\Delta H_f^{\ominus}$ of +144.4 kJ.mol^{-1}, and the bond orders as shown:
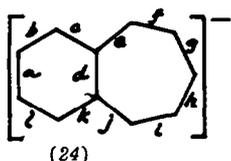
a, 1.486; b, 1.343; c, 1.357;
d, 1.210; e, 1.157; f, 1.381;
g, 1.443; h, 1.127; i, 1.740;
j, 1.100; k, 1.522; l, 1.272.

(24)

(24a)
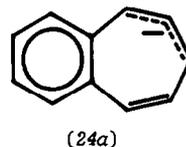
The best single representation of this structure is (24a), which is a benzo-annelated derivative of (6a). If C_{2v} symmetry is imposed, however, a quite different structure (24b) is obtained.
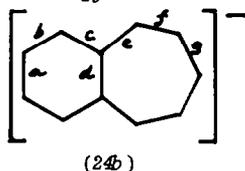
a, 1.521; b, 1.283; c, 1.467;
d, 1.226; e, 1.046; f, 1.573;
g, 1.265

(24b)

(24c)
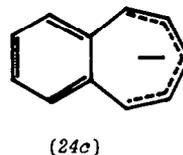
This structure has essentially the same $\Delta H_f^\ominus$ (+145.1 kJ.mol^{-1}) as (24). It is best represented as (24c).

In particular the fragment defined by bonds f and g is virtually identical, in terms of calculated bond lengths, bond orders and net atomic charges to the U-shaped conformation of the pentadienide anion (25).

(25)

(2)
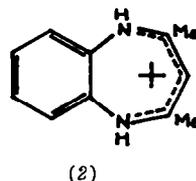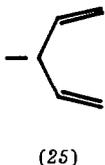
We note, in particular, the low bond orders of the bonds e, indicating that the two 6-π-electron systems in (24c) are mutually repulsive. In this respect (24c) behaves in an entirely analogous manner to biphenylene and to the benzodiazepinium cation (2)[3] in both of which two 6-π-electron groups are mutually repulsive. The structural similarity between (24b) and (2) is particularly evident.

The benzocycloheptatrienide anion thus provides another example of the type of molecule, discussed previously, where there are two structures differing little in energy.

Linear Polycyclic Non-benzenoid Species

The simplest such hydrocarbon (26) is the third member of the series which begins with cyclobutadiene, C_4H_4 and butalene, C_6H_4, (12); its molecular formula is C_8H_4 and it has eight π-electrons. The calculated structure (26) is of D_{2h} symmetry with bond orders as shown. The calculated bond lengths a - d are, respectively, 1.392, 1.463, 1.580, 1.343 Å.
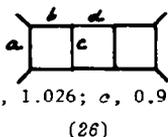
a, 1.783; b, 1.026; c, 0.988; d, 1.770

(26)

(26a)
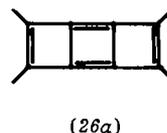
The best single representation of the structure is (26a), which is the valence isomer in which the number of distinct cyclobutadiene-type rings in the whole structure is minimised. Here again the contrast with the graph-theoretical approach is marked. The graph theory method will give equal weights in the overall structure to (26a), in which there is a single cyclobutadienoid ring, and to the three other valence isomers (26b,c,d), two of which contain two cyclobutadienoid rings, while isomer (26d) contains three.

(26b)

(26c)

(26d)
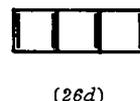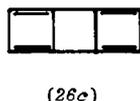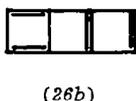
On the other hand the nodal properties of the four occupied π-molecular orbitals are entirely consistent with the formulation (26a).

As in previous examples having eight π-electrons, the delocalisation around the periphery is minimal. In particular this example should be compared with its 6 π-electron vinylogue butalene (12), in which there is extensive delocalisation
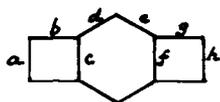
a, 0.958; b, 1.875; c, 0.950;
d, 1.035; e, 1.809; f, 0.968;
   g, 1.022; h, 1.808
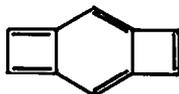
(27)   (27a)   (27b)

When the central ring is expanded to six atoms as in (27) a 10-π-electron system results. Free optimisation gave a C_{2v} structure, with bond orders as shown, which exhibits no electron delocalisation around the molecular periphery, and which must be represented as (27a). Comparison of these bond orders with those in cyclobutadiene on the one hand and in 3,4-dimethylenecyclobutene (16) on the other hand, indicates that the molecule consists of two isolated π-fragments, connected by bonds d of low bond order. Bonds a, c and f are of very low order, thereby minimising any 4-π-electron interactions in the four-membered rings.

When D_{2h} symmetry was imposed upon the geometry, the $\Delta H_f^{\ominus}$ value increased by some 48 kJ.mol^{-1} but the electronic structure retained C_{2v} symmetry with the bond orders as shown in (27c).
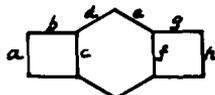
a, 1.020; b, 1.742; c, 0.959;
d, 1.128; e, 1.668; f, 0.948;   (27c)
   g, 1.146;   h, 1.606

In this form bond alternation is not so marked as in the freely optimised structure, but there is no evidence, despite the geometric symmetry constraints, of either benzenoid (6π) or peripheral (10π) delocalisation. The best single representation of this bond structure is again (27a), which, although containing loops having 4, 8 and 10 π-electrons, contains no 6 π-electron loop as in (27b).

As in the case of the tricyclic compound (26) these results presumably reflect the avoidance of a structure containing two cyclobutadienoid rings. Structure (27b) has two such rings in addition to its benzenoid ring; stabilisation introduced by the latter must be insufficient to overcome the destabilisation introduced by the presence of a second cyclobutadienoid ring. However, as will be discussed later, imposition of a particular symmetry on the molecular structure (i.e. upon the mutual arrangement of the atomic centres) does not necessarily result in the same calculated symmetry in the overall electron distribution, even although each individual molecular orbital is necessarily an eigenstate of the imposed point-group.

A highly substituted derivative of (27) has been prepared, which was fairly stable as a solid but was very sensitive to oxygen[33], but the substituent groups must play an important role in the chemistry of this compound.

Norbiphenylene and Homobiphenylene Ions. We have discussed biphenylene previously[3] and here we note only the bond orders, for the sake of completeness, and for comparison with other related 12 π- [or (6 + 6) π-] electron systems.
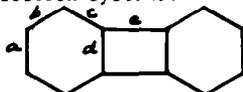
a, 1.601; b, 1.218; c, 1.603;   (1)
   d, 1.175; e, 0.983

Formally isoelectronic with biphenylene are the norbiphenylene anion (28) and the homobiphenylene cation (29), both of which optimise to structures of C_{2v} symmetry.
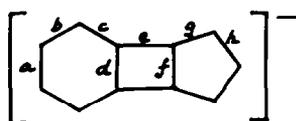
a, 1.663; b, 1.154; c, 1.611; d, 1.108
e, 1.025; f, 1.196; g, 1.429; h, 1.358

(28)
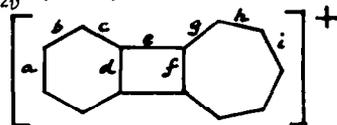
a, 1.599; b, 1.210; c, 1.580; d, 1.140;
e, 1.012; f, 1.170; g, 1.476; h, 1.306;
                i, 1.399

(29)

As in the case of biphenylene, the bonds within the central four-membered rings are all of low bond order, with bond e the lowest, indicating in all of the species mutual 'repulsion' of the two 6-π- -electron systems. There is fairly strong bond fixation in the benzenoid rings, but this is much less marked in the non-benzenoid rings where delocalisation is extensive. Presumably the π-bond delocalisation is reinforced by the tendency of the charge to be distributed over the entire π- -electron system in these non-benzenoid rings. The bond orders and the forms of the molecular orbitals indicate that the best single representations of these two ions are as (28a) and (29a) respectively. Reinforcement of π-bond delocalisation by charge has been clearly shown in the case of dehydroannulenes[34].
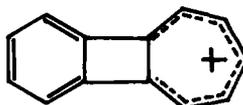
(28a)   (29a)

The anion (28) appears to have been obtained only in solution[35] but a salt of the cation (29) has been isolated as deep violet-purple crystals[36]. The n.m.r. spectra (^{1}H and ^{13}C) of (29) indicate that it is best regarded as possessing two essentially independent 6-π-electron systems, with the positive charged located mainly on the terminal and β-atoms of the conjugated system in the seven- -membered ring[36]. Present calculations also concur with this charge distribution (+0.107 at the terminal atoms, +0.112 at the β atoms). Similarly in (28a) negative charge is sited preponderantly at the bridgehead and β atoms of the five-membered ring (-0.240, -0.236 respectively).

Also in accord with the studies on biphenylene, (28) and (29), the tropone derivative (30) is a stable crystalline compound[37,38], whereas its isomer (31) is not[38,39]. The double bonds in (30) appear to be more localised than in tropone itself.
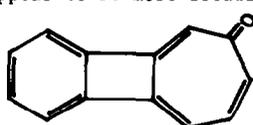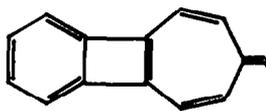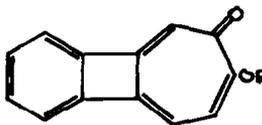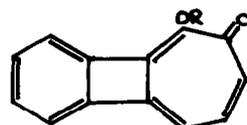
(30)   (31)   (32)   (33)

Similarly the tropolones (32)[40] and (33)[41] (R = H) exist only in the tautomeric forms shown and on methylation in each case react at only one of the oxygen atoms to provide, respectively, (32) and (33) (R = Me).

The cation analogue of (28) is a 10-π-electron system and its structure optimises to C_{2v} symmetry with the bond orders as shown in (34).
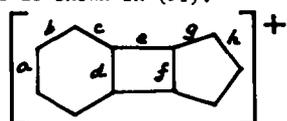
a, 1.271; b, 1.502; c, 1.285; d, 1.135
e, 1.220; f, 0.950; g, 1.512; h, 1.292   (34)

Whereas in the anion (28) the bonds of highest order in the benzenoid ring are a and c, in the cation (34) the situation is reversed and b has the highest bond order. Similarly, in the anion bond e has the lowest bond order in the four-membered ring whereas in the cation bond e has the highest order in this ring. The observation of the high bond order bonds b and g immediately suggests that this cation is an analogue of the 10-π-electron molecule naphthalene, wherein bond fixation of similar type occurs. Bond f in (34) is no more than a cross-ring σ-bond. Despite having what is at first glance a cyclopentadienium ring, this compound is in fact a 10-π-electron system and, as such, could be an interesting synthetic target.

When the benzothienocyclobutadiene (35) is oxidised to its S-oxide and S-dioxide, the signals for the protons attached to the benzenoid ring are shifted downfield[42]. This could be associated with development in the S-oxides of cationic character comparable to (34) due to association of the S-electrons with the oxygen atoms. The loss in 'aromaticity' of thiophen when it is oxidised has been long recognised and attributed to similar S-O electronic interaction.

(35)

The anion analogue of (29) poses problems similar to those encountered for the benzocyclohepta-
trienide anion (24), for which two valence isomers were found corresponding to annelation of differ-
ent valence isomers of the cycloheptatrienide ring. Free optimisation gave a structure of C_s
symmetry for (36), having $\Delta H_f^\ominus$ of +310.9 kJ. mol^{-1} and the bond orders as shown.
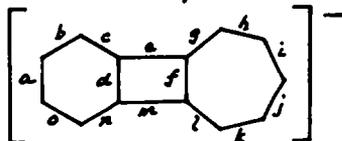
a, 1.436; b, 1.367; c, 1.389; d, 1.186;
e, 1.130; f, 0.953; g, 1.541; h, 1.260;
i, 1.294; j, 1.532; k, 1.097; l, 1.738;
m, 1.062; n, 1.432; o, 1.342
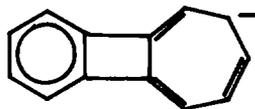
(36)   (36a)

These bond orders, when compared with those in trienide valence isomer (6b) of $[C_7H_7]^-$ indicate
that the best single representation of this structure is (36a). While there is delocalisation in
the benzenoid ring, bond fixation is very strong in the seven-membered ring.

When C_{2v} symmetry is imposed, the calculated $\Delta H_f^\ominus$ value (at the SCF level; CI was not included)
rose to +326.8 kJ. mol^{-1}, a difference of some 16 kJ. mol^{-1}, and the bond orders resulting are
shown in (36b).
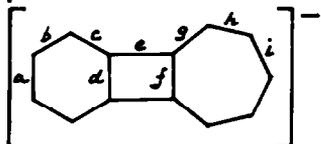
a, 1.478; b, 1.312; c, 1.460; d, 1.128;
e, 1.108; f, 0.959; g, 1.1625;
h, 1.181; i, 1.403
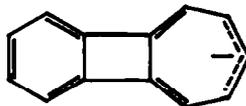
(36b)   (36c)

In this case the strong bond alternation in the benzenoid ring and the high order bonds g in the
seven-membered ring should be noted, indicative of (36c) as the best simple representation, derived
by annelation of the allylic valence isomer (6a) of the cycloheptatrienide ring. A ^{1}H-n.m.r.
spectrum of this anion was taken to suggest a bond structure as indicated by (36c) but reversed
that in the benzenoid ring;[43] assuming very low bond order for bond f this would represent annelated
benzenoid and cyclononatetraenide rings.

Some other Linear Tricyclic Compounds. The bicyclic molecules (37), (38), (39) have been studied
using semi-empirical SCF MO calculations[44]. Our interest in them lies in establishing whether
electron delocalisation is plausible in the 10-π-electron periphery of (37) or in the 14-π-
-electron periphery of (39). Such peripheral delocalisation is not be be expected in the 12-π-
-electron system of (38), which might, however, become an analogue of biphenylene by adopting a
constitution such as (38a), having long bonds of low order connecting the two 6-π-electron rings.
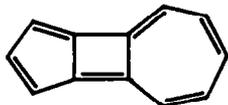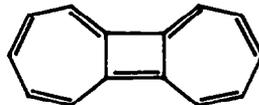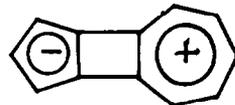
(37)   (38)   (39)   (38a)

The structure of (37) optimised to C_{2v} symmetry with $\Delta H_f^\ominus$ of +673.3 kJ. mol^{-1} and the bond orders
as shown in (37a).
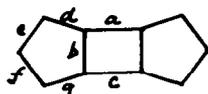
a, 1.063; b, 0.977; c, 1.591;
d, 1.696; e, 1.117; f, 1.682;   (37a)
g, 1.230

This pattern of alternate bonds is that represented by formula (37). When D_{2h} symmetry was imposed
upon the molecular geometry the calculated $\Delta H_f^\ominus$ value (at the SCF level) rose by some 11 kJ. mol^{-1}
to +684.5 kJ. mol^{-1}. The electronic structure still retains only C_{2v} symmetry; the resulting bond
orders are as shown in (37b).
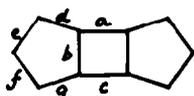
a, 1.300; b, 0.969; c, 1.276;
d, 1.386; e, 1.387; f, 1.360;   (37b)
g, 1.414

Delocalisation of the peripheral 10-π-electron system is now almost complete and bond b is only a cross-ring σ-bond.

When the geometry of (38) was optimised without constraint the resulting structure had C_s symmetry only, a $\Delta H_f^\ominus$ of +594.1 kJ. mol^{-1}, and bond orders as shown in (38b).
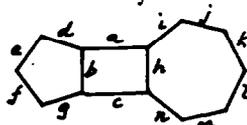
a, 0.996(1.065); b, 1.002(1.027); c, 1.663(1.397);
d, 1.775(1.581); e, 1.056(1.196); f, 1.769(1.576);
g, 1.068(1.215); h, 1.002(1.078); i, 1.798(1.543);   (38b)
j, 1.051(1.208); k, 1.798(1.566); l, 1.052(1.200);
m, 1.795(1.576); n, 1.047(1.168)

This pattern of strong bond alternation corresponds to the structure (38).

When C_{2v} symmetry was imposed on the molecular structure, the calculated $\Delta H_f^\ominus$ rose to +642.9 kJ. mol^{-1} (a change of some 49 kJ. mol^{-1}) but the electronic structure still retained only C_s symmetry with the bond orders as shown in parentheses in (38b).

In other words, the degree of peripheral delocalisation induced by the imposition of symmetry is much less in the case of the 12-π-electron system than for the 10-π-electron analogue. There is thus no evidence, at least for isolated gas-phase molecules, for the development of the dipolar structure (38a). The presence of a highly polar solvent might induce such polarisation.

The geometry of the 14-π-electron analogue (39), when optimised freely without constraint, gave a C_{2v} structure, with $\Delta H_f^\ominus$ of +496.6 kJ. mol^{-1}, and the bond orders shown in (39a).
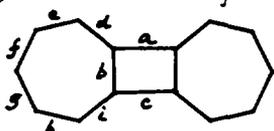
a, 0.998(1.070); b, 1.000(1.000); c, 1.669(1.503);
d, 1.788(1.656); e, 1.053(1.151); f, 1.792(1.646);   (39a)
g, 1.060(1.159); h, 1.783(1.613); i, 1.059(1.177)

As with the corresponding 10-and 12-π-electron systems, there is a pattern of strong bond alternation, adequately represented by the structure (39). Imposition of D_{2h} symmetry on the molecular framework causes an increase in the calculated $\Delta H_f^\ominus$ to +555.1 kJ. mol^{-1} (a change of some 59 kJ. mol^{-1}, larger than for either the 10-or 12-π-electron analogues) but a considerable degree of bond alternation still occurs; bond orders are shown in parentheses in (39a).

Thus neither (37), (38) nor (39) appear to be delocalised systems; this accords with the earlier SCF MO calculations[44].

<u>Cycloheptindene</u>. Rather similar to the foregoing tricyclic compounds is cycloheptindene (40), which also contains a 14-π-electron periphery. In this compound a p-quinonoid ring has been inserted between the two rings which go to make up azulene.

(40)
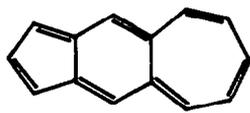
a, 1.079(1.217); b, 1.702(1.218);
c, 1.071(1.512); d, 1.729(1.513);
e, 1.036(1.163); f, 1.790(1.577);
g, 1.072(1.218); h, 1.763(1.542);
i, 1.083(1.244); j, 1.709(1.487);
k, 1.040(1.171); l, 1.756(1.561);
m, 1.038(1.167); n, 1.781(1.600);
o, 1.018(1.034); p, 1.017(1.011)

Free optimisation gave a C_s structure ($\Delta H_f^\ominus$ = +445.8 kJ. mol^{-1}) with the bond orders as shown. The values in parentheses are those calculated for a structure constrained to C_{2v} molecular symmetry ($\Delta H_f^\ominus$ = +498.6 kJ. mol^{-1}); there is still a considerable degree of bond fixation in the 14-π--electron periphery. Peripheral delocalisation of the π-electrons does not appear, therefore, to play an important role. A number of unsuccessful attempts to prepare this compound or its derivatives have been reported.

<u>The Dianion and Dication of s-Indacene</u>. The dianion (41a) of s-indacene (41) which is a vinylogue

of cycloheptindene (40), has been reported[45,46]. Like cycloheptindene, this anion can have a 14-π-
-electron periphery. Its n.m.r. spectra indicate that it has a delocalised π-electron system and
that the negative charge is based primarily on the centres marked x and to a lesser extent at those
marked y[46]. CNDO and *ab initio* calculations were in accord[46].

a, 1.183; b, 1.342;
c, 1.211; d, 1.405;
w,-0.092; x,-0.309;
y,-0.116; z,-0.059

(41)   (41a)
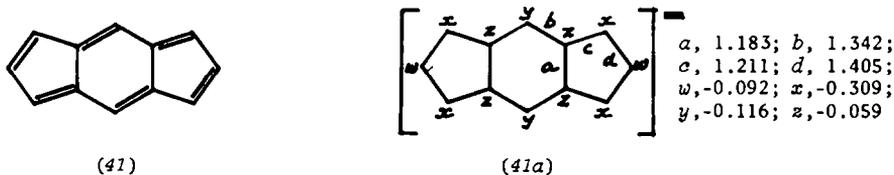
Present MNDO calculations optimise to D_{2h} symmetry and provide values for the bond orders and
charges as shown in (41a). These values suggest that there is a peripheral 14-π-electron system
with some bond alternation and that the negative charge is located primarily on sites x and to a
less extent on sites y. These results are thus in excellent agreement with the previously published
work.

The dication of s-indacene could provide a 10-π-electron periphery. Free optimisation gave D_{2h}
symmetry, and bond orders, bond lengths (Å), shown in parentheses, and charges were as shown for
(41b).

a, 1.347(1.438);   b, 1.378(1.407);
c, 0.988(1.497);   d, 1.439(1.412);
w, -0.196;   x, +0.339;
y, +0.145;   z, -0.121

(41b)
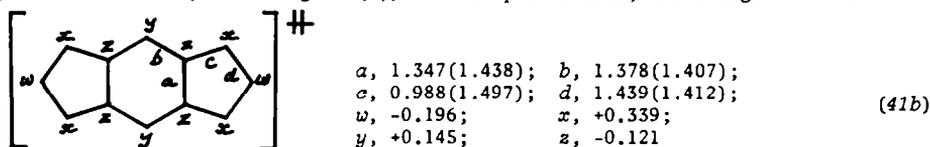
A quite different electronic structure thus obtains in this case from that in the dianion. Whereas
the latter has a peripheral delocalised π-electron system, the cation appears to have a 6-π-electron
system in the central ring with allylic 2-π-electron systems in the outer rings, best represented as
in (41c). Charge is largely concentrated on the end atoms of the allyl systems. There is little
interaction between the three delocalised systems.

(41c)

In the corresponding dianion (41a) there is no evidence for a structure analogous to (41c) but with
negative charges in the five-membered rings. A number of factors may contribute to this, including
the following. As observed with the norbiphenylene anion (28) and dehydroannulenide anions (see
e.g. [34]), the tendency for the excess electrons, as represented by the negative charge. to be de-
localised over the whole periphery may favour the peripherally delocalised structure in (41a). This
may further account for the difference between (41a) and isoelectronic anthracene (4a). Also it
has been noted in a number of cases, e.g. biphenylene (1), a benzodiazepinium cation (2), the
benzocycloheptatrienide ion (24), norbiphenylene anion (28) and homobiphenylene cation (29), that
6 + 6 $\neq$ 12, i.e. that two stabilising 6-π-electron systems prefer to remain distinct rather than
providing a destabilising 12-π-electron system. Similarly in benzocyclobutadiene (14) 6 + 2 $\neq$ 8
and bonds of low order link an 'isolated' double bond to the six-membered ring. In the cases of
(41a) and (41c) 4 + 6 + 4 = 14, but 2 + 6 + 2 $\neq$ 10. Since a peripheral 10-π-electron system should
be more stabilising than a peripheral 14-π-electron system, it may be that another influencing
factor is the stability of the allyl cation moieties, whereas no such stabilisation is provided by
allyl anions. Indeed, in view of the stabilisation afforded by 2-π-electron arrays in (41c), by
six-electron arrays in (2,24,28,29), but not by four-electron arrays in (41a), it may be that such
systems, in which the delocalisation of π-electrons is not completely cyclic, represent a situation
similar to that obtaining for cyclic conjugated systems, in which arrays of two or six, but not of
four, π-electrons provide special stabilisation.

Some Bifurcated Species

In this section we discuss a single class of molecules, namely tris-annelated benzene rings in
which the annelations consist either of cyclobutenoid rings or of further benzenoid rings, *viz.*
(42 - 45).
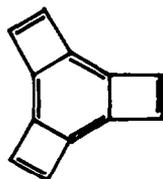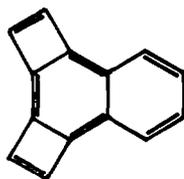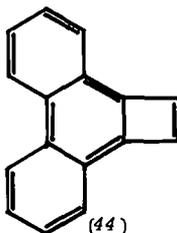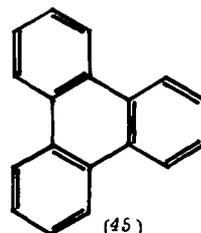
(42)   (43)   (44)   (45)

For (42) and (45) free optimisations provide structures of D_{3h} symmetry; for (43) and (44) C_{2v} structures result.

In (42) the bond orders are as shown below confirming that the bond structure drawn is the best representation of this species.
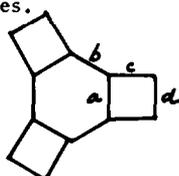
a, 0.974; b, 1.814;

c, 1.000; d, 1.841

(42)

There is almost complete bond fixation in all the rings and the individual bond orders are comparable to those in benzocyclobutadiene (14) and 3,4-dimethylenecyclobutene (16). No hint of any cyclobutadiene type rings is present.

The bond fixation in the four-membered rings of (43) is even more extreme, as shown by the calculated bond orders.
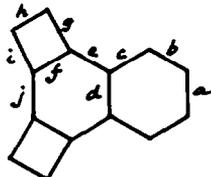
a, 1.080; b, 1.784; c, 1.053;
d, 1.053; e, 1.666; f, 1.060;
g, 0.985; h, 1.870; i, 0.977;
j, 1.748

(43)

Similarly the bond fixation in the peripheral six-membered ring is much more extreme than in either naphthalene or anthracene. The formulation (43) is an excellent representation of the bond orders. Avoidance of cyclobutadienoid character is obviously a vital factor in the structure of this molecule.

The compound (46), which has some relationship to (43), has been prepared[47]. The protons at sites x give rise to n.m.r. signals at surprisingly high field (δ 6.13). This has been attributed to the influence of paramagnetic ring currents in the four-membered rings but may equally well reflect the olefinic nature of the double bonds in the six-membered ring.
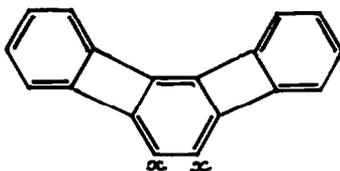
(46)

In neither (42) nor (43) is there any development of delocalised 6-π-electron character, or any indication for (43) of 14-π-electron delocalisation around the periphery. On moving to (44) the number of potentially benzenoid rings has risen to three, and possible dominant structures are one involving a phenanthrene-type pattern (44a) which would also contain a destabilising cyclobutadiene ring, one involving a tris-annelation of a delocalised central ring (44b), or that depicted in (44). No peripheral 16-π-electron delocalisation can reasonably be expected.
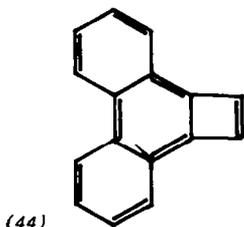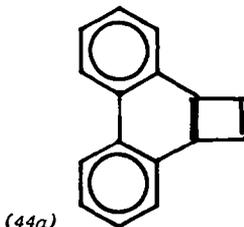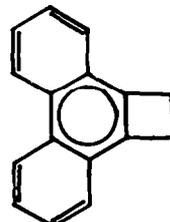
(44)   (44a)   (44b)

The calculated bond orders, shown below, while not being definitive between (44a) and (44b) certainly rule out (44). (The bond e is of higher bond order than either d or k).
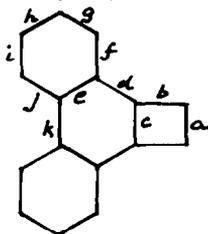
a, 1.945; b, 0.951; c, 1.550;
d, 1.235; e, 1.318; f, 1.190;
g, 1.612; h, 1.225; i, 1.601;
j, 1.209; k, 1.170

Triphenylene (45) exhibits many of the structural features of biphenylene (1), in particular the existence of isolated 6-π-electron units linked by long bonds of low bond order.
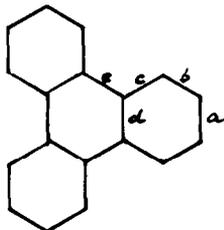
a, 1.341; b, 1.483; c, 1.317;
d, 1.365; e, 1.054

(45)

The bond orders indicate that the delocalisation in the outer six-membered rings is much greater for triphenylene than for biphenylene (1a)[3], and that triphenylene must be represented as in (45a), with linked benzenoid rings. A comparable structure for biphenylene is effectively ruled out by the involvement of the four-membered ring and its structure is best represented as in (1).
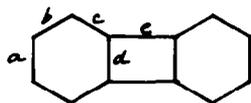
a, 1.578; b, 1.248; c, 1.569;
d, 1.218; e, 0.968

(1a)
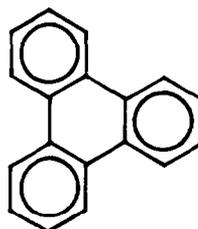
(45a)

Some miscellaneous fused-ring species

The fused tricyclic system (47), acenaphthylene, contains a total of 12 π-electrons. The geometry optimises to C_{2v} symmetry with bond orders as shown
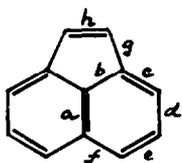
a, 1.368; b, 1.175; c, 1.551;
d, 1.231; e, 1.601; f, 1.192
g, 1.029; h, 1.826

(47)

The benzenoid portion of the molecule is almost an unperturbed naphthalene fragment (cf. 3), and there is an essentially isolated double bond in the five-membered ring.

It is interesting to note that annelation of a tropylium ring onto acenaphthylene as in (48) provides a cation in which the calculated bond orders for the C_{2v} structure indicate effective isolation of the tropylium- and naphthalene-like parts of the molecule, which contain 6 and 10 π-electrons respectively, although the seven-membered has some of the characteristics of tropolone in that bond h appears to be less fully part of the delocalised system.

a, 1.286; b, 1.219; c, 1.396;
d, 1.342; e, 1.493; f, 1.235;
g, 1.095; h, 1.180; i, 1.379;
j, 1.376; k, 1.384   (48)
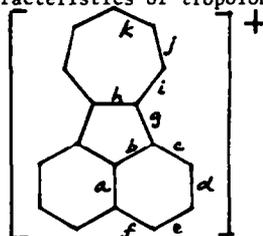
Aceheptylene or cycloheptazulene (49), with 14 π-electrons, also gives an optimised structure of C_{2v} symmetry, with bond orders as shown.
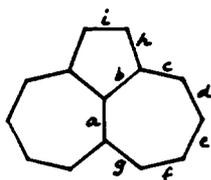
a, 1.560; b, 1.059; c, 1.091;
d, 1.726; e, 1.106; f, 1.734;
g, 1.081; h, 1.565; i, 1.222

(49)

This indicates strong bond fixation in the periphery of the heptalene portion, but some delocalisation in the fulvene-like part of the molecule defined by bonds a, b, h and i. These results are in reasonable agreement with X-ray analyses of a tetramethyl derivative[48].

One comment, worth making in rounding off this paper, is how often, when more than six electrons are involved in delocalised systems, the differences between $\Delta H_f^\ominus$ for delocalised and non-delocalised systems are relatively small. Similar comments have been made previously concerning, for example, bridged [10]annulenes[49] and azulenes[25]. The stabilisation provided by arrays of 2 or 6 π-electrons and the destabilisation connected with arrays of 4 π-electrons provide very powerful influences on the detailed structures of cyclic molecules, but when larger numbers of electrons, even ten, are involved the influence is markedly less and other factors may override simple electronic considerations. Thus the present calculations apply to isolated molecules, but in solution solvation effects, and in the solid state crystal lattice effects, may have overriding effects. For this reason care is needed in applying generally results obtained from spectra recorded in solution as from crystallographic data. Conflicting results obtained by different techniques and in different phases may often reflect the results of these extraneous factors rather than any errors of measurement or interpretation. Similarly in these cases, equilibria between the localised and delocalised forms may take place readily and may add further difficulties.

References

1. A. Yokozeki, C. F. Wilcox and S. H. Bauer, *J. Am. Chem. Soc.*, **96**, 1026 (1974).
2. J. K. Fawcett and J. Trotter, *Acta Cryst.*, **20**, 87 (1966).
3. C. Glidewell and D. Lloyd, *Tetrahedron Letters*, **23**, 4379 (1982).
4. M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, **99**, 4899, 4907 (1977); W. Thiel, P. Wiener, J. Stewart and M. J. S. Dewar, QCPE No. 428.
5. J. C. Speakman and F. B. Wilson, *Acta Cryst.*, **B32**, 622 (1976).
6. D. Lloyd and H. McNab, *Angew. Chem.*, **88**, 496 (1976); *Angew. Chem. Int. Edtn. Engl.*, **15**, 459 (1976).
7. D. W. J. Cruickshank and R. A. Sparks, *Proc. Roy. Soc.*, A **258**, 270 (1960).
8. see I. Fleming, Frontier Orbitals and Organic Chemical Reaction, Wiley, London, 1976.
9. R. H. Mitchell, T. W. Dingle, P. R. West and R. V. Williams, *J. Org. Chem.*, **47**, 5210 (1982).
10. R. B. Campbell, J. M. Robertson and J. Trotter, *Acta Cryst.*, **15**, 289 (1962).
11. A. W. Zwaard, A. M. Brouwer and J. J. C. Mulder, *Rec. Trav. Chim. Pay-Bas*, **101**, 137 (1982).
12. W. T. Borden and E. R. Davidson, *Acc. Chem. Res.*, **14**, 69 (1981).
13. M. Traetteberg, *Acta Chem. Scand.*, **20**, 1724 (1966).
14. C. J. Finder, D. Chung and N. L. Allinger, *Tetrahedron Letters*, 4677 (1972).
15. N. L. Allinger, J. T. Sprague and C. J. Finder, *Tetrahedron*, **29**, 2519 (1973).
16. R. Gygax, J. Wirz, J. T. Sprague and N.L. Allinger, *Helv. Chim. Acta.*, **60**, 2522 (1977).
17. S. Z. Goldberg, K. N. Raymond, C. A. Harmon and D. H. Templeton, *J. Am. Chem. Soc.*, **96**, 1348 (1974).
18. N. Z. Huang, T. C. W. Mak and W. K. Li, *Tetrahedron Letters*, **22**, 3765 (1981).
19. R. R. Jones and R. G. Bergman, *J. Am. Chem. Soc.*, **94**, 660 (1972).
20. R. Breslow, J. Napierski and T. C. Clarke, *J. Am. Chem. Soc.*, **97**, 6275 (1975); R. Breslow and P. L. Khanna, *Tetrahedron Letters*, 3429 (1977).
21. M. J. S. Dewar and W. K. Li, *J. Am. Chem. Soc.*, **96**, 5569 (1974).
22. M. Randić, *J. Am. Chem. Soc.*, **99**, 444 (1977); *Tetrahedron*, **33**, 1905 (1977).
23. W. Winter and H. Straub, *Angew. Chem.*, **90**, 142 (1978); *Angew. Chem. Int. Edtn. Engl.*, **17**, 127 (1978).
24. C. Kabuto and M. Oda, *Tetrahedron Letters*, 103 (1980).
25. R. C. Haddon and K. Raghavachari, *J. Am. Chem. Soc.*, **104**, 3516 (1982).
26. J. Michl and E. Thulstrup, *Tetrahedron*, **32**, 205 (1976).
27. J. M. Robertson, H. M. M. Shearer, G. A. Sim and D. G. Watson, *Acta Cryst.*, **15**, 1 (1962).
28. H. L. Ammon and M. Sundaralingam, *J. Am. Chem. Soc.*, **88**, 4794 (1966).
29. L. Farnell, J. Kao, L. Radom and H. F. Schaefer, *J. Am. Chem. Soc.*, **103**, 2147 (1981).

30. D. J. Bertelli and P. O. Crews, *Tetrahedron*, *26*, 4717 (1970).
31. K. Yamune, K. Fujimori and T. Takeuchi, *Bull. Chem. Soc. Japan*, *54*, 2537 (1981).
32. H. S. Rzepa, *J. Chem. Research*, *(S)*324; *(M)*3301 (1982).
33. F. Toda and M. Ohi, *J. Chem. Soc.*, *Chem. Comm.*, 506 (1975); F. Toda and Y. Takahara, *Bull. Chem. Soc. Japan*, *49*, 2515 (1976).
34. K. Müllen, W. Huber, T. Meul, M. Nakagawa and M. Iyoda, *J. Am. Chem. Soc.*, *104*, 5403 (1982).
35. M. P. Cava, K. Narasimhan, W. Zeiger, L. J. Radonovich and M. D. Glick, *J. Am. Chem. Soc.*, *91*, 2378 (1969).
36. L. Lombardo and D. Wege, *Tetrahedron Letters*, 4859 (1972); *Austral. J. Chem.*, *31*, 1569 (1978).
37. L. Lombardo and D. Wege, *Tetrahedron Letters*, 115 (1975).
38. L. Lombardo, R. K. McCulloch and D. Wege, *Austral. J. Chem.*, *31*, 1585 (1978).
39. R. K. McCulloch and D. Wege, *Tetrahedron Letters*, 3213 (1976).
40. J. W. Barton and R. B. Walker, *Tetrahedron Letters*, 569 (1975).
41. J. Kramer and R. S. Berry, *J. Am. Chem. Soc.*, *94*, 8336 (1972); G. Hägele, P. Sartori and A. Golloch, *Z. Naturforsch.*, *28b*, 758 (1973); J. A. H. McBride, *J. Chem. Soc.*, *Chem. Comm.*, 359 (1974); S. Kanokranaporn, J. A. H. McBride and T. J. King, *J. Chem. Research*, *(S)*204, *(M)*2911 (1980); J. A. H. McBride, P. M. Wright and B. J. Wakefield, *Tetrahedron Letters*, 4545 (1981).
42. P. J. Garratt and K. P. C. Vollhardt, *Chem. Comm.*, 109 (1970); *J. Am. Chem. Soc.*, *94*, 7087 (1972).
43. S. W. Staley, F. Heinrich and A. W. Orredal, *J. Am. Chem. Soc.*, *98*, 2681 (1976).
44. M. J. S. Dewar and N. Trinajstić, *Tetrahedron Letters*, 2129 (1969).
45. G. Gandillon, B. Bianco and U. Berger, *Tetrahedron Letters*, *22*, 51 (1981).
46. U. Edlund, B. Eliasson, J. Kowalewski and L. Trogen, *J. Chem. Soc.*, *Perkin Trans.2*, 1260 (1981).
47. J. W. Barton and R. B. Walker, *Tetrahedron Letters*, 1005 (1978).
48. E. Carstensen-Oeser and G. Habermehl, *Angew. Chem.*, *80*, 564 (1968); *Angew. Chem. Int. Edtn. Engl.*, *7*, 543 (1968); R. Qasba, F. Brandl, W. Hoppe and R. Huber, *Acta Cryst.*, *B25*, 1198 (1969).
49. *inter alia* D. Cremer and B. Dick, *Angew. Chem.*, *94*, 877 (1982); *Angew. Chem. Int. Edtn. Engl.*, *21*, 865 (1982).