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Heteroaromaticity. 13. Bond Alternation and its Consequences for Conjugation Energies and Other Criteria of Aromaticity

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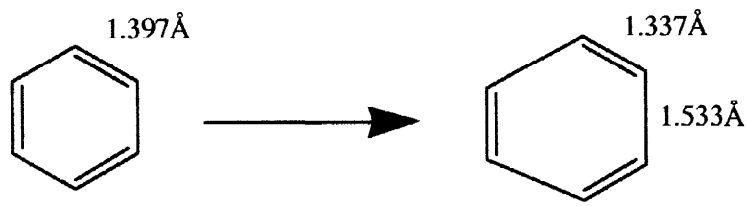
Abstract: Conjugation energies, aromaticity indices, I_6, and strain energies have been calculated from published experimental dimensions for a range of benzenoid derivatives displaying bond alternation and their quantitative interrelationships investigated.

INTRODUCTION

The original postulate by Mills and Nixon[1] that fusion of a five-membered ring onto a benzenoid one as in indane would result in double bond fixation and ensuing changes in reactivity patterns has been a continuing focus for investigation for both benzenoid and heterocyclic systems.[2,3] Although the original argument for its occurrence is now recognised to have been based upon a misconception the past few years has witnessed the description of an increasing number of benzenoid molecules displaying bond alternation, *vide infra*. Apart from some fragmentary observations little is known about the effect of bond alternation on the aromaticity of such benzenoid rings. In this paper we report the results of a comparative quantitative study of the effects of molecular structure on the aromaticity of those compounds for which accurate molecular dimensions are currently available.

AROMATICITY CRITERIA EMPLOYED IN THIS STUDY

Resonance energies are a widely employed criterion of aromaticity. In recent papers[4,5] we have introduced a method for estimating the resonance energy of an aromatic ring system from molecular dimensions which entails calculating the energy necessary to deform the real molecule into its Kekulé or resonance structure as illustrated for benzene;



In essence this entails calculating the energy, E_B, required to convert each bond of the conjugated benzene ring into the single or double bond of the corresponding Kekulé structure using the equation;

$$E_B = 85.94\,(\,R_s \text{ or } R_d - R\,)^2\,(44.39 - 26.02R)\ \text{kcal. mole}^{-1}$$

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where R (Å) is the length of the bond.Summation of the E_B values for the Kekulé structure give its conjugation energy CE. The lengths adopted for the single (R_S) and double bonds (R_d) are 1.533 and 1.337Å respectively. The energies for the separate Kekulé forms are then summed to give the overall conjugation energy, CE, according to the following expression:

$$CE = n\,E_i\left(1/E_i \div \sum_{i=1}^{i=6} 1/E_i\right)$$

The summation coefficients obtained can also be used to estimate the relative contributions of the individual Kekulé forms and have been used in this paper to provide the exo/endo ratio..

The aromaticity index, I_6,[6-8] which has been commended[9] as an alternative criterion of classical aromaticity,was also calculated for each compound This index is based upon a statistical evaluation of the extent of variation of ring bond order provided by the expression

$$I_6 = 100(1 - V/V_K)$$

$$\text{where} \quad V = \frac{100}{N}\sqrt{\frac{\Sigma\,(N - N)^2}{6}}$$

and N is the arithmetic mean of the 6 various ring bond orders, N, which were obtained[10] from the corresponding experimentally determined bond lengths using the relationship $N = 6.80/R^2 - 1.71$. V_K has the value of 33.3 for the corresponding non-delocalised form of the benzene ring.

It was recognised at the outset that the extent of bond fixation was a function of the endo ring angle and the most obvious way of placing this on a quantitative basis was to calculate the sum of the strain energies, ΣV_S, resulting from deforming each of these angles from 120°. The simplest method of achieving this was to calculate appropriate energy increments using Dauben's potential function:[11]

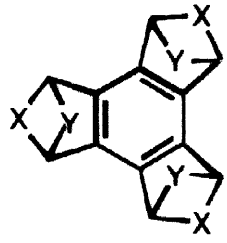
$$V_S = 0.5\,A\alpha^2$$

where A is the bond angle deformation constant (0.026 kcal. $mole^{-1}deg^2$) and α is the bond angle deformation. While the absolute magnitude of the resulting strain energies may be open to question this approach provides a convenient assessment of relative values as will be seen later.

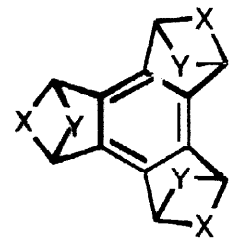
RESULTS AND DISCUSSION

The structures of the range of compounds under consideration are shown in formulae **1** to **11**. As illustrated for **1** to **5** the benzenoid ring can be depicted as having two contributing Kekulé structures in one of which the double bonds are endo to the annelating rings and the other in which they are exo. In valence bond terms most of these molecules behave as though the exo form makes a greater contribution to the resonance hybrid than the endo one. Perusal of the data in Table 1 shows that this behaviour is manifested by an increasing disparity between adjacent ring bond lengths . Whereas the introduction of six substituents into the benzene ring as in hexamethylbenzene results in a slight increase in the ring carbon-carbon bond lengths the fusion of three additional rings as instanced by entries 3 through 8 has the converse effect and the extent of bond alternation increases as the fused ring size decreases. One surprising exception to the general trend is provided by the hexafluorotris(cyclobutano)benzene **7**. As virtually identical dimensions have been derived for this molecule by two different groups of workers[20]

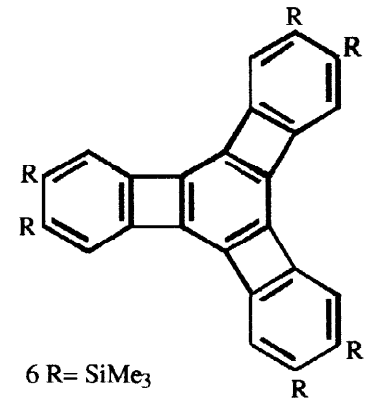
we can only assume that in this case the bond differentiation effects of the cyclobutano groups are counterbalanced by the bond lengthening effect of hexasubstitution.



ENDO

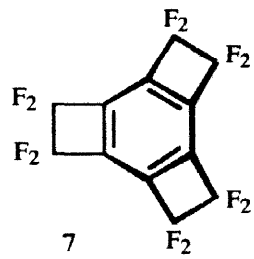


EXO



1 X=Y= CH_2CH_2
2 X= CH_2CH_2; Y= CH_2
3 X=o-C_6H_4; Y= CH_2
4 X= CH=CH; Y= O
5 X=Y= CH_2

6 R= $SiMe_3$



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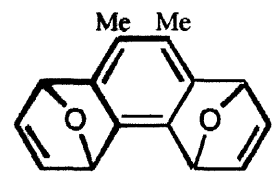

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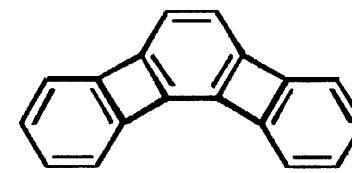

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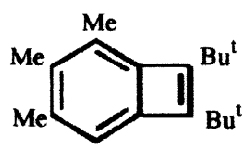

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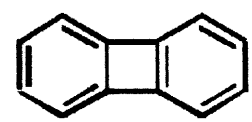

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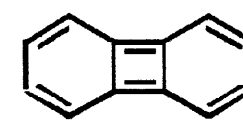
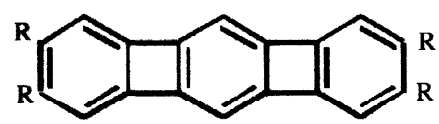


11a



12 R= $SiMe_3$

Conjugation energies and the other criteria mentioned above are also recorded in Table 1. It should be emphasised at this point that the conjugation energies (C.E.) do not contain any formal contribution from molecular strain energies. Analysis of the relative energies for the various Kekulé structures of biphenylene,**1** **1**, and **6** and **9** indicates that species such as **11a** make little or no contribution to the system. A conclusion in line with the very long bond lengths of *ca.* 1.51 Å observed between the benzene rings. Of particular note is the substantial decrease in conjugation energy of the central ring A in **6**, which explains *inter alia* the facility with which this ring is selectively hydrogenated and the

Table I. Geometrical Properties and Aromaticity Criteria for Benzenoid Rings

Entry	Compound	$R_{endo}^{av.}$	$R_{exo}^{av.}$	% exo	exo/endo	endo < ‡	ΣV_S†	C.E.†	I_6	Ref.*
1.	Me_6C_6	1.410Å	1.410Å	NA	NA	NA	-	40.6	100	12
2.	C_6H_6	1.397	1.397	NA	NA	NA	0	45.8	100	13
3.	**1**	1.408	1.393	57.5	1.35	112.4	2.25	43.5	95	14
4.	**2**	1.417	1.379	68.3	2.16	106.5	7.11	40.8	84	15
5.	**3**(central)	1.412	1.360	72.8	2.68	106.8	6.8	43.8	78	16
6.	**4**	1.425	1.353	80.1	4.03	104	9.98	36.3	70	17
7.	**5**	1.438	1.349	85.7	5.99	102.3	12.22	28.4	63	18
8.	**6**(central)	1.494	1.335	98.4	≈60	90	35.1	~1	33	19
9.	**7**	1.393	1.386	46.6	0.87	90	-	49.4	97	20
10.	**8**	1.422	1.367	74.7	2.95	104.5	9.98	38.8	75.5	21
11.	**9**(central)	1.448	1.347	89.1	8.17	90	23.4	22.7	36	22
12.	**3**(peripheral)	1.397	1.369	62.7	1.68	106.5	7.11	51.3	87	16
13.	**10**	1.432	1.359	81.0	4.26	90	11.7	33.2	68	23
14.	**11**	1.429	1.370	77.2	3.39	90	11.7	34.6	75	24

‡ Endo angle in degrees

† Kcal $mole^{-1}$

* References are to the source of X-ray structural data for the compound in question.

relative ease with which the ring undergoes ring cleavage to the isomeric cyclic triacetylene[19] . Theoretical calculations[25] have led to the conclusion that angular fused poyphenylenes, as **9**,[22] will have a lower energy than their linear fused counterparts, as **12**.[26] However we arrive at the opposite conclusion, since we calculate conjugation energies of 119.5 and 128.6 Kcal. mole^{-1} for **9** and **12** respectively from the published dimensions. Additionally these compounds are reported to have virtually identical arrays of bond angles and hence almost identical strain energies.

Bond alternation is also engendered by the fusion of two rings , entries 10 and 11, and even by one, entries 12-14. The size of the effects are once again dependent on the size of the fused ring.

Table 2. Correlation Coefficients for Pairs of Indices

	C.E.	I_6	exo/endo	ΣV_S
C.E.	1.000			
I_6	0.902	1.000		
exo/endo	0.933	0.977	1.000	
ΣV_S	0.944	0.948	0.853	1.000

It was of especial interest to establish the extent of correlation between the individual criteria listed in Table 1 in view of our earlier work[27] on the aromatic character of the benzene ring when located in a variety of polybenzenoid syystems. This indicated that there was a relatively poor corelation between 'geometrical" criteria such as the aromaticity index I_6 and various 'energetic' indices, which did not however include conjugation energies. The correlation coefficients listed in Table 2 were obtained assuming linear relationships between the pairs of criteria indicated using the data from Table 1 but omitting entries 1 and 9. It is immediately apparent that satisfactory relationships are observed between most of the criteria including C.E. and I_6 .The only exception is ΣV_S versus the exo/endo ratio where an exponential, power or quadratic relationship appears more appropriate leading to r values *ca.* 0.95-0.99, but the range of data presently available are insufficient for exploring this aspect further at present.

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