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THE APPLICATION OF THE BIOT-SAVART LAW TO THE RING CURRENT ANALYSIS OF PROTON CHEMICAL SHIFTS—II

AN APPROACH TO AROMATIC CHARACTER IN THE ANNULENES

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Abstract—A consistent, conceptually simple system for the empirical measurement of aromatic character in annulenes is presented, which is based on the HMO theory with allowance for simple bond alternation. The method, which is potentially applicable to all well-characterized annulenes, assigns an *effective* bond alternation to each annulene from the measurement of some π-electron property (in this case ring current), which is identified with the aromatic character (AC) thereof. The system is applied to a wide variety of annulenes and compared with other ground state approaches to the study of aromatic character.

INTRODUCTION

SINCE the advent of Hückel's rule regarding a structural classification for aromatic compounds,[1] the concept of aromatic character[2,4] and particularly the degree to which compounds may be considered aromatic has been a very popular and controversial subject.[5] In fact, Hückel's rule stated that coplanar, monocyclic π-systems are aromatic if and only if they contain $(4n + 2)$ π-electrons, n being an integer.[1] Thus, as originally constituted, the rule only applied to that class of compounds now known as annulenes.[6]

A number of annulene skeletons may in principle be aromatic, yet of the many annulenes synthesized few attain their full potential in this respect. In the lower annulenes particularly, this usually arises from geometrical rather than electronic exigencies. This behavior contrasts with the polycyclic (particularly benzenoid) hydrocarbons where conformations are usually planar (and unique), and the question of geometrical impediments to π-electron resonance does not arise. In the annulenes, however, the resonance energy to be gained from full aromatization often must be matched against very real strain energies which are inherent in the aromatic structure.

These considerations emphasise the rather unique chemistry of the annulenes and indicate that it might be possible to associate a degree of aromatic character with each annulene. Such a parameter would be expected to reflect the degree to which the annulene had availed itself of the π-electron resonance potential of the particular skeleton.

There has been a considerable effort made to define aromatic character, especially in the annulenes, and the degree to which it is present or absent. Almost always an observable or calculable physical property has been claimed to be a diagnostic criterion for aromatic character.[5] The more successful approaches include* the

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* Chemical reactivity[5] and electronic spectra have also been used in the assessment of aromatic character, but as non-ground state properties these methods are not considered here. Properly treated, electronic spectra can provide very detailed information on aromatic character,[7] but the analysis is rarely straightforward[7] and misinterpretations are frequent.

study of experimental and theoretical resonance and thermodynamic energies,[1, 2, 8–17] bond orders and bond lengths,[10–13, 17, 18] and ring currents.[17, 19–29] In point of fact the more important π-electron properties of annulenes (particularly those often associated with aromatic character) are dependent on the degree of π-electron resonance (delocalization) in the molecule. Accordingly, this latter "quantity" provides the fundamental and underlying basis for the concept of aromatic character, and may be correctly expected to be both determining and diagnostic of aromatic character.

In the HMO theory* the π-electron properties may be conveniently expressed as a function of the degree of bond alternation (symbolized by λ or k) in the annulene skeleton.[17, 20–24, 30–33] It is the degree of bond alternation (λ, k) calculated† for an annulene which we propose to identify with the aromatic character (AC)‡ thereof. It is stressed that the bond alternation implicit in the AC value of a compound will be effective rather than intrinsic. The parameter is introduced here to cover the whole spectrum of factors which decrease π-electron delocalization§—particularly poor p_π overlap as a result of non-planarity—as well as true alternation in bond lengths (where it occurs).

The idea is best conceptualized in the following way. From the study of some π-electron property, a given [N]annulene A is found to have a degree of aromatic character (effective bond alternation) AC. Then the quantity AC denotes the degree of bond alternation necessary in the perfect‖ [*N*]annulene to reproduce the π-electron properties of A. Thus the method is intended to provide a practical and conceptual bridge between the HMO picture of aromatic character and the world of real molecules.

Many of the preceding remarks apply in an opposite sense to the anti-aromatic [4*n*]annulenes. Furthermore, both the [4*n*]- and [4*n* + 2]-annulenes are expected to converge to a common non-aromatic limit at large ring size, due to an intrinsic preference for bond-alternate structures (of electronic origin).[17] These questions are returned to in the Discussion.

METHODS OF CALCULATION

Geometries. The geometries detailed in Part I[34] were used for the calculations of the (projected) areas.

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* An equally effective scheme could probably be devised, using the bond-alternate FEMO method. See ref. 21 and refs therein

† In this study we use ring currents[34] in the calculation of λ and k values. In principle however, any measurable π-electron property should suffice (with suitable parameterization of the HMO method).

‡ The AC value will be numerically equal to the calculated degree of bond alternation (usually k). The term is introduced to avoid confusion, and distinguish between annulenes and all other π-electron systems (many of which may be characterized by bond alternation). Furthermore, the term AC will usually be followed by the Hückel parity (see Table 1) of the particular compound, thus distinguishing between aromatic (AC(+)) and anti-aromatic (AC(−)) compounds.

§ Throughout this work, all factors which lead to a decrease in resonance, other than an electronic preference for bond alternation *per se*, are collected under the term steric inhibition of resonance.

‖ "Perfect" in the HMO concept of an annulene (*viz.* a molecule to which the HMO theory of π-electrons forms a justifiable approximation at the SCF level[11, 12]). Benzene appears to be the only example, although a case may be made for some of the ions.

Theoretical approach. The dependence of the π-electron properties of annulenes on bond alternation, has been extensively investigated from the theoretical standpoint and a number of clear expositions are already in the literature.[17,20–24,30,31,35] Nevertheless, in order to clarify the notation and avoid confusion a brief review of the salient equations is given below.

A. *Ring current magnetic anisotropy* (*RCMA*)

The contribution of the ring current (RC) to the molar magnetic anisotropy is given by[24]

$$RCMA = \frac{3N_0S}{c}\cdot RC \tag{1}$$

where S is the (projected) area of the annulene skeleton. The factor of 3 in eq. 1 arises because the ring currents calculated from solution spectra are subject to rotational averaging.

B. *Ring current, HMO π-electron energy and aromatic character*(*AC*)

Consider an annulene in which the bond lengths are alternately longer and shorter than the aromatic bond length. In this case the resonance integrals between adjacent p_π orbitals are no longer expected to be equal to the non-alternating value β (usually taken from benzene, which has a bond length of 1·397 Å). Accordingly, two resonance integrals (β_1 and β_2) are now required to characterize the π-electron properties of the molecule.[17,20,23,24,30,31,35]

Traditionally, β_1 is taken to correspond to the long bond and is therefore smaller in magnitude than β_2 (which corresponds to the short bond).

The HMO π-electron energy of an [N]annulene (N even), in the presence of this distortion is given by[17,30]

$$E_\pi(\beta_1, \beta_2) = -2\sum_j^{\text{occ.}} \sqrt{\beta_1^2 + \beta_2^2 + 2\beta_1\beta_2 \cos\left(\frac{4\pi j}{N}\right)} \tag{2}$$

The summation is carried over the occupied molecular orbitals; thus for N = $4n+2$, j takes values 0, ± 1, $\pm 2, \ldots, \pm n$, and for N = $4n$, the values are 0, $\pm 1, \ldots, \pm(n-1)$, $+n$.

The ring current per unit magnetic field (RC)* is then[31]

$$RC(\beta_1, \beta_2) = 32\left(\frac{\pi e S}{hcN}\right)^2 \beta_1\beta_2 \sum_j^{\text{occ}} \left\{\cos\frac{4\pi j}{N}(\beta_1^2 + \beta_2^2) + \beta_1\beta_2\left(1 + \cos^2\frac{4\pi j}{N}\right)\right\} \times \left\{\beta_1^2 + \beta_2^2 + 2\beta_1\beta_2\cos\frac{4\pi j}{N}\right\}^{-\frac{1}{2}} \tag{3}$$

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* In eqs 3, 1·7 and 2·7 the ring current, RC, is expressed in units of cgs per unit magnetic field. In Part I and Table 3 this quantity is multiplied by 10^3 and quoted in units of cgs ppt (parts per thousand of the magnetic field).

Further assumptions must now be made regarding the relationship between β_1 and β_2 and the bond-equalized resonance integral β, in order to put the theory into useful form. Two approaches have found acceptance in the literature.

C. *Method* I

If it is assumed that the resonance integrals are given by[17, 20, 24]

$$\beta_1 = \lambda^{\frac{1}{2}}\beta; \quad \beta_2 = \lambda^{-\frac{1}{2}}\beta \quad (\lambda \leqslant 1) \tag{1.4}$$

from which it follows that

$$\lambda = \frac{\beta_1}{\beta_2}; \quad \beta_1\beta_2 = \beta^2 \tag{1.5}$$

Eq. 2 and 3 now become

$$E_\pi^\lambda(\lambda) = 2\beta \sum_j^{\text{occ}} \sqrt{\lambda + \lambda^{-1} + 2\cos\frac{4\pi j}{N}} \tag{1.6}$$

$$RC^\lambda(\lambda) = 32\left(\frac{\pi e S}{hcN}\right)^2 \beta\lambda^{\frac{1}{2}} \sum_j^{\text{occ}} \left(\lambda + \cos\frac{4\pi j}{N}\right)\left(\lambda\cos\frac{4\pi j}{N} + 1\right) \times \left(\lambda^2 + 1 + 2\lambda\cos\frac{4\pi j}{N}\right)^{-\frac{1}{2}} \tag{1.7}$$

D. *Method* II

If the resonance integrals are characterized by[23]

$$\beta_1 = \mathrm{k}\beta; \quad \beta_2 = \beta \quad (\mathrm{k} \leqslant 1) \tag{2.4}$$

from which it follows that

$$\mathrm{k} = \frac{\beta_1}{\beta_2}; \quad \beta_1\beta_2 = \mathrm{k}\beta^2 \tag{2.5}$$

Eq. 2 becomes

$$E_\pi^\mathrm{k}(\mathrm{k}) = 2\beta \sum_j^{\text{occ}} \sqrt{1 + 2\mathrm{k}\cos\frac{4\pi j}{N} + \mathrm{k}^2} \tag{2.6}$$

and eq. 3 may be put in the form

$$RC^\mathrm{k}(\mathrm{k}) = 8\left(\frac{\pi e S}{hcN}\right)^2 \beta \sum_j^{\text{occ}} \left\{\left(1 + 2\mathrm{k}\cos\frac{4\pi j}{N} + \mathrm{k}^2\right)^{\frac{1}{2}} - (1 - \mathrm{k}^2)^2\left(1 + 2\mathrm{k}\cos\frac{4\pi j}{N} + \mathrm{k}^2\right)^{-\frac{1}{2}}\right\} \tag{2.7}$$

where the diamagnetic and paramagnetic terms are separated.[23]

E. *Comparison of methods*

A simple relationship exists between the π-electron properties calculated by the two approaches

$$E_\pi^\mathrm{k}(\mathrm{z}) \equiv \mathrm{z}^{\frac{1}{2}} E_\pi^\lambda(\mathrm{z}) \tag{8}$$

and

$$RC^{k}(z) \equiv z^{\frac{1}{2}} RC^{\lambda}(z) \tag{9}$$

In spite of the correspondence between eqs. 8 and 9, the ring currents calculated by the two methods as a function of bond alternation (eqs. 1.7 and 2.7) show similar behavior, while the HMO π-electron energies (eqs. 1.6 and 2.6) show a quite different dependence. Both equations (1.6 and 2.6) reproduce the bond-equalized HMO π-electron energy for λ,k = 1, but diametrically opposite behavior is observed as bond alternation is introduced ($1 > \lambda, k > 0$). Method I predicts an increase in π-electron energy, whereas Method II allows for a decrease in π-electron energy with increased bond alternation.

Method I has found chief application where bond alternation is a relatively minor perturbation and has proved to be a convenient device to mimic the part which configuration interaction plays in reducing the energy of the distorted structure.[36] As the inhibition of resonance considered in this paper arises from a variety of factors which we attempt to collectively describe by an effective bond alternation, we prefer the π-electron properties to be well-defined over the whole range of interest. As expected, Method II reproduces the conventional HMO picture of π-electron energies (see below). Thus, while we shall usually identify k with the AC value of a molecule, the λ values are closely comparable (clearly, however, we shall prefer the π-electron energies from eq. 2.6).

RESULTS

All results (and errors) given in Table I are obtained (explicitly or implicitly) from the ring currents derived in Part I[34] by an analysis of the proton chemical shifts of the annulenes.

In order to apply eqs. 1.7 and 2.7, a value must be assigned to the resonance integral β which is consonant with the calculation of magnetic properties (β_m). It is now recognised that parameterizations of the HMO method are, in general, not interchangeable among calculations of different molecular properties.[37,*] Nevertheless, it has been clearly demonstrated that the HMO and London theories, with suitable parameterization, are capable of giving an excellent description of the π-electron ground state properties of alternant hydrocarbons.[16,33,38,39] As this study is restricted to annulenes, the method (with allowance for bond alternation) should be on very strong grounds[11,40] (it will be remembered that this class of compounds provided much of the impetus for Hückel's early work and his structural definition for aromatic character).

Parameterization. As we must use a magnetic property to characterize the magnetic resonance integral β_m, the parameterization must be taken from ring current or magnetic susceptibility data (experimental or calculated). Benzene, as the perfect [6]annulene, obviously may be assigned a λ,k value of unity. Using the benzene ring current calculated in Part I[34] it would be possible to estimate β_m from eqs. 1.7/2.7.

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[*] Recent work[16] has raised the possibility that a reconciliation among parameterizations may be brought about by the correct choice of models (at least for certain ground state properties)

TABLE 1. CALCULATED DEGREE OF AROMATIC CHARACTER (AC)

Compound	RCMA[a] (Error) (cgs ppm)	Configuration[b] C	Configuration[b] π	Configuration[b] Hückel Parity	Parameterization A[a, c] Fraction of Max Cal RC	Parameterization A[a, c] AC λ (Error Range)	Parameterization A[a, c] AC k (Error Range)	Parameterization A[a, c] $E_\pi^k(k)$ (β)	Parameterization B[a, d] Fraction of Max Cal RC	Parameterization B[a, d] AC λ (Error Range)	Parameterization B[a, d] AC k (Error Range)	Parameterization B[a, d] $E_\pi^k(k)$ (β)
Benzene (1)	− 36·2 (10·7)	6	6	+	1·0692	1 + (0·66 > 1)	1 + (0·76 > 1)	8·000	1·3037	1 + (0·80 > 1)	1 + (0·89– > 1)	8·000
Naphthalene (2)	− 68·6 (10·3)	10	10	+	0·8715	0·848 (0·78 > 1)	0·885 (0·82– > 1)	12·247	1·0627	1 + (0·86– > 1)	1 + (0·91– > 1)	12·944
1,6-Methano-[10]annulene (3)	− 53·8 (5·7)	10	10	+	0·5108	0·683 (0·66–0·71)	0·721 (0·70–0·75)	11·427	0·6228	0·730 (0·70–0·76)	0·768 (0·74–0·80)	11·640
1,6-Oxido-[10]annulene (4)	− 70·3 (11·8)	10	10	+	0·6674	0·749 (0·70–0·80)	0·787 (0·73–0·84)	11·731	0·8138	0·817 (0·75–0·91)	0·854 (0·79–0·95)	12·076
1,6-Imino-[10]annulene (5)	− 64·5 (15·3)	10	10	+	0·6130	0·726 (0·66–0·79)	0·764 (0·70–0·83)	11·621	0·7475	0·785 (0·70–0·89)	0·822 (0·74–0·92)	11·907
N-Methyl-1,6-imino-[10]-annulene (6)	− 57·4 (13·6)	10	10	+	0·5453	0·697 (0·64–0·76)	0·736 (0·68–0·79)	11·493	0·6649	0·748 (0·68–0·83)	0·786 (0·71–0·86)	11·726
11-Methylene-1,6-methano-[10]-annulene (7)	− 63·4 (12·6)	10	10	+	0·6026	0·722 (0·67–0·78)	0·760 (0·70–0·82)	11·603	0·7348	0·779 (0·71–0·86)	0·816 (0·75–0·90)	11·876
[12]Annulene (8)	19·7 (1·9)	12	12	−	—	0·534 (0·52–0·55)	0·563 (0·55–0·58)	12·958	—	0·554 (0·54–0·57)	0·582 (0·57–0·60)	13·023
1,5,9-Tridehydro-[12]-annulene (9)	124·4 (26·1)	12	12	−	—	0·708 (0·68–0·74)	0·727 (0·70–0·75)	13·589	—	0·732 (0·70–0·76)	0·749 (0·72–0·77)	13·684
Cycl[3,3,3]azine (10)	218·6 (47·4)	12	12	−	—	0·806 (0·77–0·83)	0·817 (0·80–0·84)	13·994	—	0·827 (0·80–0·85)	0·836 (0·82–0·86)	14·084
[14]Annulene (11)	− 91·5 (6·2)	14	14	+	0·4051	0·726 (0·71–0·74)	0·748 (0·73–0·76)	16·081	0·4940	0·757 (0·74–0·77)	0·779 (0·76–0·80)	16·274
trans-15,16-Dimethyl-dihydropyrene (12)	− 195·4 (6·5)	14	14	+	0·8202	0·868 (0·85–0·88)	0·889 (0·88–0·90)	17·049	1·0000	1·0000 (0·94 > 1)	1·0000 (0·96 > 1)	17·976
trans-15,16-Dihydropyrene (13)	− 190·8 (6·2)	14	14	+	0·8007	0·861 (0·85–0·88)	0·882 (0·88–0·90)	16·995	0·9763	0·953 (0·92 > 1)	0·971 (0·94– > 1)	17·720

syn-1,6: 8,13-Dioxido-[14]-annulene (**14**)	−133·5 (20·5)	14	14	+	0·7161	0·831 (0·79–0·88)	0·852 (0·81–0·89	16·772	0·8731	0·890 (0·83 > 1)	0·911 (0·85 > 1)	17·221
syn-1,6-Methano-8,13-oxido-[14]annulene (**15**)	−118·2 (17·9)	14	14	+	0·6339	0·803 (0·77–0·84)	0·825 (0·79–0·86)	16·580	0·7729	0·851 (0·81–0·90)	0·872 (0·83–0·92)	16·919
1,6: 8,13-Butano-[14]annulene (**16**)	113·8 (24·9)	14	14	+	0·6103	0·796 (0·75–0·85)	0·817 (0·77–0·87)	16·525	0·7442	0·841 (0·78–0·91)	0·861 (0·80–0·93)	16·838
1,6, 8,13-Propano-[14]-annulene (**17**)	−127·2 (4·1)	14	14	+	0·6822	0·819 (0·81–0·83)	0·841 (0·83–0·85)	16·693	0·8318	0·873 (0·86–0·89)	0·894 (0·88–0·91)	17·087
1,8-Didehydro-[14]annulene (**18**)	−212·5 (18·6)	14	14	+	0·7190	0·832 (0·81–0·86)	0·853 (0·83–0·88)	16·779	0·8768	0·892 (0·86–0·94)	0·912 (0·88–0·96)	17·229
[16]Annulene (**19**)	106·2 (3·1)	16	16	−	—	0·695 (0·69–0·70)	0·711 (0·70–0·72)	18·075	—	0·714 (0·71–0·72)	0·729 (0·72–0·74)	18·183
trans-15,16-Dimethyl-dihydropyrene dianion (**20**)	725·5 (53·1)	14	16	−	—	—	—	—	—	—	—	—
[16]Annulene dianion (**21**)	−315·7 (16·2)	16	18	+	0·7873	0·687 (0·65–0·72)	0·779 (0·75–0·81)	18·055	0·9600	0·864 (0·79– > 1)	0·937 (0·88– > 1)	19·489
[18]Annulene (**22**)	−274·0 (26·8)	18	18	+	0·4557	0·795 (0·78–0·81)	0·809 (0·79–0·83)	21·130	0·5557	0·823 (0·80–0·84)	0·837 (0·82–0·86)	21·373
1,7,13-Tridehydro-[18]-annulene (**23**)	−144·7 (23·8)	18	18	+	0·2490	0·725 (0·70–0·75)	0·741 (0·72–0·76)	20·590	0·3036	0·746 (0·72–0·77)	0·762 (0·74–0·78)	20·750
1,5,10,14-Tetramethyl-6,8,15,17-tetradehydro-[18]-annulene (**24**)	−331·5 (31·1)	18	18	+	0·6270	0·842 (0·82–0·86)	0·856 (0·84–0·88)	21·544	0·7645	0·880 (0·85–0·91)	0·893 (0·87–0·92)	21·895
1,3,7,9,13,15-Hexadehydro-[18]-annulene (**25**)	−119·7 (22·2)	18	18	+	0·2224	0·714 (0·69–0·74)	0·730 (0·71–0·75)	20·508	0·2712	0·734 (0·71–0·76)	0·750 (0·72–0·77)	20·657
[24]Annulene (**26**)	326·4 (38·5)	24	24	—	—	0·783 (0·77–0·80)	0·791 (0·78–0·80)	27·919	—	0·797 (0·78–0·81)	0·805 (0·79–0·82)	28·064

[a] All quantities are calculated from the ring currents given in Part I[14] The quantities presented in the Table are defined in the text.

[b] Where C denotes the number of carbon atoms in conjugation and π the number of π-electrons in the system A positive Huckel parity is assigned to (4*n* + 2) π-electron systems, whereas a negative parity is given to the 4*n* π-electron systems (in accord with Huckels' rule). See ref 29

[c] $\beta_m = -61{\cdot}4409$ kcal mole^{-1}

[d] $\beta_m = -50{\cdot}3878$ kcal mole^{-1}

This procedure constitutes the usual parameterization for this type of work, but as pointed out earlier,[34] the errors associated with the ring current calculations are at a maximum for benzene and mitigate against this approach.

A. *Scheme* A

The contribution of the ring current to the diamagnetic anisotropy of benzene has been carefully studied from both theoretical and semi-empirical standpoints. The results of these investigations are collected in Table 2, together with the value of β_m to which they give rise in the HMO–London theory. The value selected as being most appropriate for use in this work was obtained by O'Sullivan and Hameka[38] from an analysis of the diamagnetic susceptibility of benzenoid hydrocarbons. Their semi-empirical approach also employed the HMO–London method for the calculation of the relative ring currents and they were able to reproduce the experimental diamagnetic susceptibilities to a high order of accuracy.[38] The results for this choice of parameters appear in Table 1 under Parameterization A.

B. *Scheme* B

Apart from benzene, the compounds exhibiting the largest fraction of the maximum calculated ring current (Table 1) are the *trans*-dihydropyrenes (**12** and **13**), closely followed by the [16]annulene dianion (**21**). All of these compounds might have been expected to have AC(+) values very close to unity (see Discussion). Accordingly, the results for Parameterization B in Table I are calculated with a β_m value estimated from the ring current of *trans*-15,16-dimethyldihydropyrene (**12**) and eqs. 1.7/2.7 with λ,k set to unity.

C. *Assessment*

Although the differences between the two parameterizations are not very serious (*cf* the range of reported values in Table 2), ultimately these discrepancies must be resolved. The more recent calculations of the ring current contribution to the diamagnetic anisotropy of benzene have resulted in much lower values than the early estimates (which often considered the experimental anisotropy (−59·7 cgs ppm[41]) to arise entirely from ring current effects). At present it appears unlikely that calculations will further lower this estimate,* although a final answer to this long standing and important question will probably have to await the appearance of more complete calculations.†

In a further effort to assess the parameterizations, chemical shifts for the [N]-annulenes with D_{Nh} symmetry (which are necessarily bond-equalized) have been calculated with both schemes, and are compared with experimental values in Table 3. Agreement with experimental data for the charged systems is poor, and no meaningful conclusions may be drawn regarding the parameterization schemes.‡ These results

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* It has been suggested[42] that the FEMO method[21,43] provides an upper limit to the ring current. The value quoted has been calculated using the exact,[42,44] rather than the circular[43] area of benzene.

† An *ab initio* SCF calculation on benzene, employing an optimized minimum basis set of Slater-type orbitals has recently appeared.[42] A good agreement with the experimental magnetic properties was attained, but the ring current contribution from the π-electrons was not explicitly obtained (personal communication, E. A. Laws 1971).

‡ An improved agreement is obtained by the consideration of additional effects in these systems.[46]

TABLE 2. VALUES OBTAINED FOR THE RING CURRENT CONTRIBUTION TO THE DIAMAGNETIC ANISOTROPY OF BENZENE

Method	Ref	RCMA (cgs ppm)	Value derived for β_m by HMO–London Theory (kcal mole^{-1})
ASMO–CI	*a*	−26·8	−48·6
Semi-Empirical Analysis of the Ring Current Chemical Shifts in Annulenes (Parameterization B)	*b*	−27·8	−50·4
Semi-Empirical Analysis of the Ring Current Chemical Shifts in Benzenoid Hydrocarbons	*c*	−31·2	−56·5
SCF MO	*d*	−31·2	−56·5
SCF MO	*e*	−31·2	−56·5
ASMO	*f*	−31·4, −33·1	−56·9, −60·0
ASMO	*g*	−33·0	−59·8
SCF MO	*h*	−33·3	−60·4
Semi-Empirical Analysis of the Ring Current Contribution to Diamagnetic Susceptibilities in Benzenoid Hydrocarbons (Parameterization A)	*i*	−33·9	−61·4
FEMO	*j*	−41·0	−74·3
Empirical Analysis of the Ring Current Contribution to Diamagnetic Susceptibilities	*k*	−41·1	−74·5

[a] T. Itoh, K. Ohno and H. Yoshizumi, *J. Chem. Phys.* **22**, 947 (1954); *J. Phys. Soc. Japan* **10**, 103 (1955)

[b] This paper, Parameterization B

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[i] Ref 38

[j] See footnote * on p. 3642 and ref 43

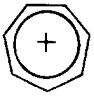
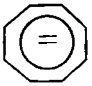
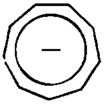
[k] Ref 26

emphasize once again the very considerable difficulties entailed in attempts to obtain suitable model chemical shifts for charged systems.[29,34]

Ring current magnetic anisotropy (*RCMA*). The contribution of the ring current to the magnetic anisotropy[24,44] may be obtained in a straightforward manner from eq. 1 and the results appear in Table 1. Apart from the value for benzene (Table 2) relatively little data is available for comparison.

The ring current diamagnetic susceptibility exaltation (Λ) estimated by Dauben, Wilson and Laity[26] for certain compounds included in this study appear in Table 4. A rough comparison may be made between the RCMA values in Table 1 and diamagnetic susceptibility exaltations by multiplying the latter values by -3. The correspondence between these quantities is not expected to be exact,[26,29] although a qualitative agreement is obtained. In all cases the quantities derived from the diamagnetic susceptibility exaltation measurements ($-3 \times \Lambda$) (Table 4), are more negative than the RCMA values (Tables 1 and 2); this may arise from an underestimation of

TABLE 3. CALCULATED PROTON CHEMICAL SHIFTS FOR THE SYMMETRIC ANNULENES

			Parameterization A[a]			Parameterization B[b]				
Compound	MCS[c] (τ)	RCGF[d] (cgs×10^3)	Cal RC[e] (cgs ppt)	Cal RCCS[f] (ppm)	Cal Chem Shift[g] (τ)	Cal RC[e] (cgs ppt)	Cal RCCS[f] (ppm)	Cal Chem Shift[g] (τ)	Obs Chemical Shift[h] (τ)	Ref
	0·54	0·26323	−0·3714	−0·098	0·44	−0·3046	−0·080	0·46	−0·87	i
	5·87	0·74778	−0·8595	−0·643	5·23	−0·7049	−0·527	5·34	4·56	j
	3·871	0·95858	−1·1094	−1·063	2·808	−0·9098	−0·872	2·999	2·734	k
	2·44	1·15293	−1·2863	−1·483	0·96	−1·0549	−1·216	1·22	0·82	j
	6·37	1·32679	−1·4060	−1·865	4·50	−1·1530	−1·530	4·84	4·32	j
	4·98	1·48405	−1·6963	−2·517	2·46	−1·3911	−2·065	2·92	3·15	l

[a] $\beta_m = -61{\cdot}4409$ kcal mole^{-1}

[b] $\beta_m = -50{\cdot}3878$ kcal mole^{-1}

[c] Model chemical shift[34]

[d] Ring current geometric factor[34]

[e] See footnote * on p. 3637

[f] Ring current chemical shift[34]

[g] Cal Chemical Shift = MCS + Cal RCCS[34]

[h] A representative value quoted from those given in ref 29 (without correction[46])

[i] R. Breslow, J. T. Groves and G. Ryan, *J. Am. Chem. Soc.* **89**, 5048 (1967)

[j] T. Schaefer and W. G. Schneider, *Canad. J. Chem.* **41**, 966 (1963)

[k] F. A. Bovey, *NMR Data Tables for Organic Compounds* Vol. 1. New York, Interscience (1967).

[l] T. J. Katz and P. J. Garratt, *J. Am. Chem. Soc.* **85**, 2852 (1963)

TABLE 4. THE DIAMAGNETIC SUSCEPTIBILITY EXALTATION (Λ)

Compound	Λ[a] (−cgs ppm)	−3 ×Λ
[16] Annulene	−5	15
Benzene	13·7	−41·1
1,6-Methano-[10]annulene	36·8	−110·4
1,6-Oxido-[10]annulene	38·9	−116·7
trans-15,16-Dimethyldihydropyrene	81	−243

[a] Ref 26.

the local Van Vleck paramagnetism in the construction of model compounds for the calculation of the Λ values.[24, 29, 34] Bailey, Gerloch and Mason[47] have estimated a value of −234 cgs ppm for the RCMA of 1,8-didehydro-[14]annulene (**18**) from magnetic measurements on a single crystal.

Unfortunately, the unequivocal estimation of localized contributions to the magnetic susceptibility and/or magnetic anisotropy remains the chief difficulty in such experimental studies.[24, 28, 29, 34, 38, 44]

HMO π-electron energies [$E_\pi^k(k)$]. The HMO π-electron energies obtained from eq. 2.6 (by substitution of the calculated k values) are given in Table 1 and may be compared with representative values presented in Table 5. Presumably it would be possible to use the aromatic criterion of Hess and Schaad,[16] and compare the HMO π-electron energy calculated for an annulene (Table 1) against the value estimated for the corresponding classical polyene. However, the impressive results of Hess and Schaad[16] were obtained on planar systems and further work is necessary to demonstrate the applicability of the models in the presence of steric inhibition of resonance. Furthermore, it is obvious from Table 5 that the analogy between aromatic character (as used here) and HMO π-electron energies is not complete, as the energies of all annulenes are predicted to decrease with increasing bond equalization. Such considerations have dissuaded us from the implementation of this approach.

TABLE 5. THE DEPENDENCE OF THE HMO π-ELECTRON ENERGY ON THE DEGREE OF BOND ALTERNATION K

Annulene	$E_\pi^k(k)$ (β)			
	$k \doteq 0·0$	$k = 0·5$	$k = 0·75$	$k = 1·0$
[4]	4·000	4·000	4·000	4·000
[6]	6·000	6·464	7·106	8·000
[8]	8·000	8·472	9·000	9·657
[10]	10·000	10·651	11·557	12·944
[12]	12·000	12·756	13·688	14·928
[14]	14·000	14·893	16·093	17·976
[16]	16·000	17·015	18·312	20·109
[18]	18·000	19·145	20·657	23·035
[24]	24·000	25·525	27·508	30·383
[8] Dianion	6·000	7·472	8·500	9·657
[16] Dianion	14·000	16·015	17·812	20·109

DISCUSSION

Although the λ or *k* values in either parameterization (Table 1) may potentially be identified with the AC* of an annulene, for the purposes of this discussion we shall focus on the k values obtained within Parameterization B.

Benzene and naphthalene. The large errors associated with the ring currents of these compounds[34] carry over into the AC determinations. Benzene (**1**), of course, is known to have an AC(+) value of unity, but, because of the errors, proved unsuitable for use as a parameterization standard (see Results Section).

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* See footnote ‡ page 3636.

Although naphthalene (**2**) fares little better with respect to errors this molecule provides an interesting illustration of the method. In the case of naphthalene it is neither bond alternation nor steric inhibition of resonance which leads to a dimunition of the ring current expected for a [10]annulene, but rather the presence of 1,6p_π overlap in the ring. We are, however, still able to characterize this by the effective AC(+) value, although such a result is of doubtful value. The additional conjugation provided by cross-linking is an innate property of the system, and should be allowed for in the secular determinant.*[48]

10π-Systems (**3**, **4**, **5**, **6**, **7**). From the AC(+) values obtained for the 1,6-bridged-[10]annulenes (**3**–**7**)[49] it is obvious that the ring deformation at the bridge[50] provides a serious steric inhibition of resonance. That these compounds still achieve a nearly bond-equalized perimeter[50] is indicative of the very real aromatic stabilization potentially available to the smaller annulenes.

Vogel[49c,d] has shown that the nature of the bridging atom exerts a profound effect on the π-electron character of these molecules†, presumably by altering the degree of overlap in the π-system (rather than by any direct interaction of bridging atom and perimeter). This is in accord with the variation in AC(+) values found for these annulenes (Table 1). In particular, it has been shown[49d] that increasing methyl substitution at the bridging carbon of 1,6-methano-[10]annulene has an unfavourable effect on the aromatic character of this compound, to the point where the 11-dimethyl analogue prefers to exist completely as the double norcaradiene (this non-aromatic isomer is evidently preferred to the classical 10π-electron cyclic polyene).

12π-Systems (**8**, **9**, **10**). The lowest AC(−) value found in this study is provided by [12]annulene (**8**),[51] and corresponds to a higher degree of bond alternation than would be expected for a classical polyene. In this case however, a significant contribution to the decrease in resonance arises from the particularly severe ring deformation (although a static Jahn–Teller effect is also evident[51]).

This contrasts with the AC(−) value found for cycl[3,3,3]azine (**10**)[52] which has a formally similar perimeter to [12]annulene, but which should have no steric impediments to resonance. However, SCF–MO calculations[53] indicate that the formally non-bonding p_π electrons of the nitrogen atom in cycl[3,3,3]azine are drawn into conjugation with the perimeter, presumably to decrease the anti-aromatic character of the [12]annulene system. Thus, while the π-electron delocalization in the perimeter of this compound is quenched by electronic rather than steric factors, the tendency towards bond alternation is not the sole reason.

The reduced AC(−) value‡ found for 1,5,9-tridehydro-[12]annulene (**9**)[54,55] certainly arises from a genuine bond length alternation in the molecule. However,

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* In fact from the HMO-London theory we can calculate a hypothetical AC(+) value for napthalene (0·93) from calculated ring currents. In addition it should be noted that while cross-linking (to produce benzenoid hydrocarbons) decreases the molecular ring current it brings about an increase in the HMO π-electron energy.[48]

† There is some evidence[50b] to indicate that **4** achieves a higher degree of bond equalization than **3** (*cf* the AC(+) values reported in Table 1).

‡ Unfortunately the possibility that the calculated ring current (and thus the AC value) lies outside the stated error limits cannot be entirely dismissed (see Part I[34]).

the presence of triple bonds undoubtedly prejudices the system towards such a distortion.*

14π-Systems (**11**, **12**, **13**, **14**, **15**, **16**, **17**, **18**). As with [12]annulene, the AC value found for [14]annulene (**11**)[6,29,55] is considerably diminished by steric inhibition of resonance due to a severe interaction of the internal hydrogen atoms (systematic bond alternation is thought to be absent in the crystal phase[56]). When the hydrogens are replaced by a suitable bridging group as in the dihydropyrenes (**12** and **13**)[57] the AC(+) value is dramatically increased. This is in accord with the X-ray crystallographic study[58] of **12** which indicates a high degree of bond equalization (at a bond length very close to that of benzene). In addition, the perimeter is nearly coplanar, with the p_π orbitals closely aligned. These considerations together with the low errors estimated for the ring currents of these two compounds,[34] lend support to the adoption of Parameterization B.

The steric inhibition of resonance caused by the bridging in the 1,6; 8,13-dibridged-[14]annulenes (**14**–**17**)[49b–d,59] is obviously responsible for the somewhat reduced AC(+) values found for these compounds, although they appear to fare significantly better than the 1,6-bridged-[10]annulenes. X-ray crystallographic studies[60,61] lend credence to this finding. For those compounds studied,[60,61] a somewhat higher order of bond length equalization is indicated for the dibridged-[14]annulenes together with a slightly better alignment of the p_π orbitals. Overlap of the bridge p_π orbitals is expected to be particularly poor in the *anti*-1,6; 8,13-dibridged-[14]-annulenes and indeed the only known compound with this geometry (the dimethano derivative) appears to be non-aromatic.[49d,62,65,†]

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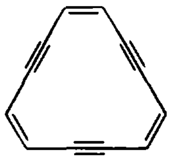
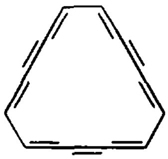
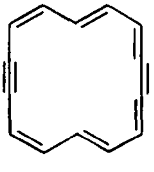
[*] The tendency of triple bonds to increase bond alternation is a point of some importance. As an illustration of the problem we first consider 1,5,9-tridehydro-[12]annulene. In the ground state of the molecule the following two Kekulé structures will be of chief importance:

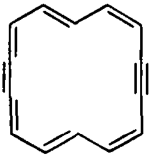

"Acetylenic"


"Allenic"

Were the two Kekulé structures to contribute equally, then the introduction of triple bonds could not be construed to prejudice the molecule to bond alternation. The present indications are, however, that the acetylenic form is the main contributor in such molecules.

Also of interest are the compounds with "mixed" Kekulé structures such as 1,8-didehydro-[14]annulene:





In such cases the presence of triple bonds will not prejudice the molecule toward bond alternation (at least, not the simple bond alternation considered above) as there will be no preferred Kekulé structure. Nevertheless, the presence of triple bonds *per se* is expected to quench the resonance of a molecule, as the periodic potential experienced by the π-electrons at sp and sp^2 hybridized carbon atoms will be quite different (for a discussion on the effect of alternating potentials on such properties as ring currents, see ref 21).

† See footnote † page 3648.

In agreement with the high AC(+) value found for 1,8-didehydro-[14]annulene (**18**), the X-ray crystallographic study[66] indicates a coplanar structure with bond lengths close to the aromatic value (with the exception of the acetylenic linkages). The slight quenching of resonance in this molecule, although of electronic rather than steric origin, is not brought about by simple bond alternation, although the effect on the π-electron properties is somewhat similar.*

16π-Systems (**19**, **20**). As expected, [16]annulene (**19**)[55,67] has a low AC(−) value and is second only to [12]annulene in this respect. The bond lengths found in an X-ray crystallographic study of this molecule[68] indicate the onset of a marked bond alternation, and correspond quite closely to the values[12,69] expected for a classical (non-aromatic) polyene, which suggests that the formally anti-aromatic [16]annulene may be approaching non-aromaticity. If this is indeed the case it appears that small (but significant) ring currents may be observed for non-aromatic annulenes (at least the 4*n* variety).

However, care must be taken in the interpretation of the AC(−) value found for [16]annulene as it is rather difficult to assess the part played by ring deformation in reducing the resonance. The crystallographic study[68] showed the molecule to be non-planar but it is difficult to estimate the degree to which these distortions pass from the crystal to the solution phase in non-rigid molecules such as **19**.

The very large paramagnetic ring current found for the *trans*-15,16-dimethyldihydropyrene dianion (**20**)[34] occurs in part because the interaction of the molecular orbitals which are responsible for the unusual magnetic properties is not decreased by the simple bond alternation considered in the present treatment.‡

18π-Systems (**21**, **22**, **23**, **24**, **25**). The completely delocalized structure expected for charged species such as the [16]annulene dianion (**21**)[71] lends support to the high AC(+) value found for this compound. Although angle strain is implicit in a planar form of the [16]annulene skeleton, it is not expected to be very severe. Furthermore, non-bonded interactions of the internal hydrogens will be somewhat relieved by the angle deformation. Thus there is every reason to expect that **21** will adopt a planar bond-equalized structure to effectively disperse the electronic charge[29] (in support of a high AC(+) value and Parameterization B). It can be seen from the tabulated data that the π-electron properties of **21** are somewhat less sensitive to bond alternation than those of the neutral annulenes.

The remaining [18]annulenes (**22**–**25**)[6,55,72,73] form an interesting series with respect to the presence of triple bonds (all are free of angle strain, and internal non-bonded interactions will be minimal for most of these molecules). As can be seen

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* See footnote * page 3647.

† A very small ring current may be present in *anti*-1,6;8,13-dimethano-[14]annulene; the ring current arising from an AC(+) value of about 0·4 (or less) would not be detectable in this molecule. The following situation probably exists. Overlap is inhibited to such a degree that the drive for aromatization (and bond equalization) is lost (in contrast to the *syn*-1,6; 8,13-dibridged-[14]annulenes) and the molecule prefers to exist as a bond-alternate classical polyene.[65] The resonance normally present in a (planar) classical polyene is also reduced by the poor overlap in the molecule and results in a very low AC(+) value. Certain segments of the molecule are probably in quite effective conjugation, but with breaks mainly occurring at the bridges (the situation is somewhat reminiscent of the island bonding postulated by Dewar, Lucken and Whitehead[63] for the cyclotriphosphazenes[64]).

‡ The *trans*-15,16-dimethyldihydropyrene dianion (**20**) will be correctly treated in a subsequent paper. See refs 36, 70.

from the AC(+) values found for these compounds, the highest value is registered by 1,5,10,14-tetramethyl-6,8,15,17-tetradehydro-[18]annulene(**24**).[73] That this compound should be more aromatic than the other dehydro-[18]annulenes (**23** and **25**) is in accord with expectations,* but that **24** is also more aromatic than [18]annulene (**22**)[6, 55] itself, is quite surprising. Evidently the absence of a unique acetylenic Kekulé structure does inhibit simple bond alternation, although the mere presence of *sp* hybridized carbon atoms causes a slight quenching of resonance* (this is in accord with the relative AC(+) values found for **24** and 1,8-didehydro-[14]annulene (**18**), the only two known dehydro annulenes without unique acetylenic Kekulé structures*).

A number of unsuccessful attempts have been made to calculate the electronic spectrum of [18]annulene (**22**) based on the crystallographic[74] and bond-equalized structures. Recent SCF MO calculations[7] on the electronic spectrum indicate that simple bond-length alternation is occurring in the solution structure of **22**. This is in contrast to the structure found in the crystal phase in which simple bond alternation was absent[74] (although all the bonds were not found to be equal in length). While the ring deformations in the crystal phase may be accounted for,[7, 75] it is difficult to understand why simple bond-length alternation is not superimposed (to some extent) on this distortion. Nevertheless, the AC(+) value found for [18]annulene† definitely lends support to the idea that an additional quenching of resonance occurs in the solution conformation of this compound‡ (the small crystallographic distortion could not account for the reduced resonance), and bond alternation obviously provides a possible mechanism.

As expected, for the two dehydro-annulenes with unique acetylenic Kekulé structures, 1,7,13-tridehydro-[18]annulene (**23**)[6, 55] and 1,3,7,9,13,15-hexadehydro-[18]-annulene (**25**)§[72] the AC(+) values, with respect to [18] annulene, fall off monotonically with increasing unsaturation.

24π-System (**26**). The AC(−) value obtained for [24]annulene (**26**)§[76] may represent a limiting value for non-aromaticity in the [4*n*]annulenes (steric inhibition of resonance at this ring size should be almost negligible.

Bond alternation

A. *Characteristics of the AC scale.* From the development given in the Introduction it is easily seen how the aromatic [4*n* + 2]annulenes may be satisfactorily characterized by AC values. The perfect annulene registers an AC(+) value of unity while progressively smaller AC(+) values are associated with decreased resonance. The results are in accord with this interpretation, and also lend support to the idea that the smaller [4*n* + 2]annulenes should be able to accept a greater steric inhibition of resonance (effective bond alternation) while retaining the drive toward aromatization (and bond equalization) as a result of the greater resonance energy potentially available.

The situation is not quite so clear for the anti-aromatic [4*n*]annulenes, although it appears fairly certain that the smaller members will have a substantial negative

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* See footnote * page 3647.

† In their pioneering work on bond alternation, Longuet-Higgins and Salem[17, 36] obtained a λ value of 0·8, using a similar approach.

‡ This hypothesis is open to experimental test. If correct, the RCMA obtained from solid phase measurements would be approximately twice that determined from the solution phase nmr spectrum. (See Table 1).

§ See footnote ‡ page 3646.

resonance energy[10–12, 15, 16, 36] and will greatly prefer to exist as bond-alternate structures.[10–12, 36, *] Thus, in any comparison between [4*n*]annulenes (with all other factors equal) the more anti-aromatic must be associated with a greater degree of bond alternation (decreased resonance), a decreased ring current and a lower AC value. In this way cyclobutadiene[77] retains its primacy as an anti-aromatic annulene (in harmony with benzene's place as an aromatic annulene); the blatant anti-aromaticity of cyclobutadiene is now well documented.[10–12, 15, 16, 77, 78] Few [4*n*]annulenes (unperturbed by steric inhibition of resonance) are available for study although the AC(−) values obtained for [16]annulene and [24]annulene tend to support this point of view. The possibility remains, however, that the quenching of resonance in [16]annulene arises from non-planarity (as found in the crystal phase[68]) rather than a natural tendency toward bond alternation. Thus in contrast to the [4*n* + 2]annulenes, steric inhibition of resonance and anti-aromatic character work in concert to decrease AC values, and it will be important to distinguish between these two factors. This point is illustrated by [12]annulene in which both effects will be quite pronounced; not surprisingly the molecule gave the lowest AC value in the study.

These considerations also account for the (relative) stability of cyclooctatetraene, which is able to escape a great deal of anti-aromatic destabilization by adopting the tub structure in which the p_π orbitals of adjacent double bonds are almost perpendicular to one another.[69] This undoubtedly produces a far greater quenching of resonance than simple bond alternation could ever hope to achieve and may correspond (effectively) to an AC(−) value close to zero.

It would also be of interest to determine the value(s) of λ, k which would correspond to a classical polyene (in contradiction to the standard HMO picture of delocalization energies, it is not zero). Such values could not actually be used as a non-aromatic limit for all annulenes of course, but would provide a possible standard at large ring size, where true bond alternation is present.[17]

An aromatic criterion for π-bond orders (p_{rs}) (with certain features in common with our approach) has been put forward by Streitweiser.[18] The following inequalities were suggested: for aromatic bonds, $0{\cdot}5 < p_{rs} < 0{\cdot}7$, and for non-aromatic bonds $0{\cdot}4 > p_{rs} > 0{\cdot}8$. For an (infinite[†]) annulene the higher limits are exceeded first, and for $p_{rs} = 0{\cdot}7$; λ, $k = 0{\cdot}95$, whereas for $p_{rs} = 0{\cdot}8$; λ, $k = 0{\cdot}82$.[17, 35, ‡]

SCF MO[10–12, 79] and SC[15]/Refined[16] HMO treatments of the classical polyenes have generally led to considerably smaller values of λ, k, usually in the range 0·45–0·60.[§]

However, rather different ideas are implicit in these two contrasting approaches and the method employed in this study. It must be remembered that the standard

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[*] Calculations indicate that an even greater degree of bond alternation may be present in the small [4*n*]-annulenes than in a classical polyene. Thus bond alternation will be expected to decrease in the larger [4*n*]annulenes until the non-aromatic limit is reached. A (perfect) bond equalized [4*n*]annulene would have a degenerate ground state giving rise to infinite paramagnetism (non-zero magnetic moment). Calculations[10e] indicate that the distorted singlet will be preferred to the symmetrical triplet.

[†] The bond orders of the symmetric annulenes change only slightly with ring size (for benzene $p_{rs} = 2/3$ whereas for the [∞]annulene $p_{rs} = 2/\pi$).

[‡] The two methods lead to identical bond orders ($p_{rs}^{\lambda}(z) \equiv p_{rs}^{\kappa}(z)$), and for the purposes of this discussion we shall not further distinguish between λ and k, except where noted.

[§] Approximate comparison may be made with the SCF MO results by taking the ratio of the appropriate off-diagonal Hartree–Fock matrix elements (F_{rs}).

HMO treatment predicts that all the bonds in any annulene will have a common bond order, satisfying the rather stringent Streitweiser criterion[18] (the 1,2 bond of naphthalene would not be classified as aromatic). Furthermore, the method we use can in no way be considered self consistent, rather we use the HMO method (perturbed in the simplest possible manner) to reproduce an empirical quantity.[36]

Thus our approach has rather more in common with the "differentiation method" used by Coulson and Golebiewski[33] to obtain bond lengths from HMO theory. The interdependence of bond lengths, bond orders and resonance integrals in π-electron systems has been studied in considerable detail and a number of simple linear equations have been developed to interrelate these quantities.[37] Using the zero order bond orders (HMO with equal resonance integrals) the calculated corrections to the resonance integrals in butadiene lead to a λ value* for this classical polyene of 0·77, while the first order corrections lead to 0·70.

The actuality of bond alternation in all classical polyenes was first demonstrated by studies of the electronic spectra of linear polyenes as a function of chain length.[80] By using the open-chain analog of eq. 2 to calculate the energy levels, Salem[81] was able to reproduce the energy of the first absorption band of the α,ω-dimethyl-polyenes with a β_1/β_2 value of 0·72.

From these foregoing considerations, the most reasonable speculation would place the non-aromatic AC limit† (at large ring size and in the absence of steric inhibition of resonance), in the range 0·7 to 0·8.

B. *Intrinsic bond alternation.* There now seems little doubt that true bond alternation is the rule rather than the exception in all polyenes and is the ultimate fate of the [4n + 2]annulenes at sufficiently large ring size.[17] Nevertheless, there are a number of contrasting opinions in the literature[10–12, 17, 23, 35, 36, 70, 83] regarding the occurrence, ring size for onset, extent and interpretation of bond alternation in the annulenes.

The SC[15] and Refined[16] HMO methods which have recently been advanced both give an adequate description of aromaticity in the annulenes based on the thermodynamic/resonance energy criterion. Both predict a positive resonance energy for the [4n + 2]annulenes and a negative resonance energy for the [4n]annulenes[15, 16] (in agreement with Hückel's rule, if not with the results of standard HMO theory). By inference then, these methods suggest bond-equalization for the [4n + 2]-annulenes and bond alternation for the [4n]annulenes.

However, the most extensive and thorough-going investigation of π-electron systems has been carried out by Dewar[10–12] using an empirical SCF MO treatment based on the Pople method.[79] The initial work on the annulenes by Dewar and Gleicher[10c] has now been revised by Dewar and De Llanos,[10d] and the original predictions considerably modified.[12] The only annulenes which are still predicted to have a negative resonance energy are cyclobutadiene and cyclooctatetraene and

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* The resonance integrals obtained by this procedure do not exactly satisfy eqs. 1.5 or 2.5, nevertheless Method I is more in accord with the differentiation method than Method II (and eq. 1.5 holds more closely than eq. 2.5).

† By our definition, a non-aromatic annulene in the absence of steric inhibition of resonance is assumed to have the same degree of bond alternation (and bond lengths) as a classical polyene (neglecting end effects). A similar approach is adopted in ref 70. A classical polyene is considered to be a molecule for which only one unexcited resonance structure can be written. As has been pointed out by Dewar,[11, 12] the collective properties of such molecules may be represented as the sum of localized bond properties. It must be remembered, however, that the physical localization of electrons in bonds is merely a convenient fiction.

the ring size limit (formerly $n \leqslant 5$[10c]) for aromatic character in the $[4n + 2]$annulenes is removed.[12] Furthermore, the only annulene which is calculated to have equal bond lengths is benzene, while for all [N]annulenes (N even) with $N \geqslant 12$ total bond alternation is predicted with a bond length difference (Δr) of 0·11 Å. Thus Dewar's[12] interpretation of aromatic character in the annulenes stands in rather marked contrast to our own.

It is our thesis that bond alternation and resonance energy should form a fairly close parallel (particularly for the $[4n + 2]$annulenes), either of which could be used as a measure of aromatic character. Furthermore, the magnitude of the resonance energies involved[10–12,15,16,84] is rather small in view of the size of the molecules (less than 10 kcal mole^{-1} for $N \geqslant 10$), and could easily be swamped by steric and/or electronic interactions not explicitly included in the calculations. As to the original suggestion by Dewar and Gleicher[10c] that [26]annulene should be the first non-aromatic $[4n + 2]$annulene (on the basis of a negative resonance energy), it is by no means clear how one could test such a statement. As our results indicate, non-aromatic annulenes* may well show small ring currents (although very low temperatures may be needed for observation), and indeed [24]annulene may be just such a case. It should be stressed that the magnetic criterion does not constitute a direct experimental test for the presence or absence of resonance energy; as pointed out by Pople and Untch,[20] ring currents (if present) will always parallel the Hückel rule.

It is thus our opinion that non-aromatic bond lengths will be achieved rather gradually (although the $[4n]$annulenes will be somewhat faster in attaining this limit), and that small ring currents (and perhaps small resonance energies) will persist past this ring size but will soon be so small as to be undetectable.† As pointed out before, the extent of bond alternation (Δr) and ring size for onset in the $[4n + 2]$annulenes is still the subject of considerable controversy.[10–12,17,23,35,36,70,83]

The preceding remarks emphasize that definitions of aromaticity based on the presence of ring currents, on thermodynamic/resonance energies, or on the degree of bond alternation will be unlikely to agree on the non-aromatic ring size limit for either the $[4n]$- or the $[4n + 2]$-annulenes. Nevertheless, the AC method does appear to be in harmony with most of the current ideas and definitions of aromatic character in the annulenes.

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* See footnote † page 3651.

† For slight bond alternation the magnitude of the ring current increases with ring size. However, for the bond alternation expected at the non-aromatic limit, the ring current will die away quite rapidly with increasing ring size.

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