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DOUBLE BOND FIXATION IN NON-ALTERNANT π-ELECTRON SYSTEMS[1]

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Abstract—In some non-alternant molecules the π-electrons show a tendency to localize in certain bonds, thus reducing the symmetry of the system. A previously described criterion which is based on the diagonalization of the bond-bond polarizability matrix has been applied to a number of systems in their ground and electronically excited states, in an effort to predict for which systems such a lowering of the symmetry is to be expected. The irreducible representation to which this distortion belongs is given. The value of the criterion as an index of "aromaticity" is briefly discussed.

IN A previous paper[2] we developed a general theory of double bond fixation in conjugated hydrocarbons. The new feature of this theory was that it allows a sharp distinction to be made between first-order effects which leave the full symmetry of a molecule unaffected, and second-order bond distortions which may result in a symmetry reduction. The formalism was applied to linear, cyclic and benzenoid π-electron systems—neutral or charged—in their ground and electronically excited states.[3] In the present paper we shall examine the influence of second-order effects on bond lengths and stability of non-alternant π-electron systems.

Formalism. We assume that the total energy E_T of a π-electron system consists of two independent parts,

$$E_T = E_\sigma + E_\pi \tag{1}$$

a σ term E_σ and a π term E_π, and that a conjugated molecule may formally be constructed by a two-step process. One starts with the required number of sp^2-hybridized carbon atoms and links them together in the desired fashion. In this planar σ-bonded skeleton all C—C bond distances are taken to be equal to a common value R_0. One now proceeds to fill the system of overlapping carbon 2p orbitals with the proper number of electrons. This will distort the bond lengths by individual increments $\Delta R_{\mu\nu}$, the most favorable distortion being determined by the requirement that the total energy E_T be at a minimum. The new equilibrium bond lengths may be calculated to successive degrees of approximation from the Taylor series expansion

$$E_T = E_T(R_0) + \sum_{\mu<\nu}\left(\frac{\partial E_T}{\partial R_{\mu\nu}}\right)_{R_0}\Delta R_{\mu\nu} + \frac{1}{2}\sum_{\mu<\nu}\sum_{\chi<\lambda}\left(\frac{\partial^2 E_T}{\partial R_{\mu\nu}\partial R_{\chi\lambda}}\right)_{R_0}\Delta R_{\mu\nu}\,\Delta R_{\chi\lambda} \tag{2}$$
$$+\text{higher terms}$$

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If only the first-order terms in (2) are taken into account, differentiation yields the linear relationships

$$R_{\mu\nu}^{(1)} = A - Kp_{\mu\nu}^{(0)} \tag{3}$$

for the first-order bond lengths $R_{\mu\nu}^{(1)}$. As usual $p_{\mu\nu}^{(0)}$ is the bond order of bond μ, ν computed according to a zero-order Hückel calculation where all bonds have been assigned equal resonance integrals β. A and K are empirical parameters. Due to the linear relationships between $R_{\mu\nu}^{(1)}$ and $p_{\mu\nu}^{(0)}$, the first-order bond distortions always transform as the totally symmetric representation of the group to which the zero-order HMO-model of the molecule belongs.

Information about second-order bond fixation may be obtained by investigating the eigenvalues A_i and eigenvectors $\mathbf{D}_i$ of a matrix whose elements are the second partial derivatives of the π-electron energy with respect to the bond lengths: $(\partial^2 E\pi/\partial R_{\mu\nu}\partial R_{\kappa\lambda})$. For alternant hydrocarbons these matrix elements are given by:[2,3]

$$\left(\frac{\partial^2 E_\pi}{\partial R_{\mu\nu}\partial R_{\kappa\lambda}}\right) = 2\pi_{\mu\nu,\kappa\lambda}\beta'_{\mu\nu}\beta'_{\kappa\lambda} + 2\delta_{\mu\nu,\kappa\lambda}p_{\mu\nu}^{(0)}\beta''_{\mu\nu} \tag{4}$$

with $\pi_{\mu\nu,\kappa\lambda}$ being the bond–bond polarizabilities,

$$\beta'_{\mu\nu} = \partial\beta_{\mu\nu}/\partial R_{\mu\nu} \qquad \text{and} \qquad \beta''_{\mu\nu} = \partial^2\beta_{\mu\nu}/\partial R_{\mu\nu}^2.$$

It was shown[2] that, instead of considering A_i and $\mathbf{D}_i$, it is equally valid (for alternant hydrocarbons) to examine the eigenvalues λ_i and eigenvectors $\mathbf{d}_i$ of the bond–bond polarizability matrix $\boldsymbol{\pi} = (\pi_{\mu\nu,\kappa\lambda})$:

$$\boldsymbol{\pi}\mathbf{d}_i = \lambda_i\mathbf{d}_i \tag{5}$$

Furthermore, it turned out that the λ_i and $\mathbf{d}_i$ are not significantly altered if one calculates the bond–bond polarizabilities either from zero-order Hückel coefficients or from a Hückel matrix which is self consistent to first order in bond lengths. The most favorable second-order bond distortion is given in our treatment by the eigenvector belonging to the largest eigenvalue λ_{max}. If λ_{max} becomes greater than a critical value λ_{crit} (which we estimated to about 1·8 β^{-1}), second-order effects in the π energy overcome the σ-compression energy and the molecule will, in general, lose its original symmetry. Depending on the type of the molecule this second-order bond distortion may be of a static or dynamic nature.[3] In cases where $|\lambda_{\text{max}}| < |\lambda_{\text{crit}}|$, the molecule retains its full symmetry and second-order effects only influence the curvature of the potential-energy function.

Equation 4 was derived under the assumption that in calculating changes of the π-electron energy as a function of nuclear displacements, variations in the diagonal elements of the Hamiltonian matrix may be neglected. This is strictly true only for alternant hydrocarbons where the Coulson–Rushbrooke theorem[4] ensures uniform charge distribution regardless of the value of the off-diagonal elements, but not for non-alternant systems. If one tries to incorporate the dependence of the diagonal Hamiltonian matrix elements on bond distances in the present formalism one obtains formulas which are too complicated to be tractable in practice.* However,

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* Erratum: The numerical results quoted in Table 2 of part I (Ref. 2) for methylene cyclopropene have been computed for $\omega = +1$ (as stated in the text) instead of $\omega = -1$. The latter value would have been the correct one, the negative sign being demanded by formula (41). A revised table will be published in connection with a study of first-order bond fixation in non-alternant π systems.

in part I of this series[2] we presented arguments to show that deviations from non-uniform charge distribution have—in all probability—only a negligible influence on second-order effects. We will therefore apply eq. (4) also to the discussion of second-order bond fixation in non-alternant hydrocarbons, that is, we shall solve the eigenvalue problem

$$\|\boldsymbol{\pi} - \lambda\mathbf{1}\| = 0 \tag{6}$$

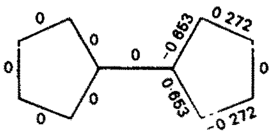
for such systems without taking into account their uneven charge distribution.

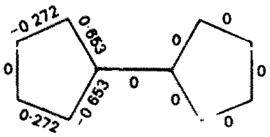
The ground and first electronically excited states of a non-alternant π system are both treated according to formula (6). In the first case the bond-bond-polarizability matrix $\boldsymbol{\pi} = (\pi_{\mu\nu,\kappa\lambda})$ is the one computed for all electrons occupying by pairs the bonding orbitals of the system under consideration. For the electronically excited state $\boldsymbol{\pi}$ is replaced by $\boldsymbol{\pi}^* = (\pi^*_{\mu\nu,\kappa\lambda})$ where the bond–bond polarizabilities $\pi^*_{\mu\nu,\kappa\lambda}$ are those for a π system where one electron has been promoted from the highest bonding to the lowest anti-bonding molecular orbital.

RESULTS

Figure 1 contains the structural formulas of the molecules for which the eigenvalues λ_i and eigenvectors $\mathbf{d}_i$ of their bond–bond polarizability matrices $\boldsymbol{\pi}$ and $\boldsymbol{\pi}^*$ were determined. Table 1 contains the λ_{max} values, representing the gain in π electron energy for the most favorable second-order distortion, and it also shows according to which irreducible representation of the symmetry group this distortion transforms.

In Fig. 2 we show the eigenvectors $\mathbf{d}_{\text{max}}$ belonging to the eigenvalue λ_{max} (i.e. the relative bond distortions) for such molecules where λ_{max} exceeds the critical value $\lambda_{\text{crit}} = 1{\cdot}8\,\beta^{-1}$. (The cases where $\lambda_{\text{max}} > 1{\cdot}5\,\beta^{-1}$ have also been included.) It should be emphasised (see 3) that the absolute sign of the eigenvectors $\mathbf{d}_{\text{max}}$ is arbitrary and that positive and negative values in Fig. 2 indicate only that the corresponding bonds distort in opposite directions. For fulvalene (XI) and heptafulvalene (XII) the most favorable type of distortion is doubly degenerate. Two orthonormal eigenvectors for the former molecule are as follows:





The λ^*_{max} and distortion types for the first electronically excited states are also given and the corresponding eigenvectors for some selected examples are also shown in Fig. 2. As mentioned before, the excited states pertain to an electron configuration in which an electron is promoted from the highest occupied HMO of the ground state to the lowest unoccupied HMO. For V, VI, XI, and XII this leads to a configuration in which a single electron or a "hole" has to occupy a degenerate pair of orbitals. These molecules will, therefore, be subject to pseudo Jahn–Teller distortions and cannot be treated by the formalism used in this paper.

Radical cations and radical anions of pentalene, heptalene, azulene, and fulvene have also been treated. The results are collected in Table II. The two types of excited states refer to the electron configurations shown in Fig. 3.

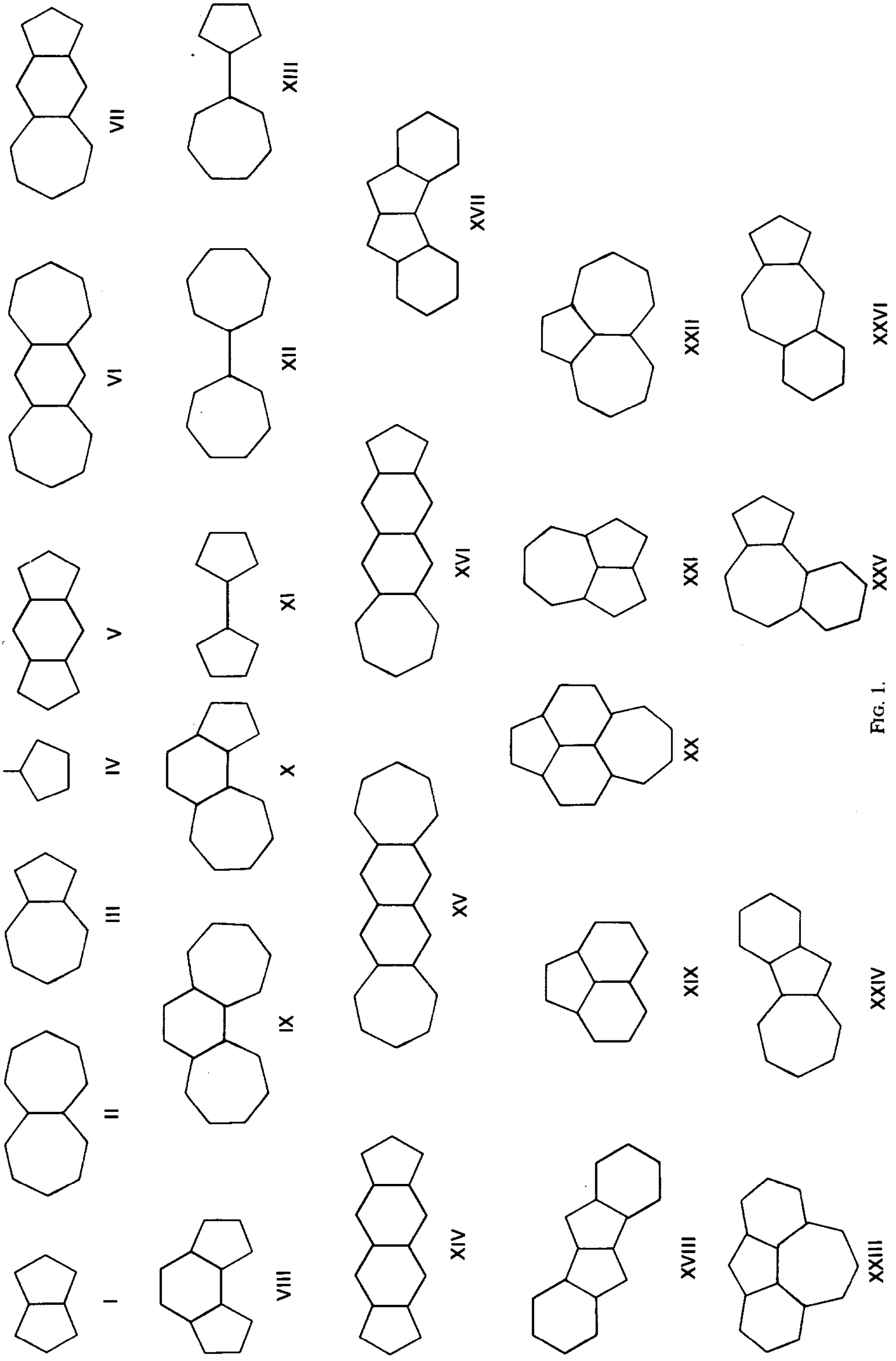
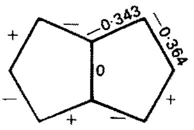

I
II
III
IV
V
VI
VII
VIII
IX
X
XI
XII
XIII
XIV
XV
XVI
XVII
XVIII
XIX
XX
XXI
XXII
XXIII
XXIV
XXV
XXVI

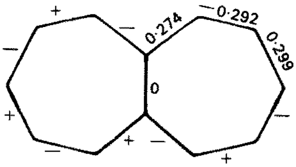
FIG. 1.

FIG. 2. Eigenvectors $\mathbf{d}_j$.
G.St. = Ground state; E.St. = Excited state; the number quoted is the corresponding λ_{max} value.

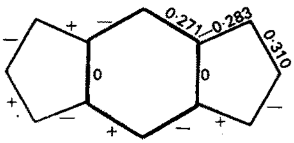
I; G.St.; 2·357



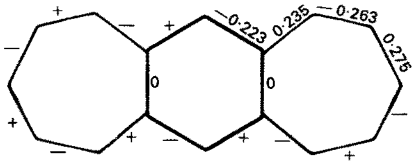
II; G.St.; 2·595; B_{1g}



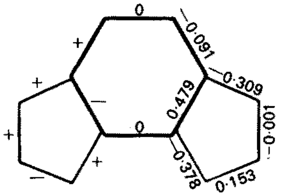
V; G.St.; 1·573; B_{1g}



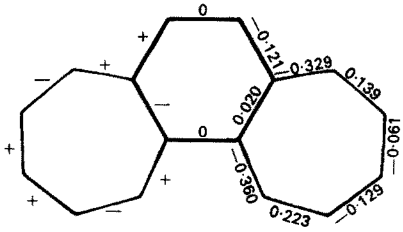
VI; G.St.; 1·750; B_{1g}



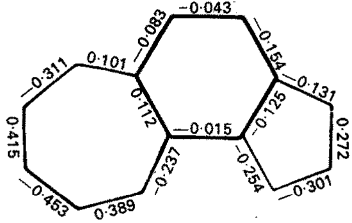
VIII; G.St.; 2·055; B_1



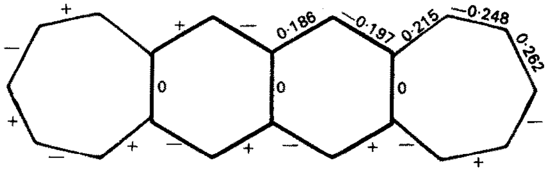
IX; G.St.; 2·824; B_1



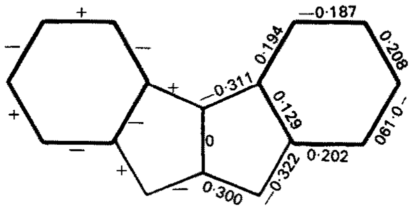
X; E.St.; 1·783; A′



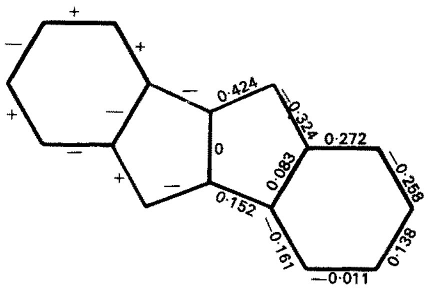
XV; G.St.; 1·525; B_{1g}

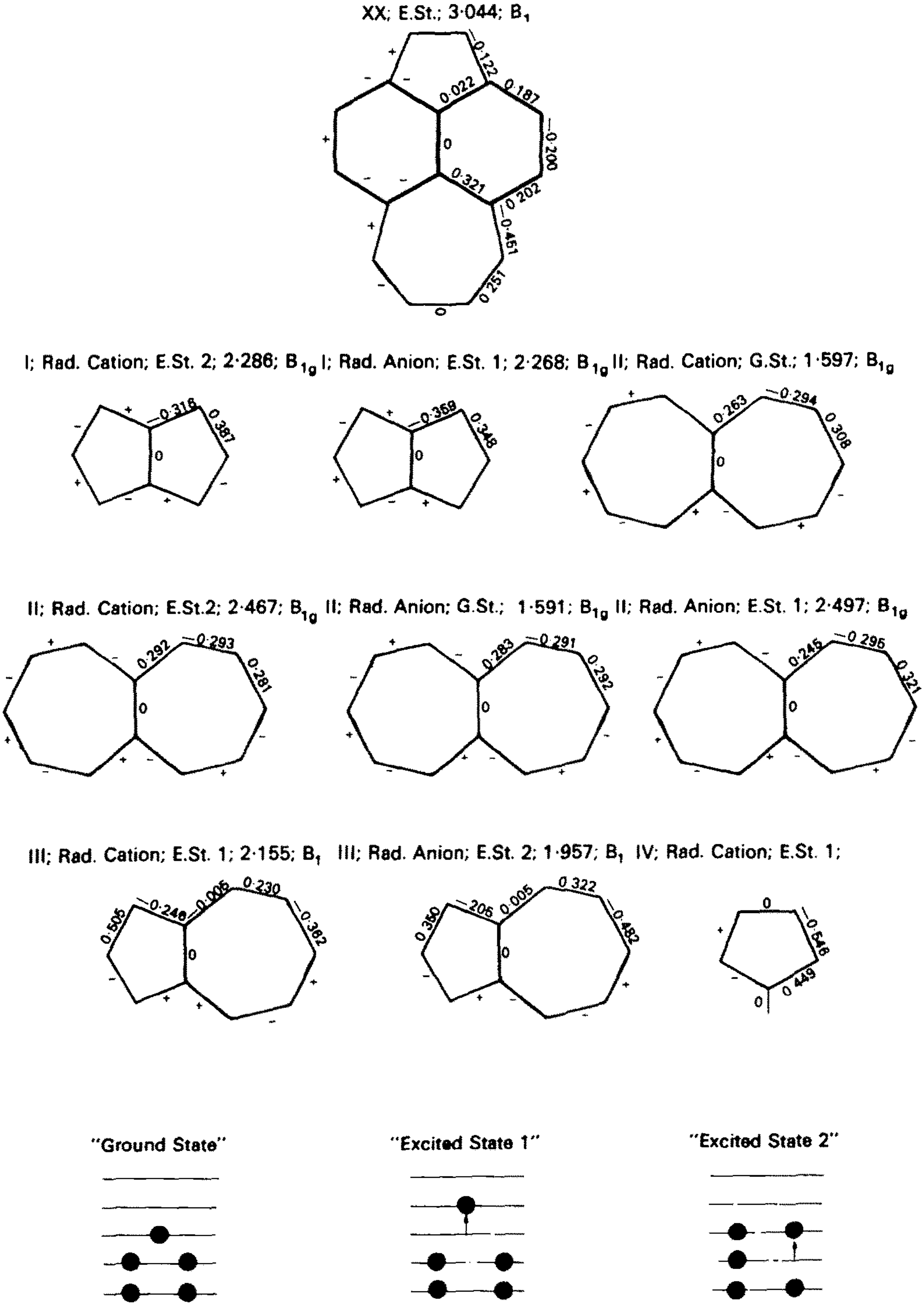


XVII; G.St.; 1·834; B_1



XVIII; E.St.; 3·392; B_u




XX; E.St.; 3·044; B_1

I; Rad. Cation; E.St. 2; 2·286; B_{1g}

I; Rad. Anion; E.St. 1; 2·268; B_{1g}

II; Rad. Cation; G.St.; 1·597; B_{1g}

II; Rad. Cation; E.St.2; 2·467; B_{1g}

II; Rad. Anion; G.St.; 1·591; B_{1g}

II; Rad. Anion; E.St. 1; 2·497; B_{1g}

III; Rad. Cation; E.St. 1; 2·155; B_1

III; Rad. Anion; E.St. 2; 1·957; B_1

IV; Rad. Cation; E.St. 1;

"Ground State"

"Excited State 1"

"Excited State 2"

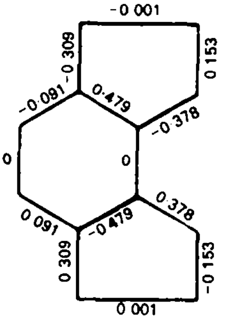
FIG. 3.

DISCUSSION

For alternant hydrocarbons second-order bond fixation becomes important only for the higher members of the series.[2,3] In contrast, inspection of Table 1 shows that second-order effects may play a dominant role already for small non-alternant systems. It is revealing that all those molecules whose λ_{max} values are close to or greater than the critical value 1·8 β^{-1}, have so far eluded preparation or are known to be unstable with respect to dimerization, polymerization, autoxydation, or thermal decomposition. Resistance towards such reactions is frequently taken as evidence for the "aromatic" character of a conjugated molecule. However, no theoretical model can convincingly predict "aromaticity" for the simple reason that this vague concept does not represent an observable. One of the more recent attempts to tackle this problem is due to Chung and Dewar,[5] who redefined the concept of "resonance energy" in the framework of an SCF model for π electron systems, which takes the coulombic interation of the π electrons explicitly into account. Both the sign and the magnitude of this quantity serve as a criterion for "aromaticity". It is postulated that the bond lengths of a conjugated system must alternate if a negative resonance energy is computed under the assumption that all bond lengths are equal. This type of analysis leads to conclusions concerning energy relationships and bond lengths in the annulene series[6] that are in excellent accord with previous results[7] (cf. also Refs. 2 and 3). On the other hand, this method yields only positive "resonance energies" for those non-alternant hydrocarbons that have been treated so far[6] and their predicted bond lengths reflect the full symmetry of these molecules. This is due to the fact that the iterative procedure used in the computation will conserve the starting symmetry of the π-system model. In contrast, the method used here shows that second-order effects—if operative—will distort the molecule in such a way that it will lose one or more elements of symmetry, in a static or dynamic sense.[2,3] We therefore believe that the tendency of the π electrons of conjugated systems to cluster in certain bonds, gauged by the largest eigenvalue λ_{max} of the bond–bond polarizability matrix, can serve as a useful criterion for "aromaticity". Also, we do not have to invoke a different explanation for "non-aromaticity" in alternant or non-alternant hydrocarbons, as the criterion rests on a common, intuitively reasonable physical phenomenon.

On the basis of this criterion, molecules characterized by λ_{max} values close to or greater than the critical value 1·8 β^{-1} are predicted not to exhibit typical "aromatic" properties. Some caution should be exercised, however, in applying this "aromaticity index" in a reverse fashion, that is, inferring aromaticity from a low value of λ_{max}. Obviously such a procedure cannot lead to valid predictions for conjugated molecules containing "loose ends", such as the linear polyenes or fulvene (IV), since an approaching reagent will find an especially favorable site for attack. It seems also doubtful whether this criterion will yield reliable information about the "aromatic" behaviour of molecules consisting of two parts held together by a formal double bond such as in XI, XII, and XIII.

In most molecules the type of second-order bond distortion transforms as a B representation and thus tends to reduce the number of symmetry elements. However, this is not a necessary consequence of second-order effects. Apart from trivial cases where the molecule has only a plane of symmetry to begin with, fulvene (IV) is one of the exceptions, in as far as second-order effects enhance the bond fixation which is already present in the ground state, due to first-order effects. Furthermore, it is not justified in general to talk of bond alternation only. There are, to be sure, cases (such as pentalene I and heptalene II) where second-order bond fixation is of such a kind as to fix the molecule in one of its Kekulé structures, albeit in a dynamic sense. But it may also happen that the eigenvector belonging to λ_{max} is of a more complicated type. Molecule VIII in its ground state may serve as a typical example:



$\lambda_{max} = 2·055$

TABLE 1. SECOND-ORDER DOUBLE BOND FIXATION IN THE GROUND AND EXCITED STATES OF THE MOLECULES LISTED IN FIG. 1

Molecule	Symmetry	Ground state		Excited state	
		λ_{max}	Type of distortion	λ^*_{max}	Type of distortion
I	D_{2h}	2·357	B_{1g}	0·929	B_{2u}
II	D_{2h}	2·595	B_{1g}	1·095	B_{2u}
III	C_{2v}	1·263	B_1	1·448	B_1
IV	C_{2v}	0·795	A_1	1·307	B_1
V	D_{2h}	1·573	B_{1g}	[a]	
VI	D_{2h}	1·750	B_{1g}	[a]	
VII	C_{2v}	1·344	B_1	1·125	B_1
VIII	C_{2v}	2·055	B_1	0·991	B_1
XI	C_{2v}	2·824	B_1	1·175	B_1
X	C_s	1·097	A′	1·783	A′
XI	D_{2h}	1·102	[b]	[a]	
XII	D_{2h}	1·216	[b]	[a]	
XIII	C_{2v}	0·964	A_1	(9·355)[c]	
XIV	D_{2h}	1·381	B_{1g}	1·337	B_{2u}
XV	D_{2h}	1·525	B_{1g}	1·497	B_{2u}
XVI	C_{2v}	1·357	B_1	1·084	B_1
XVII	C_{2v}	1·834	B_1	0·923	A_1
XVIII	C_{2h}	1·010	A_g	3·392	B_u
XIX	C_{2v}	0·957	B_1	1·395	B_1
XX	C_{2v}	1·168	A_1	3·044	B_1
XXI	C_{2v}	1·135	B_1	1·122	B_1
XXII	C_{2v}	1·385	B_1	1·007	B_1
XXIII	C_{2v}	1·222	B_1	0·969	B_1
XXIV	C_s	1·208	A′	1·267	A′
XXV	C_s	1·184	A′	1·458	A′
XXVI	C_s	1·197	A′	1·080	A′

[a] Polarizabilities are not defined because of degeneracy.

[b] λ_{max} is doubly degenerate; cf. text.

[c] Extreme value due to near degeneracy in the basis molecular orbitals.

Table 1 shows that those molecules which are characterized by a high tendency to localize the π electrons in certain bonds in the ground state lose this property in their first excited state. On the other hand, there are cases where a molecule has a relatively low λ_{max} value in the ground state but a high one in the excited state. The type of distortion may be in both states of the same or of a different kind. The localization tendency shown by neutral pentalene (I) and heptalene (II) in the ground state is diminished in the corresponding radical cations and radical anions (Table 1).

TABLE 2. SECOND-ORDER DOUBLE BOND FIXATION IN THE RADICAL CATIONS AND RADICAL ANIONS OF PENTALENE, HEPTALENE, AZULENE AND FULVENE

Molecule	Symmetry	Ground state		Excited state 1*		Excited state 2*	
		λ_{max}	Type of distortion	λ^*_{max}	Type of distortion	λ^*_{max}	Type of distortion
				Radical cations			
I	D_{2h}	1·358	B_{1g}	1·312	B_{2u}	2·286	B_{1g}
II	D_{2h}	1·597	B_{1g}	1·095	B_{2u}	2·467	B_{1g}
III	C_{2v}	1·148	B_1	1·928	B_1	1·057	B_1
IV	C_{2v}	1·227	B_1	2·155	B_1	0·540	A_1
				Radical anions			
I	D_{2h}	1·358	B_{1g}	2·267	B_{1g}	0·929	B_{2u}
II	D_{2h}	1·591	B_{1g}	2·497	B_{1g}	1·419	B_{2u}
III	C_{2v}	1·223	B_1	1·026	B_1	1·957	B_1
IV	C_{2v}	0·575	A_1	1·389	B_1	1·402	B_1

* cf. Fig. 3.

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[1] This is part III of a series of papers on double bond fixation in conjugated hydrocarbons. Part I: Ref. 2; part II: Ref. 3.

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