BOND DISTORTIONS IN NONALTERNANT HYDROCARBONS

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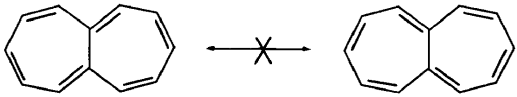
ABSTRACT

Using the semi-empirical LCAO SCF MO theory in conjunction with the variable bond-length technique, a general method is given for predicting the energetically most favourable molecular symmetries and geometrical structures (that is, interatomic distances) of conjugated hydrocarbons. The method is applied to the nonalternant hydrocarbons composed of odd-membered rings and some of their charged radicals and dianions. A symmetry rule for predicting stable molecular shapes, which is based on the pseudo-Jahn–Teller effect, is also applied to these molecules. Both the methods agree in showing that bond alternation is a rather common phenomenon in these molecules. Furthermore, using the most stable geometrical structures obtained, the magnetic susceptibilities and electronic spectra of these molecules are calculated. The results are in good agreement with the available experimental data.

INTRODUCTION

The prediction of the geometrical structures, that is, of the C—C bond distances of conjugated hydrocarbons has long been one of the major problems in π-electron theories. For benzenoid hydrocarbons, it has been recognized that the molecular symmetry for the ground state is always that suggested by the superposition with equal weight of the equivalent Kekulé-type resonance structures, and the bond orders calculated using valence-bond or molecular orbital methods assuming the full molecular-symmetry yield the theoretical C—C bond lengths which are in good agreement with experimental values.

On the other hand, it was somewhat amazing to discover that the ground states of certain nonalternant hydrocarbons should not adopt the fully-symmetrical nuclear arrangement expected on the basis of the conventional resonance theory, but rather a less symmetrical configuration in which the nuclei have been displaced to a certain degree[1]. For example, it was noticed[2–4] that heptalene does not show an energy minimum for the D_{2h} symmetry suggested by the superposition of the two Kekulé-type resonance structures, but has a lower energy if it adopts an unsymmetrical nuclear arrangement that corresponds to either of the resonance structures and exhibits a strong bond alternation of a C_{2h} type in its periphery. The resonance between the two Kekulé-type structures in this molecule should substantially be impeded:



The available experimental information[5] agrees with this in indicating that the π-electrons in this molecule are strongly localized in 'double' bonds, rather than uniformly delocalized over the entire molecule.

A theoretical explanation for such anomalous phenomena has been given, in the case of pentalene, by the pioneer work of den Boer-Veenendaal and den Boer[6], followed by several authors[2–4, 7] for certain other related non-alternant hydrocarbons. By making allowance for the effects of σ-bond compression, these authors have succeeded in predicting that an unsymmetrical configuration resembling either of the two Kekulé-type structures is actually energetically favoured as compared with the fully symmetrical one.

In all these treatments, however, it has tacitly been assumed that bond alternation corresponding to one of the Kekulé-type structures is the energetically most favourable bond distortion in a conjugated molecule. Even if this be so with the ground states of simple neutral conjugated molecules, it is obvious that such a presumption cannot be extended to large polycyclic conjugated molecules in which possible Kekulé-type structures are not always equivalent or charged radicals of conjugated molecules.

It would thus be highly desirable to reexamine the theory of double-bond fixation, taking into account all the possible types of bond distortion.

Recently, Binsch *et al.*[8–12] have made, along this line, a reexamination of the theory of bond fixation in conjugated molecules. Their scheme is based on second-order perturbation theory and allows a sharp distinction to be made between the first-order bond fixation from which the bond order–bond length relationship may be derived, but which leaves the full molecular-symmetry unaffected and the second-order bond fixation which may result in a symmetry reduction. Information about second-order bond fixation is obtained by examining the eigenvalues and eigenvectors of the bond–bond polarizability matrix. The most favourable second-order bond distortion is given by the eigenvector belonging to the largest eigenvalue. If this value becomes larger than a certain critical value, second-order effects in the π-electron energy overcome the σ-bond compression energy, and the molecule will, in general, lose its original full molecular-symmetry.

On the basis of this theory, Binsch *et al.* have examined the second-order effects on bond lengths and stability of nonalternant π-electron systems and proposed a new aromaticity criterion that is entirely based on double-bond fixation.

The theory of Binsch *et al.*, however, only gives the type of the second-order bond fixation, i.e. the normalized components of the displacement coordinate corresponding to the energetically most favourable distortion and does not provide information about actual magnitude of the distortion or equilibrium bond distances at which the nuclei of the real molecule will settle.

The aim of this contribution is threefold. First, on the basis of a semi-empirical SCF MO method, we propose a general method of predicting the energetically most favourable geometrical structures, that is, equilibrium

bond distances of conjugated hydrocarbons, and the method is applied to nonalternant hydrocarbons and some of their charged radicals and dianions. Secondly, a symmetry rule for predicting stable molecular shapes[13–15], the usefulness of which has recently been appreciated by Pearson[13], will be applied to these molecules. This rule is based on the second-order perturbation theory, as is the case with the theory of Binsch *et al.*, but it provides a more intelligible way of predicting the energetically most favourable bond distortions in conjugated molecules. Finally, the diamagnetic susceptibilities and electronic spectra, the quantities which depend sensitively upon geometrical structure, are calculated using the bond distances obtained on the basis of the SCF MO method, and the results are compared with available experimental data.

SCF–MO CALCULATIONS OF BOND FIXATIONS

Method of calculation[16, 17]

The method of calculation used for finding the energetically most favourable set of C—C bond distances is the SCF–MO formalism of the Pariser–Parr–Pople method[18, 19] together with the variable bond-length technique[20]. The C—C bond lengths and, consequently, the resonance and Coulomb repulsion integrals are allowed to vary with bond orders at each iteration until self-consistency is reached. Bond lengths r are correlated with bond orders p by the aid of the formula[4]

$$r(\text{Å}) = 1.520 - 0.186p \tag{1}$$

The Coulomb repulsion integrals are calculated using the Mataga–Nishimoto formula[21]. The resonance integral is assumed to be of the form $\beta = B\exp(-ar)$, the value of a being taken as 1.7 Å^{-1} [22].

As starting geometries for iterative calculation, we adopt all the possible distorted structures in which bond lengths are distorted, so that the set of displacement vectors may form a basis for an irreducible representation of the full symmetry group of a molecule. With pentalene, I, for example, there are 3, 2, 2 and 2 distinct bond distortions belonging respectively to a_g, b_{3g}, b_{2u} and b_{1u} representations of the point group D_{2h}. Further, if a certain distorted structure and its countertype in which the bond-length variation is reversed are not equivalent, these two structures should be differentiated as a starting geometry. If self-consistency is achieved at two or more different nuclear arrangements, the total energies should be compared with each other in order to determine which one is energetically most favourable. The total energy of a conjugated molecule is assumed to be the sum of the π-electron energy and the σ-core energy which may be regarded as the sum of the independent contributions from the C—C σ-bonds. Further, for the reduced distance variation of interest the individual contributions of the σ-bonds may safely be approximated by a quadratic function of the bond-distance variation

$$E_\sigma = \sum_{\mu<\nu} \tfrac{1}{2}k\,\Delta\, r_{\mu\nu}^2 \tag{2}$$

where k is the force constant for an sp^2 hybridized C—C σ-bond. The value

of k adopted for use in the present calculations is 714 kcal mole^{-1} A^{-2} [3].

In order to discuss the geometry of electronically excited states we use the same procedure as used for the ground state except for the employment[23] of a different value, 3.3 Å^{-1}, of a. This value of a was determined so that the predicted energy of the fluorescence from the lowest singlet excited state ($^1B_{2u}$) in benzene may fit the experimental value[24].

Results and discussion

Neutral nonalternant hydrocarbons

The symmetry groups and the bond lengths for the energetically most favourable nuclear arrangements of nonalternant hydrocarbons examined (*Figure 1*) are listed in *Table 1*.

It should be noted that in cata-condensed hydrocarbons, I–XIII, except IV, VI, X and XI, two different self-consistent nuclear arrangements, one belonging to the full symmetry group of the molecule and the other belonging to a reduced symmetry group, were obtained. In pentalene, I, for example, starting bond distortions, belonging to a_g, b_{2u}, and b_{1u} representations, all converge into the unique self-consistent set of bond lengths belonging to the point group D_{2h}, and those belonging to b_{3g} converge into another set of bond lengths belonging to the point group C_{2h}. In such a case, the nuclear arrangement belonging to the lower-symmetry group should, in principle, be energetically favoured as compared with that belonging to the full symmetry group. The stabilization energies which favour the lower-symmetry nuclear arrangement for I, II, III, V, VII, VIII, IX, XII and XIII are calculated to be 8.4, 0.6, 2.4, 7.2, 12.1, 5.3, 5.9, 2.5 and 6.6 kcal mole^{-1}, respectively. All these molecules exhibit to a greater or lesser degree a marked double-bond fixation, the extent of which may be estimated from the stabilization energy; in the fully-symmetrical nuclear configurations of these molecules the bond lengths of the peripheral C—C bonds are nearly equalized.

In cata-condensed nonalternant hydrocarbons, IV, VI, X and XI, peri-condensed nonalternant hydrocarbons, XIV–XVIII, fulvenes, XIX and XX, and fulvalenes, XXI–XXIV, on the other hand, self-consistency was achieved only for the symmetrical nuclear arrangements belonging to the full symmetry group of the molecule. All these molecules, except azulene, XI, also show more or less a pronounced double-bond fixation, but retain the initial symmetry groups unchanged.

Of the cata-condensed nonalternant hydrocarbons examined, pentalene, I, and heptalene, VII, show a remarkable double-bond fixation. In both these cases there exists a strong bond-length alternation in the periphery of the molecule. This prediction is in agreement with the previous theoretical investigations[2–4,6] and available experimental facts[5].

The *s*-indacene, III, recently prepared by Hafner and his group[25], and its 7-membered analogue, IX, are predicted to adopt a skew structure with a moderate double-bond fixation. As for III, this conclusion is in good agreement with the result previously obtained by a different method[7] and with experimental information. It is interesting to note that molecule XIII, whose perimeter is composed of $4n + 2$ carbon atoms, shows double-bond fixation to a greater extent than III or IX, the perimeter of which is composed of $4n$ carbon atoms.

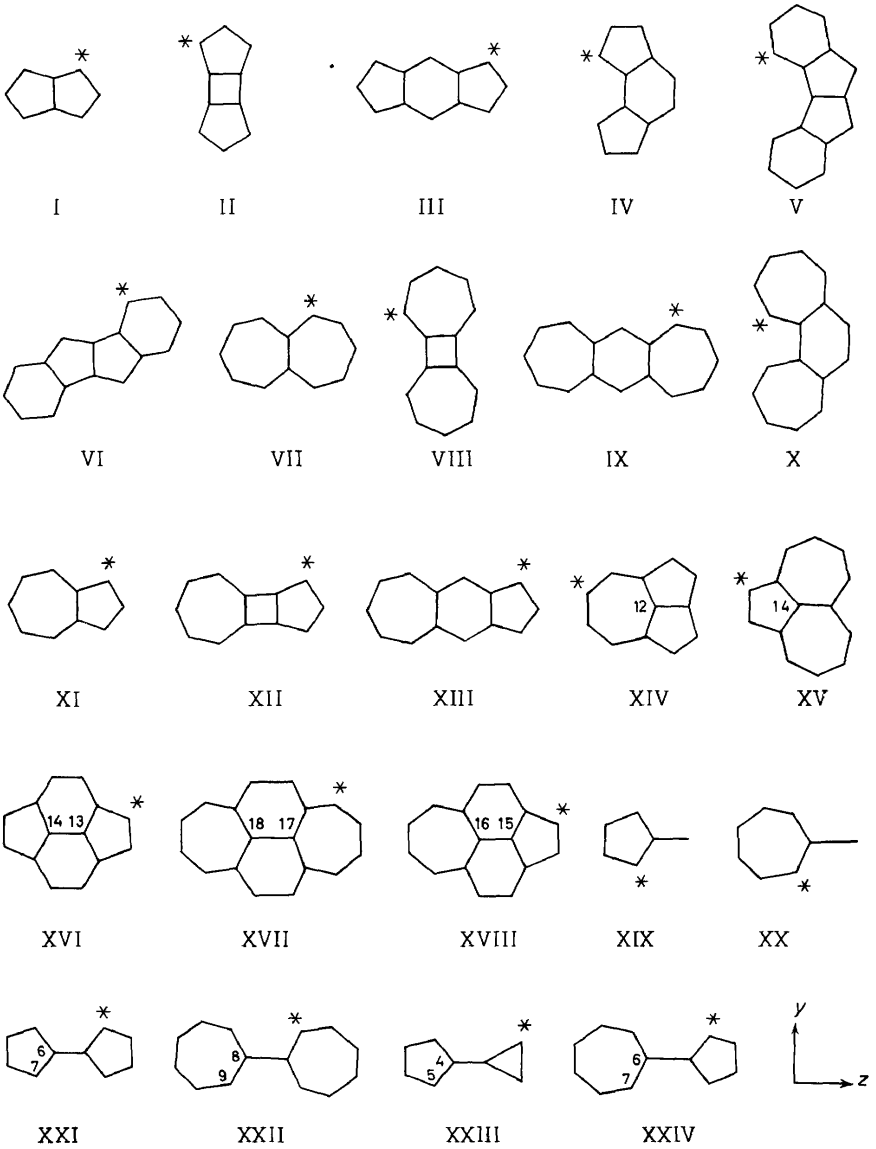


Figure 1. Numbering of atoms and choice of axes in nonalternant hydrocarbons. Carbon atoms are numbered consecutively, starting with the starred atom and proceeding in a clockwise fashion along the periphery. For VI the z axis is taken to be perpendicular to the molecular plane.

Table 1. Predicted and experimental (in italics) bond lengths of nonalternant hydrocarbons.

Molecule	Bond	Bond length (Å)
I (C_{2h})	1–2	1.356
	1–8	1.469
	2–3	1.450
	3–4	1.370
	4–8	1.446
II (C_{2v})	1–2	1.383
	1–10	1.419
	2–3	1.420
	3–4	1.381
	4–5	1.431
	4–10	1.488
	9–10	1.391
III (C_{2h})	1–2	1.372
	1–12	1.447
	2–3	1.424
	3–4	1.392
	4–5	1.435
	4–12	1.444
	11–12	1.381
IV (C_{2v})	1–2	1.449
	1–12	1.371
	2–3	1.357
	3–4	1.463
	4–5	1.368
	4–12	1.454
	5–6	1.442
	11–12	1.458
V (C_s)	1–2	1.366
	1–16	1.440
	2–3	1.437
	3–4	1.364
	4–5	1.446
	5–6	1.375
	5–16	1.449
	6–7	1.459
	7–8	1.376
	7–15	1.439
	8–9	1.451
	9–10	1.404
	9–14	1.413
	10–11	1.396
	11–12	1.398
	12–13	1.397
	13–14	1.400
	14–15	1.462
	15–16	1.390
VI (C_{2h})	1–2	1.397
	1–16	1.399
	2–3	1.397
	3–4	1.396
	4–5	1.402
	5–6	1.457
	5–16	1.409
	6–7	1.364
VI (C_{2h})	7–15	1.455
	15–16	1.467
VII (C_{2h})	1–2	1.357
	1–12	1.460
	2–3	1.450
	3–4	1.362
	4–5	1.445
	5–6	1.371
	6–12	1.453
VIII (C_{2v})	1–2	1.367
	1–14	1.442
	2–3	1.440
	3–4	1.366
	4–5	1.442
	5–6	1.366
	6–7	1.460
	6–14	1.471
	13–14	1.381
IX (C_{2h})	1–2	1.364
	1–16	1.452
	2–3	1.439
	3–4	1.371
	4–5	1.430
	5–6	1.385
	6–7	1.440
	6–16	1.449
	15–16	1.375
X (C_{2v})	1–2	1.443
	1–16	1.376
	2–3	1.363
	3–4	1.449
	4–5	1.358
	5–6	1.457
	6–7	1.357
	6–16	1.450
	7–8	1.432
	15–16	1.451
XI (C_{2v})	1–2	1.398, *1.391*[a]
	1–10	1.405, *1.413*
	4–5	1.406, *1.383*
	4–10	1.469, *1.483*
	5–6	1.398, *1.401*
	6–7	1.400, *1.385*
XII (C_s)	1–2	1.374
	1–12	1.434
	2–3	1.426
	3–4	1.380
	4–12	1.448
	5–6	1.381
	5–11	1.446
	6–7	1.427
	7–8	1.376
	8–9	1.429

Table 1 (continued)

Molecule	Bond	Bond length (Å)	Molecule	Bond	Bondlength (Å)
XII (C_s)	9–10	1.374	XVII (D_{2h})	5–17	1.427
	10–11	1.435		6–7	1.410
	11–12	1.404		17–18	1.413
XIII(C_s)	1–2	1.371	XVIII(C_{2v})	1–2	1.362
	1–14	1.441		2–3	1.446
	2–3	1.428		3–4	1.397
	3–4	1.382		3–15	1.428
	4–5	1.435		4–5	1.402
	4–14	1.462		5–6	1.397
	5–6	1.376		6–7	1.446
	6–7	1.443		6–16	1.428
	6–12	1.460		7–8	1.364
	7–8	1.369		8–9	1.440
	8–9	1.434		15–16	1.412
	9–10	1.373	XIX(C_{2v})	1–2	1.356
	10–11	1.429		1–5	1.462
	11–12	1.382		2–3	1.449
	12–13	1.436		5–6	1.353
	13–14	1.376	XX(C_{2v})	1–2	1.357
XIV(C_{2v})	1–2	1.404, *1.406*[b]		1–7	1.461
	1–11	1.397, *1.394*		2–3	1.449
	2–3	1.397, *1.386*		3–4	1.360
	3–4	1.435, *1.426*		7–8	1.355
	3–12	1.445, *1.421*	XXI(D_{2h})	1–2	1.356
	4–5	1.371, *1.359*		1–5	1.460
	5–6	1.437, *1.423*		2–3	1.455
	6–12	1.395, *1.378*		5–6	1.372
XV(C_{2v})	1–2	1.399, *1.412*[c], *1.396*[d]	XXII(D_{2h})	1–2	1.359
	1–13	1.400, *1.393*, *1.393*		1–7	1.454
	2–3	1.433, *1.437*, *1.436*		2–3	1.450
	2–14	1.442, *1.472*, *1.470*		3–4	1.360
	3–4	1.374, *1.380*, *1.358*		7–8	1.379
	4–5	1.429, *1.434*, *1.418*	XXIII(C_{2v})	1–2	1.326[e], *1.31*[f], *1.34*[g]
	5–6	1.373, *1.367*, *1.368*		2–3	1.412, *1.39*, *1.41*
	6–7	1.435, *1.446*, *1.446*		3–4	1.373, *1.37*, *1.36*
	7–14	1.400, *1.429*, *1.399*		4–5	1.444, *1.44*, *1.46*
XVI(D_{2h})	1–2	1.353		5–6	1.367, *1.36*, *1.33*
	2–3	1.462		6–7	1.443, *1.46*, *1.45*
	3–4	1.387	XXIV(C_{2v})	1–2	1.365
	3–13	1.426		1–5	1.446
	4–5	1.412		2–3	1.438
	13–14	1.414		5–6	1.387
XVII(D_{2h})	1–2	1.357		6–7	1.445
	2–3	1.452		7–8	1.366
	4–5	1.457		8–9	1.438
	5–6	1.390		9–10	1.367

[a] X-ray bond lengths; J. M. Robertson, M. M. Shearer, G. A. Sim and D. G. Watson. *Acta Cryst.* **15**, 1 (1962).
[b] X-ray bond lengths of a dimethylphenyl derivative; H. J. Linder. Personal communication (1970).
[c] X-ray bond lengths of a tetramethyl derivative; E. Carstensen–Oeser and G. Habermehl. *Angew. Chem.* **80**, 564 (1968).
[d] X-ray bond length of a tetramethyl derivative; R. Quasba, F. Brandl, W. Hoppe and R. Huber. *Acta Cryst.* **B25**, 1198 (1969).
[e] For the bonds associated with the 3-membered ring a different bond order–bond length relationship was used; ref. 22.
[f] X-ray bond lengths of a tetrachlorodi-*n*-propylcalicene; H. Shimanouchi, T. Ashida, Y. Sasada, M. Kakudo, I. Murata and Y. Kitahara. *Tetrahedron Letters*, 61 (1967).
[g] X-ray bond lengths of a tetrachlorodiphenylcalicene; O. Kennard, D. G. Watson, J. K. Facocett, K. A. Kerr and C. Romers. *Tetrahedron Letters*, 3885 (1967).

The so-called 'bowtiene', II, whose perimeter is composed of ten carbon atoms, suffers the symmetry reduction, $D_{2h} \rightarrow C_{2v}$, accompanied by a very weak double-bond fixation. The double-bond fixation in this molecule is of approximately the same order of magnitude as in naphthalene; and the molecule, therefore, provides an example in which from the viewpoint of double-bond fixation a clear-cut distinction between aromatic and nonaromatic cannot be made. On the other hand, the 7-membered analogue of bowtiene, VIII, exhibits an enhanced unsymmetrical double-bond fixation and this molecule should be nonaromatic.

Of particular interest is dibenzopentalene, V, which suffers a strong unsymmetrical bond distortion. In one of the 6-membered rings of this molecule, bond lengths are smoothed out as in benzene, while in the other ring a strong double-bond fixation exists. On the other hand, in its isomer, VI, the two 6-membered rings are equivalent and in both the rings bond lengths are almost equalized. Strong double-bond fixations are localized in the butadiene-like skeleton of the pentalene segment of this molecule. It is therefore expected that this molecule should undergo addition reactions in this region. This is in accordance with experimental facts[26].

Both *as*-indacene, IV, and its 7-membered analogue, X, show a strong double-bond fixation without suffering symmetry reduction. In these molecules, two different self-consistent geometries corresponding, respectively to two Kekulé-type structures which are not equivalent are obtained. The differences in total energies between the two equilibrium structures for IV and X are calculated to be 4.3 and 3.0 kcal mole^{-1}, respectively. Molecules IV and X should be considered to be composed, so to speak, of two pentafulvene segments and of two heptafulvene segments, respectively.

Other molecules worth mentioning are peri-condensed nonalternant hydrocarbons XIV–XVIII. As for XIV and XV, it should be noted that bond lengths of the peripheral bonds belonging to the 7-membered ring of XIV and those of the peripheral bonds belonging to the 5-membered ring of XV are all predicted to be 1.4 Å. In both the molecules, there is a pronounced double-bond fixation in the remainder of the periphery. Derivatives of XIV and XV have been prepared by Hafner *et al.*[27], and experimental facts concerning addition reactions[27, 28] support these results. In molecules XVI–XVIII bond lengths of the naphthalene core are almost the same as those of the free naphthalene molecule and there are pronounced double-bond fixations in the remainder of the periphery. The most stable nuclear arrangement in XVI corresponds to the aromatic model proposed by Lo and Whitehead[29]. Molecules XVI and XVIII have been synthesized by Trost and Bright[30] and by Boekelheide and Vick[31], respectively. The above theoretical results are in good qualitative agreement with available experimental facts.

Experimental C—C bond lengths, if available, are listed also in *Table 1*. Theoretical values are in general agreement with experimental data.

Cation and anion radicals of fulvalenes

Recently the cation and anion radicals of heptafulvalene, XXII, have been prepared and their e.s.r. spectra have been investigated by Sevilla *et al.*[32]. The hyperfine spectrum of the cation radical is consistent with three sets of four protons, which indicates that the unpaired electron is delocalized

throughout the molecule. On the other hand, the low-temperature spectrum of the anion radical is consistent with two groups of two protons. Comparison of these splittings with those of the higher-temperature spectra reveals that the unpaired spin in the radical anion is essentially localized on one of the rings, and, therefore, that the molecular symmetry group of the anion radical should be lower than D_{2h}.

In order to explain the origin of the sharp contrast between the spin density distribution of the cation and anion radicals of XXII, we now examine the symmetry groups and geometrical structures of these radicals, using the open-shell SCF formalism[33] of the Pariser–Parr–Pople method in conjunction with the variable bond-length technique[34].

In the anion radical of XXII, the starting bond distortions, belonging to a_g, b_{3g} and b_{2u} irreducible representations of the point group D_{2h}, all converge into the unique self-consistent set of bond lengths corresponding to the symmetry group D_{2h}, and distortions belonging to b_{1u} converge into another set of bond lengths corresponding to the point group C_{2v}. The stabilization energy which favours the lower-symmetry nuclear arrangement is predicted to be 9.4 kcal mole^{-1}.

Table 2. Bond lengths, spin densities, ρ, and proton hyperfine splittings, $|a^H|$, of cation and anion radicals of fulvalenes

Radical	Bond	Bond length (Å)	Atom	ρ	$\lvert a^H\rvert$(G) Theor.	$\lvert a^H\rvert$(G) Exp.[a]
XXI$^+$(C_{2v})	1–2	1.416	1	0.379	9.85	
	1–5	1.441	2	0.120	3.12	
	2–3	1.396	5	0		
	5–6	1.388	6	0		
	6–10	1.461	9	0.000		
	8–9	1.477	10	0.000		
	9–10	1.353				
XXI$^-$(D_{2h})	1–2	1.378	1	0.065	1.69	
	1–5	1.429	2	0.097	2.52	
	2–3	1.428	5	0.186		
	5–6	1.421				
XXII$^+$(D_{2h})	1–2	1.379	1	0.043	1.10	0.075
	1–7	1.427	2	0.082	2.13	2.90
	2–3	1.426	3	0.059	1.53	1.72
	3–4	1.380	7	0.133		
	7–8	1.422				
XXII$^-$(C_{2v})	1–2	1.400	1	0.275	7.15	8.22
	1–7	1.437	2	0.040	1.04	
	2–3	1.399	3	0.189	4.91	5.02
	3–4	1.422	7	0		
	7–8	1.396	8	0		
	8–14	1.499	12	0.000		
	11–12	1.354	13	0.000		
	12–13	1.426	14	0.000		
	13–14	1.360				

[a] Reference 32.

The predicted bond lengths for the C_{2v} nuclear arrangement of the anion radical of XXII listed in *Table 2* indicate that in one of the rings of this radical there exists a marked double-bond fixation to the same extent as in neutral heptafulvalene, while in the other ring bond lengths are nearly equalized. The spin density distribution also presented in *Table 2* indicates that the unpaired electron is localized essentially on the latter ring†. It should be added, however, that the negative charge is not localized on this ring alone; the charge density on this ring is -0.613 and that on the other ring is -0.387.

The cation radical XXII, on the other hand, suffers no symmetry reduction. Both the rings show a moderate double-bond fixation, and the unpaired spin is delocalized throughout the molecule (*Table 2*).

The hyperfine splittings, a^{H}, of the cation and anion radicals of XXII, calculated using McConell's relationship[35] with $|Q| = 26$ G, are listed and compared with experimental values in *Table 2*. Theoretical values are in fairly good agreement with experimental data.

Table 3. Bond lengths of dianions of nonalternant hydrocarbons

Dianion	Bond	Bond length (Å)	Dianion	Bond	Bond length (Å)
$I^{2-}(D_{2h})$	1–2	1.400	$IV^{2-}(C_{2v})$	1–2	1.401
	1–8	1.423		1–12	1.406
	4–8	1.416		2–3	1.398
$III^{2-}(D_{2h})$	1–2	1.397		3–4	1.414
	1–12	1.421		4–5	1.437
	4–12	1.432		4–12	1.416
	11–12	1.408		5–6	1.370
				11–12	1.447
			$VII^{2-}(D_{2h})$	1–2	1.415
				1–12	1.399
				2–3	1.404
				6–12	1.504

Further, we have examined the geometrical structures and spin densities of cation and anion radicals of pentafulvalene, XXI. In these radicals, the situation turned out to be quite reversed. Removal of an electron from the neutral molecule to produce the cation radical results in a symmetry reduction, the stabilization energy being calculated to be 17.8 kcal mole^{-1}, while addition of an electron to form the anion radical leaves the molecular symmetry unaffected. Inspection of *Table 2* shows that in the cation radical of XXI there exists a marked double-bond fixation in one of the rings, while

† In the HMO approximation, heptafulvalene has a degenerate pair of lowest vacant orbitals which have coefficients on one ring and zero coefficients on the other. The odd electron of the heptafulvalene anion may be placed in either of these orbitals[32]. Alternatively, we can use proper linear combinations of these orbitals and place the odd electron in either of a pair of the degenerate orbitals which have coefficients throughout the molecule. There is no reason to prefer the wavefunctions localized on one of the rings to those delocalized over the entire molecule. In the SCF approximation, the accidental degeneracy is lifted and the wavefunctions delocalized throughout the molecule are obtained.

bond lengths are nearly equalized in the other ring, on which the unpaired spin is localized. On the other hand, in the anion radical of XXI, there is a moderate double-bond fixation in both the rings, and the unpaired electron is delocalized over the entire molecule.

Dianions of nonalternant hydrocarbons

The dianions of pentalene, I, *s*-indacene, III, *as*-indacene, IV, and heptalene, VII, were examined. It turned out that in I, III and VII addition of two more electrons to the neutral molecule to form the dianion results in a complete disappearance of unsymmetrical bond distortions, and in all the dianions examined the bond lengths of the peripheral C—C bonds are nearly equalized (*Table 3*). Dianions of I, III and IV have been prepared[36–38] and are known to be stable species.

THE SYMMETRY RULE FOR PREDICTING BOND DISTORTIONS

Theory

Recently, a symmetry rule for predicting the stable molecular shapes has been developed[13–15] and applied mainly to inorganic compounds. The basis of this rule is the second-order, or pseudo, Jahn–Teller effect and follows from the earlier work by Bader[39]. We now consider the application of this rule to the prediction of the energetically most favourable bond distortions in conjugated hydrocarbons[40].

We start by assuming the fully-symmetrical nuclear arrangement as an unperturbed nuclear configuration for a conjugated molecule. The unperturbed electronic wavefunctions $\psi_0, \psi_1, \ldots, \psi_k, \ldots$ and the corresponding eigenvalues $E_0, E_1, \ldots, E_k, \ldots$ are assumed to be known. We now distort the nuclei from the original symmetrical arrangement by means of the *i*th normal coordinate of nuclear motion, Q_i. By the use of the second-order perturbation theory, the energy of the ground state after deformation may be written:

$$E(Q_i) = E_0 + \langle\psi_0|\partial H/\partial Q_i|\psi_0\rangle Q_i + \tfrac{1}{2}\{\langle\psi_0|\partial^2 H/\partial Q_i^2|\psi_0\rangle - 2\sum_k{}'|\langle\psi_k|\partial H/\partial Q_i|\psi_0\rangle|^2/(E_k - E_0)\}Q_i^2 \qquad (3)$$

If the original ground-state wavefunction, ψ_0, is nondegenerate, as it is with the nonalternant hydrocarbons concerned in this paper (since the full symmetry groups of these molecules are D_{2h}, C_{2v} or C_{2h}, which have no degenerate representation), then the second term in equation 3 is nonzero only for totally-symmetric nuclear displacements. It has been shown by Binsch *et al.*[8,9] that by equating this term to zero, the usual relationship between bond order and bond length for conjugated hydrocarbons can be derived. It follows therefore that in conjugated hydrocarbons all the symmetrical bond distortions will occur until the energy minimum is reached. That is, bond lengths will change to the first-order equilibrium values through the bond order–bond length relationship, but still keeping the original molecular symmetry unaffected.

Now we assume as in the preceding section that the total energy of a

conjugated molecule can be written as the sum of the π-electron energy and the σ-core energy which may be given by equation 2.

Assuming that the first-order changes have occurred, we then have

$$E(Q_i) = E_0 + \tfrac{1}{2}\{k + \langle\psi_0|\partial^2 H_\pi/\partial Q_i^2|\psi_0\rangle - 2\sum_k{}'|\langle\psi_k|\partial H_\pi/\partial Q_i|\psi_0|\rangle^2/(E_k - E_0)\}\, Q_i^2 \quad (4)$$

In the framework of the Hückel MO approximation or the SCF formalism with Pople's approximations[41,42], the second term in the braces is given by

$$\langle\psi_0|\partial^2 H_\pi/\partial Q_i^2|\psi_0\rangle = 2\sum_{\mu<\nu} P_{\mu\nu}\beta''_{\mu\nu}(\partial r_{\mu\nu}/\partial Q_i)^2 \quad (5)$$

where $\beta''_{\mu\nu}$ is the second derivative of $\beta_{\mu\nu}$ with respect to $r_{\mu\nu}$. We may safely neglect this term since for the reduced bond-distance interval of interest the curvature of the $\beta(r)$ curve would be very small.

According to equation 4, the force constant for the normal vibration Q_i can be identified with the term in the braces and can be negative if a given $\langle\psi_k|\partial H_\pi/\partial Q_i|\psi_0\rangle$ is nonvanishing and the associated energy gap $(E_k - E_0)$ is sufficiently small. If this force constant is negative, the energy should be lowered by the nuclear deformation Q_i, and a pseudo-Jahn–Teller distortion from the symmetrical nuclear arrangement must occur spontaneously.

In order to estimate the probable value of the force constant, we now make an approximation that the infinite sum over excited states in equation 4 is replaced by one or two dominant terms corresponding to the lowest one or two excited states. Our approach is then simply to examine whether a given molecule in a symmetrical nuclear configuration has reasonably low first excited state(s) and, if it does, whether any of the integrals $\langle\psi_k|\partial H_\pi/\partial Q_i|\psi_0\rangle$ are nonvanishing. Since Q_i and $(\partial H_\pi/\partial Q_i)$ have the same symmetry and the ground state, ψ_0, is, in general, totally symmetric, the integral is nonzero only when ψ_k and Q_i have the same symmetry. The symmetry of the first excited state(s) now determines which kind of nuclear displacement occurs energetically most easily.

Results and discussion

Neutral nonalternant hydrocarbons

The lowest excitation energies, ΔE_1, calculated assuming the full symmetry groups for nonalternant hydrocarbons, I–XIII, are summarized in *Table 4*. Considering the results of the SCF calculations, we can draw from these data a fairly clear-cut criterion for the molecular symmetry reduction in nonalternant hydrocarbons that if ΔE_1 is smaller than about 1.3 eV, the force constant should be negative and the molecule would distort into a less symmetrical nuclear configuration. According to this criterion, molecules XIV–XXIV, the ΔE_1s of which are calculated to be larger than 1.3 eV, are predicted to suffer no symmetry reduction in agreement with the results of the SCF calculations. The symmetries of the lowest excited states also listed

Table 4. Symmetries of ψ_1 and first excitation energies, ΔE_1, of nonalternant hydrocarbons calculated assuming the full molecular symmetries, and possible molecular-symmetry reductions

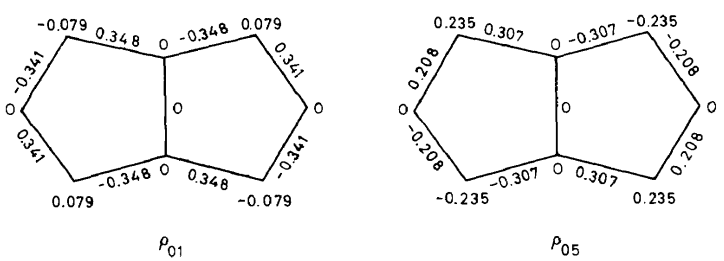
Molecule	Symmetry of ψ_1	ΔE_1(eV)	Symmetry reduction
I	B_{3g}	0.35	$D_{2h} \rightarrow C_{2h}$
II	B_{2u}	1.22	$D_{2h} \rightarrow C_{2v}$
III	B_{3g}	1.00	$D_{2h} \rightarrow C_{2h}$
IV	B_2	1.47	$(C_{2v} \rightarrow C_s)$
V	B_2	0.41	$C_{2v} \rightarrow C_s$
VI	A_g	2.54	
VII	B_{3g}	0.26	$D_{2h} \rightarrow C_{2h}$
VIII	B_{2u}	0.81	$D_{2h} \rightarrow C_{2v}$
IX	B_{3g}	0.83	$D_{2h} \rightarrow C_{2h}$
X	B_2	1.46	$(C_{2v} \rightarrow C_s)$
XI	B_2	2.05	$(C_{2v} \rightarrow C_s)$
XII	B_2	1.07	$C_{2v} \rightarrow C_s$
XIII	B_2	0.81	$C_{2v} \rightarrow C_s$

in *Table 4* are nothing but those of the energetically most soft nuclear displacements, and the predicted types of symmetry reduction are in complete agreement with those obtained in the preceding section.

Although the symmetry of the most soft normal displacement can thus be determined, its actual type cannot be uniquely determined in general without further examination of the matrix element. For pentalene, I, for example, there are two different types of bond distortion both belonging to the b_{3g} representation. In order to determine which distortion is energetically most favourable, it is useful to interpret the third term in the braces of equation 4 as the 'relaxability' of the molecule along the coordinate Q_i and express the matrix element $\langle\psi_k|\partial H_\pi/\partial Q_i|\psi_0\rangle$ in terms of the transition density, ρ_{0k}, between ground and excited states[43]

$$\langle\psi_k|\partial H_\pi/\partial Q_i|\psi_0\rangle = \int\rho_{0k}(\partial v/\partial Q_i)\mathrm{d}\tau \tag{6}$$

where v is the one-electron nuclear-electron potential operator. A given excited state may contribute much to the molecular relaxability towards the



ρ_{01} ρ_{05}

Figure 2. One-centre and two-centre components of the transition densities, ρ_{01} and ρ_{05}, of pentalene.

mode Q_i if ρ_{0k} is large near nuclei which contribute much to Q_i, but little to the relaxability if ρ_{0k} is small near such nuclei. One-centre and two-centre components of the transition density, ρ_{01}, of pentalene, together with those

of ρ_{05} associated with the fifth excited state which lies at 6.14 eV above the ground state and belongs also to the B_{3g} representation, are shown in *Figure 2*. It may be seen from these data that the lowest excited state contributes much to the relaxability towards the bond-alternation type of distortion, while the next B_{3g} excited state contributes much to the relaxability towards the other type of bond distortion belonging to the b_{3g} representation. Such is the case with other nonalternants suffering a symmetry reduction.

The stabilization energies, ΔE_s, are plotted in *Figure 3* against the lowest excitation energies, ΔE_1, as calculated assuming the fully-symmetrical nuclear configurations. It can be seen that there is a correlation between ΔE_s and ΔE_1; the smaller the former, the larger the latter.

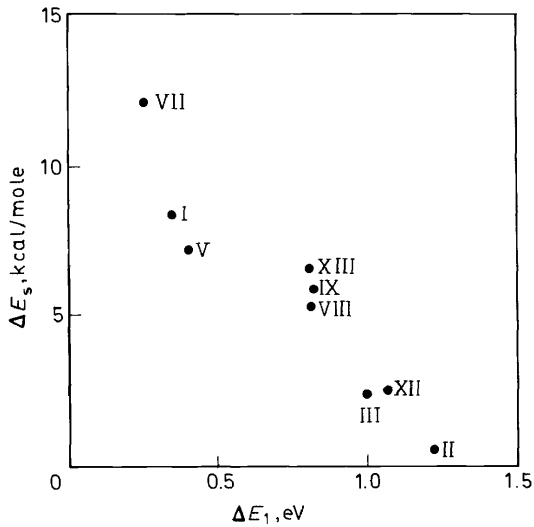


Figure 3. Correlation of ΔE_s with ΔE_1.

Anion and cation radicals of fulvalenes

If the full symmetry groups (D_{2h}) are assumed, the ground states of the cation radical of pentafulvalene, XXI, and the anion radical of heptafulvene, XXII, are predicted to be of the B_{1g} symmetry. The first excited states of these radicals are of A_u symmetry and are predicted to be very close to the ground states; in the framework of a one-electron approximation these two states are degenerate. The ground state interacts strongly with the first excited state through the normal displacement of the $b_{1u}(z)$ symmetry, with the result that the initial molecular symmetry (D_{2h}) should be reduced to C_{2v}.

On the other hand, the energy gaps between the first excited state (which is doubly degenerate in the one-electron approximation) and the ground state for the anion radical of XXI and cation radical of XXII are reasonably large (1.4 and 1.7 eV, respectively), and these radicals would not suffer symmetry reduction.

The above predictions are in accordance with the results of the SCF calculations.

Dianion of nonalternant hydrocarbons

The lowest excitation energies calculated assuming the full molecular-symmetry for dianions of I, III, IV and VII are 4.6, 1.4, 3.1 and 3.9 eV respectively. This indicates that no symmetry reduction should occur in these dianions in agreement with the results of the SCF calculations.

DIAMAGNETIC SUSCEPTIBILITIES

In order to examine the influence of double-bond fixations in nonalternant hydrocarbons on their π-electronic properties, we are now concerned with the diamagnetic susceptibilities for these molecules. The method of calculation used is the London–Hoarau method[44] together with the Wheland–Mann SCF technique[1]. The resonance integral is again assumed to be of the form $\beta = B \exp(-ar)$, but the value of a now used is 4.4 $Å^{-1}$ [45].

Table 5. Diamagnetic susceptibilities of nonalternant hydrocarbons

Molecule	Theoretical $\Delta K/\Delta K_{benzene}$	Experimental $\Lambda/\Lambda_{benzene}$
I, D_{2h}	−1.35	
I, C_{2h}	−0.41	
III, D_{2h}	−0.88	
III, C_{2h}	−0.38	
VI	1.10	1.00[a,c], 0.87[b,c]
VII, D_{2h}	−4.41	
VII, C_{2h}	−0.61	−0.45[a]
XI	2.04	2.16[a]
XIV	2.14	2.18[a,d]
XV	1.72	0.0[a,c]
XVI	−0.40	
XVII	−0.34	
XVIII	3.92	3.87[a]
XIX	0.10	0.08[a]
XX	0.16	
XXI	0.075	
XXII	0.18	0.15[a]

[a] Reference 45.
[b] Reference 44.
[c] The value for a dimethyl derivative.
[d] The value for a dimethylphenyl derivative.

In *Table 5*, selected theoretical diamagnetic anisotropies, ΔK, calculated using the bond lengths presented in *Table 1*, are listed (in units of $\Delta K_{benzene}$) and compared with experimental exaltations due to Dauben *et al.*[46]. Theoretical values are in good agreement with experimental data, except for the case of aceheptylene, XV, whose experimental exaltation has been reported unbelievably to be zero. The diamagnetic susceptibilities for nonalternants I, III, VII, XVI and XVII were predicted to be negative. Such an anomalously-reduced diamagnetism may be interpreted as an induced

Table 6. Singlet transitions of nonalternant hydrocarbons

Molecule	Transition symmetry[a]	Theoretical ΔE(eV)	f(cgs)	Experimental ΔE(eV)
I(C_{2h})	A_g	1.59	Forb.	1.72 (log ε = 1.95, tailing)[b]
	B_u	3.78	0.30	3.27 (3.99)
	B_u	4.75	0.18	4.00 (4.52)
III(C_{2h})	A_g	1.39	Forb.	1.77 (log ε = 2.59, tailing)[c]
	B_u	2.62	0.59	2.42 (4.63)
	B_u	3.78	0.21	3.61 (4.81)
	A_g	3.88	Forb.	4.06 (shoulder), 4.32 (4.68)
	A_g	4.34	Forb.	
	B_u	4.81	1.93	
VI(C_{2h})	A_g	2.54	Forb.	2.95 (log ε = 4.28)[d]
	B_u	3.32	0.64	
	A_g	4.23	Forb.	4.57 (4.64)
	B_u	4.28	0.12	
	B_u	4.91	1.29	
VII(C_{2h})	A_g	1.57	Forb.	Tail[e]
	B_u	3.02	0.31	3.52 (f = 0.15)
	B_u	3.82	0.17	4.84
XI(C_{2v})	B_2	2.05[f]	0.025[f]	1.96[g], 2.14[h] (f = 0.009)[g,h]
	A_1	3.53	0.005	3.66[g], 3.50[h] (0.08)[g,h]
	B_2	4.41	0.13	4.48[g]
	A_1	4.78	1.88	4.52[g,h] (1.10)[g,h]
	B_2	5.68	0.41	5.24[g,h] (0.38)[g,h]
XIV(C_{2v})	B_2	1.73[i]	0.003[i]	1.84[j]
	A_1	2.91	0.01	2.59
	A_1	3.64	0.073	3.37
	B_2	3.86	0.11	3.79
	B_2	4.79	0.39	4.63
XV(C_{2v})	B_2	1.52[i]	0.014[i]	1.55[j]
	A_1	2.89	0.009	2.92
	B_2	3.47	0.30	3.33
	A_1	3.82	0.14	3.96 ~ 4.77
	B_2	4.48	0.019	
	A_1	4.57	0.53	
	B_2	4.95	1.44	4.94
XVI(D_{2h})	B_{3g}	2.24	Forb.	Tail[k]
	B_{2u}	3.23	0.048	2.91
	B_{1u}	3.75	0.33	3.65
	B_{2u}	4.09	0.18	3.81
	A_g	4.62	Forb.	5.23
	B_{2u}	5.41	0.008	
XVIII(C_{2v})	A_1	2.98	0.28	2.20 ~ 3.54[l]
	B_2	3.15	0.026	
	B_2	3.32	0.066	
	B_2	3.87	0.025	
	A_1	4.50	0.96	4.14
	A_1	4.67	0.16	
	B_2	5.09	0.87	4.98
XIX(C_{2v})	B_2	3.32[f]	0.035[f]	3.32[m], 3.42[n] (f = 0.012)[m]
	A_1	5.06	0.63	5.12[m,n] (0.32)[m]
XX(C_{2v})	B_2	2.97	0.047[f]	2.91 (f = 0.02)[o]
	A_1	4.32	0.48	4.44 (0.3)
	B_2	6.05	0.096	5.83
XXI(D_{2h})	B_{3g}	2.39	Forb.	Tail[p]

Molecule	Transition symmetry[a]	Theoretical ΔE(eV)	f(cgs)	Experimental ΔE(eV)
XXI (D_{2h})	B_{2u}	2.44	0.016	2.98 (log ε = 2.41)
	B_{1u}	3.87	1.18	3.95 (4.67)
XXII(D_{2h})	B_{3g}	2.14	Forb.	Tail[p]
	B_{2u}	2.20	0.015	
	B_{1u}	3.14	1.31	3.42 (log ε = 4.35)
	A_g	4.93	Forb.	5.30 (4.35)
	A_g	5.03	Forb.	
	B_{3g}	5.28	Forb.	
	B_{2u}	5.39	0.26	
XXIII(C_{2v})	B_2	3.57[f]	0.035[f]	Tail[q]
	B_2	3.93	0.043	
	A_1	4.18	0.91	4.13 (log ε = 4.64)
	A_1	4.39	0.003	
XXIV(C_{2v})	B_2	2.72	0.008	Tail[r]
	B_2	2.78	0.034	Shoulder
	A_1	3.15	1.11	3.05 (log ε = 4.38)
	A_1	3.67	0.002	
	A_1	5.12	0.28	5.53 (4.20)

[a] For molecules which belong to the point group C_{2h}, the z axis is taken to be perpendicular to the molecular plane.
[b] The spectrum of hexaphenylpentalene; E. LeGoff, *J. Am. Chem. Soc.* **84**, 3975 (1962).
[c] The spectrum of a hexacarbomethoxydihydroxy derivative: E. LeGoff and R. B. LaCount, *Tetrahedron Letters*, 1161 (1964).
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[q] Estimated from the spectrum of a tetrachlorodi-*n*-propyl derivative; Y. Kitahara, I. Murata, M. Ueno, K. Sato and H. Watanabe, *Chem. Commun.* 180 (1966); A. S. Kende, P. T. Izzo and P. T. MacGregor, *J. Am. Chem. Soc.* **88**, 3359 (1966).
[r] The spectrum of a *p*-methoxybenzyl derivative; H. Prinzbach and W. Rosswog. *Angew. Chem.* **73**, 543 (1961); H. Prinzbach. Personal communication.

(quenched) paramagnetism[47–50]. For molecules I, III and VII, *Table 5* gives two theoretical values, one corresponding to the full symmetry (D_{2h}) and the other corresponding to the reduced symmetry (C_{2h}). It can be seen that an unsymmetrical bond distortion brings about a considerable decrease in the paramagnetic susceptibility. Part of the evidence for the reduced magnetic susceptibilities for III[25] and XVI[30] is given by their proton n.m.r. spectra which show the proton signals in the olefinic region.

It should then be concluded that the magnetic susceptibility of conjugated molecules is a very sensitive indicator of bond distortion and the magnetically induced ring currents in nonalternant hydrocarbons examined except for azulene, XI, are very much impeded as compared with those expected on the basis of Pauling's free electron model[1].

ELECTRONIC SPECTRA

In calculating electronic spectra, we take the ground-state geometries as obtained using the variable bond-length SCF technique. The method of calculation employed is the Pariser–Parr–Pople method with the same parametrization that was used in determining the ground-state geometries. Configuration mixing of all the singly excited states is included.

Calculated excitation energies and intensities for nonalternant hydrocarbons whose experimental data are available are summarized in *Table 6*. It can be seen that theoretical values are generally in good agreement with experimental data.

It should be noted that excitation energies, particularly the lowest ones (cf. *Table 4*), calculated assuming the full symmetry (D_{2h}) for molecules I, III and VII are predicted to be considerably lower than those calculated using the reduced symmetry (C_{2h}) and experimental values.

It is interesting to mention in this connection the geometrical structure of the lowest excited state of heptalene[51]. The SCF calculations show that the bond distortion, belonging to the b_{3g} representation (that is, alternation), which occurs in the ground state does not give rise to a symmetry reduction in the lowest excited state, that is, the lowest excited state exhibits no bond alternation. Furthermore, our calculations predict that bond distortions belonging to b_{1u} and b_{2u} representations do not result in a symmetry reduction. All the possible starting distortions produce the unique set of bond lengths belonging to the point group D_{2h}: bond lengths for 1–2, 1–12, 2–3 and 6–12 bonds are 1.402, 1.412, 1.405 and 1.463 Å, respectively.

The above result may easily be anticipated on the basis of the symmetry rule from the energy-level arrangement in the heptalene molecule with the D_{2h} symmetry. Excitation energies from the ground state to $\psi_1(B_{3g})$, $\psi_2(B_{1u})$ and $\psi_3(B_{2u})$ are 0.26, 2.68 and 3.37 eV, respectively, and the energy gaps E_2–E_1 and E_3–E_1 are too large to give rise to pseudo-Jahn–Teller distortions in the lowest excited state.

The geometrical structure of the lowest excited state predicted above perhaps gives one of the reasons for the appearance of a long absorption tail on the long wavelength side of the first absorption band in heptalene[5].

CONCLUSION

The results of our calculations indicate that most of the nonalternant hydrocarbons examined exhibit in greater or less degree a marked double-bond fixation. It may thus be concluded that bond distortion should be a rather common phenomenon in nonalternant hydrocarbons; fulvenes, fulvalenes, and certain peri-condensed nonalternants suffer a symmetrical bond distortion and most of the cata-condensed nonalternants are liable to undergo unsymmetrical bond distortions due to the pseudo-Jahn–Teller effect.

Finally, we wish to make a brief remark about the theoretical aromaticity criterion. Our calculations have revealed that in certain nonalternant hydrocarbons, for example, V, VI, and XIV–XVIII, the carbon skeleton

may be divided into two distinguishable parts; one in which bond lengths are highly smoothed out and the other in which a strong double-bond fixation exists. Further, it has been shown that in the cation radical of XXI and the anion radical of XXII, there exists a considerable double-bond fixation in one of the rings, while in the other ring bond lengths are nearly equalized. For such molecules, the current theoretical aromaticity criteria, such as the magnitude of the delocalization energy or that of the diamagnetic ring current are not sufficient. These quantities are associated with the properties of a conjugated molecule as a whole and cannot, therefore, reflect the local characteristics of π-electron delocalization.

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