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Symmetry Rule for Predicting Bond Distortions in Conjugated Hydrocarbons

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A symmetry rule for predicting molecular shapes which is based on the second-order Jahn-Teller effect has been applied to the predictions of bond distortions in a number of nonalternant hydrocarbons in their ground and electronically excited states. In spite of the very crude approximation that only the lowest-lying excited state plays a dominant role in determining the energetically most favorable nuclear displacement, a fairly clear-cut criterion for molecular-symmetry reduction was obtained. The actual types of the most soft bond distortions, determined by examining the two-center components of transition densities, are in good agreement with the results of variable bond-length SCF MO calculations and available experimental results. The problem of symmetry reductions possible in large cyclic polyenes $C_{4n+2}H_{4n+2}$ is briefly discussed.

A symmetry rule for predicting molecular structures has recently been developed by Pearson,[1–3] Salem,[4] and Bartell.[5] The rule is based on the second-order or pseudo Jahn-Teller effect, and follows the earlier work by Bader.[6,7] The symmetries of the ground state and the lowest excited state(s) determine which kind of nuclear motion occurs most easily in the ground state of a molecule. The rule has proved remarkably successful in predicting the stable molecular shapes of inorganic and small organic molecules. Symmetry rules have also been used to predict the course of chemical reactions by Bader,[7] Salem and Wright,[8] and Pearson.[9]

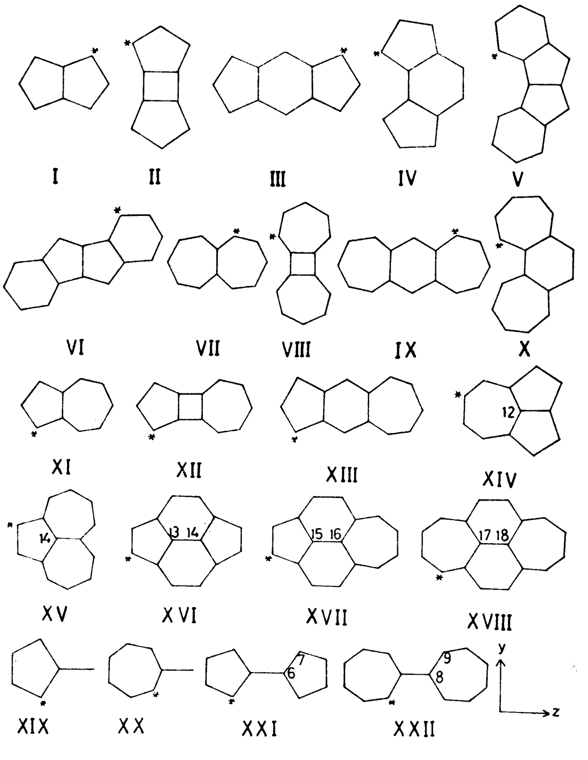

Fig. 1. Numbering of atoms and choice of axes in nonalternant hydrocarbons. Carbon atoms are numbered consecutively, starting with the starred atom and proceeding clockwise along the periphery. For VI the z axis is taken to be perpendicular to the molecular plane.

In this paper we consider the application of the symmetry rule to the prediction of the geometrical structures of conjugated π-electron systems. We deal, in particular, with the problem of molecular-symmetry reduction and double-bond fixation in the nonalternant hydrocarbons.[10]

On the basis of the second-order perturbation theory, Binsch *et al.*[11–15] have recently developed a general theory of double-bond fixation in conjugated systems. The symmetry rule is based also on the second-order perturbation theory, but it provides a more intelligible way of predicting the double-bond fixations and of understanding the origin of bond distortions in conjugated systems.

Theoretical

We start by assuming for a conjugated molecule a fully-symmetrical nuclear arrangement as the unperturbed nuclear configuration. The unperturbed electronic wavefunctions $\phi_0, \phi_1, \cdots, \phi_n, \cdots$ and the corresponding eigenvalues $E_0, E_1 \cdots, E_n, \cdots$ are assumed to be known. We now distort the nuclei from the initial symmetrical arrangement by means of the ith normal coordinate of nuclear motion Q_i. With the use of the second-order perturbation theory, the energy of the ground state after deformation may be written as

$$E(Q_i) = E_0 + \left\langle \phi_0 \middle| \frac{\partial H}{\partial Q_i} \middle| \phi_0 \right\rangle Q_i$$

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1) R. G. Pearson, *J. Amer. Chem. Soc.*, **91**, 4947 (1969).
2) R. G. Pearson, *ibid.*, **91**, 1252 (1969).
3) R. G. Pearson, *J. Chem. Phys.*, **52**, 2167 (1970).
4) L. Salem, *Chem. Phys. Lett.*, **3**, 99 (1969).
5) L. S. Bartell, *J. Chem. Educ.*, **45**, 754 (1969).
6) R. F. Bader, *Mol. Phys.*, **3**, 137 (1960).
7) R. F. Bader, *Can. J. Chem.*, **40**, 1164 (1962).
8) L. Salem and J. S. Wright, *J. Amer. Chem. Soc.*, **91**, 5947 (1969).
9) R. G. Pearson, *Theoret. Chim. Acta*, **16**, 107 (1970).
10) L. Salem, "The Molecular Orbital Theory of Conjugated Systems," Benjamin, New York (1966).
11) G. Binsch, E. Heilbronner, and J. N. Murrell, *Mol. Phys.*, **11**, 305 (1966).
12) G. Binsch and E. Heilbronner, "Structural Chemistry and Molecular Biology," A. Rich and N. Davidson, Ed., Freeman and Co., San Francisco (1968), p. 851.
13) G. Binsch and E. Heilbronner, *Tetrahedron*, **24**, 1215 (1968).
14) G. Binsch, I. Tamir, and R. D. Hill, *J. Amer. Chem. Soc.*, **91**, 2446 (1969).
15) G. Binsch and I. Tamir, *ibid.*, **91**, 2450 (1969).

$$+\frac{1}{2}\left\{\left\langle\psi_0\left|\frac{\partial^2 H}{\partial Q_i{}^2}\right|\psi_0\right\rangle - 2\sum_n{}' \frac{\left|\left\langle\psi_n\left|\frac{\partial H}{\partial Q_i}\right|\psi_0\right\rangle\right|^2}{E_n-E_0}\right\}Q_i{}^2 \tag{1}$$

If the initial ground-state wavefunction ψ_0 is nondegenerate, as is the case with the nonalternant hydrocarbons deal with in this paper (since the fully-symmetrical nuclear arrangements of these molecules belong to point-group D_{2h}, C_{2h}, or C_{2v}), then the second term in Eq. (1) is nonzero only for the totally symmetric nuclear displacements.

Let us assume that the total energy of a conjugated molecule can be written as the sum of the π-electron energy and the σ-core energy, the latter being approximated by a quadratic function of the bond-distance variation

$$E_\sigma = \sum_{\mu<\nu} \frac{k}{2}(\Delta r_{\mu\nu})^2 \tag{2}$$

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

It is easily shown[11,12] that by equating the second term in Eq. (1) to zero, the usual linear relationship between bond order and bond length for conjugated hydrocarbons can be derived. It follows that in conjugated hydrocarbons all the symmetrical bond distortions will occur until the first-order energy equilibrium is reached. That is, bond lengths will change to the first-order equilibrium values through the bond-order - bond-length relationship, but still keep the original molecular symmetry.

Assuming that the first-order changes have taken place, we have

$$E(Q_i) = E_0 + \frac{1}{2}\left\{k+\left\langle\psi_0\left|\frac{\partial^2 H_\pi}{\partial Q_i{}^2}\right|\psi_0\right\rangle - 2\sum_n{}' \frac{\left|\left\langle\psi_n\left|\frac{\partial H_\pi}{\partial Q_i}\right|\psi_0\right\rangle\right|^2}{E_n-E_0}\right\}Q_i{}^2 \tag{3}$$

If we assume that the change in the π-electron energy on variation of a particular bond length can be considered to arise from a one-electron perturbation which can be incorporated in the core resonance integral $\beta(r)$, the second term in the braces in Eq. (3) can be written as[11,14]

$$\left\langle\psi_0\left|\frac{\partial^2 H_\pi}{\partial Q_i{}^2}\right|\psi_0\right\rangle = 2\sum_{\mu<\nu} p_{\mu\nu}\beta_{\mu\nu}''\left(\frac{\partial r_{\mu\nu}}{\partial Q_i}\right)^2 \tag{4}$$

where p is the bond order and β'' is the second derivative of $\beta(r)$ with respect to r. We may safely neglect this term since for the reduced bond-distance interval in question the curvature of the $\beta(r)$ curve should be very small.

According to Eq. (3), 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 matrix element $\langle\psi_0|\partial H_\pi/\partial Q_i|\psi_n\rangle$ is nonvanishing and the associated energy gap E_n-E_0 is sufficiently small. If the 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 would occur spontaneously.

In order to estimate the probable value of the force constant, we now make a rather drastic approximation that the infinite sum over excited states in Eq. (3) is replaced by one or two dominant terms corresponding to the lowest one or two excited states. Pearson[2,3] has shown that this approximation is justified in a large variety of small molecules and complex ions. Our approach is then simply to examine whether a given molecule in a symmetrical nuclear configuration has reasonably low lowest excited state(s) and, if so, whether any of the integrals $\langle\psi_0|\partial H_\pi/\partial Q_i|\psi_n\rangle$ are nonvanishing. Since Q_i and $\partial H_\pi/\partial Q_i$ have the same symmetry and the ground state is, in general, totally symmetric, the integral is nonzero only when ψ_n and Q_i have the same symmetry. The symmetry of the lowest excited state(s) now determines which kind of nuclear displacement occurs energetically most easily.

Although the symmetry of the most soft normal nuclear displacement can thus be determined, its actual type cannot always be uniquely determined, because there are, in general, several types of bond distortion belonging to the same symmetry. In order to determine which distortion is energetically most favorable, it is useful to interpret the third term in the braces of Eq. (3) as the "relaxability" of the molecule along the coordinate Q_i, and express the matrix element $\langle\psi_0|\partial H_\pi/\partial Q_i|\psi_n\rangle$ in terms of the transition density ρ_{0n} between the ground and excited states by[4]

$$\left\langle\psi_0\left|\frac{\partial H_\pi}{\partial Q_i}\right|\psi_n\right\rangle = \int\rho_{0n}\frac{\partial v}{\partial Q_i}\mathrm{d}\tau \tag{5}$$

where v is the one-electron nuclear-electron potential operator. For a one-electron transition between molecular orbitals ϕ_i and ϕ_j, ρ_{0n} is given by $\sqrt{2}\,\phi_i\phi_j$.[10] A given state may contribute much to the molecular relaxability towards mode Q_i, if ρ_{0n} is large near nuclei which contribute much to Q_i, but little to the relaxability if ρ_{0n} is small near such nuclei. We may thus predict the most favorable type of bond distortion by examining the distribution of transition densities over the molecular skeleton.

Eigenvalues and wavefunctions for the fully-symmetrical nuclear arrangements are calculated using the self-consistent configuration-interaction formalism of Pariser-Parr-Pople MO method, in conjunction with the variable bond-length technique in which 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.[16]

Since it is based on the second-order perturbation theory, the symmetry rule only gives the type of the most favorable bond distortion. In order to obtain information about the actual magnitudes of distortions or the equilibrium bond lengths at which the

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[16] H. Yamaguchi, T. Nakajima, and T. L. Kunii, *Theoret. Chim. Acta*, **12**, 349 (1968).

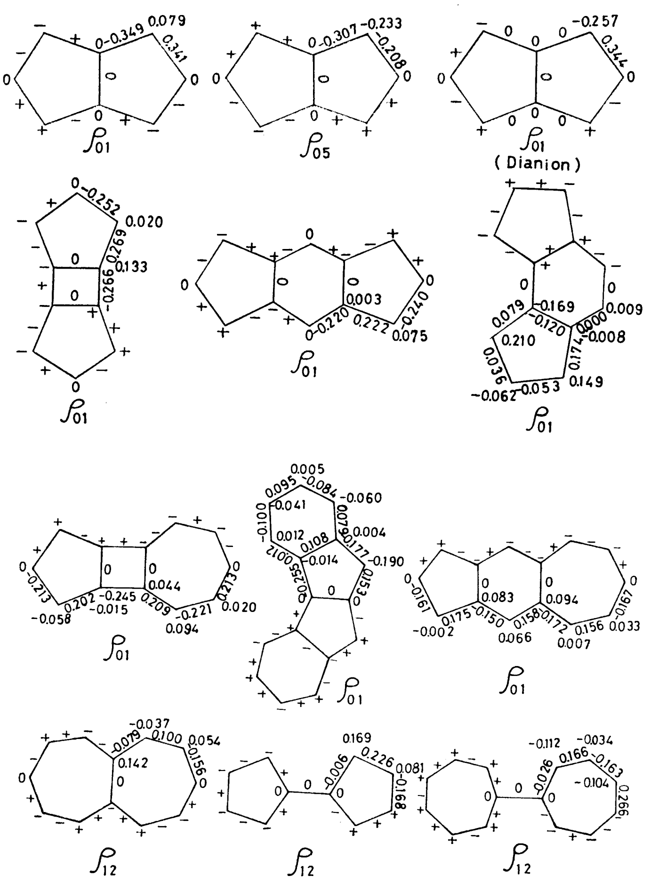

Fig. 2. One-center and two-center components of the transition densities.

TABLE 1. SYMMETRIES AND ENERGIES OF FIRST AND SECOND SINGLET EXCITED STATES OF NONALTERNANT HYDROCARBONS

Molecule (Point group)	First excited state E_1-E_0 (eV)	First excited state Symmetry	Second excited state E_2-E_1 (eV)	Second excited state Symmetry
I (D_{2h})	0.35	B_{3g}	3.25	B_{1u}
II (D_{2h})	1.22	B_{1u}	2.15	B_{3g}
III (D_{2h})	1.00	B_{3g}	1.54	B_{1u}
IV (C_{2v})	1.47	B_2	1.48	B_2
V (C_{2v})	0.41	B_2	2.27	B_2
VI (C_{2h})	2.54	A_g	0.79	B_u
VII (D_{2h})	0.26	B_{3g}	2.41	B_{1u}
VIII (D_{2h})	0.81	B_{1u}	1.75	B_{2u}
IX (D_{2h})	0.83	B_{3g}	1.20	B_{1u}
X (C_{2v})	1.46	B_2	1.06	B_2
XI (C_{2v})	2.05	B_2	1.48	A_1
XII (C_{2v})	1.07	B_2	1.51	A_1
XIII (C_{2v})	0.81	B_2	1.62	A_1
XIV (C_{2v})	1.73	B_2	1.18	A_1
XV (C_{2v})	1.52	B_2	1.37	A_1
XVI (D_{2h})	2.24	B_{3g}	0.99	B_{2u}
XVII (C_{2v})	2.98	A_1	0.17	B_2
XVIII (D_{2h})	2.15	B_{3g}	0.98	A_1
XIX (C_{2v})	3.32	B_2	1.74	A_1
XX (C_{2v})	2.94	B_2	1.38	A_1
XXI (D_{2h})	2.04	B_{3g}	0.09	B_{2u}
XXII (D_{2h})	1.74	B_{3g}	0.06	B_{2u}
I^{2-} (D_{2h})	4.62	B_{2u}	0.66	B_{1u}
III^{2-} (D_{2h})	3.05	B_{2u}	1.00	B_{1u}
IV^{2-} (C_{2v})	3.93	B_2	0.05	A_1
VII^{2-} (D_{2h})	1.43	B_{2u}	0.44	B_{1u}

nuclei of the real molecule will settle, we use the SCF MO method mentioned above, taking into account, as the starting geometries, all the possible distinct structures in which bond lengths are distorted so that the set of displacement vectors may form a basis for each irreducible representation of the full symmetry group of a molecule.[17,18] In pentalene (I, Fig. 1), for example, there are 3, 2, 2, and 2 distinct bond distortions belonging to respectively a_g, b_{3g}, b_{2u}, and b_{1u} irreducible representations of the point group D_{2h}. When self-consistency is achieved at two different geometries, one having a full symmetry and the other a lower symmetry, the latter should, in principle, be energetically favored as compared with the former. In such a case, we define the stabilization energy as the difference in total energy between the two geometries. The value of the force constant k adopted for use in calculating the σ-core energy is 714 kcal mol^{-1} Å^{-2}.[19]

Results and Discussion

The symmetries and energies (measured from the ground state) of the lowest excited states for the fully-symmetrical nuclear arrangements of the nonalternant hydrocarbons (Fig. 1) and some of their dianions are listed in Table 1. In Fig. 2 are shown the one-center and two-center components of the transition densities for some selected molecules.

The second excited states being, in most cases, well separated from the lowest excited states in these molecules, the symmetries of the most soft nuclear displacements may be given by those of the lowest excited states. In pentalene (I), for example, the most soft nuclear displacement is predicted to be of b_{3g} symmetry. In this molecule there are two distinct types of in-plane vibration both belonging to b_{3g} irreducible representation. In Fig. 2 are shown one-center and two-center components of ρ_{01} for 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 B_{3g} representation. It will be seen from these data that the lowest excited state contributes much to the relaxability of the molecule towards the bond-alternation type of distortion, while the next B_{3g} excited state contributes mainly to that towards the other type of bond distortion. The data in Fig. 2 show that in most of the molecules examined, with the exception of molecules IV and V, the bond alternation in the peripheral carbon skeleton is the energetically soft most bond distortion in the ground state. Such will be the case with the seven-membered analogues of I, II,

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[17] T. Nakajima and A. Toyota, *Chem. Phys. Lett.*, **3**, 272 (1969).

[18] T. Nakajima, in "The Chemistry of Nonbenzenoid Aromatic Compounds," International Symposium on the Chemistry of Aromatic Compounds, Butterworths, London (1970), in press.

[19] L. C. Snyder, *J. Phys. Chem.*, **66**, 2299 (1962).

TABLE 2. 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
	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	1.375
	6—16	1.450
	7—8	1.432
	15—16	1.451
XI (C_{2v})	1—2	1.398,[a] *1.391*[b]
	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—5	1.463
	4—12	1.448
	5—6	1.381
	5—11	1.446
	6—7	1.427
	7—8	1.376
	8—9	1.429
	9—10	1.374
	10—11	1.435
	11—12	1.404
XIII (C_s)	1—2	1.371
	1—14	1.441
	2—3	1.428
	3—4	1.382
	4—5	1.435
	4—14	1.462
	5—6	1.376
	6—7	1.443
	6—12	1.460
	7—8	1.369
	8—9	1.434
	9—10	1.373
	10—11	1.429
	11—12	1.382
	12—13	1.436
	13—14	1.376
XIV (C_{2v})	1—2	1.404,[c] *1.406*[d]
	1—11	1.397, *1.394*
	2—3	1.397, *1.386*
	3—4	1.435, *1.426*
	3—12	1.445, *1.421*
	4—5	1.371, *1.359*
	5—6	1.437, *1.423*
	6—12	1.395, *1.378*
XV (C_{2v})	1—2	1.399,[c] *1.412*,[e] *1.396*[f]
	1—13	1.400, *1.393*, *1.393*
	2—3	1.433, *1.437*, *1.436*
	2—14	1.442, *1.472*, *1.470*
	3—4	1.374, *1.380*, *1.358*
	4—5	1.429, *1.434*, *1.418*
	5—6	1.373, *1.367*, *1.368*
	6—7	1.435, *1.446*, *1.446*
	7—14	1.400, *1.429*, *1.399*
XVI (D_{2h})	1—3	1.353[g]
	2—3	1.462
	3—4	1.387
	3—13	1.426
	4—5	1.412
	13—14	1.414
XVII (C_{2v})	1—2	1.362[g]
	2—3	1.446
	3—4	1.397
	3—15	1.428

Table 2. continued

Molecule	Bond	Bond length (Å)	Molecule	Bond	Bond length (Å)	Molecule	Bond	Bond length (Å)
	4—5	1.402		6—7	1.410	XXI (D_{2h})	1—2	1.356
	5—6	1.397		17—18	1.413		1—5	1.460
	6—7	1.446					2—3	1.455
	6—16	1.428	XIX (C_{2v})	1—2	1.356		5—6	1.372
	7—8	1.364		1—5	1.462			
	8—9	1.440		2—3	1.449	XXII (D_{2h})	1—2	1.359
	15—16	1.412		5—6	1.353		1—7	1.454
							2—3	1.450
XVIII (D_{2h})	1—2	1.357[g]	XX (C_{2v})	1—2	1.357		3—4	1.360
	2—3	1.452		1—7	1.461		7—8	1.379
	4—5	1.457		2—3	1.449			
	5—6	1.390		3—4	1.360			
	5—17	1.427		7—8	1.355			

a) Ref. 16.
b) X-ray bond lengths; J. M. Robertson, M. M. Shearer, G. A. Sin, and D. G. Watson, *Acta Crystallogr.*, **15**, 1 (1962).
e) H. Yamaguchi, T. Terasaka, and T. Nakajima, *Theoret. Chim. Acta*, **18**, 225 (1970).
d) X-ray bond lengths of a dimethylphenyl derivative; Ref. 35.
e) X-ray bond lengths of a tetramethyl derivative; Ref. 36.
f) X-ray bond lengths of a tetramethyl derivative; Ref. 37.
g) Ref. 38.

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
				3—4	1.414
III^{2-} (D_{2h})	1—2	1.397		4—5	1.437
	1—12	1.421		4—12	1.416
	4—12	1.432		5—6	1.370
	11—12	1.408		11—12	1.447
			VII^{2-} (D_{2h})	1—2	1.415
				1—12	1.399
				2—3	1.404
				6—12	1.504

and III (molecules VII, VIII and IX, respectively).

The molecular symmetry groups and the bond distances for the energetically most stable nuclear arrangements of the nonalternant hydrocarbons obtained by the variable bond-length SCF MO method are presented in Tables 2, and 3, Inspecting the data in Tables 1, 2 and 3. one may draw a fairly clear-cut criterion for the molecular symmetry reduction in nonalternant hydrocarbons that if the lowest excitation energy is smaller than about 1.2 eV, the force constant for a certain antisymmetric in-plane vibration should be negative and the molecule would be distorted into a less symmetrical nuclear configuration. In Fig. 3 the stabilization energies ΔE_s which favor a lower-symmetry nuclear arrangement are plotted against the lowest excitation energies E_1-E_0 as calculated by assuming the fully-symmetrical nuclear arrangements. It is seen that there exists a good correlation between E_1-E_0 and ΔE_s; the smaller the former, the larger the latter.

The molecular symmetry groups for the most stable nuclear configuration as obtained by using the SCF method are in complete agreement with those brought about by the most soft bond distortions predicted from the symmetry rule. Moreover, in molecules I, II, III, VII, VIII, IX, XII, and XIII which suffer a symmetry reduction, the bond-length distributions obtained by using the SCF method indicate that they exhibit a more or less marked bond-length alternation in the molecular periphery, as is expected from the distributions of transition densities. It is of interest to note in this connection that a fairly strong bond alternation is predicted even in molecules II, VIII, and XIII, the perimeters of which are composed of $4n+2$ carbon atoms.

Of particular notice is dibenzopentalene (V). The transition density ρ_{01} of this molecule (Fig. 2) indicates

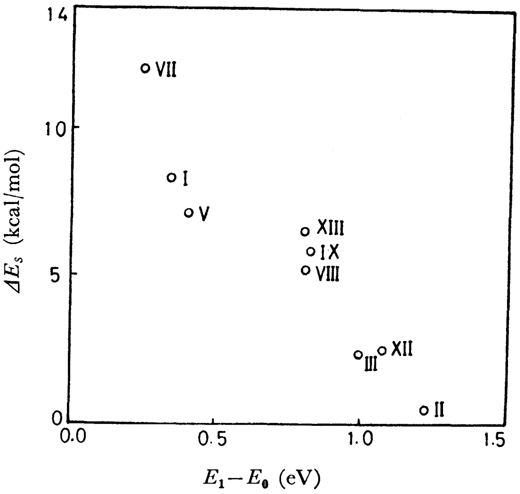

Fig. 3. Correlation of ΔE_s with E_1-E_0.

that strong double-bond fixations are localized in the pentalene segment, but there exists only a slight degree of double-bond fixation in each of the benzene rings. On the other hand, the results of SCF calculations show that in one of the benzene rings of this molecule, bond lengths are smoothed out as in benzene, whereas in the other ring there exists a strong double-bond fixation in the same degree as in the pentalene segment. In the case of V, the symmetry rule is thus insufficient in predicting the actual type of the most favorable bond distortion. In the isomeric dibenzopentalene (VI) which suffers only a first-order bond fixation, the two benzene rings are equivalent and in both the benzene rings bond lengths are almost equalized. Strong double-bond fixations are localized in the butadiene-like skeleton of the pentalene segment. It is therefore expected that the molecule undergoes addition reactions in this region. This is in accordance with experimental facts.[20,21]

Of the cata-condensed nonalternant hydrocarbons examined, pentalene (I) and heptalene (VII) which have been the objects of many theoretical investigations[13,15,19,22-27] are predicted to possess a marked tendency to the second-order double-bond fixation. In both molecules there exists a strong bond-length alternation in the molecular periphery. Available experimental information[28-30] agrees with this in indicating that the π-electrons in these molecules are strongly localized in "double" bonds, rather than uniformly delocalized over the entire molecule.

s-Indacene (III), recently prepared by Hafner *et al.*[31], is predicted to assume a skew structure with a moderate double-bond fixation. The results obtained by using different theoretical methods[13,15,32] agree with this. The theoretical predictions are in good agreement with the available experimental information.

Other molecules worth mentioning are peri-condensed nonalternant hydrocarbons XIV—XVIII; all these molecules are predicted not to suffer second-order bond distortions. As for XIV and XV, it is noted that bond lengths of the peripheral bonds belonging to the 5-membered ring of XV are all predicted to be 1.4 Å. In both molecules there is a pronounced double-bond fixation in the remaining region of the periphery. Derivatives of XIV and XV have been prepared by Hafner and Schneider[33,34] and the predicted distributions of bond lengths are in good agreement with the X-ray data (Table 2).[35-37] In molecules XIV—XVIII, it is predicted that bond lengths of the naphthalene core are almost the same as those in the free naphthalene molecule and there are marked double-bond fixations in the other region of the periphery.[38] The most stable nuclear arrangement in XVI corresponds to the aromatic model proposed by Lo and Whitehead.[39] Molecules XVI and XVIII have been synthesized by Trost and Bright[40] and Boekelheide and Vick,[41] respectively. The present results are in good qualitative agreement with the available experimental facts.

The lowest excitation energies calculated assuming the full molecular-symmetry for dianions of I, III IV, and VII are all larger than the critical value (1.2 eV). This indicates that no symmetry reduction should occur in the ground states of these dianions, the prediction being in agreement with the results of SCF calculations. In I, III, and VII, addition of two more electrons to the neutral molecule to form the dianion results in a complete disappearance of the unsymmetrical bond distortion, and in the dianions the bond lengths of the peripheral C–C bonds are nearly equalized. Dianions of I,[42,43] II,[44] and IV[45,46] have been prepared and are known to be stable species.

In this connection the molecular symmetries of anion and cation radicals of fulvalenes should be mentioned. If the full molecular symmetry (D_{2h}) is assumed, the ground states of the cation radical of pentafulvalene (XXI) and the anion radical of heptafulvalene (XXII) are predicted to be of $^2B_{1g}$ symmetry. The lowest excited states of these radicals are of ^2A_u symmetry and are predicted to be very close to the ground states; in the framework of one-electron approximation the two states are degenerate. In these radicals, therefore, the ground state interacts strongly with the first

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20) C. T. Blood and R. P. Linstead, *J. Chem. Soc.*, **1952**, 2255 2263.

21) C. C. Chuen and S. W. Fenton, *J. Org. Chem.*, **23**, 1538 (1958).

22) P. C. den Boer-Veenendaal and D. H. W. den Boer, *Mol. Phys.*, **4**, 33 (1961).

23) P. C. den Boer-Veenendaal, J. A. Vliegenthart, and D. H. W. den Boer, *Tetrahedron*, **18**, 1325 (1962).

24) T. Nakajima and S. Katagiri, *Mol. Phys.*, **7**, 149 (1963).

25) T. Nakajima, H. Yamaguchi, R. Kaeriyama, and Y. Nemoto, This Bulletin, **37**, 272 (1964).

26) P. François and A. Julg, *Theoret. Chim. Acta*, **11**, 128 (1968).

27) N. C. Baird and R. M. West, *J. Amer. Chem. Soc.*, **93**, 3072 (1971).

28) H. J. Dauben and D. J. Bertelli, *ibid.*, **83**, 4659 (1961).

29) E. LeGoff, *ibid.*, **84**, 3975 (1962).

30) R. Bloch, R. A. Marty, and P. de Mayo, *ibid.*, **93**, 3071 (1971).

31) K. Hafner, K. Häfner, C. König, M. Kreuder, G. Ploss, G. Schulz, E. Strum, and K. H. Vöpel, *Angew. Chem.*, **75**, 35 (1963); *Angew. Chem. Int. Ed. Engl.*, **2**, 123 (1963).

32) T. Nakajima, T. Saijo, and H. Yamaguchi, *Tetrahedron*, **20**, 2119 (1964).

33) K. Hafner and J. Schneider, *Angew. Chem.*, **70**, 702 (1958).

34) K. Hafner and J. Schneider, *Ann. Chem.*, **624**, 37 (1957); **672**, 194 (1964).

35) H. J. Lindner, *J. Chem. Soc.*, *B*, **1970**, 907.

36) E. Carstensen-Oeser and G. Habermehl, *Angew. Chem.*, **80**, 564 (1968).

37) R. Quasba, F. Brandle, W. Hoppe, and R. Huber, *Acta Crystallogr.* **B25**, 1198 (1969).

38) H. Yamaguchi and T. Nakajima, This Bulletin, **44**, 682 (1971).

39) D. H. Lo and M. A. Whitehead, *Chem. Comm.* **1968**, 771.

40) B. M. Trost and G. M. Bright, *J. Amer. Chem. Soc.*, **89**, 4244 (1967).

41) V. Boekelheide and G. K. Vick, *ibid.*, **78**, 653 (1956).

42) T. J. Katz and M. Rosenberger, *ibid.*, **84**, 865 (1962).

43) T. J. Katz, M. Rosenberger, R. K. O'Hara, *ibid.*, **86**, 249 (1964).

44) K. Hafner, *Angew. Chem.*, **75**, 1041 (1963); *Angew. Chem. Int. Ed. Engl.*, **3**, 165 (1964).

45) T. J. Katz and J. Schulman, *J. Amer. Chem. Soc.*, **86**, 3169 (1964).

46) T. J. Katz, V. Balogh, and J. Schulman, *ibid.*, **90**, 734 (1968).

TABLE 4. BOND LENGTHS OF CATION AND ANION RADICALS OF FULVALENES

Radical	Bond	Bond length (Å)	Radical	Bond	Bond length (Å)
XXI$^+$(C_{2v})	1—2	1.416	XXII$^+$(D_{2h})	1—2	1.379
	1—5	1.441		1—7	1.427
	2—3	1.396		2—3	1.426
	5—6	1.388		3—4	1.380
	6—10	1.461		7—8	1.422
	8—9	1.477			
	9—10	1.353	XXII$^-$(C_{2v})	1—2	1.400
				1—7	1.437
XXI$^-$(D_{2h})	1—2	1.378		2—3	1.399
	1—5	1.429		3—4	1.422
	2—3	1.428		7—8	1.396
	5—6	1.421		8—14	1.449
				11—12	1.354
				12—13	1.426
				13—14	1.360

excited state through the nuclear displacement of $b_{1u}(z)$ symmetry, with the result that the initial molecular symmetry (D_{2h}) should be reduced to C_{2v} (Table 4).

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

The above predictions are in agreement with the results obtained by using the open-shell SCF method in conjunction with the variable bond-length technique.[47,48]

The cation and anion radicals of XXII have been prepared and their ESR spectra have been investigated by Sevilla *et al.*[49] The analysis of the hyperfine spectra of these radicals has revealed that the cation radical should have D_{2h} symmetry, whereas the molecular symmetry of the anion radical should be lower than D_{2h}.

Finally we consider the application of the symmetry rule to the prediction of the geometrical structures of the excited states of conjugated hydrocarbons. On the basis of the same approximation as used in predicting the ground-state geometrical structures, the force constant for the *i*th normal nuclear-displacement in the *n*th excited state may be written as

$$f_n^i = k - 2\sum_m{}' \frac{\left|\left\langle \psi_n \left| \frac{\partial H_\pi}{\partial Q_i} \right| \psi_m \right\rangle\right|^2}{E_m - E_n} \tag{6}$$

In order to seek the most soft nuclear displacement in the excited state, the approximation is again made of replacing the sum in Eq. (6) by one or two terms correpsonding to the higher one or two excited states. Now, the transition density ρ_{nm} between the *n*th excited state corresponding to the orbital jump $\phi_i \rightarrow \phi_k$ and the *m*th one corresponding to $\phi_j \rightarrow \phi_l$ is $\phi_k\phi_l$ if $i=j$, and $-\phi_i\phi_j$ if $k=l$. Therefore, the value of the matrix element $|\langle\psi_n|\partial H_\pi/\partial Q_i|\psi_m\rangle|^2$ in Eq. (6) should be about one half of that of $|\langle\psi_0|\partial H_\pi/\partial Q_i|\psi_n\rangle|^2$ in Eq. (3) in so far as the transition densities are assumed not to vary significantly according to the molecular orbitals concerned. Thus, if the energy gap $E_m - E_n$ is smaller than about one half the critical value obtained above, that is, about 0.6 eV, the force constant in the excited state is expected to be negative.

In Table 1 are presented the energies of the second excited states (measured from the first excited states) as obtained by minimizing the ground-state energy assuming the full molecular symmetry. Use of these eigenvalues and corresponding wavefunctions in Eq. (6) is approximative. The energy values and corresponding wavefunctions to be used in Eq. (6) should, in principle, be those corresponding to the first-order equilibrium nuclear arrangement of the *n*th excited state, as given by minimizing its energy and keeping the molecular symmetry highest.

Inspection of Table 1 reveals that all those molecules which suffer a molecular-symmetry reduction in the ground state have $E_2 - E_1$ values considerably larger than the critical value and are predicted to possess a fully-symmetrical nuclear arrangement in their first excited state.

TABLE 5. BOND LENGTHS OF FIRST SINGLET EXCITED STATES OF VII, XXI AND XXII

Molecule	Bond	Bond length (Å)	Molecule	Bond	Bond length (Å)
VII (D_{2h})	1—2	1.402	XXII (C_{2v})	1—2	1.399
	1—12	1.412		1—7	1.436
	2—3	1.405		2—3	1.404
	6—12	1.463		3—4	1.421
				7—8	1.406
XXI (C_{2v})	1—2	1.422		8—14	1.442
	1—5	1.435		11—12	1.362
	2—3	1.394		12—13	1.448
	5—6	1.409		13—14	1.365
	6—10	1.442			
	8—9	1.444			
	9—10	1.366			

In the case of heptalene (VII), we have calculated the bond-length distribution in the first excited state using the same SCF procedure as that used for the ground state, except for the use of a different value 3.3 Å^{-1} (1.7 Å^{-1} for the ground state) for the exponent in the exponential expression of the resonance integral.[50] The results are presented in Table 5; all the possible starting bond distortions produce a unique set of bond

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[47] A. Toyota and T. Nakajima, *Chem. Phys. Lett.*, **6**, 144 (1970).

[48] T. Nakajima, A. Toyota, and H. Yamaguchi, "Aromaticity, Pseudoaromaticity and Antiaromaticity." The 3rd Jerusalem Symposium, The Israel Academy of Sciences and Humanities, Jerusalem (1970), p. 227.

[49] M. O. Sevilla, S. H. Flajser, G. Vincow, and H. J. Dauben, Jr., *J. Amer. Chem. Soc.*, **91**, 4139 (1969).

[50] Y. Fujimura, H. Yamaguchi, and T. Nakajima, This Bulletin, **45**, 384 (1972).

lengths belonging to the point group D_{2h} and the bond lengths of the peripheral bonds are nearly equalized, which supports the prediction given by the symmetry rule. The marked difference in the geometrical structure between the ground state and the lowest excited state in heptalene gives the main reason for the appearance of a long absorption tail throughout the visible region in its absorption spectrum.[28)]

On the other hand, there are cases where a molecule has an E_1-E_0 value reasonably higher than the critical value, but the separation between the second and first excited states is relatively small. The E_2-E_1 value for I^{2-} is of the same order of magnitude as the critical value, and those for the peri-condensed hydrocarbon, XVII, the fulvalenes, XXI and XXII, and the dianions, IV^{2-} and VII^{2-}, are significantly smaller than the critical value for the first excited state. For XXI and XXII, the results of SCF calculations presented in Table 5 agree with the predictions given by the symmetry rule in indicating that on exciting to the first excited state, the molecular symmetries are reduced to C_{2v} from D_{2h}. This provides a probable explanation for the fact that the longest wave-length absorption bands of these molecules are relatively broad.[51)]

Azulene (XI) has an E_2-E_1 value reasonably larger than the critical value and no symmetry reduction is expected on excitation to the first excited state. A recent analysis of the vibrational structures of the longest wavelength absorption band indicates that azulene retains C_{2v} symmetry in the first excited state.[52)]

Conclusion

In predicting the geometrical structures with respect to the C–C bond distances of nonalternant hydrocarbons on the basis of the pseudo Jahn-Teller theorem, we have assumed that only the lowest excited state plays a dominant role in determining the most soft nuclear displacement. In spite of this very crude approximation, the predicted types of the energetically most favorable bond distortions and molecular-symmetry reductions are in good agreement with the results of the variable bond-length SCF MO calculations and available experimental facts.

The criterion for the symmetry reduction obtained above, that if the lowest excitation energy predicted assuming the full molecular-symmetry for a nonalternant hydrocarbon is smaller than *ca.* 1.2 eV, the molecule should be distorted into a less symmetrical nuclear configuration, is applicable to the conjugated hydrocarbons in general. It is interesting to mention, in this connection, the symmetry reductions possible in large cyclic polyenes $C_{4n+2}H_{4n+2}$.[10)] The lowest excitation energies calculated assuming the full molecular-symmetry (D_{6h}) for $C_{18}H_{18}$ and $C_{30}H_{30}$, both known to date,[53)] have been reported to be about 1.6[54–56)] and 0.95 eV,[55)] respectively. It is thus expected that $C_{30}H_{30}$ should suffer a symmetry reduction, and that contrary to the previous assumption,[10,55)] there exists no symmetry reduction ($D_{6h} \rightarrow D_{3h}$) in the ground state of $C_{18}H_{18}$. Actually, as for $C_{18}H_{18}$, the lowest excitation energy (1.6 eV) predicted assuming D_{6h} symmetry is in good agreement with the position of the longest wave-length absorption band ($^1B_{2u}$) recently discovered by Blattmann *et al.*[54)] The symmetry reduction in $C_{4n+2}H_{4n+2}$ is thus predicted to occur at $n \sim 5$, which is in agreement with the result obtained by Binsch and Heilbronner using a more sophisticated theoretical procedure.[12)]

[51)] W. von E. Doering, "Theoretical Organic Chemistry, Kekulé Symposium," Butterworths, London (1958), p. 35, and personal communication.

[52)] G. R. Hunt and I. G. Ross, *J. Mol. Spectrosc.*, **9**, 50 (1962).

[53)] F. Sondheimer, R. Wolovsky, and Y. Amiel, *J. Amer. Chem. Soc.*, **84**, 274 (1962).

[54)] H. R. Blattmann, E. Heilbronner, and G. Wagnière, *ibid.*, **90**, 4786 (1968).

[55)] H. C. Longuet-Higgins and L. Salem, *Proc. Roy. Soc.*, (London), **A257**, 445 (1960).

[56)] M. Gouterman and G. Wagnière, *J. Chem. Phys.*, **36**, 1188 (1962).