The Molecular-Symmetry Reduction in Open-Shell Conjugated Hydrocarbons

Azumao Toyota and Takeshi Nakajima*

Department of Chemistry, Faculty of General Education, Yamagata University, Yamagata 990

** Department of Chemistry, Faculty of Science, Tohoku University, Sendai 980*

(Received September 20, 1976)

On the basis of the second-order Jahn-Teller theorem, we propose a criterion for predicting the stable ground-state geometrical structures of open-shell conjugated hydrocarbons. It is found that in contrast with the cases of the parent closed-shell hydrocarbons no molecular symmetry reduction occurs in the ion radicals of the C_mH_{m-2} cata-condensed nonalternant hydrocarbons, such as pentalene and heptalene. On the other hand, it is revealed that the ion radicals of fulvalene systems suffer the molecular symmetry reduction from D_{2h} to C_{2v}. In addition, the electronic spectra were calculated using the stable geometrical structures obtained by use of the semiempirical open-shell SCF MO method.

It is well known that the ground states of odd cyclic polyene radicals, *e.g.* the cyclopentadienyl radical, and ion radicals of even cyclic polyenes, *e.g.* the benzene positive ion, are unstable in the fully symmetrical nuclear arrangements and undergo the first-order Jahn-Teller distortions.[1] Further, the closed-shell C_mH_{m-2} cata-condensed nonalternant hydrocarbons, considered to be formed by the introduction of a cross-link between the two carbon atoms of like parity in even cyclic polyenes with $4n$ π-electrons, such as pentalene and heptalene, are found to suffer the second-order (pseudo) Jahn-Teller effects in the fully symmetrical nuclear arrangements and to be unstable with respect to the nuclear deformation of bond alternation type.[2] Our present interest is to examine whether the second-order Jahn-Teller distortions occur or not in the ground states of the ion radicals of C_mH_{m-2} cata-condensed nonalternant systems.

In order to predict the stable molecular shapes of closed-shell conjugated hydrocarbons, we have proposed a symmetry rule on the basis of the so-called pseudo Jahn-Teller theorem,[3-5] assuming that only the lowest-lying excited state plays a dominant role for the problem of a molecular symmetry reduction. In spite of the very drastic approximation, this rule has been shown to hold for a large number of conjugated hydrocarbons.[2,3,6-8]

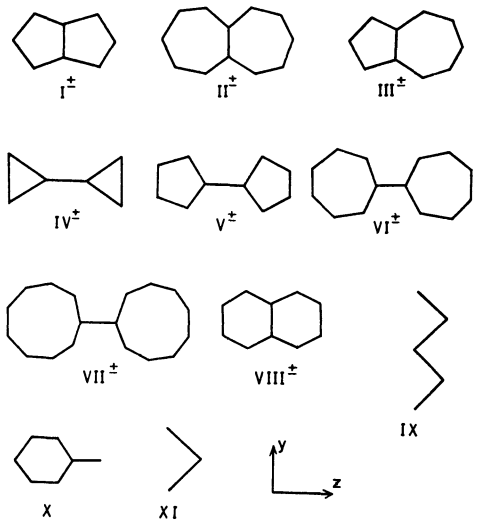

Fig. 1. Carbon skeletons and choice of axes for some open-shell conjugated hydrocarbons. The + or − sign of the superscript refers to the cation or the anion radical, respectively. I: Pentalene, II: heptalene, III: azulene, IV: triafulvalene, V: pentafulvalene, VI: heptafulvalene, VII: nonafulvalene, VIII: naphthalene, IX: pentadienyl radical, X: benzyl radical, XI: allyl radical.

In this paper, we derive a criterion for a molecular symmetry reduction in open-shell conjugated systems, and examine the stable molecular shapes of some ion radicals of (a) C_mH_{m-2} cata-condensed nonalternant systems, (b) $C_{4n+2}H_{4n}$ fulvalene systems, and (c) alternant systems (Fig. 1). Moreover, we calculate the electronic spectra using the stable geometrical structures obtained by use of the open-shell SCF MO method.

Theoretical

The Second-order Jahn-Teller Effect. The method for predicting the stable molecular shapes of conjugated hydrocarbons is based on the second-order Jahn-Teller theorem. First we assume a fully symmetrical nuclear arrangement as the unperturbed nuclear configuration for an open-shell conjugated hydrocarbon. We further assume that in the unperturbed nuclear configuration all the fully symmetrical bond distortions take place until the first-order energy equilibrium is reached. The unperturbed doublet electronic wavefunctions ψ_0, ψ_1, $\cdots$, ψ_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 fully symmetrical (first-order) nuclear arrangement by means of the ith normal coordinate of nuclear motion Q_i. On the basis of the same approximation as used previously,[3] the energy of the ground state after the deformation may be written as

$$E(Q_i) = E_0 + \frac{1}{2}\left\{k - 2\sum_{n(\neq 0)} \frac{|\langle\psi_n|(\partial v/\partial Q_i)_0|\psi_0\rangle|^2}{(E_n - E_0)}\right\} Q_i^2$$

where k and v represent the force constant for an sp^2 hybridized C–C σ-bond and the operator of one electron nuclear-electron potential energy, respectively.

According to the above equation, the curvature of $E(Q_i)$ with respect to the nuclear deformation Q_i, that is, $\{k - 2\sum_{n(\neq 0)}|\langle\psi_n|(\partial v/\partial Q_i)_0|\psi_0\rangle|^2/(E_n - E_0)\}$, can be identified as the force constant for the nuclear deformation Q_i. If a given matrix element $\langle\psi_n|(\partial v/\partial Q_i)_0|\psi_0\rangle$ is nonvanishing and the associated energy gap $E_n - E_0$ is sufficiently small, the force constant can be negative and the initial nuclear configuration would be unstable with respect to the nuclear deformation Q_i.

Such a nuclear deformation is called the pseudo, or the second-order Jahn-Teller effect.

Criterion for a Molecular Symmetry Reduction. In order to estimate the value of the force constant, we make the following approximation: the infinite sum over the excited states is replaced by one term corresponding to the lowest excited state, ψ_1. It has been shown that this approximation is amply justified at least in the closed-shell conjugated hydrocarbons.[2,3,6-8]

We now focus our attention on the matrix element, $\langle\psi_1|(\partial v/\partial Q_i)_0|\psi_0\rangle$, called the relaxability of the molecule along the nuclear displacement Q_i.[9] It is obvious from the symmetry argument that this integral is nonvanishing, only if the symmetry of the direct product $\Gamma(\psi_0)\times\Gamma(\psi_1)$ is identical with that of the nuclear deformation Q_i. We can thus determine the symmetry of nuclear deformation effective for the molecular symmetry reduction. It should be noted that in the closed-shell systems the ground state is, in principle, totally symmetric, the symmetry of nuclear deformation Q_i is identical with that of the lowest excited singlet state.

In order to calculate electronic states of open-shell conjugated hydrocarbons, we employ Longuet-Higgins and Pople's method.[10] According to their method, a doublet ground state wavefunction is written as

$$\psi_0 = |\varphi_1\bar{\varphi}_1 \cdots \varphi_{m-1}\bar{\varphi}_{m-1}\varphi_m|$$

where φ_m is the molecular orbital of an odd α electron. As the main electron configuration of the lowest excited doublet state, the following two types of electron excitation are possible:

(i) The excitation of the β electron in φ_{m-1} to φ_m, which gives rise to the doublet wavefunction

$$\psi_A = |\varphi_1\bar{\varphi}_1 \cdots \varphi_{m-1}\bar{\varphi}_m\varphi_m|$$

(ii) The excitation of the odd electron to φ_{m+1}, which gives rise to the doublet wavefunction

$$\psi_B = |\varphi_1\bar{\varphi}_1 \cdots \varphi_{m-1}\bar{\varphi}_{m-1}\varphi_{m+1}|$$

Since $(\partial v/\partial Q_i)_0$ is the one-electron operator, the matrix element $\langle\psi_1|(\partial v/\partial Q_i)_0|\psi_0\rangle$ is reduced to $\int\rho_{01}(\partial v/\partial Q_i)_0 d\tau$, where ρ_{01} is the so-called transition density. The value of this integral may become very large if the transition density is localized in the regions near nuclei which are involved in the motion. The transition density between the ground and the lowest excited doublet state is given by $\varphi_{m-1}\varphi_m$, if the latter state is ψ_A, or $\varphi_m\varphi_{m+1}$ if it is ψ_B.

It should be noted in this connection that for closed-shell systems the transition density between the ground and the lowest excited singlet state corresponding to the orbital jump $\varphi_i\rightarrow\varphi_j$, in which φ_i and φ_j are respectively the highest occupied and the lowest vacant molecular orbitals, is given by $\sqrt{2}\,\varphi_i\varphi_j$. Therefore, in so far as the transition densities for both open and closed-shell systems are assumed not to vary significantly according to the molecular orbitals concerned, the square of the matrix element, $|\langle\psi_1|(\partial v/\partial Q_i)_0|\psi_0\rangle|^2$, for open-shell systems should be about one half as that for closed-shell systems. As for closed-shell systems, it should be kept in mind that the following criterion[3] for the molecular symmetry reduction holds for a variety of molecules: if the lowest excitation energy of a molecule, calculated assuming the full molecular symmetry, is smaller than *ca.* 1.2 eV, the force constant for a certain antisymmetrical nuclear vibration should be negative, and the molecule would be distorted into a less symmetrical nuclear arrangement.

From the above arguments, we may now draw a criterion for a molecular symmetry reduction in open-shell conjugated hydrocarbons, which states: if the lowest doublet excitation energy of a given molecule, calculated assuming the full molecular symmetry, is smaller than a critical value, *ca.* 0.6 eV, the initial nuclear arrangement is unstable with respect to a certain antisymmetrical C–C nuclear deformation, and the molecule would be distorted into a less symmetrical nuclear arrangement. As to the actual type of nuclear deformation Q_i, it is predicted by examining the distributions of the transition density ρ_{01}.

Since it is based on the second-order Jahn-Teller theorem, the above criterion gives only the type of the most favorable bond distortion. In order to obtain the equilibrium C–C bond-length at which the nuclei of the real molecule will settle, we use the semiempirical open-shell SCF MO method in conjunction with the variable bond-length technique.[11,12]

Results and Discussion

In Table 1 are listed the lowest excitation energies, calculated by using the semiempirical open-shell SCF

Table 1. The lowest excitation energies and symmetries of the ground and the lowest excited doublet states of open-shell conjugated hydrocarbons

Molecule (Point group and ground state symmetry)	Lowest Excited State	
	ΔE (eV)	Symmetry
Pentalene$^+$ (D_{2h}, B_{3u})[a]	1.50	A_u
Pentalene$^-$ (D_{2h}, A_u)	1.77	B_{3u}
Azulene$^+$ (C_{2v},A_2)	1.31	B_1
Azulene$^-$ (C_{2v}, B_1)	1.18	A_2
Heptalene$^+$ (D_{2h}, B_{2g})	1.19	B_{1g}
Heptalene$^-$ (D_{2h}, B_{1g})	1.02	B_{2g}
Nonalene$^+$ (D_{2h}, B_{3u})	0.78	A_u
Nonalene$^-$ (D_{2h}, A_u)	0.99	B_{3u}
Triafulvalene$^+$ (D_{2h}, B_{3u})	1.55	A_u
Triafulvalene$^-$ (D_{2h}, B_{1g})	0.44	A_u
Pentafulvalene$^+$ (D_{2h}, A_u)	0.47	B_{1g}
Pentafulvalene$^-$ (D_{2h}, B_{2g})	1.22	B_{1g}
Heptafulvalene$^+$ (D_{2h}, B_{3u})	1.22	A_u
Heptafulvalene$^-$ (D_{2h}, B_{1g})	0.35	A_u
Nonafulvalene$^+$ (D_{2h}, A_u)	0.31	B_{1g}
Nonafulvalene$^-$ (D_{2h}, B_{2g})	1.17	B_{1g}
Odd linear polyene radicals		
C_3H_5 (C_{2v}, A_2)	3.05	B_1
C_5H_7 (C_{2v}, B_1)	2.10	A_2
C_7H_9 (C_{2v}, A_2)	1.95	B_1
C_9H_{11} (C_{2v}, B_1)	1.59	A_2
$C_{11}H_{13}$ (C_{2v}, A_2)	1.49	B_1
$C_{17}H_{19}$ (C_{2v}, B_1)	1.37	A_2
Benzyl radical(C_{2v}, B_1)	2.54	B_1
Naphthalene$^+$ (D_{2h},A_u)	0.90	B_{3u}
Naphthalene$^-$ (D_{2h}, B_{2g})	0.90	B_{1g}

a) The + or − sign refers to the cation or the anion radical, respectively.

MO CI method and the symmetries of the ground and the lowest excited doublet states at the fully symmetrical nuclear arrangements.

The Ion Radicals of C_mH_{m-2} Cata-condensed Nonalternant Systems. It is found in a previous paper[2] that in the $C_{4n}H_{4n-2}$ closed-shell systems which has a cross-link between the two carbon atoms of like parity all the lowest excitation energies calculated assuming the fully symmetrical structures are significantly smaller than the critical value, which results in the molecular symmetry reduction accompanied by a marked double-bond fixation in the peripheral carbon skeleton. On the other hand, in $C_{4n+2}H_{4n}$ with a cross-link between the two carbon atoms of like parity the lowest excitation energies are predicted to be considerably larger than the critical value for small members and a molecular symmetry reduction would not occur until the number of carbon atoms increases to a certain value. Pentalene (1-methylpentalene) and heptalene, both having $4n$ carbon atoms, have successfully been synthesized by Bloch *et al.*[13] and Dauben and Bertelli,[14] respectively, and are known to exhibit the polyolefinic characters. The theoretical studies on both molecules revealed that at the fully symmetric D_{2h} configuration the lowest excited singlet state (B_{3g}) is nearly degenerate with the ground state (A_g) and therefore the stable geometrical structure is predicted to be of C_{2h} symmetry, showing a marked double-bond fixation in the periphery.

In the cation radicals of pentalene, heptalene, and nonalene, the distributions of the transition densities are of b_{3g} symmetry and they have a tendency to distort into a skew structure corresponding to one of the Kekulé type structures (Fig. 2). However, since the energy gaps of these radicals are considerably larger than the critical value, *ca.* 0.6 eV, we cannot expect such a molecular symmetry reduction as observed in the parent closed-shell hydrocarbons.

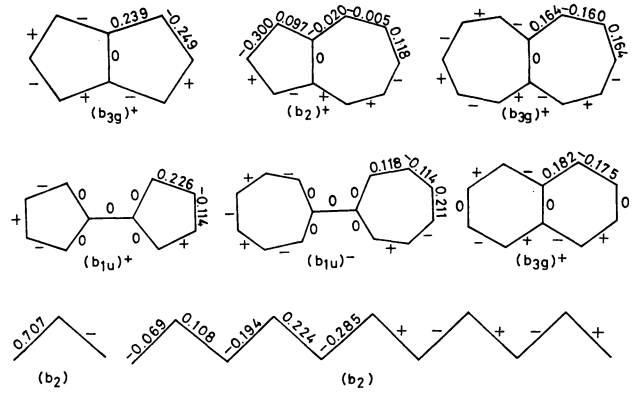

Fig. 2. Symmetries and distributions of the two-center components of transition densities (ρ_{01}). The + or − sign of the superscript written after the parentheses refers to the cation or the anion radical, respectively.

Moreover, in the anion radicals of the above molecules, the situation is the same as that seen in the cation radicals, *i.e.*, no molecular symmetry reduction occurs.

In the cation and anion radicals of azulene belonging to $C_{4n+2}H_{4n}$ system, there is no possibility of a molecular symmetry reduction from C_{2v} to C_s through the nuclear deformation of b_2 symmetry, because of the relatively large energy gap.

Results of SCF MO calculations agree that all these ion radicals, independent of the number of carbon atoms, undergo no molecular symmetry reduction (Fig. 3).

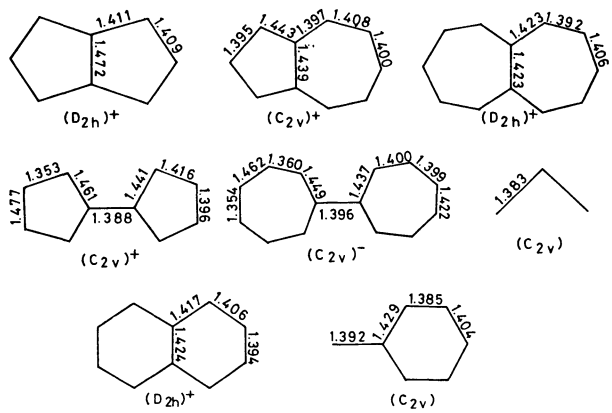

Fig. 3. Molecular symmetry groups and C–C bond lengths (in Å unit).

TABLE 2. TRANSITION ENERGIES AND INTENSITIES

Molecule (Point group)	Transition Symmetry	ΔE (eV)	f (c.g.s)	Obsd (eV)
Azulene$^+$ (C_{2v})	B_1	1.31	0.002	1.40[a]
	A_2	2.37	0.002	2.60
	B_1	2.42	0.003	
	B_1	3.23	0.036	3.37
	A_2	3.83	0.088	
	A_2	4.34	0.012	
Azulene$^-$ (C_{2v})	A_2	1.18	0.003	1.41[a]
	A_2	2.49	0.014	
	B_1	2.82	0.003	2.80
	B_1	2.99	0.091	
	B_1	3.56	0.002	
	B_1	3.93	0.000	
	A_2	4.18	0.031	4.25
	A_2	4.53	0.023	
Benzyl radical (C_{2v})	B_1	2.54	0.000	2.74 (0.003)[b]
	A_2	2.63	0.000	
	B_1	4.21	0.000	3.90 (0.025)
	A_2	4.32	0.127	
	B_1	5.33	0.675	
Naphthalene$^+$ (D_{2h})	B_{3u}	0.90	forb.	
	B_{1g}	1.74	0.097	1.74[a]
	B_{2u}	2.35	0.005	2.51
	B_{2u}	3.30	0.185	3.16
	B_{3u}	3.50	forb.	
	B_{1g}	4.27	0.175	4.00
	B_{1g}	4.96	0.487	
Naphthalene$^-$ (D_{2h})	B_{1g}	0.90	forb.	1.10[a]
	B_{3u}	1.74	0.097	1.49
	A_u	2.35	0.005	2.64
	A_u	3.30	0.185	3.32
	B_{1g}	3.50	forb.	
	B_{3u}	4.27	0.175	3.79 4.21
	B_{3u}	4.96	0.487	

a) Ref. 15. b) Refs. 21 and 22.

It should be noted that using the fully symmetric C_{2v} geometrical structures obtained, we can well reproduce the observed electronic spectra[15] for both ion radicals of azulene (Table 2).

The Ion Radicals of Fulvalene Systems. Of fulvalene systems, $C_{4n+2}H_{4n}$, pentafulvalene ($n=2$), heptafulvalene ($n=3$), and the ion radicals of heptafulvalene have been prepared, and their UV and ESR spectra have been reported.[16,17] Sevilla *et al.* have found that in the cation radical of heptafulvalene the unpaired spin density is delocalized throughout the molecule, while in the anion radical, the spin density is localized essentially on a single seven-membered ring. In a previous paper[18] we have explained the origin of the sharp contrast between the spin density distributions of the cation and anion radicals of heptafulvalene, by examining the energetically favorable molecular symmetry groups and C–C nuclear arrangements, using the open-shell SCF MO method (Fig. 3).

In the cation radicals of triafulvalene ($n=1$) and heptafulvalene ($n=3$), the ground state is of B_{3u} symmetry and the lowest excited doublet state is of A_u one in the fully symmetric D_{2h} configuration. The associated energy gaps of interest (1.55 and 1.22 eV, respectively) are considerably larger than the critical value, so that we cannot expect the molecular symmetry reduction to occur from D_{2h} to C_{2h} through the nuclear deformation of b_{3g} symmetry. On the other hand, in the anion radicals for both molecules, the ground state is of B_{1g} symmetry and the lowest excited state, nearly degenerate with the ground state, is of A_u one. It is therefore expected that in the anion radicals the molecular symmetry reduction occurs from D_{2h} to C_{2v} through the nuclear deformation of b_{1u} symmetry. Of the several nuclear deformation with the b_{1u} symmetry, the one actually effective for the molecular symmetry reduction is predicted by examining the distributions of the transition density shown in Fig. 2.

Further, in the cation radicals of pentafulvalene ($n=2$) and nonafulvalene ($n=4$), the lowest excited state (B_{1g}) is very close to the ground state (A_u). Both ion radicals are predicted to undergo the second-order Jahn-Teller distortions from D_{2h} to C_{2v} through the nuclear deformation of b_{1u} symmetry, whereas in the anion radicals, the situation is found to be the same as that seen in the cation radicals of triafulvalene and heptafulvalene.

From the above results, we can deduce the following rules concerning the molecular symmetry reduction in the ion radicals of $C_{4n+2}H_{4n}$ fulvalene systems: (i) When n is odd, a molecular symmetry reduction occurs in the anion radicals, while (ii) when n is even, it occurs in the cation radicals. These rules are interpreted in terms of Hückel MO energy level diagrams as follows: if n is odd, the lowest vacant molecular orbitals of fulvalene systems, whose symmetries are b_{1g} and a_u, are accidentally degenerate with each other. On the other hand, if n is even, the highest occupied molecular orbitals of b_{1g} and a_u symmetries are also accidentally degenerate. Hence for anion radicals of case (i), there are two ways of assigning one electron to the doubly degenerate molecular orbitals, which results in the degeneracy of the ground state in the simple one-electron picture. If we take into account the electron repulsion, this degeneracy is removed, but the energy gap between the two split states is still small as can be seen in Table 1. In a similar manner, for cation radicals of case (ii), there also occurs the degeneracy of the ground state in the one-electron approximation.

The Odd Alternant and Other Ion Radicals. As to $C_{2n+1}H_{2n+3}$ odd linear polyene radicals, we deal with those with $n=1$ to 8. In smaller systems, the energy gaps are significantly larger than the critical value, and there would be no possibility for the molecular symmetry reduction to occur. However, since as n increases, the energy gap tends to decrease and since in the hypothetical infinite odd cyclic polyene radical, which is mathematically equivalent to the infinite odd linear polyene radical,[19,20] the nuclear distortion of bond alternation type should certainly occur, it may be expected that in molecules with n larger than a certain limiting value there is a possibility of the second-order Jahn-Teller distortions to take place through the nuclear deformation of bond alternation type (Fig. 2).

In benzyl radical, the symmetry of the lowest excited state is the same as that of the ground state and the second excited state is located at the appreciably higher region, *i.e.*, 2.63 eV, so that there is no possibility for the molecular symmetry reduction to occur.

In the cation and anion radicals of naphthalene, they undergo no molecular symmetry reduction, since the calculated energy gaps are larger than the critical value.

Results of SCF MO calculations support the above predictions, and the transition energies calculated at the fully symmetric D_{2h} configurations for both ion radicals of naphthalene and those at the fully symmetric C_{2v} configuration of benzyl radical reproduce well the respective observed transition energies (Table 2).[15,21,22]

Conclusion

The problem of a molecular symmetry reduction in the open-shell conjugated systems are discussed on the basis of the second-order Jahn-Teller theorem. In contrast with the cases of the parent closed-shell hydrocarbons, the ion radicals of C_mH_{m-2} cata-condensed nonalternant hydrocarbons having $4n$ carbon atoms undergo no pseudo Jahn-Teller distortions. In the ion radicals of fulvalene systems, $C_{4n+2}H_{4n}$, a molecular symmetry reduction from D_{2h} to C_{2v} occurs in the cation radicals if n is even, and in the anion radicals if n is odd. It is found further that in odd linear polyene radicals, $C_{2n+1}H_{2n+3}$, with n larger than a certain critical value the nuclear configuration with the full molecular symmetry group should be unstable with respect to the nuclear deformation of bond alternation type.

Finally, it should be noted that the success of the predictions based on the energy-gap law is due to the assumption that the transition density does not vary significantly according to the molecular orbitals concerned, *i.e.*, the value of the matrix element, $\langle\psi_1|(\partial v/\partial Q_i)_0|\psi_0\rangle$, called the relaxability of the molecule along the nuclear displacement is almost constant from molecule to molecule. In view of the good agreement between theory and experiment obtained in this paper, we believe

that this assumption does hold at least for a variety of conjugated hydrocarbons considered in this paper.

The numerical calculation was carried out at Tohoku University with an NEAC 2200-700 electronic computer.

References

1) L. Salem, "The Molecular Orbital Theory of Conjugated Systems," Benjamin, New York (1966), p. 466.
2) A. Toyota and T. Nakajima, *Bull. Chem. Soc. Jpn.*, **46**, 3681 (1973).
3) T. Nakajima, A. Toyota, and S. Fujii, *Bull. Chem. Soc. Jpn.*, **45**, 1022 (1972).
4) R. G. Pearson, *J. Am. Chem. Soc.*, **91**, 1252, 4947 (1969).
5) R. G. Pearson, *J. Chem. Phys.*, **52**, 2167 (1970).
6) T. Nakajima, "Topics in Current Chemistry," Vol. 32, Spring-Verlag, Heidelberg (1972), p. 1.
7) A. Toyota and T. Nakajima, *Bull. Chem. Soc. Jpn.*, **46**, 2284 (1973).
8) A. Toyota, *Bull. Chem. Soc. Jpn.*, **48**, 1152 (1975).
9) L. Salem, *Chem. Phys. Lett.*, **3**, 99 (1969).
10) H. C. Longuet-Higgins and J. A. Pople, *Proc. Phys. Soc. (London)*, **A68**, 591 (1955).
11) T. Nakajima and A. Toyota, *Chem. Phys. Lett.*, **3**, 272 (1969).
12) H. Yamaguchi, T. Nakajima, and T. L. Kunii, *Theor. Chim. Acta*, **12**, 349 (1968).
13) R. Bloch, R. A. Marty, and P. de Mayo, *J. Am. Chem. Soc.*, **93**, 3071 (1971).
14) H. J. Dauben and D. J. Bertelli, *J. Am. Chem. Soc.*, **83**, 4659 (1973).
15) T. Shida and S. Iwata, *J. Am. Chem. Soc.*, **95**, 3473 (1973).
16) W. von E. Doering, "Theoretical Organic Chemistry," (Kekulé Symposium), Butterworths Sci. Publ. (1958), p. 44.
17) M. D. Sevilla, S. H. Flajser, G. Vincov, and H. J. Dauben, *J. Am. Chem. Soc.*, **91**, 4139 (1969).
18) A. Toyota and T. Nakajima, *Chem. Phys. Lett.*, **6**, 144 (1970).
19) H. Labhart, *J. Chem. Phys.*, **27**, 957 (1957).
20) M. Tsuji, S. Huzinaga, and T. Hasino, *Rev. Mod. Phys.*, **32**, 425 (1960).
21) G. Porter and E. Strachan, *Spectrochim. Acta*, **12**, 299 (1958).
22) S. Leach, in "Luminescence of Organic and Inorganic Materials," (H. P. Kallmann and G. M. Spruch, eds.), Wiley, New York (1962), p. 126.