Bond Distortions in Nonbenzenoid Phanes

Masahiro Kataoka and Takeshi Nakajima *
Department of Chemistry, Faculty of Science, Tohoku University, Sendai 980, Japan

The C–C bond alternations in *syn*-[2.2]azulenophane, *syn*-[2.2]cycloprop[*f*]indenophane, and [2.2]-pentalenophane have been investigated by use of second-order Jahn–Teller theory and the Pariser–Parr–Pople-type SCF MO method. It has been shown that *syn*-[2.2]azulenophane suffers no bond distortions, whereas *syn*-[2.2]cycloprop[*f*]indenophane suffers a_2 bond alternation, which is attributed to transannular interaction. Further, in [2.2]pentalenophane and [2.2]-*s*-indacenophane, C_{2h} and D_2 bond-alternating structures are obtained, the transannular interaction stablising the D_2 more than the C_{2h} structures.

Nonbenzenoid phanes[1] have recently attracted much attention, arising from the presence of transannular interaction. Luhowy and Keehn[2] and Kato *et al.*[3] have independently prepared *syn*- and *anti*-[2.2]azulenophane and have reported that the electronic[1–3] and photoelectron spectra[4] of the isomers are very similar to each other. Bickert *et al.*[5] tried to synthesise [2.2](2,6)-*s*-indacenophane in order to test the suggestion that full overlap of two conjugated molecules results in appreciable stabilisation. Using MNDO/1 and MINDO/3, Böhm *et al.*[6] have carried out model calculations of transannular interactions in dimeric phanes from pentalene and *s*-indacene. They found that in these dimers the bond-alternating structure (with C_{2h} symmetry) is more stable than the delocalised system (with D_{2h} symmetry) when the intersubsystem distance is between 2 and 5 Å.

Transannular interaction in [2.2]phanes generally produces first excited states of lower energy than those of the composite conjugated hydrocarbons. Indeed, the lowest excitation energies of the azulenophanes (1.4—1.7 eV) are smaller than that of azulene (2 eV).[2] The small magnitude of the first excitation energy may be responsible for the occurrence of the second-order Jahn–Teller bond distortion[7–9] in the ground state of a phane. Moreover, pentalenophane is intuitively expected to distort into the two types of bond-alternating structure, since the two bond-alternating pentalenes (C_{2h}) can be superimposed in phase or out of phase: the former case belongs to the C_{2h} category and the latter to the D_2 category.

In this paper we attempt to predict the most stable geometrical structures with respect to the C–C bond lengths of subsystems of *syn*-[2.2]azulenophane (**1**), *syn*-[2.2]cycloprop-[*f*]indenophane (**2**), [2.2]pentalenophane (**3**), and [2.2]-*s*-indacenophane (**4**) on the basis of second-order Jahn–Teller theory. The predictions have been further examined by using the dimer model[10,11] and the semiempirical SCF MO method.

Theory

The Symmetry Rule.—The symmetry rule has proved useful for predicting the energetically most favourable molecular structures of conjugated hydrocarbons.[12–14] We give here only an outline of the theory.[7–9] First, we assume a fully symmetrical nuclear configuration for a conjugated hydrocarbon. By using second-order perturbation theory, the ground-state energy of the conjugated molecule, after a C–C bond-stretching distortion Q, can be written as in equation (1), where k is the force constant for the C–C σ-bond and H_π is the Hamiltonian for π-electrons.

$$E_0(Q) = E_0 + \frac{1}{2}\left[k - 2\sum_{n\neq 0}\frac{|\langle\psi_0|(\partial H_\pi/\partial Q)_0|\psi_n\rangle|^2}{E_n - E_0}\right]Q^2 \quad (1)$$

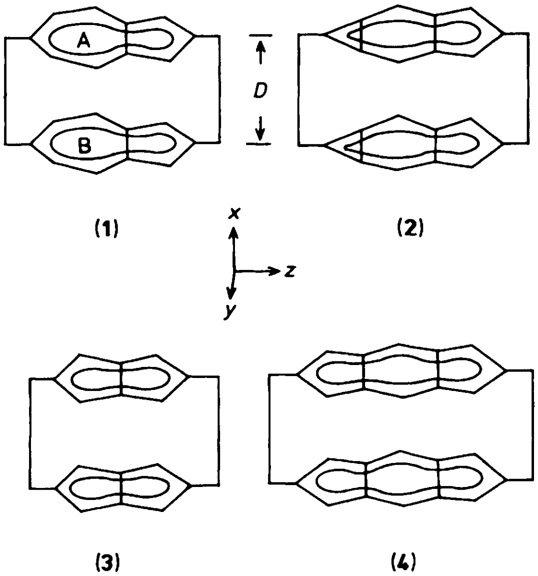

Figure 1. Carbon skeletons of *syn*-[2.2]azulenophane, *syn*-[2.2]cycloprop[*f*]indenophane, [2.2]pentalenophane, and [2.2]-*s*-indacenophane; D represents the distance between the two subsystems

The force constant for Q can be identified with the terms of equation (1) in square brackets, and will be negative when the second term is larger than k. If the force constant is negative, the energy should be lowered by the bond distortion Q, and if Q is not totally symmetric a molecular-symmetry reduction will occur spontaneously. Now, we assume that only the lowest excited states are important in the summation of equation (1). The symmetry of the bond distortion with the smallest force constant is then identical with that of the direct product between the symmetries of the ground and the relevant excited singlet state (ψ_n). It has been shown that if the energy gap $E_n - E_0$ calculated by assuming the fully symmetrical nuclear arrangement is smaller than about 1.2 eV, the molecule should be distorted into a less symmetrical structure.[12–14] The most favourable bond distortion is predicted from the distribution of two-centre components of transition density, ρ_{0n}, over the molecular skeleton. When the excited singlet corresponds to a one-electron transition between molecular orbitals φ_i and φ_j, ρ_{0n} is given by $\sqrt{2}\varphi_i\varphi_j$.

Computational Method.—In order to obtain the most stable structure of a phane, we carry out the semiempirical model calculations on the basis of the following assumptions. We use the dimer model,[10,11] consisting of two identical π-electron systems, A and B, stacked in relation to each other: the effect of the methylene bridges connecting the two subsystems upon the π-electron structures is not explicitly considered. The distance between the subsystems (D) is fixed at 3.3 Å, which is the average inter-subsystem distance of [2.2](2,6)azulenophane.[3b]

The Pariser–Parr–Pople-type semiempirical SCF MO CI method is used in conjunction with the variable bond-length technique.[15–17] In evaluating the excitation energies, configuration interactions among 55 single excitations are included. For the resonance integrals between the subsystems A and B, we take into account only those between the nearest neighbours (μ in A and μ' in B), and use the approximation (2), where β^b and

$$\beta_{\mu\mu'}{}^{AB}(r)/\beta^{b} = S_{\mu\mu'}{}^{AB}(r)/S^{b} \qquad (2)$$

S^b are the resonance and the overlap integral of benzene, respectively, and $S_{\mu\mu'}{}^{AB}(r)$ is the σ-type overlap integral. Other β parameters between the two subsystems are neglected. We use the effective nuclear charge of 2.65 for the carbon atom, determined by Burns' rules.[18] Using this value and the foregoing approximations, we obtained the first transition energy of [2.2](1,4)cyclophane (3.78 eV), consistent with experimental values (3.76 and 3.81 eV).[19]

The total energy is assumed to be the sum of the π-electron energy and the σ-core energies of the parent molecules, the latter being calculated by using equation (3), where $\Delta r_{\mu\nu}/\text{Å} = 1.5336 - r_{\mu\nu}/\text{Å}$.

$$E_{\sigma}/\text{kcal mol}^{-1} = \sum_{\mu<\nu} [857(\Delta r_{\mu\nu}/\text{Å})^2 + 329(\Delta r_{\mu\nu}/\text{Å})^3] \qquad (3)$$

In addition, we use the bond order–bond length relationship (4) including up to the third-order anharmonic term where p is the bond order.

$$r/\text{Å} = 2.4055 - (0.755 + 0.393p)^{\frac{1}{2}} \qquad (4)$$

Results and Discussion

In the Table are listed the energy gaps and the symmetries of the first and second excited singlet states of the phanes with the highest symmetries at the inter-subsystem distance of 3.3 Å. These states originate from the first excited singlet states of the parent molecules, except for the $^1B_{2g}$ state of the phane (**4**), which arises from the second excited singlet state of *s*-indacene. The transannular interaction causes energy splitting of the HOMOs and LUMOs of the parent molecules. In the phanes, the energies of the LUMO and the next HOMO decrease because of the bonding interaction between the two subsystems, whereas those of the HOMO and the next LUMO increase because of the antibonding interaction. Accordingly, the energy difference between the HOMO and the LUMO becomes smaller in the phane than in its parent conjugated hydrocarbon. This leads to a low-lying first excited singlet state corresponding to one-electron excitation from HOMO to LUMO. Such excited states include the $^1A_2$ states of the phanes (**1**) and (**2**). In the phane (**3**), this type of excited singlet state (^1A_u) is lower in energy than the closed-shell ^1A_g state, because the energy difference between the HOMO and the LUMO of pentalene is very small. On the other hand, the second excited singlet states of the phanes (**1**), (**2**), and (**3**) are produced by configuration interactions between two zero-order degenerate excitations: next HOMO→LUMO and HOMO→next LUMO. The two lowest excited singlet states (^1A_u and $^1B_{2g}$) of the phane (**4**) differ from those of the other phanes in electronic configurations. This is because the first excited singlet state of *s*-indacene corresponds to a one-electron transition from the next HOMO to the LUMO, whereas the second excited singlet state corresponds to a one-electron excitation from HOMO to LUMO. The next HOMO of *s*-indacene splits into the next and

Table. Energy gaps and symmetries of the first and second excited singlet states of the phanes (**1**)—(**4**)

Molecule (point group and ground-state symmetry)	Energy gap (symmetry)	
	$(E_1 - E_0)$/eV	$(E_2 - E_0)$/eV
(**1**) (C_{2v}, A_1)	1.30 (A_2)	2.11 (B_2)
(**2**) (C_{2v}, A_1)	0.60 (A_2)	1.47 (B_2)
(**3**) (D_{2h}, A_u)	0.29 (A_g)	0.64 (B_{3g})
(**4**) (D_{2h}, A_g)	0.26 (A_u)	0.98 (B_{2g}) 1.00 (B_{3g})[a]

[a] Energy gap and symmetry of the third excited singlet state.

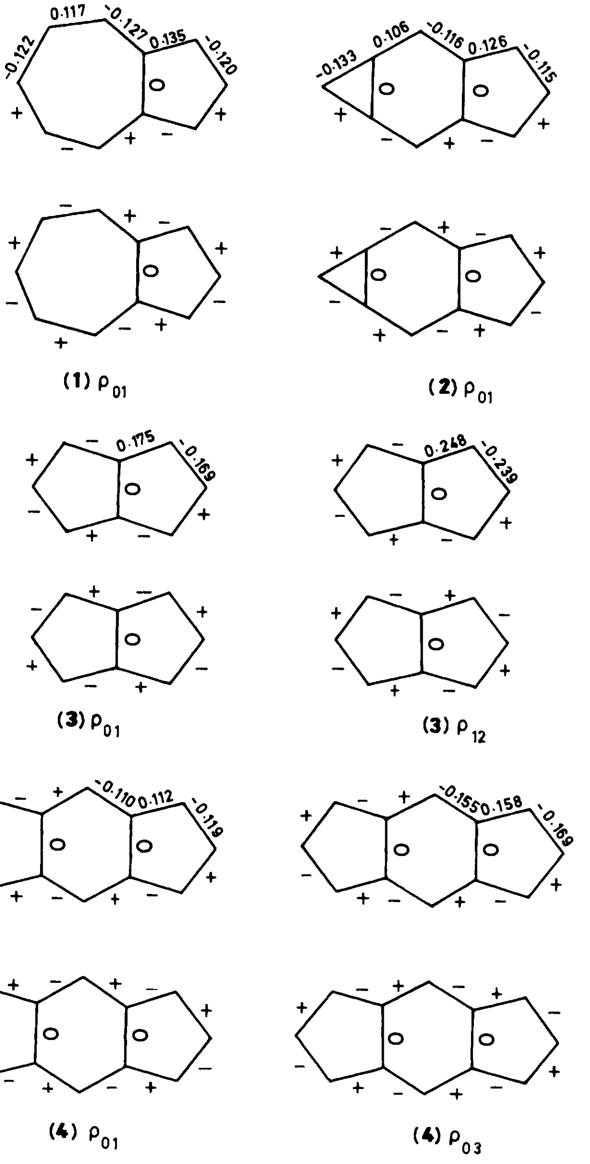

Figure 2. Distribution of two-centre components of transition densities in subsystems for molecules (**1**)—(**4**); a set of the absolute values for a molecular is obtained by using the reflections for the full symmetries

the fourth HOMO of the phane (**4**). It thus follows that the ^1A_u state of the phane (**4**) is generated by a one-electron jump: the next HOMO$\rightarrow$LUMO. The $^1B_{2g}$ excited state corresponds to one-electron excitation from HOMO to LUMO. The third excited singlet state ($^1B_{3g}$) is produced by configuration interactions between two degenerate transitions: next HOMO$\rightarrow$ next LUMO and the fourth HOMO$\rightarrow$LUMO.

Molecular symmetry reduction in these phanes can be discussed in terms of the symmetry rule and the calculated energy gaps (Table). Since the energy gap ($E_1 - E_0$) of the *syn*-azulenophane (**1**) is similar to the critical value (about 1.2 eV), the phane should be 'soft' along the a_2 nuclear displacement. From the distribution of the two-centre components of the transition density ρ_{01} shown in Figure 2, it is seen that the actual distortion is bond-alternation coupled out of phase. Inspection of the transition density ρ_{02} reveals that the b_2 distortion is bond-alternation coupled in phase. Owing to the large energy gap ($E_2 - E_0$), however, this phane will not undergo in-phase bond alternation.

In the cycloprop[*f*]indenophane (**2**), the energy gap ($E_1 - E_0$) is smaller than the critical value; thus its molecular symmetry is reduced from C_{2v} to C_2. The transition density ρ_{01} predicts that the relevant a_2 bond distortion is out-of-phase bond alternation. The distribution of the two-centre components of ρ_{02} corresponds to in-phase bond alternation. However, this will not occur, because $E_2 - E_0$ is larger than the critical value.

Our calculations show that the ground state of the D_{2h} pentalenophane (**3**) corresponds to the ^3A_u open-shell state produced by one-electron transition from HOMO to LUMO. The corresponding ^1A_u state lying above the ^3A_u by 0.1 eV is the lowest singlet state, whereas the closed-shell singlet state ^1A_g corresponds to the next lowest singlet state. However, we believe that if we take into account extensive configuration interactions in the ^1A_u and ^3A_u states, including those responsible for the dynamic spin polarisation effect, the ^1A_u state should be lower than the ^3A_u state because overlap between HOMO and LUMO is very small (violation of Hund's rule).[20] Thus, in the ground state of pentalenophane, which is now identified as the open-shell ^1A_u state, a_u bond distortion, which mixes the ^1A_u and ^1A_g states, is predicted to occur. The transition density ρ_{01} shown in Figure 2 indicates that this mode corresponds to out-of-phase bond alternation. The b_{3u} bond distortion inducing the interaction of ^1A_u with $^1A_{3g}$ is not a bond alternation. However, this distortion is not promising because of the very small value of the matrix element in equation (1). In-phase bond alternation does not occur in the ground state, but is found in the ^1A_g state. This can immediately be seen from the transition density between the ^1A_g and $^1B_{3g}$ states (ρ_{12} in Figure 2).

It is possible that the *s*-indacenophane (**4**) (D_{2h}) may distort into the three less symmetrical structures because of the three low-lying excited singlet states: ^1A_u, $^1B_{2g}$, and $^1B_{3g}$. From the distributions of the transition densities ρ_{01} and ρ_{03}, it is seen that a_u distortion leads to an out-of-phase bond-alternating structure (D_2), and the b_{3g} distortion to an in-phase bond-alternating structure (C_{2h}), the former being energetically more favourable. The b_{2g} distortion leading to the C_{2h} structure is not a bond-alternating one. This mode, however, is predicted not to occur because of the small value of the matrix element in equation (1).

In Figure 3 are shown the most favourable structures of the phanes with inter-subsystem distances (D) of 3.3 Å. In the *syn*-azulenophane (**1**), the delocalised structure is the most stable. This is in good agreement with the available experimental facts; the n.m.r. and photoelectron spectra[4] can be well interpreted by assuming C_{2v} symmetry. However, a long tail is found in the longest wavelength band of the electronic spectrum.[2] This suggests that, as in heptalene,[21] the molecular symmetry of the ground state is probably reduced from fully symmetric [C_{2v} in (**1**)], and as a result, the geometrical structure of the first excited state differs markedly from that of the ground state. Our calculations have shown a strong D-dependence of the first excitation energy; $E_1 - E_0$ is calculated to be 1.3 eV at D = 3.3 Å and 0.7 eV at D = 3 Å. When D becomes even slightly smaller than 3.3 Å, the *syn*-azulenophane should be distorted into the C_2 bond-alternating structure.

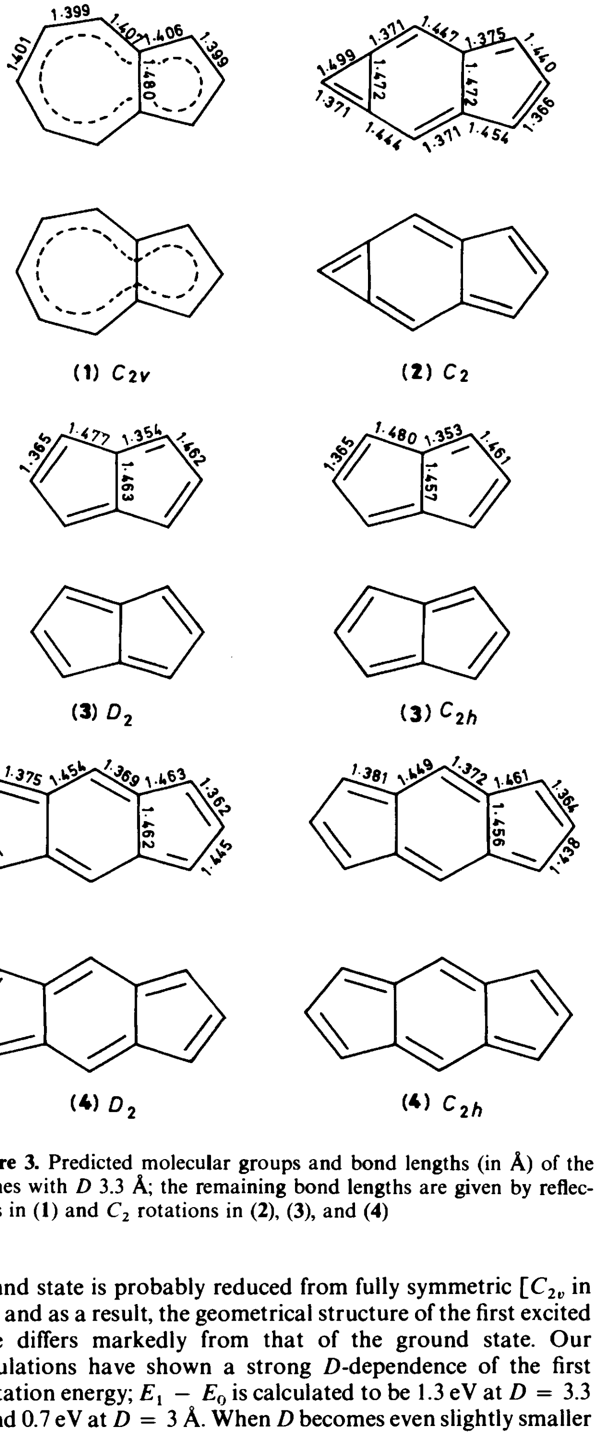

Figure 3. Predicted molecular groups and bond lengths (in Å) of the phanes with D 3.3 Å; the remaining bond lengths are given by reflections in (**1**) and C_2 rotations in (**2**), (**3**), and (**4**)

Out-of-phase bond alternation occurs in the ground state of the *syn*-cycloprop[*f*]indenophane (**2**). The stabilisation energy favouring the form of lower symmetry is calculated to be 3.3 kcal mol^{-1}. In general, the stabilisation energy of a phane can be written as the sum of the stabilisation energies in the two parent molecules and the transannular interaction energy between them. In the *syn*-cycloprop[*f*]indenophane (**2**), however, since no bond distortions are predicted to occur in the parent molecules,[22] the a_2 distortion increases the energies of the two parent molecules of the phane. In contrast, bond distortion produces a bonding interaction between the two subsystems because it mixes the $^1A_1$ state with the $^1A_2$ state, which is bonding in the inter-subsystem interaction. The bonding character of the $^1A_2$ state is due to its electronic configuration (HOMO→LUMO); as already mentioned, the HOMO is antibonding in the inter-subsystem interaction, and the LUMO is bonding. The stabilisation energy due to the transannular interaction compensates for the loss of the stabilisation energies in the two parent molecules and thus represents the net stabilisation energy in the phane.

In the pentalenophane (**3**), two types of bond-alternating structure (D_2 and C_{2h}) are possible, as shown in Figure 3. The D_2 structure is more stable than the C_{2h} by 9.3 kcal mol^{-1}, lying below the ^3A_u state of the D_{2h} structure by 6.3 kcal mol^{-1}. The D_2 form is therefore the true minimum, whereas the C_{2h} corresponds to a local minimum. The stabilisation energy for the D_2 structure is calculated to be 8.6 kcal mol^{-1}. This energy includes the extra stabilisation energy due to the transannular interaction. The extra stabilisation energy is evaluated as 2.6 kcal mol^{-1} by taking a calculated stabilisation energy of 3.0 kcal mol^{-1} for pentalene. In contrast, the transannular interaction inherent to the phane provides the C_{2h} pentalenophane with no extra stabilisation energy. Indeed, the stabilisation energy for the C_{2h} structure relative to the ^1A_g state of the D_{2h} structure is calculated to be 6.0 kcal mol^{-1}, just twice as large as the energy difference between the D_{2h} and C_{2h} pentalenes. This is because the C_{2h} pentalenophane retains the nonbonding interactions between the subsystems. Note that in the ^1A_g and $^1B_{3g}$ states of the D_{2h} structure, the interaction between the subsystems is nonbonding.

The D_2 and C_{2h} structures of the *s*-indacenophane (**4**) are also shown in Figure 3. As already predicted, b_{2g} distortion does not occur. The stabilisation energy is calculated to be 5.9 kcal mol^{-1} for the D_2 structure. The total energies of the C_{2h} and D_{2h} structures are almost the same. It is thus concluded that the D_2 structure is the most favourable in the *s*-indacenophane.

In addition to the foregoing phanes, it is of interest to consider bond alternation in [2.2][18]annulenophane. It has been found[23] that the ground state of [18]annulene is a D_{6h} structure having delocalised π-bonds. Since the first excitation energy of the annulene is 1.5 eV,[23,24] that of its phane is expected to be smaller than the critical value, about 1.2 eV; if this is so, out-of-phase bond alternation would occur.

Acknowledgements

We are grateful to Professor S. Itô, Department of Chemistry, Tohoku University, for a reprint of ref. 1.

References

1 S. Itô, *Pure Appl. Chem.*, 1982, **54**, 957.
2 L. Luhowy and P. M. Keehn, *Tetrahedron Lett.*, 1976, 1043; *J. Am. Chem. Soc.*, 1977, **99**, 3797.
3 (*a*) N. Kato, Y. Fukuzawa, and S. Itô, *Tetrahedron Lett.*, 1976, 2045; (*b*) N. Kato, H. Matsunaga, S. Oeda, Y. Fukuzawa, and S. Itô, *ibid.*, 1979, 2419.
4 B. Kovač, M. Mohraz, E. Heilbronner, S. Itô, Y. Fukuzawa, and P. M. Keehn, *J. Electron Spectrosc. Relat. Phenom.*, 1981, **22**, 327.
5 P. Bickert, V. Boekelheide, and K. Hafner, *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 304.
6 M. C. Böhm, P. Bickert, K. Hafner, and V. Beekelheide, *Proc. Natl. Acad. Sci. USA*, 1984, **81**, 2589.
7 R. F. W. Bader, *Mol. Phys.*, 1960, **3**, 137.
8 R. G. Pearson, *J. Am. Chem. Soc.*, 1969, **91**, 1252, 4947.
9 L. S. Bartell, *J. Chem. Educ.*, 1969, **45**, 754.
10 J. Koutecký and J. Paldus, *Collect. Czech. Chem. Commun.*, 1962, **27**, 599.
11 S. Iwata, K. Fuke, M. Sasaki, S. Nagakura, T. Otsubo, and S. Misumi, *J. Mol. Spectrosc.*, 1973, **46**, 1.
12 T. Nakajima, A. Toyota, and S. Fujii, *Bull. Chem. Soc. Jpn.*, 1972, **45**, 1022.
13 T. Nakajima, *Fortschr. Chem. Forsch.*, 1972, **32**, 1.
14 A. Toyota, T. Nakajima, and S. Koseki, *J. Chem. Soc., Perkin Trans. 2*, 1984, 85.
15 R. Pariser and R. G. Parr, *J. Chem. Phys.*, 1953, **21**, 446.
16 J. A. Pople, *Trans. Faraday Soc.*, 1953, **49**, 1357.
17 H. Yamaguchi, T. Nakajima, and T. L. Kunii, *Theor. Chim. Acta (Berlin)*, 1968, **12**, 349.
18 G. Burns, *J. Chem. Phys.*, 1964, **41**, 1521.
19 S. Fuke, S. Nagakura, and T. Kobayashi, *Chem. Phys. Lett.*, 1975, **31**, 205.
20 T. Koseki, T. Nakajima, and A. Toyota, *Can. J. Chem.*, 1985, **63**, 1572.
21 H. J. Dauben, Jr., and D. J. Bertelli, *J. Am. Chem. Soc.*, 1961, **83**, 4659.
22 A. Toyota, *Bull. Chem. Soc. Jpn.*, 1975, **48**, 1152.
23 H. Baumann and J. F. M. Oth, *Helv. Chim. Acta*, 1982, **65**, 1885, and references cited therein.
24 A. Toyota, T. Tanaka, and T. Nakajima, *Int. J. Quantum Chem.*, 1976, **10**, 917.

Received 12*th August* 1985; *Paper* 5/1401