Bond Distortions in the Radical Ions of Double-layer Fulvalenophane and Heptafulvalenophane

Masahiro Kataoka *,†
Department of Chemistry, Faculty of Science, Tohoku University, Sendai 980, Japan
Azumao Toyota
Department of Chemistry, Faculty of General Education, Yamagata University, Yamagata 990, Japan
Takeshi Nakajima
Tohoku Dental University, Koriyama 963, Japan

The CC bond distortions in the monocation and trication of double-layer fulvalenophane and in the monoanion and trianion of double-layer heptafulvalenophane have been examined by use of second-order Jahn–Teller theory and the Pariser–Parr–Pople-type SCF MO method. It is predicted that these radical ions are unstable with respect to b_{1u} bond distortions, which produce unequal distributions of charge and spin densities. Proton hyperfine splittings for these radical ions have been calculated.

Nonbenzenoid phane chemistry has progressed in recent years.[1–8] Not only can one prepare phanes and see their structures; one can also begin to understand their physical and chemical properties.[1,6] In particular, transannular interaction between composite conjugated hydrocarbons in an important area to be investigated. We have paid much attention to the effect of transannular interaction on the CC bond distortions of conjugated subsystems.

We have previously reported studies of the ground-state bond distortions of some nonbenzenoid phanes by semiempirical model calculations.[9,10] Thus the double-layer *syn*-azulenophane is predicted not to suffer any bond distortions, and this prediction agrees with experimental facts.[1,6] We have also suggested that the *syn*-azulenophane may exhibit a very slight nuclear displacement in which the bond-alternating displacements of the two parent subsystems are out of phase. The slight displacement of this mode is attributable to transannular interaction. Stronger transannular interaction resulting from multiple layers may lead to bond distortions. In fact, the triple-layer and the quadruple-layer *syn*-azulenophane are calculated to possess bond-alternating structures in which the distortions of the adjacent subsystems are all coupled out of phase. In-phase bond alternations were not found. On the other hand, the double-layer phanes of pentalene and *s*-indacene exhibit in-phase and out-of-phase bond alternations. The latter structures are energetically more favourable, and this can be regarded as due to transannular interaction.

The present paper extends this work to the ground-state bond distortions in the monocation (**1**) and trication (**2**) of double-layer fulvalenophane as well as in the monoanion (**3**) and trianion (**4**) of double-layer heptafulvalenophane (Figure 1). We have carried out the dimer-model calculations[10,11] by using the open-shell formalism of the Pariser–Parr–Pople SCF MO method with the variable bond-length technique.[12] The distance (d) between the two subsystems is throughout set equal to 0.33 nm, which is the average intersubsystem distance in [2.2](2,6)azulenophanes.[5] The maximum symmetries of these radical ions are assumed to be D_{2h}. We have shown that for these radical ions in-phase bond distortions occur whereas out-of-phase bond distortions do not.

We first examined the stability of the most symmetrical structures of these radical ions by using second-order Jahn–Teller (SOJT) theory.[13–16] Toyota and Nakajima[12] have proposed the rule: if the lowest doublet excitation energy of an open-shell conjugated hydrocarbon is calculated to be smaller than about 0.6 eV, the molecule is unstable with respect to a certain CC bond distortion, and may be distorted into less symmetrical structures. The representation of the distortion is determined by the direct product of the representations of the ground and the lowest excited doublet states. From the distribution of the transition density ρ_{01} between these states, one can predict the energetically most favourable distortion.

Table 1. Energy gaps and symmetries of the lowest-excited doublet states of the radical ions (**1**)—(**4**) with D_{2h} symmetry

Molecule (ground-state representation)	Energy gap $(E_1 - E_0)$/eV	Representation
(**1**) (B_{1g})	0.011	A_u
(**2**) (A_u)	0.017	B_{1g}
(**3**) (B_{3g})	0.027	B_{2u}
(**4**) (B_{2u})	0.035	B_{3g}

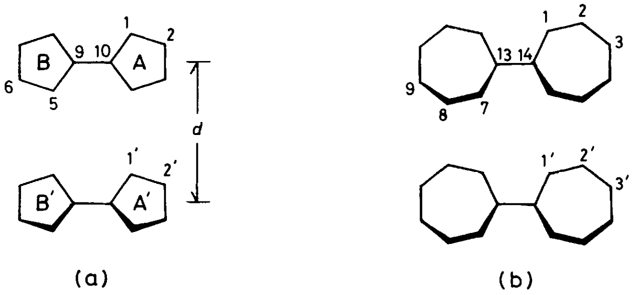

Figure 1. Carbon skeletons of the radical ions and numberings of atomic positions: (a) for (**1**) and (**2**) and (b) for (**3**) and (**4**)

Results and Discussion

We first optimised the CC bond lengths of the subsystems of the D_{2h} phanes, and calculated the first excitation energies $(E_1 - E_0)$. Table 1 gives the energy gaps $(E_1 - E_0)$ and the representations of the ground and the first excited doublet states. Figure 2 shows the distributions of the nearest two-centre components of ρ_{01} in bond regions of the subsystems.

The very small energy gap is predictable from the consideration of the HMO energy levels. For the monocation (**1**), the singly occupied MO (SOMO), $\varphi(b_{1g})$, and the highest doubly occupied MO (HDOMO), $\varphi(a_u)$, are accidentally

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† *Present address:* Tohoku College of Pharmacy, 4-4-1, Komatsushima, Sendai 983, Japan.

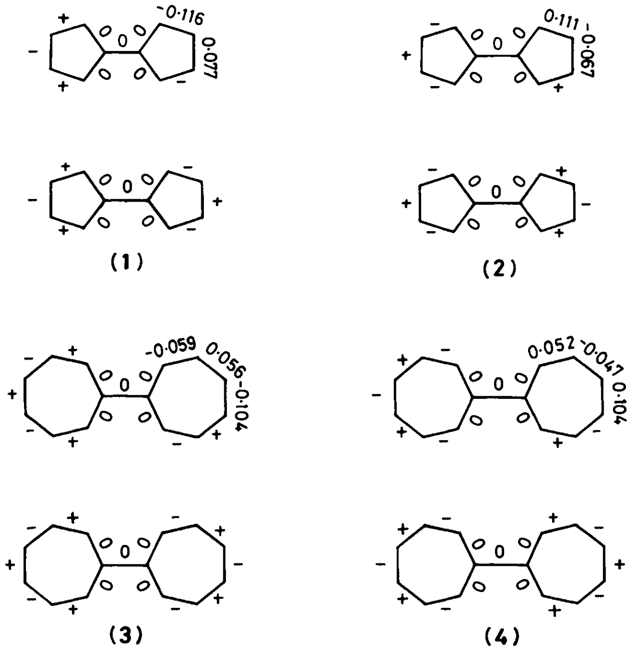

Figure 2. Distributions of two-centre components of transition densities (ρ_{01}) in subsystems for (**1**)—(**4**); a set of the absolute values for a molecule is obtained by use of the reflections for D_{2h}

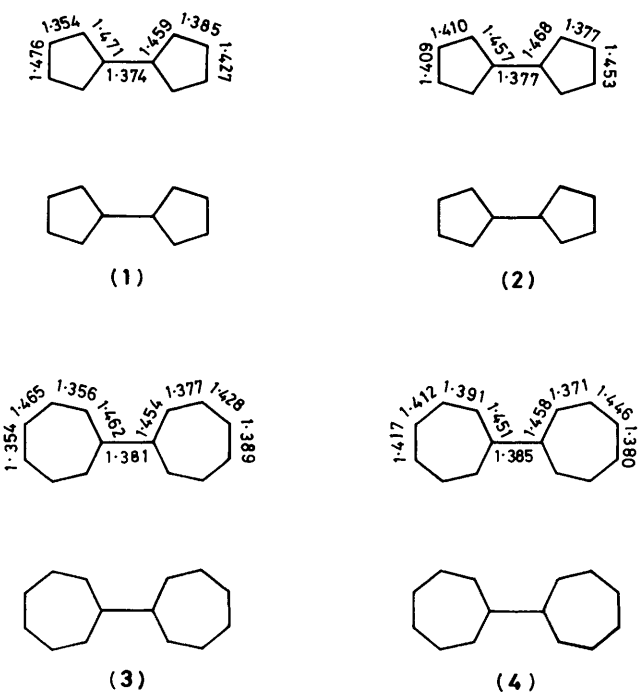

Figure 3. Predicted CC bond lengths of subsystems (in nm × 10^{-1})

degenerate. It is natural to expect a low-lying first excited double state corresponding to the MO transition $\varphi(a_u) \longrightarrow \varphi(b_{1g})$. For the trication (**2**), the SOMO is $\varphi(a_u)$ and the lowest unoccupied MO (LUMO) $\varphi(b_{1g})$. Thus, the excitation $\varphi(a_u) \longrightarrow \varphi(b_{1g})$ results in a very low-lying first excited doublet state. The same situation is found in the radical ions (**3**) and (**4**). The SOMO $\varphi(b_{3g})$ and LUMO $\varphi(b_{2u})$ of (**3**) are degenerate. For (**4**), the SOMO is $\varphi(b_{2u})$ and the HDOMO $\varphi(b_{3g})$. Therefore, the first excited doublet states of both the ions, corresponding to the MO transition $\varphi(b_{3g}) \longrightarrow \varphi(b_{2u})$, lie close to the ground states.

Such small energy differences show that these radical ions may undergo SOJT ground-state distortions of b_{1u} [$a_u \times b_{1g}$ for (**1**) and (**2**) and $b_{3g} \times b_{2u}$ for (**3**) and (**4**)]. The molecular symmetries are reduced, $D_{2h} \longrightarrow C_{2v}$.

The transition densities of (**1**)—(**4**) indicate that the actual bond distortions of the subsystems are coupled in phase. The corresponding out-of-phase distortions are predicted not to occur.

We then optimised the distorted structures of the phanes (**1**)—(**3**), using the starting geometries indicated by the transition densities shown in Figure 2. Figure 3 gives the CC bond lengths of subsystems of the most favourable structures.

Our calculations confirm the foregoing prediction that these radical ions undergo in-phase bond distortions. The stabilisation energies that favour the distorted structure are estimated to be 31.3 for (**1**), 29.7 for (**2**), 31.3 for (**3**), and 31.8 kJ mol^{-1} for (**4**). In general, the stabilisation energy of a phane can be written as the sum of the stabilisation energies of subsystems and the transannular interaction energy between them. In these ions, however, the stabilisation energy is produced by distortions of subsystems. The reason for this is that since the ground and the first excited doublet state of the D_{2h} radical ion have a bonding interaction between subsystems, after the distortion mixing these states the ion retains the bonding interaction.

The corresponding out-of-phase distortions fail to occur because the excited doublet states coupled with the ground states through these distortions are high in energy. Our preliminary calculations for (**2**) and (**3**) gave related energy gaps of about 1.2 eV (larger than 0.6 eV). We tried to find out-of-phase distorted structures of (**1**)—(**4**) but without success.

In view of the transannular interaction, we can discuss why the out-of-plane distortions are little favoured. When the subsystem distortions of the in-phase type and those of the out-of-phase type are of the same degree, the transannular interaction determines the relative stability. As already discussed, in the case of the in-phase bond-distorted structures, the transannular interaction gives no stabilisation energy. The transannular interaction in the out-of-phase distortions, on the other hand, produces the instability. We have found that for the D_{2h} structures the excited doublet states which interact with the ground states through the out-of-phase distortions have antibonding or less bonding interactions between the subsystems. In the radical ions (**1**)—(**4**), therefore, the out-of-phase distortions decrease the bonding interaction between the subsystems of the D_{2h} structures.

The transannular-interaction effect is in contrast to that seen in pentalenophane and *s*-indacenophane.[10] In these phanes, out-of-phase bond distortion supplies the extra stabilisation energy, but in-phase bond distortion does not. Thus, the out-of-phase bond-alternating structures are the most stable.

The in-phase distortions accompany the unequal distributions of the charge and spin densities summarised in Table 2. The possible hyperfine splittings have been calculated by use of McConnell's relationship[17] with $Q = 24.94$ G (1 G = 10^{-4} T). The values in parentheses are those for the D_{2h} structures.

In the radical ions (**1**)—(**4**), the unpaired spin density is confined to two rings, say A and A′. Of course, this means that the SOMO is localised on these rings. In the trication (**2**) and the monoanion (**3**), the localisation is chiefly responsible for the unequal distribution of ring charge: the rings including the unpaired electron have the larger magnitudes of electron densities, that is, a smaller positive charge for (**2**) or a larger negative charge for (**3**). In the monocation (**1**) and the trianion (**4**), the spin is found on the rings having the smaller electron densities. This is mainly because the SOMO and the HDOMO are localised on different rings: the HDOMO contributes to the electron density more than does the SOMO.

Table 2. Ring charges, spin densities, and proton hyperfine splittings (1 G = 10^{-4} T) of the C_{2v} radical ions (**1**)—(**4**)

Molecule	Ring (charge)	Atom	Spin density	Hyperfine splitting
(**1**)	A	1	0.178 (0.086)^a	4.44 (21.4)^a
	(+0.315)	2	0.071 (0.039)	1.77 (0.97)
		10	0.0 (0.0)	0.0 (0.0)
	B	5	0.000	0.00
	(+0.185)	6	0.000	0.00
		9	0.0	0.0
(**2**)	A	1	0.177 (0.092)	4.41 (2.29)
	(+0.689)	2	0.072 (0.033)	1.80 (0.82)
		10	0.0 (0.0.)	0.0 (0.0)
	B	5	0.000	0.00
	(+0.811)	6	0.000	0.00
		9	0.0	0.0
(**3**)	A	1	0.123 (0.058)	3.07 (1.45)
	(−0.307)	2	0.028 (0.017)	0.70 (0.42)
		3	0.099 (0.050)	2.47 (1.25)
		14	0.0 (0.0)	0.0 (0.0)
	B	7	0.000	0.00
	(−0.193)	8	0.000	0.00
		9	0.000	0.00
		13	0.0	0.0
(**4**)	A	1	0.117 (0.062)	2.92 (1.55)
	(−0.702)	2	0.023 (0.010)	0.57 (0.25)
		3	0.109 (0.053)	2.72 (1.32)
		14	0.0 (0.0)	0.0 (0.0)
	B	7	0.000	0.00
	(−0.798)	8	0.000	0.00
		9	0.000	0.00
		13	0.0	0.0

^{a} Values for the D_{2h} structures.

Conclusions

We have examined the ground-state bond distortions of the radical ions (**1**)—(**4**) by using SOJT theory. The SOJT distortion often indicates the instability of the restricted Hartree–Fock (RHF) solution.[18–21] The occurrence of both distortion and instability is related to the presence of a sufficiently low-lying excited state. It has been found that the broken-symmetry charge-density wave (CDW) solutions for the fully symmetrical structures are similar to the symmetry-adapted RHF solutions for the distorted structures. The negligibly small energy gaps listed in Table 1 show that the D_{2h} radical ions (**1**)—(**4**) may exhibit the doublet instabilities of the RHF solutions. The CDW solutions presumably have C_{2v} symmetry, that is, in-phase but not out-of-phase symmetry.

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