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BOND DISTORTIONS IN THE RADICAL IONS OF SOME DOUBLE-LAYER NON-BENZENOID PHANES

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The C—C bond distortions in the radical cations and anions of double-layer heptalenophane, cyclopent[*cd*]azulenophane, cyclopenta[*ef*]heptalenophane, dicyclohepta[*cd, gh*]pentalenophane and dicyclopenta[*ef, kl*]heptalenophane are examined by use of the symmetry rule and the semiempirical Pariser–Parr–Pople-type SCF MO method. It is predicted that the radical cation and anion of heptalenophane should suffer in-phase and out-of-phase bond alternations, the molecular symmetry being reduced from D_{2h} to C_{2h} and D_2, respectively. In contrast, the other radical ions are expected not to undergo any bond distortions, retaining the full molecular symmetry group. This difference is explained in terms of pseudo Jahn-Teller effect. © 1997 by John Wiley & Sons, Ltd.

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The symmetry rule[1–3] has been successfully applied to the problem of the bond distortions in conjugated hydrocarbons.[4–6] The rule has predicted that pentalene and heptalene (**1**)[4, 5] suffer bond alternations whereas their radical cations and anions[6] suffer no bond distortions. Using the symmetry rule, we have previously examined[7–9] bond distortions in non-benzenoid phanes.[10–16] The results have shown that not only double-layer pentalenophane[7] but also its radical cation and anion[8] should be distorted into C_{2h} and D_2 bond-alternated structures: in the C_{2h} structure, two bond-alternated pentalene subsystems are coupled in phase and, on the other hand, they are coupled out of phase in the D_2 structure. We have also predicted that double-layer heptalenophane should exhibit in-phase and out-of-phase bond alternations.[9] From these results, the question arises of whether the radical cation and anion of heptalenophane undergo in-phase and out-of-phase bond alternations. It is also intriguing to investigate whether or not bond distortions occur in the radical cations and anions of the nonbenzenoid phanes composed of cyclopent[*cd*]azulene (**2**), cyclopenta[*ef*]heptalene (**3**), dicyclohepta[*cd, gh*]pentalene (**4**), and dicyclopenta[*ef, kl*]heptalene (**5**) (Figure 1), because these molecules contain pentalene- and heptalene-like skeletons of interest.

In this work, we examined the bond distortions in the radical cations and anions of double-layer heptalenophane ($\mathbf{6}^+$ and $\mathbf{6}^-$), cyclopent[*cd*]azulenophane ($\mathbf{7}^+$ and $\mathbf{7}^-$), cyclopenta[*ef*]heptalenophane ($\mathbf{8}^+$ and $\mathbf{8}^-$), dicyclohepta[*cd*, *gh*]pentalenophane ($\mathbf{9}^+$ and $\mathbf{9}^-$) and dicyclopenta[*ef*, *kl*]heptalenophane ($\mathbf{10}^+$ and $\mathbf{10}^-$). We carried out dimer model[17, 18] calculations (Figure 2), using the open-shell RHF formalism of the Pariser–Parr–Pople-type SCF MO method with the variable bond-length technique.[6, 19] The total energy was assumed to be the sum of the π-electron and σ-bond energies of the parent molecules, the latter being calculated by use of the harmonic oscillator model[20] with a force constant of 714 kcal mol^{-1} Å^{-2}. In the dimer model, the two planar subsystems are fully overlapped. The distance between the subsystems (D) is set to 3·3 Å, the average intersubsystem distance in [2·2](2, 6)azulenophane.[14] Preliminary x-ray analysis[14] of this phane indicated a barrel shape with deformed, non-planar subsystems. In order to predict whether a conjugated molecule suffers a pseudo-Jahn–Teller distortion, it is essential to obtain the lowest excitation energy of the molecule. We examined the deformation effect on the lowest excitation energy of *syn*-azulenophane by considering the non-planar configuration suggested by the preliminary x-ray analysis and the planar configuration with the average intersubsystem distance. The lowest excitation energies of the two configurations were calculated to be much the same. The influence of the deformation of the subsystems on the lowest excitation energy or on the bond distortion was thus taken into account through the adoption of the average intersubsystem distance. In the present calculations, we therefore used the dimer model composed of planar subsystems with the average intersubsystem distance. The maximum symmetry was assumed to be D_{2h} for $\mathbf{6}^+$, $\mathbf{6}^-$, $\mathbf{9}^+$, $\mathbf{9}^-$, $\mathbf{10}^+$ and $\mathbf{10}^-$ and C_{2v} for $\mathbf{7}^+$, $\mathbf{7}^-$, $\mathbf{8}^+$ and $\mathbf{8}^-$. Further, we considered the pseudo-Jahn–Teller effect on bond distortions by using the symmetry rule.[4–6]

The symmetry rule states that if the energy gap between

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the ground (ψ_0) and the relevant excited doublet state (ψ_n) of an open-shell conjugated hydrocarbon is smaller than a critical value, the energy of the molecule should be lowered by an unsymmetrical nuclear deformation, and a pseudo-Jahn–Teller distortion from symmetry should occur spontaneously. The symmetry of the distortion is identical with that of the direct product between the symmetries of ψ_0 and ψ_n. The transition density ρ_{0n} indicates the most favorable bond distortion. The critical value[6] is about 0.6 eV for a one-electron transition from a doubly occupied MO ϕ_d to the singly occupied MO ϕ_s (an excited configuration ψ_A) and that from ϕ_s to a virtual MO ϕ_v (ψ_B).[21] A one-electron transition from ϕ_d to ϕ_v produces two excited configurations, $\psi_{C\alpha}$ and $\psi_{C\beta}$.[21] For $\psi_{C\alpha}$, the critical value is estimated to be about 1·2 eV. Another configuration $\psi_{C\beta}$ does not contribute to any bond distortions, because the transition density vanishes.

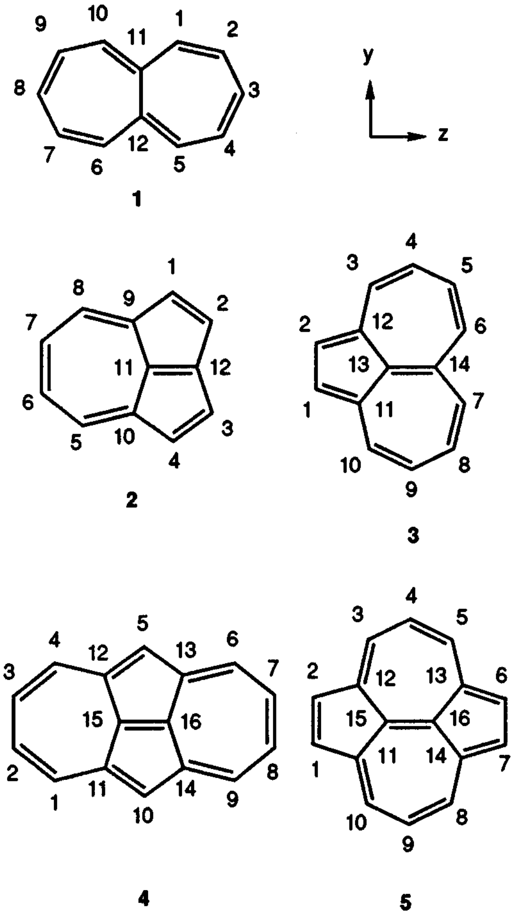


Figure 1. Carbon skeletons of parent molecules, numbering of atomic positions and choice of molecular axes

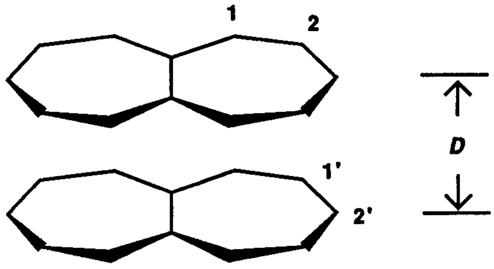


Figure 2. Dimer model (6^+ and 6^-). *D* represents the distance between the two subsystems. Similarly, in the other non-benzenoid phanes, the two subsystems are fully overlapped

Table 1. Energy gaps and symmetries of the first excited doublet states of the radical ions $\mathbf{6}^+$–$\mathbf{10}^-$

Molecule (point group, ground-state symmetry)	Energy gap (symmetry, main configuration), (E_1-E_0) (eV)
$\mathbf{6}^+$ (D_{2h}, B_{2u})	0·19 (B_{2g}, ψ_B) 0·33 (B_{1g}, $\psi_{C\beta}$)[a]
$\mathbf{6}^-$ (D_{2h}, B_{2g})	0·29 (B_{2u}, ψ_A) 0·41 (B_{1u}, $\psi_{C\beta}$)[a]
$\mathbf{7}^+$ (C_{2v}, B_1)	1·11 (A_1, ψ_A)
$\mathbf{7}^-$ (C_{2v}, B_2)	0·87 (A_1, ψ_B)
$\mathbf{8}^+$ (C_{2v}, A_2)	0·64 (A_1, ψ_B)
$\mathbf{8}^-$ (C_{2v}, A_1)	0·85 (A_2, ψ_A)
$\mathbf{9}^+$ (D_{2h}, B_{1g})	0·15 (B_{3u}, ψ_A)
$\mathbf{9}^-$ (D_{2h}, B_{3g})	0·69 (A_g, ψ_B)
$\mathbf{10}^+$ (D_{2h}, B_{1g})	0·79 (B_{2g}, ψ_A)
$\mathbf{10}^-$ (D_{2h}, B_{1u})	0·30 (B_{3g}, ψ_B)

[a] Energy gap and symmetry for the second excited doublet state·

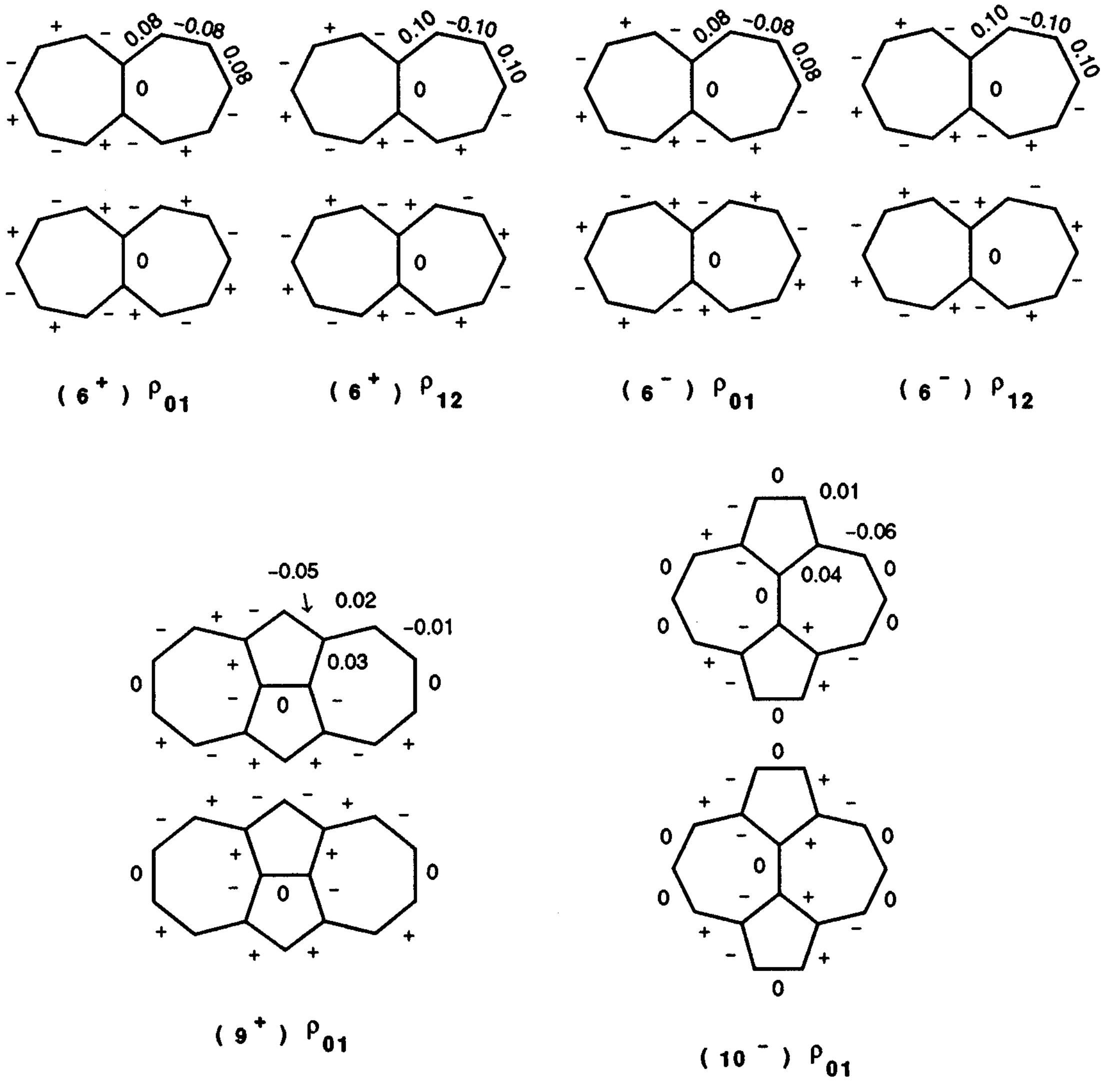
Table 1 shows the energy gaps and the symmetries of the ground and low-lying excited doublet states of the fully symmetrical structures. Figure 3 summarizes the transition densities for $\mathbf{6}^+$, $\mathbf{6}^-$, $\mathbf{9}^+$ and $\mathbf{10}^-$.

The energy gap (E_1-E_0) of $\mathbf{6}^+$ is smaller than the critical value, about 0.6 eV. This predicts that the a_u ($B_{2u}\times B_{2g}$) distortion should occur in the ground state $^2B_{2u}$. The transition density ρ_{01} shown in Figure 3 indicates out-of-phase bond alternation, which accompanies the molecular symmetry reduction $D_{2h}\rightarrow D_2$. Since the second excited doublet state $^2B_{1g}$ is a $\psi_{C\beta}$-type excited state, this state does not induce any ground-state distortions. In-phase bond alternation is expected not to occur in the $^2B_{2u}$ state. In the $^2B_{2g}$ state, however, the in-phase bond alternation is predicted from the transition density between the $^2B_{2g}$ and $^2B_{1g}$ states, ρ_{12} in Figure 3. The energy difference between these states (E_2-E_1) is 0·14 eV. This small energy gap suggests that $\mathbf{6}^+$ suffers in-phase bond alternation and simultaneously the symmetry reduction $D_{2h}\rightarrow C_{2h}$. Similarly, in $\mathbf{6}^-$, the transition density ρ_{01} indicates out-of-phase bond alternation, whereas ρ_{12} indicates in-phase bond alternation (Figure 3).

In $\mathbf{9}^+$, the energy gap of 0·15 eV is smaller than the critical value for symmetry reduction. This suggests that the radical cation undergoes the pseudo-Jahn–Teller bond distortion from D_{2h} to C_{2v} by the vibronic interaction between the ground and the first excited doublet state through the b_{2u} ($B_{1g} \times B_{3u}$) nuclear deformation. However, as shown in Figure 3, almost all of the nearest two-center components of transition density are much smaller than those in **6**$^+$ and **6**$^-$. For this reason, the vibronic interaction should be small in magnitude and hence no symmetry reduction is expected to occur. Also in **10**$^-$, no bond distortions are predicted: although the energy gap of 0·30 eV is small enough to cause the b_{2u} ($B_{1u} \times B_{3g}$) distortion, this distortion is not significant, because the two-center components of transition density (Figure 3) are small compared with those in **6**$^+$ and **6**$^-$.

In the other radical ions, the first excitation energy, shown in Table 1, is greater than the critical value, so that these radical ions should suffer no pseudo-Jahn–Teller bond distortions.

We then tried to obtain the distorted structures, using the starting geometries indicated by the transition densities. Figure 4 summarizes the molecular symmetry-groups and bond lengths corresponding to the distorted structures of **6**$^+$ and **6**$^-$ and to the most favorable structures of **7**$^+$ $-$ **10**$^-$.


(6$^+$) ρ_{01} (6$^+$) ρ_{12} (6$^-$) ρ_{01} (6$^-$) ρ_{12}

(9$^+$) ρ_{01} (10$^-$) ρ_{01}

Figure 3. Two-center components of transition densities in subsystems for **6**$^+$, **6**$^-$, **9**$^+$ and **10**$^-$. A set of the absolute values for a molecule is obtained by use of the reflections for D_{2h}

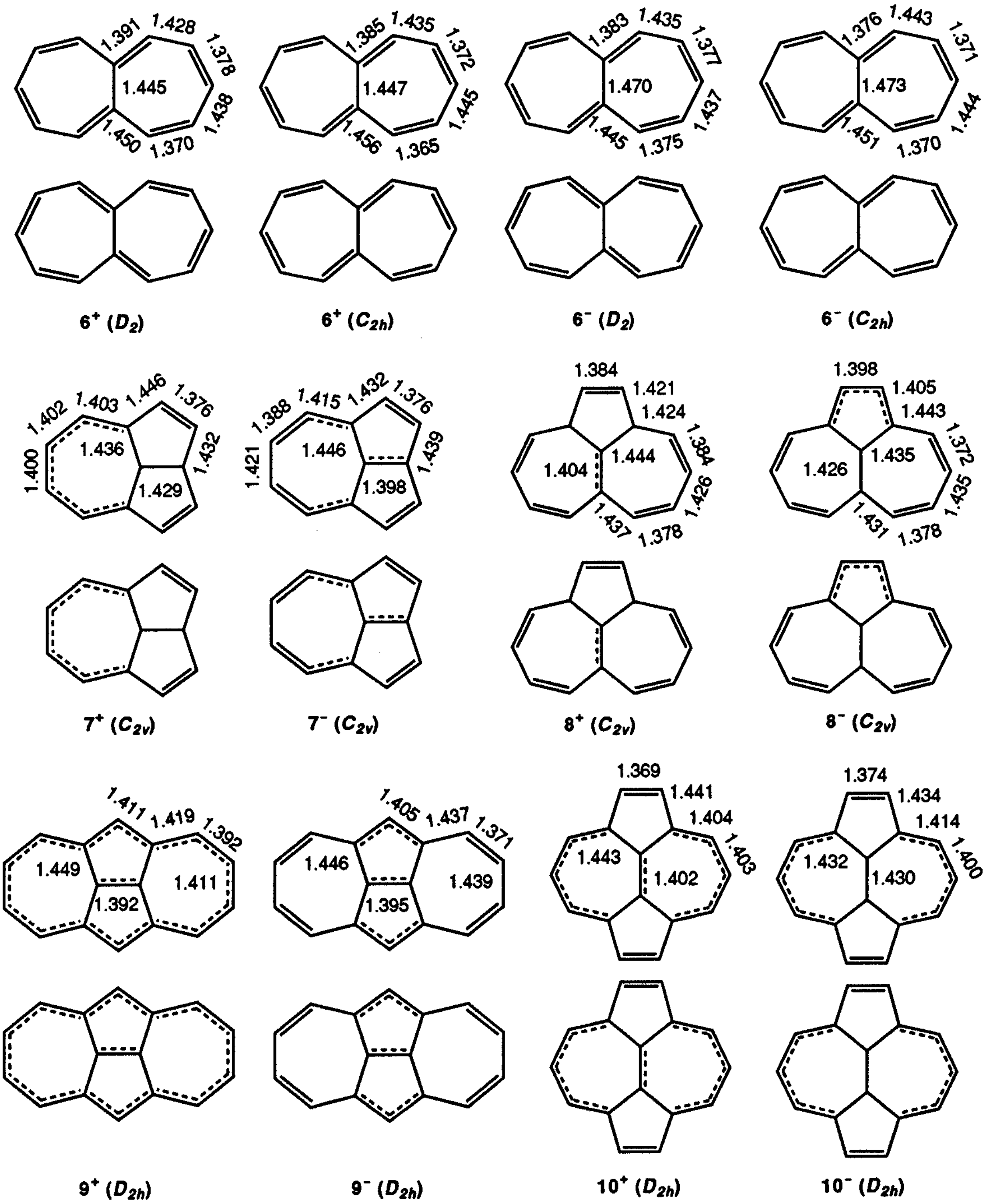


Figure 4. Predicted C—C bond lengths (Å) of the radical ions. The remaining bond lengths are given by reflections and C_2 rotations

Table 2. Spin densities (ρ_s) and hyperfine splittings (a^{H}) of the radical ions **6**$^{+}$–**10**$^{-}$

Atom	ρ_s	$\lvert a^{H}\rvert$ (mT)	ρ_s	$\lvert a^{H}\rvert$ (mT)
	6^{+} (D_2)		**6**$^{-}$ (D_2)	
1	0·062 (0·005)[a]	0·156 (0·012)[a]	0·026 (0·084)	0·066 (0·209)
2	0·043 (0·080)	0·107 (0·198)	0·037 (0·000)	0·091 (0·000)
3	0·038 (0·000)	0·094 (0·000)	0·049 (0·083)	0·121 (0·206)
4	0·040 (0·080)	0·099 (0·198)	0·036 (0·000)	0·090 (0·000)
5	0·019 (0·005)	0·049 (0·012)	0·073 (0·084)	0·181 (0·209)
11	0·048 (0·081)		0·029 (0·000)	
	6^{+} (C_{2h})		**6**$^{-}$ (C_{2h})	
1	0·084	0·209	0·006	0·016
2	0·019	0·048	0·061	0·152
3	0·063	0·157	0·024	0·059
4	0·016	0·041	0·060	0·150
5	0·043	0·108	0·047	0·117
11	0·024		0·052	
	7^{+} (C_{2v})		**7**$^{-}$ (C_{2v})	
1	0·102	0·255	0·002	0·004
2	0·003	0·009	0·072	0·180
5	0·003	0·008	0·012	0·030
6	0·008	0·019	0·061	0·151
9	0·013		0·103	
11	0·111		0	
12	0·131		0	
	8^{+} (C_{2v})		**8**$^{-}$ (C_{2v})	
1	0·031	0·077	0·009	0·022
3	0·009	0·023	0·044	0·110
4	0·072	0·178	0·001	0·003
5	0·001	0·003	0·081	0·203
6	0·055	0·138	0·007	0·018
11	0·082		0·016	
13	0		0·085	
14	0		0·098	
	9^{+} (D_{2h})		**9**$^{-}$ (D_{2h})	
1	0·053	0·131	0·005	0·012
2	0·029	0·072	0·038	0·095
5	0·074	0·185	0	0
11	0·006		0·082	
15	0		0	
	10^{+} (D_{2h})		**10**$^{-}$ (D_{2h})	
1	0·019	0·048	0·003	0·008
2	0·002	0·004	0·065	0·162
5	0·072	0·181	0	0
11	0·068		0·011	
15	0		0·092	

[a] Values for the D_{2h} structures in parentheses

In $\mathbf{6}^+$ and $\mathbf{6}^-$, in-phase and out-of-phase bond-alternated structures are obtained. This means that, as expected above, both the ions undergo the pseudo-Jahn–Teller distortions. The in-phase bond alternation reduces the molecular symmetry from D_{2h} to C_{2h}, whereas the out-of-phase bond alternation reduces the molecular symmetry from D_{2h} to D_2. In both the C_{2h} and the D_2 structures, a strong second-order double-bond fixation[22] is seen on the carbon peripheries of the subsystems. The stabilization energy that favors the distorted structure is calculated to be 13·5 kcal mol^{-1} for $\mathbf{6}^+$ (D_2), 14·0 kcal mol^{-1} for $\mathbf{6}^+$ (C_{2h}), 13·3 kcal mol^{-1} for $\mathbf{6}^-$ (D_2) and 14·0 kcal mol^{-1} for $\mathbf{6}^-$ (C_{2h}). The symmetry rule does not predict any further bond distortions that reduce the molecular symmetries; that is, molecular symmetry reductions from D_2 or from C_{2h} are expected not to occur in these radical ions.

The results in Figure 4 also show that the other radical ions undergo no bond distortions. Our calculations confirm the above prediction by the symmetry rule. In $\mathbf{9}^+$ and $\mathbf{10}^-$, the first excited doublet state is predicted to lie near the ground state.

Table 2 summarizes the spin densities and the possible hyperfine splittings, calculated by use of McConnell's relation[23] with $|Q| = 2{\cdot}494$ mT. The spin densities are obtained from the electron densities of the singly occupied MOs. From Table 2 we see that in $\mathbf{6}^+$ and $\mathbf{6}^-$ the distributions of spin densities for the D_2 and C_{2h} structures are more delocalized than that for the D_{2h} structure. This is due to the effect brought about by the pseudo-Jahn–Teller distortions, that is, the out-of-phase and in-phase bond alternations. In both the radical ions, the out-of-phase bond-alternated (D_2) structure has the more delocalized distribution of the spin densities than the in-phase bond-alternated (C_{2h}) structure. This is also found in the radical cation and anion of pentalenophane.[8]

In conclusion, the radical ions $\mathbf{6}^+$ and $\mathbf{6}^-$ show the in-phase and out-of-phase bond alternations. The total energies of the two bond-alternated structures are almost the same. On the other hand, the fully symmetrical structure is stable in $\mathbf{7}^+$–$\mathbf{10}^-$. Despite the small energy gaps ($E_1 - E_0$), neither $\mathbf{9}^+$ nor $\mathbf{10}^-$ has any bond-distorted ground-state structures, because of the weak vibronic interaction between the ground and the first excited doublet states. The other radical ions remain fully symmetrical owing to the large energy gaps ($E_1 - E_0$).

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