Violation of Hund's Multiplicity Rule in the Lowest Excited Singlet–Triplet Pairs of Cyclic Bicalicene† and Its Higher Homologues

Azumao Toyota *
Department of Chemistry, Faculty of General Education, Yamagata University, Yamagata 990, Japan
Takeshi Nakajima
Department of Chemistry, Faculty of Science, Tohoku University, Sendai 980, Japan

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The relative energy ordering of the lowest excited singlet–triplet pair in the title molecules has been examined by using the Pariser–Parr–Pople-type SCF MO method and by taking into account configuration interactions. In cyclic bicalicene, the excited singlet state is predicted to lie below the triplet state by about 4 kcal mol^{-1},‡ at least within this MO approach. This violation of Hund's multiplicity rule is ascribed essentially to the correlation effects brought about by spin polarization terms. Such a violation of Hund's rule is expected to occur in cyclic bisesquifulvalene and cyclic bitriaheptafulvalene of D_{2h} symmetry.

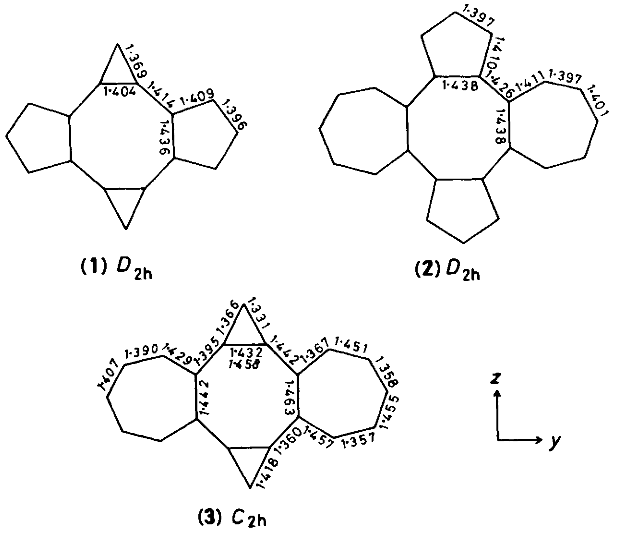
The energetic order of the singlet and triplet states arising from the same orbital occupancy in atoms and molecules can usually be predicted by Hund's rule.[1] However, Toyota and his co-workers[2] have recently shown that Hund's multiplicity rule is violated in the lowest excited singlet–triplet pair of certain conjugated molecules by using the Pariser–Parr–Pople-type (PPP-type) SCF MO method and the *ab initio* MO method with STO-3G basis set, and by taking into account configuration interactions. For the symmetrical structures (D_{2h}) of propalene homologues with 4*n* carbon atoms, the lowest excited singlet state is predicted to lie below the triplet state, irrespective of the MO methods used. This violation of Hund's multiplicity rule is explained in terms of a dynamic spin polarization (SP) effect.[3–5]

Recently, cyclic bicalicene (**1**) having 16 π electrons, considered to be composed of two calicene [5-(cycloprop-2-enylidene)cyclopenta-1,3-diene] molecules,[6] has been prepared by Yoneda and his co-workers.[7,8] In spite of being a non-alternant hydrocarbon containing highly strained three-membered rings, the molecule is a stable aromatic hydrocarbon, an exception to the Huckel rule.[9] In this connection, we have examined the double-bond fixation and aromatic stability of several cyclic bifulvalene molecules.[10,11] Furthermore, the lowest excited singlet and triplet states that evolve from a single MO transition in cyclic bicalicene and its higher homologues have been predicted to be very close in energy by using the PPP-type MO method, including only singly excited configuration interactions.

In this paper, we study the possible violation of Hund's rule for the lowest excited singlet–triplet pair in some cyclic bifulvalene molecules (Figure 1) by taking into account doubly and triply excited configuration interactions. We employ the PPP-type SCF MO method,[12] since the molecular systems under consideration are rather large. It will be shown that Hund's rule breaks down for the lowest excited singlet–triplet pairs in cyclic bicalicene, cyclic bisesquifulvalene, and cyclic bitriaheptafulvalene of the D_{2h} symmetry; this violation is ascribed to the correlation effects brought about by SP terms.

Theory

The theory of SP effects has well been developed by Borden[3] and by Kollmar and Staemmler.[4,5] We give here a brief account of the theory, since SP effects are known to be important essentially for determining the energetic order of the singlet–triplet pair.[13]



(**1**) D_{2h} (**2**) D_{2h} (**3**) C_{2h}

Figure 1. Ground-state bond lengths (in Å) and symmetry groups. For molecule (**3**) with D_{2h} symmetry, bond lengths are shown in italics

We assume that the wave functions of the excited singlet–triplet pair arising from a single MO transition $\varphi_x \rightarrow \varphi_y$ are given as in equation (i), where *i* denotes a doubly occupied MO and *x* and *y* singly occupied MOs. In equation (i), doubly occupied orbitals other than φ_i are not written down, for simplicity. The triplet state is lower in energy than the singlet by $2K_{xy}$, where K_{xy} is the exchange integral between φ_x and φ_y.

$$\Phi_{S,T} = \sqrt{\tfrac{1}{2}}\{|i\,\bar{i}\,x\,\bar{y}| \mp |i\,\bar{i}\,\bar{x}\,y|\} \qquad \text{(i)}$$

In a CI-type treatment, SP effects on the singlet–triplet pair can be taken into account by including the types of doubly excited configurations given in equations (ii), where *k* denotes

$$\Phi_S{}^1 = \sqrt{\tfrac{1}{12}}\,\{2(|\bar{i}\,\bar{k}\,x\,y| + |i\,k\,\bar{x}\,\bar{y}|) - |\bar{i}\,k\,\bar{x}\,y| - |i\,\bar{k}\,x\,\bar{y}| - |i\,\bar{k}\,\bar{x}\,y| - |\bar{i}\,k\,x\,\bar{y}|\} \qquad \text{(iia)}$$

$$\Phi_T{}^1 = \tfrac{1}{2}\{|\bar{i}\,k\,\bar{x}\,y| - |i\,\bar{k}\,x\,\bar{y}| + |i\,\bar{k}\,\bar{x}\,y| - |\bar{i}\,k\,x\,\bar{y}|\} \qquad \text{(iib)}$$

$$\Phi_T{}^2 = \sqrt{\tfrac{1}{2}}\{|\bar{i}\,\bar{k}\,x\,y| - |i\,k\,\bar{x}\,\bar{y}|\} \qquad \text{(iic)}$$

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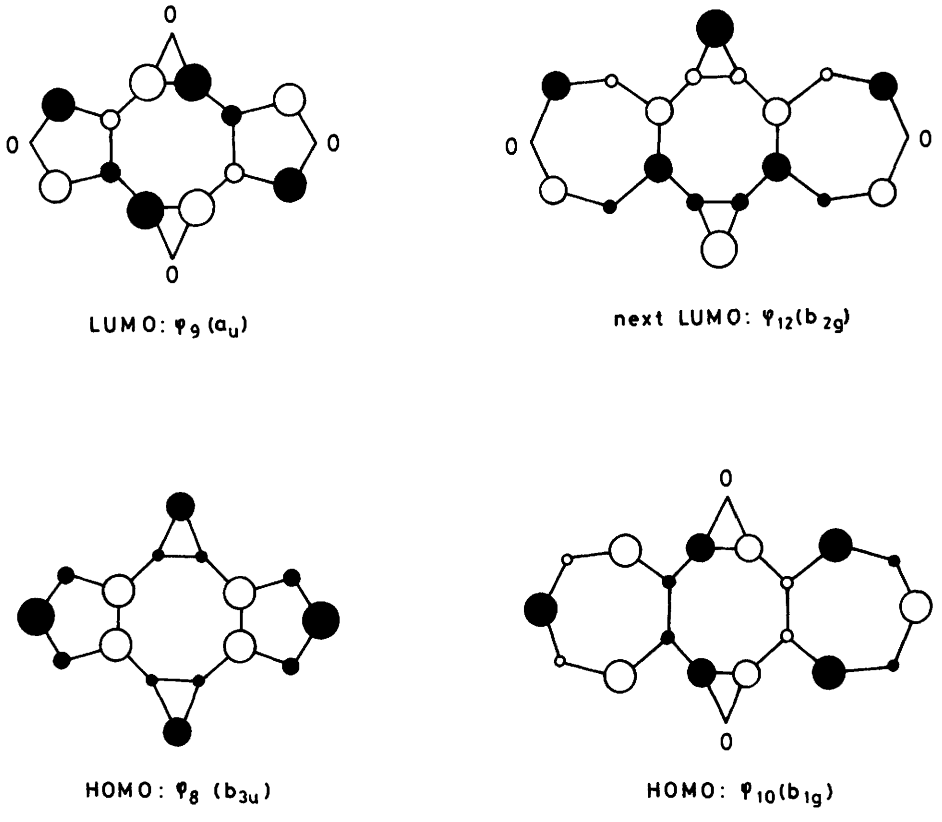
† Dicyclopenta[*a,e*]dicyclopropa[*c,g*]cyclo-octene.
‡ 1 kcal = 4.184 kJ.



LUMO: $\varphi_9\ (a_u)$ next LUMO: $\varphi_{12}(b_{2g})$

HOMO: $\varphi_8\ (b_{3u})$ HOMO: $\varphi_{10}(b_{1g})$

Figure 2. Distribution of the atomic-orbital coefficients in the HOMO and (next) LUMO of molecules (**1**) and (**3**)

a virtual MO. Of the doubly excited configurations like those represented by equations (iia—c), those in which φ_i and φ_k belong to the same irreducible representation have non-vanishing matrix elements with the wavefunctions given by equation (i), and are responsible for the SP effects on the singlet–triplet energy separation. The matrix element of Φ_S with $\Phi_S{}^1$ is $\sqrt{3}$ times larger than that of Φ_T with $\Phi_T{}^1$. Using second-order perturbation theory, we can show that this leads to a stabilization which is three times larger for the singlet than for the triplet, provided that the energy denominators are equal. The matrix element of Φ_T with $\Phi_T{}^2$ is negligibly small as compared with the foregoing matrix elements.

It is thus expected that, in molecules in which the energy gap between the singlet–triplet pair at the Hartree–Fock (HF) level is very small for certain reasons,[14] SP effects which bring about extra stabilization of Φ_S result in the violation of Hund's rule such that Φ_S lies below Φ_T.

In addition to SP effects, we further take into account correlation effects due to all the singly, doubly, and triply (SDT) excited configurations from the restricted HF (RHF) ground state.

Results and Discussion

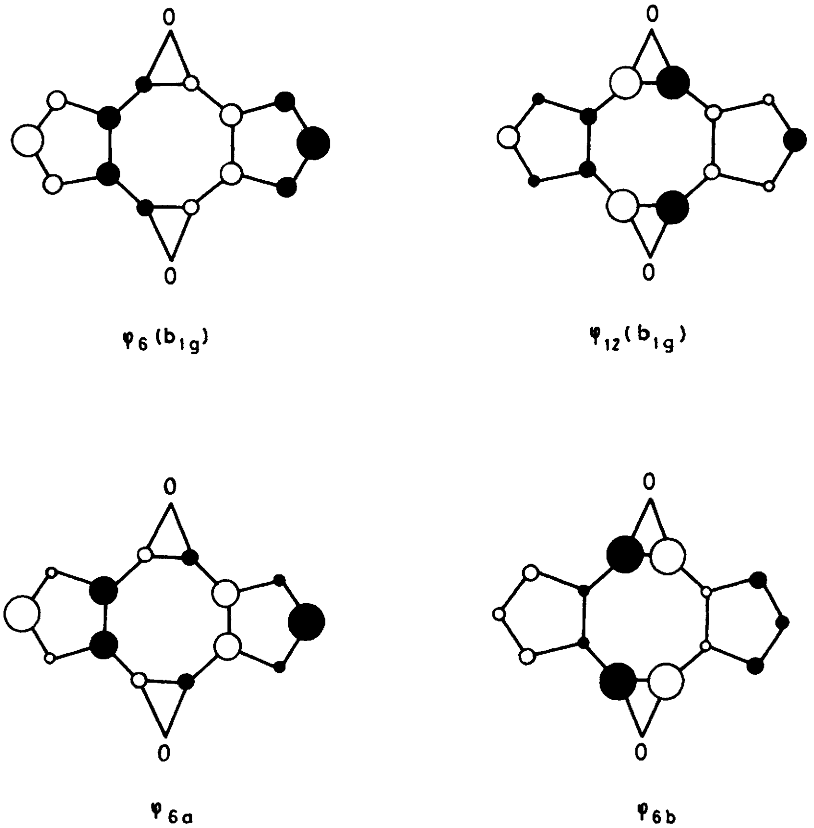
(i) *Geometrical Structures.*—The ground-state geometrical structures with respect to C–C bond lengths of several cyclic bifulvalene molecules were obtained previously by the use of the PPP-type SCF MO method incorporated with the variable-bond-length technique.[11,12] It has been shown that cyclic bicalicene and cyclic bisesquifulvalene (**2**) suffer no symmetry reduction, retaining the full molecular-symmetry group (D_{2h}). The predicted bond lengths in the former are in good quantitative agreement with *X*-ray data.[8] On the other hand, cyclic bitriaheptafulvalene (**3**) is predicted to undergo second-order Jahn–Teller bond distortion from the D_{2h} to the C_{2h} structure (the bond lengths in the D_{2h} structure are shown in italics). Using these ground-state structures, we can study the energy ordering of the excited singlet–triplet pair produced by vertical (Franck–Condon) excitations from the ground state.

Table 1. Energy lowerings of Φ_S and Φ_T due to SP terms and energy separations between the two states (in eV)

Molecule (Point group)	Energy lowering (SP)		$\Delta E_{ST}{}^a$		
	$\Delta E(\Phi_S)$	$\Delta E(\Phi_T)$	$2k_{xy}$	$2k_{xy}$ + SP	$2K_{xy}$ + SP + SDT
(**1**) (D_{2h})	0.898	0.431	0.140	−0.327	−0.158
(**2**) (D_{2h})	0.784	0.386	0.111	−0.287	−0.047
(**3**) (D_{2h})	0.990	0.559	0.087	−0.344	−0.044
(**3**) (C_{2h})	0.239	0.192	0.476	0.429	0.811

[a] The minus sign means that the singlet state is lower in energy than the corresponding triplet state.

(ii) *Energy Ordering of the Singlet–Triplet Pairs.—Cyclic bicalicene* (**1**). The symmetry of the lowest excited singlet–triplet pair which arises from the single MO transition from the HOMO, $\varphi_8(b_{3u})$, to the LUMO, $\varphi_9(a_u)$, belongs to the B_{3g} irreducible representation. Figure 2 shows the atomic-orbital coefficients of φ_8 and φ_9, where white and black circles denote plus and minus, respectively. It can be seen that the two MOs are essentially confined to different sets of carbon atoms, so that the exchange integral K_{89} responsible for the singlet–triplet energy gap should be small. An explanation for the occurrence of such MOs is as follows. The cyclic bifulvalene molecules in Figure 1 can be considered to be the perturbed molecular systems formed by the introduction of cross links between



$\varphi_6 (b_{1g})$ $\varphi_{12} (b_{1g})$

φ_{6a} φ_{6b}

Figure 3. A schematic representation of the RHF MOs φ_6 and φ_{12} and UHF MOs φ_{6a} and φ_{6b} of cyclic bicalicene

atoms having the same parity in [4*n*]annulenes.[15] Within a simple one-electron picture, the HOMOs in annulenes are the doubly degenerate nonbonding molecular orbitals (NBMOs), and the introduction of such cross links lifts the degeneracy so that one MO is bonding and the other antibonding. Since the HOMO and LUMO generally originate from the NBMOs, there still remains nonbonding character in the MOs of interest. Indeed, in cyclic bicalicene $2K_{89}$ is estimated to be only 0.140 eV, within the ZDO approximation. Therefore, it is expected that the energy ordering of the singlet–triplet pair could be reversed if there exist SP terms effective for energy lowering of Φ_S.

Table 1 shows the energy lowering of Φ_S and Φ_T due to SP terms obtained by use of second-order perturbation theory. As expected, the energy lowering is about twice as large for the singlet as for the triplet. Configuration analysis reveals that the two main SP terms are the doubly excited configurations including one-electron excitations from φ_6 to φ_{12} and from φ_7 to φ_{10}, in order of importance. The contribution from these two SP terms amounts to about one-half of the total energy lowering obtained by including all the SP terms. Mixing of φ_{12} into φ_6 results in the appearance of new spatial MOs for α and β electrons, the unrestricted HF (UHF) MOs: $\varphi_{6a,6b} = \varphi_6\cos\theta \pm \varphi_{12}\sin\theta$.[16] In Figure 3 are shown the spatial parts of the spin orbitals $\varphi_{6a}{}^{\alpha}$ and $\varphi_{6b}{}^{\beta}$ obtained by assuming $\theta = \pi/4$. The atomic-orbital coefficients of these orbitals are localized almost entirely in the different regions. Since the spin states of the two electrons can be interchanged in considering SP effects on Φ_S and Φ_T, no net spin densities appear at any carbon atoms. This is why the mechanism is referred to as dynamic spin polarization. As is seen from Figures 2 and 3, the distributions of atomic-orbital coefficients in φ_{6a} and φ_{6b} resemble closely those in φ_8 and φ_9, respectively. It is thus expected that the electron repulsions in Φ_S and Φ_T can be reduced through Coulomb repulsions between the different spin orbitals and exchange interactions between the same spin orbitals. Indeed, introducing the spin-polarized MOs into Φ_S and Φ_T and expanding them in terms of the RHF MOs,[17] we have the correlated wave functions as in equations (iii), where $\Phi_S{}^1$ stands for the SP term

$$\Phi_S{}^c = \cos^2\theta\Phi_S + \sqrt{\tfrac{1}{6}}\sin2\theta\{\sqrt{2}\Phi_Q(6,8\rightarrow9,12) - \Phi_S{}^1\} - \sin^2\theta\Phi_S(6,6,8\rightarrow9,12,12) \quad \text{(iiia)}$$

$$\Phi_T{}^c = \cos^2\theta\Phi_T + \sqrt{\tfrac{1}{2}}\sin2\theta\Phi_T{}^1 - \sin^2\theta\Phi_T(6,6,8\rightarrow9,12,12) \quad \text{(iiib)}$$

given by equation (iia) and $\Phi_T{}^1$ for the one given by equation (iib), in which orbital indices *i*, *k*, *x*, and *y* correspond to φ_6, φ_{12}, φ_8, and φ_9, respectively. Further, $\Phi_Q(6,8\rightarrow9,12)$ and $\Phi_{S,T}(6,6,8\rightarrow9,12,12)$ denote the wavefunction of the doubly excited quintet state ($M_s = 0$) and those of the triply excited singlet–triplet pair like those given by equation (i), respectively. From the correlated wavefunctions (iiia) and (iiib), we can confirm that the SP terms $\Phi_S{}^1$ and $\Phi_T{}^1$ are the configurations that break the Brillouin theorem[5] and in fact lower the energies of Φ_S and Φ_T to a first-order approximation because they interact with Φ_S and Φ_T, respectively: this is the physical meaning of SP terms in a CI-type treatment.

It follows from Table 1 that the extra stabilization of the singlet due to SP effects is 0.467 eV. This lowers the energy of the singlet state below that of the triplet state by 0.327 eV. In addition to SP effects, we take into account correlation effects due to SDT excited configurations. Interestingly, such excited configurations lower the energy more for the triplet than for the singlet. In Table 2 are shown the respective extra stabilization

Table 2. Extra stabilization energies of the triplet state due to singly (S), doubly (D), and triply (T) excited configurations (in eV)

Molecule (Point group)	Extra stabilization energy[a]		
	S	D[b]	T
(1) (D_{2h})	0.031	0.125	0.013
(2) (D_{2h})	0.037	0.151	0.052
(3) (D_{2h})	0.032	0.198	0.070
(3) (C_{2h})	0.440	−0.145	0.087

[a] A negative value means that the energy lowering for the singlet is larger than for the triplet. [b] Effects due to SP terms are excluded.

energies, due to SDT excited configurations, of the triplet state relative to those of the singlet state. The contributions from singly and triply excited configurations are rather small, but it can be seen that the extra stabilization due to doubly excited configurations is more important in determining the energetic order of the singlet–triplet pair. The inclusion of these correlation effects results in the violation of Hund's rule such that the lowest excited singlet state (B_{3g}) lies below the corresponding triplet state by 0.16 eV.

Cyclic Bisesquifulvalene (2).—The situation here is quite similar to the case of cyclic bicalicene. The energy gap for the lowest excited singlet–triplet pair is 0.111 eV before SP effects are included. Since the SP terms generally lower the energy more for the singlet than for the triplet (Table 1), the energy ordering can be reversed such that the singlet state lies below the triplet state by 0.287 eV. On the other hand, Table 2 shows that, in contrast with SP terms, SDT excited configurations lower the energy more for the triplet than for the singlet, and the extra stabilization of the triplet amounts to 0.240 eV. This contribution is rather large, but it turns out that the lowest excited singlet state (B_{3g}) still lies below the corresponding triplet state by about 0.05 eV.

Cyclic Bitriaheptafulvalene (3).—As already noted, the ground state of this molecule has two equilibrium geometries: one is the delocalized D_{2h} structure corresponding to the saddle point of the potential energy surface, and the other the bond-alternating C_{2h} structure corresponding to the energy minimum point (Figure 1).

In the D_{2h} structure, the lowest excited singlet–triplet pair arising from the single MO transition from the HOMO to the next LUMO belongs to the B_{3g} irreducible representation. It turns out that the singlet–triplet energy separation is 0.087 eV before SP effects are included. The origin of such a small energy separation is ascribed to the marked localization of the two MOs (see Figure 2). Tables 1 and 2 show that the extra stabilization of the singlet due to SP terms is 0.431 eV, while that of the triplet due to SDT excited configurations is 0.300 eV. After the inclusion of these effects, the lowest excited singlet state (B_{3g}) is predicted to be lower in energy than the triplet state by 0.04 eV.

In the C_{2h} structure, the lowest excited singlet and triplet states also arise from the single MO transition from the HOMO to the next LUMO, and they belong to the A_g irreducible representation. The singlet–triplet energy separation is calculated to be 0.476 eV before SP effects are included. The reason for such a large energy separation is that, in contrast with the situation for the D_{2h} structure, the HOMO and the next LUMO have atomic orbitals in common in the bond-alternating C_{2h} structure. Table 1 shows that the contribution of SP effects to the singlet is four times smaller in the C_{2h} structure than in the D_{2h} one. No extra stabilization of the singlet exceeds the original singlet–triplet energy separation. As a result, the lowest excited singlet state (A_g) is predicted to lie above the triplet state, as predicted by Hund's rule.

From the foregoing results, it is expected that the potential energy curves for the excited singlet and triplet states of the molecule (3) will intersect at a slightly distorted nuclear arrangement, as in the cases observed for the lowest excited states of the propalene homologues.[2]

Conclusions

In the framework of the semiempirical PPP-type SCF MO method,[12-18] we have examined the relative energy ordering of the lowest excited singlet–triplet pair by taking into account correlation effects. Within this MO approach Hund's rule breaks down for the singlet–triplet pairs in cyclic bicalicene and its higher homologues. A characteristic feature inherent in these molecules is that the HOMO and LUMO (or next LUMO) which become occupied in the excited states are markedly localized to different regions; this is a decisive factor that leads to violation. SP terms lower the energy more for the open-shell singlet than for the triplet (by a factor of about two). In contrast to this, doubly excited configurations excluding SP terms lower the energy more for the triplet than for the singlet. From these results, it can be concluded, at least in these nonalternant hydrocarbons, that whether or not the energetic order of the singlet–triplet pair can be predicted by Hund's rule is determined by competition between the foregoing effects.

As already noted, we have made use of the semiempirical PPP-type MO method; we do not consider that this impairs qualitatively the main conclusions obtained in this paper. Finally, since the lowest excited singlet–triplet pair of cyclic bicalicene is a good candidate for violation of Hund's rule, we expect that the present prediction will be examined experimentally in the near future.

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