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Violation of Hund's rule in the lowest excited singlet-triplet pairs of dicyclohepta[*cd*,*gh*]pentalene and dicyclopenta[*ef*,*kl*]heptalene

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Using the Pariser-Parr-Pople type MO method, the energy ordering of the lowest excited singlet-triplet pairs of the title molecules is examined by taking into account ample configuration interactions. In dicyclohepta[*cd*,*gh*]pentalene, it is shown that the lowest excited singlet state lies below the corresponding triplet state by about 6 kcal/mol. This violation of Hund's rule is ascribed entirely to the correlation effects brought about by spin polarization terms. Such a violation of Hund's rule is expected to occur in the lowest excited states of dicyclopenta[*ef*,*kl*]heptalene.

Key words: Violation of Hund's rule — Spin polarization effects — Dicyclohepta[*cd*,*gh*]pentalene — Dicyclopenta[*ef*,*kl*]heptalene

1. Introduction

Following Hund's rule [1], the triplet state arising from the same molecular orbital (MO) occupancy of a molecule lies below the corresponding singlet state. However, Toyota et al. [2] have shown that Hund's rule is violated in the lowest excited singlet-triplet pairs of certain nonalternant hydrocarbons by means of the Pariser-Parr-Pople (PPP) type SCF MO method and the *ab initio* MO method with STO-3G basis set, and by taking into account configuration interactions. For propalene, pentalene, and heptalene, which are known to show the lattice instabilities (i.e., the molecular-symmetry reductions) from D_{2h} to C_{2h} [3], it is

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shown that the lowest excited singlet state at the D_{2h} structure is lower in energy than the corresponding triplet state, irrespective of the MO methods used. An important feature common to the molecules is that the highest occupied MO (HOMO) and the lowest unoccupied MO (LUMO) which become singly occupied in the excited states are localized to different regions. This violation of Hund's rule is explained in terms of dynamic spin polarization (SP) effects [4–6].

In connection with the symmetrical pentalene molecule, it is of interest to examine the energetic order of the lowest excited singlet–triplet pair in dicyclohepta[*cd,gh*]pentalene [7], because the PPP-type SCF MO calculation including all of the singlet excited configurations shows that the lowest excited B_{3g} singlet state is very close in energy to the corresponding triplet state [8]. Further, such MO treatments of dicyclopenta[*ef,kl*]heptalene [9] provide almost the same transition energies for the lowest excited B_{3g} singlet and triplet states.

In this paper, we are concerned with the possible violation of Hund's rule for the lowest excited singlet–triplet pairs of dicyclohepta[*cd,gh*]pentalene and dicyclopenta[*ef,kl*]heptalene by means of the PPP-type SCF MO method [10–13] and by taking into account correlation effects due to all of the doubly and triply excited configurations. It is shown that Hund's rule breaks down for the lowest excited states of the nonalternant hydrocarbons and this violation is ascribed substantially to the correlation effects due to SP terms.

2. Theory

The theory of SP effects exists in an article by Kollmar and Staemmler [6]. However, we give here a brief account of the theory, since SP effects are important essentially for determining the energy ordering of the singlet–triplet pair [14].

The wavefunctions of the excited singlet–triplet pair arising from a single MO jump $\phi_x \rightarrow \phi_y$ are assumed to be given by

$$\Phi_{S,T} = \frac{1}{\sqrt{2}} \{ |i\bar{i}x\bar{y}| \mp |i\bar{i}\bar{x}y| \} \tag{1}$$

where i denotes a doubly occupied MO and x and y the singly occupied MOs. In Eq. (1), doubly occupied MOs other than ϕ_i are omitted for simplicity. In this approximation, the triplet state lies below the singlet state by $2K_{xy}$, where K_{xy} is the exchange integral between ϕ_x and ϕ_y.

SP effects on the singlet–triplet pair can be achieved in a CI-type calculation by including the types of doubly excited configurations given below:

$$\begin{aligned}\Phi_S^1 = \frac{1}{\sqrt{12}} \{ & 2(|\bar{i}\bar{k}xy| + |ik\bar{x}\bar{y}|) - |\bar{i}k\bar{x}y| - |i\bar{k}x\bar{y}| \\ & - |i\bar{k}\bar{x}y| - |\bar{i}kx\bar{y}| \}\end{aligned} \tag{2a}$$

$$\Phi_T^1 = \frac{1}{2} \{ |\bar{i}k\bar{x}y| - |i\bar{k}x\bar{y}| + |i\bar{k}\bar{x}y| - |\bar{i}kx\bar{y}| \} \tag{2b}$$

$$\Phi_T^2 = \frac{1}{\sqrt{2}} \{ |\bar{i}\bar{k}xy| - |ik\bar{x}\bar{y}| \} \tag{2c}$$

where k denotes a virtual MO. There are in general many doubly excited configurations like those represented by Eqs. (2a), (2b), and (2c). In the molecular systems treated in this paper, it is noted that of such excited configurations, those in which ϕ_i and ϕ_k belong to the same irreducible representation have nonvanishing matrix elements with the wavefunctions given in Eq. (1) and are responsible for the SP effects on the singlet-triplet energy separation. It is shown that the matrix element of Φ_S with Φ_S^1 is $\sqrt{3}$ times larger than that of ϕ_T with Φ_T^1. On the basis of the second-order perturbation theory, it is shown that this leads to a stabilization which is about three times larger for the singlet state than for the triplet state, provided that the energy denominators are equal. This gives rise to an essential difference between the correlation effects on the singlet and triplet states, since the matrix element of Φ_T with Φ_T^2 is very small and, hence, the correlation contribution from Φ_T^2 is negligible.

It can thus be expected that, in molecules in which the energy separation between the singlet-triplet pair at the Hartree-Fock (HF) level is very small for certain reasons, SP effects which bring about the 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 of the singly, doubly, and triply (SDT) excited configurations from the restricted HF (RHF) ground state. This is because such excited configurations give direct contributions in general to the correlation energies of the open-shell singlet and triplet states and can influence the singlet-triplet energy separation.

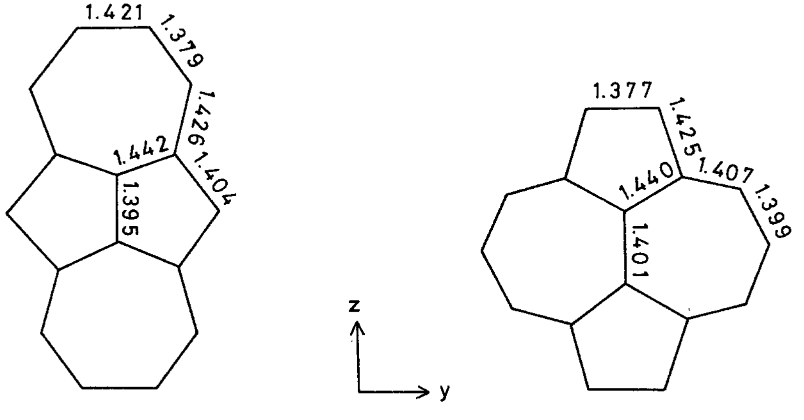
3. Results and discussion

3.1. Geometrical structures

The optimum D_{2h} nuclear arrangements with respect to C-C bond lengths of dicyclohepta[*cd,gh*]pentalene and dicyclopenta[*ef,kl*]heptalene were calculated previously [8] by means of the PPP-type SCF MO method in conjunction with the variable-bond-length technique [13]. It is noted that excepting rather a longer bond length for the central ethylene-like moiety (1.395 Å) in dicyclohepta[*cd,gh*]pentalene, all the predicted bond lengths (Fig. 1) are in good quantitative agreement with the recently reported X-ray data [15, 16]. Using the ground-state geometrical structures thus obtained, we are concerned with the energy ordering of the excited singlet-triplet pair produced by the vertical (Franck-Condon) excitations from the ground state.

3.2. Relative energy ordering of the singlet-triplet pairs

The effects of SP terms and SDT excited configurations on the singlet-triplet energy separation are examined by adopting two different types of methods [13] when estimating two-center repulsion integrals, one corresponding to the Pariser-Parr (PP) formula [10] and the other to the Mataga-Nishimoto (MN) approximation [12]. A discussion will be based mainly on the results obtained using the latter method.



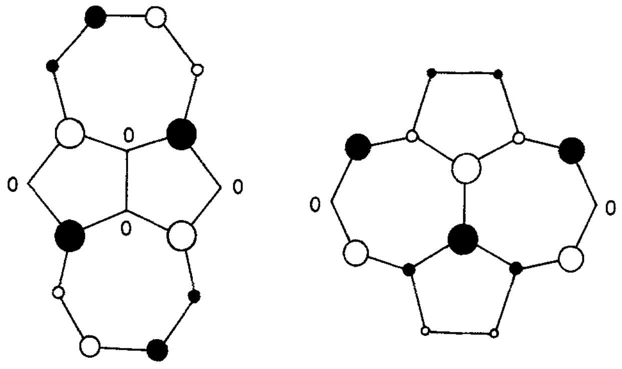
(1) (2)

Fig. 1. The bond lengths (in Å) of the D_{2h} ground state for dicyclohepta[*cd,gh*]pentalene (1) and dicyclopenta[*ef,kl*]heptalene (2) and the choice of molecular axis

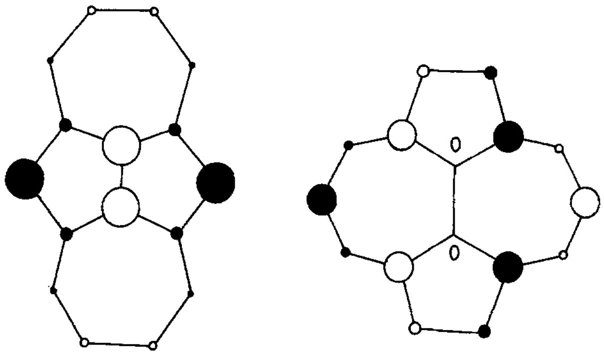
3.2.1. Dicyclohepta[*cd,gh*]*pentalene.* Both PP and MN methods reveal that the next HOMO and the HOMO are very close in energy [17], and lead to that the lowest excited singlet and the corresponding triplet state arise from the single MO transition from the next HOMO $\phi_7(b_{3u})$ to the LUMO $\phi_9(a_u)$, belonging to the B_{3g} irreducible representation [8]. Experimentally, a very weak absorption band observed at the longest wavelength (ca. 1.9 eV) [18, 19] can be assigned to the electronically forbidden singlet transition just mentioned. Fig. 2 shows the distribution of the atomic-orbital coefficients of ϕ_7 and ϕ_9, where white and black circles denote plus and minus signs, respectively. It can be seen that the two MOs are markedly localized to different regions especially on the pentalene-like skeleton and, hence, the exchange integral K_{79} responsible for the zeroth-order singlet–triplet energy separation should be small. Indeed, $2K_{79}$ is estimated to be only 0.153 eV within the zero-differential-overlap (ZDO) approximation, and this magnitude compares well with the corresponding value (0.162 eV) obtained in the symmetrical pentalene molecule [2]. Therefore, it is expected that the energy ordering of the singlet–triplet pair could be reversed if there exist SP terms effective for the energy lowering of Φ_S.

Table 1 shows the energy lowerings of Φ_S and Φ_T due to SP terms obtained by use of second-order perturbation theory. As is expected, the energy lowering is about twice as large for the singlet state as for the triplet state [2, 20]. Configuration analysis reveals that the two main SP terms are the doubly excited configurations including one-electron excitations from ϕ_8 to ϕ_{12} and from ϕ_6 to ϕ_{16}, 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 and the extra stabilization energy of the singlet state relative to the stabilization of the triplet state exceeds the value of the zeroth-order separation.

Let us show how such SP terms lower the energies of Φ_S and Φ_T effectively. Here, we take into account only the most important orbital jump above. Mixing



LUMO: $\phi_9(a_u)$ LUMO: $\phi_9(b_{2g})$



next HOMO: $\phi_7(b_{3u})$ HOMO: $\phi_8(b_{1g})$

Fig. 2. The distribution of atomic-orbital coefficients in the (next) HOMO and the LUMO of the molecules (1) and (2)

Table 1. Energy lowerings of Φ_S and Φ_T due to SP terms and energy separations ΔE_{ST} between the two states (in eV) in dicyclohepta[*cd,gh*]pentalene (1) and dicyclopenta[*ef,kl*]heptalene (2)

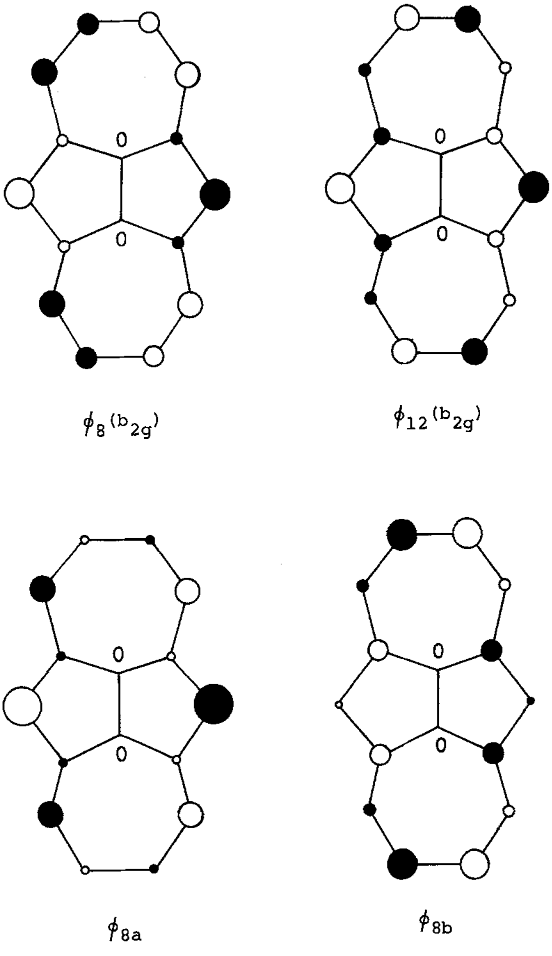
Molecule (method)	Energy lowering (SP)		ΔE_{ST}[a]		
	$\Delta E(\Phi_S)$	$\Delta E(\Phi_T)$	$2K_{xy}$	$2K_{xy}+SP$	$2K_{xy}+\mathrm{SP}+\mathrm{SDT}$
1 (MN)	0.767	0.421	0.153	−0.193	−0.269
1 (PP)	0.588	0.340	0.110	−0.138	−0.163
2 (MN)	0.793	0.388	0.210	−0.195	−0.177
2 (PP)	0.689	0.375	0.151	−0.163	−0.042

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

of ϕ_{12} into ϕ_8 results in the appearance of new spatial orbitals for α and β electrons, the unrestricted HF (UHF) MOs [21]:

$$\phi_{8a,8b} = \phi_8 \cos\theta \pm \phi_{12} \sin\theta \qquad (0 \leq \theta \leq \pi/2) \tag{3}$$

where θ is the dimensionless mixing parameter. Figure 3 shows the spatial parts of the spin orbitals ϕ_{8a} and ϕ_{8b} 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 [5, 6]. As is seen from Figs. 2 and 3, the distributions of the atomic-orbital coefficients in ϕ_{8a} and ϕ_{8b} resemble fairly those in ϕ_7 and ϕ_9, respectively. Electron repulsion in both Φ_S and Φ_T can be reduced if ϕ_7 and ϕ_{8a} are occupied by electrons with the same spin, likewise ϕ_9 and ϕ_{8b}. Thus the reduction of the Coulomb repulsion between electrons of different spin can be larger than the increase of Coulomb



$\phi_8(b_{2g})$ $\phi_{12}(b_{2g})$

ϕ_{8a} ϕ_{8b}

Fig. 3. The schematic representation of the RHF MOs ϕ_8 and ϕ_{12} and the UHF MOs ϕ_{8a} and ϕ_{8b} of the molecule (1)

minus exchange repulsion of electrons with the same spin. Indeed, introducing the spin-polarized MOs into Φ_S and Φ_T and expanding them in terms of the RHF MOs [22], we have the correlated wavefunctions as:

$$\Phi_S^c = \cos^2\theta\Phi_S + \sin 2\theta/\sqrt{6}\{\sqrt{2}\cdot\Phi_Q(7, 8 \to 9, 12) - \Phi_S^1\} - \sin^2\theta\Phi_S(7, 8, 8 \to 9, 12, 12) \tag{4a}$$

$$\Phi_T^c = \cos^2\theta\Phi_T + \sin 2\theta/\sqrt{2}\cdot\Phi_T^1 - \sin^2\theta\Phi_T(7, 8, 8 \to 9, 12, 12) \tag{4b}$$

where Φ_S^1 stands for the SP term given by Eq. (2a) and Φ_T^1 for the one given by Eq. (2b), in which orbital indices i, k, x, and y correspond to ϕ_8, ϕ_{12}, ϕ_7, and ϕ_9, respectively. Further, $\Phi_Q(7, 8 \to 9, 12)$ and $\Phi_{S,T}(7, 8, 8 \to 9, 12, 12)$ 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 Eq. (1), respectively. It can be shown that the matrix element of Φ_S with $\Phi_S(7, 8, 8 \to 9, 12, 12)$ and that of Φ_T with $\Phi_T(7, 8, 8 \to 9, 12, 12)$ have the same value and the energy gaps between Φ_S and $\Phi_S(7, 8, 8 \to 9, 12, 12)$ and between Φ_T and $\Phi_T(7, 8, 8 \to 9, 12, 12)$ are the same in general as far as Φ_S and Φ_T are written as Eq. (1). Therefore, it is ascertained that the energy separation between Φ_S and Φ_T is not affected virtually by the triply excited configurations (*vide infra*), but it would be largely influenced by the SP terms because the matrix element of Φ_S with Φ_S^1 is $\sqrt{3}$ times larger than that of Φ_T with Φ_T^1 [6]. Actually, the partial energy lowering of Φ_S due to Φ_S^1 is greater than that of Φ_T due to Φ_T^1 by 0.132 eV, which being just comparable to the value of $2K_{79}$.

It follows from Table 1 that the extra stabilization of the singlet state due to SP effects is 0.346 eV. This lowers the energy of the singlet state below that of the triplet state by 0.193 eV. In addition to SP effects, we take into account other correlation effects. In Table 2 we show the respective extra stabilization energies, due to SDT excited configurations, of the singlet state relative to those of the triplet state. Even though each contribution is very small, both PP and MN methods suggest that almost all the SDT excited configurations bring about an

Table 2. Extra stabilization energies of the singlet state due to singly (S), doubly (D), and triply (T) excited configurations (in eV) in dicyclohepta[*cd*,*gh*]pentalene (1) and dicyclopenta[*ef*,*kl*]heptalene (2)

Molecule (method)	Extra stabilization energy[a]		
	S	D[b]	T
1 (MN)	−0.007	−0.049	−0.020
1 (PP)	−0.019	−0.011	0.005
2 (MN)	0.006	−0.002	0.014
2 (PP)	0.010	0.116	−0.005

[a] A negative value means that the energy lowering for the singlet state is larger than for the triplet state

[b] Effects due to SP terms are excluded

energy lowering for the singlet state rather than for the triplet state. Consequently, 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 0.269 eV.

3.2.2. Dicyclopenta[ef,kl]heptalene. In this molecule, the lowest excited singlet and the corresponding triplet state arise from the single MO jump from the HOMO $\phi_8(b_{1g})$ to the LUMO $\phi_9(b_{2g})$, belonging to the B_{3g} irreducible representation. Figure 2 shows that the two MOs are localized conspicuously in the different regions on the heptalene-like skeleton. Hence, the situation here is quite similar to the case of dicyclohepta[*cd,gh*]pentalene; the energy separation for the lowest singlet–triplet pair is estimated to be 0.210 eV before SP effects are included (Table 1). This magnitude compares well with the corresponding separation (0.140 eV) obtained in the symmetrical heptalene molecule [2]. As is listed in Table 1, since SP terms generally lower the energy more for the singlet state than for the triplet state, the energy ordering can be reversed such that the singlet state lies below the corresponding triplet state by 0.195 eV. Configuration analysis reveals that the main two SP terms are the doubly excited configurations including one-electron excitations from ϕ_5 to ϕ_{10} and from ϕ_4 to ϕ_{11}, in order of importance. Table 2 shows that, in contrast with the case of dicyclohepta[*cd,gh*]pentalene, almost all the SDT excited configurations contribute to an energy lowering for the triplet state rather than for the singlet state, especially the effect of doubly excited configurations calculated using the PP method being appreciably large. However, it turns out that, even after the inclusion of such correlation contributions, the lowest excited singlet state (B_{3g}) still lies below the corresponding triplet state by 0.042 eV with the PP method and by 0.177 eV with the MN method, indicating a violation of Hund's rule.

4. Conclusion

Since the molecular systems under consideration are rather large, we have employed here the PPP-type SCF MO method. The present investigation leads to the prediction that Hund's rule is violated in the lowest excited B_{3g} singlet–triplet pairs of dicyclohepta[*cd,gh*]pentalene and dicyclopenta[*ef,kl*]heptalene at least within the semiempirical MO approximations used. A characteristic feature inherent in the molecules is that the (next) HOMO and the LUMO which become singly occupied in the excited states are localized to different regions on the pentalene-like skeleton for the former [23] and on the heptalene-like skeleton for the latter. This is a crucial factor that leads to the violation. While SP terms lower the energy more for the excited singlet state than for the corresponding triplet state, the correlation effects due to SDT excited configurations on the singlet–triplet energy separation are rather small. From these results it is concluded in the two molecules that whether the relative energy ordering of the singlet–triplet pair can be predicted by Hund's rule is determined by the competition between the size of the zeroth-order energy separation and that of the extra stabilization of the singlet state due to SP terms.

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