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Orbital Phase Control of the Stabilities of π-Conjugated Diradicals

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The concept of orbital phase continuity–discontinuity was applied to π-conjugated diradicals. Cyclic orbital interactions are involved in the spin polarization and delocalization in acyclic π-conjugated diradicals. The relative stabilities of the singlet isomers, those of the triplet isomers, and the spin multiplicities of the ground states were shown to be predicted by the orbital phase properties. The heteroatom effects on the spin preference was shown to be related to the *degree* of the continuity (discontinuity) of the orbital phase.

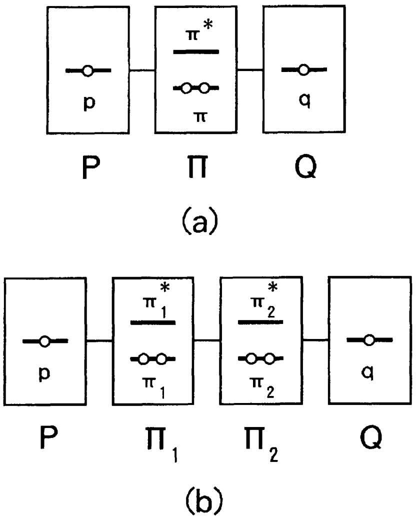
Cyclic orbital interactions are involved in the molecular systems of *acyclic* geometries.[1—4] The relative stabilities of cross vs. linear conjugated systems are controlled by the orbital phase continuity–discontinuity properties.[1] Orbital phase theory accounts for the regioselectivities of organic reactions[2] and for the abnormally acute L–M–L angles in ML$_2$[3] and ML$_3$[4] complexes. The stabilities of the closed-shell systems are now known to be controlled by the orbital phase properties.

Diradicals are intermediates in photochemical reactions[5] and prototypes of molecular magnetic materials.[6] The stability of the intermediate diradicals is one of the essential factors for determining the reaction paths. The spin multiplicities of the ground states are critical for the magnetism. The present work was undertaken to develop an orbital phase theory for the open-shell systems or for the singlet and triplet π-conjugated diradicals. We derived an orbital phase requirement for stabilizing the diradicals. This theory was successfully applied to predicting the relative stabilities of the singlet (triplet) isomers. Also, the theory was found to be useful for predicting the spin multiplicity of the ground states. Furthermore, the theory was found to give insight into the heteroatom effects on the spin preference.

Although some theories have been developed by Borden and Davidson,[7] by Ovchinnikov[8] and by Radhakrishnan[9] for the spin preference, these theories cannot be applied either to the relative stabilities of isomeric diradicals or to the heteroatom effects. The orbital phase theory leads to the same prediction about the spin preference of both alternant and nonalternant hydrocarbon diradicals as does Radhakrishnan's rule. The scope of the Borden–Davidson and Ovchinnikov theories is limited to the alternant diradicals. The orbital phase predictions are in agreement with those by the Ovchinnikov theory, and partly with those by the Borden–Davidson theory.

Orbital Phase Continuity Requirement

We studied acyclic-conjugated diradicals (Fig. 1a), where two radical centers (P and Q) interact with each other through a π-bond (Π). We derived the orbital phase requirements for the spin polarization and delocalization.



(a)

(b)

Fig. 1. Acyclic π-conjugated diradicals with the radical centers intervened by (a) one and (b) two π-bonds.

Triplet State.[10] The mechanism of the delocalization and polarization of α-spin electrons in the triplet state is schematically represented in Fig. 2a. Each of the radical orbitals (p and q), and the bonding π-orbital (π) is occupied by one electron in the ground configuration, $^3G^{\alpha}$. The electron in p shifts to the antibonding π-orbital (π*) through an interaction of the ground configuration with the transferred configuration, $^3T_1^{\alpha}$. The mixing of the transferred configuration gives rise to electron delocalization from the radical center to the π-bond. The configuration interaction is approximated by the p–π* interaction. The resulting electron hole in p is supplied with an electron by π through an interaction of the transferred configuration with the locally-excited configuration, $^3E^{\alpha}$. The mixing of the excited cofiguration polarizes the π-bond. The configuration interaction is approximated by the π–p interaction. The $^3G^{\alpha}$–$^3T_1^{\alpha}$–$^3E^{\alpha}$ or π–p–π* interaction is involved in the delocalization–polarization process.

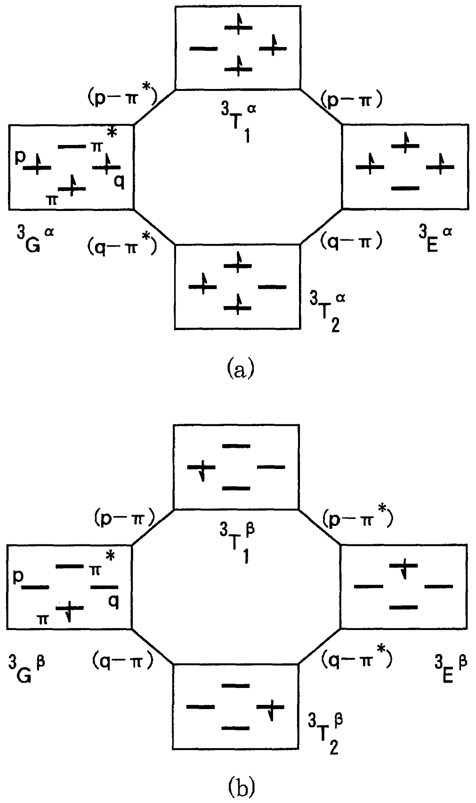


Fig. 2. Delocalization–polarization mechanisms of (a) α- and (b) β-spin electrons in the triplet states of the P–Π–Q diradicals.

The process through the other radical orbital (q) involves the $^3G^\alpha$–$^3T_2^\alpha$–$^3E^\alpha$ or π–q–π^* interaction. As a result, the cyclic –$^3G^\alpha$–$^3T_1^\alpha$–$^3E^\alpha$–$^3T_2^\alpha$– or –π–p–π^*–q– interaction (Fig. 3a) occurs.

For an effective occurrence of the cyclic configuration interaction, the delocalization–polarization processes via different radical centers are required to enhance each other by interference. The sign of the coefficient of the excited configuration is determined by the overlap integrals between the configurations involved in the delocalization–polarization processes, i.e., $S(^3G^\alpha,{}^3T^\alpha)S(^3T^\alpha,{}^3E^\alpha)$. For the same signs to be given by different processes, the following inequality is required to be satisfied:

$$S(^3G^\alpha,{}^3T_1^\alpha)S(^3T_1^\alpha,{}^3E^\alpha)S(^3E^\alpha,{}^3T_2^\alpha)S(^3T_2^\alpha,{}^3G^\alpha)>0. \quad (1)$$

This can be rewritten as

$$s(p,\pi^*)s(\pi^*,q)s(q,\pi)s(\pi,p)>0, \quad (2)$$

where s denotes the orbital overlap integral.[11)]

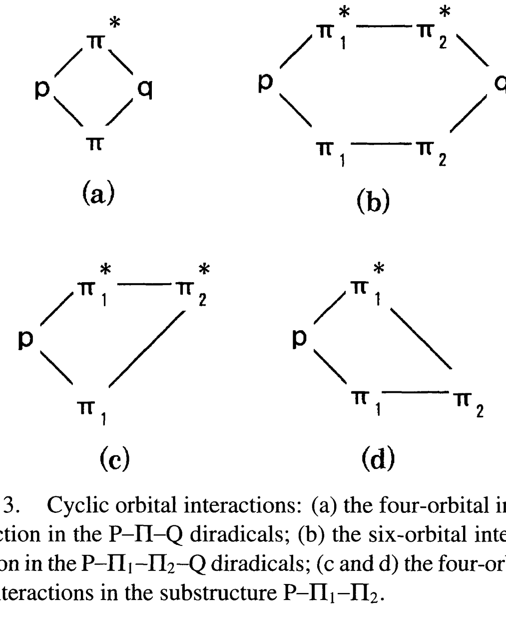


Fig. 3. Cyclic orbital interactions: (a) the four-orbital interaction in the P–Π–Q diradicals; (b) the six-orbital interaction in the P–Π$_1$–Π$_2$–Q diradicals; (c and d) the four-orbital interactions in the substructure P–Π$_1$–Π$_2$.

The requirement (inequality 2) is equivalent to a simultaneous satisfaction of the orbital phase continuity conditions: i) the electron-donating orbitals are out of phase; ii) the accepting orbitals are in phase; and iii) the donating and accepting orbitals are in phase. The donating and accepting orbitals are occupied and unoccupied by electrons in the ground configurations, respectively. The radical orbitals, p and q, are electron-donating for α-spin. The π and π^* orbitals are electron-donating and -accepting orbitals, respectively. When the continuity conditions are satisfied, $s(p,\pi^*)>0$, $s(\pi^*,q)>0$, $s(q,\pi)<0$, and $s(\pi,p)<0$. It follows that inequality 2 is satisfied. The phase conditions are essentially the same as those for acyclic[1)] and cyclic[12)] closed-shell molecules. If the conditions are satisfied or the orbital phase is continuous, both delocalization and polarization effectively occur.

The delocalization–polarization mechanism of the β-spin is shown in Fig. 2b. The cyclic –$^3G^\beta$–$^3T_1^\beta$–$^3E^\beta$–$^3T_2^\beta$– or –π–p–π^*–q– interaction (Fig. 3a) occurs.[13)] Inequality 2 is required.[11)] The same orbital phase-continuity conditions as those described above were applicable to the β-spin. In this case the radical orbitals, p and q, are electron-accepting.

Singlet State. The delocalization–polarization mechanism of the α-spin in the singlet state is shown in Fig. 4. Cyclic –$^1G^\alpha$–$^1T_1^\alpha$–$^1E^\alpha$–$^1T_2^\alpha$– or –π–p–π^*–q– interaction (Fig. 3a)[14)] occurs. The cyclic orbital interaction is also involved in the delocalization from p to q via π and π^* (Fig. 4).[15)] The following inequality is required:[16)]

$$(-1)s(p,\pi^*)s(\pi^*,q)s(q,\pi)s(\pi,p)>0. \quad (3)$$

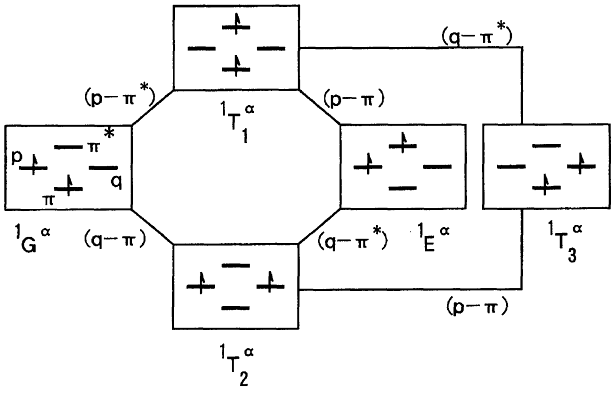


Fig. 4. Delocalization–polarization mechanism of α-spin electrons in the singlet states of the P–Π–Q diradicals.

The sign of the left side is opposite to that of inequality 2 for the triplet states. *The phase continuity properties of the singlet and triplet states of a given diradical are opposite to each other.* Inequality 3 is included in the orbital phase continuity conditions described above. One radical orbital, p, is electron-donating and the other, q, is accepting in the singlet states. When the continuity conditions are satisfied, $s(p,\pi^*)>0$, $s(\pi^*,q)>0$, $s(q,\pi)>0$, and $s(\pi,p)<0$. It follows that inequality 3 is satisfied.

Stability. The phase continuity stabilizes the ground state and destabilizes the excited state. The phase discontinuity neither stabilizes the ground state nor destabilizes the excited state. *The stability decreases in the order of the continuous phase ground state > the discontinuous phase ground state > the discontinuous phase excited state > the continuous phase excited state.*

Relative Stability of Isomers

C_4H_6 Diradicals (1,2). Orbital phase theory has been applied to the triplet states of 2-methylidenepropane-1,3-diyl (**1**) and 2-butene-1,4-diyl diradical (**2**) (Chart 1). The cyclic orbital interaction involved in **1** meets the phase requirement for both spins (Fig. 5). For the α-spin the electron-donating radical orbitals, p and q, can simultaneously be out of phase with the donating orbital π and in phase with the accepting π^*. For β-spin the accepting radical orbitals, p and q, can be in phase with the donating π and the accepting π^*. The orbital phase is continuous. This is not the case with its isomer **2**. The orbital phase is discontinuous. The triplet diradicals, **1** and **2**, of present interest are the ground states of the triplet multiplicity. The diradical **1** is stabilized by the phase continuity, while **2** is not stabilized by the phase discontinuity. This is supported by the well-known thermodynamical stability of **1** relative to **2** (Table 1).[17—19]

The phase properties of the singlet states are opposite to those of the triplet states. The orbital phase is discontinuous in **1** and continuous in **2**. The singlet diradical **1** is the singlet ground state. The singlet diradical **2** is an excited state of butadiene. The discontinuous phase ground state is more stable than the continuous phase excited state, as described above. It follows that **1** should be more stable than **2**. This agrees with the previous calculations.[18,19]

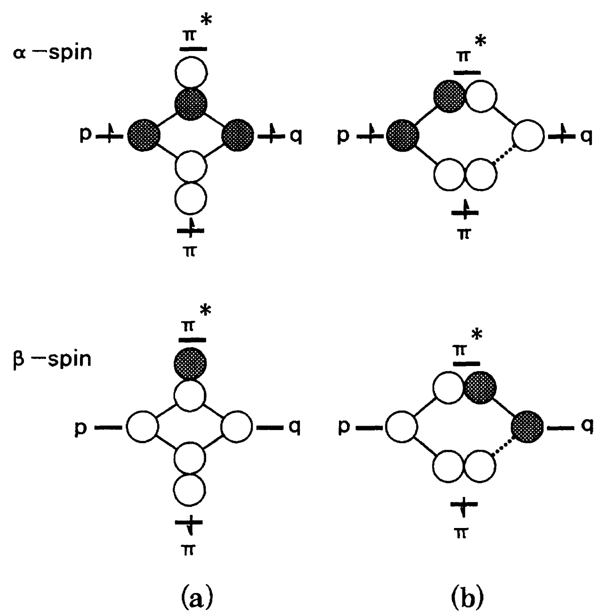


Fig. 5. The orbital phase properties in the triplet states: (a) the continuity in **1**; (b) the discontinuity in **2**.

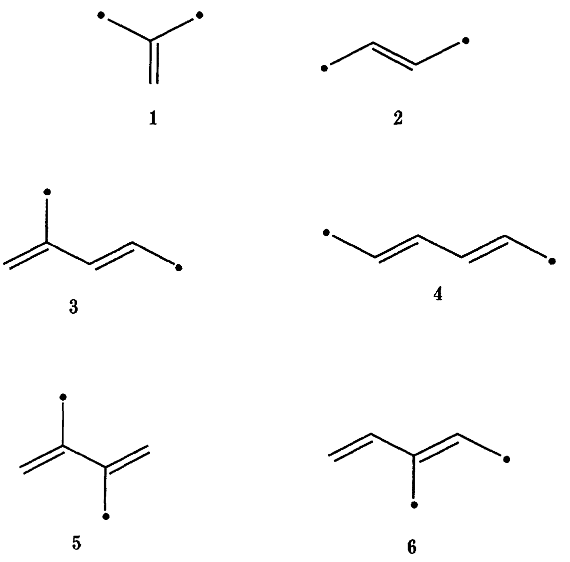


Chart 1.

Kekulé and Non-Kekulé Diradicals. Most of diradicals are stabilized by the orbital phase continuity. There are, however, a certain group of diradicals which are destabilized by the phase continuity. This is the case with the singlet diradical **2**, as discussed above. It is useful to classify the π-conjugated diradicals into two classes, *Kekulé and non-Kekulé diradicals.* The Kekulé diradicals are defined as the excited states of the Kekulé molecules. For example, diradical **2** is a Kekulé diradical, since **2** is an excited state of the Kekulé molecule, butadiene. The non-Kekulé diradicals (e.g. **1**) are among the conventional non-Kekulé molecules. The orbital phase is continuous in the singlet states of the Kekulé diradicals. The diradical states are the excited states. *The singlet Kekulé diradicals are destabilized by the orbital phase property. The triplet Kekulé diradicals and the singlet and triplet non-Kelulé diradicals are stabilized by the orbital phase continuity.*

Analysis of Electronic Structures. The method for evaluating the electron delocalization from bonds to bonds and the polarization of bonds has been useful for investigating the electronic structures of closed-shell systems.[1,4,20] We developed a method for open-shell molecules to examine the preceding qualitative theory in a numerical manner.[21] The delocalization and polarization were estimated to be C_T/C_G and C_E/C_G i.e., the ratios of coefficients of the transferred and the locally-excited configurations to that of the ground configuration. The bond orbitals were optimized so as to maximize the C_G value. The MCSCF wavefunctions were employed for analyzing the electronic structures. The re-

Table 1. Total Energies (hartrees), Relative Energies (kcal mol^{-1}) of Isomers (ΔE_i), and the Singlet–Triplet Energy Splitting (ΔE_{S-T}) of the Diradicals by the MCSCF Calculations[a]

	Triplet			Singlet			
	State	Total	ΔE_i[b]	State	Total	ΔE_i[b]	ΔE_{S-T}[c]
1	$1^3A'_2$	−153.0321	0.0	1^1A_1	−152.9984	0.0	21.1
2	1^3B_u	−153.0077[d]	15.3	2^1A_g	−152.8959[d]	64.3	
3	$1^3A'$	−229.0257	0.0	$1^1A'$	−229.0055	3.9	12.7
4	1^3B_u	−229.0141	7.3	2^1A_g	−228.9239	55.1	
5	1^3B_{2u}	−229.0068	11.9	1^1A_g	−229.0117	0.0	−3.1
6	1^3A_1	−228.9941	19.8	1^1B_2	−228.8949	73.3	
7	1^3B_2	−303.8454	6.6	2^1A_1	−303.7235	72.5	
8	1^3B_2	−303.8559	0.0	1^1A_1	−303.8391	0.0	10.5
9	1^3B_{2u}	−303.8369	11.9	2^1A_g	−303.7153	77.7	
10	1^3B_2	−304.9220		1^1A_1	−304.9219		0.06
		−304.9670[e]			−304.9661[e]		0.56[e]
12	1^3B_2	−455.6587		1^1A_1	−455.6620		−2.0
15	1^3B_2	−454.5882		1^1A_1	−454.5100		49.1
16	1^3B_2	−454.5560		1^1A_1	−454.5340		13.8
17	1^3B_2	−454.5772		1^1A_1	−454.5366		25.5

a) The MCSCF (4,4)/STO-3G method for **1** and **2** and the MCSCF (6,6)/STO-3G for the other molecules were employed. b) Relative to the energy of the most stable isomer. c) A positive value indicates that the triplet state is more stable than the singlet state. d) Ref. 19. e) The MCSCF (8,8)/STO-3G calculations.

sults (Table 2) confirmed the orbital phase theory. For the triplet states the polarization of the π-bond or the mixing of the locally excited configuration is significant in **1** (0.689) relative to **2** (0.243). The delocalization between the radical center and the π-bond also prefers **1** (0.209, 0.338) to **2** (0.139, 0.148). The singlet diradical **2** or the excited state of butadiene showed significant delocalizations (0.287, 0.254) and polarization (0.873) relative to those (0.126, 0.139, and 0.023) of **1**. The distant delocalization between the radical centers is also significant in **2** (0.060) relative to **1** (0.005).

Table 2. Electron Delocalization from Bonds to Bonds and Polarization of Bonds[a]

	Triplet					
	$\pi \to p$	$p \to \pi^*$	$\pi \to \pi^*$	$\pi_{CO} \to p$	$p \to \pi^*_{CO}$	$\pi_{CO} \to \pi^*_{CO}$
1	0.209	0.338	0.689			
2	0.139	0.148	0.243			
18				0.130	0.329	0.626
19	0.159	0.230	0.371			
20	0.147	0.211	0.349	0.089	0.206	0.252
21				0.100	0.216	0.290

	Singlet						
	$\pi \to p$	$p \to \pi^*$	$\pi \to \pi^*$	$\pi_{CO} \to p$	$p \to \pi^*_{CO}$	$\pi_{CO} \to \pi^*_{CO}$	$p \to q$
1	0.126	0.139	0.023				0.005
2	0.287	0.254	0.873				0.060
18				0.091	0.163	0.023	0.006
19	0.092	0.162	0.025				0.045
20	0.091	0.165	0.025	0.066	0.189	0.026	0.055
21				0.066	0.192	0.028	0.065

a) Indicated by the absolute values of the coefficient ratios (C_T/C_G and C_E/C_G). The MCSCF (4,4)/STO-3G wavefunctions of **1**, **2**, and **18** and the MCSCF (6,6)/STO-3G wavefunctions of **19**, **20**, and **21** were employed.

The cyclic orbital interactions were shown to be involved in the acyclic P–Π–Q systems. The relative stabilities of isomers of the singlet (triplet) diradicals were shown to be controlled by the orbital phase continuity–discontinuity properties.

C_6H_8 Diradicals (3—6). We have applied orbital phase theory to extended conjugated diradicals with one more π-bond (P–Π_1–Π_2–Q, Fig. 1b). A cyclic six-orbital interaction (Fig. 3b) is involved. In the triplet state of diradical **3** the orbital phase is continuous (Fig. 6a). Diradical **3** is stabilized. The phase is discontinuous in **4** and **5** (Figs. 6b and 6c, respectively). These diradicals are not stabilized. Diradical **6** contains substructure **2**, where the four-orbital phase is discontinuous (Fig. 5b). The phase restriction is more strict in **6** than **4** and **5**, since the radical centers are closer to each other. We can say that the orbital phase discontinuity is higher in **6**. Diradical **6** is the least stable isomer. The triplet stability is predicted to decrease in the order **3**>**4**, **5**>**6**.

The relative stability of triplet diradicals **4** and **5** is determined by the cyclic four-orbital interactions (Figs. 3c and 3d) in the substructure P–Π_1–Π_2. The four-orbital interaction shown in Fig. 3c is involved in both the delocalization of the α-spin to the distant π-bond, Π_2, and the polarization of Π_1 (Fig. 7). The interaction plays a dual role. The orbital phase is continuous in **4** (Fig. 9). The other four-orbital interaction (Fig. 3d) is involved in the polarization of Π_1 (Fig. 8), which is not accompanied by distant delocalization. The interaction is less important. The phase is continuous in **5**. The diradical **4** is thus expected to be more stable than **5**. The relative stability of the C_6H_8 triplet diradicals should decrease in the order **3**>**4**>**5**>**6**. This prediction was supported by MCSCF (6,6)[22] calculations. Isomers **4**, **5**, and **6** are 7.3, 11.9, and 19.8 kcal mol^{-1} less stable than **3**, respectively.

The orbital phase property of the singlet states is opposite

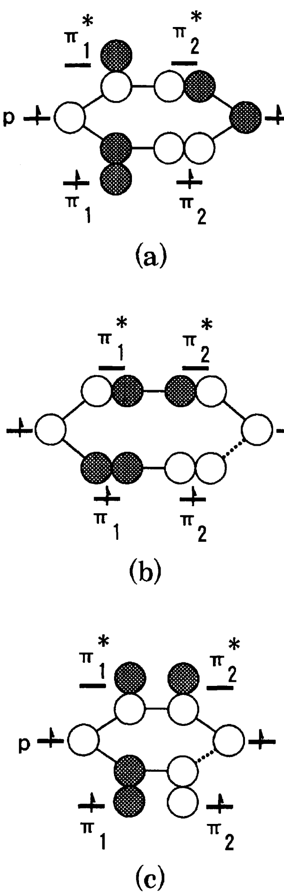


Fig. 6. The orbital phase properties in the triplet states: (a) the continuity in **3**; (b) the discontinuity in **4**; (c) the discontinuity in **5**.

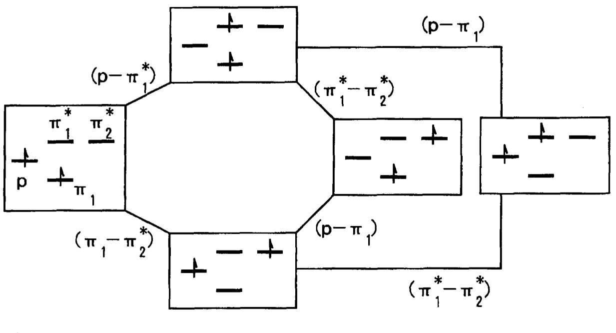


Fig. 7. The distant electron delocalization from P to Π_2 and the polarization of Π_1 in the substructure P–Π_1–Π_2 involve the cyclic $-\pi_1-p-\pi_1^*-\pi_2^*-$ interaction.

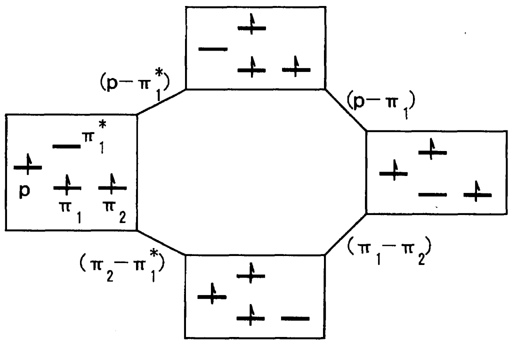


Fig. 8. The polarization of Π_1 in the substructure P–Π_1–Π_2 involves the cyclic $-\pi_1-p-\pi_1^*-\pi_2-$ interaction.

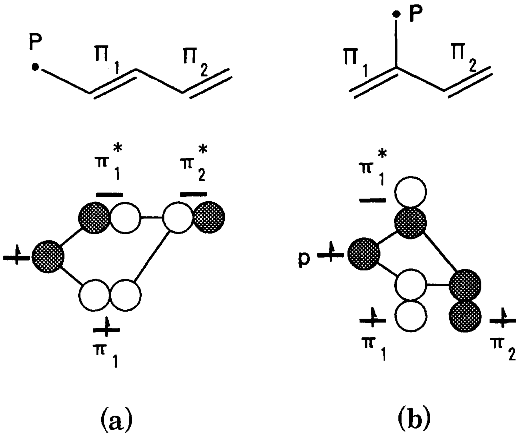


Fig. 9. The phase continuities of the cyclic orbital interactions in the substructures P–Π_1–Π_2 of **4** (a) and **5** (b).

to that of the triplet states, as discussed above. The stability of the singlet diradicals should decreases in the reverse order **6**>**5**>**4**>**3** if all are non-Kekulé diradicals. However, **4** and **6** are Kekulé diradicals. As discussed above, the singlet Kekulé diradicals are outstandingly destabilized by the phase continuity. Diradicals **4** and **6** are less stable than **3** and **5** (**5**>**3**>**4**,**6**). The four-orbital phase continuity destabilizes **6** more than the six-orbital phase continuity does **4**. The singlet stability is predicted to decrease in the order **5**>**3**>**4**>**6**. This is consistent with the MCSCF (6,6) calculations (Table 1). Diradical **5** is 3.9 kcal mol^{-1} more stable than **3**. The destabilization of the singlet Kekulé diradicals due to the phase continuity is conspicuous. Several tens kcal mol^{-1} of the relative instabilities were obtained for **4** and **6**. The difference between the four- and six-orbital phase continuities was confirmed by the calculated great destabilization of diradical **6** (1^1B_2) relative to **4** (2^1A_g).

Phenylenebismethyls (7—9). From the resonance structures and the preceding results we readily see that the stability of the triplet states decreases in the order **8**>**7**>**9** (Chart 2). Diradical **8** (*m*-isomer) contains substructure **3**, where the six-orbital phase is continuous (Fig. 6a). Diradical **8** is stabilized. The *p*-isomer **9** has substructure **4**, where the six-orbital phase is discontinuous (Fig. 6b). Diradical **7** (*o*-isomer) contains a vinylogous structure of **4**, P–Π_1–Π_2–Π_3–Q, where the eight-orbital phase is discontinuous. Diradicals **7** and **9** are not stabilized. The phase discontinuity is lower in **7** than in **9** (**7**>**9**). The decrease in stability as **8**>**7**>**9** was confirmed by MCSCF (6,6) calculations (Table 1). The *o*- and *p*-isomers are 6.6 and 11.9 kcal mol^{-1} less stable than the *m*-isomer, respectively. The tendency of **7** toward a P–Π_1–Π_2–Π_3–Q system was supported by the appreciably long distance (1.479 Å) between the carbons, substituted by methylenes in the optimized structure.

The phase properties of the singlet states are opposite to those of the triplet states. The stability of the singlet diradicals decreases in the reverse order **9**>**7**>**8** if all are non-

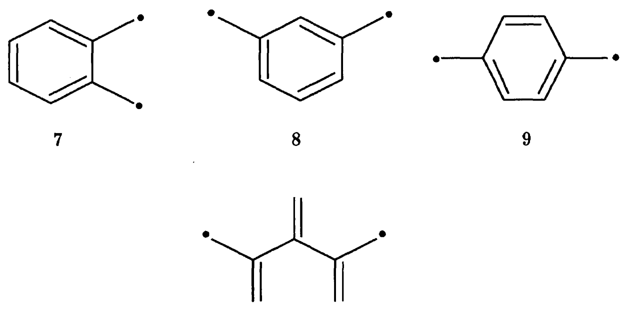


Chart 2.

Kekulé diradicals. However, **7** and **9** are Kekulé diradicals. The singlet states are destabilized (**8**>**7**, **9**). Diradicals **9** and **7** contain **4** and its vinylogs, respectively, as the substructures. The destabilization of **9** by the six-orbital phase continuity is greater than that of **7** by the eight-orbital phase continuity. The relative singlet stability is predicted to decrease in the order **8**>**7**>**9**. This was confirmed by MCSCF (6,6) calculations (Table 1). The non-Kekulé diradical **8**, not stabilized due to the phase discontinuity, was calculated to be 70 kcal mol^{-1} more stable than Kekulé diradicals **7** and **9**, destabilized by the phase continuity. The calculations supported that the *o*-isomer **7** of the low phase continuity is less destabilized than the *p*-isomer **9** of the high continuity.

Spin Preference

The orbital phase has been shown to control the delocalization of the unpaired electrons and the polarization in the conjugated π-diradicals. The phase continuity–discontinuity properties of the singlet and triplet states are opposite to each other. The spin preference can be predicted based on the phase properties.

Hydrocarbon Diradicals. The orbital phase is continuous in the triplet states of **1** (Fig. 5a), **3** and **8** (Fig. 6a). This suggests that the ground states should be triplets. This is in agreement with the experimental observations about **1**.[23,24] The MCSCF calculations showed that the preference of the triplet to the singlet state, $\Delta E_{\mathrm{S-T}}$, is 21.1 kcal mol^{-1}. The calculated $C_{\mathrm{T}}/C_{\mathrm{G}}$ and $C_{\mathrm{E}}/C_{\mathrm{G}}$ values (Table 2) showed greater delocalization and polarization in the triplet state than those in the singlet state, and supported the theory. The triplet preference of **3** and **8** is also in agreement with the previous calculations,[17,25] and the experimental observations.[26,27] Our MCSCF calculations estimated the stabilizations (12.7 and 10.5 kcal mol^{-1}) of the triplet states of **3** and **8** relative to the singlets, respectively.

The orbital phase is continuous in the singlet state of the non-Kekulé diradicals **5** (see the triplet phase discontinuity in Fig. 6c). The ground state is predicted to be a singlet. In agreement with this, the CI calculations[28] confirmed the singlet preference in the planar geometry.[29] The present MCSCF (6,6) calculations showed the preference of 3.1 kcal mol^{-1}.

Among the Kekulé diradicals are **2**, **4**, **6**, **7**, and **9**. The singlet diradicals are overwhelmingly destabilized by the phase properties. The triplet diradicals are more stable.

Some theories concerning the spin preference have been proposed by Borden and Davidson,[7] by Ovchinnikov,[8] and by Radhakrishnan.[9] Predictions based on these theories are in agreement with the orbital phase predictions concerning the alternant hydrocarbon diradicals: **1**, **3**, **5**, and **8**. Interestingly, the existing theories lead to the opposite spin preferences of **10**. According to Borden and Davidson, **10** is grouped into the same class as **5**, where the ground states are singlets. The Ovchinnikov and Radhakrishnan theories lead to a triplet preference. The cyclic eight-orbital interaction in **10** is favored by the phase-continuity in the triplet state. The ground state should be a triplet. This was supported by the present MCSCF calculations and others.[31] The MCSCF (8,8)[22] calculations showed a slight (0.56 kcal mol^{-1}) triplet preference.

Orbital phase theory can be applied to nonalternant systems as well as Radhakrishnan's rule, while the theories of Ovchinnikov and of Borden and Davidson were developed only for the alternant systems. The nonalternant system **11** contains substructures **1** and **5**, where the phase properties are opposite to each other (Chart 3). The orbital phases are continuous in the triplet state of **1** and in the singlet state of **5**. The four-orbital phase continuity in **1** is more effective than the six-orbital one in **5**. The ground state is predicted to be a triplet. This agrees with the result of a calculation.[31b] Substructures **5** and **10** are contained in **12**. The phase continuity in the singlet state of **5** is more effective than that of the eight-orbital interaction in the triplet state of **10**. The ground state is predicted to be a singlet. This agrees with the result of MCSCF (6,6) calculations. The singlet ground state is 2.0 kcal mol^{-1} more stable than the triplet.

The orbital phase continuity of **1** is the most effective in the triplet diradicals. The substructure is contained in the bismethylene-type derivatives (**13** and **14**) of triafulvene (methylidenecyclopropene) and fulvene (methylidenecyclopentadiene) and those of azulene (**15**—**17**). The ground states are predicted to be triplets. These predictions are in agreement with the results of the calculations,[17,32] or were confirmed by the present MCSCF (6,6) calculations (Table 1).

Hetero Diradicals. The orbital phase theory was applied to the hetero diradicals where the carbon atoms were replaced by heteroatoms. The spin preference of the hetero diradicals are significantly different from the isoelectronic hydrocarbon diradicals. The heteroatoms change the donor–acceptor interaction involved in the cyclic interaction. This may enhance the orbital interaction on a path and weaken that on the other. The cyclic orbital interaction or the continuity–discontinuity property is less effective.

2-Oxopropane-1,3-diyl (**18**) is a hetero analog of **1**, where the orbital phase is continuous in the triplet state and discontinuous in the singlet state (Chart 4). The diradical is the P–Π–Q system, where Π is an electron-withdrawing carbonyl group. The lowering of the π and π* orbitals in energy strengthens the interactions of the radical center orbitals with π* and weakens those with π. The same effect is expected from the bond polarity. The π* and π orbitals extend more

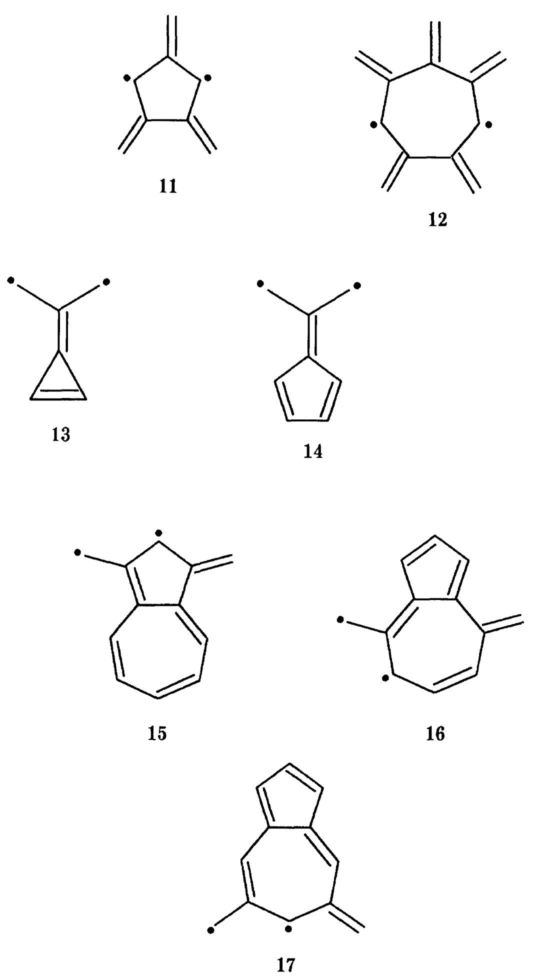


Chart 3.

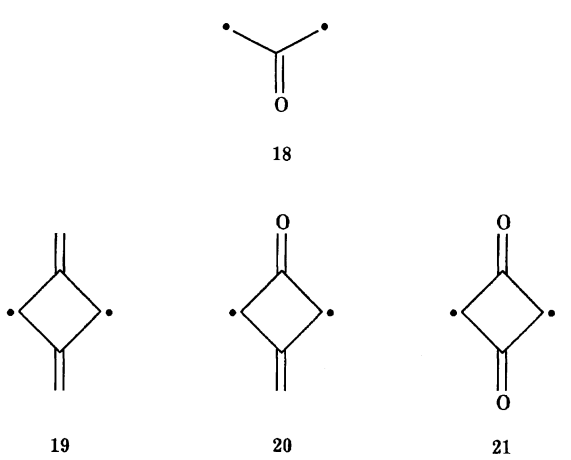


Chart 4.

and less, respectively, at the position (the carbonyl carbon) interacting with the radical centers. The $p-\pi^*-q$ interaction is more effective than the $p-\pi-q$ one. The interactions are involved in the delocalization between the radical centers in the singlet states (Fig. 4). The phase discontinuity in the singlet state is not complete. The cyclic $-\pi-p-\pi^*-q-$ interaction stabilizes the singlet state to some degree. The phase continuity in the triplet state exhibits a smaller effect. The triplet stabilization decreases. The singlet–triplet energy gap of **18** should decrease relative to that of **1**. This agrees with the results of the MCSCF calculations.33)

An analysis of the electronic structures (Table 2) supported the preceding arguments. In the singlet states the unpaired electrons delocalize between the radical centers in **18** (0.006) more than in **1** (0.005), as expected from the lowered phase discontinuity. The delocalization from p to $\pi^*_{C=O}$ in **18** (0.163) is greater than that to $\pi^*_{C=C}$ in **1** (0.139). The delocalization from $\pi_{C=O}$ to p in **18** (0.091) is smaller than that from $\pi_{C=C}$ in **1** (0.126). In the triplet state the delocalization and polarization are all decreased by oxygen substitution. An interesting fact is the decrease in the delocalization from the radical centers to the double bond. From the donor–acceptor property, the delocalization is expected to increase due to the electron-withdrawing capability of C=O. This implies that the strengthening of a part of the cyclic orbital interaction and the weakening of the other part decreases the effect of the orbital phase continuity.

Alkyl substitution on the carbon radical centers or alkano bridge introduction between the radical centers in **18** further mitigates the phase discontinuity in the singlet state. The substituents and the bridges increase the energies of the radical orbitals. This strengthens the $p-\pi^*-q$ interaction and weakens the $p-\pi-q$ interaction. In fact, the ground states of the substituted34) and bridged35) derivatives of **18** are singlets.

Cyclic Conjugated Diradicals. The monooxa (**20**) and dioxa (**21**) analogs of 2,4-dimethylidenecyclobutane-1,3-diyl diradical (**19**) have one and two 2-oxopropane-1,3-diyl units, respectively. The instability of the singlet state relative to the triplet state is expected to decrease with the number of 2-oxopropane-1,3-diyl units or in the order **19**>**20**>**21**. These diradicals are cyclic in their geometries. There are cyclic orbital interactions due to the cyclic geometries. The cyclic $-p-\pi_1^*-q-\pi_2^*-$ interaction is favored due to the orbital phase continuity in the singlet state (Fig. 10). The interaction is the most effective in the dioxa analog. This implies the extrastabilization of the singlet state of **21** due to cyclic conjugation. The increasing relative stabilization of the singlet state with oxygen substitution is in agreement with the results of calculations.36) The relative energy (ΔE_{S-T}) decreases in the order **19** (20.2 kcal mol^{-1})>**20** (11.8 kcal mol^{-1})>**21** (−12.9 kcal mol^{-1}). The ground states of **19** and **20** are triplets. The ground state of **21** is a singlet. In the singlet states the delocalization between the radical centers increases in the order **19** (0.045)<**20** (0.055)<**21** (0.065). These re-

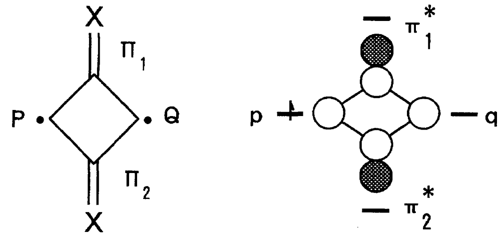


Fig. 10. The phase continuity of the cyclic $-p-\pi_1^*-q-\pi_2^*-$ orbital interaction caused by the cyclic geometries of **21**.

sults have confirmed the orbital phase theory.

Conclusion

We have developed an orbital phase theory for the open-shell electronic structures. Cyclic orbital interactions are involved in the acyclic π-conjugated diradicals. The orbital phase continuity is required for electron delocalization and polarization. The orbital phase theory was successfully applied to the relative stabilities of the singlet (triplet) diradical isomers and to the spin preferences of the ground states of both the nonalternant and alternant hydrocarbon diradicals. The effect of heteroatoms on the spin preference was discussed in terms of the degree of the orbital phase continuity or discontinuity. The orbital phase theory has been shown to control the stabilities of the open-shell structures as well as acyclic(1) and cyclic(12) closed-shell molecules and the stabilities of the triplet states as well as the singlet states.

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11) The spin eigenfunctions of the triplet state with M_S (z-component of the total spin)=1 are written as

$$\begin{aligned}
{}^3\mathrm{G} &= (4!)^{-1/2}|\pi\bar{\pi}\mathrm{pq}| \\
{}^3\mathrm{T}_1 &= (4!)^{-1/2}|\pi\bar{\pi}\pi^*\mathrm{q}| \\
{}^3\mathrm{T}_2 &= (4!)^{-1/2}|\pi\bar{\pi}\mathrm{p}\pi^*| \\
{}^3\mathrm{E} &= x({}^3\mathrm{E}_1) + y({}^3\mathrm{E}_2) + z({}^3\mathrm{E}_3)
\end{aligned}$$

where

$$\begin{aligned}
{}^3\mathrm{E}_1 &= 2^{-1}(4!)^{-1/2}(|\bar{\pi}\pi^*\mathrm{pq}| + |\pi\bar{\pi}^*\mathrm{pq}| - |\pi\pi^*\bar{\mathrm{p}}\mathrm{q}| - |\pi\pi^*\mathrm{p}\bar{\mathrm{q}}|) + \cdots \\
{}^3\mathrm{E}_2 &= 2^{-1}(4!)^{-1/2}(|\bar{\pi}\pi^*\mathrm{pq}| - |\pi\bar{\pi}^*\mathrm{pq}| + |\pi\pi^*\bar{\mathrm{p}}\mathrm{q}| - |\pi\pi^*\mathrm{p}\bar{\mathrm{q}}|) + \cdots \\
{}^3\mathrm{E}_3 &= 2^{-1}(4!)^{-1/2}(|\bar{\pi}\pi^*\mathrm{pq}| - |\pi\bar{\pi}^*\mathrm{pq}| - |\pi\pi^*\bar{\mathrm{p}}\mathrm{q}| + |\pi\pi^*\mathrm{p}\bar{\mathrm{q}}|) + \cdots \\
x^2 &+ y^2 + z^2 = 1 .
\end{aligned}$$

When we neglect the higher-order terms with respect to the orbital overlaps, s, the configuration overlaps are approximately expressed by the following equations.

$$\begin{aligned}
\mathrm{S}({}^3\mathrm{G}, {}^3\mathrm{T}_1) &= \mathrm{s}(\mathrm{p}, \pi^*) \\
\mathrm{S}({}^3\mathrm{T}_1, {}^3\mathrm{E}_1) &= \mathrm{s}(\mathrm{p}, \pi) \\
\mathrm{S}({}^3\mathrm{T}_1, {}^3\mathrm{E}_2) &= 0 \\
\mathrm{S}({}^3\mathrm{T}_1, {}^3\mathrm{E}_3) &= \mathrm{s}(\mathrm{p}, \pi) \\
\mathrm{S}({}^3\mathrm{E}_1, {}^3\mathrm{T}_2) &= \mathrm{s}(\mathrm{q}, \pi) \\
\mathrm{S}({}^3\mathrm{E}_2, {}^3\mathrm{T}_2) &= \mathrm{s}(\mathrm{q}, \pi) \\
\mathrm{S}({}^3\mathrm{E}_3, {}^3\mathrm{T}_2) &= 0 \\
\mathrm{S}({}^3\mathrm{T}_2, {}^3\mathrm{G}) &= \mathrm{s}(\mathrm{q}, \pi^*)
\end{aligned}$$

The product of the overlap integrals of the cyclically interacting configuratios, ${}^3\mathrm{G}$, ${}^3\mathrm{T}_1$, ${}^3\mathrm{E}_1$, and ${}^3\mathrm{T}_2$ is approximated:

$$\begin{aligned}
&\mathrm{S}({}^3\mathrm{G}, {}^3\mathrm{T}_1)\mathrm{S}({}^3\mathrm{T}_1, {}^3\mathrm{E}_1)\mathrm{S}({}^3\mathrm{E}_1, {}^3\mathrm{T}_2)\mathrm{S}({}^3\mathrm{T}_2, {}^3\mathrm{G}) \\
&= \mathrm{s}(\mathrm{p}, \pi^*)\mathrm{s}(\pi^*, \mathrm{q})\mathrm{s}(\mathrm{q}, \pi)\mathrm{s}(\pi, \mathrm{p})
\end{aligned}$$

The configurations ${}^3\mathrm{E}_2$ and ${}^3\mathrm{E}_3$ do not participate in any cyclic interactions since $\mathrm{S}({}^3\mathrm{T}_1, {}^3\mathrm{E}_2)=0$ and $\mathrm{S}({}^3\mathrm{E}_3, {}^3\mathrm{T}_2)=0$. We obtained the inequality 2. The same inequality was derived for the triplet states with $M_S=0, -1$.

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13) One electron occupies π in the ground configuration ${}^3\mathrm{G}^\beta$. The electron shifts to p through the interaction of the ground configuration with the transferred configuration ${}^3\mathrm{T}_1^\beta$ or through the π–p interaction. The electron further shifts to π^* through the interaction of the transferred configuration with the locally-excited configuration ${}^3\mathrm{E}^\beta$ or through the p–π^* interaction. The ${}^3\mathrm{G}^\beta$–${}^3\mathrm{T}_1^\beta$–${}^3\mathrm{E}^\beta$ or π–p–π^* interaction is involved in the delocalization–polarization process. The mixing of the transferred and excited configuration gives rise to the electron delocalization from Π to P and the polarization of Π, respectively. There is another delocalization–polarization process through the other radical orbital q, which involves the ${}^3\mathrm{G}^\beta$–${}^3\mathrm{T}_2^\beta$–${}^3\mathrm{E}^\beta$ or π–q–π^* interaction.

14) The electrons occupy π and p in the ground cofiguration ${}^1\mathrm{G}^\alpha$. The electron shifts from p to π^* through the interaction of the ground configuration with the transferred configuration ${}^1\mathrm{T}_1^\alpha$ or through the p–π^* interaction. The resulting electron hole in p is supplied with an electron by π through the interaction of the transferred configuration with the locally-excited configuration ${}^1\mathrm{E}^\alpha$ or through the π–p interaction. The ${}^1\mathrm{G}^\alpha$–${}^1\mathrm{T}_1^\alpha$–${}^1\mathrm{E}^\alpha$ or π–p–π^* interaction is involved. The other process involves the ${}^1\mathrm{G}^\alpha$–${}^1\mathrm{T}_2^\alpha$–${}^1\mathrm{E}^\alpha$ or π–q–π^* interaction.

15) The electron in π^* in the transferred configuration ${}^1\mathrm{T}_1^\alpha$ farther shifts to q through the interaction with another transferred configuration ${}^1\mathrm{T}_3^\alpha$ or through the q–π^* interaction. The electron hole in π in the transferred configuration ${}^1\mathrm{T}_2^\alpha$ is supplied with an electron by p through the interaction with ${}^1\mathrm{T}_3^\alpha$ or through the p–π interaction. The cyclic –${}^1\mathrm{G}^\alpha$–${}^1\mathrm{T}_1^\alpha$–${}^1\mathrm{T}_3^\alpha$–${}^1\mathrm{T}_2^\alpha$– or –π–p–π^*–q– interaction (Fig. 3a) occurs.

16) The spin eigenfunctions of the singlet state are written as

$$\begin{aligned}
{}^1\mathrm{G} &= (2\cdot 4!)^{-1/2}(|\pi\bar{\pi}\mathrm{p}\bar{\mathrm{q}}| - |\pi\bar{\pi}\bar{\mathrm{p}}\mathrm{q}|)\cdots \\
{}^1\mathrm{T}_1 &= (2\cdot 4!)^{-1/2}(|\pi\bar{\pi}\pi^*\bar{\mathrm{q}}| - |\pi\bar{\pi}\bar{\pi}^*\mathrm{q}|)\cdots \\
{}^1\mathrm{T}_2 &= (2\cdot 4!)^{-1/2}(|\pi\bar{\pi}\mathrm{p}\bar{\pi}^*| - |\pi\bar{\pi}\bar{\mathrm{p}}\pi^*|)\cdots \\
{}^1\mathrm{E} &= x({}^1\mathrm{E}_1) + y({}^1\mathrm{E}_2)
\end{aligned}$$

where

$$\begin{aligned}
{}^1\mathrm{E}_1 &= 2^{-1}(4!)^{-1/2}(|\bar{\pi}\bar{\pi}^*\mathrm{pq}| + |\pi\pi^*\bar{\mathrm{p}}\bar{\mathrm{q}}| - |\bar{\pi}\pi^*\bar{\mathrm{p}}\mathrm{q}| - |\pi\bar{\pi}^*\mathrm{p}\bar{\mathrm{q}}|) \\
&\quad + \cdots \\
{}^1\mathrm{E}_2 &= (12\cdot 4!)^{-1/2}(|\bar{\pi}\bar{\pi}^*\mathrm{pq}| + |\pi\pi^*\bar{\mathrm{p}}\bar{\mathrm{q}}| + |\bar{\pi}\pi^*\bar{\mathrm{p}}\mathrm{q}| + |\pi\bar{\pi}^*\mathrm{p}\bar{\mathrm{q}}| \\
&\quad -2|\bar{\pi}\pi^*\mathrm{p}\bar{\mathrm{q}}| - 2|\pi\bar{\pi}^*\bar{\mathrm{p}}\mathrm{q}|) + \cdots \\
x^2 + y^2 &= 1\,.
\end{aligned}$$

The overlap integrals of the configurations are approximated to the orbital overlaps

$$\begin{aligned}
&\mathrm{S}({}^1\mathrm{G},{}^1\mathrm{T}_1) = \mathrm{s}(\mathrm{p},\pi^*) \\
&\mathrm{S}({}^1\mathrm{T}_1,{}^1\mathrm{E}_1) = (-1)2^{-1/2}\mathrm{s}(\mathrm{p},\pi) \\
&\mathrm{S}({}^1\mathrm{T}_1,{}^1\mathrm{E}_2) = (-1)(3/2)^{1/2}\mathrm{s}(\mathrm{p},\pi) \\
&\mathrm{S}({}^1\mathrm{E}_1,{}^1\mathrm{T}_2) = 2^{1/2}\mathrm{s}(\mathrm{q},\pi) \\
&\mathrm{S}({}^1\mathrm{E}_2,{}^1\mathrm{T}_2) = 0 \\
&\mathrm{S}({}^1\mathrm{T}_2,{}^1\mathrm{G}) = \mathrm{s}(\mathrm{q},\pi^*)
\end{aligned}$$

We obtain a non-zero product of the cyclically interacting configurations:

$$\begin{aligned}
&\mathrm{S}({}^1\mathrm{G},{}^1\mathrm{T}_1)\mathrm{S}({}^1\mathrm{T}_1,{}^1\mathrm{E}_1)\mathrm{S}({}^1\mathrm{E}_1,{}^1\mathrm{T}_2)\mathrm{S}({}^1\mathrm{T}_2,{}^1\mathrm{G}) \\
&\quad = (-1)\mathrm{s}(\mathrm{p},\pi^*)\mathrm{s}(\pi^*,\mathrm{q})\mathrm{s}(\mathrm{q},\pi)\mathrm{s}(\pi,\mathrm{p})
\end{aligned}$$

The orbital overlaps involved are the same as those in the equation for the triplet state,[11] while the sign is opposite. This gives the inequality 3.

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21) The HF type total wavefunction, Ψ, of a molecule can be expanded as

$$\Psi = \sum_i c_i \Phi_i$$

where Φ_i is a configuration and c_i is its coefficient. The function Φ_i is a linear combination of the Slater determinants (ϕ_{ik}; k=1, 2, $\cdots$) composed of the bond orbitals:

$$\Phi_i = \sum_k A_{ik}\phi_{ik}\,.$$

The function Φ_i is *contained* in Ψ as an eigenfuction of $\hat{s}^2$. The total wavefunction is rewritten:

$$\Psi = \sum_{i,k} B_{ik}\phi_{ik}\,,$$

where B_{ik} is a coefficient of ϕ_{ik}. The comparison of the first equation with the last one gives

$$c_i\Phi_i = \sum_k B_{ik}\phi_{ik}\,.$$

By normalizing Φ_i, we obtained

$$|c_i| = (\sum_{k,l} B_{ik}S_{ik,il}B_{il})^{1/2}\,,$$

where the overlap integral between ϕ_{ik} and ϕ_{il} is denoted by $S_{ik,il}$. This equation is applicable to any spin states. For the present calculation we used no explicit formulas of the spin eigenfunctions, which are necessary for the Baba's method (H. Baba, S. Suzuki, and T. Takemura, *J. Chem. Phys.*, **50**, 2078 (1969)). If a CI wavefunction is employed, the products of B_{ik} and the CI expansion coefficient are summed up for all the CI configurations.

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