Tetrahedron Vol 46, No 11, pp. 3803-3812, 1990
Printed in Great Britain

0040-4020/90 $3.00+.00

SINGLET BIRADICAL AND ZWITTERIONIC STATES OF TWISTED FULVENES AND RELATED COMPOUNDS

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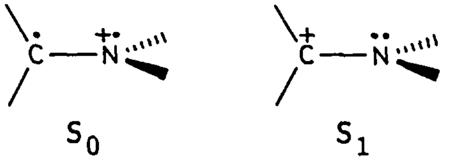
(*Received in Japan* 18 *January* 1990)

Abstract: The singlet biradical and zwitterionic states of 90°-twisted fulvenes and related compounds were investigated by the open-shell and closed-shell SCF calculations with the MINDO/3 approximation. Although, for the parent fulvene (**1**), the biradical state was more stable than the zwitterionic state by 23kcal/mol, substitution by some electron-donating groups at the 6-position inversed the relative stability of the two states. Moreover, the case was found in which the two states have nearly degenerate energies. It is shown that the relative stability of the two states is well predicted from the degree of polarization at the planar structure. Also, the variation of the electronic structure upon the double-bond twisting is discussed based on the 3×3 CI calculations.

Introduction

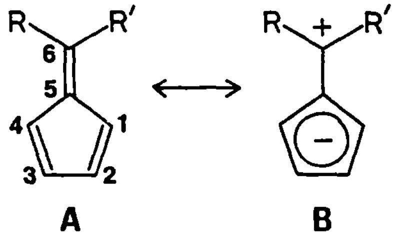
Twisted structures of olefinic compounds play an important role in photochemistry, because the return from the excited state to the electronic ground state is usually thought to occur at the 90°-twisted structure for these compounds. We have sufficient knowledge of the electronic structure of the twisted ethylene,[1,2] and it is well known that twisting ethylene around the double bond by 90° leads to a singlet biradical species. In contrast, twisting a polarized (push-pull) olefin around the double bond is thought to lead to a zwitterion.[3] Then, how is the critical case? Are there any compounds for which the singlet biradical and zwitterionic states have degenerate or nearly degenerate energies?

Recently, Bonačić-Koutecký et al. proposed the concept of "critically heterosymmetric biradicaloid" in connection with 90°-twisted olefins.[2] It corresponds to the structure at which the S_0 and S_1 surfaces touch or nearly touch, where S_0 and S_1 denote the ground and lowest excited singlet states. The S_0-S_1 surface touching is of particular interest in photochemistry, since it could lead to a high probability of the surface jump and to a dynamic memory effect[2,4]: The molecule retains a memory of the direction of arrival into the minimum (funnel) on the S_1 surface, and this is reflected in the nature and yield of the final product. It is thus very important to find out the critically heterosymmetric biradicaloids. Bonačić-Koutecký et al. stressed that charged biradicaloids are good candidates for critically heterosymmetric biradicaloids, the most representative being the 90°-twisted formaldiminium cation.[2,4]

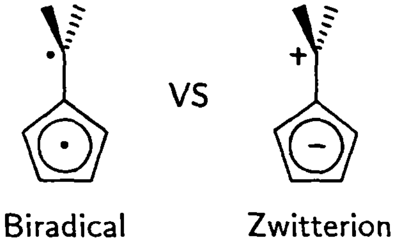


It is easily expected, however, that the twisted structures of moderately polarized olefins are also good candidates (neutral candidates) for the critically heterosymmetric biradicaloids.

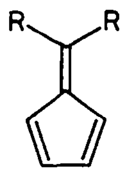
Fulvenes,[5] for which we can write one Kekule structure (**A**) as well as the dipolar structure (**B**), are of interest in this sense.



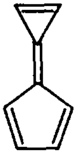
Although *ab initio* SCF calculations[6] have shown that the singlet biradical state of the 90°-twisted parent fulvene (**1**) is considerably lower in energy than the zwitterionic state, substitution by electron-donating groups at the 6-position is expected to stabilize the latter strongly relative to the former.



In the present study, the 90°-twisted structures of a variety of fulvenes and related compounds, the parent fulvene (**1**), substituted fulvenes (**2-9**), calicene (**10**),[8,9] benzocalicene (**11**),[9] sesquifulvalene (**12**), and hetero-sesquifulvalenes (**13-16**),[10] have been examined by using the semi-empirical MINDO/3 approximation.[7] We focus our discussion on (i) the relative stability of the singlet biradical and zwitterionic states at the 90°-twisted structure, and (ii) relationships between the relative stability of the two states and the molecular and electronic properties at the planar structure. Also, for **1**, **2**, **3**, and **10**, the potential energy curves for rigid twisting around the double bond are presented, and the variation of the electronic structure upon the twisting is discussed.



1 R = R′ = H
2 R = R′ = CH_3
3 R = R′ = NH_2
4 R, R′ = $-O-CH_2-CH_2-O-$
5 R, R′ = $-S-CH_2-CH_2-S-$
6 R = H, R′ = vinyl
7 R = H, R′ = NH_2
8 R = H, R′ = OH
9 R, R′ = $-O-CH_2-CH_2-NH-$



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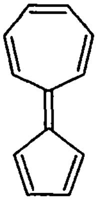

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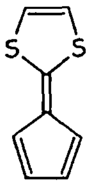

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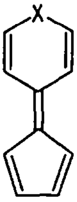
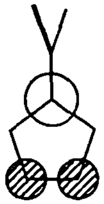


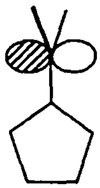
14 X = NH
15 X = O
16 X = S

Method

For the 90°-twisted structure, two orbitals (ψ_k and ψ_l) are available for the occupation of two electrons which are associated with the exocyclic (or intercyclic) double bond.



ψ_k



ψ_l

The singlet biradical state of the 90°-twisted structure is expressed by

$$^1\Phi_{BR} = \frac{1}{\sqrt{2}}\{|\ldots\psi_k\bar{\psi}_l| + |\ldots\psi_l\bar{\psi}_k|\} \qquad (1)$$

The zwitterionic state of the 90°-twisted structure is well represented by the closed-shell wavefunction

$$^{1}\Phi_{ZW} = |\ldots\psi_k\bar{\psi}_k| \qquad (2)$$

Another closed-shell wavefunction

$$^{1}\Phi_{ZW'} = |\ldots\psi_l\bar{\psi}_l| \qquad (3)$$

represents a zwitterion which is polarized oppositely to that represented by eq.(2), and have high energy.[11]

The singlet biradical state, eq.(1), was then calculated by the open-shell SCF method, and the zwitterionic state by the closed-shell SCF method by using eq.(2). The planar structure was also calculated by the closed-shell SCF method.

The potential energy curves for twisting around the double bond were obtained from the 3×3 CI calculations, because the 3×3 CI (two-electron two-orbital) description is essential for comprehensive understanding of closed-shell molecules and biradicals.[1,2] The MO's used for the CI calculation were obtained from the two-configuration SCF (TCSCF), open-shell SCF, or closed-shell SCF calculations (*vide infra*).

For all calculations, the semiempirical MINDO/3 approximation[7] was adopted.

Results and Discussion

The molecular structures of the planar form of **1-16** were optimized by assuming the C_{2v} symmetry for **1-5** and **10-16**,[12] and the electronic properties for the planar form were determined.

In order to evaluate the energy difference between the biradical and zwitterionic states of the 90°-twisted olefins, three different molecular structures were used. First, the calculation was carried out for the rigidly twisted perpendicular structure which was obtained from the energy-optimized planar form by the double-bond twisting. The energies of the former relative to the latter, ΔE_1, are listed in Table 1.

Next, the geometrical optimization was carried out for both of the two states at the 90°-twisted structure assuming the C_{2v} symmetry for **1-5** and **10-16**, and the C_s symmetry for **6-9**. The energy differences between the two states, ΔE_2, are also listed in Table 1.

Finally, the single point calculation of the S_0 state (biradical or zwitterionic) was carried out by using the geometry optimized for the S_1 state (zwitterionic or biradical), and the energy differences between the two states, ΔE_3, were obtained (Table 1). This energy difference may correspond to the adiabatic transition from the S_1 state to the S_0 state.

Table 1. The energy differences (kcal/mol) between the singlet biradical and zwitterionic states at the 90°-twisted structures (the energy of the former relative to the latter), and several properties at the planar structures of **1**-**16**

Compd.	Energy differences			$Q_\pi^{\mathrm{ring\,d)}}$	$Q^{\mathrm{ring\,e)}}$	$\mathrm{BO}^{\mathrm{f)}}$	$\mathrm{R}^{\mathrm{g)}}$
	$\Delta E_1{}^{\mathrm{a)}}$	$\Delta E_2{}^{\mathrm{b)}}$	$\Delta E_3{}^{\mathrm{c)}}$				
1	-21.2	-23.0	-17.1	5.048	-0.012	0.936	1.338
2	-25.2	-26.0	-21.7	5.069	-0.050	0.894	1.374
3	45.6	35.6	23.6	5.589	-0.417	0.648	1.407
4	20.7	18.7	13.1	5.445	-0.270	0.772	1.371
5	-2.0	-4.1	-0.5	5.195	-0.111	0.882	1.341
6	-19.4	-23.0	-18.1	5.065	-0.037	0.893	1.357
7	5.4	5.1	0.6	5.363	-0.248	0.790	1.370
8	4.1	2.9	-3.9	5.290	-0.184	0.850	1.356
9	23.2	21.6	16.9	5.500	-0.323	0.722	1.382
10	5.2	6.2	2.3	5.345	-0.222	0.803	1.358
11	1.6	2.4	-2.5	5.301	-0.203	0.812	1.359
12	-17.3	-16.0	-11.7	5.146	-0.114	0.835	1.387
13	-1.0	-3.0	0.5	5.200	-0.118	0.879	1.342
14	-5.9	-5.2	-1.5	5.290	-0.233	0.790	1.390
15	-9.1	-8.2	-4.4	5.236	-0.190	0.822	1.383
16	-18.3	-18.4	-14.7	5.131	-0.102	0.846	1.382

a) At the rigidly twisted structure. b) Geometry was optimized for each state. c) At the geometry optimized for the S_1 state. d) The total π-electron density on the five-membered ring. e) The net charge in the cyclopentadienylidene moiety. f) The π-bond order of the exocyclic (or intercyclic) double bond. g) The length of the exocyclic (or intercyclic) double bond in Å.

As may be seen from Table 1, the values of ΔE_1 and ΔE_2 are close to each other and the variation of ΔE_3 is roughly parallel to those of ΔE_1 and ΔE_2. ΔE_2 increases in the order of **2**<**1**=**6**<**16**<**12**<**15**<**14**<**5**<**13**<**11**<**8**<**7**<**10**<**4**<**9**<**3**. ΔE_1 and ΔE_3 increases in a similar order.

For the parent fulvene (**1**), the biradical is more stable than the zwitterion by 23.0kcal/mol. In contrast, for 6,6-diaminofulvene (**3**), the zwitterion is more stable than the biradical by 35.6kcal/mol. All of the other compounds except **2** lie between **1** and **3**. For **5**, **7**, **8**, **10**, **11**, **13**, and **14**, the biradical and zwitterion have similar energies, the differences being within 7kcal/mol. 90°-twisted structures of these compounds are then good candidates for critically heterosymmetric biradicaloids.[2] Rather surprising is the large stability of the biradicals for **12** and **16**: Although the zwitterion has two aromatic rings, the biradical was more stable by 16.0 and 18.4kcal/mol respectively.

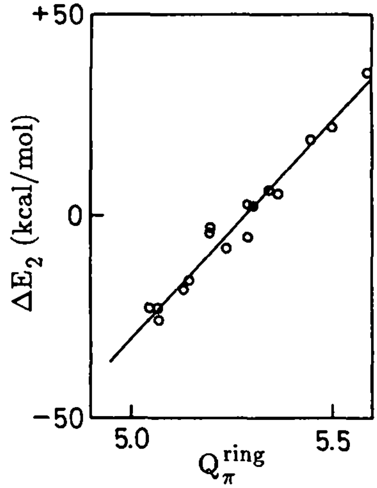


Figure 1. Relationship between ΔE_2 and Q_π^{ring}

Information about the relative stability between the biradical and zwitterionic states may be involved inherently in the planar structure. It is thus interesting to examine the correlations between ΔE_2 and various properties at the planar structure. A good correlation was obtained between ΔE_2 and the total π-electron density on the five-membered ring at the planar structure (Q_π^{ring}) which is larger than 5 reflecting the dipolar structure **B** (Table 1 and Figure 1). The correlation coefficient (r) is 0.98. The correlation between ΔE_2 and the net charge in the cyclopentadienylidene moiety (Q^{ring}) was also good (Table 1, r=-0.94). This is perhaps because the polarization of the σ-electron pairs is affected strongly by the π-electron distribution.

An appreciable correlation was also found between ΔE_2 and the π-bond order of the exocyclic (or intercyclic) double bond (BO) (Table 1, r=-0.81). In contrast, no correlation was observed between ΔE_2 and the bond length of this bond (R) (Table 1, r=0.36). This may be partly attributable to the difference in steric environments around the double bond.

In Figure 2, the potential curves of **1**, **2**, **3**, and **10** for rigid twisting around the double bond are shown. They were obtained by 3×3 CI calculations. For **1** and **2**, the MO's obtained by the two-configuration SCF (TCSCF) calculation were used in the CI calculation when the twist angle θ is other than 90°, while the MO's obtained by the open-shell SCF calculation using eq.(1) were used when $\theta=90°$, because the TCSCF energy connects with the open-shell SCF energy at $\theta=90°$. For **3** and **10**, the MO's obtained by the closed-shell SCF calculation were used, because the closed-shell SCF wavefunctions of these compounds are good approximation to the TCSCF wavefunctions in the whole range of the twist angle θ.

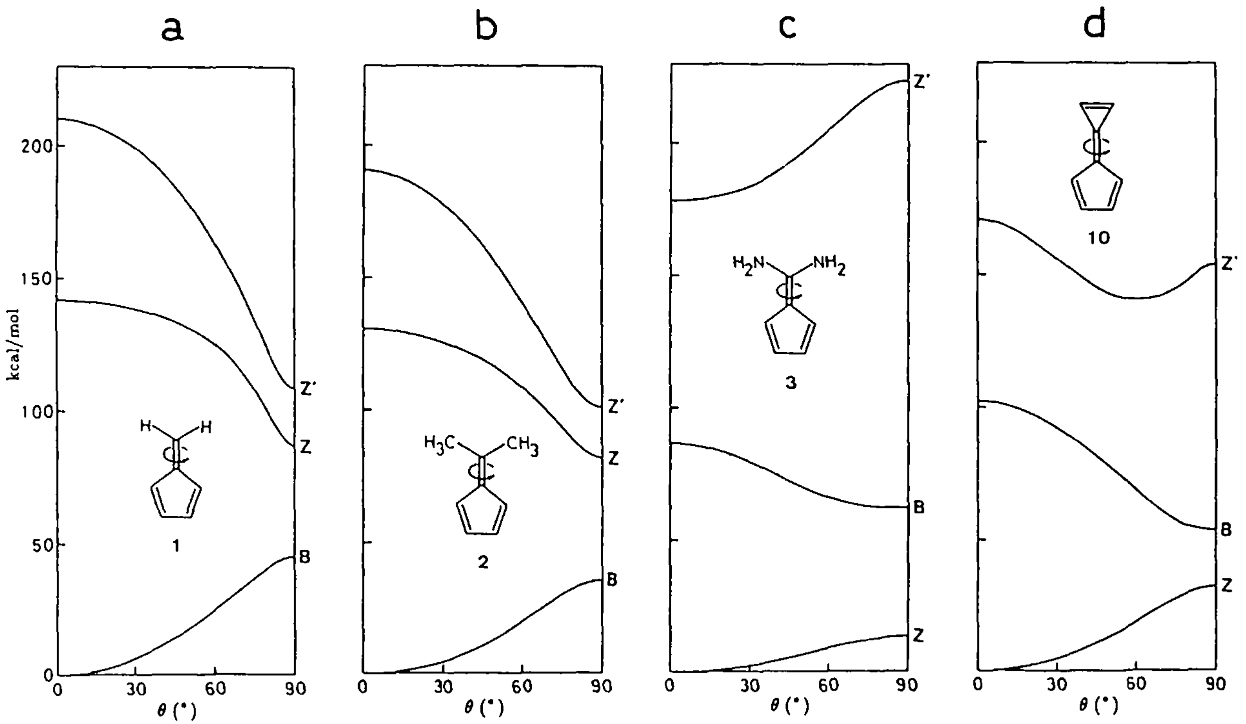


Figure 2. Potential energy curves of a) fulvene (**1**), b) 6,6-dimethylfulvene (**2**), c) 6,6-diaminofulvene (**3**), and d) calicene (**10**), with the twist angle *θ*.

The symbol "B" in Figure 2 represents a singlet biradical, while "Z" and "Z ′" represent two zwitterions which are polarized oppositely to each other. The potential energy curves for **1** and **2** have a typical shape which is expected for weakly polarized olefins, and the curve for **3** is typical one for strongly polarized olefins. For **10**, the energy gap between S_0 and S_1 at $\theta=90°$ (21.8kcal/mol) is larger than that shown above (5.2kcal/mol, see ΔE_1 in Table 1), because the wavefunction for the S_1 (biradical) state is different from that used for the ΔE_1 evaluation. In the terms used in ref.2, the 90°-twisted structures of **1** and **2** are "weakly heterosymmetric biradicaloids" and that of **3** is a "strongly heterosymmetric biradicaloid". The 90°-twisted **10** is a strongly heterosymmetric biardicaloid or a critically heterosymmetric biradicaloid.

The results of the 3×3 CI calculation is independent of any transformation of the two orbitals involved. Thus we can use the most localized orbitals,[2] say ψ_a and ψ_b, in order to understand easily the variation of the electronic structure upon twisting. In the present case, one of the two orbitals (ψ_a) localizes on the cyclopentadienylidene moiety, and the other (ψ_b) localizes on the exocyclic methylene moiety (or on the another ring). The 3×3 CI wavefunction is represented by

$$^1\Phi = c_1\Psi_1 + c_2\Psi_2 + c_3\Psi_3$$

where

$$\Psi_1 = \frac{1}{\sqrt{2}}\{|\ldots\psi_a\overline{\psi}_b| + |\ldots\psi_b\overline{\psi}_a|\}$$

$$\Psi_2 = |\ldots\psi_a\overline{\psi}_a|$$

and

$$\Psi_3 = |\ldots\psi_b\overline{\psi}_b|$$

Ψ_1 is a "covalent term", and Ψ_2 and Ψ_3 are "ionic terms". In Figure 3, the contribution of Ψ_1, c_1^2, in S_0 is shown as a function of the twist angle θ. For **1** and **2**, c_1^2 increases upon twisting and reaches 1 at $\theta=90°$. In contrast, for **3** and **10**, c_1^2 decreases upon twisting and vanishes at $\theta=90°$, while c_2^2 becomes 1 at $\theta=90°$. Interestingly, the c_1^2 values at $\theta=0°$, 0.677, 0.691, 0.429, and 0.628 for **1**, **2**, **3**, and **10**, respectively, are parallel to the ΔE_2 values at $\theta=90°$. Although the c_1^2 value has some relation to the biradical character, it should be noted that the overlap between ψ_a and ψ_b varies with the twist angle θ and the c_1^2 value cannot directly be used as a measure of biradical character.

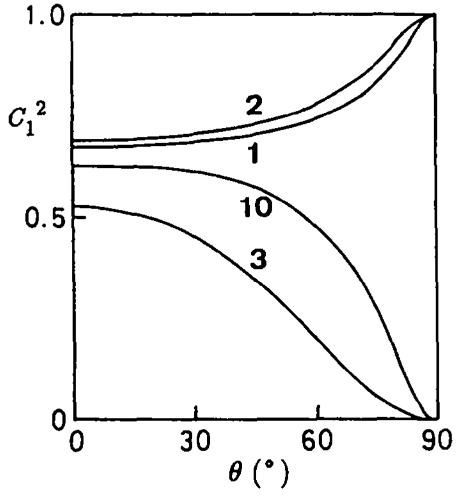


Figure 3. The variation of c_1^2 in S_0 as a function of the twist angle θ.

Concluding Remarks

The relative stability of the singlet biradical and zwitterionic states at the 90°-twisted structures of **1**-**16** was examined by using the semiempirical MINDO/3 approximation and simple wavefunctions. A near-degeneracy of the two states was found to occur by suitable substitutions. It should be noted, however, that the critical case would be quite method-dependent, and that solvent effect can fairly stabilizes the zwitterionic states in the actual case.[3]

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11. It was found that the two-configuration SCF (TCSCF) calculation using the linear combination of Φ_{ZW} and $\Phi_{ZW'}$ gives an wavefunction which is almost completely composed of only Φ_{ZW}.
12. For **12**, the C_s structure in which the seven-membered ring is buckled was also considered, but this structure was more stable than the C_{2v} planar structure by only 0.05kcal/mol. The amino groups in **3** and **7** preferred to be coplanar with the fulvene skeleton. For the methyl groups in **2**, the eclipsed conformation was assumed. See J. F. Chiang and S. H. Bauer, J. Am. Chem. Soc. **92**, 261 (1970).