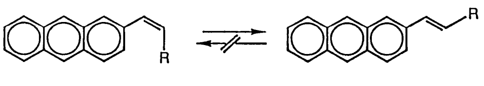
Qualitative Triplet Potential Energy Curves of Arylethylenes along the Double Bond Twisting

Osamu KIKUCHI,* Katsunori SEGAWA, Ohgi TAKAHASHI,
Tatsuo ARAI, and Katsumi TOKUMARU*
Department of Chemistry, University of Tsukuba, Tsukuba 305
(Received January 31, 1992)

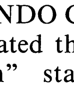
Synopsis. The potential energy curves of triplet states of styrene, 2-vinylnaphthalene and 2-vinylanthracene were calculated by the restricted open-shell SCF MNDO method as a function of the twist angle of the external double bond. It was shown that the shape of the lowest triplet potential energy curve is determined by the relative energies of two triplet states, the "ring-excitation" and "olefin-excitation" states.

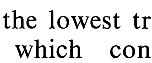
2-Anthrylethylenes undergo one-way cis→trans isomerization in their excited triplet state, while styrene and 2-naphthylethylene derivatives do two-way isomerization.[1-4] Although experimental works have elucidated the mechanism of this novel one-way isomerization and the potential energy profile of the triplet state,[1-3] theoretical works are required to clarify the shape of the triplet potential energy surface along the double bond twisting which governs the isomerization path.

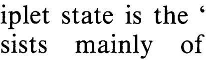


R=CH$_3$, *t*-Bu, Ph, 2-naphthyl

The potential energy curves of the excited singlet states of arylethylenes[5-9] and those of the triplet states of diarylethylenes[10] have frequently been discussed theoretically; however, only a few theoretical potential energy curves have been reported for the triplet states of monoarylethylenes.[6,8,9] In this respect, we carried out the restricted open-shell Hartree–Fock (ROHF) calculations with the MNDO approximation[11] for three arylethylenes, **1**—**3**, and the triplet potential energy curves were obtained as a function of the twist angle, θ, of the external double bond. Although **1**—**3** have no cis and trans isomers, they are appropriate examples to examine the dependence of the triplet potential energy curves of arylethylenes on the size of aromatic moiety.


1


2


3

Calculation

The MNDO CI calculation[12] of 2-vinylanthracene (**3**) has indicated that the lowest triplet state is the "ring-excitation" state which consists mainly of the HOMO→LUMO excitation within the aromatic ring. The "olefin-excitation" triplet state, which consists mainly of the $\pi\rightarrow\pi^*$ excitation of the external double bond, is the upper triplet state. This state is particularly important for the cis–trans isomerization because it correlates to the lowest triplet state at the 90°-twisted structure. The SCF level of calculations are appropriate for understanding the electronic properties of these potential energy curves qualitatively, and ROHF method with the MNDO approximation[11] was employed to evaluate the triplet potential energy curves for **1**—**3**.

The lowest singlet state, S$_0$, was calculated by two-configuration SCF (TCSCF) method. The second configuration corresponds to the $\pi\rightarrow\pi^*$ doubly-excited configuration of the olefinic double bond. This second configuration becomes important for the S$_0$ state when θ increases, and the TCSCF wavefunction is required to describe correctly the diradical structure at the 90°-twisted form. Thus the TCSCF singlet energy can be compared appropriately with the ROHF triplet energy.

The molecular structures of **1**—**3** were optimized for their planar singlet state by the closed-shell SCF method. The potential energy curves were then calculated by twisting the external double bond, the other molecular parameters being fixed. Calculations were carried out on the NEWS-1560 workstation with the MOSEMI program.[13]

Results and Discussion

Figure 1 depicts calculated potential energy curves of **1**—**3**. In the case of styrene (Fig. 1a), the T$_1$ energy due to the "olefin-excitation" decreases with increasing θ; however, the introduction of aromatic group with low triplet energy stabilizes the "ring-excitation" state to cause this state to be the lowest triplet at planar geometry, θ=0, as in the case of 2-vinylanthracene (Fig. 1c). A typical example of electronic structures of the "olefin-excitation" and "ring-excitation" is shown in Fig. 2.

The calculated triplet energies of **1**—**3** at θ=0 and θ=90° (perpendicular geometry, ^{3}p*) are summarized in Table 1, together with the values obtained experimentally.[3,14-16] As shown in Fig. 1, the lowest singlet as well as triplet perpendicular geometries are located almost the same in energy (at ca. 39 kcal mol^{-1} over the planar ground state); both are diradical states. In the S$_0$ surface of styrene, the rotational barrier obtained by the present calculation is smaller than those reported previously.[5-7] The calculated energies of ^{3}p* are also smaller by ca. 10 kcal mol^{-1} than those obtained experimentally, but are independent of the size of aromatic substituent as observed experimentally. Furthermore, the triplet energy of planar geometry decreases with decreasing the triplet energy of aromatic substituent from 54 (styrene) to 40 kcal mol^{-1} (2-vinylanthracene), which is qualitatively in good agreement with the experimental values of 63 and 42 kcal mol^{-1}, respectively. Thus, the present ROHF

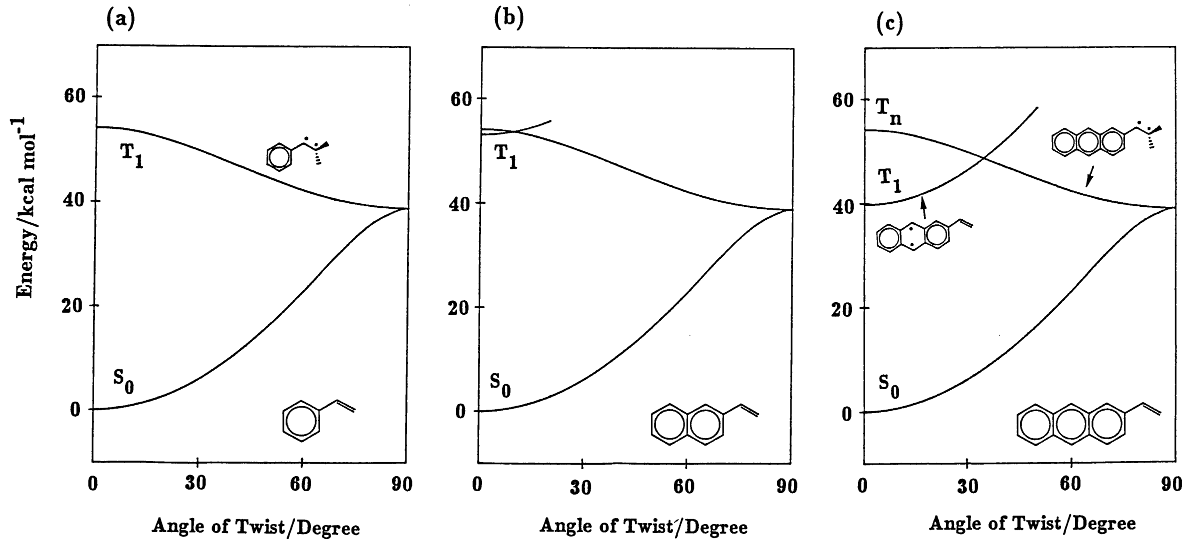


Fig. 1. Calculated lowest singlet and triplet potential energy curves of **1**—**3** as a function of the twist angle of the external double bond.

Table 1. The Lowest Triplet Energies of Planar and Perpendicular Conformations

	Planar conformation		Perpendicular conformation	
	E_T(obsd)[a]	E_T(cald)[a]	E_T(obsd)[a]	E_T(cald)[a]
Styrene (**1**)	63±2[b]	54[e]	51.2[b]	39[e]
2-Vinylnaphthalene (**2**)	ca. 52[c]	53[e]	ca. 52[c]	39[e]
2-Vinylanthracene (**3**)	41.6[d]	40[e]	52.7[d]	39[e]

a) Triplet energy in kcal mol^{-1}. b) Ref 14. c) Refs. 15 and 16. d) Ref. 3. e) Present calculation.

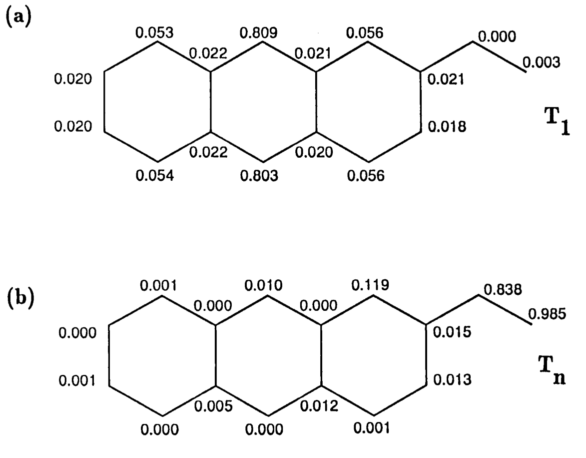


Fig. 2. Spin distributions in planar 2-vinylanthracene for the "ring-excitation" triplet state (a) and the "olefin-excitation" triplet state (b).

MNDO calculations give somewhat smaller values than those observed. However, the above results indicate that it is worth while to discuss qualitatively the effect of substituent on the potential energy surface of isomerization in the triplet state on the basis of present calculations.

As discussed above, the lowest triplet state of styrene corresponds to the "olefin-excitation" for the whole range of θ. This state becomes lower in energy as θ increases and correlates directly to the lowest triplet state at the 90°-twisted structure (Fig. 1a). On the other hand, in 2-vinylanthracence as Fig. 2 illustrates excitation in the lowest triplet state ("ring-excitation") does not significantly weaken the double bond character of the external double bond. This means that with the increase of the rotational angle around the double bond the T_1 energy should increase, as the S_0 energy does. This proposition is confirmed by the calculation as shown in Fig. 1c; the energy of the "ring-excitation" T_1 of 2-vinylanthracene increases, while that of the "olefin-excitation" T_n decreases, as the external double bond rotates from planar to perpendicular. The inverse θ dependence of T_1 and T_n energy curves results in the crossing of the "ring-excitation" and "olefin-excitation" curves at θ=35° (Fig. 1c).[17] 2-Vinylnaphthalene is the intermediate case; two triplet states cross at a smaller θ value.

From the calculated potential energy curves for **1**—**3**, two interesting conclusions are derived. (1) The shape of the lowest triplet potential energy curve is determined by the relative energies of the "ring-excitation" and "olefin-excitation" triplet states of the planar structure;[18] if the excited triplet state of the aromatic moiety is low, the crossing between the two triplet states occurs at a large θ value, and consequently, the barrier to the conversion from the perpendicular form, $^3p^*$, to the trans planar one, $^3t^*$, is small. (2) The T_1 potential energy curve of arylethylenes has an energy minimum near θ=90°, since the T_1 state near θ=90° corresponds to the "olefin-triplet" even if the "ring-excitation" triplet state

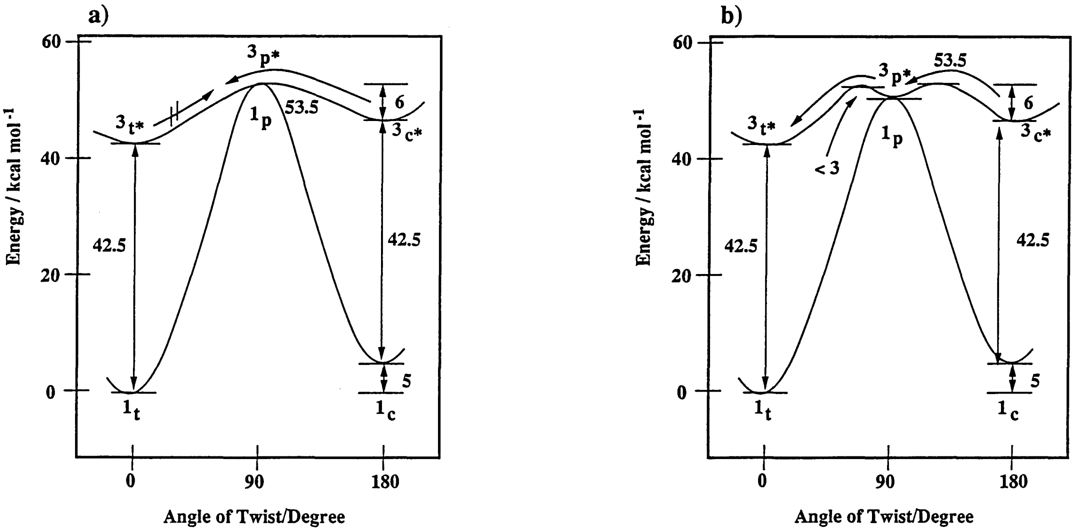


Fig. 3. Potential energy surfaces of one-way isomerization of 2-(3,3-dimethyl-1-butenyl)-anthracene with energy barrier at $^3p^*$ (a)[2] and with energy minimum at $^3p^*$ (b).

of the planar structure has very low evergy.

Although the present calculations were carried out for unsubstituted olefins, they give indications on the potential energy curves for the one-way isomerization of the substituted arylethylenes. It is generally accepted that the deactivation rate constant at $^3p^*$ ($k_{pd}=10^7$—10^8 s^{-1}) is ca. 3 orders of magnitude faster than that at $^3t^*$ ($k_{td}=10^3$—10^4 s^{-1}) at room temperature in fluid solution. What is required for one-way isomerization is that the decay at $^3p^*$ is negligibly small ($<10^{-2}$) compared to that at $^3t^*$. This condition is attained if the equilibrium constant K_{tp} ($^3t^* \rightleftarrows {}^3p^*$) is smaller than 10^{-5} which corresponds to the free energy change between $^3t^*$ and $^3p^*$, $\Delta G_{tp}=7$ kcal mol^{-1}. If we assume that the entropy difference between $^3t^*$ and $^3p^*$ is very small, ΔG_{tp} is almost equal to the energy difference between $^3t^*$ and $^3p^*$.

From these discussions we can depict the potential energy surfaces of one-way isomerization as shown in Fig. 3, together with the previously estimated potential energy surfaces.[2] Experimental findings need the energy difference between $^3t^*$ and $^3p^*$ more than 7 kcal mol^{-1} and the calculation needs the crossing of T_1 and T_n, and a shallow minimum at $^3p^*$. The frequency factor for rotation from $^3p^*$ to $^3t^*$ is asssumed as 10^{12} s^{-1}, then, the energy barrier for rotation from $^3p^*$ to $^3t^*$ should be less than 3 kcal mol^{-1}, in order to observe the isomerization from $^3p^*$ to $^3t^*$ which should be faster than 10^{10} s^{-1} before deactivation (10^7—10^8 s^{-1}) occurs. The present discussion suggests that one-way photoisomerization can also take place on the potential energy surface with shallow minimum at $^3p^*$.

This work was supported by a Grant-in-Aid for Specially Promoted Research No. 03101004 from the Ministry of Education, Science and Culture.

References

1) T. Arai, T. Karatsu, H. Misawa, Y. Kuriyama, H. Okamoto, T. Hiresaki, H. Furuuchi, H. Zeng, H. Sakuragi, and K. Tokumaru, *Pure Appl. Chem.*, **60**, 989 (1988).

2) T. Arai, T. Karatsu, H. Sakuragi, and K. Tokumaru, *Tetrahedron Lett.*, **24**, 2873 (1983); T. Karatsu, M. Tsuchiya, T. Arai, H. Sakuragi, and K. Tokumaru, *Chem. Phys. Lett.*, **169**, 36 (1990), and references there-in.

3) H. Misawa, T. Karatsu, T. Arai, H. Sakuragi, and K. Tokumaru, *Chem. Phys. Lett.*, **146**, 405 (1988).

4) R. A. Caldwell, G. W. Sovocool, and R. J. Peresie, *J. Am. Chem. Soc.*, **95**, 1496 (1973); J. Saltiel and D. W. Eaker, *Chem. Phys. Lett.*, **75**, 209 (1980); T. Arai, H. Sakuragi, and K. Tokumaru, *Bull. Chem. Soc. Jpn.*, **55**, 2204 (1982).

5) G. Orlandi, A. P. Palmieri, and G. Poggi, *J. Chem. Soc., Faraday Trans. 2*, **77**, 71 (1981).

6) M. Said and J. P. Malrieu, *Chem. Phys. Lett.*, **102**, 312 (1983).

7) G. L. Bendazzoli, G. Orlandi, P. Palmieri, and G. Poggi, *J. Am. Chem. Soc.*, **100**, 392 (1978); R. J. Hemley, U. Dinur, V. Vaida, and M. Karplus, *J. Am. Chem. Soc.*, **107**, 836 (1985).

8) M. C. Bruni, F. Momicchioli, I. Baraldi, and J. Langlet, *Chem. Phys. Lett.*, **36**, 484 (1975).

9) O. Kikuchi and H. Yoshida, *Bull. Chem. Soc. Jpn.*,**58**, 131 (1985).

10) G. Bartocci, F. Masetti, U. Mazzucato, A. Spalletti, G. Orlandi, and G. Poggi, *J. Chem. Soc., Faraday Trans. 2*,**84**, 385 (1988); F. Momicchioli, I. Baraldi, and E. Fischer, *J. Photochem. Photobiol.*, **A48**, 95 (1989).

11) M. J. S. Dewer and W. Thiel, *J. Am. Chem. Soc.*, **99**, 4899, 4907 (1977).

12) The CI calculation for the triplet states involved 76 singly- and doubly- excited configurations.

13) O. Kikuchi, K. Morihashi, and T. Kozaki, unpublished.

14) T. Ni, R. A. Caldwell, and L. A. Melton, *J. Am. Chem. Soc.*, **111**, 457 (1989).

15) As the triplet energies of planar and perpendicular conformations of 2-vinylnaphthalene have not been reported, those values were assumed from the experimental results of 3,3-dimethyl-1-(2-naphthyl)-1-butene.[16]

16) T. Arai, H. Sakuragi, and K. Tokumaru, *Chem. Lett.*, **1980**, 1335; T. Arai, H. Sakuragi, K. Tokumaru, Y. Sakaguchi, J. Nakamura, and H. Hayashi, *Chem. Phys. Lett.*, **98**, 40 (1983).

17) This crossing disappears when CI calculation is applied to the triplet states; an avoided crossing occurs at this region.

18) This characteristic nature of the triplet potential energy curves has been pointed out; T. Arai, T. Karatsu, H. Sakuragi, and K. Tokumaru, *Chem. Lett.*, **1981**, 1377.