2754 © 1993 The Chemical Society of Japan NOTES *Bull. Chem. Soc. Jpn.*,**66**, 2754—2757(1993) [Vol. 66, No. 9

Ab Initio Triplet Potential Energy Curves of Methyl-Substituted Arylethylenes along the Double Bond Twisting

Katsunori SEGAWA, Ohgi TAKAHASHI, Osamu KIKUCHI,* Tatsuo ARAI, and Katsumi TOKUMARU*
Department of Chemistry, University of Tsukuba, Tsukuba 305

(Received April 19, 1993)

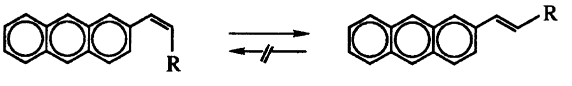
Synopsis. The potential energy curves of triplet states of β-methylstyrene (**3**) and 2-(1-propenyl)anthracene (**4**) were obtained by ab initio restricted open-shell Hartree–Fock (ROHF) calculations as a function of the twisted angle of the external double bond. The relative energies of trans, perpendicular, and cis forms of **4**, t<p, c, support that the one-way isomerization occurs from cis to trans forms of **4**.

2-Anthrylethylenes undergo one-way cis→trans isomerization in their excited triplet states (Chart 1), while styrene derivatives do two-way isomerization.[1] In our previous paper,[2] the potential energy curves of triplet states of styrene (**1**), 2-vinylnaphthalene, and 2-vinylanthracene (**2**) were calculated by ROHF MNDO method[3] 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 of arylethylenes.

However, **1** and **2** have no cis and trans isomers, and they are not appropriate to examine the difference between cis→trans and trans→cis isomerization processes. In this paper, the potential energy curves for the triplet states of β-methylstyrene (**3**) and 2-(1-propenyl)anthracene (**4**) were obtained by ab initio calculations, and one-way isomerization process was examined. Effect of the substitution of a methyl group at the α carbon atom or at the ring carbon atoms on the potential energy curves was also examined. In the cis forms of **3** and **4**, the aryl groups are expected to be twisted about the C–C single bond to reduce the steric repulsion. Since the MNDO method, which has been used in our previous paper, can not describe such a single bond rotation correctly, ab initio calculations with the STO-3G[4] and 6-31G[5] basis sets were carried out for **1**—**4** in this study (Chart 2). Calculations were carried out on the HP-730 workstations using the ABINIT program.[6]

Results and Discussion

Styrene and 2-Vinylanthracene. The planar molecular structures of **1** and **2** were optimized by the closed-shell SCF method using the STO-3G basis set. In the calculation of **2**, the anthryl group was assumed to have the D_{2h} symmetry. For the triplet states of **1** and **2**, two forms were optimized by the ROHF method; one is the planar ($\theta=0°$) and the other is the 90°-twisted ($\theta=90°$) forms. The molecular structures are shown



R = CH_3, *t*-Bu, Ph, 2-naphthyl

Chart 1.

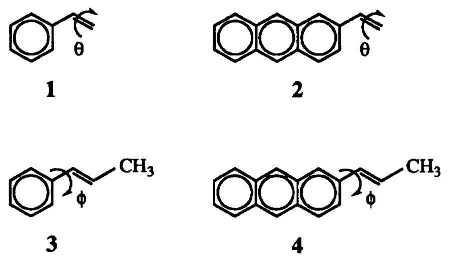


Chart 2.

Table 1. STO-3G Structures of Singlet and Triplet States of Styrene[a]

	Planar S_0	Planar T_1	90°-twisted T_1
Bond lengths			
C1–C2	1.397	1.399	1.397
C2–C3	1.383	1.385	1.384
C3–C4	1.388	1.387	1.387
C4–C5	1.386	1.390	1.388
C5–C6	1.384	1.382	1.384
C6–C1	1.394	1.404	1.398
C1–Cα	1.498	1.471	1.484
Cα–Cβ	1.314	1.547	1.487
Cα–H	1.084	1.083	1.085
Cβ–H(1)	1.080	1.079	1.082
Cβ–H(2)	1.081	1.080	1.082
Bond angles			
C6–C1–C2	118.5	117.9	118.5
C1–C2–C3	120.7	120.8	120.7
C2–C3–C4	120.1	120.5	120.2
C3–C4–C5	119.7	119.5	119.7
C4–C5–C6	120.1	120.2	120.1
C5–C6–C1	120.8	121.1	119.4
C2–C1–Cα	120.7	121.0	120.7
C1–Cα–Cβ	127.0	125.0	123.7
C1–Cα–H	114.0	118.3	117.5
Cα–Cβ–H(1)	123.3	121.9	121.2
Cα–Cβ–H(2)	121.1	119.4	121.2
Total energy	−303.873829	−303.752623	−303.776008

a) Bond lengths are in Å, bond angles are in degrees, and total energies are in au. The parameters for the ring C–H bonds are not shown.

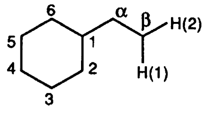
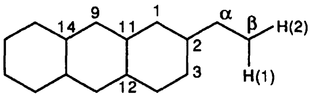


Table 2. STO-3G Structures of Singlet and Triplet States of 2-Vinylanthracene[a)]

	Planar S_0	Planar T_1[b)]	Planar T_2[c)]	90°-twisted T_1
Bond lengths				
C1–C2	1.343	1.397	1.345	1.343
C2–C3	1.448	1.382	1.450	1.449
C9–C11	1.393	1.481	1.393	1.393
C11–C1	1.450	1.383	1.449	1.449
C11–C12	1.424	1.413	1.425	1.425
C2–Cα	1.499	1.499	1.471	1.484
Cα–Cβ	1.313	1.314	1.547	1.487
Cα–H	1.084	1.084	1.082	1.084
Cβ–H(1)	1.080	1.080	1.077	1.082
Cβ–H(2)	1.081	1.081	1.079	1.082
Bond angles				
C1–C2–C3	120.3	119.7	120.2	120.3
C14–C9–C11	121.3	121.5	121.3	121.4
C9–C11–C1	122.3	121.5	122.3	122.3
C11–C1–C2	121.4	121.1	121.5	121.4
C1–C2–Cα	119.0	118.1	119.1	120.3
C2–Cα–Cβ	127.2	127.0	125.8	123.8
C2–Cα–H	114.0	114.2	117.7	117.2
Cα–Cβ–H(1)	123.3	123.2	122.0	121.2
Cα–Cβ–H(2)	121.2	121.2	119.0	121.2
Total energy	−605.454964	−605.361618	−605.333498	−605.357240

a) Bond lengths are in Å, bond angles are in degrees, and total energies are in au. The anthracene group was assumed to have the D_{2h} symmetry. The parameters for the ring C–H bonds are not shown. b) A "ring-excitation" state. c) A "olefin-excitation" state.



in Tables 1 and 2. The C_α–C_β distances for the singlet, planar triplet and 90°-twisted triplet states show clearly the difference in their electronic structures. The T_1 state of **1** is the "olefin-excitation" state and its C_α–C_β bond is essentially a single bond. The T_1 state of **2** is the "ring-excitation" state and its C_α–C_β bond remains a double bond. In the ROHF calculation of the triplet potential energy curves along the twisting of the external double bond, the molecular parameters were changed synchronously between those for the planar and 90°-twisted forms. The 90°-twisted singlet biradical is expected to have the structure which is very similar to the 90°-twisted triplet biradical. Thus, in the calculation of the S_0 potential energy curve, the molecular structure was changed synchronously as a function of θ from the structure of the planar singlet state to that of the 90°-twisted triplet state. The S_0 potential energy curve was calculated by two configuration SCF (TCSCF) method, which includes the ground configuration and a doubly-excited configuration and represents the biradical structure at the 90°-twisted form correctly.[2)]

In the case of styrene, the lowest triplet state was found to correspond to the "olefin-excitation" for the whole range of θ. When θ increases, the triplet energy decreases. On the other hand, the lowest triplet state of 2-vinylanthracene corresponds to "ring-excitation" and becomes unstable when θ increases. The shapes of the lowest singlet and triplet potential energy curves of **1** and **2** resemble those obtained by MNDO calculations.[2)] The calculated triplet state energies of **1** and **2** are shown in Tables 3 and 4. The calculated triplet energies of the planar and 90°-twisted forms of **1** are higher than the experimental values by 8—11 kcal mol^{-1}. In the case of **2**, the triplet state energy of the planar form is higher than the experimental value by 17 kcal mol^{-1}. Although the present ab initio ROHF calculations overestimate the triplet energies of the planar and 90°-twisted triplet states, they support the qualitative features of the potential energy curves obtained by the semiempirical calculations.[2)]

Methyl-Substituted Arylethylenes. In the calculation of methyl-substituted arylethylenes, **3** and **4**, the molecular parameters of **1** and **2** were used and CH_3 group was introduced simply at the terminal carbon atom. The methyl group was fixed at the structure of the methyl group in propene (C–C=1.506 Å, C–H=1.117 Å, C–C–H=110.7°).[10)] An important conformational factor is the rotation about the C–C single bond. This rotational angle, ϕ, was optimized in the potential energy curve calculation.

Figure 1 depicts the potential energy curves of **3** and

Table 3. The Lowest Triplet Energies (kcal mol^{-1}) of Methyl-Substituted Styrenes

Substitution	Planar conformation			Perpendicular conformation		
	STO-3G	6-31G	Exp.[a)]	STO-3G	6-31G	Exp.[a)]
None (**1**)	76.1	73.5	64.9	61.4	59.1	51.2
β(**3**)[b)]	75.2	73.7	60.5	61.0[c)]	59.5	53.2

a) Ref. 7. b) The trans form. c) The corresponding S_0 energy calculated by the TCSCF method is 61.6 kcal mol^{-1}.

Table 4. The Lowest Triplet Energies (kcal mol^{-1}) of Methyl-Substituted 2-Vinylanthracenes

Substitution	Planar conformation		Perpendicular conformation	
	STO-3G	Exp.	STO-3G	Exp.
None (**2**)	58.6	41.6[a)]	61.3	52.7[a)]
α	58.4		58.4	
β(**4**)[b)]	57.9	42.5[c)]	60.9[d)]	53.5[c)]
9	56.1		61.4	
10	56.1		61.3	

a) Ref. 8. b) The trans form. c) Ref. 9. d) The corresponding S_0 energy calculated by the TCSCF method is 61.6 kcal mol^{-1}.

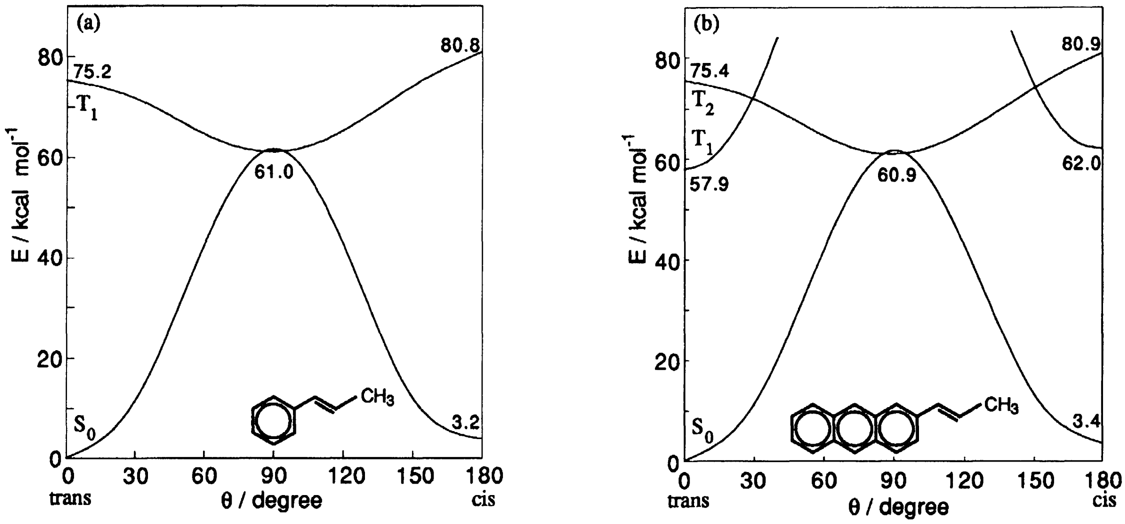


Fig. 1. Potential energy curves of (a) β-methylstyrene (**3**) and (b) 2-(1-propenyl)anthracene (**4**) as a function of the twisted angle of the external double bond.

4. The energy difference between cis and trans conformations of **3** is 3.2 kcal mol^{-1} in the S_0 state and 5.6 kcal mol^{-1} in the T_1 state. The corresponding energy difference of stilbene in its S_0 state is 4.6 kcal mol^{-1},[7)] indicating that the steric repulsion in the cis form of **3** is smaller than that between two phenyl groups in *cis*-stilbene. The phenyl ring in the cis form of **3** is twisted around the single C–C bond to reduce this steric repulsion. The ϕ values for the S_0 and T_1 states of the cis form ($\theta=180°$) of **3** were calculated to be 63° and 51°, respectively.[11)] The ϕ value was calculated to be 0° for $\theta \leq 120°$.

The S_0 and T_2 potential energy curves of **4** resemble the S_0 and T_1 potential energy curves of **3**. An important point observed in Fig. 1b is that the T_1 state for the trans and cis forms of **4** corresponds to the "ring-excitation," as was pointed out in the previous paper.[2)] This triplet state has double bond character at the olefinic C–C bond and becomes unstable when the double bond is twisted. The T_1 and T_2 potential energy curves of **4** were calculated using different molecular structures and they cross together near $\theta=30°$ in Fig. 1b, although they belong to the same irreducible representation. Since the electronic structures of these two triplet states are different largely from each other, two triplet states can be obtained separately by ROHF calculations, even if the same molecular structure is employed. The ϕ values of S_0 and T_1 states of the cis form of **4** were calculated as 64° and 59°, respectively. The T_1 state of the trans conformation of **4** is located at the energy minimum and lies 3 kcal mol^{-1} lower than the perpendicular triplet state. Thus the trans conformation can be the decay channel to the ground state, suggesting a possible cis→trans one-way isomerization.

Since the cis→trans one-way isomerization requires that the T_1 state of the trans conformation is at an energy minimum and more stable than the perpendicular T_1 state, it is interesting to examine how the triplet state energies of the planar and perpendicular forms are changed by substitution. Table 4 shows the energies of the planar and perpendicular forms of methyl-substituted 2-vinylanthracenes. In this calculation, molecular structures of **1** and **2** were used and the hydrogen atom was replaced by a methyl group with the standard structure. The substitution at the α position stabilizes the perpendicular T_1 state largely, while the ring-substitution stabilizes the planar T_1 state. This trend can be understood from the fact that the T_1 state of **4** is the "ring-excitation" state. It is thus expected that the cis→trans one-way isomerization hardly occur in the α-substituted anthrylethylenes while it can occur in the ring-substituted anthrylethylenes.

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 and K. Tokumaru, *Chem. Rev.*, **93**, 23 (1993), and references cited therein; K. Tokumaru and T. Arai, *J. Photochem. Photobiol. A: Chem.*, **65**, 1 (1992); 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); T. Arai, T. Karatsu, H. Sakuragi, and K. Tokumaru, *Tetrahedron Lett.*, **24**, 2873 (1983).

2) O. Kikuchi, K. Segawa, O. Takahashi, T. Arai, and K. Tokumaru, *Bull. Chem. Soc. Jpn.*, **65**, 1463 (1992).

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

4) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969).

5) W. J. Hehre, R. Ditchfield, and J. A. Pople, *J. Chem. Phys.*, **56**, 2257 (1972).

6) O. Kikuchi, T. Nakano, and K. Morihashi, unpublished.

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

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

9) The experimental values for 2-(3,3-dimethyl-1-butenyl)anthracene: T. Karatsu, M. Tsuchiya, T. Arai, H. Sakuragi, and K. Tokumaru, *Chem. Phys. Lett.*, **169**, 36 (1990).

10) The Chemical Society of Japan, "Kagaku Binran (Chemistry Handbook)," 2nd ed, Maruzen, Tokyo (1975), p. II-1398.

11) $\phi=22°$ has been estimated for the S_0 state of the cis form of **3** by photoelectron spectroscopy: T. Kobayashi, T. Arai, H. Sakuragi, K. Tokumaru, and C. Utsunomiya, *Bull. Chem. Soc. Jpn.*, **54**, 1658 (1981).