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AM1 Potential Energy Curves for Cis–Trans Isomerization of Stilbene Cation Radicals

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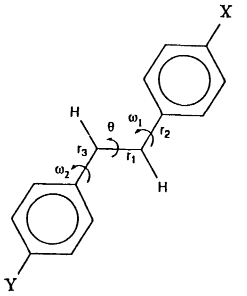
Synopsis. AM1 potential energy curves of stilbene cation radical and its derivatives were calculated by the open-shell RHF method as a function of the twist angle of the central C–C bond. The electronic properties of the potential energy curves of stilbene cation radicals were well understood, and the substituent effect on the barrier height for the cis-trans isomerization was evaluated.

The stilbene cation radical undergoes one-way cis→trans isomerization reaction, and the isomerization efficiency depends upon substituent.[1,2] Different mechanisms have been proposed for the isomerization reaction. One is the unimolecular process caused by the rotation around the olefinic double bond,[1] and another is the bimolecular reaction via a dimer cation radical.[2] Transfer of an electron hole from *cis*-stilbene cation radical to neutral *trans*-stilbene is also considered.[3] Moreover, the cis→trans isomerization has been shown to proceed via an excited state of the *cis*-stilbene cation radical.[4,5]



1: X=H Y=H
2: X=H Y=CN
3: $X=CH_3$ Y=H
4: $X=OCH_3$ Y=H
5: X=Cl Y=H
6: X=CN Y=CN
7: $X=CH_3$ $Y=CH_3$
8: $X=OCH_3$ $Y=OCH_3$
9: X=Cl Y=Cl
10: $X=OCH_3$ Y=CN

Among these reaction mechanisms, the unimolecular ground state process is a fundamental one, and the potential energy profile along this process should be characterized first. The stilbene cation radical has been calculated by the CI method for π electrons,[6] and the UMINDO/3[7] and CNDO/S-CI[8] methods for valence electrons. However, systematic theoretical studies are not available on the potential energy surfaces of the cation radical. In this note, the potential energy curves of stilbene cation radical, $1^{+\cdot}$, were calculated as a function of the twist angle of the central C–C bond by using the restricted open-shell Hartree-Fock (ROHF) method with the AM1 approximation;[9] AM1 gives reasonable molecular parameters for stilbene and related compounds.[10] The substituent effect on the potential energy curves was also examined for the cation radicals, $2^{+\cdot}$—$10^{+\cdot}$. The calculations were carried out by using the MOSEMI program.[11]

Structure of Stilbene Cation Radical. The molecular structures for trans, cis, and the C_2 90°-twisted stilbene cation radicals were optimized under the restriction of planarity for the phenyl rings; they are shown in Fig. 1. The cis form has the twist angle of 26°. As shown in Fig. 2, SOMO and LUMO of the C_2 stilbene cation radical are degenerate near θ=90°, and the ^2A and ^2B states, in which an unpaired electron occupies the a and b orbitals, respectively, have equal energies and

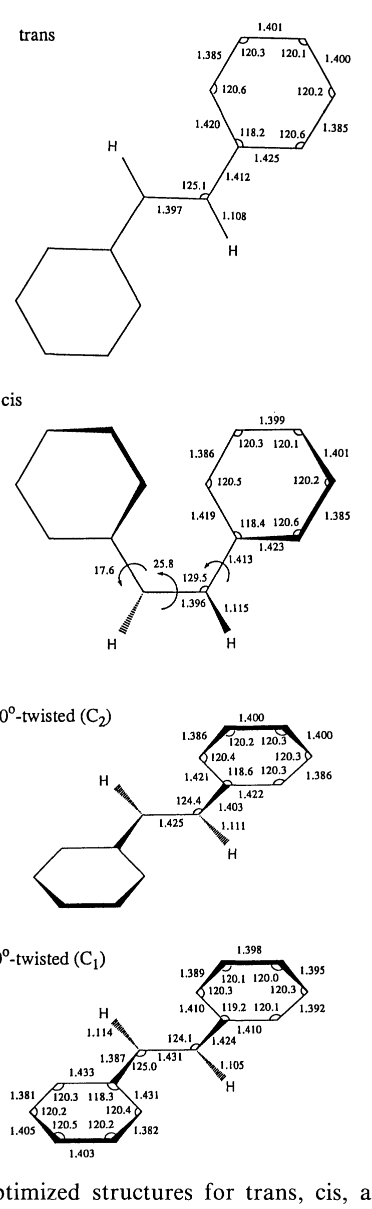


Fig. 1. Optimized structures for trans, cis, and 90°-twisted stilbene cation radicals. The planarity of the phenyl rings was assumed for all species. For the 90°-twisted structures, $\omega_1=\omega_2=0$ was assumed. Bond lengths are in Å and bond angles are in degrees.

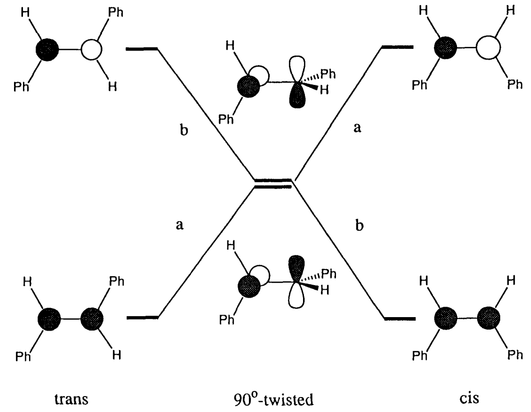


Fig. 2. The correlation diagram for the SOMO and LUMO of *trans*- and *cis*-stilbene cation radicals. The symbols "a" and "b" are the irreducible representations of the C$_2$ point group.

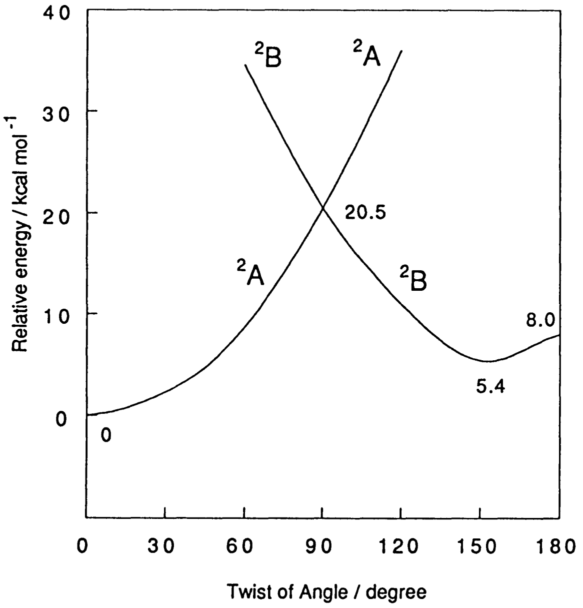


Fig. 3. The potential energy curves for the C$_2$ stilbene cation radical as a function of the twist angle of the central C–C bond. The structure was optimized at several twist angles under the C$_2$ symmetry restriction.

structures. Reduction of symmetry property of the 90°-twisted cation radical from C$_2$ to C$_1$ causes mixing of the ^{2}A and ^{2}B states and lowers the energy; the optimized C$_1$ 90°-twisted structure is also shown in Fig. 1.

In the *trans*- and *cis*-stilbene cation radicals, the unpaired electron and positive charge are delocalized over the whole molecule. In the case of the C$_1$ 90°-twisted form, two benzyl fragments have different structures and separation of the unpaired electron and positive charge occurs. The unpaired electron is localized in one benzyl fragment with the longer (1.424 Å) C$_\alpha$–C$_{\text{ipso}}$ bond, while the positive charge in the other one with the shorter (1.387 Å) C$_\alpha$–C$_{\text{ipso}}$ bond. The structures of these two benzyl fragments resemble those of benzyl radical and benzyl cation, respectively.[12]

Potential Energy Curves of Stilbene Cation Radical. The potential energy curves of the C$_2$ stilbene cation radical are shown in Fig. 3. Two electronic states, ^{2}A and ^{2}B, cross near θ=90°. This crossing suggests that the cis–trans isomerization of the stilbene cation radical may proceed very efficiently via the excited states, since one of the excited state energy surfaces of one isomer is connected with the ground state surface of the other isomer through a conical intersection. This feature of the potential energy curves is clearly different from that for the singlet states of neutral stilbene, where a strong avoided crossing appears near θ=90° in the C$_2$ potential energy curves.[13,14]

The *cis*-stilbene cation radical was calculated to be higher in energy than the *trans*-stilbene cation radical by 5.4 kcal mol^{-1}. The energy at the crossing point of the ^{2}A and ^{2}B states is higher than the trans form by 20.5 kcal mol^{-1}. Reduction of symmetry property from C$_2$ to C$_1$ mixes the two states and lowers the energy. The C$_1$ 90°-twisted structure of stilbene cation radical was calculated to be 4.1 kcal mol^{-1} more stable than the C$_2$ 90°-twisted structure.[15] The AM1 calculations thus gave the energy barriers of 16.4 and 11.0 kcal mol^{-1} for the trans→cis and cis→trans isomerization, respectively.[16]

Substituted Stilbene Cation Radicals. The trans, cis, and the C$_1$ 90°-twisted structures of para-substituted stilbene cation radicals were optimized. Table 1 shows the rotational barriers for substituted stilbene cation radicals. The values are the energy difference between the C$_1$ 90°-twisted structure and trans or cis isomer. For the symmetrically substituted stilbene cation radicals, the barriers are almost constant independent of the electronic properties of the substituent, while those of the monosubstituted stilbene cation radicals and the 4-cyano-4′-methoxystilbene cation radical are lower than the unsubstituted stilbene cation radical by 1—5 kcal mol^{-1}. This is a general trend expected in the olefin cation radicals.[17]

Lewis et al. reported that quantum yield for dicyanoanthracene-sensitized cis→trans isomerization of 4-cyanostilbene cation radical is much larger than that of 4-methoxystilbene cation radical.[2] The magnitudes of the calculated cis→trans isomerization barrier for these cation radicals are not consistent with this experiment; the observed isomerization may not proceed by the rotation around the C–C bond.[2]

Kuriyama et al. reported that the activation energy

Table 1. Calculated Rotational Barriers of 4,4′-Disubstituted Stilbene Cation Radicals (in kcal mol^{-1})

	Trans→*Cis*	*Cis*→*Trans*	Δ*E* (*Cis*–*Trans*)
$\mathbf{1}^{+\cdot}$	16.4	11.0	5.4
$\mathbf{2}^{+\cdot}$	14.7	9.3	5.4
$\mathbf{3}^{+\cdot}$	15.3	9.8	5.5
$\mathbf{4}^{+\cdot}$	13.1	7.4	5.7
$\mathbf{5}^{+\cdot}$	16.3	10.8	5.5
$\mathbf{6}^{+\cdot}$	16.2	10.8	5.4
$\mathbf{7}^{+\cdot}$	16.6	10.9	5.7
$\mathbf{8}^{+\cdot}$	16.6	10.4	6.2
$\mathbf{9}^{+\cdot}$	16.4	10.8	5.6
$\mathbf{10}^{+\cdot}$	11.7	6.0	5.7

Table 2. Calculated Ionization Potentials of 4,4′-Disubstituted Stilbenes (in eV)[a]

	Trans	*Cis*
1	7.87(8.49)	7.98(8.78)
2	8.15(8.78)	8.27(9.08)
3	7.77(8.39)	7.88(8.67)
4	7.61(8.26)	7.73(8.51)
5	7.95(8.57)	8.07(8.86)
6	8.43(9.08)	8.55(9.38)
7	7.67(8.30)	7.79(8.58)
8	7.41(8.09)	7.54(8.35)
9	8.02(8.65)	8.15(8.93)
10	7.86(8.52)	7.99(8.74)

a) The values in parentheses are Koopmans' ionization potentials.

for the cis→trans isomerization of 4,4′-dibromostilbene cation radical is 7.7 kcal mol^{-1}, while that of 4,4′-dimethylstilbene cation radical is 3.3 kcal mol^{-1}.[1)] These values seem to be too small for the ground state interconversion of the isolated cation radical, and other factors affecting the reaction need to be considered.

Ionization Potentials of Neutral Stilbenes. The electron hole transfer from the cation radical to the neutral species has been proposed for the reaction scheme,[3)] and it is worth to present the ionization potential of neutral stilbenes. The ionization energies of stilbene derivatives were obtained from the energy difference between the cation radical and the neutral species which were calcualted for the optimized structures. Koopmans' ionization potentials are also listed in parentheses. The calculated AM1 ionization energies of *trans-* and *cis-*stilbenes agree well with the experimental values, 7.87 and 8.20 eV, respectively.[18)] The calculated ionization energies of substituted stilbenes correlate well with the experimental oxidation potentials,[2)] and AM1 gives correct ionization potentials for stilbene derivatives.

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15) The structures with θ=88° and 92° were also optimized and the 90°-twisted structure was found to be a good approximation for the transition state.

16) The AM1 activation energies may be smaller than the correct values; the STO-3G values are 25.6 and 15.8 kcal mol^{-1} for the trans→cis and cis→trans processes, respectively.

17) This trend was observed in ab initio calculations of mono-, di-, tri-, and tetra-methylsubstituted ethylene cation radicals; O. Takahashi, Thesis, Tsukuba University (1992).

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