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Multi-Reference CI Calculation of Potential Energy Curves for cis–trans Isomerization of Stilbene Cation Radical

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Ab initio and AM1 multi-reference SCI calculations have been applied to the stilbene cation radical and the potential energy curves for the lower doublet states were obtained as a function of the twist angle about the central C–C bond to elucidate the photochemical cis–trans isomerization process. The shape of the calculated potential energy curves has suggested that the cis→trans one-way isomerization proceeds very efficiently from an upper excited state of the *cis*-stilbene cation radical.

Recent experimental works have shown that the stilbene cation radical is produced photochemically and undergoes cis–trans isomerization.[1] It has been established experimentally that the cis→trans one-way isomerization proceeds from the excited states and the quantum yield of the isomerization depends upon the excitation wavelength.[2—5] In our previous paper,[6] the electronic properties of the ground state potential energy curve of the stilbene cation radical were well understood by the open-shell RHF AM1 calculations. Our previous paper also suggested that the cis–trans isomerization may proceed very efficiently via the excited states of the stilbene cation radical. The excited states of the stilbene cation radical have been calculated by the CI method for π electrons,[4,7] and CNDO/S-CI method for valence electrons.[8] However, semi-empirical or ab initio MO levels of CI calculations have not been reported for the cis–trans isomerization process of the stilbene cation radical. In this paper, the potential energy curves of the stilbene cation radical were calculated as a function of the twist angle about the central C–C bond by ab initio and AM1 multi-reference singly-excited CI (MR-SCI) methods, and the cis→trans one-way isomerization process from the excited states was discussed.

Calculation

The molecular structure of the stilbene cation radical was optimized by the restricted open-shell Hartree–Fock (ROHF) method with the STO-3G basis set[9] at several θ twist angles (see Fig. 1) of the central C–C bond under the C_2 symmetry restriction. The C–H bond lengths in the phenyl groups and the bond angles of the phenyl rings were fixed at 1.10 Å and 120°, respectively. For the *cis*-stilbene cation radical, the minimum energy was found at $\theta=158°$. The ROHF potential energy curves for the lowest doublet state were obtained by using the STO-3G and 6-31G[10] basis sets for these molecular structures.

In order to obtain the excited state potential energy curves which are as accurate as the ground state one, the MR-SCI calculations, in which the singly-excited configurations constructed from the lower 6 configurations were taken into account, were carried out. If all singly-excited configurations derived from the 6 reference configurations are included, the number of configuration state functions (CSF's) becomes 18667 even for the minimal-basis-set calculation. This requires much computation time for the present molecular size, and the active space, in which ϕ_{42}—ϕ_{55} MO's are included, was selected in the construction of the CI functions; this gives 400 CSF's. Thus the potential energy curves were calculated by 6R-SCI/STO-3G method for the 14 active MO's.

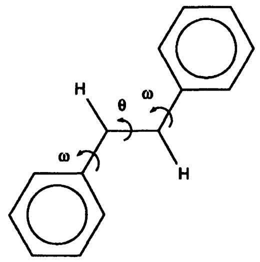

Fig. 1. Definition of the θ and ω angles in the stilbene cation radical.

The MR-SCI calculations with the 6 reference configurations were also performed by using the AM1 approximation.[11] The molecular structure was optimized by the ROHF/AM1 calculation for each twist angle, and the 6R-SCI calculation was carried out for these molecular structures. All calculations were carried out on the HP730 workstations by using the ABINIT88 and MOSEMI programs written in our group.[12]

Results and Discussion

The molecular structures of trans, cis, and the C_2 90°-twisted stilbene cation radicals were shown in Fig. 2. In the C_1 90°-twisted structure, the positive charge is localized mostly on the quinone-type ring and the unpaired electron on the other ring. The cis form has the twist angle of 22.3° (θ=157.7°). In this cis form, the phenyl rings are twisted by 20.7° (ω=20.7°) in order to reduce the repulsion between two phenyl groups. The energy of the cis form is 9.6 kcal mol^{-1} relative to the trans form. The ω twist angle is 30.8° for θ=180°; it decreases as θ decreases and becomes zero for $\theta<120°$.

The ROHF/STO-3G potential energy curves are de-

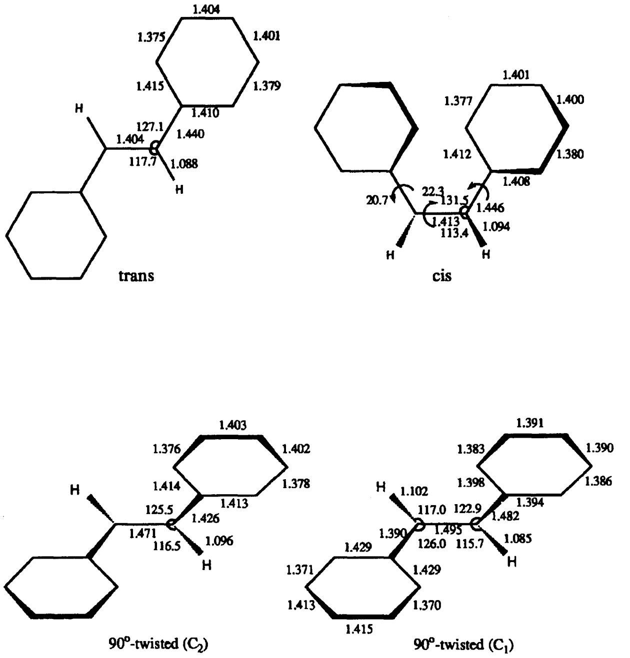

Fig. 2. Structures for trans, cis, and 90°-twisted stilbene cation radicals optimized by ROHF/STO-3G calculation. Bond lengths shown are in Å and bond angles are in degrees. The θ angle is 0° for the *trans*-stilbene cation radical and the ω angles are 0° for the trans and 90°-twisted structures. Planarity of the phenyl rings was assumed for all species. Also, the C–H bonds in the phenyl groups and the bond angles of the phenyl rings were fixed at 1.10 Å and 120°, respectively.

picted in Fig. 3. Two electronic states, ^{2}A and ^{2}B, cross each other near $\theta=90°$. The energy of this crossing point is 42.5 kcal mol^{-1} relative to the trans form. This point is a conical intersection in a multi-dimensional potential energy hypersurface and reduction of symmetry property from C_2 to C_1 at $\theta=90°$ mixes the two states; this mixing lowers the energy to 24.8 kcal mol^{-1}.[13] This can be seen in the schematic representation of the potential energy surfaces shown in Fig. 4. The energy barriers for the thermal trans→cis and cis→trans isomerizations are thus estimated as 24.8 and 15.2 kcal mol^{-1}, respectively. The 6-31G//STO-3G calculations gave slightly higher energy barriers, 25.7 and 17.3 kcal mol^{-1} for the two isomerizations, respectively. The barrier for the trans→cis isomerization of the stilbene cation radical obtained here is about the half of that of neutral stilbene, 46 kcal mol^{-1};[14] this tendency is in accord with that for the ethylene cation radical and neutral ethylene.[15] The qualitative shape of the ground state potential energy curves along the twisting of the central C–C bond resembles that obtained by AM1 calculations;[6] the ab initio barrier heights are larger than the AM1 ones.

As the first step in the CI calculations, the single-reference SCI/STO-3G calculation with 98 CSF's was

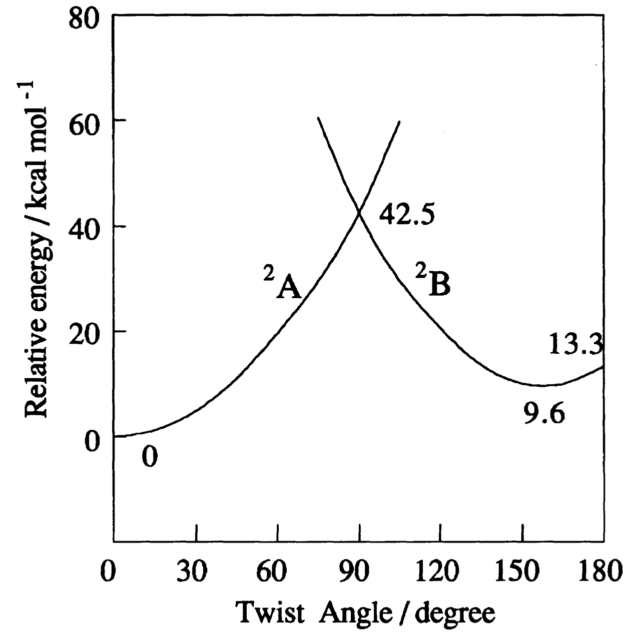

Fig. 3. The ROHF/STO-3G potential energy curves for the C_2 stilbene cation radical as a function of the twist angle about the central C–C bond. The structure was optimized in steps of 15° under the C_2 symmetry restriction.

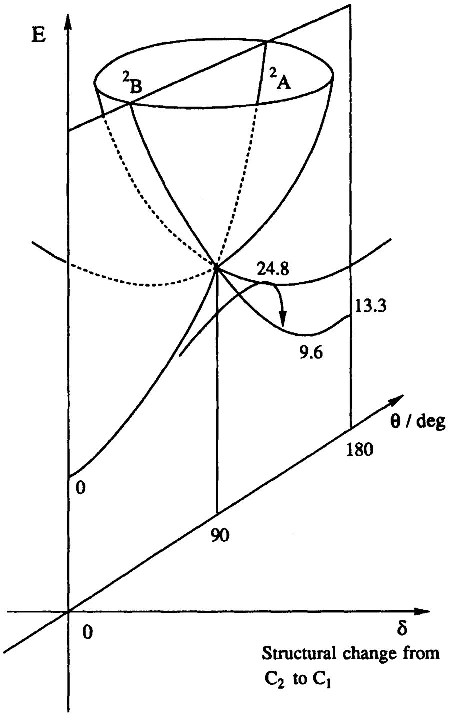

Fig. 4. Schematic representation of the potential energy surfaces for the ground and lowest excited states of stilbene cation radical near the 90°-twisted conformation. θ is the twist angle of the central C–C bond and δ-axis represents the structural change from C_2 to C_1 symmetry structures.

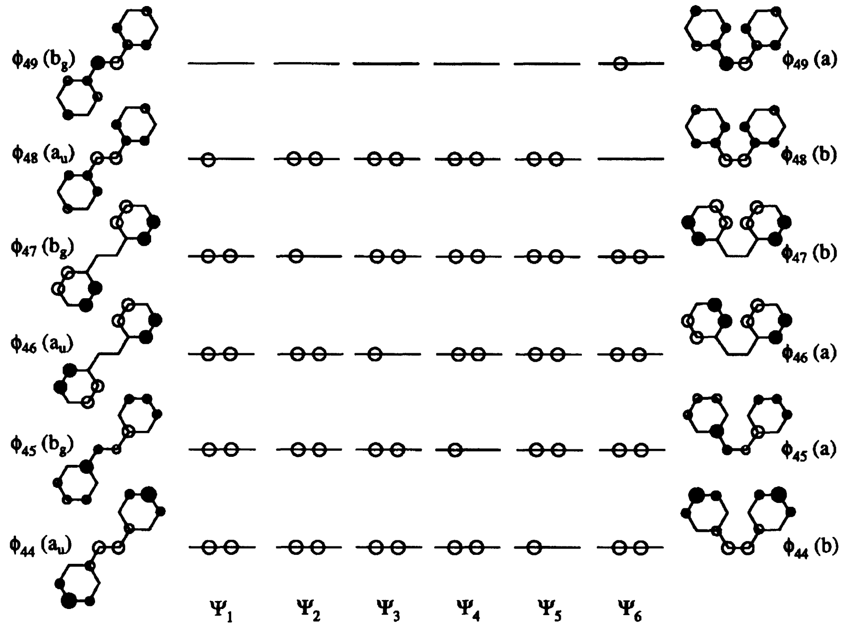

Fig. 5. Schematic representation of 6 molecular orbitals of the *trans*- and *cis*-stilbene cation radicals and 6 reference configurations used in the MR-SCI/STO-3G calculations.

Table 1. Lower 6 Doublet States of *trans*-Stilbene Cation Radical Calculated by 6R-SCI/STO-3G Method

State	Symmetry	Total energy [a)]	Relative energy [b)]	Configurations [c)]
D_0	^2A_u	−530.428439	0.0	Ψ_1 (94%)
D_1	^2B_g	−530.329601	62.0	Ψ_2 (32%), Ψ_4 (43%), Ψ_6 (8%)
D_2	^2A_u	−530.327735	63.2	Ψ_3 (82%), $\Psi_{47\rightarrow49}$ (5%)
D_3	^2B_g	−530.327263	63.5	Ψ_2 (50%), Ψ_4 (30%), $\Psi_{46\rightarrow49}$ (4%)
D_4	^2A_u	−530.288370	87.9	Ψ_5 (67%), $\Psi_{45\rightarrow49}$ (12%)
D_5	^2B_g	−530.284160	90.5	Ψ_6 (69%), Ψ_4 (14%)

a) In a.u. ^2A_u ground state ROHF energy=−530.405148 a.u. b) In kcal mol^{-1}. c) $\Psi_{i\rightarrow k}$ is the configuration which is derived by one electron excitation from i to k orbitals in the Ψ_1 configuration.

Table 2. Lower 6 Doublet States of *cis*-Stilbene Cation Radical Calculated by 6R-SCI/STO-3G Method

State	Symmetry	Total energy [a)]	Relative energy [b)]	Configurations [c)]
D_0	^2B	−530.411598	0.0	Ψ_1 (94%)
D_1	^2B	−530.315575	60.2	Ψ_2 (82%), $\Psi_{46\rightarrow49}$ (4%)
D_2	^2A	−530.315549	60.2	Ψ_4 (73%), Ψ_6 (6%), $\Psi_{44\rightarrow49}$ (5%)
D_3	^2A	−530.310223	63.6	Ψ_3 (78%), $\Psi_{47\rightarrow49}$ (4%)
D_4	^2B	−530.281034	81.9	Ψ_5 (68%), $\Psi_{45\rightarrow49}$ (12%)
D_5	^2A	−530.275093	85.6	Ψ_6 (73%), Ψ_4 (10%)

a) In a.u. ^2B ground state ROHF energy=−530.389802 a.u. b) In kcal mol^{-1}. c) $\Psi_{i\rightarrow k}$ is the configuration which is derived by one electron excitation from i to k orbitals in the Ψ_1 configuration.

performed for the *trans*-stilbene cation radical and the electronic structures of the lower excited states were characterized. The 6 configurations which contribute largely to the ground state and 5 lower-lying excited states are shown in Fig. 5. These configurations have been suggested for the lower electronic states of stilbene ions.[8)] We need the potential energy curves both for the ground state and lower excited states with same accuracy. These potential energy curves may be obtained by MR-SCI calculations which include these 6 configurations as the reference configurations.

The 6R-SCI excitation energies for the trans and cis forms are listed in Tables 1 and 2 as well as the main configurations contributing to each state. The lower three excited states lie closely, while the fourth and fifth excited states do. It has experimentally been observed that *trans-* and *cis-*stilbene cation radicals have two characteristic absorption bands in the visible region.[2—4] The λ_{max} values for the trans form are 759 nm (37.7 kcal mol^{-1}) and 482 nm (59.3 kcal mol^{-1}).[4a] Corresponding values for the cis form are 750 nm (38.1 kcal/mol^{-1}) and 518 nm (55.2 kcal mol^{-1}).[4b] The present calculations indicate that the first band corresponds to the transitions to the lower three excited states (D_1—D_3) which consist of the excitations from the doubly-occupied MO's to SOMO, and the second band to the fourth (D_4) and fifth (D_5) states, one of which corresponds to the SOMO→LUMO excitation. These agree well with the assignment reported earlier.[4,8] The excitation energies are highly overestimated by the present SCI calculations and more sophisticated methods with larger basis sets need to be used to have the quantitatively correct excitation energies.

Figure 6 shows the 6R-SCI/STO-3G potential energy variations along the C–C bond twisting. Two characteristic features are recognized in the excited state potential energy curves. First, only one excited state, D_5 (3^2B_g for the trans form and 3^2A for the cis form), is stabilized by the C–C bond twisting, other excited states being destabilized. This suggests that the cis-trans isomerization does not proceed efficiently from the lower excited states. The main configuration of the D_5 excited state is the SOMO→LUMO excited configuration. Since this configuration has the anti-bonding character between the central C–C π bond, the D_5 state becomes stable when the C–C bond is twisted. The second characteristic is the shape of the avoided crossing observed between the D_5 state and the 1^2A excited state in the vicinity of θ=140°. The 3^2A state of the cis form is largely stabilized by the C–C bond twisting and the slope of the potential energy curve of this state is very sharp; the avoided crossing between this state and the lowest excited state is remarkable in the cis form.

Sazhnikov et al.[3] have shown that the cis→trans isomerization proceeds efficiently from the upper excited states of the stilbene cation radical, while the reverse isomerization is not observed photochemically. These experimental facts can well be elucidated by the present 6R-SCI potential energy curves, since one of the upper excited states of the cis form, 3^2A, crosses avoidedly with the lowest excited state, 1^2A, which leads to the ground state of the trans form. As is shown in Fig. 4, the C_1 90°-twisted structure corresponds to the transition state for the thermal cis–trans isomerization. In the photochemical isomerization, however, the conical intersection in the C_2 plane is very important, since it can be an efficient leakage channel from the excited state to the ground state.

The difference observed in the shape of the D_5 curves between the trans and cis forms originates from the nonplanarity of the cis-stilbene cation radical. As pointed out above, the ω angle is 30.8° for the planar cis form (θ=180°) and decreases when the θ angle decreases.

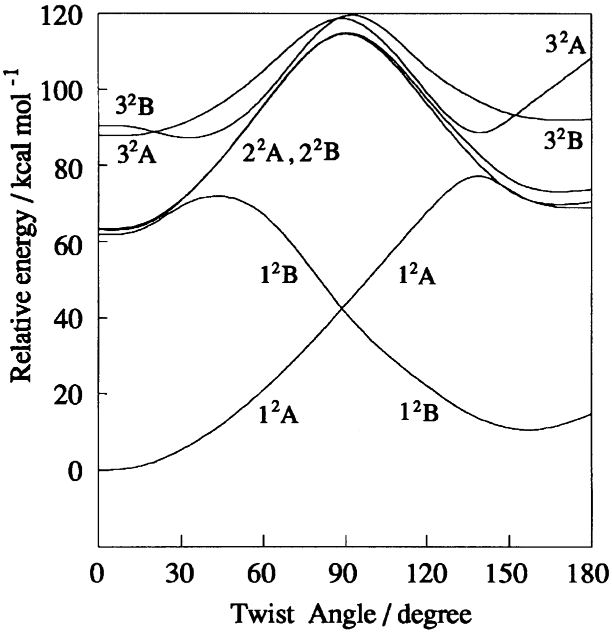

Fig. 6. The MR-SCI/STO-3G potential energy curves for the stilbene cation radical as a function of the twist angle about the central C–C bond.

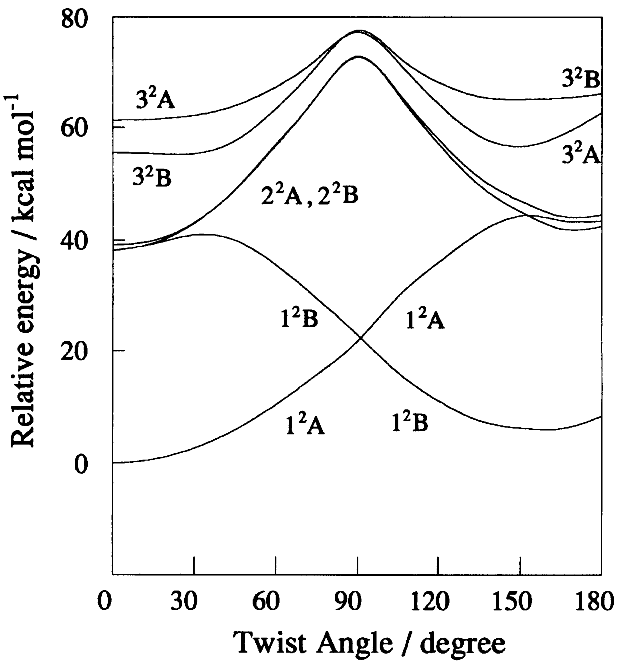

Fig. 7. The MR-SCI/AM1 potential energy curves for the stilbene cation radical. The 6 reference configurations employed are the same as the MR-SCI/STO-3G calculation shown in Fig. 5.

This indicates that the unpaired electron in the Ψ_6 configuration, which is localized largely on the central C–C π system, is much stabilized by the phenyl groups in the cis form when the θ angle decreases.

This ω effect was confirmed by additional potential energy calculations in which the ω angle was fixed at

30.8°, and the θ angle was decreased from 180°; the stabilization of the 3^2A state of the cis form by the θ twisting was very small if the ω angle was not changed.

The 6R-SCI potential energy curves were also calculated with the AM1 approximation. In this CI calculation, ROHF/AM1 molecular structures were used and the same number of CSF's as in the ab initio calculation were included. The overall shape of the potential energy curves for the ground and excited states (Fig. 7) resembles that obtained by ab initio calculations (Fig. 6); the AM1 excitation energies agree with experimental ones much better than ab initio values.[16] Thus the 6R-SCI/AM1 calculations support the above discussions on the potential energy curves and the cis-trans isomerization of the stilbene cation radical via the excited states.

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13) Two factors may be important for this large energy lowering, 17.7 kcal mol^{-1}; electron reorganization and geometry reorganization. If we used the geometry of the C_2 symmetry and allowed to break the symmetry property of electron distribution, the energy lowering was 14.6 kcal mol^{-1} indicating that the energy lowering due to the electron reorganization is predominant.

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16) 6R-SCI/AM1 excitation energies for the first and second absorption bands of the trans form are 38—39 and 56—61 kcal mol^{-1}, respectively, and those of the cis form (θ=158°) are 38—40 and 51—59 kcal mol^{-1}, respectively.