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Electronic Absorption Spectra and Geometry of Molecular Ions Generated from Stilbene and Related Compounds. III. Radical Ions of (*Z*)-Stilbene and Its α,β-Dialkyl Derivatives

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The radical ions of (*Z*)-stilbene and its α,β-dialkyl derivatives were produced by γ-ray irradiation of the parent compounds in frozen matrices at 77 K, and their geometries were investigated by electronic absorption spectroscopy. While the relaxed geometries of the radical ions of (*Z*)-stilbene are probably similar to that of the neutral molecule, those of the radical ions of the α,β-dialkyl derivatives are appreciably different from those of the neutral molecules: The torsion angle of the central ethylenic bond is distinctly larger and that of each C–Ph bond is probably smaller in the radical ions than in the neutral molecules. On illumination the radical ions of (*Z*)-stilbene isomerize to the *E* isomers, but those of the α,β-dialkyl derivatives do not. A mechanism of the photoisomerization is proposed, and an interpretation of the difference in the photochemical behavior between the unsubstituted stilbene radical ions and the α,β-dialkyl derivatives is given.

The present paper reports the result of an electronic spectroscopic study of the geometry of the radical ions of (*Z*)-stilbene (abbreviated as ZS), (*Z*)-α,β-dimethylstilbene (ZαβDMS), and (*Z*)-α,β-diethylstilbene (ZαβDES). The radical ions were produced by γ-ray irradiation of frozen solutions of the respective compounds at 77 K, and their electronic absorption spectra measured before and after illumination or limited warming were examined with respect to the geometry of the radical ions.

This work has three purposes as follows.

(1) Previously, we found that the relaxed geometries of radical ions generated from sterically crowded compounds were appreciably different from those of the parent neutral molecules.[1,2] It is one of the purposes of the present work to examine the geometries of the radical ions of the sterically crowded (*Z*)-stilbenes and to compare them with the geometries of the parent molecules.

(2) The π-bond order of the central ethylenic bond (the α–β bond) of stilbene is smaller in the radical ions than in the neutral molecule.[2] Therefore, the thermal *Z*→*E* isomerization should occur more readily in the radical ions than in the neutral molecule. As expected, the anion radical produced from ZS by reduction with alkali metals in ethereal solutions readily isomerizes to the anion radical of (*E*)-stilbene (ES).[3] When the anion radical of ZS ($ZS^{-\cdot}$) forms an ion pair with the alkali counterion, its isomerization is comparatively slow.[4,5] When $ZS^{-\cdot}$ is not associated with the counterion, its isomerization occurs especially rapidly.[5,6] Wang *et al.* proposed a mechanism involving a dianion for the isomerization of the counterion-free $ZS^{-\cdot}$ to the counterion-free $ES^{-\cdot}$ in hexamethylphosphoric triamide (HMPT).[7] The radical ions produced by γ-ray irradiation in frozen matrices are counterion-free, and the possibility that the radical ions in the frozen matrices disproportionate to a pair of the diion and the neutral molecule should be extremely small. Therefore, it is of interest to examine whether the radical ions of the (*Z*)-stilbenes in frozen matrices isomerize to the *E* isomers on limited warming. This is the second of the purposes of the present work.

(3) Both the cation and the anion radical of ZS in frozen matrices at 77 K undergo the *Z*→*E* photoisomerization on visible light illumination.[8,9] It is the third of the purposes to examine whether the photoisomerization occurs also in the radical ions of the crowded α,β-dialkyl derivatives.

Experimental

Materials. (*Z*)-*Stilbene (ZS)*: A commercial product of Aldrich Chemical Co. was used: UV_{max} (heptane) 278.7 nm (ε 1.031×10^4).

(*Z*)-α,β-*Dimethylstilbene (ZαβDMS)*: This compound was prepared as described previously:[10] UV_{max} (heptane) 252.0 nm (ε 8.88×10^3).

(*Z*)-α,β-*Diethylstilbene (ZαβDES)*: This compound was newly prepared as follows. Reductive coupling of propiophenone (4.03 g) with titanium(IV) chloride (8.6 g) and zinc (5.9 g) in dioxane (200 cm³) was carried out according to the procedure of Mukaiyama *et al.*[11] After work-up, the residue was chromatographed twice on silica gel columns by using hexane as the eluent to give 700 mg of a colorless oil. Kugelrohr distillation of the oil gave an analytically pure sample of ZαβDES, which solidified in the receiver: mp 32.5—34.0 °C, uncorrected; UV_{max} (heptane) 248.8 nm (ε 8.87×10^3); ^1H NMR ($CDCl_3$) $\delta=7.12$ (10H, br s, $2C_6H_5$), 2.62 (4H, q, $J=8$ Hz, $2CH_2$), 1.00 (6H, t, $J=8$ Hz, $2CH_3$). Found: C, 91.38; H, 8.73%; M^+, 236. Calcd for $C_{18}H_{20}$: C, 91.47; H, 8.53%; M, 236. Earlier reports[12–14] on this compound are now to be corrected, because the sample prepared previously [an oil: UV_{max} (ethanol) 244 nm (ε 7.74×10^3)] has, in the course of the present work, proved not to be pure.

Spectra of Radical Ions. The radical ions of ZS, ZαβDMS, and ZαβDES were prepared by γ-ray irradiation of frozen solutions of the parent compounds in deaerated 2-methyltetrahydrofuran (MTHF) for anion radicals and in *s*-butyl chloride (BC) or a Freon Mixture (FM: an equivolume mixture of trichlorofluoromethane and 1,2-dibromo-1,1,2,2-tetrafluoroethane) for cation radicals both at 77 K. The electronic absorption spectra of the γ-ray irradiated

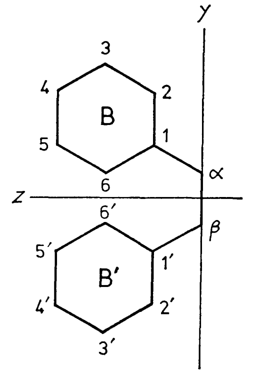

Fig. 1. The carbon skeleton of (*Z*)-stilbene.

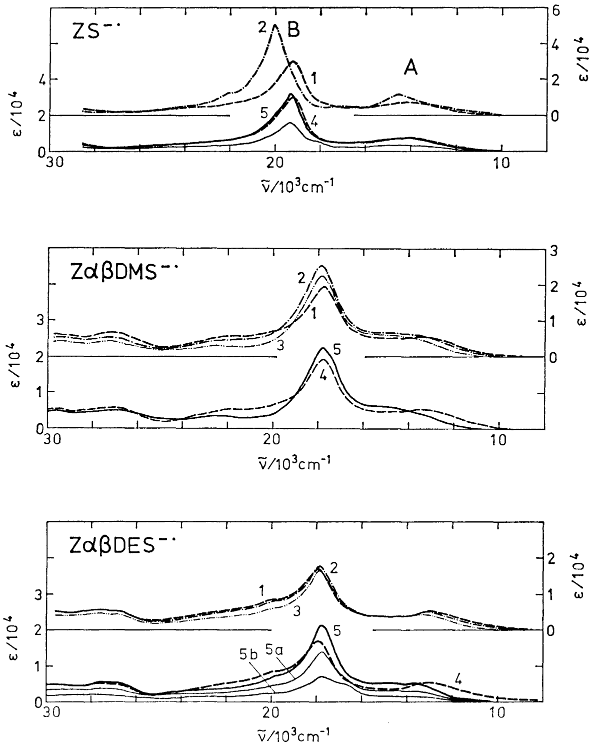

Fig. 2. Electronic absorption spectra of the anion radicals of (*Z*)-stilbene (ZS), (*Z*)-α,β-dimethylstilbene (ZαβDMS), and (*Z*)-α,β-diethylstilbene (ZαβDES).
Curves 1 and 4 (----): spectra observed immediately after γ-ray irradiation of frozen solution, designated F in the text. Curve 2 (—·—): spectra observed after illumination of the sample for curve 1 with light of wavelengths corresponding to band A, designated PA in the text. Curve 3 (—··—): spectra observed after illumination of the sample for curve 2 with light of wavelengths corresponding to and longer than band B, designated PB in the text. Curve 5 (——): spectra observed after controlled warming of the sample for curve 4, designated W in the text. Curves 5a and 5b (——): spectra observed after additional controlled warming of the sample for curve 5. The solvent is 2-methyltetrahydrofuran (MTHF) for all the spectra.

samples were measured before and after illumination with visible light or warming for a limited period. The experimental details are the same as described in previous papers.[1,2)]

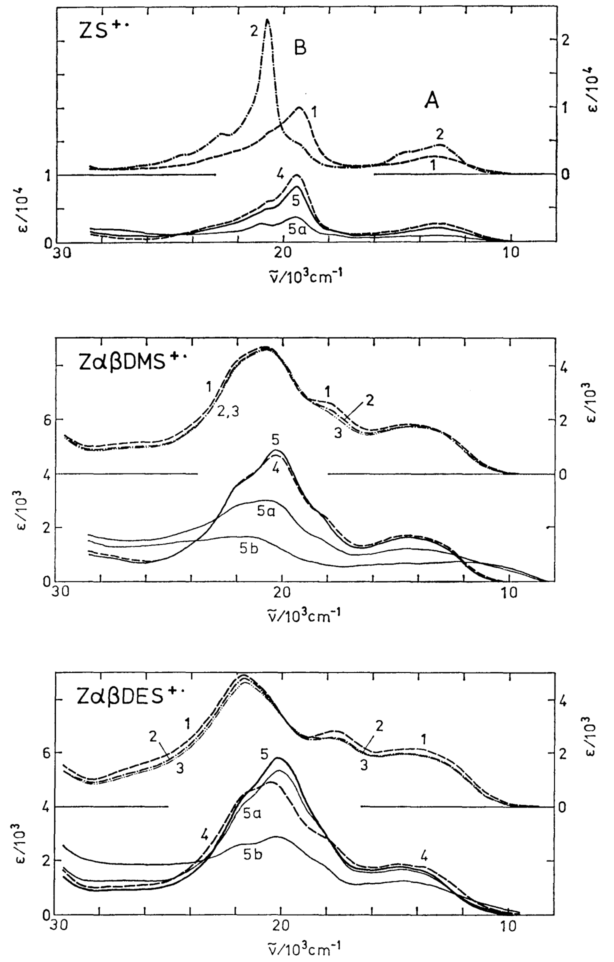

Fig. 3. Electronic absorption spectra of the cation radicals of ZS, ZαβDMS, and ZαβDES.
See Caption for Fig. 2. The solvent is *s*-butyl chloride (BC) for spectra 1, 2, and 3, and is a Freon Mixture (FM) for the other spectra.

Molecular Orbital Calculation

As in the previous work,[1,2)] a semiempirical SCF-MO-CI calculation was carried out for the radical ions by the Longuet-Higgins and Pople method.[15)]

The numbering of the carbon atoms is illustrated for ZS in Fig. 1. Torsion angles β–α–1–6, α–β–1′–6′, and 1–α–β–1′ are denoted by $\theta_{\alpha 1}$, $\theta_{\beta 1'}$, and $\theta_{\alpha\beta}$, respectively. The value of $\theta_{\alpha\beta}$ is 0° for the planar *Z* configuration and 180° for the planar *E* configuration.

Results and Discussion

Designation of Spectra and of Geometries. Representative spectra of the radical ions are shown in Figs. 2 and 3, and relevant data are listed in Tables 1 and 2. As seen in the figures, the radical ions exhibit two major bands in the visible region. The band at the longer wavelength is designated as A, and that at the shorter wavelength as B. For band A, for example, the wavelength (λ) and molar absorption coefficient (ε) at the absorption maximum and the oscillator strength (f) are denoted by λ_A, ε_A, and f_A, re-

Table 1. Data on electronic absorption spectra of anion radicals

Anion radical	Class[a]	No. in Fig. 2	λ_B/nm	$\varepsilon_B/10^4$	f_B	λ_A/nm	$\varepsilon_A/10^4$	f_A	f_A/f_B
$\mathrm{ZS}^{-\cdot}$	F(MTHF)	4	520.0	2.975	0.377	707.4	0.714	0.140	0.370
	PA(MTHF)	2	499.4	5.019	0.499	687.5	1.123	0.153	0.306
	W(MTHF)	5	517.8	3.149	0.385	707.4	0.701	0.129	0.335
$\mathrm{Z}\alpha\beta\mathrm{DMS}^{-\cdot}$	F(MTHF)	4	561.8	1.944	0.320	750	0.539	0.080	0.250
	PA(MTHF)	2	559.1	2.521	0.367	690[b]	0.631	0.085	0.231
	W(MTHF)	5	563.2	2.263	0.285	667[b]	0.606	0.072	0.251
$\mathrm{Z}\alpha\beta\mathrm{DES}^{-\cdot}$	F(MTHF)	4	557.2	1.686	0.297	763.2	0.535	0.082	0.277
	PB(MTHF)	3	559.6	1.655	0.250	750.0	0.435	0.061	0.243
	W(MTHF)	5	562.5	2.135	0.302	675.0	0.522	0.062	0.207

a) See the text or caption for Fig. 2. for the notation under the column Class. b) Inflection.

Table 2. Data on electronic absorption spectra of cation radicals

Cation radical	Class[a]	No. in Fig. 3	λ_B/nm	$\varepsilon_B/10^4$	f_B	λ_A/nm	$\varepsilon_A/10^4$	f_A	f_A/f_B
$\mathrm{ZS}^{+\cdot}$	F(BC)	1	517.6	1.000	0.152	750.0	0.261	0.041	0.267
	PA(BC)	2	482.5	2.303	0.220	755.0	0.440	0.063	0.286
	F(FM)	4	515.4	1.000	0.141	750.0	0.263	0.044	0.314
	W(FM)	5	515.4	0.819	0.121	750.0	0.199	0.035	0.287
$\mathrm{Z}\alpha\beta\mathrm{DMS}^{+\cdot}$	F(BC)	1	480.4	0.467	0.126	687.5	0.179	0.031	0.246
	F(FM)	4	492.1	0.467	0.104	700.0	0.168	0.030	0.288
	W(FM)	5	492.1	0.487	0.102	700.0	0.161	0.028	0.277
$\mathrm{Z}\alpha\beta\mathrm{DES}^{+\cdot}$	F(BC)	1	460.1	0.490	0.147	714.4	0.212	0.038	0.258
	F(FM)	4	460[b]	0.439					
			485.3	0.490	0.131	675.0	0.184	0.030	0.228
	W(FM)	5	496.5	0.580	0.137	675.0	0.169	0.027	0.195

a) See the text or caption for Fig. 3 for the notation under the column Class. b) Inflection.

Table 3. Results of the MO calculation for the planar (*Z*)-stilbene anion radical with C_{2v} symmetry

Transition[a]	ΔE[b]/eV	f[c]	P[d]	State[e]	Symmetry[f]	Character[g]
1	1.183	0.002	y	D_1	B_1	0.954(−1, −2)
2	1.217	0.001	z	D_2	A_2	0.966(−1, −3)
3	1.498	0.135	y	D_3	B_1	0.956(−1, −4)
4	2.591	0.109	z	D_4	A_2	0.927(−1, −5)
5	3.107	0.202	y	D_5	B_1	0.919(+1, −1)
6	3.676	0.001	y	D_6	B_1	0.759(−1, −6)
7	3.870	0.001	z	D_7	A_2	0.597(−1, −7)
8	4.217	0.037	z	D_8	A_2	0.563(+4, −1)

a) Transitions are numbered in the order of increasing transition energy. b) Transition energy. c) Oscillator strength of the transition. d) Direction of the transition moment (*cf.* Fig. 1). e) The excited state. f) The symmetry species to which the excited state belongs. The ground state (state D_0) belongs to symmetry species A_2. g) The wave function of the excited state. Only the electron configuration whose coefficient in the wave function is the largest is shown, together with the coefficient. Symbol (i, j) denotes the electron configuration arising from the ground configuration by promotion of an electron from π MO ϕ_i to π MO ϕ_j. The orbital index i runs from $+7$ for the lowest orbital to -7 for the highest one in the order of increasing energy. Orbitals ϕ_{+1} and ϕ_{-1} correspond, respectively, to HOMO and LUMO in the molecule. The coefficient of the ground configuration in the wave function of state D_0 is 0.989.

spectively.

As in Part II of this series,[2] spectra of radical ions measured after different treatments are designated as follows: The spectrum of a radical ion measured immediately after its production by γ-ray irradiation in a frozen matrix is designated as F (*frozen*), that measured after illumination as P (*photobleached*), that measured after controlled warming as W (*warmed*). Sometimes, spectrum P measured after illumination with light of wavelengths corresponding to band A (illumination A) is referred to as spectrum PA, and that measured after illumination with light of wavelengths corresponding to and longer than band B (illumination B) as spectrum PB. If necessary, the solvent is denoted

Table 4. Transition energies (ΔE) and oscillator strengths (f) of the planar (*Z*)-stilbene anion radical and their variation with geometrical changes[a)]

Symmetry	$\theta_{\alpha 1}/°$	$\theta_{\beta 1'}/°$	$\theta_{\alpha\beta}/°$	ΔE_5/eV	f_5	ΔE_4/eV	f_4	ΔE_3/eV	f_3	f_3/f_5
C_{2v}	0	0	0	3.108	0.202	2.592	0.109	1.498	0.135	0.668
C_2	30	30	0	+0.233	−0.029	−0.256	+0.017	−0.252	+0.007	+0.153
C_s	30	−30	0	+0.230	−0.033	−0.257	+0.018	−0.252	+0.007	+0.172
C_2	0	0	30	−0.312	+0.056	−0.012	−0.013	+0.198	+0.002	−0.137

a) The values for the nonplanar geometries are relative to the planar geometry.

in parentheses: For example, spectrum F of a cation radical in solution in *s*-butyl chloride is referred to as spectrum F(BC).

The same designations are also used to specify the geometries of radical ions after the respective treatments. That is, for example, the geometry of a cation radical immediately after its production in frozen *s*-butyl chloride is referred to as geometry F(BC). The relaxed geometry of a radical ion, that is, the geometry that the radical ion would take in fluid solutions, is referred to as geometry R (*relaxed*), and that of the parent neutral molecule as geometry N (*neutral*). Geometry W is considered to be nearly equal to geometry R.[1,2)]

We should like to emphasize that the spectral changes caused by illumination or controlled warming, shown in Figs. 2 and 3, are definite and reproducible, which should defy possible skepticism about attaching significance to the apparently small spectral changes discussed in the following text. The instrumental reproducibility is within ±0.1% for both the ordinate and the abscissa of these figures.

Assignment of Absorption Bands. The results of the MO calculation for the stilbene anion radical in the planar *Z* form are shown in Table 3. It is notable that the *f* values of transitions 3 and 5 are considerably smaller than the corresponding values for the anion radical in the planar *E* form (*cf.* Table 3 in Part II), and that the *f* value of transition 4 is not zero in contrast to the case of the planar *E* form. The results of the MO calculation for the cation radical are similar to those for the anion radical. The character of each state of the radical ions in the *Z* form is analogous to that of the corresponding state of the radical ions in the *E* form.[2)]

As in the case of the *E* isomers,[2)] bands A and B are ascribed to transitions 3 and 5, respectively. The band appearing between bands A and B in spectra of Z$\alpha\beta$DMS$^{+\cdot}$ and Z$\alpha\beta$DES$^{+\cdot}$ is ascribed to transition 4. In the spectra of the other radical ions, the absorption due to transition 4 is probably masked by the tails of bands A and B. The *f* values in Tables 1 and 2 may be less accurate than the corresponding values for the radical ions of sterically uncrowded or less crowded (*E*)-stilbenes in Part II,[2)] because of the presence of the superposing absorption due to transition 4 and also because of the comparatively small separation of bands A and B.

Expected Effects of Geometrical Changes on the Electronic Transitions. Table 4 lists the calculated values of the transition energy (ΔE) and oscillator strength (f) of transitions 3, 4, and 5 and of the ratio between the *f* values of transitions 3 and 5 (f_3/f_5) for the stilbene anion radical in the planar *Z* geometry and also the calculated values of the changes in these quantities associated with the changes from the planar *Z* geometry to nonplanar geometries in which $|\theta_{\alpha 1}|$, $|\theta_{\beta 1'}|$, or $|\theta_{\alpha\beta}|$ is 30°. The corresponding values for the cation radical are very close to the values for the anion radical.

The changes in the properties of the transitions of the anion radical associated with the geometrical changes seen in Table 4 and the corresponding ones of the cation radical should represent the effect of the geometrical changes on the absorption bands: It is expected, for example, that an increase in $|\theta_{\alpha 1}|$ and $|\theta_{\beta 1'}|$ will cause a large red shift and a very small increase in intensity of band A, a large blue shift and a small decrease in intensity of band B, and an increase in f_A/f_B, and that an increase in $|\theta_{\alpha\beta}|$ will cause a large blue shift and a very small increase in intensity of band A, a large red shift and a small increase in intensity of band B, and a decrease in f_A/f_B.

Geometry of the Neutral Molecules. Before proceeding to the discussion of the geometries of the radical ions, we briefly mention the geometry of the parent neutral molecules, which is relevant to the later discussion.

According to an electron-diffraction study, the molecule of ZS in the gas phase has a propeller-like geometry with C_2 symmetry, in which $\theta_{\alpha 1}$ and $\theta_{\beta 1'}$ are about 43°.[16)] This value is larger than predicted by most theoretical calculations.[17)] The value for the ZS molecule in solution is probably smaller than that for the molecule in the gas phase. The former is estimated at 29° from the λ_{max} value (278.7 nm) of the main absorption band of ZS in heptane solution.[12,14,20)]

By the method described in Refs. 12—14 and 20, the value of $|\theta_{\alpha 1}|$ and $|\theta_{\beta 1'}|$ is estimated at 52° for Z$\alpha\beta$DMS in solution from its λ_{max} value of 252.0 nm (in heptane) and at 54° for Z$\alpha\beta$DES in solution from its λ_{max} value of 248.8 nm (in heptane). When an allowance for the electronic bathochromic effect of the alkyl substituents is made, these values are revised to 59° and 61°, respectively.[21)]

At any rate, it is evident that the value of $|\theta_{\alpha 1}|$ and $|\theta_{\beta 1'}|$ in the relaxed geometry of the neutral molecule (*i.e.*, geometry N) increases in the order ZS≪Z$\alpha\beta$DMS<Z$\alpha\beta$DES. The value of $\theta_{\alpha\beta}$ in geometries N of these compounds is probably equal or close to 0°.

Broadness of Absorption Bands. Now, let us return to the spectra of the radical ions. The absorption bands of the radical ions of the (*Z*)-stilbenes are structureless and are much broader than those of the radical ions of sterically uncrowded (*E*)-stilbenes.[24] This seems to indicate the nonplanarity of the geometry of the radical ions of the (*Z*)-stilbenes.

Effect of Warming and Relaxed Geometries. *Cation Radicals*: In spectra F(BC) of the cation radicals, λ_B/nm decreases in the order $ZS^{+\cdot}>Z\alpha\beta DMS^{+\cdot}>Z\alpha\beta DES^{+\cdot}$. This indicates that $|\theta_{\alpha 1}|$ and $|\theta_{\beta 1'}|$ increase in the order $ZS^{+\cdot}<Z\alpha\beta DMS^{+\cdot}<Z\alpha\beta DES^{+\cdot}$ in geometries F(BC) of the cation radicals as in geometries N. If $\theta_{\alpha\beta}$ were nearly 0° or nearly constant in geometries F(BC) of these cation radicals, λ_A/nm and f_A/f_B would increase in the order $ZS^{+\cdot}<Z\alpha\beta DMS^{+\cdot}<Z\alpha\beta DES^{+\cdot}$. In fact, they increase in the order $Z\alpha\beta DMS^{+\cdot}<Z\alpha\beta DES^{+\cdot}<ZS^{+\cdot}$. This fact suggests that in geometries F(BC) $|\theta_{\alpha\beta}|$ is appreciably larger for $Z\alpha\beta DMS^{+\cdot}$ and $Z\alpha\beta DES^{+\cdot}$ than for $ZS^{+\cdot}$.

Spectrum F(FM) of $ZS^{+\cdot}$ is similar to spectrum F(BC), and remains almost unchanged on limited warming. These facts indicate that geometry F(FM) of this cation radical is similar to geometry F(BC), which is probably similar to geometry N, and that any significant geometrical change does not occur on the warming.

On the other hand, spectra F(FM) of $Z\alpha\beta DMS^{+\cdot}$ and $Z\alpha\beta DES^{+\cdot}$ are significantly different from spectra F(BC), and change appreciably on limited warming. In going from spectra F(BC) to spectra W(FM), λ_B/nm increases for both the cation radicals, and λ_A/nm and f_A/f_B decrease for $Z\alpha\beta DES^{+\cdot}$. These changes indicate an increase in $|\theta_{\alpha\beta}|$ and/or a decrease in $|\theta_{\alpha 1}|$ and $|\theta_{\beta 1'}|$. The geometrical change from F(BC) to W(FM) appears to be larger for $Z\alpha\beta DES^{+\cdot}$ than for $Z\alpha\beta DMS^{+\cdot}$. Spectra W(FM) of these cation radicals are different from spectra W(FM) of the *E* isomers (*cf.* Part II[2]).

In spectra W(FM), λ_B/nm increases in the order $Z\alpha\beta DMS^{+\cdot}<Z\alpha\beta DES^{+\cdot}$, and λ_A/nm and f_A/f_B decrease in the order $Z\alpha\beta DMS^{+\cdot}>Z\alpha\beta DES^{+\cdot}$. These sequences are opposite to the corresponding ones in spectra F(BC). Since it is unlikely that $|\theta_{\alpha 1}|$ and $|\theta_{\beta 1'}|$ are larger in $Z\alpha\beta DMS^{+\cdot}$ than in $Z\alpha\beta DES^{+\cdot}$, the above sequences indicate that in geometries W(FM) and therefore in geometries R (*i.e.*, the relaxed geometries) $|\theta_{\alpha\beta}|$ is considerably larger in $Z\alpha\beta DES^{+\cdot}$ than in $Z\alpha\beta DMS^{+\cdot}$.

Thus, it is concluded that, in geometries W and therefore in geometries R of the cation radicals, $|\theta_{\alpha 1}|$ and $|\theta_{\beta 1'}|$ increase in the order $ZS^{+\cdot}\ll Z\alpha\beta DMS^{+\cdot}\leqslant Z\alpha\beta DES^{+\cdot}$ and $|\theta_{\alpha\beta}|$ increases in the order $ZS^{+\cdot}\ll Z\alpha\beta DMS^{+\cdot}\ll Z\alpha\beta DES^{+\cdot}$

Anion Radicals: In spectra F(MTHF) of the anion radicals, λ_A/nm increases in the order $ZS^{-\cdot}<Z\alpha\beta DMS^{-\cdot}<Z\alpha\beta DES^{-\cdot}$, and λ_B/nm increases and f_A/f_B decreases in the order $ZS^{-\cdot}$, $Z\alpha\beta DES^{-\cdot}$, $Z\alpha\beta DMS^{-\cdot}$. The sequences probably indicate that in geometries F(MTHF) $|\theta_{\alpha 1}|$ and $|\theta_{\beta 1'}|$ increase in the order $ZS^{-\cdot}<Z\alpha\beta DMS^{-\cdot}<Z\alpha\beta DES^{-\cdot}$ and $|\theta_{\alpha\beta}|$ is noticeably larger in $Z\alpha\beta DMS^{-\cdot}$ and $Z\alpha\beta DES^{-\cdot}$ than in $ZS^{-\cdot}$. This means that geometries F(MTHF) of $Z\alpha\beta DMS^{-\cdot}$ and $Z\alpha\beta DES^{-\cdot}$ have already been relaxed to a considerable extent before being warmed, owing to the softness of the MTHF glass at 77 K.[1,2]

On limited warming, the spectrum of $ZS^{-\cdot}$ changes little, indicating that the geometry remains almost unchanged.

On the other hand, for $Z\alpha\beta DMS^{-\cdot}$ and $Z\alpha\beta DES^{-\cdot}$ the limited warming causes a large blue shift of band A and a small red shift and an increase in intensity of band B. The spectral changes indicate an increase in $|\theta_{\alpha\beta}|$ and/or a decrease in $|\theta_{\alpha 1}|$ and $|\theta_{\beta 1'}|$. Spectra W(MTHF) of these anion radicals are different from spectra W(MTHF) of the *E* isomers (*cf.* Part II[2]).

In spectra W(MTHF), the values of λ_A/nm and λ_B/nm of $Z\alpha\beta DMS^{-\cdot}$ are close to those of $Z\alpha\beta DES^{-\cdot}$. This similarity of the band position does not necessarily mean the geometrical similarity of these two anion radicals. Since the value of f_A/f_B is noticeably different between the two anion radicals, and also in view of the above conclusion on geometries W of the corresponding cation radicals, geometries W of these anion radicals seem to be considerably different from each other. Probably both $|\theta_{\alpha\beta}|$ and $|\theta_{\alpha 1}|$ as well as $|\theta_{\beta 1'}|$ increase in the order $Z\alpha\beta DMS^{-\cdot}<Z\alpha\beta DES^{-\cdot}$. The increase in $|\theta_{\alpha\beta}|$ and that in $|\theta_{\alpha 1}|$ and $|\theta_{\beta 1'}|$ should have opposite effects on the band position. The above-mentioned similarity of the band position is probably a result of balancing of the opposite effects.

Thus, it is concluded that, in geometries W and therefore in geometries R of the anion radicals, $|\theta_{\alpha 1}|$ and $|\theta_{\beta 1'}|$ increase in the order $ZS^{-\cdot}<Z\alpha\beta DMS^{-\cdot}<Z\alpha\beta DES^{-\cdot}$ and $|\theta_{\alpha\beta}|$ increases in the order $ZS^{-\cdot}\ll Z\alpha\beta DMS^{-\cdot}<Z\alpha\beta DES^{-\cdot}$.

While the position of band B in spectrum W of $ZS^{-\cdot}$ is close to that in spectrum W of $ZS^{+\cdot}$, band B in spectrum W of $Z\alpha\beta DMS^{-\cdot}$ and that of $Z\alpha\beta DES^{-\cdot}$ are located at much longer wavelength than are those of the corresponding cation radicals. In addition, the magnitude of the blue shift of band A in going from spectrum F to spectrum W is much larger for $Z\alpha\beta DMS^{-\cdot}$ and $Z\alpha\beta DES^{-\cdot}$ than for the corresponding cation radicals. These facts probably indicate that $|\theta_{\alpha\beta}|$ is larger in $Z\alpha\beta DMS^{-\cdot}$ and $Z\alpha\beta DES^{-\cdot}$ in geometry R than in the corresponding cation radicals in geometry R.

Comparison with Other Spectral Data: The value of λ_{max} of the sodium salt of $ZS^{-\cdot}$ in fluid solution in THF was reported to be 500 nm (ε 3.3×10^4).[7] This value is considerably smaller than the values of λ_B of $ZS^{-\cdot}$ in the present work. Since the sodium salt in THF probably exists as a contact ion pair, the difference in the λ_{max} value may be mainly ascribed to the effect of the counterion.

The values of λ_{max} of the anion radicals produced by reduction of 1,2-diphenylcyclopentene (DPCP) and 1,2-diphenylcyclohexene (DPCH) with sodium in HMPT were reported to be 530 nm (ε 3.4×10^4) and 560 nm (ε 2.3×10^4), respectively.[25] In this solvent the anion radicals are probably counterion-free. These anion radicals have a $ZS^{-\cdot}$ π system, and obviously the above data refer to band B of the π system. In $DPCP^{-\cdot}$ $|\theta_{\alpha\beta}|$ should be close to 0°, while in $DPCH^{-\cdot}$ it may deviate to some extent from 0°. The fact that the λ_{max} value of $DPCH^{-\cdot}$ is considerably larger than that of $DPCP^{-\cdot}$ indicates that the value of $|\theta_{\alpha\beta}|$ is considerably larger in $DPCH^{-\cdot}$ than in $DPCP^{-\cdot}$.[26]

The values of $\lambda_{\max}$ and $\varepsilon_{\max}$ of DPCP$^{-\cdot}$ are close to the values of λ_B and ε_B of spectrum W of ZS$^{-\cdot}$. Since the small difference in the λ value may be largely ascribed to the electronic bathochromic effect of the trimethylene chain in DPCP$^{-\cdot}$, if the difference in $|\theta_{\alpha 1}|$ and $|\theta_{\beta 1'}|$ between these anion radicals is assumed to be small, this spectral similarity is taken as a support to our conclusion that $|\theta_{\alpha\beta}|$ of ZS$^{-\cdot}$ in the relaxed geometry is approximately 0°.

The values of $\lambda_{\max}$ and $\varepsilon_{\max}$ of DPCH$^{-\cdot}$ are close to the values of λ_B and ε_B of spectra W of Z$\alpha\beta$DMS$^{-\cdot}$ and Z$\alpha\beta$DES$^{-\cdot}$. The electronic effect of the alkyl substituents should be approximately equal in these three anion radicals. Therefore, this spectral similarity indicates the geometrical similarity of the ZS$^{-\cdot}$ π systems in these anion radicals and supports our conclusion that $|\theta_{\alpha\beta}|$ in Z$\alpha\beta$DMS$^{-\cdot}$ and Z$\alpha\beta$DES$^{-\cdot}$ in the relaxed geometry deviates considerably from 0°.

The values of $\lambda_{\max}$ and $\varepsilon_{\max}$ of spectra F of Z$\alpha\beta$DMS$^{-\cdot}$ and Z$\alpha\beta$DES$^{-\cdot}$ are similar to those of DPCH$^{-\cdot}$, but different from those of DPCP$^{-\cdot}$. This fact seems to support the above inference that geometries F(MTHF) of Z$\alpha\beta$DMS$^{-\cdot}$ and Z$\alpha\beta$DES$^{-\cdot}$ have already been relaxed to a considerable extent.

General Conclusions on the Effect of Warming and on the Relaxed Geometries: From the study of limited warming, the following conclusions are drawn.

(1) Neither the *Z*→*E* nor the *E*→*Z* isomerization occurs on limited warming of glassy solutions of the radical ions of ZS, Z$\alpha\beta$DMS, Z$\alpha\beta$DES, or their *E* isomers (ES, E$\alpha\beta$DMS, E$\alpha\beta$DES).

(2) The relaxed geometries of the radical ions of ZS are almost similar to that of the neutral molecule, in which $|\theta_{\alpha\beta}|$ is approximately 0° and $|\theta_{\alpha 1}|$ and $|\theta_{\beta 1'}|$ are about 30°. It is possible that $|\theta_{\alpha\beta}|$ in the ZS radical ions in the relaxed geometry is slightly larger than that in the neutral molecule and that $|\theta_{\alpha 1}|$ and $|\theta_{\beta 1'}|$ in the former are slightly smaller than those in the latter.

(3) In the radical ions of Z$\alpha\beta$DMS and Z$\alpha\beta$DES in the relaxed geometry $|\theta_{\alpha\beta}|$ deviates considerably from 0°.

(4) $|\theta_{\alpha 1}|$ and $|\theta_{\beta 1'}|$ in the radical ions of Z$\alpha\beta$DMS and Z$\alpha\beta$DES in the relaxed geometry are probably somewhat smaller than those in the corresponding neutral molecules, but they are appreciably larger than those in the radical ions of ZS in the relaxed geometry.

Conclusions 2 and 3 are rationalized as follows. In the radical ions of ZS, the steric interference between the two phenyl groups can be relieved effectively by an increase in $|\theta_{\alpha 1}|$ and $|\theta_{\beta 1'}|$ as in the neutral molecule. There seems to be no need for the increase in $|\theta_{\alpha\beta}|$. On the other hand, in the radical ions of Z$\alpha\beta$DMS and Z$\alpha\beta$DES, the steric interference between the two alkyl groups is relieved only by an increase in $|\theta_{\alpha\beta}|$.

Conclusion 4 also seems to be quite reasonable, since the steric interference between the phenyl group and the alkyl group connected to the same carbon atom in the radical ions of Z$\alpha\beta$DMS and Z$\alpha\beta$DES remains unrelieved even when $|\theta_{\alpha\beta}|$ increases, and can be relieved only by an increase in $|\theta_{\alpha 1}|$ and $|\theta_{\beta 1'}|$.

As mentioned in Part II,[2)] the relaxed geometry of a radical ion in its ground state (state D_0) is expected to be intermediate between the geometries of the neutral molecule in its ground state (state S_0) and in its first excited singlet state (state S_1). According to a theoretical calculation by Fischer *et al.*,[19)] $\theta_{\alpha\beta}$ is 37° and 49° in ZS and Z$\alpha\beta$DMS, respectively, both in state S_1, while $\theta_{\alpha 1}$ and $\theta_{\beta 1'}$ are 13° in both the molecules in state S_1.[28)] The result that $\theta_{\alpha\beta}$ in Z$\alpha\beta$DMS in state S_1 has a considerably large value is consistent with Conclusion 3. However, the other results are inconsistent with Conclusions 2 and 4.

Effect of Illumination. As mentioned above, both the cation and the anion radical of ZS in frozen solutions at 77 K isomerize irreversibly to their *E* isomers on illumination.

In contrast, the radical ions of Z$\alpha\beta$DMS and Z$\alpha\beta$DES do not isomerize on illumination. The spectra of the cation radicals in frozen BC change only slightly on illumination. In the case of the anion radicals in frozen MTHF, on illumination spectral changes similar to those caused by limited warming occur: Band A shifts to shorter wavelengths, band B increases in intensity, and f_A/f_B decreases. These spectral changes indicate an increase in $|\theta_{\alpha\beta}|$ and a decrease in $|\theta_{\alpha 1}|$ and $|\theta_{\beta 1'}|$ as in the case of warming, but there is no indication of occurrence of the *Z*→*E* isomerization.

As seen in Part II,[2)] the radical ions of E$\alpha\beta$DMS and E$\alpha\beta$DES do not isomerize on illumination. Spectra PB of the radical ions of *Z* and *E* isomers of the α,β-dialkylstilbenes ($\alpha\beta$DAS's) appear distinctly different. Thus, it is concluded that in the radical ions of the $\alpha\beta$DAS's in frozen matrices at 77 K neither the photoisomerization between *Z* and *E* isomers nor the photoconversion from both *Z* and *E* isomers to a common product occurs.

Mechanism of the Z→E *Photoisomerization of the Unsubstituted Stilbene Radical Ions.* We propose here a mechanism of the photoisomerization of the stilbene radical ions and account for the notable difference in the photochemical behavior between the unsubstituted and the α,β-dialkyl-substituted stilbene radical ions.

The photoisomerization process of the stilbene radical ions is explicable by the diagrams in Fig. 4, which show the state energies as functions of $|\theta_{\alpha\beta}|$. The diagrams were drawn in the light of the results of the MO calculation, spectroscopic data, and the fact that the change in $|\theta_{\alpha\beta}|$ should be accompanied by a change in $|\theta_{\alpha 1}|$ and $|\theta_{\beta 1'}|$.

As mentioned above, for both the cation and the anion radical, and for both the *Z* and the *E* isomer, state D_5 is approximated as the state arising from state D_0 as a result of promotion of an electron from ϕ_{+1} to ϕ_{-1}. That is, aside from the closed electron configuration in which the six lowest-energy π orbitals (from ϕ_{+7} to ϕ_{+2}) are filled, states D_0 and D_5 of the cation radical are approximated by electron configurations $\phi_{+1}{}^1$ and $\phi_{-1}{}^1$, respectively, and states D_0 and D_5 of the anion radical by electron configurations $\phi_{+1}{}^2\phi_{-1}{}^1$ and $\phi_{+1}{}^1\phi_{-1}{}^2$, respectively.

At $|\theta_{\alpha\beta}|=90°$, ϕ_{+1} and ϕ_{-1} form a degenerate pair of orbitals. When $|\theta_{\alpha\beta}|$ increases from the *Z* side to the *E* side across this point, ϕ_{+1} and ϕ_{-1} are con-

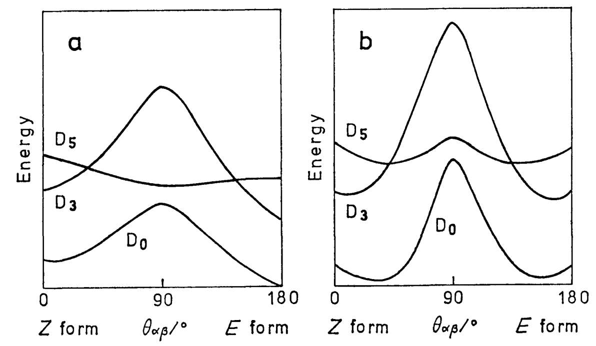

Fig. 4. State energies *vs.* the torsion angle about the central ethylenic bond ($\theta_{\alpha\beta}$).
(a): The unsubstituted stilbene radical ions. (b): The α,β-dialkylstilbene radical ions.

verted into ϕ_{-1} and ϕ_{+1}, respectively. Therefore, to a first approximation, states D_5 and D_0 are degenerate at $|\theta_{\alpha\beta}|=90°$, and, when $|\theta_{\alpha\beta}|$ increases from the Z side to the E side across this point, states D_5 and D_0 are converted into states D_0 and D_5, respectively. In fact, as a result of configuration interaction, the energy curves for these states must be separated as shown in Fig. 4, but the energy gap between these states at $|\theta_{\alpha\beta}|=90°$ should be small. Therefore, the internal conversion will occur with a high probability from state D_5 to state D_0 near this point.

In the E form of the unsubstituted stilbene radical ions, $|\theta_{\alpha 1}|$ and $|\theta_{\beta 1'}|$ are approximately 0°. In the Z form also they are small. Therefore, the π-bond order of the α–β bond is low. Accordingly, the energy barrier at $|\theta_{\alpha\beta}|=90°$ in state D_0 should be low, and the energy of state D_5 at this point should also be low. Thus, the energy of state D_5 will decrease as $|\theta_{\alpha\beta}|$ increases from 0° to 90°. The possible small decrease in $|\theta_{\alpha 1}|$ and $|\theta_{\beta 1'}|$ associated with the increase in $|\theta_{\alpha\beta}|$ will lower the energies of states D_5 and D_0 to some extent.

After all, the Z→E photoisomerization is considered to proceed as follows: $D_0(Z) \longrightarrow D_5(Z) \rightsquigarrow D_5(|\theta_{\alpha\beta}|=90°) \rightsquigarrow D_0(|\theta_{\alpha\beta}|=90°) \rightsquigarrow D_0(E)$. In this scheme, a radiative transition is represented by a straight arrow, and radiationless ones by wavy arrows. The basic assumption in this mechanism is that the photoisomerization proceeds via state D_5, the final state of the electronic transition responsible to band B.

Actually, even illumination A (illumination with light of wavelengths corresponding to band A), that is, the excitation to state D_3, induces the Z→E isomerization. In this case, the photoisomerization will proceed as follows. The radical ion passes from state D_3 to state D_5 at the crossing point ($0°<|\theta_{\alpha\beta}|<90°$) of the energy curves of the two states (*cf.* Fig. 4 (a)), and then the isomerization occurs: $D_0(Z) \longrightarrow D_3(Z) \rightsquigarrow D_3$(the crossing point) $\rightsquigarrow D_5$(the crossing point) $\rightsquigarrow D_5(|\theta_{\alpha\beta}|=90°) \rightsquigarrow D_0(|\theta_{\alpha\beta}|=90°) \rightsquigarrow D_0(E)$. Passing from state $D_3(Z)$ to the crossing point involves moving along a rising curve, *i.e.*, overriding a small barrier. The energy necessary to override the barrier must be supplied as vibrational energy.

Recently, Sazhnikov *et al.*[29,30] measured the wavelength dependence of the quantum yield of the Z→E photoisomerization of the radical ions of the unsubstituted stilbene in glassy solutions at 77 K, and found the following facts. (1) The quantum yield is very high on illumination with light of wavelengths corresponding to the "second absorption band" (*i.e.*, band B in our designation), 400—600 nm. (2) The maximum value of the quantum yield is extremely high. For the anion radical it is as high as 0.60 at 529 nm (nearly the absorption maximum of band B), a value which is much higher than the corresponding value for the Z→E photoisomerization of the neutral stilbene molecule (*ca.* 0.05 at −180 °C). (3) The quantum yield drops sharply to zero when the wavelength of the exciting light is varied from *ca.* 650 nm (for the cation radical) or *ca.* 620 nm (for the anion radical) to 800 nm in the region of the "first absorption band" (*i.e.*, band A in our designation). The 0-0 band of band A is probably located at about 800 nm. Fact 3 means that the illumination at this wavelength cannot cause the isomerization, and that, when the radical ions are excited into higher vibrationally excited levels of state D_3, the quantum yield of the isomerization increases sharply.

The facts found by Sazhnikov *et al.* can be satisfactorily rationalized by the above proposed mechanism. States D_1 and D_2 in their papers should be replaced by states D_3 and D_5, respectively.

Interpretation of Nonoccurrence of the E→Z *Photoisomerization in the Unsubstituted Stilbene Radical Ions.* The Z→E photoisomerization of the unsubstituted stilbene radical ions is irreversible. That is, the E→Z photoisomerization does not occur. In order to interpret this fact, both intramolecular and intermolecular factors should be taken into consideration.

First, we consider the intramolecular factor. In the case of the radical ions of the unsubstituted stilbene the E isomer should be considerably more stable than the Z isomer, as in the case of the neutral molecule[31,32] and the dianion.[27] Considering the difference in the λ_B value between the E and the Z isomer, we infer that the energy of state D_5 of the E isomer should be comparable to or rather lower than that of the Z isomer. Perhaps, the energy of state D_5 may be lower at $|\theta_{\alpha\beta}|=180°$ than at $|\theta_{\alpha\beta}|=90°$. If it is true, it may be possible that the excitation of the E isomer from state D_0 to state D_5 cannot induce the E→Z isomerization. However, this interpretation may not be convincing.

With regard to the intermolecular factor, Gegiou *et al.* found that the quantum yield of the E→Z photoisomerization of the unsubstituted stilbene molecule in fluid solutions decreased with increasing viscosity of the medium, while that of the Z→E photoisomerization was practically unaffected by the viscosity of the medium.[33] Considering the fact that in solution the nonplanar (Z)-stilbene molecule occupies a larger volume than the planar (E)-stilbene molecule by about 2.5%,[34] these authors ascribed the viscosity effect to an increase in molecular volume somewhere along the path of the E→Z photoisomerization. Sazhnikov *et al.* stated that the same interpretation appeared to be true for the radical ions of stilbene.[30] A plausible interpretation for the radical ions may be as follows:

The isomerization of the more bulky nonplanar *Z* isomer to the less bulky planar *E* isomer is not resisted by the rigid matrix, but the reverse process (the *E*→*Z* isomerization), which necessitates an increase in the volume of the radical ion, is inhibited.

It is rather surprising that the *Z*→*E* isomerization, which is obviously accompanied by a large change in the shape of the radical ion, proceeds easily in the rigid matrix such as frozen *s*-butyl chloride. The thermal energy liberated from the optically excited solute radical ion may locally heat and loosen the matrix around the radical ion.

Interpretation of Nonoccurrence of the Z→E *and the* E→Z *Photoisomerization in the α,β-Dialkylstilbene Radical Ions.* The fact that the radical ions of αβDAS's undergo neither the *Z*→*E* nor the *E*→*Z* photoisomerization may not be ascribed to the intermolecular effect, but may be intrinsic to the radical ions: Since both *Z* and *E* isomers of the αβDAS radical ions are nonplanar to a comparable extent, the isomerization will not be accompanied by an appreciable increase in the volume of the radical ion. In addition, the differences in the shape of the radical ion among the *Z* form, the 90° twisted form, and the *E* form are considered to be rather smaller than those in the unsubstituted stilbene radical ions. In this connection, it may be noted that in sterically hindered stilbene derivatives such as 2,2′,4,4′,6,6′-hexamethylstilbene both the quantum yields of the *Z*→*E* and the *E*→*Z* photoisomerization of the molecules in fluid solutions are independent of the viscosity of the medium and that this fact is interpreted on the basis of the inference that the volumes occupied by both the isomers are similar.[33)]

We must invoke the intramolecular or intrinsic factor. The reason of the nonoccurrence of the photoisomerization is probably as follows. An state energy diagram schematically drawn for the αβDAS radical ions is shown in Fig. 4 (b). The ground states of the *Z* and the *E* isomer of α,β-dimethylstilbene have comparable energies.[10,12,13,32)] Accordingly, the energy difference between states $D_0(Z)$ and $D_0(E)$ of the αβDAS radical ions is probably also very small. In these radical ions, $|\theta_{\alpha 1}|$ and $|\theta_{\beta 1'}|$ are always large, and therefore the π-bond order of the α–β bond is high. Therefore, the increase in the energy of state D_0 associated with the deviation of $|\theta_{\alpha\beta}|$ from 0° or 180° should be sharp, and the energy barrier at $|\theta_{\alpha\beta}|=90°$ in state D_0 should be much higher than in the case of the unsubstituted stilbene radical ions. As a result, the energy of state D_5 should be raised at $|\theta_{\alpha\beta}|=90°$. Also in this case, the possible small decrease in $|\theta_{\alpha 1}|$ and $|\theta_{\beta 1'}|$ associated with the deviation of $|\theta_{\alpha\beta}|$ from 0° or 180° will lower the energies of states D_5 and D_0 to some extent. Consequently, the energy curve for state D_5 as well as that for state D_0 possibly has a maximum at $|\theta_{\alpha\beta}|=90°$ and minima between $|\theta_{\alpha\beta}|=0°$ and 90° and between $|\theta_{\alpha\beta}|=90°$ and 180°. Therefore, in these radical ions, the excitation to state D_5 does not induce the isomerization in either direction.

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