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Electronic Absorption Spectra and Geometry of Molecular Ions Generated from Stilbene and Related Compounds. II. Radical Ions of (*E*)-Stilbene and Related Compounds

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The electronic absorption spectra of radical ions produced by γ-ray irradiation of (*E*)-stilbene and related compounds in frozen matrices were measured. On illumination and on controlled warming, the spectra of the radical ions of sterically uncrowded stilbenes and diphenylacetylene remained almost unchanged, while those of the radical ions of sterically crowded stilbenes changed noticeably. Examination of the spectra and of their changes led to the following conclusions: (a) The relaxed geometry of the radical ions of sterically uncrowded stilbenes is planar or nearly planar; (b) in the unrelaxed geometries of the radical ions of (*E*)-α,β-dialkylstilbenes the torsion angles of the Ph–C bonds are nearly as large as in the parent molecules, and on relaxation these angles become smaller and the torsion angle of the central ethylenic bond deviates from 0° to a considerable extent; (c) for the radical ions of *ortho*-substituted (*E*)-stilbenes the geometrical change on relaxation is comparatively small.

Geometries of molecular ions generated from unsaturated molecules by addition or removal of one or two electrons are not always similar to those of the parent molecules. The question of how the molecular geometry changes with the ionization is a subject of interest.

Previously we studied the geometry of neutral molecules of stilbenes[1–6] and of their dianions[7] by means of electronic absorption spectroscopy. The present paper reports the results of a similar investigation of the geometry of radical ions (anion and cation radicals) of (*E*)-stilbene and related compounds, on which no reliable information is available.

In a previous paper,[8] we reported that the electronic absorption spectrum of the tetraphenylethylene (TPE) anion radical in frozen 2-methyltetrahydrofuran (MTHF) changed markedly on controlled warming, and attributed the spectral change to the geomerical change of this sterically crowed anion radical. In the present study, it is examined whether such a phenomenon occurs for radical ions of sterically crowded stilbene derivatives.

The compounds treated here and their abbreviations (in parentheses) are as follows: (*E*)-stilbene (ES), (*E*)-α-methylstilbene (EαMS), (*E*)-α,β-dimethylstilbene (E$\alpha\beta$DMS), (*E*)-4,4′-dimethylstilbene (E44′DMS), (*E*)-2,4,6-trimethylstilbene (ETMS), (*E*)-2,2′,4,4′,6,6′-hexamethylstilbene (EHMS), (*E*)-α,β-diethylstilbene (E$\alpha\beta$-DES), (*E*)-4-phenylstilbene (E4PS), (*E*)-4,4′-diphenylstilbene (E44′DPS), and diphenylacetylene (DPA).

Experimental

Spectra of Radical Ions Produced by γ-Ray Irradiation of Frozen Solutions at 77 K. Radical ions of ES and related compounds were produced by γ-ray irradiation in deaerated solutions frozen at 77 K in liquid nitrogen, and their electronic absorption spectra were measured. For the anion radicals MTHF was used as the solvent, whereas for the cation radicals *s*-butyl chloride (BC) or a Freon Mixture (FM: an equivolume mixture of trichlorofluoromethane and 1,2-dibromo-1,1,2,2-tetrafluoroethane) was employed. The experimental details are described in a previous paper.[8] Both the anion and the cation radicals 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.

After recording the spectra of γ-ray irradiated samples, they were illuminated with light of the wavelengths corresponding to and longer than band A for 5—10 min (illumination A). Then, the samples were successively illuminated with light of the wavelengths corresponding to and longer than band B for 5—10 min (illumination B).

To see the effect of limited warming, the γ-ray irradiated sample was taken out of the liquid nitrogen for a limited time, and then refrozen at 77 K. The warming period was successively increased (for example, 20, 24, 28 s for anion radicals; 10, 12, 14 s for cation radicals).

The spectra of the cation radicals of E4PS and E44′DPS were less accurate because of the low solubility of these compounds in BC and in FM.

Spectra of Anion Radicals Produced by Alkali-metal Reduction. The spectra of the anion radicals produced by reduction of ES, EαMS, E44′DMS, ETMS, and EHMS with alkali metals (sodium, potassium, and cesium) in deaerated 1,2-dimethoxyethane (DMS) were also measured for the comparison with those obtained by γ-ray irradiation. The experimental procedure was described previously.[7]

Reliable spectra of the anion radicals of E$\alpha\beta$DMS and E$\alpha\beta$DES could not be obtained by the alkali-metal reduction even in the presence of a large excess of the parent molecules at low temperature,[8] being masked by the absorption due to the corresponding dianions. This is due to the fact that the equilibrium constant (K_{dispr}) of the disproportionation of the anion radical associated with the counterion to a pair of the neutral molecule and the dianion associated with two counterions is much greater for these sterically crowded stilbenes than for sterically uncrowded or less crowded stilbenes.[7] Even the K_{dispr} value for EαMS was reported to be much greater than that for ES.[9] It is evident that the K_{dispr} values for E$\alpha\beta$DMS and E$\alpha\beta$DES are much more greater than that for EαMS.

Molecular Orbital Calculation

To characterize the absorption bands and to get the

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relation between the bands and the geometry of the radical ions, we carried out a semiempirical SCF-MO-CI calculation for the π electronic state of the radical ions by the method developed by Longuet-Higgins and Pople.[13] The details of the calculation procedure are essentially the same as those employed in previous work.[8,14] The same assumptions on the geometry as those in Part I of this series[7] were made.

The carbon skeleton of the (*E*)-stilbene π system and the numbering of the carbon atoms are illustrated in Fig. 1. Torsion angles β-α-1-6 and α-β-1′-6′ are denoted by $\theta_{\alpha 1}$ and $\theta_{\beta 1'}$, respectively. Angle $\theta_{\alpha\beta}$ is defined as 180° minus torsion angle 1-α-β-1′. For the planar *E* form angles $\theta_{\alpha 1}$, $\theta_{\beta 1'}$, and $\theta_{\alpha\beta}$ are 0°.

Results and Discussion

Designation of Spectra and of Geometries. Representative spectra of the radical ions measured after various treatments are shown in Figs. 2 and 3, and relevant data are listed in Tables 1 and 2. Although most of the spectral changes are relatively small, they are reproducible with a precision of a few percent. The molar absorption coefficient (ε) was evaluated in the same manner as described in Ref. 8. The values for the spectra of anion radicals are reliable, but those for the spectra of cation radicals are uncertain.[15]

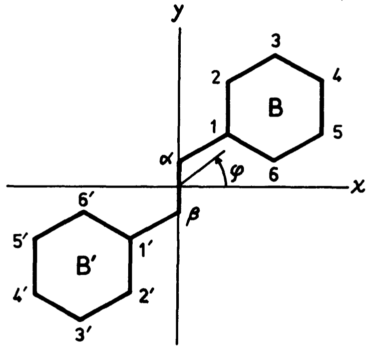
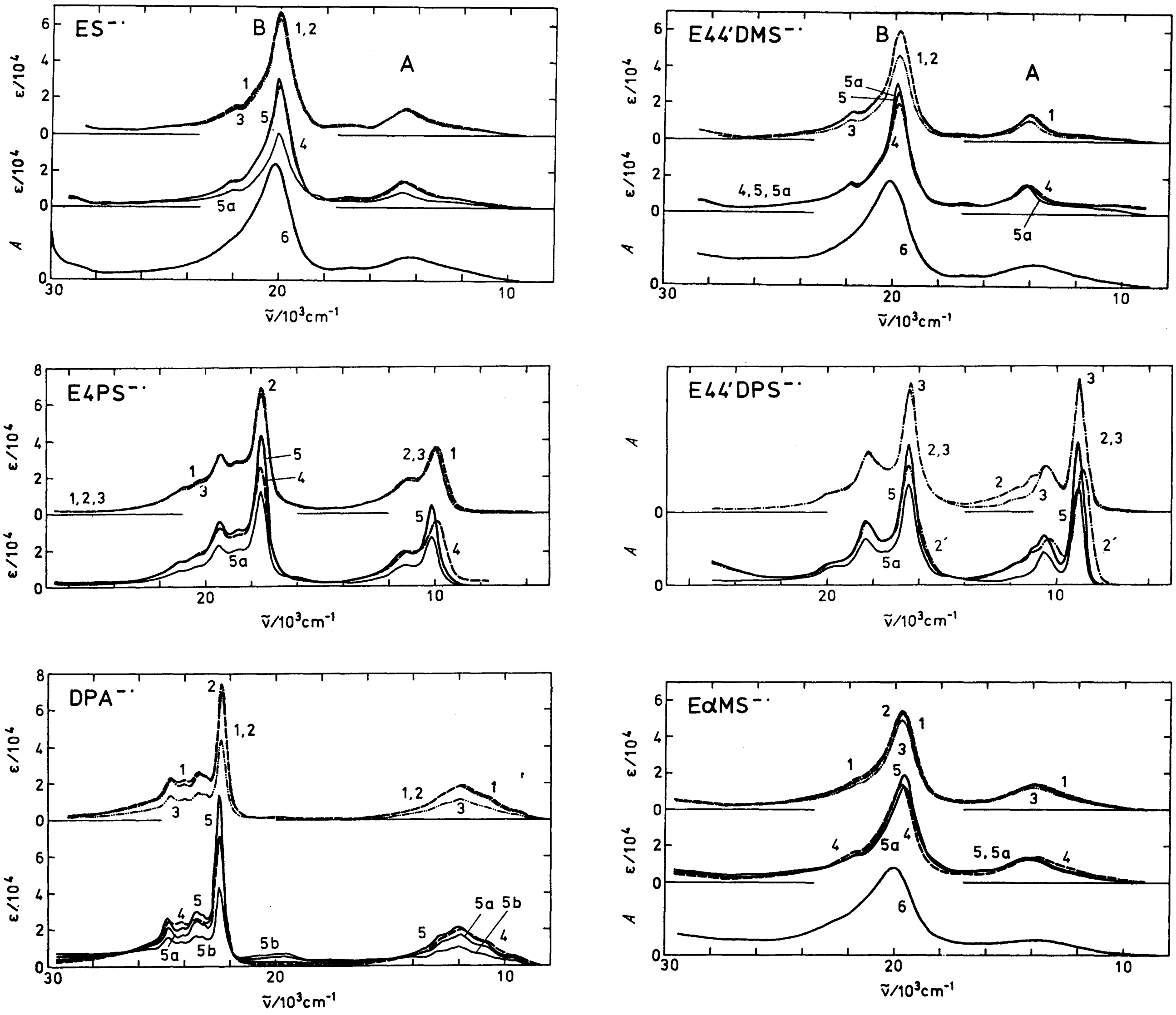


Fig. 1. The carbon skeleton of (*E*)-stilbene.

As seen in the figures, the radical ions exhibit two major bands, A and B, in the visible region. For band A, for example, the wavelength (λ) and molar absorption coefficient at the maximum and the oscillator strength (f) are denoted by λ_A, ε_A, and f_A, respectively.



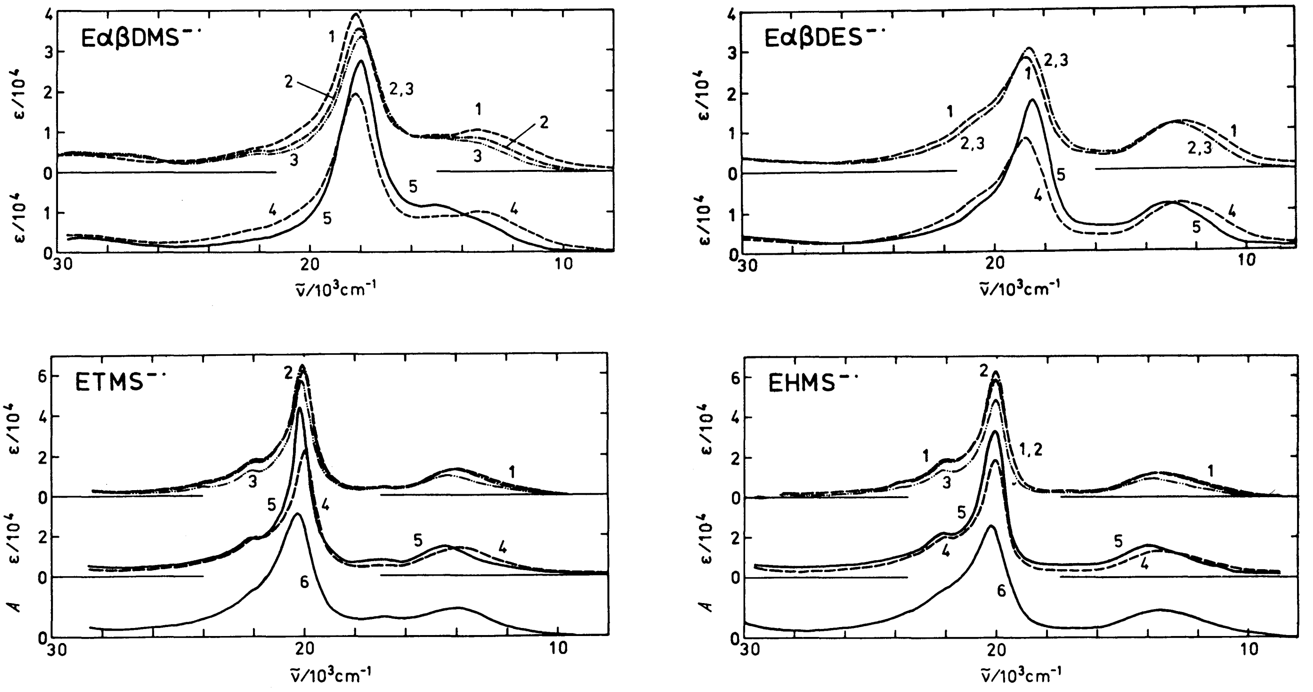


Fig. 2. Electronic absorption spectra of anion radicals. Curves 1 and 4 (------): spectra observed immediately after γ-ray irradiation of frozen solution, designated F in the text. Curve 2 (-·-·-): spectra observed after illumination of the sample for curve 1 with light of wavelengths corresponding to 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, 5b, 5c, ··· (——): spectra observed after additional controlled warming for successively increasing time. The solvent is 2-methyltetrahydrofuran (MTHF) for all the above spectra. Curve 6 (——): spectra of anion radicals produced by alkali-metal reduction in fluid dimethoxyethane (DME), designated M in the text.

For the sake of convenience, spectra of a radical ion measured after different treatments are designated as follows:[8] The spectrum of a radical ion immediately after its production by γ-ray irradiation in a frozen matrix is designated as F (*frozen*), that after illumination as P (*photobleached*), that after controlled warming as W (*warmed*), and that of an anion radical produced by alkali-metal reduction in a fluid DME solution as M (*metal*). Sometimes, spectrum P after illumination A is referred to as spectrum PA, and that after illumination B as spectrum PB. If necessary, the solvent is denoted in parentheses: For example, spectrum F of a cation radical in solution in BC is referred to as spectrum F(BC).

The same designations are also used to specify the geometries of the radical ion after the respective treatments. In addition, the geometry of the parent neutral molecule is designated as N (*neutral*), and the geometry that the radical ion takes in a fluid solution as R (*relaxed*). According to a conclusion in Ref. 8, geometry W is considered to be almost equal to geometry R.

Assignment of Absorption Bands. The results of the MO calculation for the stilbene anion radical in the planar E form belonging to point group C_{2h} are shown in Table 3, which includes all the electronic transitions having a transition energy (ΔE) smaller than 4.5 eV. By comparison between the observed spectra and the results of the calculation, bands A and B are ascribed to transitions 3 and 5, respectively. The very weak band appearing between bands A and B in the spectra of ES⁻·, E44′DMS⁻·, ETMS⁻·, and EHMS⁻· is ascribed to transition 4, which is forbidden in the planar E form but is weakly allowed in nonplanar geometries in which $\theta_{\alpha\beta}$ is not 0°.

As seen in Table 3, transitions 3, 4, and 5 can be well approximated as the one-electron excitations from ψ_{-1} to ψ_{-4}, from ψ_{-1} to ψ_{-5}, and from ψ_{+1} to ψ_{-1}, respectively. Accordingly, bands A and B of the stilbene anion radical correspond to the longest-wavelength intense band of the stilbene dianion[7] and that of the stilbene molecule,[1,2,6,16] respectively.

The results of the MO calculation for the stilbene cation radical are quite similar to those for the anion radical, because of the pairing properties of π orbitals of the alternant hydrocarbon. Similarly to the case of the anion radical, bands A and B are ascribed to transitions 3 and 5, respectively, and the very weak band appearing between bands A and B in the spectra of ES⁺· and some other cation radicals is ascribed to transition 4. Transitions 3, 4, and 5 in the cation radical can be well approximated as the one-electron excitations from ψ_{+4} to ψ_{+1}, from ψ_{+5} to ψ_{+1}, and from ψ_{+1} to ψ_{-1}, respectively.

The orbitals involved in the approximate one-electron expressions of transitions 3, 4, and 5 in the radical ions can be roughly approximated as follows:

$$\psi_{\pm1} \approx a\phi_{\pm1}(\mathrm{B}) \mp b\phi_{\pm1}(\mathrm{E}) \pm a\phi_{\pm1}(\mathrm{B}')$$
$$\psi_{\pm4} \approx a\phi_{\pm1}(\mathrm{B}) \pm b\phi_{\mp1}(\mathrm{E}) \mp a\phi_{\pm1}(\mathrm{B}')$$
$$\psi_{\pm5} \approx b\phi_{\pm1}(\mathrm{B}) \pm a\phi_{\pm1}(\mathrm{E}) \pm b\phi_{\pm1}(B')$$

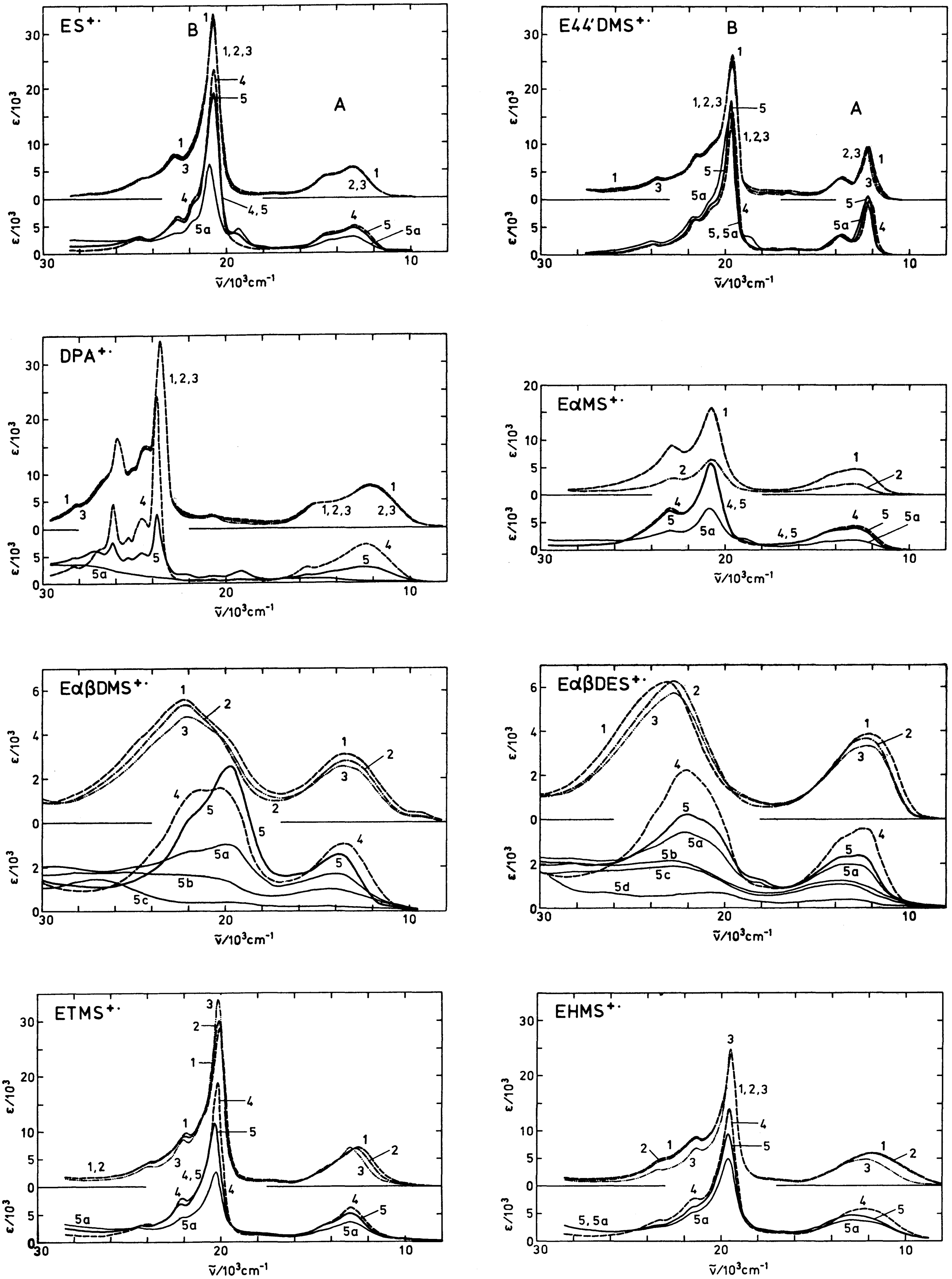


Fig. 3. Electronic absorption spectra of cation radicals. See Caption for Fig. 2. The solvent is *s*-butyl chloride (BC) for spectra 1, 2, and 3, and is a Freon Mixture (FM) for the other spectra.

TABLE 1. DATA ON ELECTRONIC ABSORPTION SPECTRA OF ANION RADICALSa)

Anion radical	Class	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
$ES^{-\cdot}$	F	4	499.3	6.569	0.627	690.3	1.407	0.191	0.305
	W	5	498.4	7.042	0.616	682.1	1.422	0.190	0.308
	M(Na^+)	6	495	6.569b)	0.780b)	700	1.324b)	0.218b)	0.279
$E44'DMS^{-\cdot}$	F	4	504.6	5.988	0.589	708.5	1.594	0.217	0.369
	W	5a	502.6	7.101	0.611	700.0	1.617	0.189	0.309
	M(K^+)	6	496	5.988b)	0.793b)	725	1.238b)	0.216b)	0.272
$E4PS^{-\cdot}$	F	4	568.2	6.550	0.679	1007.1	3.558	0.318	0.468
	W	5	569.6	8.311	0.749	986.6	4.398	0.317	0.423
$E44'DPS^{-\cdot}$	PA	2′	608.1	0.672c)	0.694d)	1126.5	0.652c)	0.482d)	0.695
	W	5	607.4	0.790c)	0.716d)	1102.4	0.799c)	0.449d)	0.627
$DPA^{-\cdot}$	F	4	445.6	7.056	0.555	836.2	1.945	0.290	0.522
	W	5	444.9	9.331	0.624	836.2	2.060	0.302	0.483
$E\alpha MS^{-\cdot}$	F	4	507.9	5.344	0.634	718.5	1.367	0.216	0.341
	W	5	510.4	5.865	0.666	704.1	1.355	0.200	0.301
	M(Na^+)	6	498	5.344b)	0.938b)	730	0.882b)	0.173b)	0.184
$E\alpha\beta DMS^{-\cdot}$	F	4	550.0	3.921	0.536	750	1.016	0.199	0.371
	PB	3	556.5	3.352	0.440	714	0.778	0.130	0.297
	W	5	557.5	4.754	0.521	662.5	1.183	0.159	0.306
$E\alpha\beta DES^{-\cdot}$	F	4	532.6	2.811	0.454	800	1.201	0.227	0.500
	PB	3	537.2	3.040	0.459	775	1.142	0.191	0.416
	W	5	541.5	3.761	0.491	756.5	1.192	0.194	0.396
$ETMS^{-\cdot}$	F	4	500.0	6.231	0.598	720.6	1.390	0.226	0.378
	PB	3	497.1	5.649	0.446	700	0.972	0.130	0.290
	W	5	495.6	8.333	0.700	692.6	1.430	0.214	0.305
	M(K^+)	6	493	6.231b)	0.757b)	715	1.381b)	0.205b)	0.271
$EHMS^{-\cdot}$	F	4	498.0	5.831	0.598	730.6	1.269	0.237	0.396
	PB	3	498.0	4.802	0.414	725	0.863	0.131	0.317
	W	5	498.0	7.300	0.747	717.1	1.533	0.269	0.360
	M(Na^+)	6	494	5.831b)	0.741b)	745	1.357b)	0.240b)	0.324

a) The solvent is DME for spectra M and is MTHF for all the other spectra. For spectra M, the counterion is indicated in parentheses. b) Values tentatively determined by equating the value of ε_B of spectrum M to that of spectrum F. c) Values of the absorbance. d) Values tentatively determined on some assumptions.

In these expressions, a and b represent coefficients bearing the relation $a>b>0$; $\phi_{+1}(E)$ and $\phi_{-1}(E)$ represent the bonding and the antibonding π orbital of the central ethylenic bond, respectively $[\phi_{\pm1}(E)=2^{-1/2}(\chi_\alpha \pm \chi_\beta)]$; $\phi_{+1}(B)$ and $\phi_{-1}(B)$, for example, represent the following π orbitals of benzene ring B (see Fig. 1):

$$\phi_{\pm1}(B) = 12^{-1/2}(2\chi_1 \pm \chi_2 - \chi_3 \pm 2\chi_4 - \chi_5 \pm \chi_6).$$

With respect to the α-β bond, the orbitals belonging to symmetry species a_u, ϕ_{+5}, ϕ_{+1}, and ϕ_{-4}, are bonding, and the orbitals belonging to symmetry species b_g, ϕ_{+4}, ϕ_{-1}, and ϕ_{-5}, are antibonding; with respect to the α-1 and the β-1′ bond, ϕ_{+5}, ϕ_{+4}, and ϕ_{-1} are bonding, and ϕ_{+1}, ϕ_{-4}, and ϕ_{-5} are antibonding.

Expected Effects of Geometrical Changes on the Electronic Transitions. In Table 4 are listed the calculated values of the energies and oscillator strengths of transitions 3, 4, and 5 and of the ratio between the oscillator strengths of transitions 3 and 5 (f_3/f_5) for the stilbene anion radical in the planar E geometry. Table 4 also lists the calculated values of the changes in these quantities associated with the changes from the planar E geometry to geometries in which $|\theta_{\alpha1}|$, $|\theta_{\beta1'}|$, or $|\theta_{\alpha\beta}|$ is 30°. The corresponding values for the cation radical are almost coincident with 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 $|\theta_{\alpha1}|$ and $|\theta_{\beta1'}|$ will exert a large bathochromic and a very small hyperchromic effect on band A and a comparatively large hypsochromic and a large hypochromic effect on band B, and will bring about a large increase in ratio f_A/f_B, and that an increase in $|\theta_{\alpha\beta}|$ will exert a large hypsochromic and a small hypochromic effect on band A and a large bathochromic and a small hypochromic effect on band B, and will bring about a small decrease in f_A/f_B.

Comparison between Spectra of Anion and Cation Radicals. With a few exceptions, the maxima of bands A and B of each anion radical are located at shorter and at longer wavelength, respectively, than are those of the corresponding cation radical, and, without exception, the separation between the maxima of the two bands of each anion radical is considerably smaller than that of the corresponding cation radical.

Because of the pairing properties of π orbitals, the spectra of both radical ions should closely resemble

TABLE 2. DATA ON ELECTRONIC ABSORPTION SPECTRA OF CATION RADICALS

Cation radical	Class	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
$ES^{+\cdot}$	F(BC)	1	482.1	3.337	0.264	759.0	0.555	0.071	0.268
	F(FM)	4	483.2	3.337	0.245	762.9	0.495	0.065	0.266
	W(FM)	5	482.9	2.908	0.229	757.7	0.473	0.060	0.260
$E44'DMS^{+\cdot}$	F(BC)	1	509.3	2.613	0.233	816.0	0.955	0.065	0.279
	F(FM)	4	510.1	2.613	0.178	819.4	1.010	0.059	0.333
	W(FM)	5	507.7	2.826	0.183	815.9	1.076	0.055	0.303
$DPA^{+\cdot}$	F(BC)	1	424.0	3.408	0.330	811.5	0.770	0.149	0.453
	F(FM)	4	421.0	3.408	0.242	807.9	0.705	0.116	0.479
	W(FM)	5	421.0	1.263	0.089	807.9	0.289	0.041	0.453
$E\alpha MS^{+\cdot}$	F(BC)	1	481.6	1.576	0.223	775.0	0.472	0.072	0.325
	F(FM)	4	480.7	1.576	0.208	769.3	0.431	0.069	0.331
	W(FM)	5	480.7	1.576	0.203	767.0	0.401	0.061	0.300
$E\alpha\beta DMS^{+\cdot}$	F(BC)	1	450.0	0.560	0.170	750.0	0.311	0.063	0.372
	PB(BC)	3	450.0	0.481	0.142	725.0	0.255	0.049	0.348
	F(FM)	4	492.3 467.3	0.559 0.551	0.146	740.7	0.303	0.049	0.338
	W(FM)	5	506.5	0.656	0.145	725.0	0.255	0.040	0.278
$E\alpha\beta DES^{+\cdot}$	F(BC)	1	432.1	0.624	0.168	825.0	0.385	0.073	0.438
	PB(BC)	3	438.5	0.573	0.149	825	0.330	0.061	0.408
	F(FM)	4	452.9	0.624	0.153	806.5	0.357	0.063	0.414
	W(FM)	5	454.1	0.423	0.116	786.8	0.236	0.046	0.395
$ETMS^{+\cdot}$	F(BC)	1	498.2	2.868	0.268	800.0	0.709	0.090	0.337
	PB(BC)	3	496.3	3.373	0.255	769.6	0.714	0.075	0.296
	F(FM)	4	495.6	2.868	0.226	775.0	0.625	0.076	0.336
	W(FM)	5	491.9	2.137	0.201	775.0	0.518	0.067	0.333
$EHMS^{+\cdot}$	F(BC)	1	513.1	2.397	0.249	850.0	0.588	0.108	0.436
	PB(BC)	3	513.1	2.487	0.199	825.0	0.473	0.078	0.391
	F(FM)	4	510.9	2.397	0.233	825.0	0.580	0.107	0.457
	W(FM)	5	509.7	1.942	0.213	775.0	0.461	0.094	0.441

TABLE 3. RESULTS OF THE MO CALCULATION FOR THE STILBENE ANION RADICAL HAVING THE PLANAR *E* GEOMETRY BELONGING TO SYMMETRY GROUP C_{2h}

Transition[a)]	$\Delta E^{b)}$/eV	$f^{c)}$	$\varphi^{d)}$/°	State[e)]	Symmetry[f)]	Character[g)]
1	1.218	0	—	D_1	B_g	0.961(−1,−3)
2	1.224	0.004	−70.3	D_2	A_u	0.953(−1,−2)
3	1.519	0.383	+36.7	D_3	A_u	0.952(−1,−4)
4	2.606	0	—	D_4	B_g	0.919(−1,−5)
5	3.011	0.604	+43.8	D_5	A_u	0.892(+1,−1)
6	3.672	0.013	+46.8	D_6	A_u	0.758(−1,−6)
7	3.882	0	—	D_7	B_g	0.603(−1,−7)
8	4.270	0	—	D_8	B_g	0.598(+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: φ represents the angle that the transition moment makes with the x axis in the xy plane (see Fig. 1). e) The excited state. f) The symmetry species to which the excited state belongs. 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 the ground state (state D_0) is 0.988.

TABLE 4. DEPENDENCE OF THE ENERGY AND OSCILLATOR STRENGTH OF TRANSITIONS OF THE STILBENE ANION RADICAL ON THE GEOMETRY[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_{2h}	0	0	0	3.011	0.604	2.606	0	1.519	0.383	0.632
C_2	30	30	0	+0.143	−0.157	−0.282	0	−0.249	+0.014	+0.254
S_2	30	−30	0	+0.143	−0.157	−0.282	0	−0.249	+0.014	+0.254
C_2	0	0	30	−0.338	−0.043	−0.016	+0.008	+0.191	−0.068	−0.072

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

are aprotic and should have nearly equal values of the static dielectric constant at 77 K,[15] the marked shifts of the bands of the cation radicals as compared with those of the corresponding anion radicals cannot be attributed to the difference in the general solvent effect. The shifts might be a manifestation of the difference in the effect of σ electrons in both the radical ions, as suggested previously,[15] or a manifestation of the difference in the geometry. For example, if the length of the α-β bond is shorter in cation radicals than in the corresponding anion radicals, the directions of the shifts can be well explained.

Electronic Bathochromic Effect of Alkyl Substituents. Before proceeding to discuss the relation between the spectra and the geometry, we must examine the electronic bathochromic effect of alkyl substituents.

Both bands A and B of the E44′DMS radical ions are located at longer wavelengths than are the corresponding bands of the ES radical ions. In Table 5, the magnitudes of bathochromic shift of bands A and B of the ES radical ions caused by substitution of two methyl groups at the *para* positions are compared with those of the corresponding bands of the ES molecule[4] and of the ES dianion.[7] As seen in the table, the magnitude of the bathochromic shift of band A or its corresponding band increases in the order dianion< anion radical<cation radical, and that of band B or its corresponding band increases in the order anion radical<molecule<cation radical.

Table 5. Bathochromic shift of bands of ES by substitution of two methyl groups into the *para* positions

Species	$\tilde{\nu}_B^{a)}$ / cm^{-1}	$\Delta\tilde{\nu}_B^{b)}$ / cm^{-1}	$\tilde{\nu}_A^{a)}$ / cm^{-1}	$\Delta\tilde{\nu}_A^{b)}$ / cm^{-1}
Dianion[c]	—	—	19881	235
Anion radical[d]	20028	210	14486	372
Molecule[e]	34002	812	—	—
Cation radical[f]	20743	1108	13175	920

a) Wave number at the band maximum of ES. b) Difference between the wave number at the band maximum of ES and that of E44′DMS. c) Data on the spectra of the potassium salts in DME.[7] d) Data on spectra F(MTHF) (Curves 4 in Fig. 2). e) Data on the spectra of solutons in heptane.[2,4] f) Data on spectra F(BC) (Curves 1 in Fig. 3).

As mentioned already, band A of the cation radicals can be ascribed to the one-electron excitation from ϕ_{+4} to ϕ_{+1}, and that of the anion radical as well as the longest-wavelength intense band of the dianion to the one-electron excitation from ϕ_{-1} to ϕ_{-4}; bands B of the radical ions and the longest-wavelength intense band of the molecule can be ascribed to the one-electron excitation from ϕ_{+1} to ϕ_{-1}.

The magnitude of the energy lift of a π molecular orbital caused by alkyl substitution depends on the orbital energy and on the absolute magnitude of the atomic orbital coefficient at the substitution position in the molecular orbital: The lower the orbital energy, and the larger the absolute value of the atomic orbital coefficient, the larger will be the magnitude of the lift of the orbital energy.

Table 6 shows the energies (E) and atomic orbital coefficients (C_i) of the π molecular orbitals relevant to bands A and B and their corresponding bands calculated by the SCF-MO method for the planar E geometry. The sequence of the magnitude of the bathochromic shift by 4-methyl substitution expected from the data in this table agrees with the above-mentioned observed sequence both for band A (and its corresponding band) and for band B (and its corresponding band). From the data in this table, it is also expected that the electronic bathochromic effect of alkyl substitution at the *ortho* positions or at positions α and β on bands A and B may be smaller in the case of cation radicals and larger in the case of anion radicals than that of alkyl substitution at the *para* positions.

Classification of Compounds. The compounds treated in the present work are classified into three groups: group I (sterically uncrowded compounds: ES, E44′DMS, E4PS, E44′DPS, and DPA), group II (α-alkylated derivatives of ES: EαMS, E$\alpha\beta$DMS, and E$\alpha\beta$DES), and group III (*ortho*-methylated derivatives of ES: ETMS and EHMS). The following discussion is made on the basis of this classification.

Group I. ES and E44′DMS: Spectra F of the radical ions of ES and E44′DMS exhibit characteristic vibrational fine structure, and remain almost unchanged on illumination and on controlled warming, except for the diminution in intensity on prolonged warming. This fact indicates that geometries P, W, and R of these radical ions are quite similar to geometries F, which in turn must be similar to the most probable geometries of

Table 6. Energy and AO coefficients of π SCF-MO's of ES having the planar geometry

Species	MO	E/eV	$\lvert C_\alpha \rvert$	$\lvert C_2 \rvert$	$\lvert C_4 \rvert$	$\lvert C_6 \rvert$
Dianion	ϕ_{-4}	+5.8695	0.2286	0.0239	0.3834	0.1484
	ϕ_{-1}	+1.1723	0.3976	0.2683	0.3304	0.2582
Anion radical	ϕ_{-4}	+2.8399	0.1679	0.0703	0.4052	0.1712
	ϕ_{-1}	−0.0401	0.3993	0.2579	0.3239	0.2471
	ϕ_{+1}	−5.3081	0.4469	0.2725	0.3113	0.2724
Molecule	ϕ_{-1}	−2.1731	0.4239	0.2609	0.3128	0.2541
	ϕ_{+1}	−9.0169	0.4239	0.2609	0.3128	0.2541
Cation radical	ϕ_{-1}	−5.5195	0.4472	0.2725	0.3111	0.2723
	ϕ_{+1}	−10.7900	0.3987	0.2580	0.3241	0.2472
	ϕ_{+4}	−13.6682	0.1681	0.0720	0.4055	0.1701

the parent molecules in the rigid solutions.

It is established by X-ray analysis that the ES molecule assumes a planar or nearly planar geometry in the crystalline state,[17)] and it is inferred that the most probable geometry of the ES molecule in fluid solutions is also planar or nearly planar,[1,2,18)] although, according to an electron diffraction study,[19)] the most probable geometry of the ES molecule in the gas phase is a nonplanar propeller-like geometry with C_2 symmetry in which $\theta_{\alpha 1}$ and $\theta_{\beta 1'}$ are about 30° and $\theta_{\alpha\beta}$ is about 0°. In addition, nearly all the theoretical calculations conclude that the ES molecule should be essentially planar.[20,21)]

Accordingly, geometries F, P, W, and R of the radical ions of ES as well as E44'DMS are concluded to be planar or nearly planar. This conclusion is consistent with the facts found by Chang and Johnson that the same anion radical having the *E* geometry is obtained by reduction of the *Z* or the *E* isomer of stilbene with potassium in DME[22)] and that the ESR spectrum of the anion radical at −60 °C shows the presence of two nonequivalent sets of *ortho* protons and of two nonequivalent sets of *meta* protons, implying that the rotation around the C–Ph bonds is frozen on the ESR time scale.[23,24)]

In Part I of this series,[7)] we concluded that the preferred geometry of the ES dianion resulting from the reduction of ES with alkali metals in DME was planar or nearly planar, although on the geometry of the ES dianion various conflicts exist.[25)] We conclude here that all the preferred geometries of the molecule, radical ions, and dianion of ES in solid states or in fluid solutions are planar or nearly planar. This conclusion seems reasonable, since the steric strain in the planar geometry of ES must be very small and hence there must be no driving force for this system to assume a largely twisted geometry.

Spectra M: Spectra M of ES$^{-\cdot}$ and E44'DMS$^{-\cdot}$ are similar, on the whole, to spectra F, P, and W of the same anion radicals. However, a closer examination reveals that the former are much broader than the latter, and that bands A and B in the former are at longer and at shorter wavelength, respectively, than are the corresponding bands in the latter. The same tendencies are also observed for spectra of EαMS$^{-\cdot}$, ETMS$^{-\cdot}$, and EHMS$^{-\cdot}$. As the counterion becomes larger in the series Na$^+$, K$^+$, and Cs$^+$, the maximum of band B shifts slightly to shorter wavelengths, while the maximum of band A shifts rather irregularly (*cf.* Table 7).

TABLE 7. DATA ON SPECTRA M OF ANION RADICALS

Spectrum	ES$^{-\cdot}$		E44'DMS$^{-\cdot}$		EHMS$^{-\cdot}$	
	λ_B/nm	λ_A/nm	λ_B/nm	λ_A/nm	λ_B/nm	λ_A/nm
M(Na$^+$)	495	700	499	745	494	745
M(K$^+$)	494	701	496	725	494	740
M(Cs$^+$)	493	702	495	715	489	735
F[a)]	499.3	690.3	504.6	708.5	498.0	730.6
W[a)]	498.4	682.1	502.6	700.0	498.0	717.1

a) Data on spectra F and W are listed for comparison.

The value of K_{dispr} of ES$^{-\cdot}$ in various ethereal solvents increases as the size of the counterion decreases.[10)] From this fact, it is inferred that ES$^{-\cdot}$ as well as ES^{2-} forms a contact pair with the counterion.[29)] According to the results of our MO calculation, the charge density in ES$^{-\cdot}$ is the largest at positions α and β. It seems most probable that in the contact ion pair the counterion is located near the central ethylenic bond of ES$^{-\cdot}$, as in the contact ion aggregate of ES^{2-} with two counterions.[7)] The calculation results also show that the charge density at positions α and β decreases greatly on transition 3 and slightly on transition 5 (*cf.* Table 6). Therefore, it is expected that the counterion exerts a great hypsochromic effect on band A and a slight hypsochromic effect on band B and that the effects decrease as the size of the counterion increases. Agreement between the expectations and the observations is not good. The difference in the position of bands between spectra M and spectra W (as well as F and P) may be partly attributed to a possible difference between geometries M and W (as well as F and P), besides of the effect of the counterion. If $|\theta_{\alpha 1}|$ and $|\theta_{\beta 1'}|$ are slightly larger in geometry M than in geometry W, or if the length of the α-β bond is slightly shorter in geometry M than in geometry W, the direction of the shifts of bands A and B in spectra M as compared with spectra W can be explained.

The values of λ_B and ε_B of ES$^{-\cdot}$ (counterion: Na$^+$) in hexamethylphosphoric triamide (HMPT) were reported to be 500 nm and 6.0×10^4, respectively.[30)] In this solvent the anion radical is considered to exist as free ions, not paired with the counterion. This λ_B value is nearly equal to the values for spectra F, P, and W. On the other hand, the values of λ_B and ε_B of ES$^{-\cdot}$ (counterion: Na$^+$) in THF were reported to be 494 nm and 5.5×10^4, respectively, or 495 nm and 5.23×10^4, respectively.[27)] These λ_B values coincide with the value for spectrum M of ES$^{-\cdot}$ with the same counterion in DME.

E4PS and E44'DPS: E4PS$^{-\cdot}$ and E44'DPS$^{-\cdot}$ also show spectra characteristic of sterically uncrowded radical ions: Spectrum F of E4PS$^{-\cdot}$ and spectrum PA of E44'DPS$^{-\cdot}$ exhibit well-resolved vibrational structure, and remain almost unchanged on illumination, although on controlled warming band A is intensified and is shifted to shorter wavelengths and band B is intensified. Such a spectral change occurs to a smaller extent on illumination, and also occurs in spectra of ES$^{-\cdot}$ and E44'DMS$^{-\cdot}$ to a much smaller extent on controlled warming. Such a spectral change perhaps indicates that $|\theta_{\alpha 1}|$ and $|\theta_{\beta 1'}|$ and possibly the dihedral angles between two benzene rings in the biphenyl groups deviate from 0° to some extents in geometries F and become smaller in geometries W.

DPA: Spectra F of the radical ions of DPA also exhibit well-resolved vibrational structure and remain almost unchanged on illumination and on controlled warming.

It is known that the molecule of this compound is planar in the crystalline state, belonging to point group D_{2h},[31)] and the most preferred geometry of the molecule in solutions is probably also planar in view of its electronic absorption spectrum.[18,32] It is inferred from the similarity of the spectra that geometries F, P, W, and R of the radical ions of this compound are quite similar to one another and are planar similarly to the preferred geometry of the parent molecule.

Bands A and B of the radical ions of DPA are located at longer and at shorter wavelength, respectively, than are the corresponding bands of the radical ions of ES. This is attributed to the fact that the α-β bond in DPA (an acetylenic bond) is shorter than that in ES (an ethylenic bond). Since the α-β bond is bonding in ϕ_{+1} and ϕ_{-4} and antibonding in ϕ_{+4} and ϕ_{-1}, the intensification of the π-π interaction across the α-β bond resulting from the shortening of the bond must lower the energies of the former orbitals and raise the energies of the latter orbitals, and consequently must decrease the energy of transition 3 and increase the energy of transition 5.

Group II. EαMS, EαβDMS, and EαβDES: In contrast with the sterically uncrowded radical ions belonging to group I, the radical ions of EαMS, E$\alpha\beta$DMS, and E$\alpha\beta$DES exhibit broad spctra,[33] and their spectra F change markedly on illumination and on controlled warming.

The stilbene π system in these compounds cannot be planar owing to the steric interferences of the alkyl substituents with the phenyl groups, and the steric interferences are relieved mainly by rotation of the phenyl groups out of the plane of the central ethylenic bond. According to an electronic absorption spectroscopic study,[1,3,6] $|\theta_{\alpha 1}|$ and $|\theta_{\beta 1'}|$ in molecules in solutions increase in the order ES (*ca.* 0°)$<$EαMS (average of $|\theta_{\alpha 1}|$ and $|\theta_{\beta 1'}|$)$\ll$E$\alpha\beta$DMS$<$E$\alpha\beta$DES.

Cation Radicals: In spectra F(BC) of cation radicals, λ_B/nm decreases and f_A/f_B increases in the order ES$^{+\cdot}$, EαMS$^{+\cdot}$, E$\alpha\beta$DMS$^{+\cdot}$, E$\alpha\beta$DES$^{+\cdot}$, and λ_A/nm increases in almost the same order. If the effect of the geometrical change outweighs the electronic effect of the alkyl substituents, the observed sequences indicate that in geometries F(BC) $|\theta_{\alpha 1}|$ and $|\theta_{\beta 1'}|$ increase in the order ES$^{+\cdot}$$<E\alpha$MS$^{+\cdot}$(average)$\ll$E$\alpha\beta$DMS$^{+\cdot}$$<E\alpha\beta$DES$^{+\cdot}$. This probably means that geometries F(BC) of these cation radicals are similar to geometries N.

On illumination of the BC solution of E$\alpha\beta$DMS$^{+\cdot}$ as well as that of E$\alpha\beta$DES$^{+\cdot}$, λ_B/nm increases, λ_A/nm decreases, and f_A/f_B decreases. These spectral changes indicate that, in going from geometry F(BC) to geometry P(BC), $|\theta_{\alpha 1}|$ and $|\theta_{\beta 1'}|$ decrease and/or $|\theta_{\alpha\beta}|$ increases.

Spectrum F(FM) of E$\alpha\beta$DMS$^{+\cdot}$ probably indicates the coexistence of the cation radicals having an almost frozen or only slightly relaxed geometry similar to geometry F(BC) or P(BC) and of the cation radicals having a partially relaxed geometry, suggesting that the FM glass at 77 K is softer than the BC glass at the same temperature, as pointed out already.[8,15] On controlled warming, the geometries are converted to geometry W(FM), which is considered to be an almost completely relaxed geometry. In spectrum W(FM), λ_B/nm is much larger, λ_A/nm is appreciably smaller, and f_A/f_B is much smaller than in spectrum F(BC). This indicates that in geometry R of E$\alpha\beta$DMS$^{+\cdot}$ $|\theta_{\alpha 1}|$ and $|\theta_{\beta 1'}|$ are much smaller and/or $|\theta_{\alpha\beta}|$ is much larger than in geometry F(BC) and hence than in geometry N. The extent of relaxation of the various geometries of this cation radical may be expressed as follows: N$\leqslant$F(BC)$<$P(BC)$\ll$F(FM)$\ll$W(FM)$\approx$R.

From a similar analysis of the spectra of E$\alpha\beta$DES$^{+\cdot}$, it is inferred that geometry F(FM) of this cation radical is already almost completely relaxed, and that $|\theta_{\alpha 1}|$ and $|\theta_{\beta 1'}|$ are appreciably smaller and/or $|\theta_{\alpha\beta}|$ is appreciably larger in geometry R than in geometry F(BC) and hence than in geometry N. The extent of relaxation of the various geometries of this cation radical may be expressed as follows: N$\leqslant$F(BC)$<$P(BC)$<$F(FM)$\leqslant$W(FM)$\approx$R. The magnitude of the geometrical change on relaxation seems to be smaller in E$\alpha\beta$DES$^{+\cdot}$ than in E$\alpha\beta$DMS$^{+\cdot}$.

In spectra W(FM), λ_A/nm increases in the order E$\alpha\beta$DMS$^{+\cdot}$ $\ll$ES$^{+\cdot}$$<E\alpha$MS$^{+\cdot}$$\ll$E$\alpha\beta$DES$^{+\cdot}$, and λ_B/nm decreases in the same order, that is, in the order E$\alpha\beta$DMS$^{+\cdot}$$\gg$ES$^{+\cdot}$$>E\alpha$MS$^{+\cdot}$$\gg$E$\alpha\beta$DES$^{+\cdot}$. If in geometries W(FM) the stericin terferences were relieved only by deviation of $\theta_{\alpha 1}$ and $\theta_{\beta 1'}$ from 0° and $\theta_{\alpha\beta}$ were maintained at approximately 0° as in geometries N, $|\theta_{\alpha 1}|$ and $|\theta_{\beta 1'}|$ in geometries W(FM) would increase in the order ES$^{+\cdot}$$<E\alpha$MS$^{+\cdot}$(average)$\ll$E$\alpha\beta$DMS$^{+\cdot}$$<E\alpha\beta$DES$^{+\cdot}$, and consequently λ_A/nm and λ_B/nm in spectra W(FM) would increase and decrease, respectively, in the same order, as is almost the case in spectra F(BC). It should be noted that the observed λ_A/nm and λ_B/nm values of E$\alpha\beta$DMS$^{+\cdot}$ are extraordinarily small and large, respectively. This cannot be attributed to the electronic effect of the methyl substituents, and can be explained only by assuming that in geometry W(FM) of this cation radical $|\theta_{\alpha\beta}|$ is appreciably large. Thus, the observed sequences of band position are taken as an indication of the deviation of $\theta_{\alpha\beta}$ from 0° in geometry W(FM) and hence in geometry R of E$\alpha\beta$DMS$^{+\cdot}$.

It is unlikely that $|\theta_{\alpha\beta}|$ in geometry W(FM) of E$\alpha\beta$DES$^{+\cdot}$ is smaller than that of E$\alpha\beta$DMS$^{+\cdot}$. On the other hand, the former may not be much larger than the latter: If it were, the observed sequences of band position in spectra W(FM) would be reversed. The observed sequences seem to indicate that, in geometries W(FM) and R, $|\theta_{\alpha 1}|$ and $|\theta_{\beta 1'}|$ of E$\alpha\beta$DES$^{+\cdot}$ are much larger than those of E$\alpha\beta$DMS$^{+\cdot}$, while $|\theta_{\alpha\beta}|$ of the former is not appreciably different from that of the latter. That is to say, on relaxation, $|\theta_{\alpha 1}|$ and $|\theta_{\beta 1'}|$ decrease to a larger extent in E$\alpha\beta$DMS$^{+\cdot}$ than in E$\alpha\beta$DES$^{+\cdot}$, while $\theta_{\alpha\beta}$ deviates from 0° to a similar extent in both the cation radicals.

Thus, it is concluded that, in geometries R, $|\theta_{\alpha 1}|$ and $|\theta_{\beta 1'}|$ increase in the order ES$^{+\cdot}$ (*ca.* 0°)$<$EαMS$^{+\cdot}$ (average)$\ll$E$\alpha\beta$DMS$^{+\cdot}$$\ll$E$\alpha\beta$DES$^{+\cdot}$, and $|\theta_{\alpha\beta}|$ increases in the order ES$^{+\cdot}$(*ca.* 0°)$<$EαMS$^{+\cdot}$$\ll$E$\alpha\beta$DMS$^{+\cdot}$$\approx$E$\alpha\beta$DES$^{+\cdot}$.

The steric interference between the α-alkyl (β-alkyl) and the β-phenyl (α-phenyl) group in (*E*)-α,β-dialkylstilbenes can be relieved by increase in $|\theta_{\alpha\beta}|$ as well as by increase in $|\theta_{\beta 1'}|$ ($|\theta_{\alpha 1}|$), while the interference between the α-alkyl (β-alkyl) and the α-phenyl (β-phenyl) group can be relieved only by increase in $|\theta_{\alpha 1}|$ ($|\theta_{\beta 1'}|$). Therefore, the above conclusion suggests that in geometry R of E$\alpha\beta$DES$^{+\cdot}$ the methyl group in the α-ethyl (β-ethyl) group avoids facing the β-phenyl (α-phenyl) group and interferes mainly with the α-phenyl (β-phenyl) group.

Anion Radicals: In spectra F of anion radicals, λ_A/nm and $f_\mathrm{A}/f_\mathrm{B}$ increase in the order $\mathrm{ES}^{-\cdot} \ll \mathrm{E\alpha MS}^{-\cdot} \ll \mathrm{E\alpha\beta DMS}^{-\cdot} \ll \mathrm{E\alpha\beta DES}^{-\cdot}$, and λ_B/nm increases in the order $\mathrm{ES}^{-\cdot} < \mathrm{E\alpha MS}^{-\cdot} \ll \mathrm{E\alpha\beta DES}^{-\cdot} \ll \mathrm{E\alpha\beta DMS}^{-\cdot}$. If it were not for the electronic bathochromic effect of the alkyl substituents, perhaps the sequence of λ_B/nm of $\mathrm{ES}^{-\cdot}$ and $\mathrm{E\alpha MS}^{-\cdot}$ might be reversed, but the other sequences of band position would not be altered. It should be noted that the λ_B/nm value of $\mathrm{E\alpha\beta DMS}^{-\cdot}$ is larger than that of $\mathrm{E\alpha\beta DES}^{-\cdot}$, and that these values are larger than the λ_B/nm values of $\mathrm{ES}^{-\cdot}$ and $\mathrm{E\alpha MS}^{-\cdot}$.

On illumination and on controlled warming, in spectra of $\mathrm{E\alpha MS}^{-\cdot}$, $\mathrm{E\alpha\beta DMS}^{-\cdot}$, and $\mathrm{E\alpha\beta DES}^{-\cdot}$, λ_A/nm and $f_\mathrm{A}/f_\mathrm{B}$ decrease, and λ_B/nm increases. Especially, the decrease in λ_A/nm of $\mathrm{E\alpha\beta DMS}^{-\cdot}$ on controlled warming is notable. In addition, f_B or ε_B of $\mathrm{E\alpha\beta DMS}^{-\cdot}$ and that of $\mathrm{E\alpha\beta DES}^{-\cdot}$ increase prominently on controlled warming. In spectra W, λ_A/nm increases in the order $\mathrm{E\alpha\beta DMS}^{-\cdot} \ll \mathrm{ES}^{-\cdot} \ll \mathrm{E\alpha MS}^{-\cdot} \ll \mathrm{E\alpha\beta DES}^{-\cdot}$, $f_\mathrm{A}/f_\mathrm{B}$ increases in the order $\mathrm{E\alpha MS}^{-\cdot} < \mathrm{E\alpha\beta DMS}^{-\cdot} < \mathrm{ES}^{-\cdot} \ll \mathrm{E\alpha\beta DES}^{-}$, and the sequence of λ_B/nm is the same as that in spectra F. The sequence of λ_A/nm is the same as and that of $f_\mathrm{A}/f_\mathrm{B}$ is similar to the corresponding sequences in spectra W(FM) of cation radicals.

From these facts the following conclusions are drawn: (1) In going from geometries N of EαMS, EαβDMS, and EαβDES to geometries R of the corresponding anion radicals, $|\theta_{\alpha 1}|$ and $|\theta_{\beta 1'}|$ decrease and $|\theta_{\alpha\beta}|$ increases; (2) in geometries R, $|\theta_{\alpha 1}|$ and $|\theta_{\beta 1'}|$ increase in the order $\mathrm{ES}^{-\cdot}$ (*ca.* 0°) $<\mathrm{E\alpha MS}^{-\cdot}$ (average) $\ll \mathrm{E\alpha\beta DMS}^{-\cdot} \ll \mathrm{E\alpha\beta DES}^{-\cdot}$, and $|\theta_{\alpha\beta}|$ increases in the order $\mathrm{ES}^{-\cdot}$ (*ca.* 0°) $< \mathrm{E\alpha MS}^{-\cdot} \ll \mathrm{E\alpha\beta DMS}^{-\cdot} \approx \mathrm{E\alpha\beta DES}^{-\cdot}$, that is, geometries R of these anion radicals are at least qualitatively similar to geometries R of the corresponding cation radicals; (3) geometries F of these anion radicals in MTHF glasses are already partially relaxed before illumination and controlled warming; (4) the extent of relaxation of the various geometries of the α-alkylated (*E*)-stilbene anion radicals in MTHF may be expressed as follows: $\mathrm{N} \ll \mathrm{F} < \mathrm{P} \ll \mathrm{W} \approx \mathrm{R}$.

General Discussion on Group II: As concluded above, in geometries R of the radical ions of the α-alkylated (*E*)-stilbenes $|\theta_{\alpha 1}|$ and $|\theta_{\beta 1'}|$ are smaller and $|\theta_{\alpha\beta}|$ is larger than in geometries N. In Part I of this series,[7] a qualitatively similar conclusion was drawn for the geometries of the dianions of these compounds.

Fischer *et al.*[21] stated as follows: Sterically unhindered stilbenes, that is, (*E*)-stilbenes not substituted at the *ortho* and the α and β positions, have a planar geometry both in the ground state (state $\mathrm{S_0}$) and in the first excited singlet state (state $\mathrm{S_1}$); sterically hindered stilbenes, *e.g.*, (*Z*)-stilbenes and α,β-disubstituted (*E*)-stilbenes, are strongly twisted about the α-1 and the β-1′ bond in state $\mathrm{S_0}$, while in state $\mathrm{S_1}$ the major twist is about the α-β bond. Thus, according to the results of their calculation by the CFF-SCF-PI-CI method described by Warshel and Karplus,[36] in going from state $\mathrm{S_0}$ to state $\mathrm{S_1}$, in EαβDMS $\theta_{\alpha 1}$ and $\theta_{\beta 1'}$ decrease from 47° to 13° and $\theta_{\alpha\beta}$ increases from 6° to 49°, while in ES all the torsion angles are 0° in both the states.

State $\mathrm{S_1}$ as well as the first excited triplet state (state $\mathrm{T_1}$) of these compounds can be well approximated by the electron configuration arising from state $\mathrm{S_0}$ by promotion of an electron from ψ_{+1} to ψ_{-1}.[37] Therefore, because of the pairing properties of π orbitals in even alternant hydrocarbons, in the one-electron approximation the π-bond order of each bond of the dianion as well as the dication both in state $\mathrm{S_0}$ and that of the neutral molecule in state $\mathrm{S_1}$ as well as $\mathrm{T_1}$ should be equal to each other. Accordingly, it is reasonable that the most probable geometry of the dianion in state $\mathrm{S_0}$ is similar to that of the neutral molecule in state $\mathrm{S_1}$.

In the stilbene molecule in state $\mathrm{S_0}$, the π-bond order of the α-1 as well as the β-1′ bond is much smaller than that of the α-β bond. In the molecule in state $\mathrm{S_1}$ and in the dianion in state $\mathrm{S_0}$, the sequence of the π-bond orders is reversed, and consequently the overcrowding in sterically hindered derivatives is relieved in a different way than in the molecule in state $\mathrm{S_0}$, resulting in a different geometry.

The bonding character of the radical ions in the ground state (state $\mathrm{D_0}$) is intermediate between those of the molecule and of the diions both in state $\mathrm{S_0}$. Therefore, the relaxed geometry of the radical ions of a sterically crowded stilbene derivative in state $\mathrm{D_0}$ is probably intermediate between those of the parent molecule and of the corresponding diions both in state $\mathrm{S_0}$.

The values of π-bond order calculated by the SCF-MO-CI method are shown in Table 8. From these values it is expected that in geometries R of sterically crowded stilbene molecules and ions $|\theta_{\alpha 1}|$ and $|\theta_{\beta 1'}|$ decrease and $|\theta_{\alpha\beta}|$ increases in the following order: the molecule in state $\mathrm{S_0}$, the radical ions in state $\mathrm{D_0}$, the molecule in state $\mathrm{T_1}$, the molecule in state $\mathrm{S_1}$, the diions in state $\mathrm{S_0}$.

Group III. *ETMS and EHMS*: The spectra of the radical ions of ETMS and EHMS are similar to those of the radical ions of ES, exhibiting characteristic vibrational structure. In contrast to spectra F of the radical ions of ES, however, those of the radical ions of ETMS and EHMS change distinctly on illumination and on controlled warming. Especially, λ_A/nm and $f_\mathrm{A}/f_\mathrm{B}$ decrease, although the magnitude of the spectral changes is considerably smaller than in the case of the radical ions of EαβDMS and EαβDES. In addition, f_B and ε_B of the anion radicals of ETMS and EHMS increase prominently on controlled warming. The spectra of these anion radicals in MTHF glass at 77 K are similar on the whole to spectra M of the same anion radicals. Thus, with respect to the spectral behavior,

TABLE 8. THE π-BOND ORDERS OF THE PLANAR (*E*)-STILBENE MOLECULE AND MOLECULAR IONS CALCULATED BY SCF-MO METHOD

Bond	$\mathrm{ES(S_0)}$[a]	$\mathrm{ES}^{-\cdot}\mathrm{(D_0)}$ $\mathrm{ES}^{+\cdot}\mathrm{(D_0)}$	$\mathrm{ES(T_1)}$[b]	$\mathrm{ES(S_1)}$[b]	$\mathrm{ES}^{2-}\mathrm{(S_0)}$[a] $\mathrm{ES}^{2+}\mathrm{(S_0)}$
α-1;β-1′	0.341	0.448	0.508	0.563	0.711
α-β	0.886	0.705	0.664	0.543	0.448

a) Ref. 7. b) Ref. 37.

group III is intermediate between groups I and II.

Analysis of the spectra of the radical ions of ETMS and EHMS leads to the following conclusions on geometries of these radical ions.

(1) Geometries F are similar to geometries N. In geometries F, $|\theta_{\alpha1}|$ and $|\theta_{\beta1'}|$ increase in the order ES$^{\pm\cdot}$ (*ca.* 0°)$\ll$ETMS$^{\pm\cdot}$ (average of $|\theta_{\alpha1}|$ and $|\theta_{\beta'1}|$)$<$ EHMS$^{\pm\cdot}$, as in geometries N.

(2) On controlled warming and on illumination, $|\theta_{\alpha1}|$ and $|\theta_{\beta1'}|$ decrease and $|\theta_{\alpha\beta}|$ increases.

(3) The extent of the geometrical relaxation may be expressed as follows: for the cation radicals, N$<$ F(BC)$<$P(BC)$\approx$F(FM)$\leqslant$W(FM)$\approx$R; for the anion radicals, N$<$F$<$P$<$W$\approx$R.

(4) The geometrical changes on the relaxation are comparatively small. Especially, the values of $|\theta_{\alpha\beta}|$ in geometries R are probably much smaller than those in geometries R of the radical ions of E$\alpha\beta$DMS and E$\alpha\beta$DES.

Conclusion 4 above is rather surprising, because in the case of neutral molecules both the steric interference caused by the *ortho* substitution in EHMS and that caused by the α and β substitution in E$\alpha\beta$DMS are relieved by rotation to comparable degrees about the α-1 and the β-1′ bond.[3,4] However, this conclusion is consistent with the following facts.

(i) As found in Part I of this series,[7] as positions α and β of the ES dianion are increasingly substituted with alkyl groups, the longest-wavelength intense band shifts rapidly to shorter wavelengths, which indicates that $|\theta_{\alpha\beta}|$ increases rapidly; on the other hand, as the *ortho* positions are increasingly substituted with methyl groups, the band shifts slowly to shorter wavelengths, indicating that $|\theta_{\alpha\beta}|$ increases slowly. From these facts, it was inferred that the values of $|\theta_{\alpha1}|$ and $|\theta_{\beta1'}|$ in the EHMS dianion, for example, were larger than those in the E$\alpha\beta$DMS dianion, and that the value of $|\theta_{\alpha\beta}|$ in the former was smaller than that in the latter.

(ii) ETMS and EHMS as well as ES can readily be converted into the corresponding anion radicals by alkali-metal reduction,[7] but it is difficult to reduce them to the dianions, indicating that the values of K_{dispr} are small for these compounds.[9] On the other hand, as mentioned already, E$\alpha\beta$DMS and E$\alpha\beta$DES[7] as well as TPE[8] are readily reduced to the dianions with alkali metals, which indicates that the values of K_{dispr} are probably large for these sterically crowded compounds. These facts suggest that the geometries of the molecule, anion radical, and dianion are not much different from one another in the case of ETMS and EHMS as well as ES, while those are markedly different in the case of E$\alpha\beta$DMS, E$\alpha\beta$DES, and TPE.

(iii) According to a study by Fischer *et al.*,[21] the observed "Stokes shift"[38] ($\Delta\lambda$) of stilbenes parallels the increase ($\Delta\theta_{\alpha\beta}$) in the calculated equilibrium value of $\theta_{\alpha\beta}$ on the excitation from state S$_0$ to state S$_1$. For sterically uncrowded stilbenes, both $\Delta\lambda$ and $\Delta\theta_{\alpha\beta}$ are small: For ES, $\Delta\lambda$ is *ca.* 0 nm, $\theta_{\alpha\beta}$ is 0° in both the states, and $\Delta\theta_{\alpha\beta}$ is 0°. On the other hand, for sterically crowded stilbenes such as (Z)-stilbene, E$\alpha\beta$DMS, and its Z isomer, both $\Delta\lambda$ and $\Delta\theta_{\alpha\beta}$ are large: For E$\alpha\beta$DMS, for example, $\Delta\lambda$ is 67 nm, and $\theta_{\alpha\beta}$ increases from 6° to 49° on the excitation, that is, $\Delta\theta_{\alpha\beta}$ is 43°. For EHMS $\Delta\lambda$ is as small as 4 nm. This fact suggests that the change in $\theta_{\alpha\beta}$ of this compound on the excitation is very small.

These facts are interpreted as follows. Since in the stilbene molecule in state S$_0$ the π-bond order of the α-β bond is large and those of the α-1 and the β-1′ bond are small, the steric interference in sterically crowded stilbenes is relieved almost exclusively by rotation about the α-1 and the β-1′ bond. In the radical ions in state D$_0$, the neutral molecule in state S$_1$, and the diions in state S$_0$, the π-bond order of the α-β bond decreases, and those of the α-1 and the β-1′ bond increase (*cf.* Table 8). Therefore, the possibility arises that the steric interference in sterically crowded stilbenes is relieved by rotation about the α-β bond as well as by rotation about the α-1 and the β-1′ bond. The steric interference caused by the *ortho* substitution may be smaller than that caused by the α and β substitution. In addition, while a major part of the steric interference caused by the α and β substitution may effectively be relieved by rotation about the α-β bond, the steric interference caused by the *ortho* substitution cannot be relieved by rotation about the α-β bond so effectively as is that caused by the α and β substitution, and must be relieved mainly by rotation about the α-1 and the β-1′ bond, as in the neutral molecules in state S$_0$.

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9) K_{dispr} for ES$^{-\cdot}$ at ambient temperature was estimated at about 10^{-3} (counterion: Na$^+$, solvent: THF),[10] 0.09 (counterion: Na$^+$, solvent: MTHF),[11] and about 0.03 (counterion: Na$^+$, solvent: THF).[12] On the other hand, according to Garst *et al.*,[11] the values of K_{dispr} for TPE$^{-\cdot}$ and EαMS$^{-\cdot}$ at 25 °C (counterion: Na$^+$, solvent: MTHF) are$\geqslant$1000.

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25) An X-ray study by Walczak and Stucky of crystals of salts of ES^{2-} with Li^+ complexed with amines revealed that the ES^{2-} moiety in the salts had a planar geometry.[26] Jachimowicz *et al.* inferred that ES^{2-}, if associated with its counterions, had a planar or nearly planar geometry, and that, if not associated with the counterions, it had a fully twisted geometry.[12] On the other hand, Garst *et al.*[11] and Wang *et al.*[27] proposed a nonplanar geometry twisted by 90° around the central ethylenic bond for ES^{2-}. A basis for the proposition by Garst *et al.* is an anticipation of a direct correspondence between the geometry of the dianion in its ground state and that of the molecule in its lowest excited triplet state, which was assumed to be a 90° twisted one. However, this correspondence may not necessarily hold good. In addition, according to a study by Benson and Williams of the photochemical *Z-E* isomerization of stilbene in its triplet state, the 90° twisted geometry is at a maximum in the potential energy profile for the triplet state.[28] All the phenomena interpreted in terms of the twisted geometry of ES^{2-} by Garst *et al.*,[11] by Wang *et al.*,[27] and by Jachimowicz *et al.*[12] seem also to be interpretable in terms of an approximately planar geometry of ES^{2-}. We believe that ES^{2-} has a planar or approximately planar geometry, whether it is associated with the counterions or not.

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33) Quantity $f/\varepsilon_{\max}$ may be taken as a measure of broadness of a band. The values of $10^4 f_B/\varepsilon_B$ for the radical ions of the α,β-dialkylstilbenes ($E\alpha\beta DMS^{+\cdot}$, 0.30; $E\alpha\beta DES^{+\cdot}$, 0.27; $E\alpha\beta DMS^{-\cdot}$, 0.14; $E\alpha\beta DES^{-\cdot}$, 0.16) are much larger than those for the radical ions of the compounds belonging to group I or group III (0.08—0.10). The large broadness of the band may be taken as reflecting the large deviation of the geometry from planarity.[34,35]

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38) Fischer *et al.*[21] defined the "Stokes shift" ($\Delta\lambda$) as the wavelength difference between the longwave "onset" of the longest-wavelength intense absorption band and the shortwave "onset" of the fluorescence band, and defined the "onset" as the wavelength at which the absorbance or the emission was 1% of its peak value. The values of $\Delta\lambda$ were obtained from absorption and fluorescence spectra both measured at -180 to -190 °C using an equivolume mixture of methylcyclohexane and 3-methylpentane as the solvent. The Stokes shift is ordinarily defined as the difference in wavelength or in wave number between the most intense maximum of the absorption band and that of the fluorescence band. The Stokes shift so defined, $\Delta\lambda_{\max}$ (or $\Delta\tilde{\nu}_{\max}$), is evaluated from the data by Fischer *et al.* as follows: 42 nm (3.85×10^3 cm^{-1}) for ES, 180 nm (16.74×10^3 cm^{-1}) for EαβDMS, and 85 nm (8.42×10^3 cm^{-1}) for EHMS.