Electronic Absorption Spectra and Geometry of Molecule Ions Generated from Stilbene and Related Compounds. I. Dianions

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Stilbene and some of its alkyl-substituted derivatives were reduced with alkali metals to dianions in 1,2-dimethoxyethane. From comparison of the electronic absorption spectra of these dianions with one another and with the results of semiempirical SCF-MO-CI calculation of the π-electronic state, the geometries of the dianions were inferred to be as follows: (a) the preferred geometry of a sterically unhindered dianion, such as the dianion of stilbene, is probably planar or nearly planar; (b) when alkyl substituents are introduced into the central ethylenic carbon atoms, the steric interference caused by the substituents is relieved chiefly by the rotation about the central ethylenic bond; (c) the steric interference caused by *ortho* methyl substituents seems to be comparatively small or to be relieved by the rotation about the bonds connecting benzene rings to the ethylenic carbon atoms as well as the ethylenic bond. From the influence of alkali-metal cations on the spectra of the dianions, it was inferred that the dianions exist mainly as contact ion aggregates in which the counter-ions are located near the central ethylenic bond, one probably almost above an ethylenic carbon atom and the other almost below the other ethylenic carbon atom.

Aromatic hydrocarbons are reduced with alkali metals in ethereal solvents to mononegative ion radicals (anion radicals) and, further, in some cases, to dinegative ions (dianions). Geometries of these ions are probably not always similar to those of the parent molecules. The question of how the molecular geometry changes with charge state is of interest, but information on the geometry of the ions is scarce. As regards the ions generated from stilbene, a planar geometry has been proposed for the anion radical,[1] and a nonplanar geometry in which the two benzylidene moieties are rotated about the central ethylenic bond (the α—α' bond) to make an angle of about 90° has been proposed for the dianion.[2] However, direct evidence does not seem to have been given.

One of us (H. S.) studied the relation between the electronic absorption spectrum and the molecular geometry of the neutral molecules of stilbene and related compounds.[3–8] The purpose of the present study is to disclose the corresponding relation for the negative and positive ions generated from stilbene and related compounds and to answer partly the above question. We have studied the geometries and spectra of the dianions by means of semiempirical SCF-MO-CI calculation.

Experimental

A deaerated solution of *trans*-stilbene in 1,2-dimethoxyethane (DME) cooled in ice was contacted with a potassium mirror in a vacuum line system, essentially similar to the one described by Ishitani *et al.*[9] After a while, the solution turned yellowish brown, and exhibited a distinct ESR signal with fine structure; its electronic absorption spectrum has main bands at about 701 and 494 nm, as shown in Fig. 1 (1) (curve b), and closely resembles the spectrum of the anion radical produced by γ-ray irradiation of a glassy solution of *trans*-stilbene in 2-methyltetrahydrofuran (MTHF) at 77°K.[10] The yellowish brown solution is considered to contain the stilbene anion radical and the neutral stilbene as main components. After the solution had been kept cool and in contact with a potassium mirror for a sufficiently long time (about one day), the color turned a beautiful red. This red solution exhibited substantially no ESR signal. Its electronic absorption spectrum has a broad intense band with a peak at about 503 nm and no intense bands in the near ultraviolet region, as shown by curve c in Fig. 1 (1). The solution decolored when it was brought into contact with air. The electronic absorption and NMR spectra of the decolored solution were essentially the same as those of the solution of neutral *trans*-stilbene. When anthracene was dissolved into the red solution, the color of the solution changed to blue, and the solution showed electronic absorption and ESR spectra characteristic of the anthracene anion radical. It is evident that the red solution contains the stilbene dianion as the main component and does not contain the neutral molecule and anion radical of stilbene in any significant amounts.

Some alkyl-substituted derivatives of stilbene were reduced by procedures similar to the one described above. The electronic absorption spectra of stilbene and its derivatives in various reduction stages, measured by the use of cells of path length 10 mm at room temperature, are shown in Figs. 1 (1)—(8). In each figure, curve a is the spectrum of the neutral molecule (S) in *n*-heptane, curve b that of a DME

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[1] R. Chang and C. S. Johnson, Jr., *J. Chem. Phys.*, **41**, 3272 (1964); *ibid.*, **46**, 2314 (1967).

[2] J. F. Garst, J. G. Pacifici, and E. R. Zabolotny, *J. Amer. Chem. Soc.*, **88**, 3872 (1966).

[3] H. Suzuki, This Bulletin, **25**, 145 (1952).

[4] H. Suzuki, *ibid.*, **33**, 379 (1960).

[5] H. Suzuki, *ibid.*, **33**, 396 (1960).

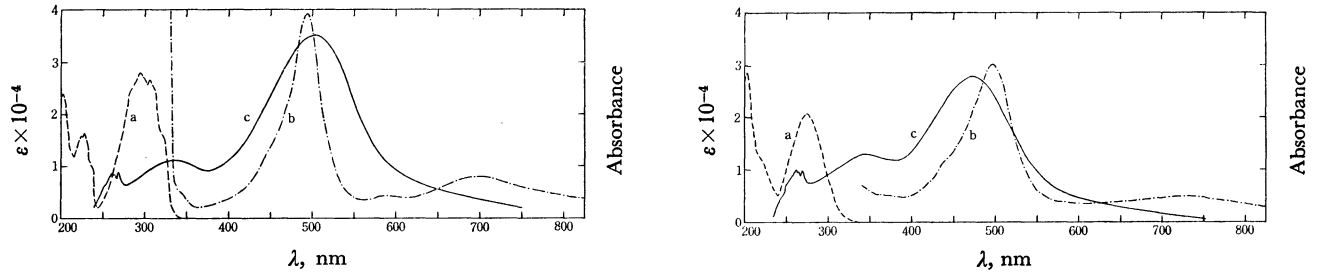
[6] H. Suzuki, *ibid.*, **33**, 406 (1960).

[7] H. Suzuki, *ibid.*, **35**, 1715 (1962).

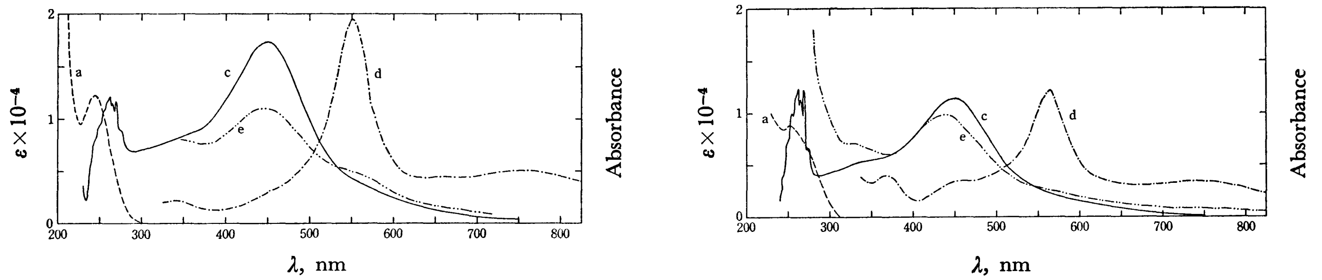
[8] H. Suzuki, "Electronic Absorption Spectra and Geometry of Organic Molecules," Academic Press Inc., New York, N.Y. (1967), Chapter 14.

[9] A. Ishitani, K. Kuwata, H. Tsubomura, and S. Nagakura, This Bulletin, **36**, 1357 (1963); A. Ishitani and S. Nagakura, *Theor. Chim. Acta*, **4**, 236 (1966).

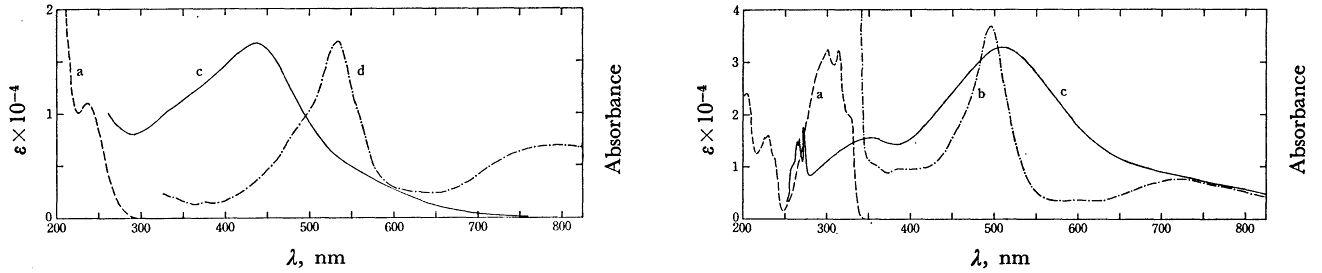
[10] The spectra of the anion radicals produced by γ-ray irradiation were measured by Dr. Tadamasa Shida of the Institute of Physical and Chemical Research, Yamato-machi, Saitama, to whom the authors are greatly indebted.



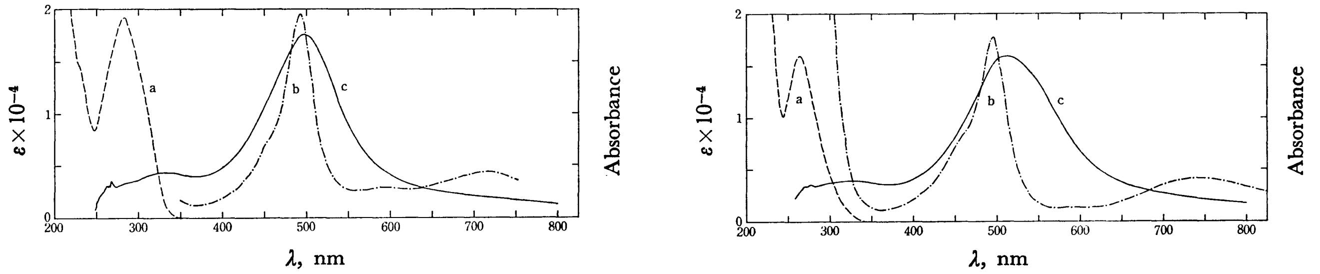
(1) *trans*-Stilbene (2) α-Methyl-*trans*-Stilbene



(3) α,α′-Dimethyl-*trans*-stilbene (4) α,α′-Dimethyl-*cis*-stilbene



(5) α,α′-Diethyl-*trans*-stilbene (6) 4,4′-Dimethyl-*trans*-stilbene



(7) 2,4,6-Trimethyl-*trans*-stilbene (8) 2,4,6,2′,4′,6′-Hexamethyl-*trans*-stilbene

Fig. 1. Electronic absorption spectra of stilbenes (S) and their anion radicals (S^-) and dianions (S^{2-}). Curve a is the spectrum of S dissolved in *n*-heptane. Curve c is the spectrum of a DME solution in which S has been reduced with K to S^{2-}. For explanation of other cruves, see text. For curve a the intensity is represented with the molar absorptivity (ε); for other curves it is represented with the absorbance on arbitrary scale.

solution which is considered to contain the anion radical (S^-) and the neutral parent compound S as main solutes, and curve c that of a DME solution containing the dianion (S^{2-}) as the most important solute and not S^- and S in any significant amounts. Intensity is represented by the molar absorptivity for curve a, and by absorbance in a different arbitrary scale for all other curves. Each spectrum represented by curve b closely resembles that of the anion radical produced by γ-ray irradiation,[10] except that the former is slightly broader. The wavelengths of the main absorption maxima (λ_{max}) and some relevant data are given in Table 1.

In the case of α,α′-dialkylstilbenes the spectra of the anion radicals could not be obtained by means of alkali-metal reduction. In Figs. 1 (3)—(5), the spectra of the anion radicals produced by γ-ray irradiation[10] are shown by curve d, and those of DME solutions in which reduction with potassium has not sufficiently occurred exhibiting weak and broad ESR signals by curve e. These spectra indicate that each solution corresponding to curve e contains the neutral molecule of the stilbene derivative in a large amount, the dianion in a fair amount and the anion radical in a very small amount. This means that the equilibrium constant (K_{disp}) of the disproportionation

$$2S^- \rightleftharpoons S + S^{2-}$$

Table 1. The main absorption bands of molecules, anion radicals, and dianions of stilbenes

Stilbene	Molecule[a)]	Anion radical[b)]		Dianion[b)]	
	λ_{max}[c)]	λ_{max}[c)]	Color[d)]	λ_{max}[c)]	Color[d)]
Unsubstituted *trans*-	294	701; 494	YB	503	R
α-Methyl-*trans*-	274	*ca.* 725; 497	YB	472	BR
α,α'-Dimethyl-*trans*-	243	—	—	450	BY
α,α'-Dimethyl-*cis*-	252	—	—	450	BY
α,α'-Diethyl-*trans*-	237	—	—	437	BY
4,4'-Dimethyl-*trans*-	301	*ca.* 725; 496	DB	509	R
2,4,6-Trimethyl-*trans*-	283	*ca.* 715; 493	B	497	R
2,4,6,2',4',6'-Hexamethyl-*trans*-	263	740; 494	DB	510	R

a) Dissolved in *n*-heptane.
b) Generated from stilbene by reduction with potassium in DME.
c) The wavelength of the absorption maximum in units of nm.
d) Color of solution: YB, yellowish brown; DB, dark brown; B, brown; R, red; BR, brownish red; BY, brownish yellow.

is much greater for these derivatives than for *trans*-stilbene and other derivatives. It has been found that even the K_{disp} value for α-methylstilbene is greater than that for stilbene.[2)] It is noteworthy that the spectra of the dianions generated from *trans*- and *cis*-α,α'-dimethylstilbene are essentially the same as each other, while the spectra of the anion radicals produced from these isomers by γ-ray irradiation distinctly differ from each other.

Reductions with sodium and with cesium were also carried out for most of the compounds. As a whole, the spectra of the dianions produced by the use of these alkali metals are closely similar to those obtained by the use of potassium, except for comparatively small differences in the position of the absorption maximum.

In contrast to the α,α'-dialkyl derivatives, it was difficult to reduce the derivatives bearing methyl substituents on the benzene nuclei to dianions, but not to anion radicals. With the 4,4'-dimethyl and 2,4,6-trimethyl derivatives, when the spectra of the anion radicals were measured a broad absorption band having a peak at about 790 or 800 nm often developed and the color of the solutions changed from yellowish brown to deep blue. The species responsible for this band could not be identified; it is certain that it is neither the anion radical nor the dianion. The 2,4,6,2',4',6'-hexamethyl derivative was also readily reduced to the anion radical by the use of any alkali metal, but all attempts to reduce it to the dianion with sodium and with cesium were unsuccessful. The spectra of the solutions kept in contact with the alkali metal for a sufficiently long time were those of the anion radical. There were no signs of bands due to the dianion or to the neutral molecule. A spectrum considered to be due to the dianion was obtained by the use of potassium. However, it changed its shape in a comparatively short time. It is therefore questionable whether the spectrum shown as curve c in Fig. 1 (8) can be regarded as that of the pure dianion. The corresponding λ_{max} value in Table 1 is also questionable. With these nuclear-methylated derivatives the values of K_{disp} appear to be very small. According to qualitative observations, the value for 4,4'-dimethylstilbene appears to become larger to some extent as the temperature is lowered. This tendency, if true, is quite the opposite of that reported for reduction of tetraphenylethylene with sodium in tetrahydrofuran.[11-16)]

MO Calculation

It is assumed that all the tervalent carbon atoms in the dianions have sp^2 hybrid orbitals and the π-electron approximation is applicable. This seems to be reasonable, although the possibility of rehybridization should be taken into consideration in the case of smaller systems such as ethylene,[17)] and in cases where the reductant is, for example, lithium and where on association of the dianion with the alkali-metal cations the ethylenic carbon atoms might be linked to the alkali-metal atoms with bonds having partially covalent character. Semi-empirical SCF–MO–CI calculation of the π-electronic states of the dianions was carried out on many geometrical models designed to represent rotations about the central CC "double" bond (the α—α' bond) and the two CC "single" bonds (the α—1 and the α'—1' bond). The carbon skeleton of the stilbene π-system is illustrated in Fig. 2, together with the numbering of the carbon atoms and the coordinate system.

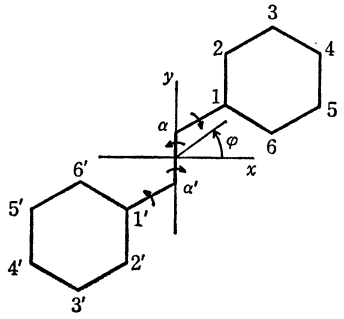


Fig. 2. The skeleton of the stilbene π-system. The planar *trans* form, that is, geometry (0,0,0), is shown.

The length of CC bond p—q is denoted by R_{pq} (Å), and the angle of twist of this bond, *viz.*, the dihedral angle between the σ-skeleton planes of carbon atoms p and q, is denoted by θ_{pq}. The value of $\theta_{\alpha\alpha'}$ is taken to be 0° for the *trans* form, and 180° for the *cis* form. For the sake of convenience, essentially the same assumptions as those made for the treatment of neutral stilbenes are made on the geometry.[3,4,8)] Thus, the following relations are assumed:[18)]

$$R_{\alpha 1} = 1.517 - 0.067 \times |\cos\theta_{\alpha 1}|$$

$$R_{\alpha' 1'} = 1.517 - 0.067 \times |\cos\theta_{\alpha' 1'}|$$

$$R_{\alpha\alpha'} = 1.517 - 0.177 \times |\cos\theta_{\alpha\alpha'}|$$

All bond angles are assumed to be 120°, and all CC bond lengths in the benzene rings 1.397 Å. Thus the geometry of the π-system can be described as a function

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11) A. G. Evans and B. J. Tabner, *J. Chem. Soc.*, **1963**, 4613.

12) A. G. Evans, J. C. Evans, and C. L. James, *ibid.*, **B 1967**, 652.

13) J. F. Garst and E. R. Zabolotny, *J. Amer. Chem. Soc.*, **87**, 495 (1965).

14) R. C. Roberts and M. Szwarc, *ibid.*, **87**, 5542 (1965).

15) A. Cserhegyi, J. Jagur-Grodzinski, and M. Szwarc, *ibid.*, **91**, 1892 (1969).

16) M. Szwarc, *Accounts Chem. Res.*, **2**, 87 (1969).

17) See, for example, C. D. Cook, and K. Y. Wan, *J. Amer. Chem. Soc.*, **92**, 2595 (1970).

18) For the foundation of these assumptions, see Ref. 8, pp. 183—186.

of angles of twist θ_{a1}, $\theta_{a'1'}$, and $\theta_{aa'}$. Hereafter geometries are represented as (θ_{a1}, $\theta_{a'1'}$, $\theta_{aa'}$). As an example, geometry (0,0,0) represents the geometry in which $\theta_{a1}=\theta_{a'1'}=\theta_{aa'}=0°$. The calculations were carried out for geometries in which $\theta_{a1}=\theta_{a'1'}$ and which belong to symmetry group C_2, with the exception of geometries (0,0,0) and (0,0,180), which belong to symmetry groups C_{2h} and C_{2v}, respectively.[19]

Calculation was carried out by means of the Pariser-Parr-Pople method, using an HITAC 5020E at the computer Centre, the University of Tokyo. The parameter values were taken as proposed by Nishimoto and Forster.[20] Thus, for all the carbon π-centers, the values of the one-center core integral (α_p) and one-center repulsion integral (γ_{pp}) were taken to be -11.16 and 11.13 eV, respectively. The two-center core integral (β_{pq}) was taken to be zero for nonneighboring π-centers, and was estimated for neighboring π-centers by the use of a modification of the Nishimoto-Forster equation,[20]

$$\beta_{pq}(\text{in eV}) = -(2.04+0.51P_{pq})\times|\cos\theta_{pq}|,$$

where P_{pq} represents the π-bond order of the p—q bond calculated from the starting set of MO's. The two-center repulsion integral (γ_{pq}) was estimated by the use of the following Nishimoto-Mataga type equation[21] for all the pairs of π-centers:

$$\gamma_{pq}(\text{in eV}) = 14.397/(1.294+R_{pq})$$

Satisfactory self-consistency was attained after 10 iterations in SCF-MO calculation. In the iterations the geometry and all the values of β_{pq} and γ_{pq} were kept fixed, and no interaction between the π-electron distribution and the σ-electron distribution was taken into consideration.

The values of the resonance integral (β^0_{pq}) for neighboring π-centers were determined by the use of the equation

$$\beta^0_{pq} = k_{pq}\beta^0,$$

where

$$k_{pq} = [S(R_{pq}, 0°)/S(1.397\text{Å}, 0°)]\times|\cos\theta_{pq}|.$$

$S(R,0°)$ represents the π–π overlap integral for a CC bond whose length is R and whose angle of twist is 0°. For the values of S the values calculated by Mulliken and others[22] for Slater atomic orbitals were used.

TABLE 2. CALCULATED RESULTS FOR THE LOWEST SINGLET EXCITED STATES (HAVING AN ENERGY LOWER THAN 6 eV) OF THE STILBENE DIANION OF GEOMETRY (0,0,0)

State	Symmetry	Coef.[a]	Conf.[b]	E[c]	f[d]	φ[e]
S_1	A_g	0.9891	(8—10)	1.6364	0	—
S_2	B_u	0.9624	(8—9)	1.6444	0.0306	−67°36′
S_3	B_u	0.9678	(8—11)	2.6840	1.9545	+36°57′
S_4	A_g	0.9281	(8—12)	3.7101	0	—
S_5	A_g	0.9050	(7—9)	4.5412	0	—
S_6	B_u	0.9454	(7—10)	4.5627	0.2101	−60°45′
S_7	A_g	0.8495	(7—11)	4.7912	0	—
S_8	B_u	0.9475	(8—13)	4.8381	0.0347	+35°21′
S_9	A_g	0.9483	(8—14)	5.5512	0	—

a) Coefficient with which the electron configuration appears in the state function.

b) Electron configuration that makes the most important contribution to the state. (i—j) denotes the singlet electron configuration arising from the ground configuration by promotion of an electron from π orbital ϕ_i to ϕ_j. The orbital index i takes the increasing integer from 1 for the lowest orbital to 14 for the highest orbital in the order of increasing energy.

c) Energy of the excited state relative to the ground state (S_0) in eV.

d) Oscillator strength of the transition from the ground state to the excited state.

e) Direction of the transition moment: φ represents the angle that the transition moment makes with the x axis in the xy plane (see Fig. 2).

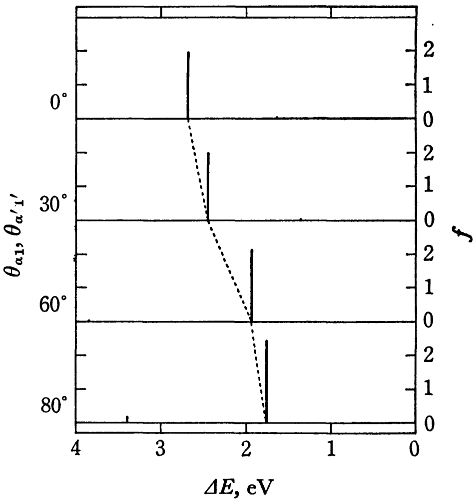

Fig. 3. The calculated energies (ΔE) and oscillator strengths (f) of transitions from the ground state to singlet excited states in the stilbene dianion for various values of θ_{a1} and $\theta_{a'1'}$ when $\theta_{aa'}$ is fixed at 0°.

In the CI calculation 30 singlet and 30 triplet lowest-energy singly excited electron configurations were taken into account.

Some results of the calculation are shown in Table 2 and Figs. 3 and 4. In Table 2 are listed the energies and some other data of the lowest singlet excited states of the dianion of geometry (0,0,0). Figures 3 and 4 illustrate the variations in the energies (ΔE) and oscillator strengths (f) of the transitions from the ground state to the lowest singlet excited states associated with the variations in geometry.

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[19] Calculation was also carried out for geometries (a, $-a$, 0) and (a, $-a$, 180), which belong to symmetry groups S_2 and C_s, respectively. The calculated values of energies and oscillator strengths of electronic transitions and of the ground-state energy of the π-electronic system coincide almost completely with those for the corresponding C_2 geometries, (a, a, 0) and (a, a, 180). The S_2 geometries (a, $-a$, 0) seem to be almost as probable as the corresponding C_2 geometries (a, a, 0). The C_s geometries (a, $-a$, 180), however, seem to be much less probable than the corresponding C_2 geometries (a, a, 180), since the steric repulsion between the two phenyl groups must be much stronger in the former than in the latter. Geometries (a, $-a$, b) with b different from 0 and 180 have no symmetry elements. The probability of these geometries also seems to be small.

[20] K. Nishimoto and L. S. Forster, *Theor. Chim. Acta*, **3**, 407 (1965); *ibid.*, **4**, 155 (1966).

[21] K. Nishimoto and N. Mataga, *Z. Phys. Chem.* (Frankfurt), **12**, 335 (1957); N. Mataga and K. Nishimoto, *ibid.*, **13**, 140 (1957).

[22] R. S. Mulliken, C. A. Rieke, D. Orloff, and H. Orloff, *J. Chem. Phys.*, **17**, 1248 (1949).

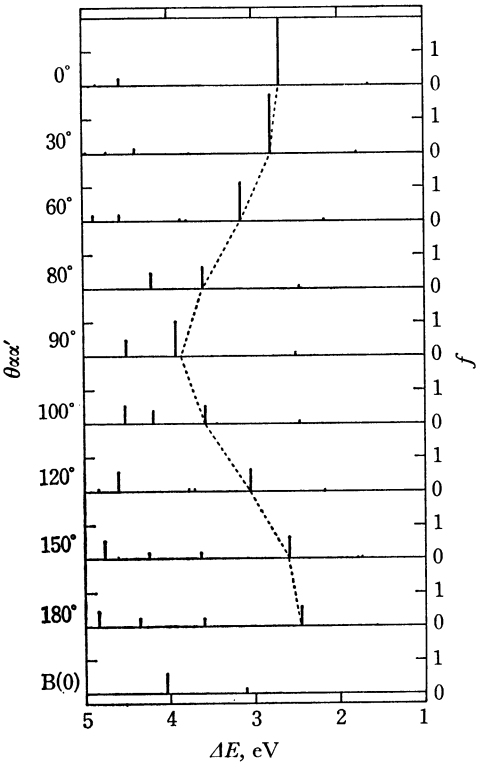

Fig. 4. The calculated energies (ΔE) and oscillator strengths (f) of transitions from the ground state to singlet excited states in the stilbene dianion for various values of $\theta_{\alpha\alpha'}$ when $\theta_{\alpha 1}$ and $\theta_{\alpha' 1'}$ are fixed at 0°. For comparison, the corresponding quantities in the benzyl anion of a planar geometry are also shown, being indicated by B(0). In every case there is no singlet excited state having energy lower than 1 eV.

Discussion

Band A. As shown in Fig. 1 and Table 1, each dianion has an intense absorption band with its maximum in the region of about 420—520 nm (according to Zabolotny and Garst,[23] for the dianion generated from *trans*-stilbene, $\lambda_{\max}=504$ nm, and $\varepsilon_{\max}=ca.\ 3.8\times 10^4$). Hereafter, attention is focused on this band, which is referred to as band *A*. It should be noted that in every case this band is structureless and very wide.

Besides this band, most of the "dianion spectra" (curve c, Fig. 1) show a very broad band in the region of 330—350 nm and a comparatively weak band with fine structure in the region of 260—270 nm. It is somewhat questionable whether all these weak absorptions are due to the dianions.

Regarding the position of band *A*, the following facts should be noted: (1) band *A* of the 4,4′-dimethylstilbene dianion is at slightly longer wavelength than that of the stilbene dianion; (2) the position of band *A* of the 2,4,6-trimethyl- and 2,4,6,2′,4′,6′-hexamethylstilbene dianions does not differ much from that of the stilbene dianion, in spite of the presence of a number of methyl substituents; (3) band *A* shifts progressively to shorter wavelengths as alkyl substituents are introduced to the α and α′ positions, in the order stilbene, α-methylstilbene, α,α′-dimethylstilbene, and α,α′-diethylstilbene.

Band *A* can undoubtedly be attributed to the transition from the ground state (S_0) to the singlet excited state to which the singlet electron configuration arising from one-electron transition from the 8th orbital (the highest occupied orbital) to the 11th orbital, (8—11), makes the most important contribution (see Table 2). In geometries (0,0,0) and (0,0,180), this excited state is the 3rd singlet excited state S_3 belonging to symmetry species B_u and B_2, respectively. In other geometries of symmetry C_2 this state belongs to symmetry species B. Hereafter, this state is called the *A* state, and the transition from the ground state to this state is called the *A* transition.

There seem to be at least three factors influencing the position of band *A*: (1) the geometry of the dianion, (2) the electronic effect of alkyl substituents, and (3) the effect of the counter-ion. The purpose of the present paper is to infer the geometry of the dianions from the position of their *A* bands, but before proceeding to such a discussion, it seems necessary to examine other factors.

The Electronic Effect of Alkyl Substituents. Band *A* of the 4,4′-dimethylstilbene dianion is at longer wavelength than that of the stilbene dianion by about 6 nm. If additivity is assumed, the bathochromic shift due to one methyl substituent at the *para* position is about 120 cm^{-1}.

The electronic effect of a methyl substituent on the energy of a π-electronic transition is usually ascribed to the inductive and the hyperconjugative effect, and can be approximately treated by perturbation theory.[24] Roughly speaking, the change in wavenumber at the absorption maximum caused by introduction of one methyl substituent $\Delta\nu$ depends on the change in the π-electron density at the substitution position (p) upon the electronic transition ΔP_{pp} in the following way. When the value of ΔP_{pp} is negative, the value of $\Delta\nu$ is also negative (the shift is bathochromic); the larger the absolute value of ΔP_{pp}, the larger the absolute value of $\Delta\nu$; when the value of ΔP_{pp} is zero, or positive (if small amount) the value of $\Delta\nu$ can be negative owing to the hyperconjugative effect; when the value of ΔP_{pp} is positive and very large, the value of $\Delta\nu$ can be positive (the shift can be hypsochromic).

TABLE 3. THE CALCULATED π-ELECTRON DENSITIES IN THE GROUND AND *A* STATES OF THE STILBENE DIANION OF GEOMETRY (0,0,0)

Position (p)	$P_{pp(G)}$	$P_{pp(A)}$	$\Delta P_{pp(GA)}$
α; α′	1.2444	1.1759	−0.0685
1; 1′	1.0687	1.1505	+0.0818
2; 2′	1.1531	1.0747	−0.0784
3; 3′	1.0674	1.1409	+0.0735
4; 4′	1.2756	1.3321	+0.0565
5; 5′	1.0687	1.0532	−0.0155
6; 6′	1.1221	1.0727	−0.0494

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[23] R. Zabolotny and J. F. Garst, *J. Amer. Chem. Soc.*, **86**, 1645 (1964).

[24] See, for example, H. Suzuki, the book cited in Ref. 8, pp. 408—410; A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley & Sons, Inc., New York, N.Y. (1961), pp. 131—134.

In Table 3 are shown the values of the π-electron densities (P_{pp}) in the ground and A states, together with the values of the π-electron density changes (ΔP_{pp}) associated with the A transition, calculated for geometry (0,0,0). It should be noted that the value of ΔP_{pp} is negative at the α and *ortho* positions and positive at the *para* positions. Essentially the same tendency is found in other geometries such as (0,0,30) and (30,30,0). Since the electronic effect of a methyl substituent on band A is bathochromic even at the *para* position, it must be bathochromic to much greater extent at the α and *ortho* positions. Accordingly, if it were not for the electronic effect of the methyl (or ethyl) substituents, the hypsochromic shift of band A associated with progressive introduction of alkyl substituents into the α and α' positions should be greater than observed. Even in the series of stilbene, 2,4,6-trimethyl-, and 2,4,6,2′,4′,6′-hexamethylstilbene, band A would shift hypsochromically, though the extent of the shift might be comparatively small, with increasing introduction of methyl substituents.

TABLE 4. DEPENDENCE OF THE POSITION OF THE A BAND MAXIMUM ON THE COUNTER-ION

trans-Stilbene	λ_{max}, nm (in DME)		
	Na^+	K^+	Cs^+
Unsubstituted	500	503	513
α,α'-Dimethyl-	436	450	457.5
α,α'-Diethyl-	427	437	440

Effect of the Counter-ion. The spectra of the dianion generated from the same compound by reduction with different alkali metals are similar to one another in shape, but the position of band A differs for different alkali metals. Table 4 shows that in every case the A band maximum shifts to longer wavelengths as the alkali metal becomes larger, in the order Na, K, and Cs.

If the dianions existed as unassociated ions or as so-called solvent-separated ion aggregates, the spectra would be substantially independent of the kind of the counter-ion.[25,26] The fact that the position of the absorption maximum varies depending on the kind of the alkali metal indicates that the dianions S^{2-} exist at least for a great part as contact ion aggregates (S^{2-}, $2M^+$) (called triple ions or diassociates), being associated with the alkali-metal ions M^+, although DME, the solvent used, is said to be a powerful solvating agent for alkali-metal ions and hence a very suitable solvent for making solvent-separated ion aggregates[25,26] or unassociated ions.[27]

In addition to the contact diassociates, possibly some other species, such as solvent-separated diassociates, contact and solvent-separated monoassociates (S^{2-},M^+), and unassociated dianions, may exist, though probably in much smaller amounts. The contact ion aggregates may assume various geometries around the equilibrium geometry. These might be responsible at least partly for the broadness of band A.

The fact that the band shifts to longer wavelengths with increasing size of the counter-ion suggests that band A of the unassociated dianion is located at a still longer wavelength than that of the same dianion associated with cesium ions. As is seen in Table 4, for every alkali metal the band shifts to shorter wavelengths with increasing alkyl substitution, in the order stilbene, α,α'-dimethyl-, and α,α'-diethylstilbene. It is plausible that the order will also be maintained in the spectra of the unassociated dianions.

Geometry of the Dianions. It might be said that, if it were not for the electronic effect of alkyl substituents and the effect of the counter-ions, band A would behave as follows: (1) it shifts comparatively rapidly to shorter wavelengths as the α and α' positions are increasingly substituted with alkyl groups; (2) it shifts comparatively slowly to shorter wavelengths as the *ortho* positions are increasingly substituted with methyl groups. These behaviors should be related to the geometry of the dianions.

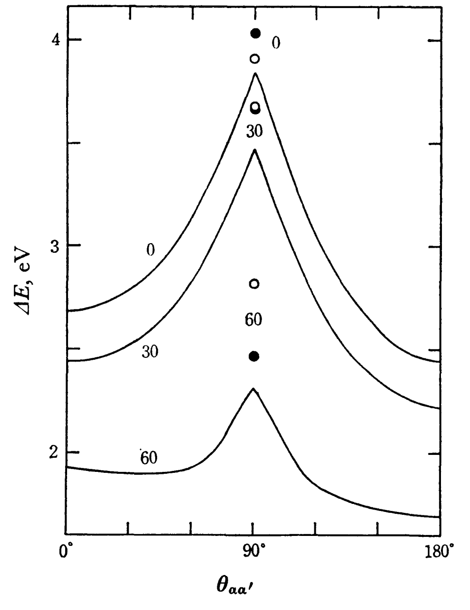

Fig. 5. The relationship of the calculated energy of the A transition of the stilbene dianion (ΔE) to angles of twist $\theta_{\alpha 1}$, $\theta_{\alpha' 1'}$, and $\theta_{\alpha\alpha'}$. The numerals written near curves and circles indicate the values of $\theta_{\alpha 1}$ ($=\theta_{\alpha' 1'}$) in units of degree. For geometries with $\theta_{\alpha\alpha'}=90°$, the A transition being forbidden, the energies of the main allowed transition are also shown with open circles. These are to be compared with the energies of the main allowed transition of the benzyl anion of the corresponding geometries, which are shown with black spots.

As is seen in Figs. 3 and 4, the results of calculation show that the energy of the A transition decreases with increasing deviation of $\theta_{\alpha 1}$ and $\theta_{\alpha' 1'}$ from 0° and increases with increasing deviation of $\theta_{\alpha\alpha'}$ from 0° or from 180°. These tendencies can be seen more clearly in Fig. 5, in which the energy of the A transition is plotted against $\theta_{\alpha\alpha'}$ for various values of $\theta_{\alpha 1}$ and $\theta_{\alpha' 1'}$. The π-electronic state of the stilbene dianion having a geometry in which $\theta_{\alpha\alpha'}=90°$ is considered to resemble that of two mutually independent benzyl anions. For the sake of comparison,

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25) T. E. Hogen-Esch and J. Smid, *J. Amer. Chem. Soc.*, **88**, 307 (1966).

26) L. L. Chan and J. Smid, *ibid.*, **90**, 4654 (1968).

27) K. H. J. Buschow, J. Dieleman, and G. J. Hoijtink, *J. Chem. Phys.*, **42**, 1993 (1965).

Table 5. The main absorption band maximum of the benzyl anion in tetrahydrofuran

Counter-ion	$\lambda_{\max}$, nm	$\varepsilon_{\max}$	Ref.
Li^+	330	9.6×10^3	23)
Na^+	354.6	1.2×10^4	22)
Na^+	350	3.5×10^3	24)
Cs^+	356	—	24)

results of a similar calculation for the benzyl anion are also given in Figs. 4 and 5.

The benzyl anion has been reported to have its first intense absorption band at about 350 nm,[28-30] as shown in Table 5. This position is of much shorter wavelength than that of band *A* of the stilbene dianion. The stilbene dianion is iso-π-electronic with hydrazobenzene, and the benzyl anion with aniline. The spectral resemblance of hydrazobenzene and aniline suggests that the most preferred geometry of hydrazobenzene is probably a nonplanar conformation in which the central NN bond is twisted.[31] The situation is quite different in the case of the stilbene dianion and the benzyl anion.

We thus conclude as follows. The most preferred geometry of a sterically unhindered dianion such as the dianions of stilbene and 4,4'-dimethylstilbene is probably planar or nearly planar. It is probably the *trans* form, in view of the result of calculation of the total energy.

When alkyl substituents are introduced into the α and α' positions, the steric interference caused by the substitution are probably relieved chiefly by partial rotation about the α—α' bond. From examination of the electronic absorption spectra of α-methyl- and *cis*-*β*-methylstyrene and *cis*- and *trans*-α-methylstilbene it has been concluded that a phenyl group in such a system sterically interacts more strongly with a methyl group at the *cis*-*β* position than with a methyl group at the α position.[32,33] This leads to the inference that in the planar *trans* form of the α,α'-dimethylstilbene dianion the steric interference of the α-phenyl group with the α'-methyl group is probably stronger than that with the α-methyl group. The former can be relieved by comparatively small rotation about the α—α' bond. This means that major part of the steric interference in the dianion can be relieved by rotation about the α—α' bond. The rotation about the α—α' bond is, of course, not the only possible mode of geometry change relieving the steric interference. Rotation about the α—1 and the α'—1' bonds and some other modes of geometry change probably take place to smaller extents. The possibility also cannot entirely be excluded that a small change in hybridization of the valence orbitals of the α and α' carbon atoms, resulting in a small deviation of the geometry about these atoms from planarity, may contribute to the relief of the steric interference.

The fact that the dianion spectra of *cis*- and *trans*-α, α'-dimethylstilbene are essentially the same indicates that the same dianion, probably of a *trans*-like geometry, is produced from either isomer.

The steric effect of introduction of methyl groups into the *ortho* positions is apparently smaller than that of introduction of methyl groups into the α and α' positions. This is rather surprising, in view of the fact that in the case of neutral molecules the steric effect of the *ortho* substitution is almost comparable to that of the α and α' substitution.[6] This is considered to indicate one of the following two possible causes: (1) in the dianions the steric interference caused by the *ortho* substitution is much smaller than that caused by the α and α' substitution; (2) the former cannot be relieved by rotation about the α—α' bond as effectively as the latter, and can be relieved more effectively by rotation about the α—1 and α'—1' bonds; consequently, the values of $\theta_{\alpha1}$ and $\theta_{\alpha'1'}$ in the 2,4,6,2',4',6'-hexamethylstilbene dianion, for example, are larger than those in the α, α'-dimethylstilbene dianion and the value of $\theta_{\alpha\alpha'}$ in the former is smaller than that in the latter. The second possibility seems to be more plausible.

In the dianion the increase in the total energy associated with deviation of $\theta_{\alpha1}$ and $\theta_{\alpha'1'}$ from 0° is considered to be much larger than that associated with deviation of the same extent of $\theta_{\alpha\alpha'}$ from 0°. The fact that the formation of the dianion is difficult with the nuclear-substituted stilbenes but easy with the α,α'-substituted stilbenes may have some connection with the possible difference in the extent of the steric interference involved or that in the manner in which the steric interference is relieved, in addition to the possible difference in the magnitude of the electron-donating effect of the substituents at different positions. The relative difficulty of the dianion formation is due to many factors, such as the energy of formation of the aggregates of the dianion and anion radical with the counter-ion and of external and internal solvation of the ion aggregates, besides that of formation of the unassociated dianion from the unassociated anion radical, and deserves further investigation.

Total Energy and π-Bond Order. The phenomenon that the main absorption band shifts to shorter wavelengths with increasing steric interference is very similar to that observed with the neutral molecules of stilbenes.[3-8] However, while in the neutral molecules the steric interference is relieved chiefly by rotation about the α—1 and α'—1' "single" bonds, in the corresponding dianions it is inferred as above to be relieved chiefly by rotation about the α—α' "double" bond. The difference is understandable in terms of calculated values of the total energy as well as the π-bond order.

Table 6. The calculated total energies of the stilbene molecule and dianion of various geometries in the ground state

Geometry	Total Energy, eV	
	Molecule	Dianion
(0,0,0)	−179.8883	−180.5341
(0,0,180)	−179.9029	−180.2377
(30,30,180)	−179.5502	−179.3771

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28) R. Asami, M. Levy, and M. Szwarc, *J. Chem. Soc.*, **1962**, 361.

29) R. Waack and M. A. Doran, *J. Amer. Chem. Soc.*, **85**, 1651 (1963).

30) F. J. Hopton and N. S. Hush, *Mol. Phys.*, **6**, 209 (1963).

31) H. Suzuki, the book cited in Ref. 8, p. 518.

32) H. Suzuki, This Bulletin, **33**, 619 (1960).

33) G. Favini and M. Simonetta, *Theor. Chim. Acta*, **1**, 294 (1963).

Table 7. The π-bond orders of some bonds of the stilbene molecule and molecule ions of geometry (0,0,0)

Bond	Calculated by SCF-MO method		Calculated by Hückel method		
	Molecule	Dianion	Molecule	Anion radical Cation radical	Dianion Dication
α—α'	0.8859	0.4477	0.8577	0.6760	0.4942
α—1; α'—1'	0.3413	0.7109	0.3825	0.4867	0.5908

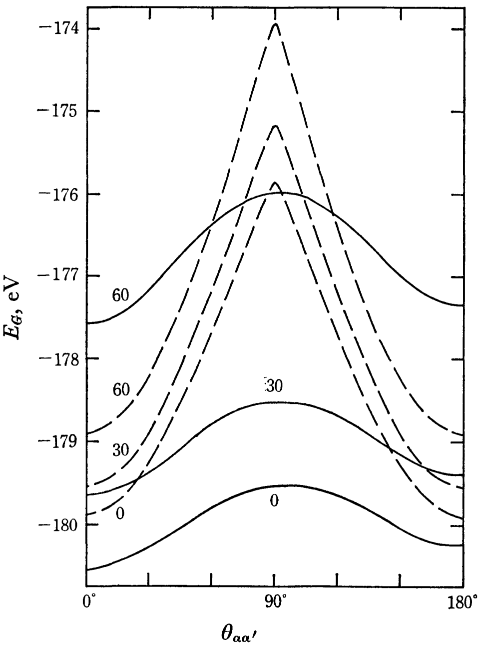

Fig. 6. The relationship of the calculated total energies (E_G) of the stilbene molecule (— — —) and dianion (———) in the ground state to angles of twist $\theta_{\alpha 1}$, $\theta_{\alpha' 1'}$, and $\theta_{\alpha\alpha'}$. The numerals written near curves indicate the values of $\theta_{\alpha 1}$ ($=\theta_{\alpha' 1'}$) in terms of degree.

In Fig. 6 and Table 6 are shown results of the SCF calculation of the total energy of the ground state, as the sum of the π-electron energy and the energy of core-core interaction, for the stilbene dianion and molecule of various geometries. In the calculation the energy of core-core interaction was assumed to be given by

$$\sum_{p} \sum_{q \neq p} \gamma_{pq},$$

where γ_{pq} is the two-center repulsion integral for the $2p\pi$ atomic orbitals centered at carbon atoms p and q.

From the results, both for the dianion and the molecule, geometries (0,0,0) and (0,0,180) correspond to the energy minima. In addition, the results show that in the case of the dianion the α—α' bond is twisted with a smaller energy increase than the α—1 and α'—1' bonds, while in the case of the molecule the reverse is true. These tendencies agree with those expected from correlation diagrams[34] connecting the HMO levels of the planar stilbene π-system with those of two non-interacting benzyl groups and those of non-interacting two benzene rings and one ethylenic bond.

In Table 7 are shown the π-bond orders calculated for geometry (0,0,0). In the dianion the π-bond order of the α—α' bond is smaller than that of the α—1 as well as the α'—1' bond, while in the molecule the reverse is true. The π-bond orders of bonds of the anion radical (as well as the cation radical) must be intermediate between those of the corresponding bonds of the molecule and the dianion (as well as the dication). Therefore, it is of interest to examine how steric interferences affect the geometry and the spectrum in the case of these ion radicals.

It is noteworthy that in the case of the dianion the calculated ground-state energy of geometry (0,0,0) is lower by as much as about 0.3 eV than that of geometry (0,0,180), while in the case of the molecule the energy of geometry (0,0,0) is slightly higher than that of geometry (0,0,180). Even in the case of the molecule, *trans*-stilbene is more stable than its *cis* isomer by about 3[35,36] or 6[37] kcal/mol. In the *cis*-stilbene molecule the two phenyl groups cannot be simultaneously coplanar with the central ethylenic bond plane, owing to steric interference, and the most preferred geometry of this molecule is considered to be close to geometry (30,30,180).[3,4,8,38] According to the results of calculation, the energy of this geometry is higher by about 0.3 eV than that of geometry (0,0,0). Thus, it may be said that the present calculation gives quite adequate results. It seems reasonable to infer that the most preferred geometry of the dianion is the *trans* form, at least if steric interference is absent or small.

Location of the Alkali-Metal Cations in the Contact Ion Aggregates. The geometry of the contact ion aggregates (S^{2-},$2M^+$), the location of M^+'s with respect to S^{2-} in (S^{2-},$2M^+$), is examined.

Schlenk and Bergmann found that addition of carbon dioxide to products resulting from the reduction of *trans*-stilbene with alkali metals, followed by hydrolysis, gave α,α'-diphenylsuccinic acid, which was the racemic mixture when the alkali metal was lithium and the *meso* isomer when the alkali metal was sodium or potassium.[39] These stereochemical findings suggest that, in the reduction with lithium, two lithium atoms undergo *cis* addition to the α and α' carbon atoms of stilbene with bonds possessing covalent character to a large extent, and that in the reduction with sodium or potassium the product exists for a great part as ion aggregates (S^{2-},$2M^+$) which are in equilibrium with the unassociated ions. The thermodynamically most stable geome-

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[34] A. Imamura and R. Hoffmann, *J. Amer. Chem. Soc.*, **90**, 5379 (1969).

[35] G. B. Kistiakowsky and W. R. Smith, *ibid.*, **56**, 638 (1934).

[36] T. W. J. Taylor and A. R. Murray, *J. Chem. Soc.*, **1938**, 2078.

[37] P. Borrell and H. H. Greenwood, *Proc. Roy. Soc.*, *Ser. A*, **298**, 453 (1967).

[38] D. L. Beveridge and H. H. Jaffé, *J. Amer. Chem. Soc.*, **87**, 5340 (1965).

[39] W. Schlenk and E. Bergmann, *Ann.*, **463**, 1 (1928).

try of the ion aggregate is probably a geometry in which one of the two cations is located on one side of the dianion plane and the other on the opposite side.

The energy of interaction between the ions in the contact aggregate of the dianion in the ground state with the cations ΔE_G and the change in the energy of the A transition of the dianion caused by the ion aggregation $\Delta\Delta E_{GA}$ were tentatively calculated for various locations of the cations in the following approximate manner. In the calculation solvent effects were not considered.

It is assumed that two alkali-metal cations are located symmetrically with respect to the origin of the coordinate system assigned to the dianion (see Fig. 2). That is, if the coordinate of one of the two cations is denoted by (x_M, y_M, z_M), that of the other is assumed to be $(-x_M, -y_M, -z_M)$. The energy of interaction between the ions in the aggregate of the two cations with the dianion in the ith π-electronic state ΔE_i is given by

$$\Delta E_i = 2(E_{\text{core},M} - E_{\pi(i),M}) + E_{MM'},$$

where $E_{\text{core},M}$ is the energy of repulsive interaction between the cores of the dianion and one of the cations, $E_{\pi(i),M}$ is that of attractive interaction between the π-electronic cloud of the dianion and one of the cations, and $E_{MM'}$ is that of repulsive interaction between the two cations. These quantities are assumed to be given by the following equations:[40]

$$E_{\text{core},M} = e^2\sum_p (1/R_{pM})$$

$$E_{\pi(i),M} = e^2\sum_p (P_{pp(i)}/R_{pM})$$

$$E_{MM'} = e^2/R_{MM'},$$

where e is the quantum of electricity, R_{pM} the distance between the pth carbon π-center of the dianion and one of the cations, $P_{pp(i)}$ the π-electron density at the pth carbon π-center of the dianion in the ith π-electronic state, $R_{MM'}$ the distance between the two cations, and the summations are carried out over all the π-centers. The change in the energy of transition from the ith to the jth π-electronic state associated with the aggregation $\Delta\Delta E_{ij}$ is given by

$$\Delta\Delta E_{ij} = 2(E_{\pi(i),M} - E_{\pi(j),M}).$$

The calculation was carried out for the dianion of geometry (0,0,0), by the use of the values of π-electron densities $P_{pp(G)}$ and $P_{pp(A)}$ shown in Table 3. After Hush and Rowlands,[41] the perpendicular distance of a cation from the plane of the dianion z_M was assumed to be given by

$$z_M = r_{M^+} + 2.5(\text{Å}),$$

where r_{M^+}, the Goldschmidt ionic radius of the alkali-metal cation, was taken to be 0.97, 1.33, and 1.70 Å for Na$^+$, K$^+$, and Cs$^+$, respectively. The results of the calculation for various locations of the cations are shown in Fig. 7.

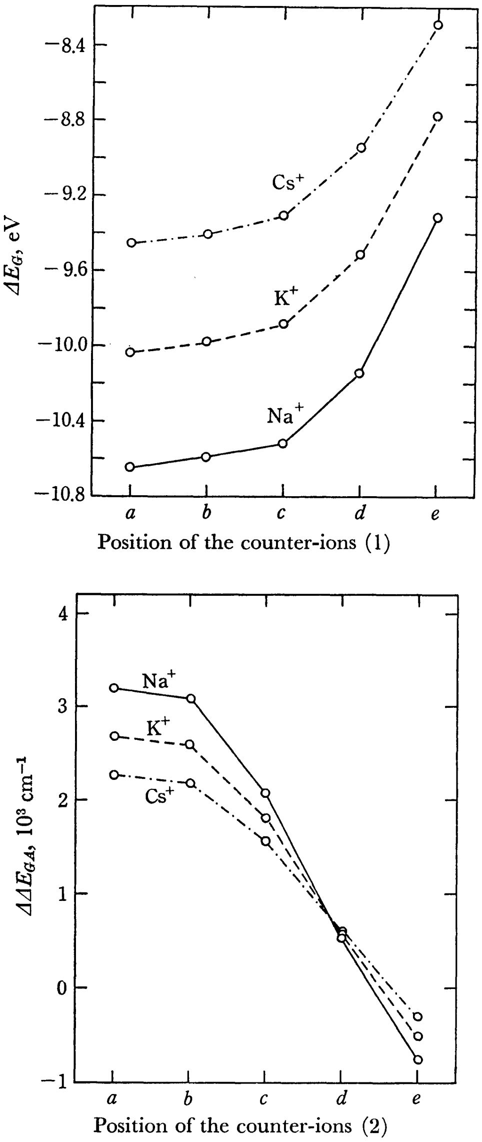

Fig. 7. The relationship of (1) ΔE_G and (2) $\Delta\Delta E_{GA}$ of the stilbene dianion of geometry (0,0,0) to the location of the counter-ions. The positions of the counter-ions are represented by the projection of one of them on the plane of the dianion as follows: (*a*) the center of the α-α' bond; (*b*) the position of carbon atom α; (*c*) the position of carbon atom 1; (*d*) the center of a benzene ring; (*e*) the position of carbon atom 4. The perpendicular distances of the counter-ions from the dianion plane are taken as described in text.

The A band maximum shifts to shorter wavelengths as the alkali metal is changed from Cs to K, and further to Na. From comparison of this fact with the result of the calculation of $\Delta\Delta E_{GA}$ shown in Fig. 7(2) and inspection of the result of the calculation of ΔE_G shown in Fig. 7(1), the possibility of geometries in which the alkali-metal cations are located near the benzene rings is excluded. It is inferred that the cations are located near the ethylenic bond. The results show that geometries a and b have large and nearly equal probabilities.

In addition to the electrostatic interaction between the ions, charge transfer from the dianion to the alkali-metal cations seems to make a minor contribution to the stability of the ion aggregate. The most important component of the charge-transfer interaction is probably the interaction between the highest occupied orbital (the 8th π orbital) of the dianion and the lowest vacant orbital (an s orbital) of each cation. Since the former

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40) For justification of adopting the point-charge approximation, see Ref. 41.

41) N. S. Hush and J. R. Rowlands, *Mol. Phys.*, **6**, 201 (1963).

has a nodal plane bisecting the α—α' bond perpendicularly and the latter is centrosymmetric, if the cations were located near the center of the α—α' bond (geometry *a*), the charge-transfer interaction would make substantially no contribution to the stability. It is therefore concluded that the most preferred or equilibrium geometry of the ion aggregate is probably close to geometry *b*, that is, the geometry in which one of the cations is located above carbon atom α and the other below carbon atom α'.