

Electronic Absorption Spectra and Geometry of Anion Radicals generated from (*E*)-Stilbene and 'Stiff' Stilbenes

Keiichiro Ogawa* and Motoko Futakami

Department of Chemistry, The College of Arts and Sciences, The University of Tokyo, Komaba, Meguro-ku, Tokyo 153, Japan

Hiroshi Suzuki

Department of Chemistry, School of Medicine, Juntendo University, Inba-mura, Chiba 270-16, Japan

Akira Kira

The Institute of Physical and Chemical Research, Wako, Saitama 351, Japan

The electronic absorption spectra of anion radicals produced by γ -ray irradiation of (*E*)-stilbene (**1**), indeno[2,1-*a*]indene (**2**), 5,6,11,12-tetrahydrochrysene (**3**), (*E*)-1,1'-bi-indanylidene (**4**), and (*E*)-1,1',2,2',3,3',4,4'-octahydro-1,1'-binaphthylidene (**5**) in glassy 2-methyltetrahydrofuran solution at 77 K have been measured. Examination of the spectra leads to the following conclusions. (a) The (*E*)-stilbene skeleton in the anion radical of (**1**) as well as of (**2**), (**3**), and (**4**) is planar or nearly planar; (b) in the anion radical of (**5**) immediately after its production, the ethylene bond and the C-Ph bonds are substantially twisted, and on controlled warming or on illumination, the twisting of the ethylene bond is increased.

The geometry of radical ions generated from diarylethylenes has been extensively studied,¹⁻³ because it is related to the fundamental question of how the molecular geometry changes with changes in the charged state. It is also related to the interest in the geometry of the neutral molecules in the first excited singlet state as well as in the first excited triplet state, since the π -bond orders of the ethylene bond and the C-Ar bonds in the radical ions are expected to be intermediate between those in the parent neutral molecules in the ground state and in the excited states.

In previous papers, the geometry of radical ions generated from (*E*)-stilbene (**1**) in fluid and glassy solutions were inferred to be planar or nearly planar from electronic absorption spectroscopy.^{2,3} The present study confirms this inference for the anion radical (**1**)^{-•} in glassy solution by comparing its electronic absorption spectra with those of the anion radicals generated from related compounds in which the (*E*)-stilbene skeleton is geometrically fixed by alkylene chains: indeno[2,1-*a*]indene (**2**), 5,6,11,12-tetrahydrochrysene (**3**), (*E*)-1,1'-bi-indanylidene (**4**), and (*E*)-1,1',2,2',3,3',4,4'-octahydro-1,1'-binaphthylidene (**5**). The geometries of these anion radicals and their change on being warmed for a limited period or on illumination are elucidated.

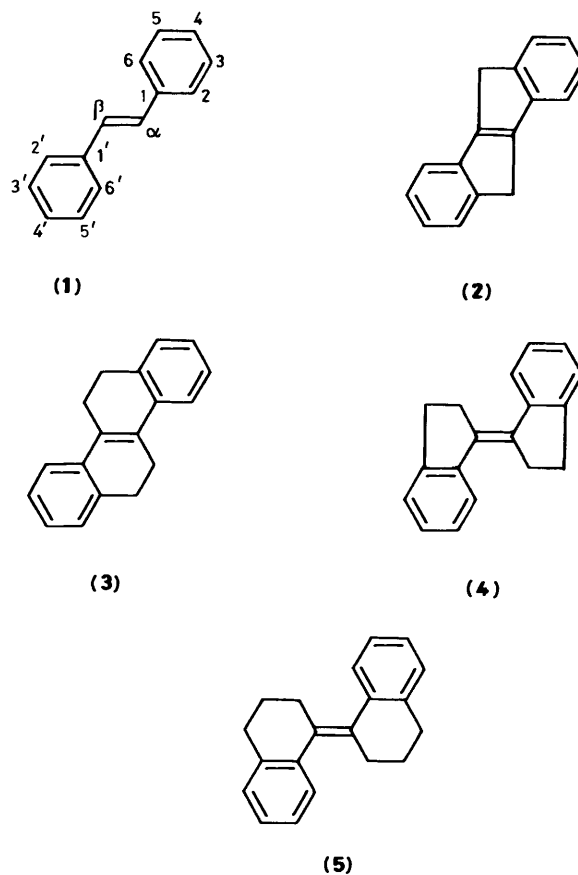
Experimental

Syntheses of the parent compounds (**2**)–(**5**) have been described in a previous paper.⁴

Anion radicals of (**1**)–(**5**) were produced by γ -ray irradiation of glassy solutions of the parent compounds in deaerated 2-methyltetrahydrofuran (MTHF) at 77 K. The electronic absorption spectra of the γ -ray-irradiated samples were measured before and after illumination with visible light or warming for a limited period. The experimental details are the same as those described previously.²

Results and Discussion

Designation of Spectra and of Geometries.—Representative spectra of the anion radicals are shown in Figure 1 and relevant data are listed in Table 1. As seen in the figures, the anion



radicals exhibit two major bands in the visible region. The band at the lower wavenumber is designated as A, and that at the higher wavenumber as B. For band B, for example, the wavenumber and the molar absorption coefficient at the absorption maximum are denoted by $\tilde{\nu}(\text{B})$ and $\epsilon(\text{B})$, respectively.

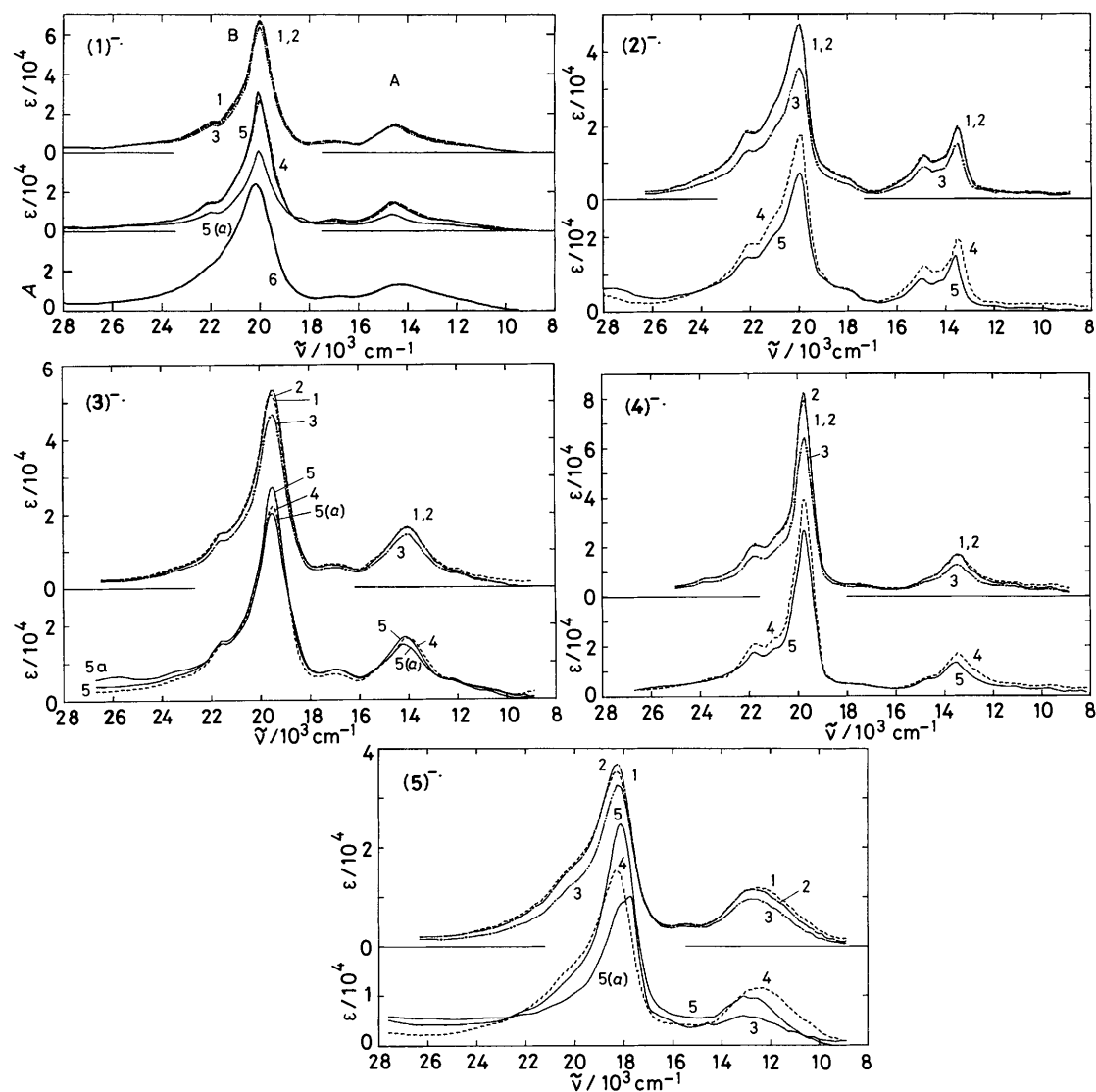


Figure 1. Electronic absorption spectra of the anion radicals generated from (1)–(5). Curves 1 and 4 (---): spectra observed immediately after γ -ray irradiation of a glassy solution, designated I in the text. Curve 2 (— · — · —): spectra observed after illumination of the sample for curve 1 with light of wavenumber corresponding to band A, designated PA in Table 1. Curve 3 (— · — · —): spectra observed after illumination of the sample for curve 2 with light of wavenumber corresponding to and lower than band B, designated PB in Table 1. Curve 5 (—): spectra observed after controlled warming of the sample for curve 4, designated W in the text. Curve 5(a) (—): spectra observed after additional controlled warming. The solvent is 2-methyltetrahydrofuran for all the above spectra. Curve 6 (—): spectra of anion radical (1)⁻ produced by alkali-metal reduction in fluid 1,2-dimethoxyethane, reproduced from ref. 2

Spectra of the anion radicals measured after different treatments are designated as follows: the spectrum of an anion radical measured immediately after its production by γ -ray irradiation in a frozen matrix is designated as I (immediately after the production), that measured after illumination as P (photobleached), and that measured after controlled warming as W (warmed). For brevity, combined expressions are also used; e.g. $\tilde{\nu}_i(B)$ of spectra I is denoted by $\tilde{\nu}_i(B)$. Similarly, the spectra of the neutral molecules in the glassy solution are designated as spectra g (glassy) and the wavenumber at the absorption maximum of their main band is denoted by $\tilde{\nu}_g$.

The same designations are also used to specify the geometries of the anion radicals after the respective treatments.

Character of Absorption Bands.—By comparison of the observed spectra and the results of semiempirical SCF-MO-CI calculations for the π -electronic state of the anion radical of (1), bands A and B are ascribed mainly to the one-electron

transition from π orbital ψ_{-1} to π orbital ψ_{-4} and that from π orbital ψ_{+1} to π orbital ψ_{-1} , respectively.² The index of π orbitals runs from +7 for the lowest orbital to -7 for the highest one in the order of increasing energy. Orbitals ψ_{+1} and ψ_{-1} correspond, respectively, to the HOMO and the LUMO in the molecule. The relevant orbitals are shown in Figure 2.

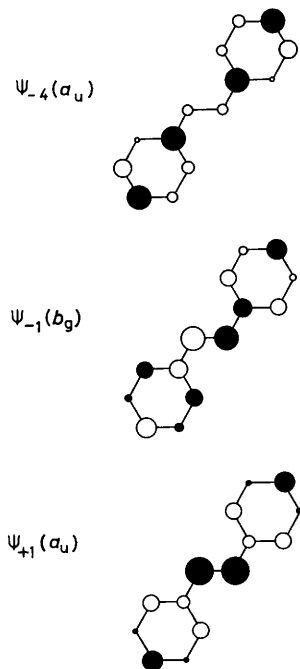
The numbering of the carbon atoms of the (*E*)-stilbene π system is illustrated in the structural formula of (1). Torsion angles $\beta_{\alpha-1-6}$ and $\alpha-\beta-1'-6'$ are denoted by $\theta_{\alpha 1}$ and $\theta_{\beta 1'}$, respectively. Angle $\theta_{\alpha\beta}$ is defined as 180° minus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

As reported previously, it is expected that an increase in $|\theta_{\alpha 1}|$ and $|\theta_{\beta 1'}|$ will cause a larger red shift of band A and a smaller blue shift of band B, and that an increase in $|\theta_{\alpha\beta}|$ will cause a smaller blue shift of band A and a larger red shift of band B.²

Band B of (1)⁻—(4)⁻.—In the neutral molecules in glassy MTHF solution at 77 K, the main absorption band, largely

Table 1. Data from electronic absorption spectra of the anion radicals of (1)–(5)

Anion radical	Class	No. in Figure 1	$\tilde{\nu}(\text{B})/10^3 \text{ cm}^{-1}$	$\epsilon(\text{B})/10^4$	$\tilde{\nu}(\text{A})/10^3 \text{ cm}^{-1}$	$\epsilon(\text{A})/10^4$
(1) ^{-•} ^a	I	4	20.03	6.569	14.49	1.407
	W	5	20.06	7.042	14.66	1.422
(2) ^{-•}	I	1, 4	19.94	4.727	13.51	1.928
	W	5	19.89	4.773	13.51	1.982
	PA	2	19.94	4.712	13.47	1.917
	PB	3	19.94	3.535	13.47	1.485
	I	1, 4	19.51	5.194	14.13	1.636
(3) ^{-•}	W	5	19.51	5.715	14.18	1.684
	PA	2	19.51	5.326	14.14	1.616
	PB	3	19.51	4.660	13.99	1.441
	I	1, 4	19.77	7.929	13.48	1.687
	W	5	19.77	6.670	13.62	1.329
(4) ^{-•}	PA	2	19.74	8.242	13.50	1.707
	PB	3	19.74	6.410	13.58	1.287
	I	1, 4	18.31	3.541	12.50	1.154
	W	5	18.13	4.474	13.12	0.996
	PA	2	18.27	3.683	12.81	1.142
(5) ^{-•}	PB	3	18.27	3.252	12.81	0.953

^a Data from ref. 2.**Figure 2.** Relevant π molecular orbitals of the (*E*)-stilbene anion radical (1)^{-•} in the planar form with C_{2h} symmetry

ascribed to the one-electron transition from ψ_{+1} to ψ_{-1} , is located in the following order ($\tilde{\nu}_g/10^3 \text{ cm}^{-1}$): (5) (33.91) \gg (1) (31.78) > (2) (31.34) > (4) (30.55) > (3) (30.41).⁴ In the anion radicals, $\tilde{\nu}_i(\text{B})$ decreases in the order (1)^{-•} \approx (2)^{-•} > (4)^{-•} > (3)^{-•} \gg (5)^{-•}. That is, the sequence of $\tilde{\nu}_i(\text{B})$ is the same as that of $\tilde{\nu}_g$ except for (5). The fact that $\tilde{\nu}_i(\text{B})$ of (1)^{-•} is very close to $\tilde{\nu}_i(\text{B})$ of (2)^{-•} and that $\tilde{\nu}_i(\text{B})$ of (3)^{-•} and (4)^{-•} is smaller than $\tilde{\nu}_i(\text{B})$ of (2)^{-•} suggests that the (*E*)-stilbene skeleton in the anion radicals (1)^{-•}–(4)^{-•} is planar or nearly planar, since it is no problem to assume that the (*E*)-stilbene skeleton of (2)^{-•} is planar or nearly planar in the neutral molecule (2) in glassy solution. The fact that $\tilde{\nu}_i(\text{B})$ of (2)^{-•}–(4)^{-•} is smaller than that of (1)^{-•} is mainly ascribed to the electronic bathochromic effect of the alkylene chains as in the case of $\tilde{\nu}_g$ of the neutral molecules.

Table 2. Squares of selected atomic-orbital coefficients of π SCF-MOs of the (*E*)-stilbene anion radical (1)^{-•} having the planar geometry

	C_a^2	C_b^2	C_c^2
ψ_{-4}	0.0282	0.0049	0.0293
ψ_{-1}	0.1594	0.0665	0.0611
ψ_{+1}	0.1997	0.0743	0.0742

The fact that $\tilde{\nu}_i(\text{B})$ of (3)^{-•} is smaller than that of (2)^{-•} reflects the general trend that the absorption band which is ascribed to the one-electron transition from ψ_{+1} to ψ_{-1} is located at lower wavenumber in a compound with a cyclohexa-1,3-diene moiety than in a corresponding compound with a cyclopentadiene moiety as observed for the corresponding neutral molecules. The fact that $\tilde{\nu}_i(\text{B})$ of (3)^{-•} and (4)^{-•} is smaller than that of (2)^{-•} may suggest that the electronic bathochromic effect of the dimethylene chain is larger than that of the methylene chain.

The range of $\tilde{\nu}_i(\text{B})$ of (1)^{-•}–(4)^{-•} is narrower than that of $\tilde{\nu}_g$ of (1)–(4): the difference between $\tilde{\nu}_i(\text{B})$ of (1)^{-•} and that of (3)^{-•} is $0.52 \times 10^3 \text{ cm}^{-1}$ while the difference between $\tilde{\nu}_g$ of (1) and that of (3) is $1.37 \times 10^3 \text{ cm}^{-1}$. This fact clearly shows that the electronic bathochromic effect of the alkylene chains is smaller in the anion radicals than in the neutral molecules. This is in accordance with our previous prediction on the basis of molecular-orbital theory.²

Band A of (1)^{-•}–(4)^{-•}.— $\tilde{\nu}_i(\text{A})$ decreases in the order (1)^{-•} > (3)^{-•} > (2)^{-•} > (4)^{-•}. This sequence is similar to that of $\tilde{\nu}_i(\text{B})$ except for (3)^{-•}. The fact that $\tilde{\nu}_i(\text{A})$ of (3)^{-•}, (2)^{-•}, and (4)^{-•} is smaller than that of (1)^{-•} may be ascribed to the electronic bathochromic effect of the alkylene chains.

In the one-electron approximation, the magnitude of the bathochromic effect of an alkyl or alkylene substituent is interpreted as the difference in the energy lift of the relevant π molecular orbitals by the substitution. The magnitude of the energy lift of a π molecular orbital caused by alkyl or alkylene substitution depends on the square of the coefficient of the atomic orbital (that is, the electron density) at the substitution position in the molecular orbital: the larger the square of the atomic-orbital coefficient, the larger will be the magnitude of the lift of the orbital energy.

Table 2 shows the squares of atomic orbital coefficient (C_i^2)

of the π molecular orbitals relevant to bands A and B calculated by the SCF-MO method for the planar geometry of (1)^{-•}.

In compound (3), dimethylene chains are present at the α (β) and 6' (6) positions. In compound (4), dimethylene chains are present at the α (β) and 2 (2') positions. Since, in the transition from ψ_{-1} to ψ_{-4} , the decrease of C_2^2 is larger than that of C_6^2 , the electronic bathochromic effect of dimethylene chains for band A is expected to be larger in (4)^{-•} than in (3)^{-•}. On the other hand, the electronic bathochromic effect for band B in (3)^{-•} is expected to be nearly the same as that in (4)^{-•}, since, in the transition from ψ_{+1} to ψ_{-1} , the decrease of C_6^2 is nearly equal to that of C_2^2 .

It should also be noted that the range of $\tilde{\nu}_1(\text{A})$ is wider than that of $\tilde{\nu}_1(\text{B})$: the difference between $\tilde{\nu}_1(\text{A})$ of (1)^{-•} and $\tilde{\nu}_1(\text{A})$ of (4)^{-•} is $1.01 \times 10^3 \text{ cm}^{-1}$ and the difference between $\tilde{\nu}_1(\text{B})$ of (1)^{-•} and $\tilde{\nu}_1(\text{B})$ of (3)^{-•} is $0.52 \times 10^3 \text{ cm}^{-1}$. That is, the electronic bathochromic effect of alkylene chains is larger in band A than in band B. This seems reasonable because the decrease in the π -electron density at the substitution position is larger in the transition from ψ_{-1} to ψ_{-4} than in that from ψ_{+1} to ψ_{-1} as shown in Table 2.

Anion Radical (5)^{-•}.—In a previous paper, we concluded that $|\theta_{\alpha 1}|$ as well as $|\theta_{\beta 1}|$ of neutral molecule (5) in glassy solution is substantially deviated from 0° as in the crystalline state,* since $\tilde{\nu}_g$ of (5) is much larger than that of (1)—(4).⁴ In the case of the anion radical, both $\tilde{\nu}_1(\text{A})$ and $\tilde{\nu}_1(\text{B})$ of (5)^{-•} are much smaller than those of (1)^{-•}—(4)^{-•}. This fact can only be understood by the explanation that not only $|\theta_{\alpha 1}|$ and $|\theta_{\beta 1}|$ but also $|\theta_{\alpha \beta}|$ is substantially deviated from 0° in (5)^{-•}, since the electronic bathochromic effect of the alkylene chains in (5)^{-•} must be not much different from that in (1)^{-•}—(4)^{-•}, especially that in (4)^{-•}.

Effect of Warming and of Illumination.—On warming or by illumination of the samples for a limited period, the positions of both bands A and B were almost unchanged. This implies that for these species geometry W or P is almost the same as geometry I, which is planar or nearly planar. In contrast, in the case of (5)^{-•}, band B shifts to lower wavenumbers, and at the same time, band A shifts, markedly to higher wavenumbers, on limited warming. A similar but smaller spectral change was also observed on illumination. Hence, it is concluded that on controlled warming $|\theta_{\alpha \beta}|$ of (5)^{-•} is significantly increased and that on illumination a similar but smaller geometrical change occurs. Thus, the geometry of (5)^{-•} is not similar to that of (1)^{-•}—(4)^{-•} but to that of the radical ions generated from (E)- α, β -dialkylstilbenes.²

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* In the X-ray structure, $\theta_{\alpha \beta} = 0.2(3)$, $\theta_{\alpha 1} = -44.4(3)$, and $\theta_{\beta 1} = -47.4(3)^\circ$.⁵

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