BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 3294—3300 (1972) [Vol. 45, No. 11

Comparison of the Electronic Spectra of Geometric Isomers. III. β-Substituted Styrenes

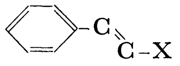
Takayuki Fueno, Kizashi Yamaguchi, and Yuji Naka*
Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka

(Received February 21, 1972)

The ultraviolet absorption spectra of *cis* and *trans* isomers of various β-substituted styrenes have been measured both in the gaseous state and in *n*-hexane solution. The excitation energies observed for *cis* isomers are either smaller or greater than those of the *trans*, depending on the type of β-substituents. The isomeric difference in the energy of the lowest allowed transition was found to be linearly correlated with Taft's steric substituent constants. The electronic states of the various isomeric pairs were calculated by the LCAO–SCF–CI method of the Pariser-Parr-Pople type. The results were found to be entirely in line with the observed spectral features.

We have previously shown that *trans* isomers of terminal-substituted butadienes and ethylenes exhibit ultraviolet absorption at greater energy than do the corresponding *cis* isomers.[1,2] It is known, on the other hand, that *cis*-stilbene has greater excitation energies than its *trans* isomer.[3] Such contradistinctive cases can be characterized by the relative importance of the *electronic* and *steric* effects of substituent groups. Thus, if the entire chromophore of a *cis* isomer is in full π-conjugation, it should show smaller excitation energy as compared with its *trans* isomer.[1,2] The situation is reversed when a *cis* isomer cannot exist in planar form as a result of the steric repulsion between the substituents. The LCAO–SCF–CI theory of the Pariser-Parr-Pople (PPP) type fully rationalizes these interpretations.[1,4]

It is to be expected that β-substituted styrenes lie in between the above two extreme cases. Some compounds of this family would resemble stilbene in their spectral feature while others would be close to the butadiene type in nature, depending on the bulkiness of the β-substituent attached. Examination of this question is the purpose of the present work. The compounds investigated are the following:



$X = CH_3$, C_2H_5, COOH, $CONH_2$, $CH{=}CH_2$, CN, OC_2H_5, or F

Spectra of the *cis* and *trans* isomers were measured in the vapor phase and in *n*-hexane solution. Expected results were obtained. The experimental results were justified by the PPP treatments.

Experimental

The β-methyl (1-phenyl-1-propene, **1**),[5] ethyl (1-phenyl-1-butene, **2**),[6] vinyl (1-phenyl-1,3-butadiene, **5**),[7] and ethoxy (styryl ethyl ether, **7**)[8] derivatives of sryrene were prepared according to the methods given in the literature. β-Fluorosryrene (**8**) was synthesized by the method of Bergmann *et al.*[9] All these compounds were then separated into geometric isomers by means of preparative gas chromatography: column packings, poly(ethylene glycol); column length, 3—5 m; operating temperature, 100—170°C; and carrier gas, hydrogen. The *cis* and *trans* isomers of cinnamic acid (**3**), cinnamide (**4**) and cinnamonitrile (**6**) were supplied by Dr. Kobuke, Kyoto University. Isomeric purity of each sample as determined by gas chromatography was no less than 95%.

All the geometric isomers were identified by the magnitudes of the NMR coupling constants observed between the ethylenic hydrogens. In the case of **8**, the HF coupling constants were also useful; $J_{\alpha F}(\text{Hz})=45$ (*cis*-**8**) and 20 (*trans*-**8**).

The absorption spectra were recorded on a Cary Model 15 spectrophotometer for both gas and solution samples at room temperature. Sample preparation and observation were carried out in the same manner as conducted previously for the butadiene derivatives.[1] Extinction coefficients were determined only for the solution spectra.

Method of Calculation

The LCAO–SCF–CI method of the Pariser-Parr-Pople type[10,11] was used to calculate the energies and oscillator strengths of the π—π* transitions. The necessary atomic parameters were taken from the tables of Hinze and Jaffé[12] and Moore,[13] and listed in a previous article.[1] The one- and two-center repulsion integrals were evaluated according to the Pariser formula[14] and the Nishimoto-Mataga[15] formula, respectively.

The off-diagonal core resonance integrals H_{rs} between

---

* Present address: Department of Chemical Engineering, Faculty of Engineering, Kyoto University, Yoshida, Kyoto.

1) T. Fueno and K. Yamaguchi, *J. Amer. Chem. Soc.*, **94**, 1119 (1972).

2) T. Fueno and K. Yamaguchi, This Bulletin, the preceding article.

3) H. Suzuki, This Bulletin, **33**, 381 (1960).

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

5) R. Adams, "Organic Reactions," Vol. 1, Wiley, New York (1957) p. 251.

6) G. Wittig and G. Harborth, *Ber.*, **77**, 319 (1944).

7) O. Grumitt and F. J. Christoph, *J. Amer. Chem. Soc.*, **73**, 3479 (1951).

8) S. I. Miller, *ibid.*, **78**, 6091 (1956).

9) F. Bergmann, A. Kalmus, and E. Breuer, *ibid.*, **80**, 4540 (1958).

10) R. Pariser and R.G. Parr, *J. Chem. Phys.*, **21**, 466, 467 (1953).

11) J. A. Pople, *Trans. Faraday Soc.*, **49**, 1375 (1953).

12) J. Hinze and H. H. Jaffé, *J. Amer. Chem. Soc.*, **84**, 540 (1962); *J. Phys. Chem.*, **67**, 1501 (1963).

13) C. E. Moore, "Atomic Energy Levels," National Bureau of Standards Circular No. 467, Vol. 1, Washington, D. C. (1949).

14) R. Pariser, *J. Chem. Phys.*, **21**, 568 (1953).

15) K. Nishimoto and N. Mataga, *Z. Phys. Chem.*, (Frankfurt), **12**, 335 (1957).

two neighboring atoms r and s were evaluated according to the Wolfsberg-Helmholtz formula[16]

$$H^0_{rs} = -\frac{\kappa}{2}S_{rs}(I_r+I_s) \qquad (1)$$

where S_{rs} is the overlap integral between the parallel Slater $p\pi$ atomic orbitals on atoms r and s, and the parameter κ values were empirically determined as to reproduce the state energies observed. The κ values finally adopted were 0.85 for compounds **3**, **5**, and **7**, and 0.9 for the rest.

We assume that molecular geometries of β-substituted styrenes are such as to be constructed schematically by replacing the vinyl group of the parent styrene with a substituted ethenyl group. The bond lengths and angles of both styrene and substituted ethylenes were taken from the literature.[17] The hyperconjugation model was assumed for the methyl group.[1] For nonplanar geometries of *cis* isomers in which the phenyl ring was assumed to be rotated out of plane, the resonance integral for the bond *t-u* connecting the benzene ring and the C=C double bond was modified to be

$$H_{tu} = H^0_{tu}\cos\theta \qquad (2)$$

where θ is the rotation angle. The coordinate axes were chosen as shown in Fig. 1.

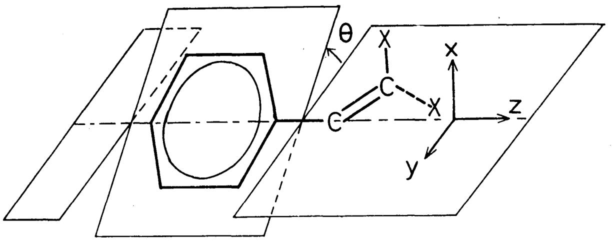


Fig. 1. Coordinate axes and conformation of *cis*-β-substituted styrenes.

The configuration interactions were treated by including lower 10 singly excited configurations. All computations were performed on a KDC-II at the Computation Center of Kyoto University.

Results and Discussion

A. Observed Spectra. Figure 2 shows the absorption spectra of the *cis* and *trans* isomers of β-methylstyrene (**1**), as an example, both in the gaseous state and in *n*-hexane solution. In either phase, the observed spectra have three bands in the wavelength range 200—300 nm. The first band appearing at about 280 nm is very weak, whereas the second (230—260 nm) and the third (~200 nm) are both strong. In the vapor spectra of the geometric isomers, we see that the second absorption peak of the *trans* isomer (λ_{max}=238 nm) is at a greater wavelength than that of the *cis* isomer (λ_{max}=233 nm). The same is true with the solution spectra. The extinction coefficient was found to be greater for *trans*-**1** (ε=17100) than for its *cis* isomer (ε=12300).

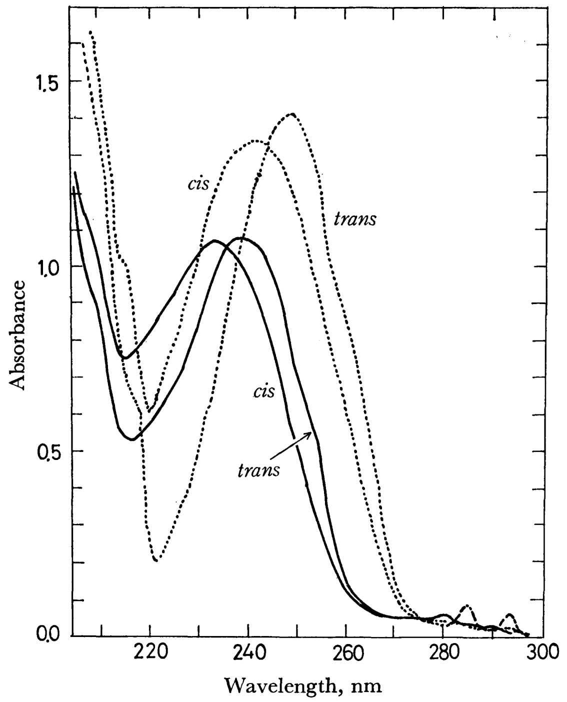


Fig. 2. Absorption spectra of *cis*- and *trans*-β-methylstyrenes (**1**) in the vapor phase (——) and in *n*-hexane solution (······). Concentration in *n*-hexane: *cis*, 106.0 μM; *trans*, 86.8 μM.

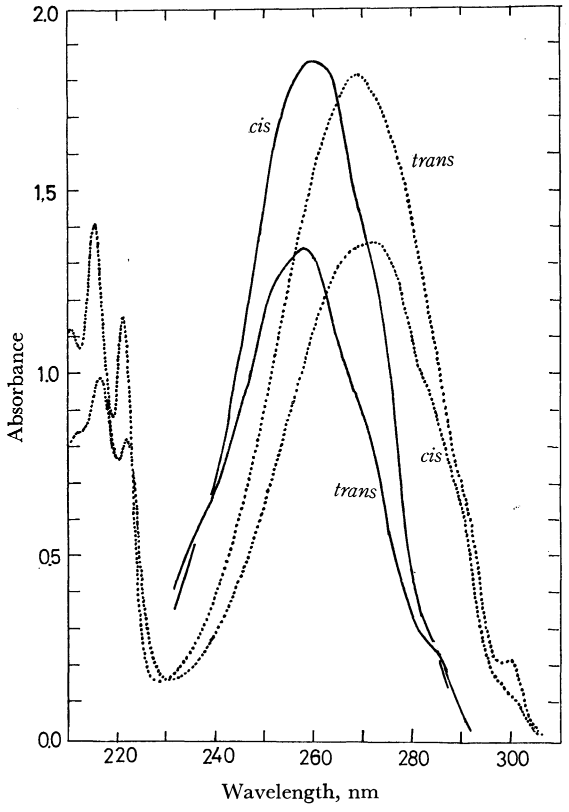


Fig. 3. Absorption spectra of *cis*- and *trans*-cinnamonitriles (**6**) in the vapor phase (——) and in *n*-hexane solution (······). Concentration in *n*-hexane: *cis*, 78.0 μM; *trans*, 91.0 μM.

The spectral features of the β-ethyl (**2**), the β-carboxy (**3**), β-carbamido (**4**) and β-vinyl (**5**) derivatives were

---

[16] M. Wolfsberg and L. Helmholtz, *J. Chem. Phys.*, **20**, 837 (1952).

[17] A. D. Mitchell, ed., "Table of Interatomic Distances and Configuration in Molecules and Ions," The Chemical Society. London (1958).

TABLE 1. SINGLET π–π^* EXCITATIONS OF β-SUBSTITUTED STYRENES

Geometry	Band	Obsd[a]				Calcd[b]				
		Δ^1E, eV		10^{-4} ε_{max}, $M^{-1}cm^{-1}$	f	Δ^1E, eV	f_z	f_y	f_x	Wt % of the most important spin configurations[c]
		Gas	Soln							
1 CH_3										
cis	1	—	—	—	—	4.878	0.000	0.000	0.000	43.0 (5—7); 42.9 (4—6)
	2	5.33	5.17	1.23	0.35	5.222	0.448	0.175	0.000	98.2 (5—6)
	3	—	—	—	—	6.373	0.000	0.184	0.099	42.6 (5—7); 42.6 (4—6)
						6.592	0.201	0.253	0.012	63.6 (4—7); 13.1 (5—8); 11.0 (3—6)
						6.616	0.000	0.000	0.000	49.0 (5—8); 50.7 (3—6)
trans	1	4.55	4.36	—	—	4.823	0.000	0.000	0	43.6 (5—7); 43.5 (4—6)
	2	5.21	5.01	1.71	0.45	5.124	0.840	0.085	0	98.7 (5—6)
	3	6.26	6.12	2.13	—	6.371	0.013	0.415	0	45.6 (5—7); 45.6 (4—6)
						6.589	0.447	0.176	0	65.4 (4—7); 13.5 (5—8); 13.2 (3—6)
						6.755	0.000	0.000	0	49.8 (5—8); 49.9 (3—6)
2 C_2H_5										
cis	1	—	—	—	—	4.656	0.000	0.000	0.000	45.4 (3—5); 45.4 (4—6)
	2	5.33	5.15	0.81	0.20	5.355	0.484	0.043	0.000	95.3 (4—5)
	3	—	—	—	—	6.334	0.104	0.226	0.113	37.3 (3—5); 37.3 (4—6); 17.4 (3—6)
						6.472	0.504	0.250	0.037	10.8 (3—5); 10.8 (4—6); 65.6 (3—6)
						6.685	0.000	0.000	0.000	48.6 (4—7); 48.6 (2—5)
trans	1	4.41	4.24	—	—	4.607	0.000	0.000	0	45.8 (3—5); 45.8 (4—6)
	2	5.15	4.98	1.68	0.41	5.219	0.568	0.043	0	96.1 (4—5)
	3	—	—			6.260	0.044	0.414	0	42.7 (3—5); 42.7 (4—6)
						6.459	0.559	0.210	0	75.2 (3—6)
						6.696	0.000	0.000	0	48.6 (4—7); 48.6 (2—5)
3 COOH										
cis	1	—	—	—	—	4.873	0.003	0.000	0.002	47.4 (5—7); 31.0 (6—8); 14.7 (5—9)
	2		4.70[d]	0.10[d]	—	4.942	0.364	0.248	0.001	97.6 (6—7)
	3		5.80[d]	1.05[d]	—	5.945	0.000	0.045	0.056	51.1 (5—7); 25.4 (6—8); 20.1 (5—9)
						6.291	0.073	0.094	0.000	58.4 (4—7); 40.1 (6—9)
						6.403	0.053	0.168	0.000	21.6 (4—7); 29.8 (6—9); 46.8 (5—8)
trans	1	—	—	—	—	4.736	0.170	0.063	0	41.2 (5—7); 26.7 (6—8); 20.6 (6—7)
	2		4.54[d]	0.2[d]	—	4.682	0.667	0.094	0	78.5 (6—7); 13.9 (5—7)
	3		5.77[d]	1.5[d]	—	6.061	0.000	0.248	0	42.0 (5—7); 45.0 (6—8)
						6.387	0.142	0.139	0	21.7 (4—7); 33.5 (6—9); 41.6 (5—8)
						6.432	0.044	0.064	0	59.1 (4—7); 38.7 (6—9)
4 $CONH_2$										
cis	1	—	—	—	—	4.958	0.003	0.004	0.001	42.5 (5—7); 35.6 (6—8); 12.6 (5—9)
	2		4.79[d]	—	—	5.146	0.421	0.229	0.001	96.5 (6—7)
	3	—	—	—	—	6.077	0.057	0.153	0.003	85.1 (4—7)
						6.178	0.000	0.067	0.096	52.9 (5—7); 28.9 (6—8); 13.7 (5—9)
						6.412	0.022	0.056	0.000	64.8 (6—9); 30.5 (5—8)
trans	1	—	4.15[d]	—	—	4.794	0.269	0.018	0	32.3 (6—7); 39.1 (5—7); 20.2 (6—8)
	2		4.62[d]	—	—	4.841	0.550	0.131	0	66.5 (6—7); 14.6 (5—7); 14.5 (6—8)
	3	—	—	—	—	6.129	0.008	0.090	0	32.7 (5—7); 34.0 (6—8); 25.9 (4—7)
						6.196	0.018	0.382	0	12.1 (5—7); 11.7 (6—8); 68.1 (4—7)
						6.480	0.119	0.050	0	56.0 (6—9); 41.6 (5—8)
5 $CH=CH_2$										
cis	1	—	—	—	—	4.679	0.000	0.000	0.000	33.7 (4—6); 16.3 (4—8); 16.3 (3—7)
	2	4.94	4.71	—	—	4.871	0.466	0.359	0.000	97.8 (5—6)
	3	—	—	—	—	5.941	0.000	0.000	0.000	50.0 (5—6); 49.4 (5—8)
						6.010	0.002	0.037	0.110	42.6 (4—6); 42.7 (6—7)
						6.098	0.051	0.331	0.015	23.3 (3—6); 23.3 (5—8); 38.1 (4—7)
trans	1	4.13[f]	—	—	—	4.565	0.000	0.000	0	39.6 (4—6); 39.6 (5—7); 10.4 (3—7); 10.4 (4—8)
	2	4.71[f]	4.43[g]	—	—	4.602	0.899	0.197	0	98.9 (5—6)
	3	—	—	—	—	5.979	0.007	0.272	0	44.5 (4—6); 44.6 (5—7)
						6.047	0.000	0.000	0	49.7 (3—6); 49.6 (5—8)
						6.109	0.151	0.329	0	26.7 (3—6); 26.6 (5—8); 35.8 (4—7)

Geometry	Band	Obsd[a]				Calcd[b]				
		Δ^1E eV		10^{-4} $\varepsilon_{\max}$, $M^{-1}cm^{-1}$	f	Δ^1E, eV	f_z	f_y	f_x	Wt % of the most important spin configurations[c]
		Gas	Soln							
6 CN										
cis	1	—	—	—	—	4.764	0.084	0.085	0	22.9 (5—6); 36.3 (4—6); 30.7 (5—7)
	2	4.76	4.55	1.71	0.28	4.689	0.273	0.174	0	75.0 (5—6); 17.7 (4—6)
	3	—	5.72	1.25	—	6.006	0.002	0.190	0	42.3 (4—6); 40.4 (5—7); 10.7 (4—8)
						6.316	0.017	0.000	0	64.9 (5—8); 31.7 (3—6)
						6.485	0.041	0.232	0	30.5 (3—6); 49.0 (4—7)
trans	1	—	4.13	0.13	—	4.778	0.015	0.000	0	48.1 (4—6); 34.9 (5—7); 10.1 (4—8)
	2	4.80	4.61	1.99	0.32	4.841	0.993	0.100	0	97.6 (5—6)
	3	—	5.75	1.56	—	6.211	0.002	0.358	0	47.3 (4—6); 45.9 (5—7)
						6.450	0.230	0.066	0	44.6 (5—8); 47.6 (4—7)
						6.548	0.105	0.035	0	27.8 (5—8); 65.4 (3—6)
7 OC_2H_5										
cis	1	—	4.21	—	—	4.560	0.002	0.001	0	51.7 (5—7); 38.6 (4—6)
	2	4.93	4.74	1.64	0.40	4.989	0.545	0.070	0	96.3 (5—6)
	3	—	6.15	1.37	—	6.085	0.007	0.329	0	43.5 (5—7); 41.7 (4—6)
						6.383	0.297	0.106	0	64.7 (4—7); 28.8 (3—6)
						6.530	0.153	0.041	0	11.3 (4—7); 54.0 (5—8)
trans	1	—	4.13	—	—	4.569	0.000	0.000	0	63.7 (5—7); 39.7 (4—6)
	2	4.94	4.78	2.30	0.54	5.021	0.624	0.059	0	97.0 (5—6)
	3	—	~6.2	—	—	6.125	0.011	0.365	0	44.5 (5—7); 43.1 (4—6)
						6.385	0.392	0.109	0	70.0 (4—7); 22.5 (3—6)
						6.549	0.092	0.030	0	35.8 (3—6); 54.4 (5—8)
8 F										
cis	1	—	4.32	—	—	4.837	0.001	0.001	0	51.3 (5—7); 40.5 (4—6)
	2	5.31	5.14	—	—	5.320	0.573	0.060	0	96.2 (5—6)
	3	—	—			6.426	0.014	0.404	0	43.0 (5—7); 43.4 (4—6)
						6.707	0.457	0.157	0	74.4 (4—7); 15.5 (3—6)
						6.936	0.073	0.015	0	42.4 (3—6); 50.8 (5—8)
trans	1	4.43	4.26	—	—	4.845	0.000	0.001	0	50.2 (5—7); 41.5 (4—6)
	2	5.32	5.15	—	—	5.347	0.630	0.053	0	96.8 (5—6)
	3	—	—	—	—	6.458	0.018	0.439	0	43.8 (5—7); 44.7 (4—6)
						6.702	0.515	0.150	0	76.2 (4—7); 12.7 (3—6)
						6.958	0.043	0.012	0	44.5 (3—6); 50.8 (5—8)

a) The extinction coefficients $\varepsilon_{\max}$ and oscillator strengths f were determined from the spectra in solution. Solvent is *n*-hexane, unless otherwise noted.

b) The rotation angle of the phenyl ring in *cis* isomers (Fig. 1) was assumed to be: 30° for **1** and **2**; 45° for **3**, **4**, and **5**; and 0° for **6**, **7**, and **8**.

c) The symbol (*i*—*j*) indicates the singlet spin configuration resulting from the one-electron transition from the *i*th to the *j*th molecular orbital of the ground-state configuration.

d) In ethanol.

f) R. J. Dolter and C. Curran, *J. Amer. Chem. Soc.*, **82**, 4155 (1960).

g) Ref. 7.

found to be essentially the same as those of **1**. All the data observed for compounds **1** to **5** are summarized in Table 1.

The spectra of cinnamonitrile (**6**) shown in Fig. 3 are in contrast to those of β-methylstyrene. The second ultraviolet absorption of the *trans* isomer ($\lambda_{\max}=269$ nm) occurs at a shorter wavelength than that of the *cis* isomer ($\lambda_{\max}=272$ nm). The tendency is the reverse of that found for **1**.

The β-ethoxy (**7**) and β-fluoro (**8**) derivatives are similar to **6** in their spectral feature (Figs. 4 and 5); the second bands of *cis* isomers are shifted, though only slightly, to longer wavelength relative to the *trans*. The bands show considerable vibrational structure, indicating a planar conformation. The spectral data for **6**, **7**, and **8** are also given in Table 1.

The second excitation energy Δ^1E_2 of the *cis* isomers relative to the *trans* appears to be correlated with the steric repulsion between the *cis* β-substituent and the phenyl group. The isomeric differences

$$\delta\Delta^1E_2 = \Delta^1E_2(cis) - \Delta^1E_2(trans) \tag{3}$$

for the various β-substituted styrenes including stilbene are given in Table 2, together with the steric substituent constants E_s[18] available for the β-substituents. The steric repulsion is the greatest in *cis*-stilbene. The negative values of $\delta\Delta^1E_2$ found for **6**, **7**, and **8** might

---

[18] R. W. Taft, in "Steric Effects in Organic Chemistry," ed., M. S. Newman, Wiley, New York, N. Y. (1956), Chapter 13.

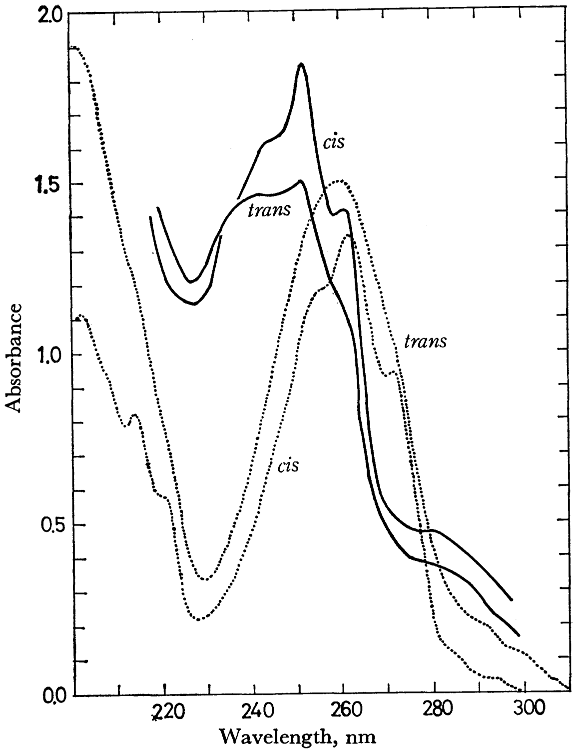


Fig. 4. Absorption spectra of *cis*- and *trans*-β-styryl ethyl ethers (**7**) in the vapor phase (——) and in *n*-hexane solution (……). Concentration in *n*-hexane: *cis*, 81.1 μM; *trans*, 65.2 μM.

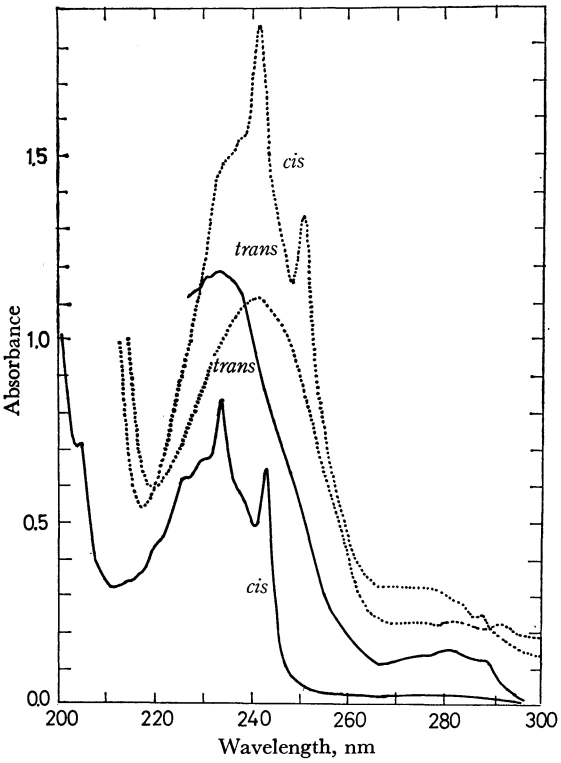


Fig. 5. Absorption spectra of *cis*- and *trans*-β-fluorostyrenes (**8**) in the vapor phase (——) and in *n*-hexane solution (……).

indicate the electronic effect of *cis* substitutions surpassing their steric contribution.

Plots of $\delta\Delta^1E_2$ against E_s give a good linear relationship (Fig. 6). The solution data are better correlated with E_s than are the gas-phase data, the regression line being obtained by use of only the former. The linearity in turn permits estimation of the E_s values for substituents for which no such data are available as yet. The estimated values are −0.65, −0.17, 0.00, and 0.90 for the groups CH=CH$_2$, CONH$_2$, COOH, and CN, respectively.

Table 2. Differences between the second excitation energies of *cis*- and *trans*-β-substituted styrenes

Substituent[a]	$\delta\Delta^1E_2$, eV[b] Gas	Soln	E_s[c]
C_6H_5	—	0.34[d]	−0.90
CH=CH$_2$	0.23	0.28	
CONH$_2$	—	0.17	
C_2H_5	0.18	0.17	−0.07
CH_3	0.12	0.16	0.00
COOH	—	0.16	
F	−0.01	-0.00_5	0.49
OC$_2$H$_5$	−0.01	−0.04	0.90
CN	−0.04	−0.06	

a) Substituents are listed in decreasing order of $\delta\Delta^1E_2$ in solution.

b) Eq. (3).

c) Steric substituent constants defined from the hydrolysis rates of *o*-substituted benzoic esters (except for C_2H_5, for which the value derived from aliphatic esters has been adopted).[18]

d) The energies corresponding to the Δ^1E_2 are 4.56 (in ethanol) and 4.22 eV (in heptane) for the *cis* and *trans* isomers, respectively.[3]

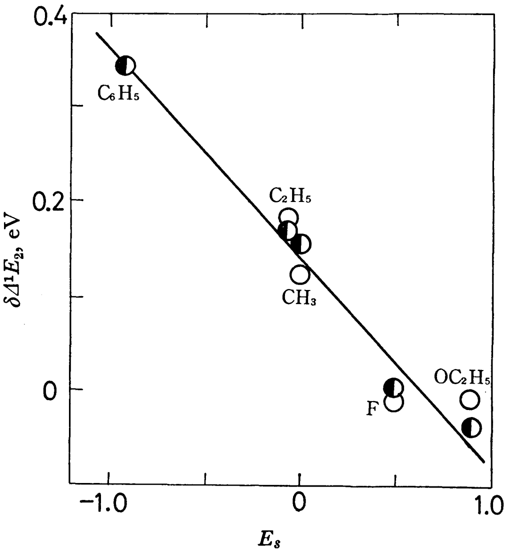


Fig. 6. Linear correlation of $\varepsilon\Delta^1E_2$ with E_s. ○, gas phase; ◐, solution.

B. Electronic States. *cis*- and *trans*-β-methylstyrenes (**1**) were first treated. Figure 7 gives the energy diagram of *trans*-**1** before and after configuration interactions. Each state is characterized as if the molecule were of the C_{2v} symmetry with respect to its pseudo-long axis (z). The transition to the lowest $^1B_2$ state is forbidden, while the second transition to the $^1A_1$ state is allowed. The third ($^1B_2$) and fourth ($^1A_1$) transitions are both allowed and are situated close to each other. The calculated results are consistent

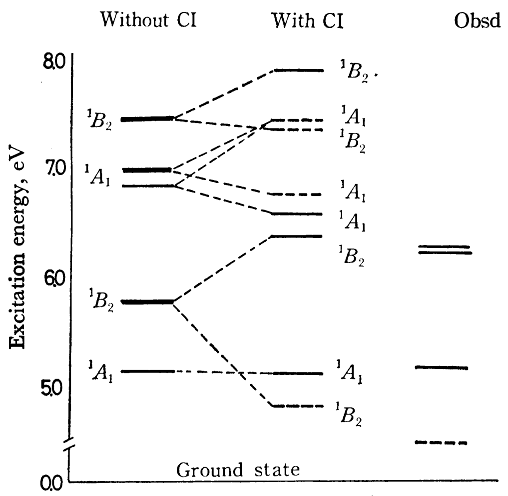


Fig. 7. Energy diagram of *trans*-β-methylstyrene.
——, allowed; ----, forbidden.

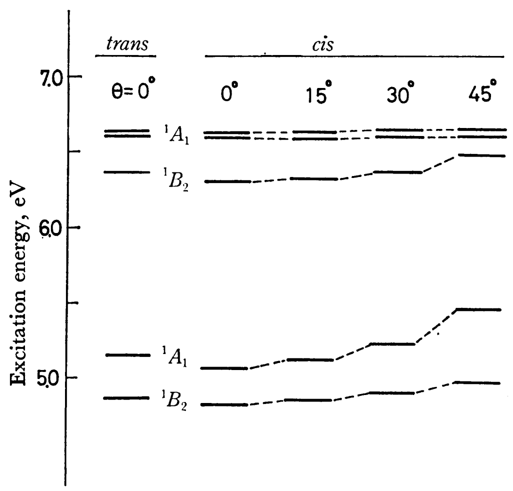


Fig. 8. Dependences of the calculated excitation energies of *cis*-β-methylstyrene on the out-of-plane rotation angle θ of the phenyl ring.

with the observed spectrum.

Fugure 8 illustrates the dependences on θ of the excitation energies calculated for *cis*-**1**. The energies cannot exceed those of the *trans* isomer unless θ is greater than 20°. The angular dependence of energy is the largest for the second excited state. The calculated value of the second excitation energy Δ^1E_2 for *cis*-**1** relative to *trans*-**1** was found to be in best agreement with the observed gas-phase value, when θ was assumed to be 30°.

The excitation energies and oscillator strengths culculated for the *cis* ($\theta=30°$) and *trans* ($\theta=0°$) isomers of **1** are listed in Table 1, together with the weight% of the spin configurations which most importantly contribute to each electronic state. For either isomer the second excited state is well represented by the spin configuration $^1\Phi_{5,6}$ alone, which corresponds to the one-electron transition from the highest occupied (*h*) to the lowest vacant (*l*) obrital in the ground configuration. On the other hand, both the first and third excited states are described as superpositions of two configurations, $\Phi_{5,7}$ and $\Phi_{4,6}$, where the orbitals ψ_4 and ψ_7 respectively denote the next-highest occupied and next-lowest vacant levels, which are essentially localized in the phenyl ring. Thus, the first and third bands are considered to be analogs of the $^1B_{2u}$ and $^1E_{2u}$ bands of benzene, respectively, whereas the second band ($^1A_1$) is characteristic of the entire chromophore of **1**. It is natural that the Δ^1E_2 value calculated should be the most sensitive to the conformational change of the molecular framework.

Analogous calculations have been performed for all the remaining compounds. The results are summarized in Table 1. For every isomeric compound studied, the second π—π^* excitation is allowed and well represented by a single spin configuration, which corresponds to the electronic promotion from orbital *h* to *l*. However, *trans*-**3** and *cis*-**6** are somewhat unusual in this respect. For compounds **1** through **5**, the deformations of the *cis* isomers were necessary to reproduce their increments in Δ^1E_2 value relative to the *trans* isomers. For compounds **6**, **7**, and **8** on the other hand, the planar structure ($\theta=0°$) was found to be plausible even for *cis* isomer.

Numerical agreement between theory and experiment is good for the second band energies but less satisfactory for the first and third bands. Nonetheless, we may be content with the present results in view of the limited accuracy of the virtual orbital approximation.

The oscillator strengths calculated were larger for *trans* isomers than for the corresponding *cis* isomers. The results are in good agreement with those found experimentally. It deserves special mention that the oscillator strengths are larger for *trans* isomers in all the three systems investigated (ethylenes, butadienes, and styrenes). Their values are most reliable in discriminating geometric isomers.

C. Structural Effect on Δ^1E_2. Elucidation of the structural effect on Δ^1E_2 can be achieved most expediently by analyzing the configurational energy $\Delta^1E_2{}^0$. In the PPP approximation, the energy is given by

$$\Delta^1E_2{}^0 = \varepsilon_l - \varepsilon_h - J_{hl} + 2K_{hl} \tag{4}$$

where ε_l and ε_h are the energies of the lowest vacant and highest occupied orbitals, respectively, and where J_{hl} and K_{hl} are the inter-frontier-orbital Coulomb and exchange repulsions, respectively.

Variations of these energy terms with structure are diagrammatically shown in Fig. 9, taking β-methylstyrene as an example. It can be seen that the energy gap $\Delta\varepsilon_{hl}$ between the frontier orbitals for the hypothetical planar *cis* isomer ($\theta=0°$) is essentially equal to that for the *trans* isomer. The K_{hl} terms are also nearly equal for both isomers. Clearly, it is the J_{hl} term that would lower the $\Delta^1E_2{}^0$ for the planar *cis* isomer relative to the *trans*. As θ for the *cis* isomer increases, however, its ε_l increases while ε_l decreases monotonically. The progressive spread of the gap with θ tends to counterbalance the increase in the term ($J_{hl}-2K_{hl}$). The relative magnitudes of $\Delta^1E_2{}^0$ for the two isomers are thus offset when θ is greater than about 20°. Note that the variation of $\Delta^1E_2{}^0$ with structure is essentially the same as that of Δ^1E_2 shown in Fig. 8. Incidentally, the considerable lowering in ε_h with θ is compatible with the observation that the vertical

Table 3. Contributions of various energy terms to the configurational energy $\Delta^1E_2^0$ (eV)

No.	X	Geometry	Angle, deg	$\Delta\varepsilon_{hl}$	J_{hl}	K_{hl}	$\Delta^1E_2^0$	Δ^1E_2
1	CH_3	*cis*	30	8.229	4.778	0.899	5.248	5.222
		trans	0	7.992	4.731	0.942	5.145	4.124
2	C_2H_5	*cis*	30	8.367	5.023	1.040	5.420	5.355
		trans	0	8.157	5.208	1.078	5.286	5.219
3	COOH	*cis*	45	7.976	4.597	0.797	4.972	4.942
		trans	0	7.500	4.628	0.877	4.711	4.682
4	$CONH_2$	*cis*	45	8.165	4.754	0.881	5.172	5.146
		trans	0	7.649	4.628	0.911	4.843	4.841
5	$CH=CH_2$	*cis*	45	7.760	4.733	0.920	4.904	4.871
		trans	0	7.335	4.573	0.930	4.622	4.602
6	CN	*cis*	0	7.684	4.666	0.862	4.743	4.689
		trans	0	7.667	4.572	0.887	4.869	4.841
7	OC_2H_5	*cis*	0	7.964	4.957	1.025	5.056	4.989
		trans	0	7.961	4.943	1.032	5.082	5.021
8	F	*cis*	0	8.310	5.000	1.039	5.389	5.320
		trans	0	8.305	4.986	1.044	5.409	5.347

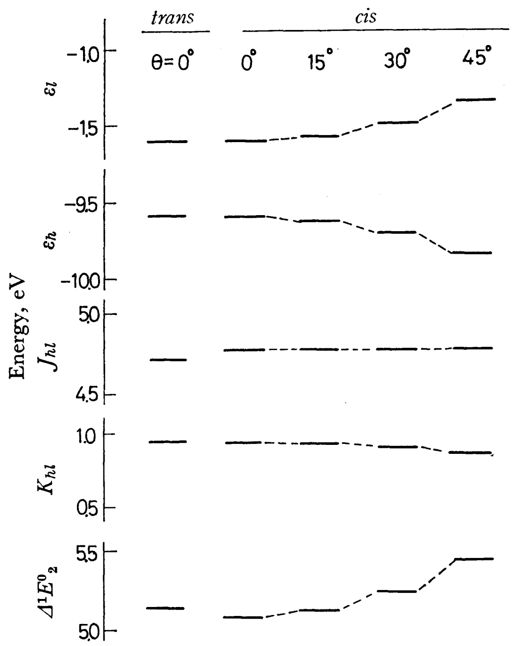


Fig. 9. Concentrations of various energy terms to $\Delta^1E_2^0$ of *cis*- and *trans*-β-methylstyrenes.

ionization potential of *cis*-**1** is greater than that of *trans*-**1** by as much as 0.11 eV.[2]

Exactly the same situation is encountered with all the remaining compounds. In order for the calculated isomeric differences of $\Delta^1E_2^0$ to agree with the observed, rotational angles of $\theta=30°$ (for **1** and **2**) and $\theta=45°$ (for **3**, **4**, and **5**) had to be assumed. For compounds **6**,**7**, and **8**, on the other hand, $\theta=0°$ sufficed to interpret the observed differences. The results of calculations for these conformations are given in Table 3. The relative magnitudes of $\Delta^1E_2^0$ remain much the same as those of Δ^1E_2.

The lower excitation energies for the *cis* isomers of **6**, **7**, and **8** as compared with the *trans* counterparts are noteworthy. We have previously interpreted the lower excitation energies of planar *cis* isomers to imply that they experience greater relief from intramolecular electronic repulsion upon excitation.[1] An alternative interpretation may be possible if the promoted electron is considered to be under the Coulombic field of the rest of the molecule. Withdrawal of an electron from orbital *h* of a molecule would leave an electron hole which is distributed over the molecule with partial positive charges. When the electron withdrawn is placed in orbital *l*, it is subjected to Coulombic attraction ($-J_{hl}$) from the hole. Apparently, the electron-hole attraction is larger for *cis* isomers, for which the molecular framework is relatively compact. We feel that the latter interpretation is of conceptual importance, particularly because it can readily be extended to intermolecular charge-transfer interactions.

Conclusion

The second excitation energy Δ^1E_2 of *cis*-β-substituted styrenes is either smaller or greater than that of the *trans* isomers, depending on the nature of the β-substituents. The relative magnitudes are well correlated with the steric substituent effects. PPP calculations taking account of the out-of-plane rotation of the phenyl group lead to results which are compatible with observation. The greater Δ^1E_2 values for *cis* isomers are attributable to their greater inter-frontier-orbital energy gap due to the steric hindrance between the substituent groups. The smaller values of Δ^1E_2 for presumably planar *cis* isomers can be understood from the concept of intramolecular electron-hole Coulombic attractions.