# *Relations between Electronic Absorption Spectra and Spatial Configurations of Conjugated Systems. VIII. Stilbene Derivatives with Methyl Groups on the Benzene Nuclei*

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The method developed in Part V¹⁾ of this series is applied to some stilbene derivatives with methyl groups on the benzene nuclei. With such compounds, the electronic bathochromic effect of the methyl groups on the benzene nuclei should not be ignored. Accordingly, an allowance for this effect is made, analogously to the case of *o*-alkyl- and *o,o'*-dialkylbiphenyls in Part II²⁾ of this series, by choice of the references for correlation between the calculated transition energy $\Delta E_A$ and the observed wave number $\nu_A$ of the conjugation band.

**4-Methyl- and 4, 4'-Dimethyl-*trans*-stilbene.**—In order to determine the longer-wave-length-side reference, the ultraviolet absorption spectra of 4-methyl- and 4, 4'-dimethyl-*trans*-stilbene in *n*-heptane were measured. The results are shown in Table I and Fig. 1. The spectra resemble the spectrum of *trans*-stilbene, on the whole showing fine structures (cf. Table I and Fig. 1 in Part V). The introduction of a methyl group into a para-position of *trans*-stilbene causes the red-shift of about 4.2 mμ of the maxima of the conjugation band, and the introduction of the second methyl group into the other para-position results in a further red-shift of about 3 mμ.

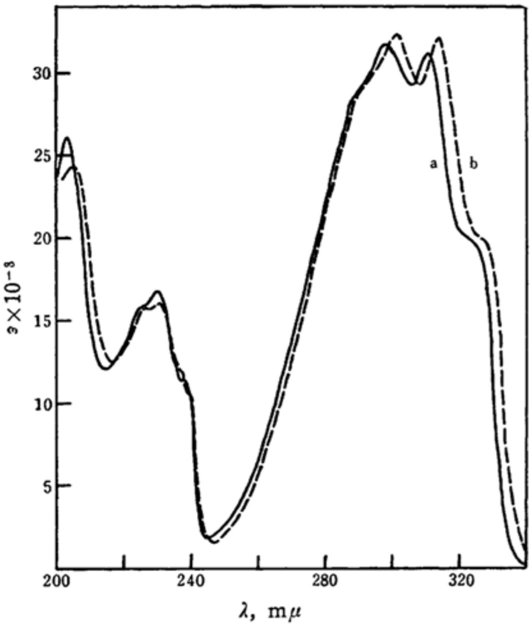

Fig. 1. Ultraviolet absorption spectra (in *n*-heptane): a ——, 4-methyl-*trans*-stilbene; b ------, 4, 4'-dimethyl-*trans*-stilbene.

**4,4',α,α'-Tetramethylstilbene.**—According to Nagai and Simamura³⁾, the spectrum of *trans*-4, 4', α, α'-tetramethylstilbene shows the absorption maximum at 245 mμ ($\varepsilon$=15000), and that of the *cis* isomer shows the maximum at 258 mμ ($\varepsilon$=10000). These maxima are considered as the conjugation bands. Thus, with these compounds, similarly to α, α'-dimethylstilbene⁴⁾, the conjugation band of the *cis* isomer is at a longer wavelength and of lower intensity than that of the *trans* isomer.

In application of our method to these compounds, the possible bathochromic effect of the α- and α'-methyl groups is provisionally ignored for the same reasons as in the preceding part⁴⁾ of this series, and then, in order to make allowance for the bathochromic effect of the *p*- and *p'*-methyl groups, *trans*-4, 4'-dimethylstilbene is taken as the longer-wavelength-side reference compound. That is, the value of $\nu_L$ [wave number corresponding to the calculated transition energy for planar *trans*-stilbene, $\Delta E_L$, 1.1423 ($-\beta$)] is assumed in this case to be 33190 cm⁻¹ (301.3 mμ, the γ-band of *trans*-4, 4'-dimethylstilbene). On the other hand, as the shorter-wave-length-side reference, the value for toluene corresponding to the center of gravity of singlets of benzene is taken. That is, the value of $\nu_S$ [wave number corresponding to the value of $\Delta E_A$ when $\rho$ is 0, $\Delta E_S$,

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1) H. Suzuki, This Bulletin, **33**, 379 (1960).
2) H. Suzuki, ibid., **32**, 1350 (1959).
3) Y. Nagai and O. Simamura, presented at the 11th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1958.
4) H. Suzuki, This Bulletin, 33, 396 (1960).

TABLE I. ABSORPTION MAXIMA OF METHYLATED STILBENES (IN *n*-HEPTANE)

| Compound | A-band | | B-band | | C-band | |
|---|---|---|---|---|---|---|
| | λ, mμ | ε | λ, mμ | ε | λ, mμ | ε |
| 4-Methylstilbene | α (324.5) | 19800 | (238.0) | 11450 | 203.3 | 26100 |
| | β 311.2 | 31200 | △230.2 | 16800 | | |
| | γ △298.3 | 31800 | (225.0) | 15800 | | |
| | δ (292.0) | 29550 | | | | |
| 4,4′-Dimethylstilbene | α (327.5) | 19900 | (239.5) | 10550 | 204.8 | 24350 |
| | β 314.2 | 32100 | (237.0) | 11980 | | |
| | γ △301.3 | 32400 | △230.7 | 16100 | | |
| | δ (293.5) | 29950 | 225.9 | 15730 | | |
| 2,4,6-Trimethylstilbene | 282.7 | 19200 | | | 208.5 | 29600 |
| | | | | | 201.5 | 29700 |
| 2,4,6,2′,4′,6′-Hexamethylstilbene | 262.7 | 16000 | | | 214.0 | 35700 |

Wavelengths in parentheses denote inflections.
Symbol △ denotes the most intense maximum of fine structure.

TABLE II. RESULTS OF CALCULATION

| Compound | $\lambda_A$ mμ | $\Delta E_A$ $-\beta$ | $\rho$ | $\theta°$ | $R$ Å | $R.E.$ $-\beta$ | $p_{\alpha-\alpha'}$ |
|---|---|---|---|---|---|---|---|
| *trans*-Stilbene | 294.1 | 1.1423 | 0.9084 | 0 | 1.445 | 0.704 | 0.856 |
| *trans*-4,4′,α,α′-Tetramethylstilbene | 245 | 1.620 | 0.404 | 61 | 1.494 | 0.140 | 0.970 |
| *cis*-4,4′,α,α′-Tetramethylstilbene | 258 | 1.491 | 0.530 | 51.7 | 1.481 | 0.242 | 0.948 |
| *trans*-2,4,6,2′,4′,6′-Hexamethylstilbene | 262.7 | 1.523 | 0.498 | 54.3 | 1.485 | 0.212 | 0.954 |

2(−β)] is assumed to be 46882 cm$^{-1}$ (213.3 mμ) (cf. Table II in Part II).

On the basis of the above references, calculation by the usual method has been carried out. The results are shown in Table II, in which the notation is the same as in Part V of this series. The calculated values of the interplanar angle θ (the angle of twist of each "single" bond) for *trans*- and *cis*-4,4′,α,α′-tetramethylstilbenes agree fairly well with the values for *trans*- and *cis*-α,α′-dimethylstilbenes (58° and 51.5°), respectively (cf. Table II in the preceding part of this series).

**2,4,6-Trimethyl- and 2,4,6,2′,4′,6′-Hexamethyl-*trans*-stilbene.**—The ultraviolet absorption spectra of 2,4,6-trimethyl-*trans*-stilbene (*trans*-1-mesityl-2-phenylethylene) and 2,4,6,2′4′,6′-hexamethyl-*trans*-stilbene (*trans*-1,2-dimesitylethylene) measured in *n*-heptane are shown in Table I and Fig. 2. A comparison of these spectra with the spectrum of *trans*-stilbene[1)] reveals that the conjugation band shifts progressively toward shorter wavelengths and reduces the intensity with the increasing number of methyl substituents. This fact is undoubtedly due to the steric interferences

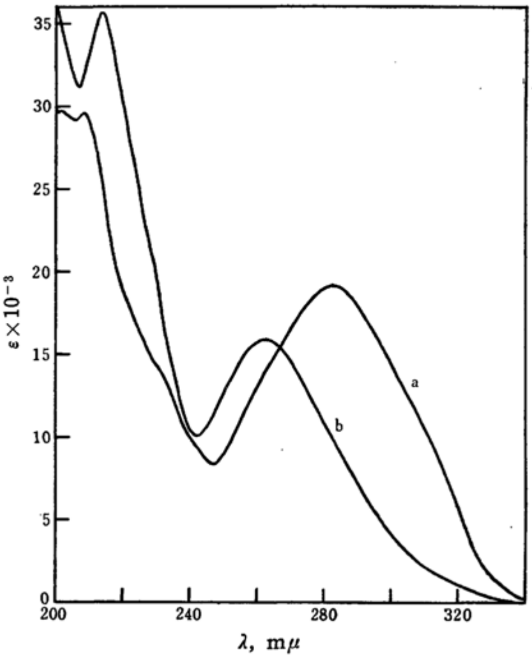

Fig. 2. Ultraviolet absorption spectra (in *n*-heptane): a, 2,4,6-trimethyl-*trans*-stilbene; b, 2,4,6,2′,4′,6′-hexamethyl-*trans*-stilbene.

of the substituents which prevent the molecule from assuming a planar configuration. It is noteworthy that the conjugation bands of these substituted stilbenes have, similarly to those of *cis*-stilbene[1] and $\alpha$-substituted stilbenes[4], no fine structure, in contrast to that of *trans*-stilbene.

Now, it is assumed that the mean value of the magnitude of the red-shift of the conjugation band caused by substitution of a methyl group at the *o*- or *p*-position of *trans*-stilbene is 3 m$\mu$, and that the effect of methyl substitution is additive analogously to the case of methylbenzenes[5]. Then if the configuration of dimesitylethylene were planar, this compound whould show the conjugation band at a longer wavelength than that of *trans*-stilbene by about 18 m$\mu$ ($3\times6$ m$\mu$). That is, the conjugation band of the hypothetical planar molecule of this compound would be at about 312 m$\mu$ (294+18 m$\mu$). Accordingly, the value of $\nu_L$ is assumed in this case to be 32051 cm$^{-1}$ (312 m$\mu$).

On the other hand, as the shorter-wavelength-side reference compound, mesitylene is taken. While the approximate center of the low-intensity band of benzene in the region between 230 and 270 m$\mu$ is at 255 m$\mu$, the corresponding one of mesitylene is at 266 m$\mu$[6]. In addition, while the 0–0 band of benzene is at 262.54 m$\mu$, that of mesitylene is at 274.06 m$\mu$[5]. That is, the band of mesitylene is at longer wavelengths by about 11 or 11.5 m$\mu$ than that of benzene. On the analogy of the case of toluene as well as ethylbenzene (cf. Table II in Part II), it may be considered that the other bands of mesitylene are probably at longer wavelengths by about 11 or 11.5 m$\mu$ than the corresponding bands of benzene. Accordingly, the value for mesitylene corresponding to the center of gravity of singlets of benzene (48000 cm$^{-1}$, 208.3 m$\mu$) is presumed to be 45600 cm$^{-1}$ (219.3 m$\mu$= 208.3+11 m$\mu$). Therefore, the value of $\nu_S$ for treatment of dimesitylethylene is assumed to be 45600 cm$^{-1}$.

The results of calculation carried out by the usual procedure on the basis of the above references are shown in Table II. From scale models, it is inferred that the interplanar angle in *trans*-dimesitylethylene should be approximately equal to that in *trans*-$\alpha,\alpha'$-dimethylstilbene. The value calculated here is slightly smaller than that for dimethylstilbene; still it may be said that the agreement is fairly good.

2,4,6-Trimethylstilbene is unsymmetrical, so that the two interplanar angles should be different, and therefore, the resonance integral for the Mes–C bond and that for the Ph–C bond should be different from one another. Therefore, the present method can not be applied to this compound. However, it must be sure that this compound is nonplanar, since the conjugation band is at a considerably shorter wavelength than that of *trans*-stilbene. On the basis of the above assumption that the red-shift caused by a *p*- or *o*-methyl group is about 3 m$\mu$, it is presumed that the conjugation band of this compound would be at about 273.7 m$\mu$ (282.7 − 9 m$\mu$) if it were not for the red-shift by the electronic effect of the methyl groups. It is of interest that this presumed position coincides almost completely with the observed position of the conjugation band of *trans*-$\alpha$-methylstilbene (273.5 m$\mu$)[4]. It may, therefore, be presumed that the value of the extra-resonance energy *R. E.* of mesitylphenylethylene is approximately equal to that of $\alpha$-methylstilbene [0.457 $(-\beta)$][4] and hence is smaller than that of *trans*-stilbene. This presumption seems to be supported by the following fact. According to Everard and others[7], the exaltation of molecular refraction of *trans*-stilbene is +6.6, and that of 2,4,6-trimethylstilbene is smaller by 1.3 than that of *trans*-stilbene. This fact is considered to indicate that the extent of conjugation is smaller in trimethylstilbene than in stilbene.

Everard and Sutton[8] have found with 4-dimethylaminostilbenes a similar depression of the exaltation caused by *o*-substituents attributable to steric inhibition of resonance. According to them, the exaltation of 4-dimethylaminostilbene is 7.5, and, on the other hand, the values for its 2,2′-dimethyl- and 2′,4′,6′-trimethyl-derivatives are 3.3 and 1.6, respectively (the values of the exaltation are expressed relative to that of *trans*-stilbene). The value for the 2′-chloro-derivative is much the same as that for the parent compound, indicating that there is negligible inhibition of conjugation in the chloro-compound in contrast to the methyl compounds.

4-Dimethylaminostilbene and related compounds have been studied by several

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[5] K. F. Herzfeld, *Chem. Revs.*, **41**, 233 (1947).

[6] A. E. Gillam and E. S. Stern, "An Introduction to Electronic Absorption Spectroscopy", 2nd Ed., Edward Arnold Publishers, Ltd., London (1957), p. 134.

[7] K. B. Everard, L. Kumar and L. E. Sutton. *J. Chem. Soc.*, **1951**, 2807.

[8] K. B. Everard and L. E. Sutton, ibid., **1951**, 2816.

workers in England, probably in connection with the carcinogenic activity. Haddow and others⁹⁾ have found that the derivatives of 4-dimethylaminostilbene with methyl groups at two *o*-positions in a benzene nucleus are biologically ineffective probably because of the nonplanarity of the molecular configurations of these compounds. Beale and Roe¹⁰⁾ have found that the oscillator strength of the longest wavelength band (conjugation band) of *trans*-stilbene as well as 4-dimethylaminostilbene is markedly lowered by substitution of methyl groups at the *o*-positions. Thus, in the 2′-position a methyl group causes a decrement of 0.04 in *f*-value, and successive introductions of further methyl groups into the *o*-positions cause larger decrements in *f* of magnitude varying with the position of substitution. This effect has been attributed to the steric hindrance to planarity of the molecular configuration.

Regarding the reactions of the *o*-methyl substituted stilbenes, only a few data are available. According to the present author's preliminary study¹¹⁾, the rate of bromination of 2, 4, 6-trimethylstilbene in carbon tetrachloride is markedly greater than that of trans-stilbene, even when a little catechol is added to suppress the retarding effect of atmospheric oxygen⁴⁾. The high reactivity of trimethylstilbene as compared with stilbene is probably partly due to the larger $\pi$-bond order of the ethylenic bond or the lower bond localization energy in trimethylstilbene relative to stilbene.

On the other hand, according to Fuson and others¹²⁾, the reactivity to potassium permanganate falls in the order *trans*-stilbene> 2, 4, 6-trimethylstilbene> 2, 4, 6, 2′, 4′, 6′-hexamethylstilbene. Thus, when 0.1 cc. of a 2% solution of potassium permanganate in water is added to a solution of 0.05 g. of the stilbene in 4 cc. of acetone, the time required for discharging the permanganate color is as follows: *trans*-stilbene, less than one minute; trimethylstilbene, four and one-half hours; hexamethylstilbene, 60 hr. In the methylated stilbenes, there should be a considerably large steric hindrance to the approach of the reagent to the ethylenic bond due to the mesityl or phenyl groups rotated out of the plane of the ethylenic bond. The order of the reactivity can be considered to be in conformity with the magnitude of the steric hindrance.

## Experimental

All the spectra were measured with a Cary recording spectrophotometer Model 14 M-50.

*p*-Methylstilbene was prepared by the Meerwein reaction, quite analogously to the synthesis of *p*-methoxystilbene described in Part V of this series. From 53.5 g. of *p*-toluidine, 25.8 g. of the purified product, colorless crystals melting at 121∼122°C, was obtained after repeated recrystallization from ethanol (26.5% of the theoretical amount).

*p, p*′-Dimethylstilbene was prepared by reduction of *p, p*′-dimethylbenzoin (*p*-toluoin), quite analogously to the synthesis of *trans*-stilbene from benzoin described in Organic Syntheses¹³⁾. From about 15 g. of *p*-toluoin, the purified product, colorless crystals melting at 177∼178°C, was obtained after repeated recrystallization from ethanol; yield, 4.7 g. (32% of the theoretical amount).

Found: C, 92.34; H, 7.86. Calcd. for $C_{16}H_{16}$: C, 92.26; H, 7.74%.

*p*-Toluoin was prepared by the benzoin condensation of *p*-tolualdehyde. To a solution of 82.7 g. of *p*-tolualdehyde in 165 ml. of ethanol, a solution of 18 g. of potassium cyanide in 120 ml. of water was added. The reaction mixture was refluxed for about two hours, and then left to stand for about a month in a refrigerator. The crystalline deposits contaminated with a considerably large amount of orange-colored oily matter were collected and pressed on a porous plate to remove the adhering oily matter. After recrystallization from ethanol, *p*-toluoin was obtained in colorless crystals melting at 87∼88°C; yield, 15 g. (18.1% of the theoretical amount).

*p*-Tolualdehyde was prepared according to the method described in Organic Syntheses¹⁴⁾.

2, 4, 6-Trimethylstilbene was prepared, after the procedure described by Fuson and others¹²⁾, by dehydration of 1-mesityl-2-phenylethanol prepared by the Grignard reaction of mesitaldehyde with benzyl magnesium chloride. The product was purified by repeated recrystallization from ethanol, and obtained in colorless crystals melting at 56.5∼57.5°C.

Mesitaldehyde was prepared, according to the method described in Organic Syntheses¹⁵⁾, by the action of hydrogen chloride on mesitylene in tetrachloroethane in presence of anhydrous aluminum chloride and zinc cyanide.

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9) A. Haddow, R. J. C. Harris, G. A. R. Kon and E. M. F. Roe, *Trans. Roy. Soc.* (*London*), **A241**, 147 (1948).

10) R. N. Beale and E. M. F. Roe, *J. Am. Chem. Soc.*, **74**, 2302 (1952).

11) H. Suzuki, unpublished.

12) R. C. Fuson, J. J. Denton and C. E. Best, *J. Org. Chem.*, 8, 64 (1943).

13) L. I. Smith (Editor-in-Chief), "Organic Syntheses", Vol. 23, John Wiley & Sons, Inc., New York (1943), p. 86.

14) F. C. Whitmore (Editor-in-Chief), ibid., Vol. XII (1932), p. 81.

15) L. I. Smith (Editor-in-Chief), ibid., Vol. 23 (1943), p. 57.

Mesitylene was prepared according to the method described in Organic Syntheses[16].

2, 4, 6, 2′, 4′, 6′-Hexamethylstilbene was prepared, according to the method described by Fuson and Best[17], by heating thiomesitaldehyde with copper powder. To a solution of 8.5 g. of mesitaldehyde in 80 ml. of anhydrous ethanol cooled by a freezing mixture, hydrogen chloride was passed for 50 min., and then hydrogen chloride and hydrogen sulfide were passed for one and a third hours at −5∼+5°C. The reaction mixture was left to stand for about two hours. The white deposits were collected and washed repeatedly with anhydrous ethanol. Thus, after being dried in a desiccator, the crude thiomesitaldehyde was obtained as white, apparently amorphous, powder; yield, 4.3 g. About 4.2 g. of the crude thiomesitaldehyde was mixed thoroughly with 3.6 g. of copper powder, and heated for about one hour over an oil bath at 220∼230°C. The copper powder turned black. Repeated extraction with hot ligroin afforded, after removal of the solvent, the crude dimesitylethylene. After repeated recrystallization from ethanol and treatment with activated charcoal, the substance was obtained in colorless fine needles melting at 131∼132°C; yield, 1.85 g.

The preparation of this compound by dehydration of 1, 2-dimesitylethanol was reported by Fuson and others[12]. However, an attempt by the present author to prepare 1, 2-dimesitylethanol, according to the directions of Fuson and others, by the Grignard reaction of mesitaldehyde with 2, 4, 6-trimethylbenzyl magnesium chloride was unsuccessful. 2, 4, 6-Trimethylbenzyl chloride was prepared from mesitylene according to the directions of Vavon and Bolle[18].

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[16] H. Gilman (Editor-in-Chief), ibid., Col. Vol. 1. (1932), p. 334.

[17] R. C. Fuson and C. E. Best, *J. Am. Chem. Soc.*, **67**, 155 (1945).

[18] G. Vavon and J. Bolle, *Compt. rend.*, **204**, 1826 (1937).