Relations between Electronic Absorption Spectra and Spatial Configurations of Conjugated Systems. VII. α-Substituted and α,α'-Disubstituted Stilbenes

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The method developed in Part V[1] of this series is applied to α- and α,α'-substituted stilbenes, some of which were preliminarily treated in an earlier paper[2], and the relations between the ultraviolet absorption spectra and the spatial configurations of these compounds are discussed. Further, the relations between the spatial configurations and some physical and chemical properties of these compounds are discussed in detail with special reference to α,α'-dimethylstilbene.

Ultraviolet Absorption Spectra.—The ultraviolet absorption spectra of α-alkyl- and α,α'-dialkylstilbenes in ethanol were reported previously[2]. The spectra of some of these compounds as well as α,α'-dihalostilbenes in *n*-heptane have newly been measured. These are shown in Figs. 1 and 2. In Table I, the data of the spectra are summarized.

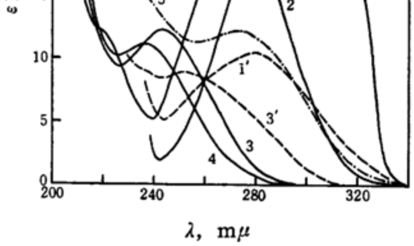

Fig. 1. Ultraviolet absorption spectra of stilbenes in *n*-heptane: 1, *trans*-stilbene; 1', *cis*-stilbene (in ethanol); 2, *trans*-α-methylstilbene; 3, *trans*-α,α'-dimethylstilbene; 3', *cis*-α,α'-dimethylstilbene; 4, *trans*-α,α'-diethylstilbene; 5, methyltriphenylethylene.

The spectra of the alkylated stilbenes in *n*-heptane do not differ significantly from the corresponding spectra in ethanol. Thus, the following generalizations, some of which were not explicitly stated in the earlier paper, can be deduced. (1) The conjugation band is shifted toward shorter wavelengths and is reduced in intensity with increasing number and increasing size of substituents at the ethylenic

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[1] H. Suzuki, This Bulletin, **33**, 379 (1960).

[2] H. Suzuki, ibid., **25**, 145 (1952).

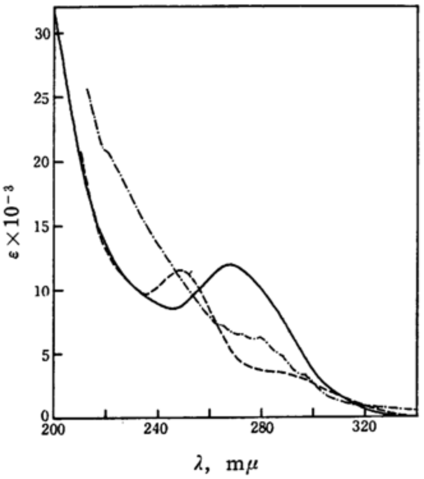

Fig. 2. Ultraviolet absorption spectra of *trans*-α,α'-dihalostilbenes in *n*-heptane: ——, dichlorostilbene; ------, dibromostilbene; —·—·—, diiodostilbene.

carbon atoms in each of the *trans* and the *cis* series. (2) The conjugation band of a *trans* isomer is invariably more intense than that of the corresponding *cis* isomer. (3) With stilbene as well as α-methylstilbene, the conjugation band of the *trans* isomer is at longer wavelengths than that of the *cis* isomer. On the other hand, with α,α'-dimethyl- as well as α,α'-diethylstilbene, the conjugation band of the *trans* isomer is at shorter wavelengths than that of the *cis* isomer. (4) The conjugation bands of these stilbene derivatives have, similarly to that of *cis*-stilbene, no fine structure, in contrast to that of *trans*-stilbene.

Also with *trans*-α,α'-dihalostilbenes, the conjugation band is structureless, and is shifted toward shorter wavelengths as the substituents become larger. *trans*-α,α'-Diiodostilbene in *n*-heptane dissociates

TABLE I. ULTRAVIOLET ABSORPTION MAXIMA

Stilbene	Solvent	*trans*			*cis*		
		λ, mμ	ε	Ref.	λ, mμ	ε	Ref.
Unsubstituted	H	294.1*	27950	1)			
		(B 228.5*	16200)				
		(C 201.5	23900)				
	E	294.5*	27850	1)	280	10450	a)
		(B 228.8*	16400)		(B 224	24400)	
		(C 201.0	23800)				
α-Methyl-	H	273.5	21100	b)			
		(B (217)	12530)				
		(C 202.3	28700)				
	E	272	21000	2)	267	9340	2)
α,α'-Dimethyl-	H	243.3	12270	b)	252.0	8880	b)
		(C (201.3)	32250)				
	E	243.5	12260	2)	252	8780	2)
α-Methyl-α'-ethyl-	E	240	11950	2)			
α,α'-Diethyl-	H	236.6	11090	b)			
	E	237.5	11020	2)	244	7740	2)
α-Methyl-α'-phenyl-	H	274.5	12200	b)			
		(B 227.5	16800)				
	E	275	9860	2)			
		(B 226	13720)				
α,α'-Dichloro-	H	268.0	12000	b)			
α,α'-Dibromo-	H	248.5	11570	b)			
α,α'-Diiodo-	H	(220.5)	20800**	b)			

Solvent: H, *n*-heptane; E, ethanol.

Symbols B and C in parentheses denote the B-band and the C-band, respectively. All the maxima other than the B- and C-bands refer to the conjugation bands (viz. A-bands). Wavelengths in parentheses denote inflections.

* The most intense maximum of fine structure.

** The apparent value. The accurate molecular extinction coefficient could not be determined, because this compound dissociates partly in this solvent into tolan and iodine.

a) R.N. Beale and E.M.F. Roe, *J. Chem. Soc.*, **1953**, 2755.

b) The present work.

TABLE II. RESULTS OF CALCULATION

Stilbene	Solvent	λ_A mμ	ΔE_A $-\beta$	ρ	$\theta°$	R Å	$R.E.$ $-\beta$
trans-α-Methyl-	H	273.5	1.299	0.730	34.5	1.462	0.457
cis-α-Methyl-	E	267	1.354	0.671	40	1.467	0.387
trans-α,α'-Dimethyl-	H	243.3	1.577	0.446	58	1.490	0.173
cis-α,α'-Dimethyl-	H	252.0	1.490	0.531	51.5	1.481	0.243
trans-α-Methyl-α'-ethyl-	E	240	1.612	0.412	60.5	1.493	0.146
trans-α,α'-Diethyl-	H	236.6	1.649	0.378	63	1.497	0.124
cis-α,α'-Diethyl-	E	244	1.570	0.453	57.5	1.489	0.178
trans-α,α'-Dichloro-	H	268.0	1.345	0.680	39	1.467	0.397
trans-α,α'-Dibromo-	H	248.5	1.525	0.497	54.5	1.485	0.212
trans-α,α'-Diiodo-	H	220.5	1.838	0.200	75.7	1.517	0.034

gradually into tolan and iodine, and consequently the absorption due to tolan is detected in the spectrum (cf. Fig. 2 with Fig. 2 in the preceding part[3] of this series). The inflection at near 220.5 mμ probably indicates the vestigial conjugation band of *trans*-α,α'-diiodostilbene.

Application of Calculation.—In the application of the method developed in Part V of this series to these stilbene derivatives, the data of the spectra of *n*-heptane solutions newly measured are used. For the compounds, the spectra of which in *n*-heptane have not yet been measured, the data of the spectra of ethanol solutions are used, since the positions of the bands may be considered not to vary significantly in either of the solvents (cf. Table I and also Parts I[4] and V of this series).

The effects of the substituents upon the spectra must include not only the steric hypsochromic effect due to the steric interferences between the substituents and the phenyl groups but also the electronic (probably bathochromic) effect of the substituents (cf. Part II[5] of this series). However, in view of the fact that the substituents in the compounds treated here are at the positions of cross-conjugation to the conjugated system of the stilbene skeleton, this possible electronic effect is considered to be probably very small compared with the steric hypsochromic effect, especially in the cases of the alkyl substituents, and therefore, is ignored in the present treatment.

In the cases of the halogen substituents, the electronic effect of the lone pair electrons of the halogen atoms may be relatively large campared with the electronic (probably hyperconjugation) effect of the alkyl substituents, and perhaps it should not be ignored. Nevertheless, the possible electronic effect of all the substituents is ignored, for simplification, in the present treatment. That is, it is assumed that the position of the conjugation band is determined solely by the spatial configuration of the stilbene skeleton.

The results of the calculations are shown in Table II. The notation used here is the same as in Part V of this series.

In α-methylstilbene as well as α-methyl-α'-ethylstilbene, the positions of the two phenyl groups are not equivalent, and therefore, their angles of twist must differ from each other. In spite of this, the results for these compounds, obtained on the basis of the assumption that the angles of twist of the two phenyl groups are equal, are also shown for comparison.

It is to be noted that the calculated values of the angle of twist θ (interplanar angle) in Table II are possibly rather smaller than the actual values because of the neglect of the electronic effect of the substituents mentioned above. In addition, when the β-band instead of the γ-band of *trans*-stilbene is taken as the "longer-wavelength-side reference", the calculated values of θ will evidently become greater than those in Table II.

Discussion

As will be expected, Table II shows that the calculated interplanar angle becomes larger with the increasing number and size of substituents. It is of interest that the change of the substituents from methyl groups to ethyl groups affects only rather slightly the position of the conjugation band and consequently the interplanar angle. A somewhat similar phenomenon has been seen in the comparison between *o*-methyl- and *o*-ethylbiphenyl[5]. On the

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[3] H. Suzuki, ibid., **33**, 389 (1960).
[4] H. Suzuki, ibid., **32**, 1340 (1959).
[5] H. Suzuki, ibid., **32**, 1350 (1959).

other hand, the replacement of the methyl group in β-methylcinnamic acid by an ethyl group has a greater steric consequence. According to Takahasi[6], the wavelengths (mμ) of the conjugation bands and the molecular extinction coefficients (in parentheses) of the bands of cinnamic acid and its β-alkyl derivatives in 94% ethanol are as follows: cinnamic acid, 273 (22000); β-methylcinnamic acid, 260 (15000); β-ethylcinnamic acid, 244 (10000).

The conjugation band of methyltriphenylethylene (1, 1, 2-triphenylpropene) is at a considerably shorter wavelength than that of triphenylethylene (cf. the preceding part of this series) and coincides in position almost completely with that of *trans*-α-methylstilbene. From this fact, it would be inferred that the most probable configuration of methyltriphenylethylene might be the one in which the phenyl group at the *trans*-position to the methyl group was completely rotated out of the plane of the ethylenic bond, or in other words, was insulated, leaving the two remaining *trans*-related phenyl groups in the configuration analogous to the most probable configuration of *trans*-α-methylstilbene. However, the fact that the intensity of the conjugation band of methyltriphenylethylene is much smaller than that of *trans*-α-methylstilbene suggests that this inference is unlikely. This situation is very similar to that observed in the comparison between the spectra of triphenylethylene and of *trans*-stilbene[3].

As mentioned already, it is especially noteworthy that the conjugation band of *trans*-α, α′-dimethylstilbene as well as its diethyl a analogue is at a shorter wavelength than that of the *cis* isomer, contrary to the generally accepted view that *trans* isomers of conjugated compounds should exhibit the conjugation bands at longer wavelengths than the corresponding *cis* isomers. A similar phenomenon has been observed by Nagai and Simamura[7] with some *p*, *p*′-disubstituted α, α′-dimethylstilbenes. These facts are considered to indicate that with these compounds the *trans* isomers are less conjugated than the corresponding *cis* isomers. In fact, as is seen in Table II, the calculated interplanar angles in the *trans* isomers of α, α′-dimethylstilbene and its diethyl analogue are larger than those of the corresponding *cis* isomers, and the calculated extra-resonance energies of the *trans* isomers are smaller than those of the *cis* isomers. This conclusion deduced here from the absorption spectra seems to be supported by some pieces of information on the properties of these compounds such as the reactivities, the nuclear magnetic resonance spectra, and the exaltations of molecular refraction. Accordingly, the relations between the spatial configurations and some physical and chemical properties of the stilbenes will be discussed in a later section with special emphasis on those for *trans*- and *cis*-α, α′-dimethylstilbenes.

Correlation of the Calculated Interplanar Angles with the Values Estimated from Scale Models.—That the calculated interplanar angle (58°) for *trans*-α, α′-dimethylstilbene agrees fairly well with the value estimated from scale models has been described in the earlier paper[2]. Thus, according as one assumes a twisted structure for this compound in which the ortho hydrogen atom of each phenyl group just touches the methyl group attached to the same ethylenic carbon atom as the phenyl group or a structure in which that hydrogen atom just touches the other methyl group, the interplanar angle is estimated at 60° or 56°, in good agreement with the calculated value.

For *trans*-α, α′-dibromostilbene, the interplanar angle is estimated at 48° or 51.5° from analogous models in which the interference radius of a bromine atom is 1.95 Å[8] (van der Waals radius) and the length of a C-Br bond is 1.91 Å[8] (the length of an Alkyl-Br bond). The actual length of the C-Br bond may be shortened more or less from the above normal value by interaction between the bromine atom and the ethylenic bond[9]. When the possible shortening of the bond is taken into account, the interplanar angle estimated from models will become slightly larger. The agreement of the calculated value (54.5°) of the interplanar angle with the value estimated from scale models is not so good as in the case of the dimethyl analogue; still it may be said to be fairly good.

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[6] M. Takahasi, ibid., **31**, 756 (1958).

[7] Y. Nagai and O. Simamura, presented at the 11th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1958.

[8] L. Pauling, "The Nature of the Chemical Bond", Cornell University Press, Ithaca, N. Y. (1940).

[9] (a) H. de Laszlo, *Proc. Roy. Soc.* (*London*), **A146**, 690 (1934). (b) J. A. C. Hagill, I. E. Coop and L. E. Sutton, *Trans. Faraday Soc.*, **34**, 1518 (1938).

For the dichloro analogue, the interplanar angle is estimated at 43° or 48° from the analogous medels in which the interference radius of a chlorine atom is 1.80 Å[8] (van der Waals radius) and the length of a C–Cl bond is 1.77 Å[8] (the length of a normal Alkyl-Cl bond). The agreement of the calculated interplanar angle (39°) with the value estimated from models is worse than in the cases of the dimethyl and the dibromo analogues. The discrepancy is probably due mainly to the effect of the interaction of the lone pair electrons of the chlorine atoms with the ethylenic bond on the position of the conjugation band, which has been ignored in the present calculations. The interaction may affect not only the estimation of the interplanar angle from scale models by the contraction of the C–Cl bond (the length of the C–Cl bond in chloroethylene, for example, is 1.69 Å[10]), but also may exert a bathochromic effect on the conjugation band. Thus, if it were not for this effect, this compound would exhibit the conjugation band at a shorter wavelength than the observed position, and consequently the calculated interplanar angle would become larger than the value in Table II.

Correlation of Some Properties with the Spatial Configurations. — *Exaltation of molecular refraction.*—As Mulliken[11] stated for the case of alkylstyrenes, the exaltation of molecular refraction can be considered as a measure of the extent of conjugation. Some relevant data selected from the data by Auwers[12,13] are shown in Table III.

The exaltation is markedly greater in *trans*-stilbene than in the *cis* isomer. On the other hand, in contrast to the case of stilbene, the exaltation is, though slightly, smaller in *trans*-α,α'-dimethylstilbene than in the *cis* isomer. This reversal is similar to what happens to the electronic absorption spectra.

Nuclear magnetic resonance. — Curtin and others[14] measured the proton magnetic resonance spectra of stilbene, azobenzene, and diphenylcycloalkanes, and found that the positions of the aromatic proton resonance and those of the α-protons provide a new method of assignment of configuration of such compounds.

According to the results of the measurements by them, the α-hydrogens of *cis*-stilbene give rise to resonance at a higher magnetic field than those of the *trans* isomer, indicating that the α-hydrogens of the *cis* isomer are more shielded than those of the *trans* isomer.

Recently, we measured the proton magnetic resonances of *trans*- and *cis*-α,α'-dimethylstilbenes and related compounds[15]. A relevant part of the results are shown in Table IV, together with the data by

TABLE III

Compound	EM_α	EM_D	$E\Sigma_\alpha$	$E\Sigma_D$	Ref.
trans-Stilbene			+3.24	+3.57	12, 13)
cis-Stilbene	+2.26	+2.74	+1.26	+1.52	13)
trans-α-Methylstilbene			+2.04	+2.17	12)
trans-α,α'-Dimethylstilbene	+2.10	+2.22	+1.01	+1.07	13)
cis-α,α'-Dimethylstilbene	+2.12	+2.27	+1.02	+1.09	13)
Triphenylethylene	+5.17	+5.68	+2.02	+2.22	12)
Methyltriphenylethylene	+3.64	+3.98	+1.35	+1.47	12)

EM_α and EM_D are exaltations of molecular refraction.
$E\Sigma_\alpha$ and $E\Sigma_D$ are specific exaltations.

TABLE IV. CHEMICAL SHIFTS OF PROTON MAGNETIC RESONANCE (in c.p.s.)

Compound	Proton	Solvent	*trans*	*cis*		Standard
Stilbene	α-H	CT	−90	−70	(at 40 Mc.)	M
α,α'-Dimethylstilbene	CH_3	B	− 8	−19	(at 27 Mc.)	Cy
α,α'-Diethylstilbene	CH_2	B	−22	−25	(at 27 Mc.)	Cy
	CH_3	B	+13	+ 5	(at 27 Mc.)	Cy

Solvent: CT, carbon tetrachloride; B, benzene.
Standard substance: M, an external methylene chloride; Cy, cyclohexane.

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10) L. O. Brockway, J. Y. Beach and L. Pauling, *J. Am. Chem. Soc.*, **57**, 2693 (1935).

11) R. S. Mulliken, *J. Chem. Phys.*, **7**, 356 (1939).

12) K. v. Auwers, *Ber.*, **62**, 693 (1929).

13) K. v. Auwers, *Ann.*, **499**, 123 (1932).

14) D. Y. Curtin, H. Gruen and B. A. Shoulders, *Chem. & Ind.*, 1205 (1958).

15) M. Katayama, S. Fujiwara, H. Suzuki, Y. Nagai, and O. Simamura, presented at the 12th Annual Meeting of the Chemical Society of Japan, Kyoto, April, 1959.

Curtin and others for *trans*- and *cis*-stilbenes.

In contrast to the α-hydrogens of *trans*- and *cis*-stilbenes, the hydrogens of the α-methyl groups of *cis*-α,α'-dimethylstilbene and of the α-ethyl groups of *cis*-α,α'-diethylstilbene give rise to resonance at lower fields than the corresponding hydrogens of the *trans* isomers. That is, the hydrogens are less shielded in the *cis* isomers than in the corresponding *trans* isomers.

Katayama calculated the magnetic fields due to the circulating π-electrons' currents for these compounds by making an allowance for the spatial configurations, and found that the calculated differences of the magnetic fields for the *trans* isomers and for the *cis* isomers are smaller than the observed ones. Accordingly, the observed differences may be partly due to the differences of the π-electron densities at carbon atoms and of the electron densities at the hydrogen atoms concerned, which is, in turn, probably due to the differences of the extent of conjugation as well as hyperconjugation. That is, it appears that the conjugation in the π-electron systems affects the chemical shift of the nuclear magnetic resonance. At any rate, it is of interest that the observations on the proton resonance mentioned above are considered to correspond to the fact that the sequence of the positions of the conjugation bands of *trans* and *cis* isomers in the case of stilbene is reversed in the cases of α,α'-dimethyl- and α,α'-diethylstilbene.

Thermal isomerization. — As mentioned already in Part V of this series, *trans*-stilbene is thermodynamically much more stable than the *cis* isomer. Thus, according to Taylor and Murray(16), the equilibrium mixture of the *cis*-*trans* thermal isomerization at 200°C consists of 96% of the *trans* isomer and 4% of the *cis* isomer. In addition, according to Kistiakowsky and Smith(17), the equilibrium mixture at 320~340°C contains 92~94% of the *trans* isomer. The heat of the thermal *cis*-*trans* isomerization ($-\Delta H$) is about 3 kcal./mol. (In addition, the heat of isomerization at 25°C has been estimated at 7.0 ± 0.4 kcal./mol. for *p*-nitrostilbene and at 4.6 ± 0.3 kcal./mol. for *p*,*p*'-dinitrostilbene from the heats of combustion(18). Also with these compounds, the *trans* isomers are, of course, much more stable than the *cis* isomers.)

The difference of stability between the isomers is by far smaller in the case of α,α'-dimethylstilbene than in the case of stilbene. Thus, according to the previous study by Simamura and the present author(2,19), the equilibrium mixture yielded by heating either *trans*- or *cis*-α,α'-dimethylstilbene with a little concentrated sulfuric acid for 20 hr. at 210°C contained the *trans* and the *cis* isomers in the ratio of the amounts 55 : 45 or 60 : 40.

The fact that the *trans* isomer is still, though slightly, also more stable in this case than the *cis* isomer would appear, at first sight, to be rather surprising, being contrary to the anticipation from the absorption spectra. As discussed already in the previous paper(2), however, this fact is understandable if one considers that the steric repulsion between the two methyl groups in the *cis* isomer, which can not be reduced by the rotation of the phenyl groups, is also an important contributory factor to the stability besides the resonance stabilization.

According to Taylor and Murray(16), the equilibrium mixture of the *cis*-*trans* isomerization of α,α'-dichlorostilbene at 220~230°C contains 75% of the *cis* isomer. The large stability of the *cis* isomer relative to the *trans* isomer may be partly due to the attractive (London) force between the chlorine atoms in the *cis* isomer as Taylor and Murray stated, and may be partly due to the fact that the difference of the resonance stabilization energy between the two isomers is considered, on the analogy of the case of α,α'-dimethylstilbene, to be not so great as in the case of stilbene, the resonance being considerably suppressed in both isomers by the steric factors.

Reaction with bromine.—As seen in Tables IV and V in Part V of this series and Table II in the present paper, the extra-resonance energy *R.E.*, i.e. the bond localization energy of the central ethylenic bond, decreases and the π-bond order of the ethylenic bond $p_{\alpha-\alpha'}$ increases, with decreasing ρ, and hence with the increasing interplanar angle. In Table V, the calculated values of *R.E.* and $p_{\alpha-\alpha'}$ for

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16) T. W. J. Taylor and A. R. Murray, *J. Chem. Soc.*, **1938**, 2078.

17) G. B. Kistiakowsky and W. R. Smith, *J. Am. Chem. Soc.*, **56**, 638 (1934).

18) C. M. Anderson, L. G. Cole and E. C. Gilbert, ibid., **72**, 1263 (1950).

19) O. Simamura and H. Suzuki, This Bulletin, **27**, 231 (1954).

TABLE V

Entry No.	Compound	ρ	*R.E.* $(-\beta)$	$p_{\alpha-\alpha'}$
1	Tetraphenylethylene	1.032	0.906	0.820
2	Triphenylethylene	0.946	0.764	0.845
3	*trans*-Stilbene	0.908	0.704	0.856
4	*cis*-Stilbene	0.787	0.530	0.890
5	*trans*-α-Methylstilbene	0.730	0.457	0.904
6	*cis*-α,α'-Dimethylstilbene	0.531	0.243	0.948
7	*trans*-α,α'-Dimethylstilbene	0.446	0.173	0.963
8	(Unconjugated olefin)	0	0	1

trans- and *cis*-stilbenes and some related compounds are summarized. The variation of the bond localization energy as well as of the π-bond order of the ethylenic bond should affect the rates of the reactions of these compounds with the "double-bond reagents"[20]. Thus, the decrease in the bond localization energy as well as the increase in the π-bond order should facilitate such reactions. This effect is subsequently referred to as the bond localization effect.

On the other hand, the substituents themselves or the phenyl groups rotated out of the plane of the ethylenic bond owing to steric necessities may hinder the approach of the reagent to the reaction site in such reactions. This effect, being purely steric in nature, is referred to as the steric (hindrance) effect in a narrow sense. This effect should, of course, retard such reactions. For example, the fact that α-*t*-butylstilbene does not add bromine[21] in contrast to α-methyl[19] and α-ethyl analogues[22] which add bromine is probably due to this effect.

In addition to the effects mentioned above, the substituents may, of course, exert an electronic effect (e. g. the inductive, mesomeric, or hyperconjugation effect) on the reactions. Therefore, in consideration of the reactions of these stilbene-type compounds, all the effects of the above three types are to be taken into account.

Simamura and the present author found in the earlier study[19] on the action of bromine on stilbenes that *trans*-α-methyl stilbene adds bromine much faster than *trans*-stilbene. The extreme slowness of the reaction of *trans*-stilbene with bromine is partly due to the retarding effect of atmospheric oxygen, and when a little catechol is added, the rate increases appreciably. On the other hand, the fastness of the reaction of *trans*-α-methylstilbene is ascribed partly to the accelerating effect of a little hydrogen bromide formed as a by-product by substitution, which starts the chain addition reaction of bromine by producing, in co-operation with oxygen, bromine atoms, and this effect is considered to be also suppressed by catechol. However, even when a little catechol is added, the rate of the reaction of *trans*-α-methylstilbene with bromine is still much greater than that of *trans*-stilbene[23]. This difference of the rates may be partly due to the electron-donating effect of the methyl group, partly to the unsymmetrical nature of the electronic state of the ethylenic bond in methylstilbene, and partly (perhaps mainly) to the bond localization effect due to the nonplanarity of the configuration of methylstilbene.

The π-bond order of the ethylenic bond in *trans*-α,α'-dimethylstilbene is greater than that in methylstilbene, so that dimethylstilbene would be expected to add bromine more rapidly than methylstilbene. In fact, however, the action of bromine on dimethylstilbene leads to the facile substitution at the methyl groups rather than the addition at the ethylenic bond[19]. This fact seems to be attributable to the steric effect in a narrow sense or the unstability of dimethylstilbene dibromide as the possible intermediate due to the steric strain in the molecule caused by the crowding of bulky groups.

Methyltriphenylethylene does not add bromine, but is substituted at the methyl group only slowly[19]. The absence of the addition is probably due to the steric hindrance effect in a narrow sense.

Reaction with hydrogen bromide and oxygen.—It was reported previously that the steric effect plays a predominant role in the

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[20] G. M. Badger, "The Structures & Reactions of the Aromatic Compounds", The University Press, Cambridge (1954).

[21] Ramart-Lucas, *Ann. Chim.*, [8] **30**, 394 (1913).

[22] A. Klages and S. Heilmann, *Ber.*, **37**, 1447 (1904).

[23] H. Suzuki, unpublished.

TABLE VI. EPOXIDATION OF OLEFINS WITH PERBENZOIC ACID IN BENZENE

Entry No.	Olefin	$10^4 k$	$\Delta H^\ddagger$	$\Delta F^\ddagger$	$-\Delta S^\ddagger$	Ref.
1	Tetraphenylethylene	0.28	17.2	24.1	22.6	25)
2	Triphenylethylene	3.075	15.7	22.6	22.7	25)
3	*trans*-Stilbene	4.27	15.25	22.2	22.8	25)
			13.8			26)
4	*cis*-Stilbene	13.35	14.1	21.75	25.2	25)
5	*trans*-α-Methylstilbene	37.42	12.6	21.1	28.1	26)
6	*cis*-α,α'-Dimethylstilbene	219.5	10.8	20.0	30.5	26)
7	*trans*-α,α'-Dimethylstilbene	228	11.0	20.0	29.8	26)
8	Cyclohexene	263.5	12.7	19.95	24.0	25)

The values of k (in mol^{-1} l. sec^{-1}) are those at 30°C. The values of $\Delta F^\ddagger$ (in kcal. mol^{-1}) and of $\Delta S^\ddagger$ (in cal. deg^{-1} mol^{-1}) are those calculated from the rates at 30°C. The values of $\Delta H^\ddagger$ are in kcal. mol^{-1}.

reactions of stilbene and stilbene derivatives with hydrogen bromide and oxygen[24]. The conclusions are summarized as follows.

(1) *trans*-Stilbene and *trans*-α-methylstilbene can produce bromine atoms by the combined action of hydrogen bromide and oxygen, and thus can initiate chain reactions, the former yielding mainly its dibromide, and the latter yielding its dibromide along with ω-bromoacetophenone and benzoic acid as the final products.

(2) On the other hand, both *trans*- and *cis*-α,α'-dimethylstilbenes as well as *trans*-α,α'-diethylstilbene undergo no such reaction in the absence of a catalyst, because they are unable by themselves to produce bromine atoms from hydrogen bromide and oxygen, probably owing to the steric effect which hinders the approach of hydrogen bromide and oxygen to the ethylenic bond. However, once bromine atoms have been produced from hydrogen bromide and a peroxidic initiator, they are active enough to attack the ethylenic bonds of these stilbene derivatives, producing radicals as chain carriers, and resulting in the oxidative cleavage of the double bonds.

(3) Further, methyltriphenylethylene and α,α'-bisbromomethylstilbene (1,4-dibromo-2,3-diphenyl-2-butene) appear not to react with hydrogen bromide and oxygen even in the presence of a peroxidic catalyst. That is, the steric hindrance is so great in these compounds that they are not only incapable of such initiation, but also unsusceptible even to the action of bromine atoms, or, if a bromine atom adds to the double bond, unable to propagate the chain reactions efficiently.

Reaction with perbenzoic acid (epoxidation). —The reaction of olefins with perbenzoic acid gives excellent yields of the corresponding epoxides. It has been presumed that perbenzoic acid acts as a double-bond reagent, i. e. that the reaction involves attack on the olefinic bond and not on one of the constituting carbon atoms[25]. The correlation of the reactivities of *trans*-stilbene, triphenylethylene and tetraphenylethylene to perbenzoic acid with the π-bond orders as well as the bond localization energies of the ethylenic bonds of these compounds was briefly discussed already in the preceding part[3] of this series. The discussion will be extended here to other stilbene derivatives.

The relevant data selected from the results of the kinetic studies by Lynch & Pausacker[25] and by Simamura, Fukuyama & Nagai[26] are shown in Table VI.

While *cis*-stilbene is epoxidized much more rapidly than the *trans* isomer, *cis*-α,α'-dimethylstilbene is epoxidized slightly more slowly than the *trans* isomer, in accordance with the expectration from the calculated bond localization energies. The difference in the reaction rate among the compounds may, of course, depend not only on the difference of the bond localization energy, but also on the steric effect in a narrow sense (that is, the degree of unfavorableness of the steric situation to the approach of the reagent, or the magnitude of the steric strain in the transition state), and also on the electronic

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[24] H. Suzuki, O. Simamura and T. Ichihashi, This Bulletin, **27**, 235 (1954).

[25] B. M. Lynch and K. H. Pausacker, *J. Chem. Soc.*, **1955**, 1525.

[26] The author is indebted to Professor O. Simamura, Dr. M. Fukuyama and Mr. Y. Nagai for communicating with him and allowing him to quote these results in advance of publication. They were presented first by them at the Symposium on the Organic Reaction Mechanism held under the auspices of the Chemical Society of Japan, Fukuoka, October, 1958.

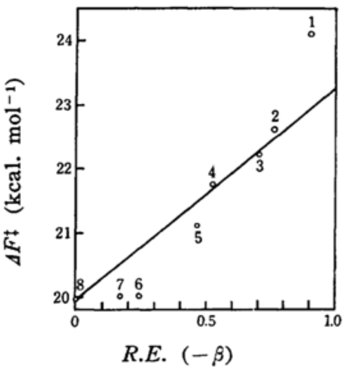

Fig. 3. Relation between the free energy of activation for the reaction of olefins with perbenzoic acid and the bond localization energy. Olefins are represented by the entry numbers in Table V as well as in Table VI.

effect of the substituents (e. g. the electron-donating effect of methyl groups). In spite of this, the sequence of the free energy of activation ($\Delta F^{\ddagger}$) shown in Table VI agrees completely with the sequence of the calculated bond localization energy (*R.E.*) shown in Table V. This fact is seen more clearly in Fig. 3, which shows the values of *R.E.* and $\Delta F^{\ddagger}$ for each compound plotted against one another and numbered according to the entry number in Table VI.

Considering the discrepancy between the experimental value of $\Delta H^{\ddagger}$ for *trans*-stilbene determined by Lynch and Pausacker and that by Simamura and others, it may be somewhat doubtful to compare the data of the different sources. On the other hand, it may also be doubtful to place much reliance on the absolute magnitude of the individual calculated bond localization energy. However, Fig. 3 appears to lead to the following discussions.

The points for *trans*-α-methylstilbene and especially for *trans*- and *cis*-α,α'-dimethylstilbenes are deviated down from the straight correlation line drawn nearly through the points for cyclohexene, *cis*- and *trans*-stilbenes. That is, the values of $\Delta F^{\ddagger}$ for these methylated stilbenes are smaller than those anticipated from the values of *R.E.* on the basis of the correlation line. These vertical deviations may be considered to indicate the facilitation of the reaction by the hyperconjugation effect or the electron-donating effect of the methyl groups. The steric interference with the approach of the reagent may also exist to some extent in these methylated stilbenes. This interference seems to be revealed by the large absolute values of the entropy of activation for these compounds as compared with *trans*-stilbene.

Tetraphenylethylene and triphenylethylene have greater free energies of activation than anticipated from the calculated bond localization energies on the basis of the correlation line. This fact appears to suggest that the low reactivities of these compounds as compared with *trans*-stilbene are not only due to the larger bond localization energies but also partly to the steric effect in a narrow sense caused by the greater crowding of phenyl groups or by the nonplanarity of the configurations of these compounds. However, in view of the fact that the values of the entropy of activation for these compounds are nearly equal to that for *trans*-stilbene, this possibility may be questionable. Perhaps, the so-called electron-withdrawing effect of the phenyl group relative to the hydrogen atom may be a contributory factor.

Simamura and others measured also the rates of the reaction of many 4, 4'-disubstituted α,α'-dimethylstilbenes with perbenzoic acid, and found that there exists a linear relation between the logarithms of the rate constants and the sum of the values of Hammett's substituent constant for the 4- and 4'-substituents for each of the *trans* and the *cis* series. According to them, the proportionality constant (Hammett's reaction constant ρ) for the *cis* isomers is -0.88 at 30°C, -0.90 at 20°C, and -0.93 at 10°C, and, on the other hand, the value for the *trans* isomers is -0.80 at 30°C, -0.83 at 20°C, and -0.86 at 10°C, meaning that the effect of the 4- and 4'-substituents on the reaction rate constant is stronger in the *cis* series than in the *trans* series. This fact coincides with the present conclusion that the *cis* isomer of α,α'-dimethylstilbene is more conjugated than the *trans* isomer. The above mentioned values of Hammett's reaction constant for 4, 4'-disubstituted dimethylstilbenes are appreciably smaller than those for 4-substituted *trans*-stilbenes (about $-1.07\sim1.16$, estimated from the data by Lynch and Pausacker). This fact may be correlated with the fact that *trans*-stilbene is more conjugated than *trans*- and *cis*-dimethylstilbenes.

Experimental

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

The alkylstilbenes were prepared as reported previously[2,19].

trans-α,α'-Dichlorostilbene was prepared by the addition of chlorine to tolan. To a solution of 10 g. of tolan in 100 cc. of acetic acid, 140 cc. of a 0.4 mol./l. solution of chlorine in acetic acid was added. The reaction mixture was left to stand for about a month, and then poured into water. The crystalline deposits were collected, pressed on a porous plate to remove some adhering oily matter, and repeatedly recrystallized from ethanol. The substance was obtained in colorless crystals melting at 138.5~139.8°C; yield, 2.4 g. (17.2% of the theoretical amount).

trans-α,α'-Dibromostilbene was prepared by the addition of bromine to tolan. To a solution of 3.4 g. of tolan in 70 cc. of ether, about 2 cc. (in exess) of bromine was added dropwise. The crystalline deposits were collected and washed twice with ether. The substance was obtained in colorless prisms melting at 205~206°C; yield, 5.1 g. (79% of the theoretical amount).

trans-α,α'-Diiodostilbene was prepared by the addition of iodine to tolan. To a solution of 356 mg. (2×10^{-3} mol.) of tolan in 10 cc. of acetic acid, a solution of 508 mg. (2×10^{-3} mol.) of iodine in 22.5 cc. of acetic acid was added and the reaction mixture was left to stand for about a month. The crystalline deposits were collected and carefully recrystallized from acetic acid. The substance was obtained in colorless, bright prisms hardly soluble in most organic solvents and decomposing at about 199°C with the evolution of iodine vapor; yield, 744 mg. (86% of the theoretical amount).

Summary

The ultraviolet absorption spectra of some α- and α,α'-substituted stilbenes have been analyzed, and the most probable spatial configurations of these compounds have been inferred from the spectra by application of the calculation method described in the earlier part of this series.

It is especially noteworthy that with α,α'-dimethylstilbene as well as its diethyl analogue the *trans* isomer shows the conjugation band at a shorter wavelength than the *cis* isomer, contrary to the generally accepted view that *trans* isomers of conjugated compounds should exhibit the conjugation bands at a longer wavelength than the corresponding *cis* isomers. This fact is considered to indicate that with these compounds the *trans* isomers are less conjugated than the corresponding *cis* isomers, and that the angle of twist of the "single" bond (interplanar angle) is larger in the *trans* isomers than in the corresponding *cis* isomers. This has been confirmed by the results of the calculations. Further, this is supported also by some pieces of information on the properties of these compounds, such as the reactivities, the exaltation of molecular refraction, and the nuclear magnetic resonance. With special emphasis on this respect, the correlation of some physical and chemical properties of these compounds with the spatial configurations of the molecules has been discussed in detail.

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