Relations between Electronic Absorption Spectra and Spatial Configurations of Conjugated Systems. XI. Styrene, 1, 1-Diphenylethylene and their Methylated Derivatives

By Hiroshi SUZUKI

(Received October 30, 1959)

An introduction of a substituent into an *o*-, the α-, or the *cis*-β-position of styrene must cause a deviation of the phenyl group from the coplanar position with the plane of the ethylenic bond, owing to the steric interaction between the *o*-substituent and the α- or the *cis*-β-hydrogen or between the α- or *cis*-β-substituent and an *o*-hydrogen. On the other hand, in 1, 1-diphenylethylene, the two phenyl groups can not simultaneously be coplanar with the plane of the ethylenic bond. These steric situations must reveal themselves in the ultraviolet absorption spectra. In this part of the series, the method analogous to the one used so far in the previous parts of this series is applied to methylated styrenes, 1, 1-diphenylethylene, and its methylated derivatives, and the relations between the most probable spatial configurations of these compounds and the ultraviolet absorption spectra are discussed.

Calculation

The method of calculation is quite analogous to the ones for biphenyls[1], terphenyls[2], and stilbenes[3,4] in the earlier parts of this series. The $\pi-\pi$ resonance integral for the ethylenic bond is denoted by $\eta\beta$, and that for the $\alpha-1$ "single" bond of styrene is denoted by $\rho\beta$, in which β represents the $\pi-\pi$ resonance integral for a C–C bond in benzene as usual. By substituting suitable values for η and ρ according to the lengths and the angles of twist of the corresponding bonds, and by solving the secular equation for the determination of the molecular orbitals of styrene as linear combination of $2p\pi$ atomic orbitals by the usual procedure, the energy ΔE_A of the transition from the highest occupied orbital to the lowest vacant orbital, which is allowed by absorption of light polarized along the direction of the long axis of the molecule, is calculated. This value of ΔE_A is considered to correspond to the transition energy of the intense conjugation band of the molecule of the styrene-type of the configuration prescribed by the values of η and ρ.

The length of the ethylenic bond is assumed to be 1.34 Å, and hence the value of η is assumed to be 1.080 for the styrenes and 1, 1-diphenylethylenes throughout the present treatment, for the same reason as in the case of stilbenes in Part V[3] of this series. By using this value for η, the value of ΔE_A is calculated as a function of the variable ρ. The results are shown in Table I. It is seen in Table I that the value of ΔE_A increases with the decreasing value of ρ, and that the value of ΔE_A coincides with the value for benzene, $2(-\beta)$, when the value of ρ is zero.

TABLE I

ρ	1	0.9	0.8	0.7	0.6	0.5	0.4	0.3	0.2	0.1	0
$\Delta E_A(-\beta)$	1.3958	1.4506	1.5082	1.5684	1.6314	1.6968	1.7646	1.8342	1.9036	1.9672	2

Although reliable data concerning the spatial configuration of styrene molecule are not yet available, the configuration can be presumed by analogy with the following facts. Butadiene in the vapor phase has recently been found by Almenningen and his collaborators[5] to have probably almost exclusively the planar *trans*-configuration in which the length of the 2–3 "single" bond is 1.483±0.01 Å. On the other hand, biphenyl in the crystalline state has been found to have the planar configuration in which the length of the co-annular "single" bond is 1.48Å[6]. Accordingly, it may be presumed that styrene has probably the planar or nearly planar configuration in which the length of the $\alpha-1$ "single" bond is about 1.48 Å. Even if the presumption of the bond length is not correct, a small change in the bond length for the reference compound is considered not to affect significantly the resultant calculated values for

---

1) H. Suzuki, This Bulletin, 32, 1340 (1959).
2) H. Suzuki, ibid., 33, 109 (1960).
3) H. Suzuki, ibid., 33, 379 (1960).
4) H. Suzuki, ibid., 33, 410 (1960).
5) A. Almenningen, O. Bastiansen and M. Traetteberg, *Acta Chem. Scand.*, 12, 1221 (1958).
6) (a) J. Dhar, *Indian J. Phys.*, 7, 43 (1932); *Chem. Abstr.*, 26, 4517 (1932). (b) Idem., *Proc. Natl. Inst. Sci. India*, 15, 11 (1949); *Chem. Abstr.*, 43, 4655 (1949).

the angles of twist, as suggested by the results of the similar calculations for terphenyls in Part IV⁽²⁾ of this series. Therefore, the presumption is adopted in the present treatment. Then, the relation between ρ and the angle of twist θ (i. e. the interplanar angle between the benzene ring and the ethylenic bond) as well as the length of the "single" bond R is assumed to be quite analogous to the relation between μ (the variable analogous to ρ) and θ as well as R postulated in the case of biphenyl in Part I⁽¹⁾ of this series. Thus, ρ is expressed as follows:

$$\rho = \cos\theta \times S(R, 0^\circ)/S(1.39, 0^\circ)$$
$$= \cos\theta \times 0.77108 + \cos^2\theta$$
$$\times (1.54 - 1.48) \times 1.4458$$

where $S(R, 0^\circ)$ represents the $\pi - \pi$ overlap integral for the bond, the length and the angle of twist of which are R(Å) and 0°, respectively, and $S(1.39, 0^\circ)$ represents the overlap integral for a C–C bond in benzene, whose length is 1.39 Å and whose angle of twist is, of course, zero.

Accordingly, the value of ρ when R and θ are 1.48 Å and 0°, respectively, i. e. the value of ρ for the planar styrene molecule, is calculated to be 0.858, and the corresponding value of ΔE_A is calculated to be 1.475 $(-\beta)$, which is referred to as ΔE_L. When the wave number ν_A of the maximum of the conjugation band of a styrene derivative has been correlated with the calculated transition energy ΔE_A, the value of ρ for the compound can be evaluated, and then the corresponding values of θ and R can be estimated.

Styrenes

The data of the ultraviolet absorption spectra to be found in the literature for styrene and substituted styrenes are considerably variable. Especially the data of the molecular extinction coefficients are extremely variable, probably owing to the presence of polymeric materials in some of the specimens used, as pointed out already by Braude and Sondheimer⁽⁷⁾. Also with wavelengths of the absorption maxima, different workers using different instruments have reported values which vary by a few mμ. Further, the positions of the maxima vary more or less, depending on the solvent. With consideration for these situations, mainly the data obtained newly by the present author and those obtained recently by Schwartzman and Corson⁽⁸⁾, both using Cary recording spectrophotometers and

TABLE II. ABSORPTION MAXIMA OF STYRENES

Styrene	Solvent			Conj. band				Ref.
		λ, mμ	ε	λ, mμ	ε	λ, mμ	ε	
Unsubstituted	C			248				8
p-Methyl-	C			253				8
trans-β-Methyl-	E	293	780	250	17300			9
		284	1100					
o-Methyl-	C			246				8
o, *p*-Dimethyl-	C			251				8
α-Methyl-	H	285.7	167	241.5	9780	215.4	8670	*a*
		278.1	311			200.0	20950	
α, β-Dimethyl-	E			244	8700			10
cis-β-Methyl-	E	290	120	240.6	13800			9
β, β-Dimethyl-	H	288.2	550	239.4	9060	(216)	8260	*a*
		280.3	800	(247.2)	6690			
		264.8	890					
o, *o*′-Dimethyl-	C			238				8
o, *p*, *o*′-Trimethyl-	O			245	7000			11
α, β, β-Trimethyl-	H	286.0	430	237.8	8440			*a*
		278.5	550	(245.3)	6210			
		275.5	550					
α, *o*-Dimethyl-	E	No max. between 210 and 300 mμ						12

Solvent: C, cyclohexane; E, ethanol; H, *n*-heptane; O, octane.
Wavelengths in parentheses denote inflections.
Ref. *a*, the present work.

---

7) E. A. Braude and F. Sondheimer, *J. Chem. Soc.*, **1955**, 3773.

8) L. H. Schwartzman and B. B. Corson, *J. Am. Chem. Soc.*, **78**, 322 (1956).

9) R. Y. Mixer, R. F. Hech, S. Winstein and W. G. Young, ibid., **75**, 4094 (1953).

10) Y. Hirschberg, ibid., **71**, 3241 (1949).

11) K. C. Bryant, G. T. Kennedy and E. M. Tanner, *J. Chem. Soc.*, **1949**, 2389.

12) (a) M. J. Murray and W. S. Gallaway, *J. Am. Chem. Soc.*, **70**, 3867 (1948). (b) Ramart-Lucas and J. Hoch, *Bull. soc. chim. France*, [5] **5**, 848 (1938).

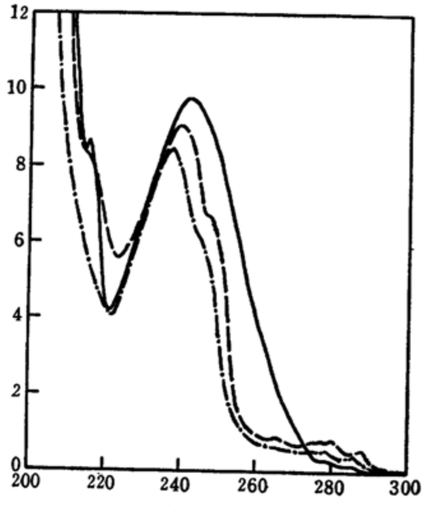

Fig. 1. Ultraviolet absorption spectra (in *n*-heptane): ——, α-methylstyrene ; ----, β,β-dimethylstyrene ; -·-·-, α,β,β-trimethylstyrene.

using saturated hydrocarbons as the solvents, are used in the present treatment. For a few compounds, the data of the spectra of which in solutions in saturated hydrocarbon are not available, the data for ethanol solutions are used. Such data used here are summarized in Table II, and the spectra measured by the present author are shown in Fig. 1.

It is evident that the styrene derivatives with methyl substituents in the sterically hindered positions exhibit the conjugation bands at shorter wavelengths than the conjugation band of the parent compound, styrene. The bands appearing in the range between 270 and 290 mμ are considered to be the ones corresponding to the $A_{1g}\rightarrow B_{2u}$ transition in benzene, quite similarly to the corresponding bands of benzaldehyde and of acetophenone[13].

In order to infer the spatial configurations of the styrenes from the data of the spectra by applying the above-mentioned calculation method, the electronic bathochromic effect of the methyl groups (probably due to the hyperconjugation effect) should be taken into account, because the wavelength separation between the conjugation band of styrene and the center of gravity of singlets of benzene as the shorter-wavelength-side reference is so small that the magnitude of the bathochromic effect of the methyl groups may not be negligible relatively to the magnitude of the steric hypsochromic effect.

The allowance for the electronic bathochromic effect of the methyl groups is made by the method analogous to the ones used in the treatments of *o*-alkylbiphenyls in Part II[14] of this series and of the stilbene derivatives with methyl groups on the benzene nuclei in Part VIII[15] of this series, i. e. by choosing pertinently the longer-wavelength-side and the shorter-wavelength-side references in the correlation of ν_A with ΔE_A.

Longer-wavelength-side Reference. — As the value of ν_A corresponding to ΔE_L, viz. ν_L, the wave number, at which the molecule concerned would exhibit the absorption maximum of the conjugation band if the molecule were planar, is taken. Thus, for example, as the value of ν_L for *o*-methylstyrene, the wave number of the absorption maximum of the conjugation band of *p*-methylstyrene, 39526 cm^{-1} (253 mμ), is taken, since the electronic bathochromic effect of a methyl group can be considered to be approximately equivalent in the *o*- and *p*-positions.

From the comparison of the spectrum of *p*-methylstyrene with that of styrene and the comparison of the spectrum of *o*,*p*-dimethylstyrene with that of *o*-methylstyrene, it may be presumed that the magnitude of the bathochromic displacement of the conjugation band per a methyl substituent at the *p*- or *o*-position of styrene is about 5 mμ. Further, it may be assumed that the displacement is approximately additive, on the analogy of the case of methylated benzenes[16]. According to Schwartzman and Corson[8], *m*-methylstyrene and *m*,*m'*-dimethylstyrene in cyclohexane solutions exhibit the conjugation bands at 251 and 254 mμ, respectively. Comparing these wavelengths with that of styrene itself (248 mμ), it is seen that the magnitude of the bathochromic displacement per a methyl group at a *m*-position is 3 mμ, and that the additivity holds good in this case. The magnitude of the bathochromic displacement caused by an *o*-methyl group may, strictly speaking, be not completely equal to that by a *p*-methyl group. Probably, the former is very slightly smaller than the latter, in view of the results of the calculations for *p*- and *o*-terphenyls described in Part IV[2] of this series, but must be considerably larger than the magnitude of the bathochromic displacement caused by a *m*-methyl group. Therefore, the assumption that the magnitude of the displacement per an *o*-methyl group is equal to that per a *p*-methyl group can be considered to be quite satisfactory in the present approximate treatment. When it is assumed so, *o*,*p*-dimethylstyrene would have the absorption maximum of the conjugation band at about 258 mμ ($248+5\times2$ mμ) if it were not for

---

[13] H. Suzuki, This Bulletin, 33, 613 (1960).

[14] H. Suzuki, ibid., 32, 1350 (1959).

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

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

TABLE III. RESULTS OF CALCULATION FOR STYRENES

Group	Entry No.	Styrene	λ_A mμ	λ_L mμ	λ_S mμ	ΔE_A $-\beta$	ρ	$\theta°$	R Å
I	1	Unsubstituted	248			1.475	0.858	0	1.48
	2	*p*-Methyl-	253					0	
	3	*trans*-β-Methyl-	250					0	
II	4	*o*-Methyl-	246	253	213.3	1.555	0.722	31	1.489
	5	*o*,*p*-Dimethyl-	251	258	217.3	1.553	0.725	30.7	1.489
	6	α-Methyl-	241.5	250	208.3	1.567	0.702	33	1.490
	7	α,β-Dimethyl-	244	252	208.3	1.557	0.719	31.5	1.489
III	8	*cis*-β-Methyl-	240.6	250	208.3	1.578	0.685	35.2	1.491
	9	β,β-Dimethyl-	239.4	252	208.3	1.607	0.639	40	1.494
IV	10	*o*,*o*′-Dimethyl-	238	258	217.3	1.711	0.480	54	1.505
	11	*o*,*p*,*o*′-Trimethyl-	245	263	219.3	1.669	0.543	49	1.500
	12	α,β,β-Trimethyl-	237.8	254	208.3	1.638	0.590	45	1.498
V	13	α,*o*-Dimethyl-						(90)	

the steric hypsochromic effect. Accordingly, for the treatment of *o*,*p*-dimethylstyrene, the value of 38760 cm^{-1} (258 mμ) is taken as the value of ν_L.

Further, for example, for *cis*-β-methylstyrene, the wave number of the maximum of *trans*-β-methylstyrene is taken as ν_L. The magnitude of the bathochromic wavelength displacement caused by the introduction of a methyl group into the α-position and that by the introduction into a β-position may be not equal to each other, since the two positions must be not equivalent, the α-methyl group being at the position of cross-conjugation to the conjugated system of the styrene skeleton and, on the other hand, the β-methyl group being at the position of conjugation to the conjugated system. In spite of this, the magnitude of the displacement by an α-methyl as well as a β-methyl group is provisionally assumed to be equal to the difference in wavelength between the maximum of *trans*-β-methylstyrene and that of styrene, 2 mμ, although the data of the maxima of these compounds may be not pertinent to comparison, since they are obtained in different solvents. Further, it is assumed that the additivity holds good also in this case. Then, for example, the value of ν_L for the treatment of α, β, β-trimethylstyrene becomes 39370 cm^{-1} (254 mμ = 248 + 2 × 3 mμ).

Shorter-wavelength-side Reference.—The value of ΔE_A when ρ is zero, $2(-\beta)$, is denoted by ΔE_S, and the corresponding wave number is denoted by $\tilde{\nu}_S$, as usual. As the value of ν_S for the treatments of the styrenes which have no methyl substituent on the benzene nuclei, the center of gravity of singlets of benzene, 48000 cm^{-1} (208.3 mμ), is taken, as usual.

As shown in Table II in Part II[14] of this series, the absorption bands of toluene, *m*-xylene, and mesitylene are at longer wavelengths by about 5, 9 and 11 mμ, respectively, than the corresponding bands of benzene. Accordingly, the values for these compounds corresponding to the center of gravity of singlets of benzene are considered to be approximately 46882 cm^{-1} (213.3 mμ = 208.3 + 5 mμ), 46019 cm^{-1} (217.3 mμ = 208.3 + 9 mμ), and 45600 cm^{-1} (219.3 mμ = 208.3 + 11 mμ), respectively. Therefore, for example, as the value of ν_S for the treatment of *o*, *p*, *o*′-trimethylstyrene, the value of 45600 cm^{-1} is taken.

Application of the Calculation. — When the references have been determined for each styrene derivative as mentioned above, the value of the calculated transition energy ΔE_A corresponding to the observed position (ν_A in wave number) of the maximum of the conjugation band of the compound can be easily obtained by the use of the usual postulated linear relation of ΔE_A to ν_A between the two reference points. Consequently, from the value of ΔE_A, the corresponding value of ρ can be obtained according to the relation between ρ and ΔE_A shown in Table I, and then the corresponding values of θ and R can be obtained. The results of the calculations are shown in Table III, in which λ_A refers to the wavelength of the absorption maximum of the compound concerned, and λ_L and λ_S refer to the corresponding longer-wavelength-side and the corresponding shorter-wavelength-side references, respectively, in wavelength.

Discussion

Although much reliance may not be placed on the individual numerical values of the calculated interplanar angles because of the approximation used, the results of the calculations shown in Table III appear to lead to the conclusion that these styrenes can be classified into the following well-defined groups with respect to the type or the degree of the steric interaction involved in the molecule.

Group I. The compounds which have no methyl substituent at hindering positions, i. e. at *o*-, α-, and *cis*-β-positions. To this group, the compounds of the entry numbers 1—3 listed in Table III belong. These compounds are probably planar.

Group II. The compounds which have one hindering methyl group either at an *o*-position or at the α-position of the molecule. These compounds are considered to involve solely the steric interference either between the *o*-methyl group and the α-hydrogen or between the α-methyl group and an *o*-hydrogen. To this group, the compounds of the entry numbers 4–7 in Table III belong. The β-methyl group in "α, β-dimethylstyrene" (entry 7) is probably *trans* to the phenyl group. The calculated interplanar angles for these compounds range from 31° to 33°.

Group III. The compounds with one hindering methyl group at the *cis*-β-position. These compounds involve solely the steric interference between the *cis*-β-methyl group and an *o*-hydrogen. To this group, the compounds of the entry numbers 8 and 9 belong. For these compounds, the calculated interplanar angles are 35° and 40°, being slightly larger than those for the compounds belonging to Group II.

Group IV. The compounds with two hindering methyl groups either at both *o*-positions or at the α- and the *cis*-β-positions. These compounds involve the steric interferences between methyl groups and hydrogen atoms on both the sides of the benzene nucleus. To this group, the compounds of the entry numbers 10–12 in Table III belong. The calculated interplanar angles for these compounds range from 45° to 54°, and are considerably larger than those for the compounds belonging to Group II and those for the compounds belonging to Group III.

Group V. To this group, α, *o*-dimethylstyrene (entry 13) belongs. If the most probable configuration of this compound were the configuration involving the steric interference between the α-methyl group and the *o*-hydrogen and the interference between the *o*-methyl group and the *cis*-β-hydrogen, this compound would belong to Group IV and not to Group V. In fact, however, this compound has been reported to show no absorption maximum in the range between 210 and 300 mμ, in contrast with the compounds belonging to Group IV. Accordingly, the most probable configuration of this compound is probably the one in which the two methyl groups just contact with each other, and consequently, the interplanar angle is larger than in the compounds belonging to Group IV and probably nearly 90°. This inference seems to be not unlikely, in view of the fact that *o, o'*-dimethylbiphenyl has probably the *cis*-like configuration in which the two methyl groups contact with each other as discussed in Part II[14] of this series.

The fact that the calculated interplanar angles for the compounds belonging to Group III are appreciably larger than those for the compounds belonging to Group II is of interest. This fact seems to lead to the conclusion that the steric interference due to the *cis*-β-methyl group is more effective than that due to the α-methyl group.

The geometries of the relevant parts of the compounds belonging to Group IV are considered to be approximately similar to those of *trans*-α, α'-dimethylstilbene and of *trans*-2, 4, 6, 2', 4', 6'-hexamethylstilbene, except for the possible differences of the bond lengths and of the bond angles. The calculated interplanar angle for α, β, β-trimethylstyrene (entry 12) is considerably smaller than that for *trans*-α, α'-dimethylstilbene (58°)[17]. On the other hand, the calculated interplanar angle for *o, o'*-dimethylstyrene (entry 10) coincides almost completely with that for *trans*-hexamethylstilbene (54.3°)[15].

At any rate, it is noteworthy that the interplanar angles for the compounds which involve the steric interferences between methyl groups and hydrogen atoms on both sides of the benzene ring (belonging to Group IV) are considerably larger than those for the compounds which involve the steric interference solely on one side of the benzene ring (belonging either to Group II or to Group III). This may mean that in the compounds with the steric interference solely on one side of the benzene ring the steric interference is relieved to some extent probably by changes in the bond angles.

Lastly in this section, it may be concluded that, by making allowance for the electronic bathochromic effect of the methyl substituents, the interplanar angles in the methylated styrenes have been almost satisfactorily inferred from the wavelength positions of the conjugation bands.

Criticism on Braude and Forbes' Classification of Steric Effects in Ultraviolet Absorption Spectra

Braude and his coworker[18] classified the steric effects of twisting of "single" bonds in conjugated systems on the conjugation bands into

---

[17] H, Suzuki, This Bulletin, 33, 396 (1960).

[18] E. A. Braude and F. Sondheimer, *J. Chem. Soc.*, 1955, 3754.

two types: (1) Steric effect which gives rise to intensity changes only, without causing any "unusual" change in wavelength (the steric effect of type 1, or *type 1* steric effect). This effect is caused by relatively small twists. (2) Steric effect which causes changes in both wavelength and intensity (the steric effect of type 2, or *type 2* steric effect). This effect is caused by larger twists than the first effect.

To the above two types, Forbes[19] has recently added a third type; the steric effect occurring when the twist is so large that conjugation across the bond is almost completely inhibited and the molecule absorbs as two distinct entities. This effect has been termed a *type 3* steric effect.

A similar classification of steric effects into three main classes has been proposed also by Turner and Voitle[20], and such a classification appears to have been generally accepted[21].

Braude and Sondheimer have regarded *o*-methylated styrenes and related compounds[7] as well as *o*-methylated benzaldehydes and acetophenones[18] as examples of the compounds exhibiting the steric effect of type 1, and have applied their postulated equation $\cos^2\theta=\varepsilon/\varepsilon_0$ to these compounds, where ε and ε_0 are the molecular extinction coefficient of the conjugation band of a given compound and that of the corresponding planar reference compound, respectively. According to the results, the estimated interplanar angles between the phenyl group and the CH=CX group in styrenes and related compounds are about 20∼30° for one, and about 40∼60° for two *o*-methyl substituted compounds.

On the other hand, Braude and Forbes[22] have stated that *o*-methylbiphenyl provides an excellent example of the steric effect of type 2, in contrast with *o*-methylated styrenes and acetophenones, notwithstanding the fact that the geometries of the relevant parts of these systems are quite similar. They have explained this rather strange difference between the biphenyl system on the one hand, and the acetophenone and styrene systems on the other, as follows: "the two possible uniplanar conformations of this compound (*o*-methylbiphenyl) are identical and involve the same extent of steric hindrance, whereas the two uniplanar conformations of 2-methylacetophenone or 2-methylstyrene are not identical and one involves much less steric hindrance than the other. Hence the steric hindrance produced by an *o*-methyl substituent will be effectively much larger in the biphenyl than in the other two systems, and the probability of any *o*-substituted biphenyl molecule's occupying a near-planar vibrational state will be extremely low. Thus, the conditions prerequisite for the display of steric effects of type 1 no longer exist".

This appears to be their main reason, although they have given two additional reasons. If this explanation were acceptable, why do *o,o'*-dimethyl substituted styrenes and acetophenones, e.g. 2,4,6-trimethylstyrene, 2,6-dimethylbenzylideneacetone, and 2,6-dimethylacetophenone, belong to the group of compounds which exhibit the steric effect of type 1 as Braude and his coworker have stated?

It will be evident, as seen in the present treatment of the styrenes and as discussed for the case of acetophenones in the preceding part[13] of this series, that the electronic bathochromic effect of the substituents is responsible for the apparent absence of an appreciable hypsochromic displacement of the conjugation band in these compounds. That is, it seems that the apparent absence of an appreciable wavelength displacement is not a proof of the absence of the hypsochromic displacement produced by the steric interaction but should be considered as a result of compensation of the hypsochromic effect by the electronic bathochromic effect of the substituents. The apparent bathochromic displacement observed sometimes with hindered compounds should, of course, be considered to be due to the electronic bathochromic effect of the substituents outweighing the steric hypsochromic effect. These considerations imply that the difference between the steric effect of type 1 and the steric effect of type 2 is not the difference in kind or in underlying mechanism as Braude and Forbes have asserted, but merely in degree.

In general, as has been discussed so far in this series, the electronic transition energy and hence the wavelength at which absorption occurs are determined by the spatial configuration or conformation of the molecule. Thus, so far as the conformation about the "single" bond is concerned, the non-planarity of the conformation must in principle produce a more or less large hypsochromic shift of the conjugation band, depending on the degree of the deviation from the coplanarity. On the other hand, the presence of steric interference in the molecule affects invariably the population ratio among conformations, and changes the most probable conformation from the planar conformation to a nonplanar one in most cases. Therefore, the wavelength displacement of the

---

[19] W. F. Forbes, "Steric Effects in Conjugated Systems", edited by G. W. Gray, (Proceedings of a Symposium held at the University, Hull, 15-17 July, 1958 by the Chemical Society), Butterworths Scientific Publications, London (1958), p. 62.

[20] R. B. Turner and D. M. Voitle, *J. Am. Chem. Soc.*, 73, 1403 (1951).

[21] M. S. Newman (ed.), "Steric Effects in Organic Chemistry", John Wiley & Sons, Inc., New York (1956), p. 484.

[22] E. A. Braude and W. F. Forbes, *J. Chem. Soc.*, 1955, 3776.

conjugation band caused by steric interference is not an unusual phenomenon as Braude and others have stated, but rather a usual one.

Either when the steric interference is so weak that the planar or nearly planar conformation is still the most probable one, or when the transition probability in the more probable nonplanar conformation is much smaller than the transition probability in the less probable planar conformation, it might be possible that the absorption maximum in the resultant spectrum of the sterically hindered compound is at the same wavelength as the maximum of the unhindered planar reference compound, the intensity of the former being smaller than that of the latter. However, it is doubtful whether such cases can exist in fact. The so-called steric effect of type 1 is, as mentioned above, merely superficial or spurious with respect to the steric effect, and should be considered as a special case where the steric hypsochromic shift is so small that it is almost completely compensated by the bathochromic shift due to the electronic effect of the substituents. Further, only considering that, as pointed out already in an earlier part[23] of this series, the hypsochromic shifts of the conjugation bands as compared with the bands of the corresponding planar reference compounds are observed even in the spectra cited by Braude and others as examples of the steric effect of type 1, it will be evident that the effect of this type is not clear-cut even phenomenologically.

Attention to the fact that, even when any significant wavelength displacement is apparently not observed, the presence of steric interference in the molecule or the deviation of the most probable molecular configuration from the coplanarity can manifest itself in a decrease in the intensity of the band may be of some practical significance, whatever the underlying mechanism may be. It seems, however, not to be necessary in principle to consider the so-called steric effect of type 1 separately from the so-called steric effect of type 2. Further, the steric effect of type 3 (i. e. the *type 3* steric effect) is merely the extreme case of the steric effect of type 2. Accordingly, it may be concluded that Braude and Forbes' classification of steric effects and their elucidations of the "mechanisms underlying the different types" are quite redundant, as pointed out also by Dewar[24].

1, 1-Diphenylethylenes

In 1, 1-diphenylethylene, the two phenyl groups can not be simultaneously coplanar with the ethylenic bond, owing to the steric necessities. Therefore, the most probable configuration of this molecule is presumed to be the configuration in which both of the phenyl groups are rotated out to the same extent as each other from the plane of the ethylenic bond, or alternatively, the configuration in which one of the phenyl groups is almost perpendicularly rotated out of the plane of the ethylenic bond, leaving the other phenyl group coplanar with the ethylenic bond.

The data of the ultraviolet absorption spectra of 1, 1-diphenylethylene and its methylated derivatives are summarized in Table IV, in which the data of the spectrum of styrene are also included for comparison. In addition, the spectra of 1, 1-diphenylethylene and its 2, 2-dimethyl derivative measured by the present author are shown in Fig. 2. These spectra are similar to each other, except for the appearance of the additional band at 235.4 mμ besides the principal band at 248.0 mμ in the spectrum of 1, 1-diphenylethylene. It is especially of interest that the absorption maxima of the principal (conjugation) bands of these four compounds appear at the almost identical wavelength.

The close similarity between the spectrum of 1, 1-diphenylethylene and that of styrene would be considered as supporting the second of the two hypotheses mentioned above concerning the

TABLE IV. ABSORPTION MAXIMA OF 1, 1-DIPHENYLETHYLENES

1, 1-Diphenylethylene	Solvent			Conjugation band		Ref.
		λ, mμ	ε	λ, mμ	ε	
Unsubstituted	H			248.0	14270	*a*
				235.4	13730	
2-Methyl-				ca. 248	ca. 13000	25
2, 2-Dimethyl-	H	(286.5)	1320	248.0	11700	*a*
		(279.0)	1900			
(Styrene)	C			248		8

Solvent: H, *n*-heptane; C, cyclohexane. Wavelengths in parentheses denote inflections.
Ref. *a*, the present work.

---

[23] H. Suzuki, This Bulletin, 32, 1357 (1959).

[24] M. J. S. Dewar, Ref. 19, p. 71.

[25] Ramart-Lucas and P. Amagat, *Bull. soc. chim. France*, [4] 51, 108 (1932).

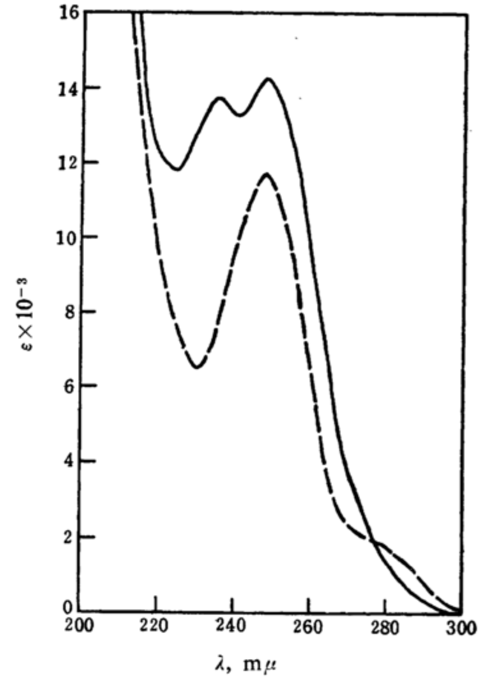

Fig. 2. Ultraviolet absorption spectra (in *n*-heptane): ——, 1, 1-diphenylethylene ; ----, 1, 1-diphenyl-2, 2-dimethylethylene.

most probable configuration of 1, 1-diphenylethylene. However, the close similarity between the spectrum of 1, 1-diphenylethylene and the spectra of its methylated derivatives seems to suggest that the first hypothesis is more plausible, because especially the dimethyl derivative (1, 1-diphenyl-2-methylpropene) can not assume the configuration of the second hypothesis owing to the steric interferences between the phenyl groups and the methyl groups at the *cis*-β-positions relative to the phenyl groups.

Now, when it is assumed that 1, 1-diphenylethylene as well as its derivatives has the configuration in which a styrene chromophore is left as the second hypothesis, these compounds can be treated by the calculation quite similar to the one in the case of styrenes.

Alternatively, when it is assumed that each compound has a configuration in which the two phenyl groups are rotated out by the identical degree from the plane of the ethylenic bond as the first hypothesis, the secular equation for the determination of the molecular orbitals as linear combinations of the $2p\pi$ atomic orbitals can be factorized into one equation identical in the form with the one for styrene and one equation for benzene, when ρ' is $1/\sqrt{2}\times\rho$, $\rho'\beta$ representing the $\pi-\pi$ resonance integral for each bond connecting a phenyl group to an ethylenic carbon atom. This situation is very similar to that in the treatment of tetraphenylethylene in Part VI[26] of this series. Accordingly, also in this case, the calculation similar to the one for styrenes can be applied to these 1, 1-diphenylethylenes, and from the values of ρ obtained as results of the calculation, the values of ρ' can be obtained. Then, from the values of ρ', the values of θ and R can be obtained by the use of the relation quite analogous to the one between ρ and θ as well as R postulated already. The results of the calculation are shown in Table V, in which the symbols have the same significance as in Table III. Allowance for the electronic bathochromic effect of methyl groups has been made by the method quite analogous to the one used in the case of the styrenes. In 1, 1-diphenyl-2-methylethylene, the positions of the two phenyl groups are not completely equivalent, and therefore, their angles of twist θ must differ, though probably very slightly, from each other. In spite of this, the results for this compound obtained on the basis of the assumption that the angles of twist of the two phenyl groups are equal are shown.

It is noteworthy that the introduction of methyl groups into the 2- or β-positions of 1, 1-diphenylethylene affects only slightly the calculated interplanar angle θ. The presence of the additional steric interference by the methyl groups in spite of the apparent absence of a wavelength displacement of the conjugation band is evident from the fact that the intensity of the band is decreased in the order 1, 1-diphenylethylene > 1, 1-diphenyl-2-methylethylene > 1, 1-diphenyl-2, 2-dimethylethylene, with the increasing number of methyl substituents. Thus, also in this case, the apparent absence of a wavelength displacement of the conjugation band is considered as the result of the compensation of the hypsochromic shift due to the steric interference by the bathochromic shift due to the electronic (probably hyperconjugation) effect of the methyl groups. Lastly, it may be mentioned that the calculated interplanar angles for these compounds, especially for the dimethyl compound, are very similar to those for the styrene derivatives belonging to Group IV (cf. Table III).

Exaltation of Molecular Refraction

Mulliken[27] has indicated that the molecular refractions of positional isomeric alkylstyrenes should roughly parallel the ultraviolet absorption maxima. Following this view, Schwartzman and Corson[8] have correlated the ultraviolet absorption spectra of styrene derivatives with methyl substituents on the benzene nucleus with the molecular refractions. The present author also has frequently referred so far in this series to

---

[26] H. Suzuki, This Bulletin, 33, 389 (1960).
[27] R. S. Mulliken, *J. Chem. Phys.*, 7, 356 (1939).

TABLE V. RESULTS OF CALCULATION FOR 1, 1-DIPHENYLETHYLENES

1, 1-Diphenylethylene	λ_A mμ	λ_L mμ	λ_S mμ	ΔE_A $-\beta$	ρ	ρ'	$\theta°$	R Å
Unsubstituted	248	248	208.3	1.475	0.858	0.607	43.5	1.496
2-Methyl-	248	250	208.3	1.496	0.821	0.581	46	1.498
2, 2-Dimethyl-	248	252	208.3	1.515	0.788	0.557	48	1.500

TABLE VI

Compound	EM_α	EM_D	$E\Sigma_\alpha$	$E\Sigma_D$	Ref.
Styrene					
Unsubstituted		1.37			9
		1.10		0.97	28
			1.10	1.13	29
			1.05	1.10	30
p-Methyl-			1.40	1.48	29
trans-β-Methyl-		1.87			9
			1.09	1.19	30
α-Methyl-		0.94			9
		0.64		0.55	28
			0.62	0.68	29, 30
α, β-Dimethyl-		0.70			9
			0.63	0.67	29, 30
cis-β-Methyl-		1.00			9
β, β-Dimethyl-			0.64	0.70	29, 30
α, β, β-Trimethyl-		0.59			9
		0.50		0.34	28
			0.44	0.48	30
1, 1-Diphenylethylene					
Unsubstituted			0.88	0.95	30
2-Methyl-	1.86	2.10	0.96	1.08	30
2, 2-Dimethyl-	1.39	1.53	0.67	0.74	30

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

the exaltation of the molecular refraction as a measure of the degree of conjugation.

In Table VI, the data of the exaltations found in the literature for the styrenes and the 1, 1-diphenylethylenes treated in this part of the series are summarized. The data for some compounds are considerably variable, depending on the worker. In addition, the values of the exaltations are considered to contain not only the conjugation effect but also the hyperconjugation effect of the methyl groups. Therefore, it may not be pertinent to correlate these values of the exaltations directly with the calculated interplanar angles or with the degrees of conjugation which will be inferred from the calculated interplanar angles. Notwithstanding, it will be seen that there exist roughly regular relations among these quantities.

Experimental

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

α-Methylstyrene (2-phenylpropene) was prepared after the procedure described by Klages[31], and purified by repeated distillation; colorless liquid, b. p. 160~162°C. The value of boiling point is in good agreement with those found in the literature (162°C[31], 160~162°C[32]).

β, β-Dimethylstyrene (1-phenyl-2-methylpropene) was prepared, after the procedure described by Tiffeneau[33], by dehydration of 1-phenyl-2-methylpropanol by heating with oxalic acid, and was purified by repeated distillation; colorless liquid, b. p. 189~193°C. The boiling point of this compound found in the literature is 179~189°C[33]. 1-Phenyl-2-methylpropanol was prepared by the Grignard reaction of benzaldehyde and the Grignard reagent prepared from isopropyl bromide and magnesium.

α, β, β-Trimethylstyrene (2-phenyl-3-methyl-2-butene) was prepared by dehydration of 2-phenyl-3-methyl-2-butanol by distillation, and purified by repeated distillation; colorless liquid, b. p. 189~

---

28) K. v. Auwers and F. Eisenlohr, *Ber.*, **43**, 806 (1910).
29) K. v. Auwers, ibid., **45**, 2781 (1912).
30) K. v. Auwers, ibid., **62**, 693 (1929).
31) L. Klages, ibid., **35**, 2640 (1902).
32) M. Tiffeneau, *Compt. rend.*, **134**, 845 (1902).
33) M. Tiffeneau, *Ann. Chim.*, [8] **10**, 365 (1907).

191°C. The value of boiling point is in good agreement with the value found in the literature. 2-Phenyl-3-methyl-2-butanol was prepared by the Grignard reaction from acetophenone and isopropyl bromide.

The specimen of 1, 1-diphenylethylene used was obtained by re-distillation under reduced pressure of the material prepared by Dr. Takahasi in this laboratory by the method described in Organic Syntheses[34]; colorless thin plates; b. p. 140~143°C/16 mmHg.

1, 1-Diphenyl-2, 2-dimethylethylene (1, 1-diphenyl-2-methylpropene) was prepared by dehydration of 1, 1-diphenyl-2-methylpropanol by refluxing with a few pieces of biscuit chips impregnated with concentrated sulfuric acid, and purified by distillation; colorless liquid, b. p. 167~169°C/22 mmHg. The value of boiling point of this compound found in the literature is 150~152°C/15 mmHg[35] and 280~282°C/775 mmHg[36]. 1, 1-Diphenyl-2-methylpropanol was prepared by the Grignard reaction from benzophenone and isopropyl bromide.

The author thanks Professor Kengo Shiomi and Professor Saburo Nagakura for reading the manuscript and for valuable advice, and also thanks Dr. Makoto Takahasi for his interest and for a generous supply of 1, 1-diphenylethylene.

Department of Chemistry
College of General Education
The University of Tokyo
Meguro-ku, Tokyo

---

[34] H. Gilman (Editor-in-Chief), "Organic Syntheses", Col. Vol. 1, John Wiley & Sons, Inc., New York (1932), p. 221.

[35] Ramart-Lucas and M. E. Salmon-Legagneur, *Bull. soc. chim. France*, [4] **45**, 728 (1929).

[36] J. Levy, ibid., [4] **29**, 882 (1921).