

formed all of the nitrogen analyses and to Grant Crane who prepared the vinyl butyl sulfone monomer. The author also wishes to express his ap-

preciation to B. L. Johnson for his continued interest in this work.

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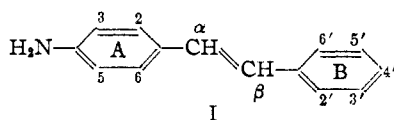
[CONTRIBUTION FROM THE CHESTER BEATTY RESEARCH INSTITUTE, ROYAL CANCER HOSPITAL, LONDON]

The Spectrophotometric Determination of Steric Hindrance in Some Stilbene Derivatives

BY R. N. BEALE AND E. M. F. ROE

The effect of steric hindrance to planarity on the intensity of the longest wave length transition in a number of methyl-derivatives of stilbene and 4-dimethylaminostilbene has been determined by comparison of the oscillator strengths (f) of this band in compounds with substituents in hindering and non-hindering positions in the molecule. A methyl group in a non-hindering position causes either no change or an increment in f -value, *i.e.*, no change at the 3- or 3'-position and a change in f -value of +0.05 at the 4- or 4'-position. In the hindering 2'-position a methyl group causes a decrement in f -value, *i.e.*, a change of -0.04. Successive introductions of further hindering methyl groups causes larger decrements in f of magnitude varying with the position of substitution. It is found that any of these methyl groups exerts its effect on the f -value of this band independently of other groups in the same ring, as though its effect were strictly localized. The changes in f -value are therefore additive for these compounds. A similarly independent effect is exerted by the $-N(CH_3)_2$ group substituted at the 4-position in stilbene, where it causes an increment in f more than twice that produced by a methyl group at that position.

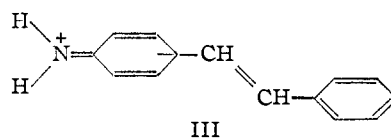
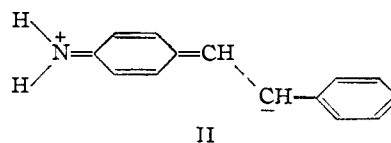
In the course of spectroscopic investigations of the growth-inhibiting and carcinogenic compound,



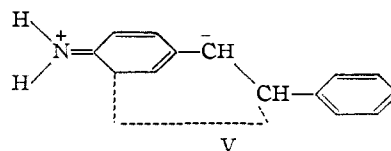
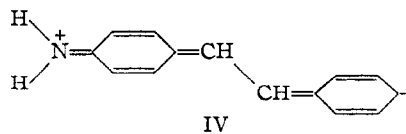
4-aminostilbene (I) and its derivatives,¹ it was observed that the ultraviolet absorption spectra of these compounds show reduction in maximum extinction and in some cases shift to higher frequencies of the long wave length band when substitution causes steric hindrance to the planarity of the molecule. Similar results are found in non-basic stilbene derivatives and examples of the effect are shown in Figs. 1 and 2. In Fig. 1 these progressive changes in extinction and frequency are evident as crowding about the ethylenic double bond is increased from the 2,4,6-trimethyl derivative to the 2,4,6,2',4',6'-hexamethyl derivative of stilbene. The changes are well marked also in the spectrum of 4-dimethylamino-2',4',6'-trimethylstilbene (Fig. 2) but they are more difficult to assess in the case of the corresponding 2'-methyl compound. Similar results have been found by other investigators, for stilbene derivatives² and in further aromatic series.³

In the substituted 4-aminostilbenes with which this investigation is mainly concerned,⁴ the ex-

pected changes in frequency and intensity due to steric hindrance may be discussed in terms of Coulson and Jacobs'⁵ calculations of π -electron charge distribution in the ground state⁶ and lowest excited state of this molecule. Their results were obtained by a simple molecular orbital method and are displayed diagrammatically in Fig. 3. The differences in excess π -electron charge on the atoms are somewhat exaggerated in this diagram. From Fig. 3, the structures expected to be of importance in light absorption would be: (a) in the ground state



and ortho-quinonoid structures corresponding to III; and (b) in the lowest excited state



benes, and resonance structures similar to those postulated for the latter may reasonably be assumed for 4-dimethylaminostilbene. *trans*-Isomers alone are discussed throughout this paper.

(5) C. A. Coulson and J. Jacobs, *J. Chem. Soc.*, 1983 (1949).

(6) Calculations by Pullman⁷ for the ground state of 4-aminostilbene lead to similar conclusions to those of Coulson and Jacobs.

(7) A. Pullman, *Compt. rend.*, 226, 486 (1948).

(1) A. Haddow, R. J. C. Harris, G. A. R. Kon and E. M. F. Roe, *Phil. Trans. Roy. Soc.*, [A] 241, 147 (1948).

(2) H. Ley and F. Rinke, *Ber.*, 56B, 771 (1923); H. Ley and H. Specker, *Z. Wiss. Phot.*, 38, 13 (1939); B. Arends, *Ber.*, 64, 1936 (1931); A. Smakula and A. Wassermann, *Z. physik. Chem.*, 155A, 353 (1931); G. N. Lewis and M. Calvin, *Chem. Revs.*, 25, 273 (1939).

(3) For example: L. W. Pickett, G. F. Walter and H. France, *THIS JOURNAL*, 58, 2296 (1936); W. Theilacker and W. Ozegowski, *Ber.*, 73, 898 (1940); M. T. O'Shaughnessy and W. H. Rodebush, *THIS JOURNAL*, 62, 2906 (1940); R. N. Jones, *ibid.*, 63, 1658 (1941); *ibid.*, 67, 1956 (1945); K. J. Brunings and A. H. Corwin, *ibid.*, 64, 593 (1942); W. R. Remington, *ibid.*, 67, 1838 (1945); L. G. S. Brooker, P. L. White, R. H. Sprague, S. G. Dent, Jr., and G. van Zandt, *Chem. Revs.*, 41, 325 (1947).

(4) The spectra investigated are those of derivatives of 4-dimethylaminostilbene, nearly all of which have substituents in ring B. These compounds were of greater biological interest than the 4-aminostil-

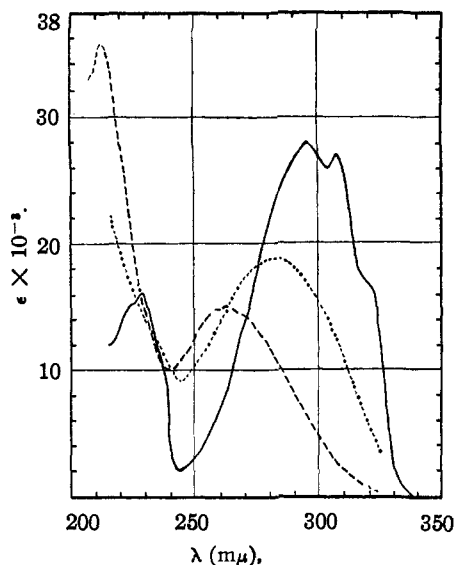


Fig. 1.—Ultraviolet absorption spectra: —, *trans*-stilbene (in 95% ethanol); - - - - - , 2,4,6-trimethylstilbene (in absol. ethanol); - · - · - · , 2,4,6,2',4',6'-hexamethylstilbene (in absol. ethanol).

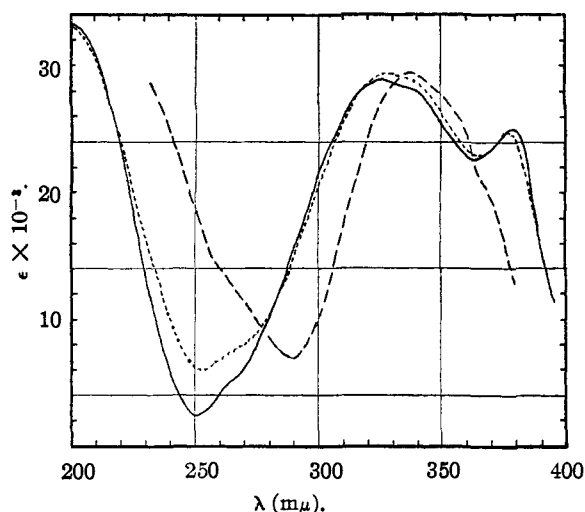
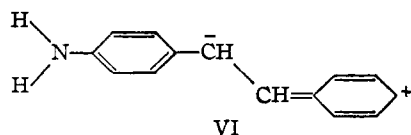


Fig. 2.—Ultraviolet absorption spectra (95% ethanol): —, 4-dimethylaminostilbene; - - - - - , 4-dimethylamino-2'-methylstilbene; - · - · - · , 4-dimethylamino-2',4',6'-trimethylstilbene.

and possibly also



Structure IV (and possibly VI also), which makes its greatest contribution to the resonance hybrid when the molecule is planar, should be of little importance in the ground state of the molecule. Hindrance to planarity should therefore introduce less strain in the ground state than in the excited state of the molecule. This hindrance, in the absence of other effects, should increase the energy of the excited state more than that of the ground state, with a resultant greater separation of electronic energy levels and shift of the corre-

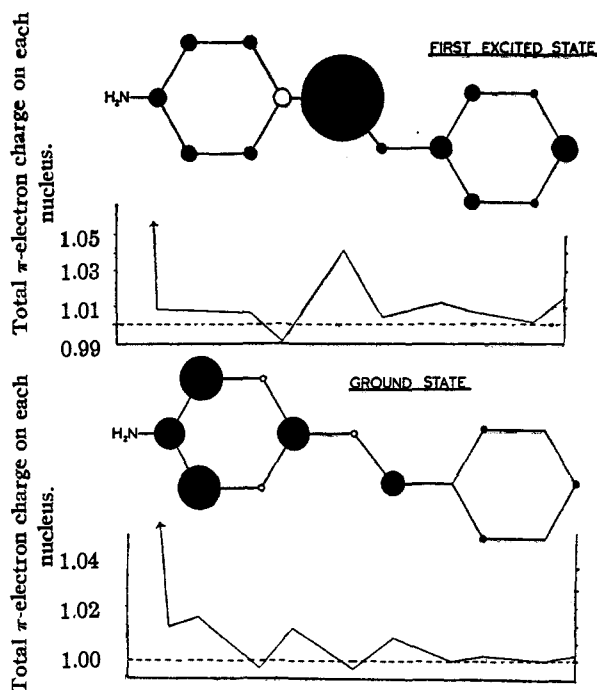


Fig. 3.—Diagrammatic representation of π -electron charge distribution in 4-aminostilbene (data of Coulson and Jacobs, ref. 5). Diameters of circles are proportional to excess π -electron charge (above 1.0) on each atom: ●, excess charge; ○, deficiency of charge.

sponding absorption to higher frequencies. As a further result of hindrance to planarity, the molecule in the ground state should approximate less frequently to the planar configuration demanded for ease in excitation to the higher energy states. This should lead to a decrease in the transition probability as measured by the oscillator strength, and thus a lowered absorption intensity. Further examination of the results of Coulson and Jacobs⁵ (Fig. 3) suggests that small variations in steric effect might be expected when compounds with hindering substituents in different rings are examined, for two reasons; (a) less perturbation occurs in ring B than in ring A in both ground and excited states, and (b) the C_1-C_α bond has slightly more double bond character and is therefore shorter than the $C_1'-C_\beta$ bond, particularly in the excited state, so that the approach to the ethylenic double bond of a hindering substituent in ring A is closer than in the case of ring B. These differences in bond lengths are small, however, and probably will not give rise to major variations in steric effect.

It was shown in the earlier work on these spectra¹ that the effects on the frequency of absorption of factors other than steric hindrance, such as the position of non-hindering substituents in the same or different rings, are difficult to assess. In addition, Mulliken⁶ had calculated that the intensities of the bands occurring in conjugated dienes should be very sensitive to changes in bond angles, even when the calculated frequencies of the transitions are approximately independent of the shape of the molecule. It was suggested, therefore, that measurement of changes in absorption intensity in the stilbene series might provide the more precise and

(8) R. S. Mulliken, *J. Chem. Phys.*, **7**, 121 (1939).

useful criterion of the presence of steric hindrance. The absorption spectra discussed in this paper have been determined down to about 2100 Å., and in this initial analysis the longest wave length band, which was shown by Mulliken and Rieke⁹ to be an N, V₁ type transition in *trans*-stilbene, has been chosen for intensity measurements. Due caution, of course, must be observed in the interpretation of data based on the intensity of a single band. Stealing of intensity by a strong neighboring band may occur, as shown by the work of Goepfert-Mayer and Sklar¹⁰ and of Sklar¹¹ on the benzene transitions and of Platt and Klevens¹² on alkyl benzenes. And effects other than steric hindrance may have greater influence on intensity determinations in one part of the spectrum than in another, e.g., Klevens and Platt's¹³ investigations of N,N-dimethylaniline derivatives, where the far ultraviolet band (near 1800 Å.) shows different intensity changes from those of the three longer wave length bands (near 2100, 2500 and 3000 Å.) when the effects of methyl groups ortho (hindering) or para (non-hindering) to the -N(CH₃)₂ group are compared. However, no prediction may be made from these results as to the expected behavior of bands in the stilbene series for at least two reasons: (1) the 2100 and 2500 Å. bands in dimethylaniline derive from theoretically forbidden transitions in benzene, while there is general agreement^{9,14,15} that the longest wave length transition in the polyenes is theoretically allowed, and (2) the distribution of intensity between the bands is expected to be different for the two series of compounds, i.e., the longest wave length band is weakest in dimethylaniline and other substituted benzenes, while calculations^{9,14} show that the major part of the absorption intensity in *trans*-stilbene is concentrated in this band. It is, indeed, strong and

well separated from any strong neighboring transitions in the substituted stilbenes discussed in this paper.

Results

The oscillator strengths (*f*) of the longest wave length band in the spectra of a number of alkyl derivatives of stilbene and of 4-dimethylaminostilbene have been calculated from the integrated areas under the curves by means of the usual equation

$$f = 4.315 \times 10^{-9} \int \epsilon \bar{\nu} d\bar{\nu}$$

where ϵ is the molar extinction coefficient and $\bar{\nu}$ is the frequency in cm.⁻¹. All data are taken from curves which are being prepared for publication by the present authors.

In attempting to measure intensity of absorption by means of the integrated area under the longest wave length band envelope, it was necessary to separate a low intensity band whose presence is evident from the dissymmetry of the spectrum on each side of the minimum in most of these curves (Figs. 1 and 2). After drawing a reasonable cut-off for the main bands on either side of this minimum, the shape and position of this small band may easily be calculated in most cases, as is seen from the examples in Fig. 4. In the non-basic stilbene derivatives this band was found to have an *f*-value of 0.015 ± 0.005 and in the basic derivatives a value of 0.04 ± 0.005 . It is not clear whether this band should be regarded as a separate weak electronic transition or as a vibrational band associated with

TABLE I

f-VALUES FOR LONGEST WAVE LENGTH BAND IN *trans*-STILBENE AND DERIVATIVES

No.	Compound	<i>f</i> -value
1	<i>trans</i> -Stilbene	0.745
2	2-Methylstilbene	...
3	3-Methylstilbene	.745
4	4-Methylstilbene	.790
5	4,4'-Dimethylstilbene	.830
6	2,4,6-Trimethylstilbene	.655
7	2,4,6,2',4',6'-Hexamethylstilbene	.475
8	4-N-(CH ₃) ₂ stilbene	.865
9	4-N(CH ₃) ₂ -2'-methylstilbene	.820
10	4-N(CH ₃) ₂ -3'-methylstilbene	.865
11	4-N(CH ₃) ₂ -4'-methylstilbene	.915
12	4-N(CH ₃) ₂ -2',3'-dimethylstilbene	.825
13	4-N(CH ₃) ₂ -2',4'-dimethylstilbene	.875
14	4-N(CH ₃) ₂ -2',5'-dimethylstilbene	.835
15	4-N(CH ₃) ₂ -2',6'-dimethylstilbene	.720
16	4-N(CH ₃) ₂ -3',4'-dimethylstilbene	.925
17	4-N(CH ₃) ₂ -2, 2'-dimethylstilbene	.745
18	4-N(CH ₃) ₂ -2',4',6'-trimethylstilbene	.770

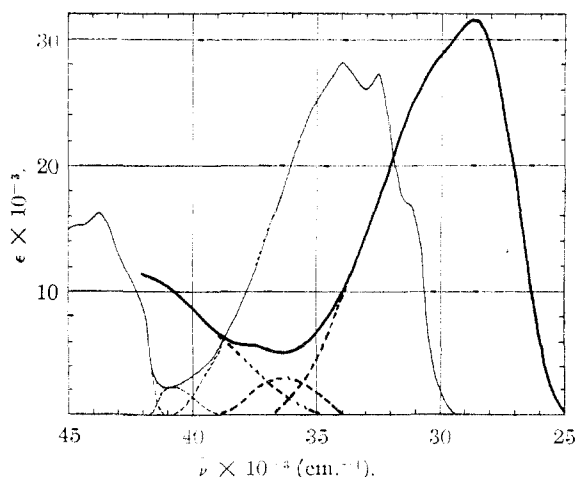


Fig. 4.—Ultraviolet absorption spectra (95% ethanol): —, stilbene; - - -, 4-dimethylaminostilbene.

(9) R. S. Mulliken and C. A. Rieke, *Repts. on Progress Phys.*, **8**, 231 (1941).

(10) M. Goepfert-Mayer and A. L. Sklar, *J. Chem. Phys.*, **6**, 645 (1938).

(11) A. L. Sklar, *ibid.*, **7**, 985 (1939).

(12) J. R. Platt and H. B. Klevens, *Chem. Revs.*, **41**, 301 (1947).

(13) H. B. Klevens and J. R. Platt, *THIS JOURNAL*, **71**, 1714 (1949).

(14) W. Kuha, *Helv. Chim. Acta*, **31**, 1780 (1948).

(15) N. S. Bayliss, *J. Chem. Phys.*, **16**, 287 (1948).

one or other of the near ultraviolet electronic transitions. However, since most of the following discussion is concerned with differences between *f*-values of the long wave length bands in pairs of basic or non-basic stilbenes, the inclusion of this small band in the calculations, or its omission, does not affect the results. It was decided to include it in the *f*-values for compounds listed in Table I. Each compound is numbered in this table, for convenience in later comparisons.

TABLE II
EFFECT OF METHYL-SUBSTITUTION ON f -VALUE IN STILBENE AND DERIVATIVES

Group	$f_a - f_b$	Δf	Δf_{av}
(1) Non-hindering methyl (4- or 4'-)	$f_4 - f_1$	+0.045	
	$f_5 - f_4$	+ .045	
	$f_{11} - f_3$	+ .050	
	$f_{13} - f_9$	+ .055	+0.050
	$f_{18} - f_{15}$	+ .050	
	$(f_6 - f_1) - (f_{15} - f_3)$	+ .055	
(2) Non-hindering methyl (3- or 3'-)	$f_3 - f_1$	0	
	$f_{10} - f_8$	0	
	$f_{14} - f_9$	+ .015	+ .005
	$f_{19} - f_{11}$	+ .010	
	$f_{12} - f_9$	+ .005	
(3) Single hindering methyl	$f_2 - f_1$.	
	$f_9 - f_3$	-0.045	
	$f_{12} - f_{10}$	- .040	- .04
	$f_{13} - f_{11}$	- .040	
(4) Second hindering methyl (same ring as (3))	$f_{14} - f_{10}$	- .030	
	$f_{15} - f_9$	-0.100	
	$f_{18} - f_{13}$	- .105	
	$f_6 - f_4 - \Delta f_{av} (3)$	- .095	- .100
	$f_{18} - f_{11} - \Delta f_{av} (3)$	- .105	
(5) Second hindering methyl (different ring from (3))	$f_{17} - f_9$	- .075	- .075
(6) Fourth hindering methyl	$(f_7 - f_5) - (f_{13} - f_8) - (f_{17} - f_9)$	- .130	- .135
	$(f_7 - f_5) - (f_5 - f_4) - (f_{17} - f_9)$	- .140	

Accuracy of Intensity Measurements.—Errors in determining the f -value of the long wave length band in this series of compounds may be due to (a) experimental error in the spectroscopic measurements and (b) variations in estimate of the cut-off separating the band from its neighbors. The latter error is reduced considerably by the standard procedure outlined above and is estimated to be no greater than ± 0.005 in f . Change from 100 to 95% ethanol as the solvent in these experiments produced changes in f as large as 0.035 in basic stilbene derivatives and negligible changes in non-basic stilbenes. All measurements were made therefore in the same solvent, 95% ethanol. The main experimental error, which may be large in the absence of precautions, is caused by *trans-cis* isomerization due to exposure to light or heat and this was avoided by preparing solutions in very weak light in cold solvent. All compounds were purified by chromatography, crystallization and in some cases, sublimation until no further change in spectrum could be detected under optimum conditions. Many of the measurements were first made spectrographically, including a qualitative examination using a hydrogen discharge tube as light source in order to detect fine structure. Finally, all were examined spectrophotometrically using a Beckman or Hilger Uvispek instrument. The error in maximum extinction values is considered to be no greater than $\pm 0.5\%$. The experimental error in our f -values, which range from 0.475 to 0.925, is estimated to be ± 0.005 , which gives a total error in f , including cut-off error, of ± 0.01 . The maximum error in *difference* of f -values for any pair of compounds (Δf) is thus no greater than ± 0.02 . In practice, as will be seen from Table II, the variation in Δf is of the order of ± 0.01 .

Discussion

Stilbene Derivatives with One Hindering Substituent.—The positional effects of the various substituents in 4-dimethylaminostilbene may be observed by comparison of the f -values given in Table I. For example, the change in f resulting from substitution of a methyl group at the 4'-position may be obtained from the data for compounds 11 and 8 in the Table, *i.e.*, $f_{11} - f_3 = 0.050$. Similarly $f_{13} - f_9 = 0.055$ and $f_{18} - f_{15} = 0.050$, and thus a Δf_{av} value may be calculated for the influence of a 4'-methyl group in this molecule. Results, calculated in this way, for a single methyl group substituted at the 2'-, 3'- or 4'-position in 4-dimethylaminostilbene and of a methyl group at the 3- or 4-position in stilbene are summarized in Table II (sections (1) to (3)), and Δf_{av} values are given.

From Table II the following facts emerge: (1) a methyl group substituted at the 4- or 4'-position causes an increment in f ; (2) a methyl group substituted at the 3- or 3'-position causes no significant change in f ; (3) a methyl group substituted at the 2'-position causes a *decrement* in f .

From (1) and (2) above it would be expected that a methyl substituent at the 2'-position should cause an increment or no change in f if steric hindrance were absent. The f -decrement at the 2'-position is therefore attributed to steric hindrance, and the following data on further hindering methyl groups support this conclusion.

Stilbene Derivatives with More than One Hindering Substituent.—Very few derivatives have been synthesized with more than one hindering substituent, or with any substituent other than a basic group in the aminostilbene ring A. The results which are available are shown in Table II

(sections (4) to (6)). It is clear that a second hindering methyl group in the same ring, either in stilbene or in its 4-dimethylamino derivatives, causes a further f -decrement (-0.100), more than twice the effect of the first hindering methyl group. This increased f -decrement is to be expected from an examination of atom models and of the generalized plane diagram in Fig. 5. In this diagram the methyl group is given its maximum dimensions (2.0 Å.) so that the steric interference shown is maximal, and rotation of the methyl group together with other uncertainties in assigning dimensions to such a diagram¹ may reduce steric hindrance in the real molecule below that depicted. It is apparent, however, that when the first (2'-) hindering substituent has taken up the position of least strain, *i.e.*, near to the β -C-H group, the second (6'-) substituent in the same ring must overlap the α -C-H group, where interference is greater. It appears that the f -decrement is a sensitive test of this effect.

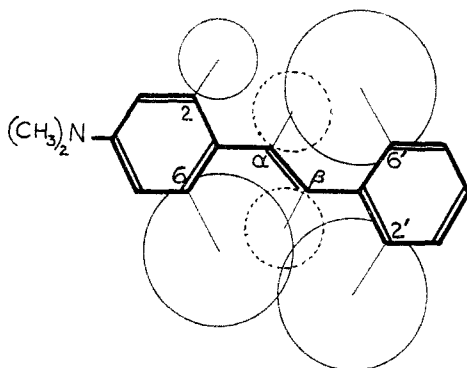


fig. 5.—Generalized plane diagram of 4-dimethylamino-6,2,6'-trimethylstilbene (a large circle represents the van der Waals zone of a methyl group and a small circle that of a hydrogen atom).

A second hindering methyl group in a different ring from the first, as in 4-dimethylamino-2,2'-dimethylstilbene (Table II (5)), causes a larger f -decrement than a 2'-methyl but a smaller decrement than a 6'-methyl group. Since in this compound each group may now take up a similar position of minimum interference this result would be unexpected in terms of overlap with α - and β -C-H groups. However, it is clear that even in the case of the non-basic 2-methylstilbene, the introduction of a second hindering group at the 6-position would leave the ethylenic double bond still coplanar and in conjugation with the unsubstituted ring; while its introduction at the 2'-position would reduce conjugation with this ring also, since neither ring would be then coplanar with the double bond. The path length over which unrestricted flow of π -electron charge is allowed would therefore be shorter in the 2,2'-dimethyl derivative than in the 2,6-compound, with consequent greater reduction in intensity in the former case. The unequal perturbation in the two rings in the case of 4-dimethylaminostilbene derivatives also may influence the difference in f -decrements, but insufficient data are available at present to enable these two effects to be separated.

From the f -value for hexamethylstilbene¹⁶ a value for a fourth hindering methyl group may be obtained (Table II (6)), by combination of data for stilbene and basic stilbene derivatives. There is, again, a large f -decrement (-0.140). In such a compound some overlap might be expected between the methyl groups themselves at 2,6'- and at 2',6-positions in addition to their interference with the α - and β -C-H groups (Fig. 5). That this is not the case may be seen from the following analysis. The difference between the f -decrements due to a 2-methyl and a 2'-methyl group (Fig. 5) is $-0.075 - (-0.04) = -0.035$ (from (3) and (5) in Table II), *i.e.*, in the case where overlap between the methyl groups is improbable, as explained in the preceding paragraph. This difference is almost the same as that between the Δf -values for the 6-methyl and the 6'-methyl groups ((6) and (4) in Table II, Fig. 5). This result would not be expected if hindrance due to methyl-methyl overlap were present, since the Δf -value for the 6-methyl group involves the f -value for 2,4,6,2',4',6'-hexamethylstilbene (f_7) where two such overlap decrements (2',6- and 2,6'-) would have to be assumed. Figure 5 shows that any methyl-methyl overlap is expected to be small, and could be negligible since the van der Waals zones assumed can only be approximate in shape and size.

Additivity of the Δf -Values.—The data collected in this investigation concern substitution effects of the methyl group in stilbene or in 4-dimethylaminostilbene. The remarkable consistency of these effects in spite of their relatively small magnitudes (*i.e.*, 0 to 15% of molecular f -values) is clear from Table II. Thus: (a) a methyl group introduced in a given *non-hindering* position has the same effect on f -value (*increment or no-change*) whether the molecule is planar or sterically hindered and whether a basic group is present or absent; *e.g.*, 4'-methyl substituted in 4-dimethylaminostilbene or in its 2'-methyl or 2',6'-dimethyl derivatives; a 4-methyl group substituted in stilbene or in 2,6-dimethylstilbene. (b) A methyl group introduced at a given *hindering* position causes the same *decrement* in f in the presence or absence of a non-hindering methyl group; *cf.* a 2'-methyl group substituted in 4-dimethylaminostilbene or its 4'-methyl or 5'-methyl derivative. (c) A *further hindering* methyl group introduced at a second hindering position in the same ring (B) causes a *larger decrement* in f than does the first group, in the presence or absence of a *non-hindering* methyl group; *e.g.*, a 6'-methyl group substituted in the 2'-methyl or 2',4'-dimethyl derivative of 4-dimethylaminostilbene.

From (a), (b) and (c) above it is seen that the effects on f -values of methyl substitution in these molecules are not only consistent but independent of one another and additive. It is as though the effects were strictly localized and non-interacting, possibly because the resultant perturbations of the

(16) The hexamethylstilbene used in this work was a different sample (m.p. 130°) from that (m.p. 105°) reported by Haddow, *et al.*¹ Its spectrum shows a higher maximum wave length and extinction and a larger f -value (0.475) than that of the former specimen ($f = 0.265$). It is apparent that the earlier sample was the *cis*-isomer and the one discussed in the present work is the *trans*-isomer.

molecule are small.¹⁷ It is of interest in this connection to note the influence on f -values of the $-\text{N}(\text{CH}_3)_2$ group substituted at the 4-position in stilbene derivatives. Where comparison may be made between derivatives with and without this substituent, as in results reported in Table II, the Δf -values are independent of the presence of the $-\text{N}(\text{CH}_3)_2$ group. It follows, therefore, that this group also exerts a constant effect at the 4-position, in the presence or absence of a methyl substituent in ring B. (The effect of 4- $\text{N}(\text{CH}_3)_2$ in the presence of a methyl substituent in the same ring (A) cannot be evaluated without further data.)¹⁸ The Δf_{av} value for 4- $\text{N}(\text{CH}_3)_2$, calculated excluding the small band discussed under Results, is $+0.095$ ($f_8 - f_1 = 0.100$; $f_{18} - f_6 = 0.090$; $f_{11} - f_4 = 0.090$; $f_{10} - f_3 = 0.095$). If this band is included the Δf_{av} value is $+0.120$, the difference being due to the greater intensity of the small band in basic stilbene derivatives, as noted before. It is apparent that even if this small band is excluded from consideration, the effect of the 4- $\text{N}(\text{CH}_3)_2$ group is much greater than that of a methyl group at the 4-position in stilbene, as would be expected on grounds of resonance theory.

Further experimental data are necessary before any conclusive rules could be made concerning the changes in f -values due to substitution in stilbene

(17) See Note by J. R. Platt, *THIS JOURNAL*, **74**, 2376 (1952).

(18) NOTE ADDED TO PROOF.—The recently measured f -value for 2,2'-dimethylstilbene (0.645) allows this effect to be evaluated, *i.e.*, $f_{17} - 0.645 = +0.100$, which should be compared with the average value of $+0.120$ and indicates absence of interaction between 4- $\text{N}(\text{CH}_3)_2$ and a substituent in the same ring A.

and its derivatives. Preliminary work on other alkyl derivatives of 4-dimethylaminostilbene suggests that an increasing f -decrement results from increase in bulk of an alkyl group substituted at the 2'-position. In addition, the substitution of an isopropyl group at the 4-position in stilbene or at the 4'-position in the basic stilbene causes a smaller f -increment than is the case with methyl substitution at these positions. This, together with a comparison of the effects in these compounds of methyl substitution at the 3-(or 3'-) position (no significant change in f), and the 4-(or 4'-) position (f -increment) indicates that the mesomeric effect of these groups is called into play to a greater extent than their inductive effect.

Thus, the results reported above suggest that careful measurement of f -values may prove a useful means of investigation of small degrees of steric hindrance to planarity and of other effects of substitution in these compounds.

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Reaction of Methyl Radicals with Hydrogen and Deuterium^{1,2}

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Free methyl radicals produced by photolysis of acetone or acetaldehyde in presence of deuterium or mixtures of hydrogen and deuterium yield various ratios of CH_4 and CH_3D determined by competition for methyl radicals by the different compounds present. By this method the reaction between free methyl and molecular hydrogen is established as $\text{CH}_3 + \text{H}_2 \rightarrow \text{CH}_4 + \text{H}$. Separate studies with acetone and acetaldehyde combined with previous work by Trotman-Dickenson and Steacie, Rollefson and Grahame, and Dodd indicate an activation energy of the reaction of methyl with hydrogen >13 kcal. and a steric factor of the order of 10^{-2} . The similar reaction with deuterium has an activation energy ~ 1 kcal. greater.

1. Introduction

The reaction of free methyl radical and molecular hydrogen has been the subject of repeated experimental and theoretical investigation.⁴ Activation energies given in the literature vary from an estimated low of 6–8 kcal. by Hartel and Polanyi⁵ to an estimated high of 20 kcal. by F. O. Rice.⁶ The tendency has been to favor a low activation energy, ~ 9 kcal., and a low steric factor,⁷ $\sim 10^{-4}$. On

the other hand, arguments have been offered that such a steric factor is much lower than that to be expected for simple free radical reactions.⁸ The activation energy is not in good agreement with most recent information on bond strengths and activation energy of the reverse reaction. Calculations based on low values of activation energy led to the conclusion by Patat and Sachsse⁹ that the Rice-Herzfeld free-radical chain theory¹⁰ is unsatisfactory for the cases they examined.

The situation regarding this important elementary reaction has been so confusing that even the reality of the mechanism



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(2) Abstract from a thesis submitted by Sol Davison to the Department of Chemistry of the University of Notre Dame in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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(4) Cf. R. D. Anderson, S. Davison and M. Burton, *Discussions Faraday Soc.*, **10**, 136 (1951), for a review of previous work.

(5) H. v. Hartel and M. Polanyi, *Z. physik. Chem.*, **B11**, 97 (1930).

(6) F. O. Rice, *THIS JOURNAL*, **56**, 488 (1934).

(7) Cf. E. W. R. Steacie, "Atomic and Free Radical Reactions," Reinhold Publishing Corp., New York, N. Y., 1946.

(8) M. G. Evans and M. Szwarc, *Trans. Faraday Soc.*, **45**, 940 (1949).

(9) D. Patat and H. Sachsse, *Z. physik. Chem.*, **B31**, 105 (1936); F. Patat, *ibid.*, **B32**, 274, 294 (1936).

(10) F. O. Rice and K. F. Herzfeld, *THIS JOURNAL*, **56**, 284 (1934).