

**271.** *Structural Assignments for the Geometrical Isomers of Some Nuclear-substituted  $\alpha\alpha'$ -Dimethylstilbenes by Means of Proton Magnetic Resonance Measurements.*

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The magnetic resonance of the methyl protons has been measured for 22 nuclear-substituted  $\alpha\alpha'$ -dimethylstilbenes. The methyl groups in the *trans*-compounds absorb at higher fields than those in the *cis*-isomers. The difference in chemical shift between the *trans*- and the *cis*-isomer arises from the different shielding effect of the  $\pi$ -electron current in the phenyl groups in different positions and conformations. These results are used to assign, for the first time, configurations to several substituted  $\alpha\alpha'$ -dimethylstilbenes.

In connexion with other work several nuclear-substituted  $\alpha\alpha'$ -dimethylstilbenes have been synthesized,<sup>1-4</sup> and the geometrical configurations have been determined<sup>1,5</sup> for the 4,4'-dimethyl-, 4,4'-dichloro-, 4,4'-dibromo-, 4,4'-di-iodo-, and 4,4'-dinitro-derivatives. These results and the study of  $\alpha\alpha'$ -dimethylstilbene<sup>4</sup> itself have shown that the *trans*-isomers each have higher m. p.s than the corresponding *cis*-isomers, in agreement with the general rule. On this basis, geometrical configurations, which could not be established by other means, were tentatively assigned to certain pairs of substituted dimethylstilbenes. These assignments have now been proved by measurement of chemical shifts of proton magnetic resonance of the  $\alpha$ -methyl group in  $\alpha\alpha'$ -dimethylstilbenes. Moreover, such measurements have enabled structures to be established for  $\alpha\alpha'$ -dimethylstilbenes which could be obtained only in one form.

Tables 1 and 2 list the observed shifts of  $\alpha$ -methyl protons relative to the proton resonance of cyclohexane used as an internal standard. All the  $\alpha$ -methyl protons absorb at fields lower than the protons of cyclohexane. Limited solubilities did not allow measurement in the same solvent for all the compounds, but measurement of the shift of 3,3', $\alpha,\alpha'$ -tetramethylstilbene in both acetone and carbon tetrachloride showed that the shift in the former is at lower fields by 0.01 p.p.m. than in the latter; the solvent effect is assumed to be negligible also for the other compounds investigated.

<sup>1</sup> Nagai, *J. Soc. Org. Synth. Chem. Japan*, 1961, **19**, 464.

<sup>2</sup> Nagai, *J. Soc. Org. Synth. Chem. Japan*, 1961, **19**, 470.

<sup>3</sup> Nagai, *J. Soc. Org. Synth. Chem. Japan*, 1961, **19**, 473.

<sup>4</sup> Nagai, Simamura, and Ehara, *Bull. Chem. Soc. Japan*, 1962, **35**, 244.

<sup>5</sup> Shimozawa and Nagai, *J. Chem. Soc. Japan*, 1960, **81**, 22.

TABLE 1.

Chemical shifts (in p.p.m.) of  $\alpha$ -methyl protons in substituted  $\alpha\alpha'$ -dimethylstilbenes,  $(X \cdot C_6H_4 \cdot CMe)_2$ , relative to cyclohexane as internal standard.

Subst. X	Ref.	<i>cis</i> -		<i>trans</i> -	
		M. p.	Shift	M. p.	Shift
4,4'-Me <sub>2</sub> .....	1	84.5°	-0.68	110.5°	-0.41
H, H .....	4	67	-0.715	107	-0.44
4,4'-Cl <sub>2</sub> .....	1	75	-0.68	134	-0.41
4,4'-Br <sub>2</sub> .....	1	82	-0.70	146	-0.40
4,4'-I <sub>2</sub> .....	1	109.5	-0.68	175.5	-0.425 †
4,4'-(NO <sub>2</sub> ) <sub>2</sub> .....	4	155	-0.82 *	217	-0.51 †

\* In acetone. † In saturated acetone solution.

TABLE 2.

Chemical shifts (in p.p.m.) of  $\alpha$ -methyl protons in substituted  $\alpha\alpha'$ -dimethylstilbenes,  $(X \cdot C_6H_4 \cdot CMe)_2$ , relative to cyclohexane as internal standard and the assignment of the geometrical configuration.

Subst. X	Ref.	<i>cis</i> -		<i>trans</i> -	
		M. p.	Shift	M. p.	Shift
4,4'-(MeO) <sub>2</sub> .....	1	52°	-0.67	132°	-0.43 *
3,3'-(MeO) <sub>2</sub> .....	2			90	-0.43
					-0.44 †
3,3'-Me <sub>2</sub> .....	2			72	-0.42
3,3'-Br <sub>2</sub> .....	2	80	-0.70	101	-0.44
3,3'-(NO <sub>2</sub> ) <sub>2</sub> .....	2	88		159	-0.53 *
4-MeO-4'-NO <sub>2</sub> .....	3			143.5	-0.47 *
4-Me-4'-NO <sub>2</sub> .....	3			131.5	-0.44 *
4-Cl-4'-NO <sub>2</sub> .....	3			145.5	-0.48 †

\* In saturated acetone solution. † In acetone.

For those pairs of isomers with known geometrical configurations, the chemical shifts of the  $\alpha$ -methyl protons relative to the resonance peak of the protons of cyclohexane were found to range from -0.82 to -0.68 p.p.m. for the *cis*- and from -0.51 to -0.40 p.p.m. for the *trans*-isomers (see Table 1). Although both the *cis*- and the *trans*-4,4'-dinitro-compound absorb at exceptionally low fields compared with the other compounds of the same geometrical configuration, it is beyond doubt that the shifts belonging to the *cis*- or to the *trans*-isomers constitute distinct groups. Thus the chemical shift for the *trans*-isomers appears at fields higher by 0.25-0.31 p.p.m.

Conjugation of a benzene ring with an olefinic double bond tends to keep the benzene ring coplanar with the double bond. In  $\alpha\alpha'$ -dimethylstilbene, however, the phenyl groups are twisted round the phenyl-carbon bond axis out of the plane of the double bond, in the *cis*-form by the neighbouring methyl and phenyl group, and in the *trans*-form by the two neighbouring methyl groups. The difference between the angles of these twists should cause difference in the shift of proton resonance of the  $\alpha$ -methyl group of *cis*- and *trans*-isomers, since the shielding effect on the methyl protons exerted by the circulatory current of the  $\pi$ -electrons in the benzene ring depends on the relative orientation of the methyl and the phenyl group. The shift due to this effect had been calculated in relation to the angle of twist, but no reasonable choice of angle for the *cis*- and the *trans*-isomer could bring the calculated difference into harmony with that observed.<sup>6</sup> In that calculation, only the effect of the phenyl group which is bound to the same olefinic carbon atom as the methyl group was considered. We have now estimated the shift while taking account of the shielding effect from both phenyl groups and found fair agreement with the experimental results.

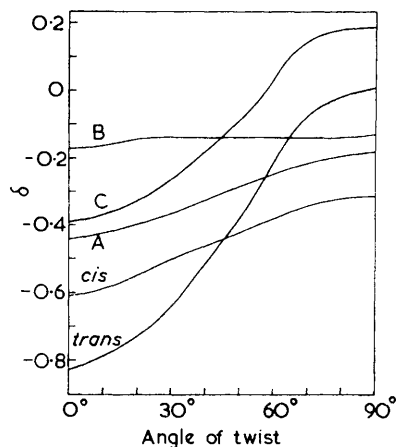
The usual bond lengths and bond angles being assumed, the position of the centre of

<sup>6</sup> Katayama, Fujiwara, Suzuki, Nagai, and Simamura, *J. Mol. Spectroscopy*, 1960, **5**, 85.

gravity of the three hydrogen atoms of the methyl group was evaluated in reference to the cylindrical co-ordinate system fixed to the benzene ring, and the chemical shift  $\delta$  at this point due to the circulating  $\pi$ -electron current of the benzene ring was estimated by Johnson and Bovey's method.<sup>7</sup> The curves drawn in the accompanying Figure show the dependency of the  $\delta$  value on the angle of the twist which the phenyl group suffers owing to the steric requirement. Curve A represents the shielding due to the phenyl group in the  $\alpha$ -position, that is, the phenyl group which is attached to the same carbon as the methyl under consideration, and curves B and C represent those due to the phenyl in the  $\alpha'$ -position which is respectively *trans* or *cis* to the methyl group. The curves denoted *cis* and *trans* show the relations between the  $\delta$  value and the angle of twist for these isomers, the angles of twist being assumed to be the same for both phenyl groups in each isomer; they have been constructed from curves A and B and curves A and C, respectively.

Variation of the chemical shift  $\delta$  of the  $\alpha$ -methyl protons in  $\alpha\alpha'$ -dimethylstilbene due to the circulating  $\pi$ -electrons in the benzene ring with the angle of twist of the benzene ring.

(A)  $\delta$  due to the  $\alpha$ -phenyl group. (B)  $\delta$  due to the  $\alpha'$ -phenyl *trans* to the methyl group. (C)  $\delta$  due to the  $\alpha'$ -phenyl *cis* to the methyl group. *trans*,  $\delta$  for the *trans*-isomer. *cis*,  $\delta$  for the *cis*-isomer.



Obviously, in this Figure, the region corresponding to angles of twist less than about  $50^\circ$  are fictitious, since inspection of a model shows that the steric effect requires that the phenyl group must be twisted at least about  $50^\circ$  out of the plane of the ethylenic bond. For significant values of angle of twist, the calculated  $\delta$  value is larger for the *trans*- than for the *cis*-isomer, in agreement with experiment, thus satisfactorily explaining the rule found above. Further, the following consideration leads to very reasonable values for the angle of twist of the phenyl group. If we assume the angle of twist to be  $50^\circ$  for the *cis*-compound, the corresponding angle for the *trans*-compound should be  $63^\circ$ , as readily seen from the Figure, in order that the difference in the shift between the *cis*- and the *trans*-isomer may agree with the observed one of 0.27 p.p.m. When the angle for the *cis*-compound is assumed to be increasingly larger, the angle for the *trans*-isomer correspondingly increases until it reaches  $70^\circ$ , at which point the angle for the *cis*-isomer is  $70$ – $80^\circ$ . The true value for the angle of twist cannot be determined. However, in view of the tendency of the benzene ring to become coplanar with the ethylenic linkage, thus reducing the angle of twist, the probable angle of twist is estimated to be  $50$ – $65^\circ$  for the *cis*- and  $60$ – $70^\circ$  for the *trans*-isomer. These angle values are in harmony with Suzuki's results<sup>8</sup> from ultraviolet-spectroscopic study of these compounds.

On the basis of this relation between the difference in shift and the isomeric structure the geometrical configurations of the isomeric pairs of 4,4'-dimethoxy- and 3,3'-dibromo- $\alpha,\alpha'$ -dimethylstilbene are now established, as shown in Table 2. Thus, in these compounds also the melting point of the *trans*- is higher than that of the corresponding *cis*-form. The 3,3'-dimethoxy-, 3,3'-dimethyl-, 4-methoxy-4'-nitro-, 4-methyl-4'-nitro-, and

<sup>7</sup> Johnson and Bovey, *J. Chem. Phys.*, 1958, **29**, 1012.

<sup>8</sup> Suzuki, *Bull. Chem. Soc. Japan*, 1952, **25**, 145; 1960, **33**, 396.

4-chloro-4'-nitro-derivatives, all of which have been obtained only in one form and lack the corresponding geometrical isomer, are assigned the *trans*-configuration, since their shifts all lie between  $-0.42$  and  $-0.48$  p.p.m. relative to cyclohexane. Similarly, the *trans*-configuration is assigned to the higher-melting form of 3,3'-dinitro-compound, since it absorbs at  $-0.53$  p.p.m. relative to cyclohexane. The lower-melting isomer, which now must be assigned the *cis*-configuration, has not been measured because of insufficiency in material.

*Experimental.*—The nuclear magnetic resonance spectra were determined with a Varian model V-4300C spectrometer with a 56.4 Mc. oscillator. The measurements were made on *ca.* 8% solutions in carbon tetrachloride, cyclohexane (0.4%) being used as an internal standard. For materials insoluble in carbon tetrachloride, 8% or saturated acetone solutions were used according to the solubility. The spectra were calibrated by the side-band technique.

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