

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AT THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

The Bromine-Bromine Distance in the Dibromides of *cis*- and *trans*-Stilbene¹

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The configuration of the products resulting from the addition of halogens to the double bonds of *cis* and *trans* isomers has been of considerable interest in connection with the problem of restricted rotation about the resulting single bond.

Weissberger has measured the electric dipole moments of the stilbene dichlorides² and dibromides³ in benzene solution. His results are shown in Table I. The difference in moment for a given pair of isomers indicates a lack of free rotation in at least one member of the pair, since completely free rotation in both members would lead to identical moments. The low moment of the *meso* dibromide is an indication that the bromine atoms are restricted to the *trans* position or nearly so, the slight deviation from zero moment being possibly due to thermal vibration.

TABLE I
ELECTRIC DIPOLE MOMENTS

	<i>meso</i>	<i>dl</i>
Stilbene dichlorides	1.27 <i>D</i>	2.75 <i>D</i>
Stilbene dibromides	0.4-0.9 <i>D</i>	2.8 <i>D</i>

Rate studies have been made in this Laboratory by Young, Pressman and Coryell⁴ for the reaction between potassium iodide and the dibromides of various pairs of *cis-trans* isomers. It was found for each pair investigated that the rate of reaction of the *trans* derivative is faster and the heat of activation smaller than for the corresponding *cis* derivative. Young and Pressman⁵ have attributed these differences to restriction of the rotation about the single bond between the two carbon atoms carrying the bromine and have correlated the specific reaction rate constants with the configurations postulated on the basis of preferred orientation due to this restriction. It was in connection with this work that the present problem presented itself and the author is indebted to Dr. Young and Mr. Pressman for the

(1) Presented at the Stanford University meeting of the Pacific Division of the American Association for the Advancement of Science, June, 1939.

(2) Arnold Weissberger, *J. Org. Chem.*, **2**, 245 (1937).

(3) Private communication to the author.

(4) William G. Young, David Pressman and Charles D. Coryell, *THIS JOURNAL*, **61**, 1640 (1939).

(5) William G. Young and David Pressman, results not as yet published; see abstract of paper presented by William G. Young at the Eighth National Organic Chemistry Symposium of the American Chemical Society, St. Louis, Missouri, December, 1939.

pure crystalline materials used in this investigation.

Although free rotation about the carbon to carbon single bond in question in the stilbene dibromides would seem highly improbable in the crystalline solids, there is, it seems, a high degree of probability that if there is a preferred orientation in the liquid or dissolved state the same or very nearly the same orientation will also be assumed by the molecules on entering the crystal.

Taking 1.54 Å. as the carbon to carbon single bond distance, 1.91 Å. for the carbon to bromine distance, and tetrahedral bond angles, one may calculate the expected bromine-bromine separation for the absolute *cis* position to be 2.82 Å. and for the absolute *trans* position 4.57 Å. Thermal vibration at room temperature would make the average separation for *cis*-restricted molecules greater and for *trans*-restricted molecules less than these calculated values.

For purposes of describing the configuration about the bond, use is made of the azimuthal angle, ϕ , such that ϕ is 0 for the *cis* position and 180° for the *trans*. Using the above angles and distances, the bromine separation, l , then becomes

$$l = [7.95 + 6.48 (1 - \cos \phi)]^{1/2}$$

The method employed in measuring this distance was the radial distribution treatment essentially as described by W. V. Medlin.⁶

In this treatment the radial distribution function, $4\pi r^2 \rho(r)$, is given by the following summation over all lines observed on the photograph

$$4\pi r^2 \rho(r) = 4\pi r^2 \rho_0 + \frac{2r}{\pi} \sum_{i=1}^{i=\infty} s_i I_i \sin s_i r$$

where $s = 4\pi \sin \Theta_i / \lambda$, Θ_i being the Bragg angle or one-half the scattering angle for the i th line on the film, λ the wave length of the X-rays and I_i the intensity of the i th line.

The above function represents the product of scattering powers in volume elements which are separated by the distance r as a function of this distance. The magnitude of these maxima will be proportional to the products of the atomic numbers of the atoms involved. When one particular

(6) W. V. Medlin, *THIS JOURNAL*, **57**, 1026 (1935), and **58**, 1590 (1936).

kind of atom is much heavier than any of the others present, as is the case in the present study, maxima due to the interaction of these heavy atoms with each other may be so strong as to blank out all other effects. Thus bromine-bromine interaction will be $(35)^2$ as compared to 35×6 for bromine-carbon and $(6)^2$ for carbon-carbon or in the approximate ratio of 35:6:1.

The crystalline samples of the *meso*- and *dl*-stilbene dibromides were finely ground and passed through a 200-mesh sieve. The resulting powder was packed with only slight pressure into capillary tubes with a bore of about 0.3 mm. The cylinders thus formed were then pushed out of the capillary by means of a stiff wire and mounted in the X-ray camera. No collodion or other binder was used in holding the samples together.

Filtered radiation from a copper target was employed in a cylindrical camera of 5 cm. radius. Both of the photographs used showed 35 measurable lines, covering a range of $\sin \theta/\lambda$ out to 0.375 for *trans*-stilbene dibromide and to 0.318 for *cis*-stilbene dibromide. The intensities were estimated both visually and with the aid of microphotometer tracings made on the Smith-Leighton-Hensen microphotometer at Stanford University, the two methods giving values in fairly good agreement. The weaker lines did not show on the tracings so it was necessary to rely entirely on the visual estimates for their intensities.

The relative intensities so obtained were corrected by means of the Lorentz and polarization factors and multiplied by a factor $e^{-B \sin^2 \theta}$ following the procedure of Medlin, so as to reduce the importance of the lines at large scattering angles. In both cases a value of $B = 7.5$ was used. Medlin has shown, and it was tested in this case as well, that the positions of the maxima are quite independent of the value of B .

The results of the summations are shown in Fig. 1, the constant term $4\pi r^2 \rho_0$ being omitted. In the case of *trans*-stilbene dibromide (the *meso* compound), only one maximum is observed and that at 4.50 Å. The small shelf just under 3 Å. may be due to carbon-bromine interaction caused by a carbon atom and a bromine atom not directly bonded to each other, but each bonded to a common third atom. The calculated distance for such a case is 2.8 Å. The large maximum is without doubt due to bromine-bromine interaction and the distance 4.50 Å. corresponds to

nearly the complete *trans* position which, as pointed out before, would require a separation of 4.57 Å. The distance 4.50 Å. corresponds to an azimuthal angle of 154° or a displacement of 26° from the full *trans* position assuming a static model.

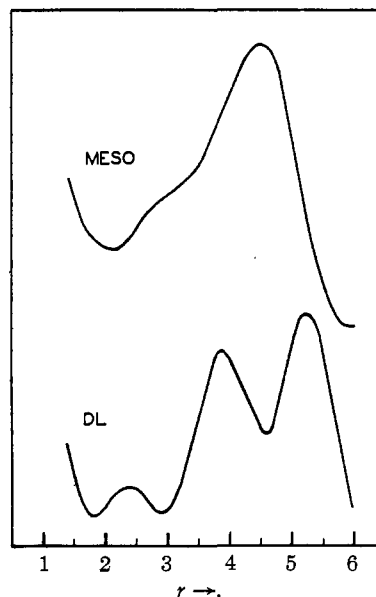


Fig. 1.—Radial distribution functions for the stilbene dibromides.

There is also the possibility that the single large maximum in this case is the resultant of two different pairs of bromine-bromine distances of nearly the same magnitude, one of them being within the molecule and the other due to bromines in different molecules. For example, the bromine separation within the molecule might be that for the full *trans*, 4.57 Å., and that for the pair on adjacent molecules about 4.4 Å., giving the observed peak at 4.50 Å. as an unresolved doublet. Only a more complete structure determination could answer this question. In spite of this difficulty, it still may be said safely that the bromine atoms are close to *trans* in configuration.

The function for *cis*-stilbene dibromide (the *dl* mixture), shows three maxima in the range covered, one small one at 2.40 Å. and larger ones at 3.85 and 5.25 Å. The value 2.40 is too small to be attributed to a bromine-bromine separation where the two atoms are not directly bonded to each other since the minimum distance between non-bonded bromine atoms in crystalline bromine at liquid air temperature is 3.30 Å. and twice the van der Waals radius is 3.80 Å. the normally

expected closest distance of approach of non-bonded atoms. The smallness of the peak, too, would eliminate it as being due to bromine-bromine interaction and it is therefore attributed to unresolved carbon-bromine interaction, from the bonded distance for these atoms of 1.91 Å. and the non-bonded separation of 2.82 Å. The maximum at 5.25 is to be attributed to a bromine separation in different molecules because the distance is greater than that for full *trans*. The remaining peak at 3.85 appears, therefore, to be the one due to the bromine atoms within the molecule. This distance corresponds to an azimuthal angle 90°. It is interesting to note that the bromine separation is only slightly different from twice the van der Waals radius for bromine which is 3.80 Å. If the phenyl groups were fully *trans* to each other, the bromine azimuthal angle would be 60°, requiring a separation of only 3.35 Å., which is less than twice the van der Waals radius. The tendency of the phenyl groups to be *trans* to each other would be opposed by the repulsion of the bromine atoms and the observed structure may be the resultant of these two forces. A second configuration with the phenyl groups 30° from *cis* to each other is also permitted by the observed bromine separation. In this case the bromine atoms would again be brought as close as possible to each other by the tendency of the phenyl groups to get apart. These two possibilities are shown in Fig. 2.

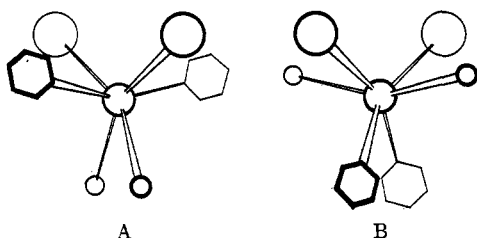


Fig. 2.—Configurations permitted for the dibromide of *cis*-stilbene, looking down the axis of the bond between the two carbon atoms to which bromine is bonded. The circles represent in order of decreasing size, bromine, carbon and hydrogen atoms. The phenyl groups are indicated by means of hexagons. No significance is to be attached to the absolute sizes or scale used.

These findings lend support to the postulate of Young and Pressman and are in fairly good agreement with the electric dipole moments found by Weissberger² and shown in Table I.

In order to estimate the dipole moments ex-

pected for the observed bromine separation, the molecules were considered as being made up of two C_6H_5CHBr groups joined together by a carbon-carbon bond and rotated with respect to each other through the angle ϕ . If the component of the electric moment of the C_6H_5CHBr group perpendicular to the axis of the bond by means of which the two are joined is represented by m , and if polarization is neglected, the molecular dipole moment, μ , is given by the function, $\mu = 2m \cos(\phi/2)$.

The value of m was estimated by making use of the electric moment for benzyl bromide which was found by Mohler⁷ to be 1.88 D . The moment of a C-H bond taken as 0.4 D^8 was subtracted vectorially and the component of the remainder perpendicular to the C-H bond was taken assuming tetrahedral angles. This procedure gives a value of 1.7 D for m . Making use of the values of ϕ calculated from the bromine-bromine distances, this leads to a moment of 0.8 D for the *meso* dibromide, which falls in Weissberger's range, and 2.4 D for the *dl* dibromide as compared to the observed value of 2.8 D . In this simplified treatment the phenyl groups have received no special attention and the same function is assumed for both the *meso* and the *dl* dibromides.

The author is indebted to Dr. William G. Young and David Pressman for their kindness in making available the crystalline dibromides from which the X-ray powder photographs were prepared.

Summary

The bromine-bromine separations in the molecules of the crystalline stilbene dibromides have been measured by means of the radial distribution treatment of X-ray powder photographs. The separation was found to be 4.50 Å. in the *meso* dibromide and 3.85 Å. in the *dl* dibromide. In the former, all like groups are *trans* to each other, while in the latter the bromine atoms are as close to each other as the van der Waals radius for bromine will permit. The results support the postulate of Young and Pressman and are in agreement with the electric dipole moments found by Weissberger.

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(7) H. Mohler, *Helv. Chim. Acta*, **21**, 67 (1938).

(8) Linus Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939, pp. 67, 68.