

The mean chain length decreases considerably as the initial ethane pressure increases. This fact is discussed in the light of the possibility that hydrogen atoms are the chain carriers. The activation energy of the chain propagation process is about 10,000 cal.

The activation energy of the chain-free reaction has the very high value of 74,500 cal., and is distributed in about 14 square terms.

REFERENCES

- Allen and Sickman 1934 *J. Amer. Chem. Soc.* **56**, 2031.
Fletcher and Rollefson 1936 *J. Amer. Chem. Soc.* **58**, 2135.
Hinshelwood 1926 *Proc. Roy. Soc. A*, **113**, 230.
Mitchell and Hinshelwood 1937 *Proc. Roy. Soc. A*, **159**, 32.
Rice and Herzfeld 1934 *J. Amer. Chem. Soc.* **56**, 284.
Sachsse 1936a *Z. phys. Chem. B*, **31**, 87.
— 1936b *Z. phys. Chem. B*, **31**, 79.
Staveley and Hinshelwood 1936a *Nature, Lond.*, **137**, 29.
— 1936b *Proc. Roy. Soc. A*, **154**, 335.
— 1936c *J. Chem. Soc.* pp. 812, 818.
— 1937 *Proc. Roy. Soc. A*, **159**, 192.

X-Ray Analysis of the Dibenzyl Series IV—Detailed Structure of Stilbene

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A preliminary account of the crystal structure of stilbene in relation to other compounds in the dibenzyl series has already been given in Part III of this work (Robertson, Prasad and Woodward 1936). The general arrangement of the four molecules in the unit cell was deduced from certain absolute intensity measurements, the physical properties of the crystal, and a comparison with the accurately known structure of dibenzyl (Robertson 1934, 1935a). Although the approximate structure was established beyond any doubt, the precise determination of the atomic positions has proved to be a matter of very great difficulty. This is due to the presence of four molecules in the unit cell and to the fact that it is impossible to formulate a

definite model of the molecule from the chemical structure owing to the possibility of free rotation about the single bonds. For the accurate analysis it was necessary to determine the phase constants of all the weaker reflexions, and in the course of this work over twenty trial structures were calculated and compared. In this connexion the mechanical sorting method of structure factor calculation previously described (Robertson 1936) proved of great assistance. The repeated application of a double Fourier synthesis to the ($h0l$) set of structure factors then gradually refined the values for the atomic co-ordinates, and we believe that the final results given below are now comparable in accuracy to those obtained for the other structures in this series. It is unnecessary to describe in detail the various stages by which this structure has been reached, and the results of the final Fourier synthesis only are given in the following pages.

The relative orientations of the molecules in the crystal now recorded should enable various physical properties of the crystal to be expressed as functions of the individual molecules. In particular, the results now obtained will justify more accurate measurements being made on the magnetic susceptibilities and the refractive indices of the crystal than are available at present.

The main results of the analysis are first discussed in relation to the structure of the molecule, while the X-ray work, co-ordinates of the atoms, etc., are given in a later section.

THE STRUCTURE OF THE STILBENE MOLECULE

Two separate molecules contribute to the asymmetric unit of the crystal, and their structures have been independently deduced from the intensity measurements. The final results are expressed by contour maps of the electron distribution in figs. 1, 2 and 3 which represent projections of the structure along the b crystal axis. It will be seen that the two molecules differ considerably in these projections. It is found, however, that this difference is due to relative orientation and not to any significant difference in the shape or dimensions of the molecules themselves. The actual dimensions can readily be deduced from these projections, and the results are shown in figs. 4 and 5.

Owing to the complicated nature of the structure only the b axis projections give any resolution of separate atoms. Consequently as only one projection is available for each molecule, some of the dimensions recorded in figs. 4 and 5 are only partially direct determinations. This applies particularly to the carbon-carbon double bond distance of 1.33 Å and to

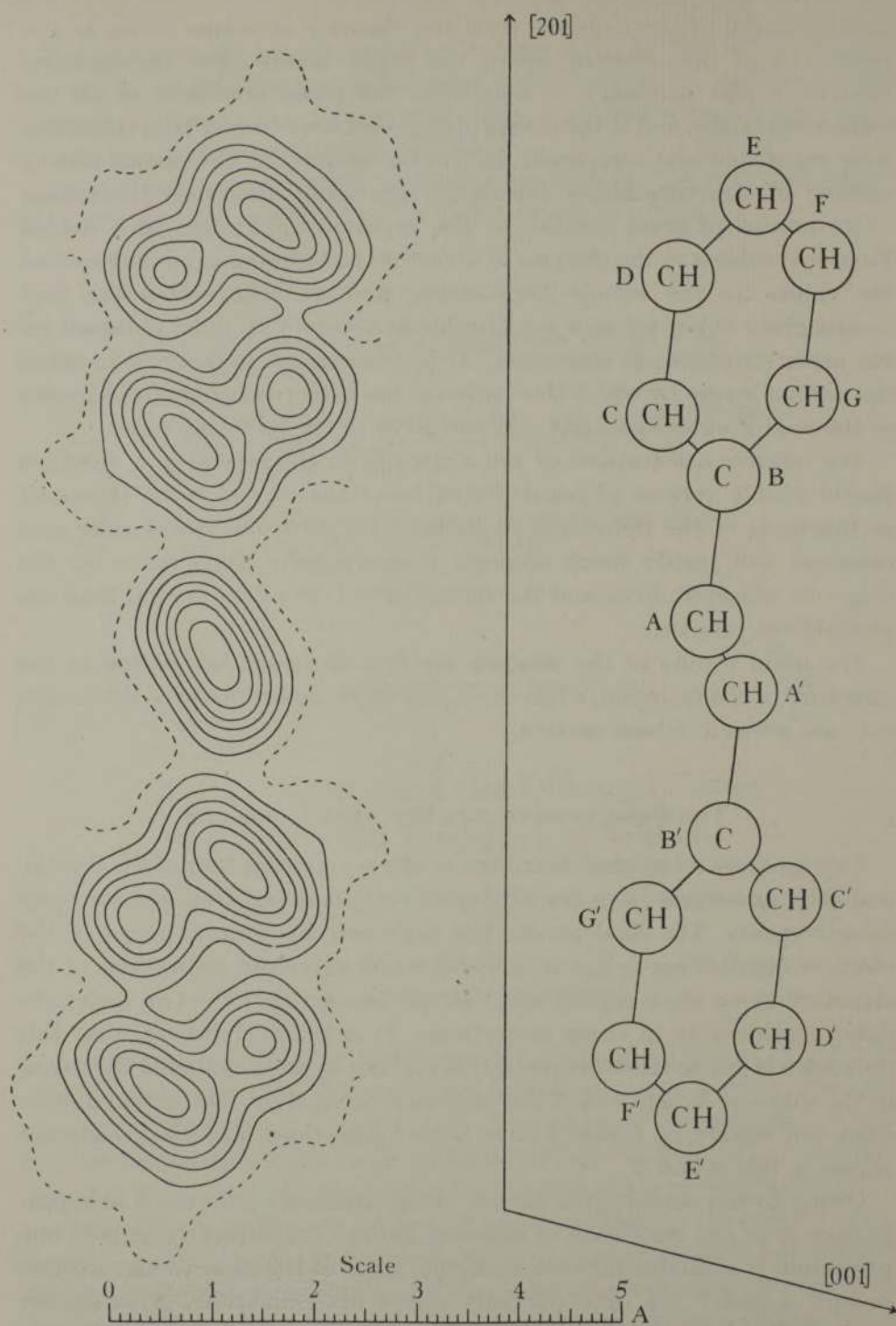


FIG. 1—Stilbene molecule 1 in the b axis projection. Each contour line represents a density increment of approximately one electron per \AA^2 , the one electron line being dotted.

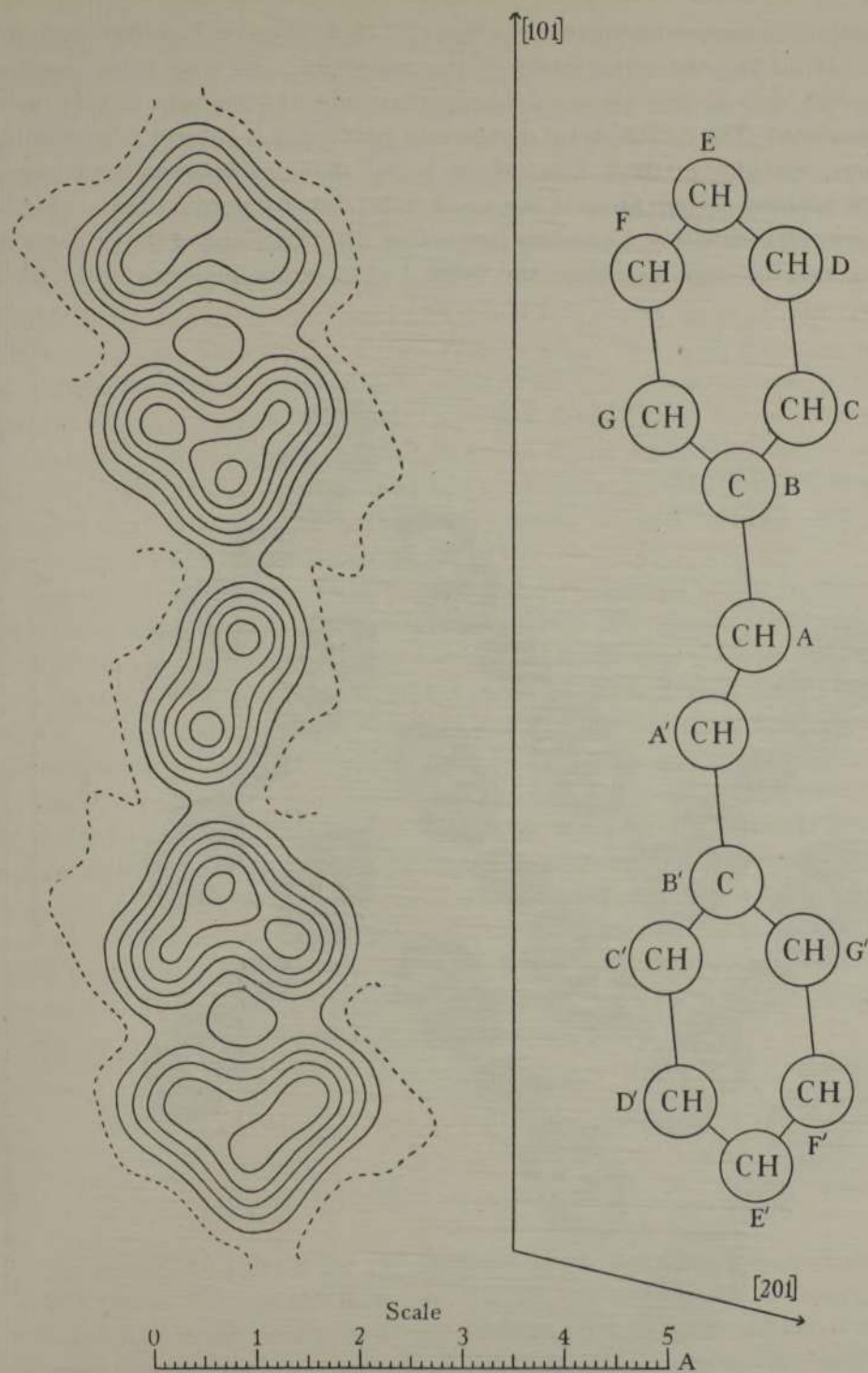


FIG. 2—Stilbene molecule 2 in the b axis projection. Scale as in fig. 1.

the carbon-carbon distance in the ring of 1.39 Å. These values were assumed in calculating the orientations of the molecules, and were later justified by the agreements obtained when other sets of structure factors were calculated. The double bond distance in particular is subject to a possible error of about ± 0.04 Å. The "single bond" distance between the benzene ring and the carbon atom *A* is a much more direct determination owing to the small inclination which this line makes with the plane of the projection. For this distance we obtain the value 1.44 Å in one molecule and 1.45 Å

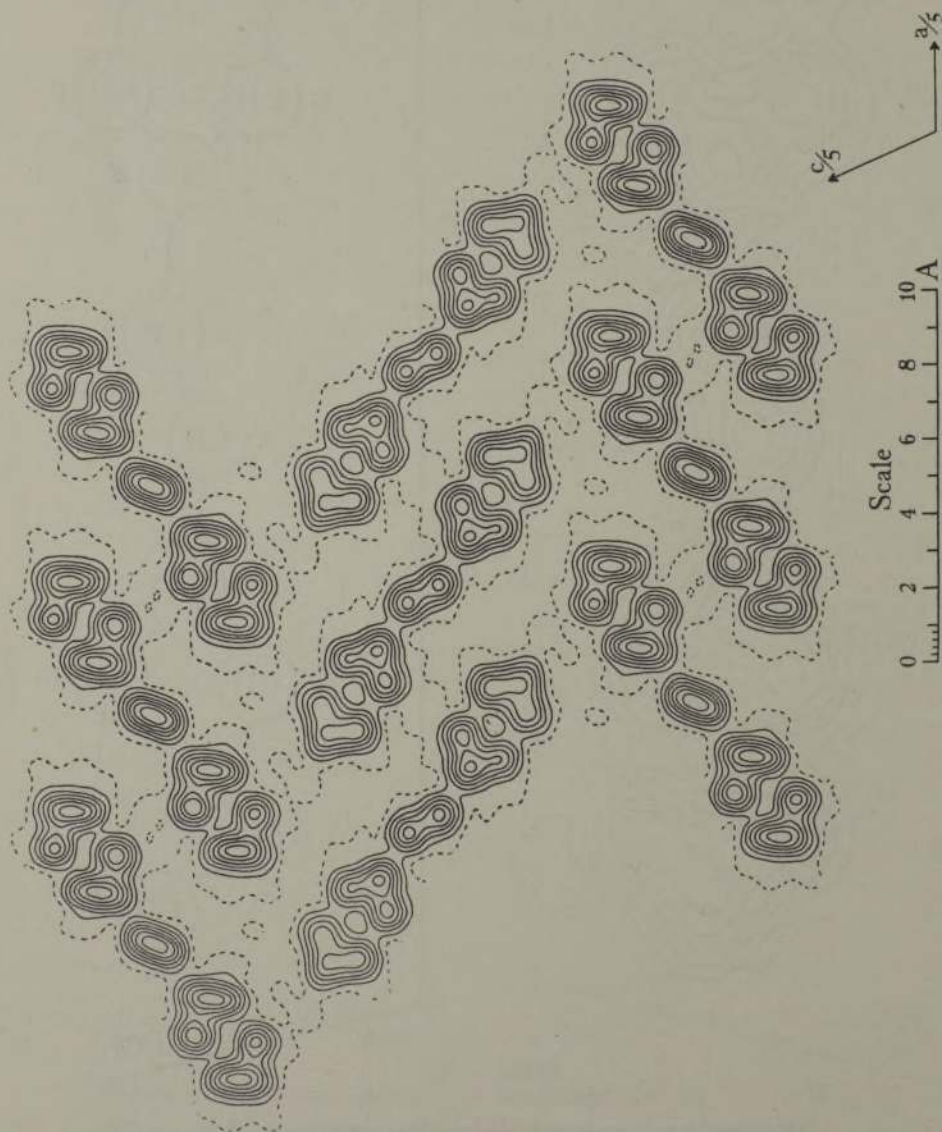
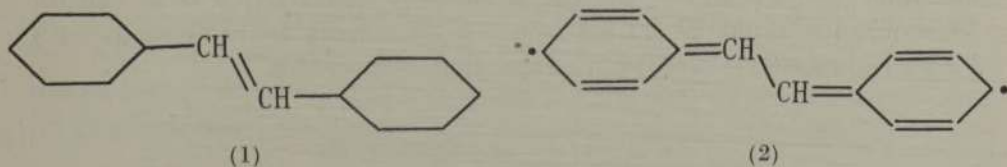


FIG. 3.—Showing on a smaller scale the arrangement of a group of stilbene molecules in the *b* axis projection. Each line approximately one electron per Å^2 .

in the other, figures which, however, are still subject to an error of at least ± 0.02 A, so that we cannot attach any significance to the difference.

With regard to shape and the angles between the bonds, a somewhat larger difference is obtained between the two molecules. They are both nearly flat. The divergence from a strictly planar model can be measured by the angle through which it is necessary to rotate the ring about the single bond AB , starting from the planar position. For molecule 1 this rotation is 10° and for molecule 2 only 3° . Further, the angle between the double bond and the single bond ($A'AB$) is 128° for molecule 1 and 133° for molecule 2. It is doubtful, however, whether much significance can be attached to these observed differences. The short distance between the central atoms A and A' and their imperfect resolution in the projections make it difficult to define the exact direction of the line joining them, and all the above figures depend upon the orientation of this line. It seems possible that strictly planar models may apply to each molecule, within the limits of experimental error.

In spite of these minor uncertainties definite conclusions can be drawn regarding the structure of the stilbene molecule. The length of the single bond from the benzene ring to the atom A has undergone a severe contraction from the standard value of 1.54 A as in diamond. The value of 1.44 A which we find indicates about 40% of double bond character in this link, if use is made of the curve recently given by Penney (1937) which expresses the relation between the order of linkage and the internuclear distance between two linked carbon atoms (the "ionic diameter" of carbon). There is thus no doubt that the ordinary formula for stilbene (1) does not represent the molecule completely, but that excited structures of the form represented by (2) must also contribute to the normal state. In (2) the dots in the para positions represent single electrons, which can formally be considered as paired. Such formulae have been discussed by Pauling and Sherman (1933) in relation to diphenyl and related compounds.



The strongest evidence for the existence of (2), however, is to be found in the planar form of the molecule. In (1) free rotation of the rings is possible, and in the nearly isomorphous dibenzyl crystal the planes of the benzene rings are in fact practically at right angles to the plane of the central

zig-zag. (The rings are always parallel to each other, both in the dibenzyl and stilbene crystals, owing to the centre of symmetry in the molecule.) Thus as far as formula (1) is concerned we might expect the plane of the rings to be at right angles to the plane of the central zig-zag, by analogy with the dibenzyl crystal, and especially as such a configuration would give a greater clearance between the ethylene hydrogen atoms and the ortho hydrogen atoms in the ring. But if formula (2) contributes to the structure, the molecule is necessarily planar, from general stereochemical considerations.

We must conclude that in the actual structure there is resonance between these two forms, and their relative contributions may be estimated from the internuclear distances given above. Further evidence for the existence of such resonance in stilbene has been given by Pauling and Sherman (1933) from a study of thermochemical data. They find that the total resonance energy of stilbene is 4.09 e-volts, which is 0.67 e-volt more than the resonance energy for two benzene rings. This additional energy must be attributed to resonance between (1) and (2).

With regard to the unusually large angle of 128–133° which we find in the central zig-zag of stilbene (compare figs. 4 and 5), we are indebted to Dr. Jahn for pointing out that this is probably a result of repulsion between the ortho hydrogen atoms in the ring and the ethylene hydrogen atoms. If a planar model is made, with the hydrogen atoms at 1.09 Å from the carbon atoms and all the angles 120° (as in ethylene), then the distance between the ortho hydrogen atom and the ethylene hydrogen atom is 1.71 Å on one side of the ring and 2.45 Å on the other side. Increasing the zig-zag angle to 133° makes these distances 2.33 Å and 2.07 Å respectively. As the carbon-hydrogen bonds themselves must also react to the repulsive forces to some extent, it is probable that with a zig-zag angle of about 130° the hydrogen-hydrogen distances are almost equalized. The increase in the angle might, however, also arise from a repulsion between the π electrons on non-neighbouring carbon atoms (atoms *A* and *B'* or *A'* and *B*). This question could be settled from measurements on compounds with longer conjugated chains, such as the diphenylpolyenes.

ANALYSIS OF THE STRUCTURE

Crystal Data

Stilbene— $C_{14}H_{12}$; melting point 124° C.; density, measured 1.159 (Hengstenberg), calculated 1.161; monoclinic prismatic, $a = 12.35$, $b = 5.70$, $c = 15.92$ Å, $\beta = 114.0^\circ$. Space group $C_{2h}^5(P2_1/a)$. Four molecules per unit

cell. Molecular symmetry, centre. Volume of the unit cell, 1023 \AA^3 . Absorption coefficient for X-rays, $\lambda = 1.54$, $\mu = 5.97$ per cm. Total number of electrons per unit cell = $F(000) = 384$.

Fourier Synthesis

The X-ray measurements on stilbene have been described in a previous paper (Robertson, Prasad and Woodward 1936). The absolute scale of the F values is difficult to determine accurately for crystals in this series of compounds owing to their volatile nature. This is particularly the case for azobenzene, the unprotected crystal rapidly losing weight at room temperatures. On the other hand, the use of sealed containers for the crystals tends to reduce the accuracy of the intensity measurements. Because of this the scale of the F values was finally decided by making a correlation with the final calculated values, which are based on an average atomic f curve for aromatic hydrocarbons (Robertson 1935*b*). Direct measurements on stilbene gave results which tended to be rather lower than this scale.

In the analysis of the structure one of the chief difficulties lay in determining the direction of the central $-\text{CH}=\text{CH}-$ groups in the two molecules which contribute to the asymmetric unit. After a number of trial calculations, a preliminary Fourier synthesis was carried out, in which all terms whose sign depended upon the directions assigned to these groups were omitted. The result gave a rather ill-defined projection of the structure but indicated quite clearly the general direction of the central groups and the lie of the rings. It was then possible to calculate the phase constants of further terms in the series and gradually refine the structure.

The coefficients in the double Fourier series used for the contour maps of figs. 1-3 are the measured values of $F(h0l)$ given in Table I, divided by the area of the (010) face, with signs corresponding to the calculated values. From a total of a hundred possible terms six of the smaller ones, amounting to about 2% of the total, were omitted from the final synthesis because of doubtful sign. The series was summed at 900 different points on the asymmetric unit (one-quarter of the unit cell); at intervals of 6° or 0.206 \AA on the a axis, and 6° or 0.265 \AA on the c axis. The numerical results are not reproduced in this paper, but the contour maps were drawn by graphical interpolation methods from the summation totals.

Orientation of the Molecules. Co-ordinates

In both molecules the benzene rings correspond fairly accurately to the projections of regular plane hexagons. In molecule 1 (fig. 1) two of the atoms, D and G , are quite clearly defined, but the atoms of the central

—CH=CH— group are not resolved. In molecule 2 (fig. 2) the atoms of the ring are more obscure, but the central group is partially resolved. The orientation of the molecules can best be calculated by measuring the angles which certain well-defined lines in the projections make with the crystal axes, and assuming certain known interatomic distances and valency angles.

TABLE I—VALUES OF $F(h0l)$

| | h | | | | | | |
|------------|------|-----|-----|-----|-----|-----|-----|
| | 0 | 2 | 4 | 6 | 8 | 10 | 12 |
| 12 | — | — | -10 | — | — | — | — |
| 11 | — | + 7 | — | — | — | — | — |
| 10 | + 8 | -14 | — | — | — | — | — |
| 9 | — | +14 | - 7 | — | — | — | — |
| 8 | -20 | +12 | — | — | — | — | — |
| 7 | + 6 | +14 | -18 | + 9 | - 6 | — | — |
| 6 | +13 | +19 | - 9 | — | — | — | — |
| 5 | — | — | — | — | -15 | — | — |
| 4 | -57 | — | +40 | + 5 | + 9 | — | — |
| 3 | — | -53 | +33 | -30 | — | — | — |
| 2 | +24 | +89 | +37 | + 7 | — | - 4 | — |
| 1 | — | -53 | — | - 4 | + 9 | — | — |
| 0 | +384 | -37 | — | +14 | + 6 | — | — |
| $\bar{1}$ | — | — | -17 | +32 | — | — | - 8 |
| $\bar{2}$ | +24 | -36 | +18 | +18 | +17 | - 6 | +11 |
| $\bar{3}$ | — | +50 | +20 | — | — | -12 | — |
| $\bar{4}$ | -57 | +81 | — | +27 | + 8 | +17 | — |
| $\bar{5}$ | — | +53 | + 7 | -38 | — | +11 | — |
| $\bar{6}$ | +13 | + 8 | +39 | +14 | — | +20 | -18 |
| $\bar{7}$ | + 6 | + 6 | -26 | +15 | + 8 | +12 | - 8 |
| $\bar{8}$ | -20 | +12 | +31 | — | — | — | — |
| $\bar{9}$ | — | — | — | +35 | -10 | — | +14 |
| $\bar{10}$ | + 8 | + 8 | - 5 | + 9 | — | — | +10 |
| $\bar{11}$ | — | - 5 | +11 | — | — | + 8 | +11 |
| $\bar{12}$ | — | - 9 | + 8 | - 5 | + 9 | - 6 | — |
| $\bar{13}$ | — | -12 | +14 | — | +19 | — | — |
| $\bar{14}$ | — | — | - 9 | — | — | — | — |
| $\bar{15}$ | — | + 6 | + 6 | — | + 5 | — | — |
| $\bar{16}$ | — | - 8 | - 7 | — | — | — | — |

The quantities used are defined as follows:

r = measured length of any line in the projection.

R = assumed real length.

η = angle which projected line makes with a crystal axis.

(χ, ψ, ω) = the angles which the line actually makes with the a, b and c' crystal axes, c' being perpendicular to a and b .

$L, M,$ and $N,$ are three convenient axes in the molecule, mutually perpendicular (compare fig. 4).

Then we have the relations

$$(1) \cos^2 \chi + \cos^2 \psi + \cos^2 \omega = 1,$$

$$(2) \sin \psi = r/R,$$

$$(3) \cos \omega = \cos \chi \tan \eta.$$

For molecule 1 (compare figs. 1 and 6) the measured quantities are

$$r_{DG} = 1.68, \quad r_{AA'} = 0.76, \quad r_{AB} = 1.43 \text{ A},$$

$$\eta_{DG} = 84.8^\circ, \quad \eta_{AA'} = 65.6^\circ, \quad \eta_{L(AB)} = 32.0^\circ.$$

We further assume that $R_{DG} = 2.78 \text{ A}$, $R_{AA'} = 1.33 \text{ A}$ (double bond distance in ethylene) and that the angle between L and DG in the benzene ring is 60° . The axis M is then taken to lie in the plane of L and DG .

These figures give the following values for the orientation of molecule 1:

$$\begin{array}{llll} \chi_L = 33.4^\circ & \cos \chi_L = 0.8352 & \chi_M = 114.8^\circ & \cos \chi_M = -0.4190 \\ \psi_L = 79.9^\circ & \cos \psi_L = 0.1748 & \psi_M = 35.0^\circ & \cos \psi_M = 0.8187 \\ \omega_L = 58.5^\circ & \cos \omega_L = 0.5219 & \omega_M = 66.8^\circ & \cos \omega_M = 0.3939 \\ \chi_N = 110.9^\circ & \cos \chi_N = -0.3563 & \chi_{DG} = 86.9^\circ & \cos \chi_{DG} = 0.0547 \\ \psi_N = 123.2^\circ & \cos \psi_N = -0.5469 & \psi_{DG} = 37.2^\circ & \cos \psi_{DG} = 0.7965 \\ \omega_N = 40.8^\circ & \cos \omega_N = 0.7567 & \omega_{DG} = 53.0^\circ & \cos \omega_{DG} = 0.6021 \\ \chi_{AA'} = 76.3^\circ & \cos \chi_{AA'} = 0.2362 \\ \psi_{AA'} = 34.9^\circ & \cos \psi_{AA'} = 0.8204 \\ \omega_{AA'} = 58.6^\circ & \cos \omega_{AA'} = 0.5207 \end{array}$$

The angles which the central $-\text{CH}=\text{CH}-$ group (AA') makes with the L , M and N axes are 127.8° , 39° , and 98° . Thus the angle between AA' and the plane of the ring is 8.0° , and the angle through which the ring must be turned about AB or L , starting from a flat model, is 10.4° . The reduced dimensions of the molecule are shown in fig. 4.

The rectangular co-ordinates of the atom A , referred to the a , b and c' crystal axes and centre of symmetry (mid point of AA') as origin, are

$$x'_A = 0.157, \quad y'_A = 0.546, \quad z'_A = 0.346 \text{ A},$$

while the co-ordinates of the other atoms, referred to the molecular axes L and M with A as origin, are given in Table II.

TABLE II—MOLECULE 1

| Atom ... | A | B | C | D | E | F | G |
|----------|-----|-------------------|-------------------|-------------------|-------------------|--------------------|--------------------|
| L ... | 0 | 1.45 ₁ | 2.14 ₆ | 3.53 ₆ | 4.23 ₁ | 3.53 ₆ | 2.14 ₆ |
| M ... | 0 | 0 | 1.20 ₃ | 1.20 ₃ | 0 | -1.20 ₃ | -1.20 ₃ |

It has already been shown (Robertson, Prasad and Woodward 1936) that molecule 2 can be derived from molecule 1 approximately by a rotation of 180° about the a axis and a translation of $c/2$. Hence in order to compare the relative orientations of the two molecules in the crystal the above movement is applied to molecule 2 before calculating its orientation. With this provision, the calculations are very similar to the above. The line DG , however, is not so clearly defined in molecule 2, so the projection of a regular hexagon was first described on the ring to give the best fit at all the corners, and the subsidiary line, PQ , parallel to M , was used.

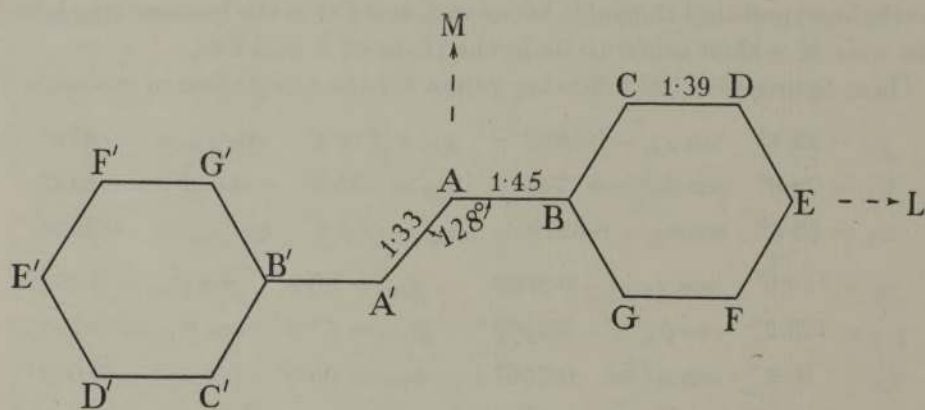


FIG. 4.—Dimensions of stilbene molecule 1. AA' is inclined at 8° to plane of ring.

The measured quantities for molecule 2 are then

$$r_{PQ} = 1.33, \quad r_{AA'} = 1.02, \quad r_{AB} = 1.44 \text{ \AA},$$

$$\eta_{M(PQ)} = 123.8^\circ, \quad \eta_{AA'} = 61.2^\circ, \quad \eta_{L(AB)} = 31.4^\circ.$$

It is further assumed that $R_{PQ} = 2 \times 1.39 \cos 30^\circ = 2.406 \text{ \AA}$, and that $AA' = 1.33 \text{ \AA}$ as before.

With these figures the following values are obtained for the orientation of molecule 2:

| | | | |
|-------------------------|--------------------------|-----------------------------|------------------------------|
| $\chi_L = 31.4^\circ$ | $\cos \chi_L = 0.8533$ | $\chi_M = 107.9^\circ$ | $\cos \chi_M = -0.3076$ |
| $\psi_L = 88.4^\circ$ | $\cos \psi_L = 0.0278$ | $\psi_M = 33.6^\circ$ | $\cos \psi_M = 0.8333$ |
| $\omega_L = 58.6^\circ$ | $\cos \omega_L = 0.5208$ | $\omega_M = 62.6^\circ$ | $\cos \omega_M = 0.4595$ |
| $\chi_N = 114.9^\circ$ | $\cos \chi_N = -0.4212$ | $\chi_{AA'} = 68.3^\circ$ | $\cos \chi_{AA'} = 0.3694$ |
| $\psi_N = 123.5^\circ$ | $\cos \psi_N = -0.5521$ | $\psi_{AA'} = 50.1^\circ$ | $\cos \psi_{AA'} = 0.6417$ |
| $\omega_N = 44.0^\circ$ | $\cos \omega_N = 0.7194$ | $\omega_{AA'} = 47.8^\circ$ | $\cos \omega_{AA'} = 0.6719$ |

The angles which LA' makes with L , M and N for molecule 2 are thus 133.1° , 43.1° and 91.5° , the angle between AA' and the plane of the ring, 1.5° , and the angle through which the ring must be turned about L from the strictly planar model is 2.8° . Hence molecule 2 is almost exactly flat. The reduced dimensions are shown in fig. 5.

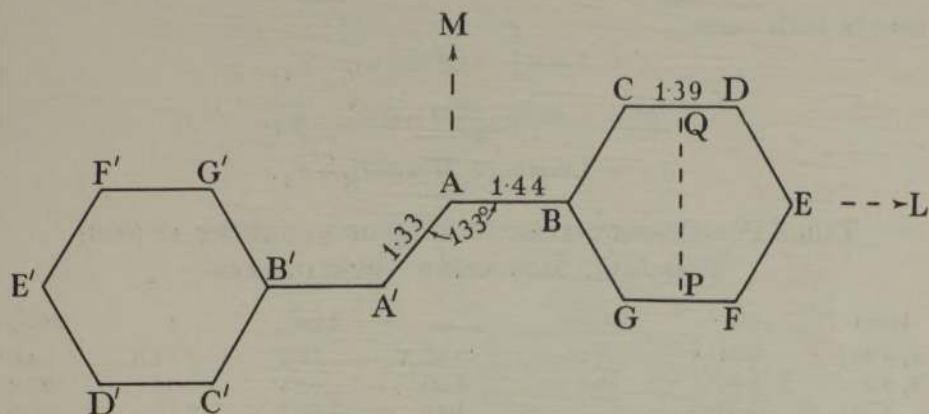


FIG. 5—Dimensions of stilbene molecule 2. AA' is inclined at 1.5° to plane of ring.

The rectangular co-ordinates of the atom A , referred to the a , b and c' crystal axes and the centre of symmetry of molecule 2 as origin, are

$$x'_A = 0.246, \quad y'_A = 0.427, \quad z'_A = 0.447 A,$$

while the co-ordinates of the other atoms, referred to the molecular axes L and M with A as origin, are given in Table III.

TABLE III—MOLECULE 2

| Atom... | A | B | C | D | E | F | G |
|---------|-----|----------|----------|----------|----------|-----------|-----------|
| L ... | 0 | 1.44_0 | 2.13_5 | 3.52_5 | 4.22_0 | 3.52_5 | 2.13_5 |
| M ... | 0 | 0 | 1.20_3 | 1.20_3 | 0 | -1.20_3 | -1.20_3 |

The crystal co-ordinates of all the atoms in the asymmetric unit, which includes both molecules, are given in Table IV. These figures are referred to the monoclinic crystal axes and the centre of symmetry at (000) as origin. For molecule 1 they are derived from the preceding figures by the relations

$$x = x' - z' \cot \beta,$$

$$y = y',$$

$$z = z' \operatorname{cosec} \beta,$$

and for molecule 2, referred to the same origin, by

$$x = x' + z' \cot \beta,$$

$$y = -y',$$

$$z = c/2 - z' \operatorname{cosec} \beta,$$

where in both cases

$$x' = L \cos \chi_L + M \cos \chi_M + x'_A,$$

$$y' = L \cos \psi_L + M \cos \psi_M + y'_A,$$

$$z' = L \cos \omega_L + M \cos \omega_M + z'_A.$$

TABLE IV—CO-ORDINATES. CENTRE OF SYMMETRY AT (000)
AS ORIGIN. MONOCLINIC CRYSTAL AXES

| Atom | x | $2\pi x/a$ | y | $2\pi y/b$ | z | $2\pi z/c$ |
|------------|--------|------------|--------|------------|--------|------------|
| A_1 (CH) | 0.31 A | 9.1° | 0.55 A | 34.5° | 0.38 A | 8.6° |
| B_1 (C) | 1.86 | 54.2 | 0.80 | 50.5 | 1.21 | 27.3 |
| C_1 (CH) | 2.31 | 67.3 | 1.91 | 120.3 | 2.12 | 48.0 |
| D_1 (CH) | 3.79 | 110.6 | 2.15 | 135.7 | 2.92 | 65.9 |
| E_1 (CH) | 4.83 | 140.8 | 1.28 | 81.2 | 2.79 | 63.2 |
| F_1 (CH) | 4.38 | 127.7 | 0.18 | 11.3 | 1.88 | 42.5 |
| G_1 (CH) | 2.89 | 84.4 | -0.06 | -4.0 | 1.08 | 24.5 |
| A_2 (CH) | 0.05 | 1.4 | -0.43 | -27.0 | 7.47 | 169.0 |
| B_2 (C) | 0.94 | 27.5 | -0.47 | -29.5 | 6.65 | 150.3 |
| C_2 (CH) | 0.76 | 22.1 | -1.49 | -94.0 | 5.65 | 127.7 |
| D_2 (CH) | 1.62 | 47.2 | -1.53 | -96.4 | 4.86 | 109.8 |
| E_2 (CH) | 2.67 | 77.8 | -0.54 | -34.4 | 5.07 | 114.6 |
| F_2 (CH) | 2.85 | 83.2 | 0.48 | 30.1 | 6.07 | 137.2 |
| G_2 (CH) | 1.99 | 58.0 | 0.52 | 32.6 | 6.86 | 155.1 |

The manner in which the co-ordinates finally assigned to the atoms fit the contour maps is shown by the plot in fig. 6, which covers the asymmetric portion of the unit cell.

Intermolecular Distances and Arrangement of Molecules

The minimum distance of approach between atoms on adjoining molecules in the stilbene structure is of the order of 3.5 Å, similar to or slightly less than the values found for dibenzyl (compare Robertson 1935*a*). Only a few of these distances have been calculated for stilbene, but the shortest found is between *A* on molecule 1 and *E* on the reflected molecule 1 where the value is 3.58 Å.

The centres of the four molecules in the unit cell of stilbene coincide with four crystal centres of symmetry at (000), $(\frac{1}{2}\frac{1}{2}0)$, $(00\frac{1}{2})$ and $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$, (Structure I). It was pointed out in the previous paper (Robertson, Prasad

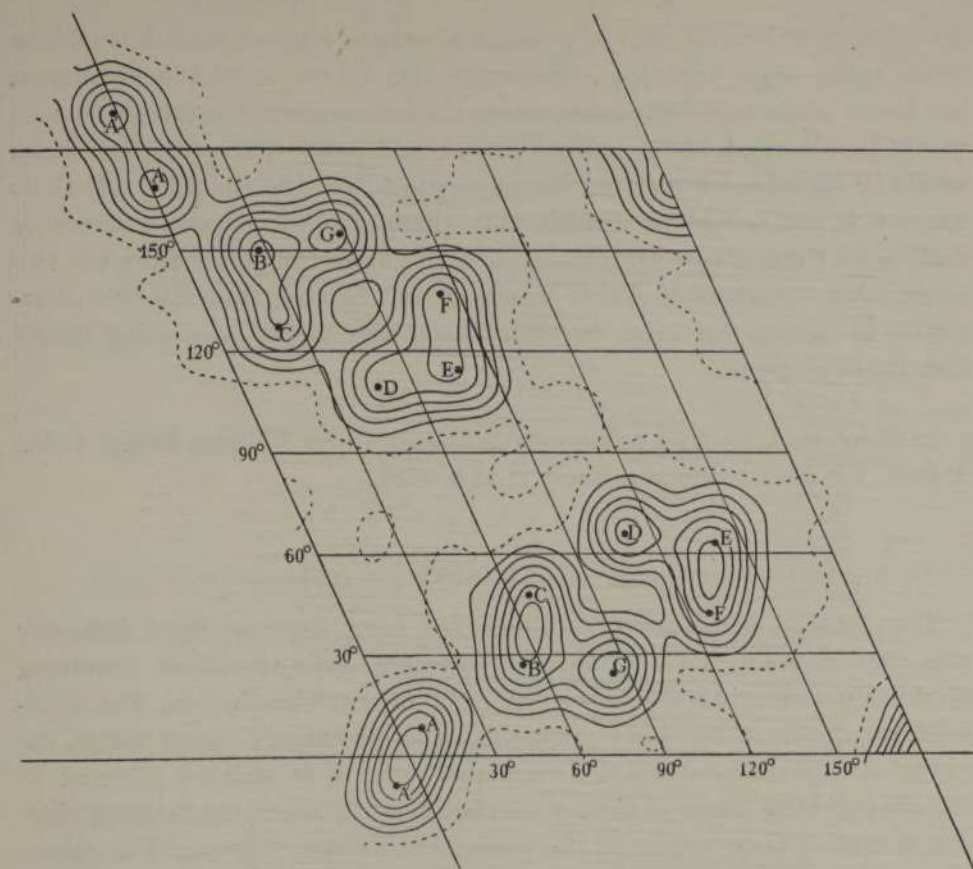


FIG. 6—The co-ordinates assigned to the atoms in stilbene.

TABLE V

| <i>hkl</i> | <i>F</i> meas. | <i>F</i> calc. (I) | <i>F</i> calc. (II) |
|------------|----------------|--------------------|---------------------|
| 110 | 43 | +51 | -29 |
| 210 | 26 | -29 | +27 |
| 310 | < 7 | + 1 | +17 |
| 410 | 29 | -27 | +13 |
| 510 | 35 | +33 | - 3 |
| 610 | < 10 | + 5 | + 9 |
| 710 | 13 | -12 | 0 |
| 810 | < 10 | +15 | + 9 |
| 910 | < 10 | +10 | - 2 |
| 130 | < 10 | -16 | -20 |
| 230 | 23 | +17 | - 7 |
| 330 | 15 | + 9 | + 1 |
| 430 | < 10 | + 7 | +17 |
| 530 | < 10 | - 4 | +20 |
| 630 | < 10 | - 9 | + 3 |
| 730 | < 10 | -10 | -17 |
| 150 | 14 | -20 | + 2 |
| 250 | 17 | -16 | - 4 |

and Woodward 1936) that a possible alternative arrangement would be (000), $(\frac{1}{2}\frac{1}{2}0)$, $(0\frac{1}{2}\frac{1}{2})$ and $(\frac{1}{2}0\frac{1}{2})$, (Structure II). In the second arrangement, the *b* axis projection and consequently the intensities of the (*h*0*l*) reflexions would be identical, the *a* axis projection and some of the (0*kl*) reflexions would be slightly changed, but the *c* axis projection and the (*hk*0) reflexions when *k* is odd would be considerably changed. The measured structure factors for these planes are compared with values calculated from the two alternative structures in Table V, and it will be seen that the first alternative is correct, the total discrepancies in the second case being nearly four times as great.

In conclusion, we wish to record our thanks to Sir William Bragg, O.M., P.R.S., for his continued interest in this work.

SUMMARY

The detailed structure of stilbene has been deduced from intensity measurements on the crystal by successive approximations involving double Fourier syntheses of the (*h*0*l*) zone of structure factors. The molecules are shown to be nearly planar and may be exactly planar within the limits of experimental error. This planar form is in striking contrast to the shape of the dibenzyl molecule in the crystal, where the benzene rings are almost at right angles to the plane of the central zig-zag. The planar form of the stilbene molecule is explained by the conjugation of the central double bond with the benzene rings, and the consequent contribution which an alternative excited structure makes to the normal state. The resonance involved is also shown by the thermochemical data and by the inter-nuclear carbon-carbon distances obtained from the analysis, the "single bonds" emerging from the benzene rings having a length of only about 1.44 Å. The length of the double bond is about 1.33 Å, although this is not a very direct determination owing to difficulties in the analysis.

Two stilbene molecules contribute to the asymmetric unit of the crystal, and although these molecules have different appearances in the electron density maps the differences are shown to be due to the relative orientation of the molecules and not to any appreciable differences in their shape or dimensions. The precise orientation of each molecule is given, with the co-ordinates of the atoms. The minimum intermolecular approach distances are of the order of 3.5 Å, similar to the distances found in other aromatic hydrocarbons.

REFERENCES

- Pauling and Sherman 1933 *J. Chem. Phys.* **1**, 606.
Penney 1937 *Proc. Roy. Soc. A*, **158**, 306.
Robertson 1934 *Proc. Roy. Soc. A*, **146**, 473.
— 1935*a* *Proc. Roy. Soc. A*, **150**, 348.
— 1935*b* *Proc. Roy. Soc. A*, **150**, 106.
— 1936 *Nature, Lond.*, **138**, 683.
Robertson, Prasad and Woodward 1936 *Proc. Roy. Soc. A*, **154**, 187.
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The Suspension of Solids in a Turbulent Stream

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A considerable amount of research has been done recently on the mechanism by which grains of sand, etc., may be picked up by a river or by a gale of wind and carried to some distance. In particular Jeffreys (1929) has considered the theoretical aspects of the action while the writer (1934) and Bagnold (1936) have published experimental data on the action by which the grains are picked up in water and air respectively. Another problem of considerable practical importance is that of the quantity—or, more strictly, the time average of the quantity—of solid material carried at different levels above the bed or ground. Up to the present, data on this question have all been collected in relation to a special case, i.e. that in which the particles have the same size and density. Thus, Hurst (1929) collected samples of uniformly graded sand at different depths in a turbo-cylinder containing a vigorously stirred mixture of sieved sand in water, and showed that, in the body of the cylinder, an exponential relation between “weight” of sample and height above the bottom of the vessel existed.

The present paper is mainly concerned with measurements of the concentration of the suspended material near the uniformly graded bed of an artificial channel and the application of these results to the conditions in a natural stream.