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# The Crystal and Molecular Structure of Biphenyl

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The crystal structure of biphenyl has been determined using two-dimensional $(\varrho_o - \varrho_c)$ maps. The whole molecule is perfectly planar within the limits of error of the experimental results. The great length of the bond linking the two phenyl rings ($1{\cdot}50_6$ Å with estimated standard deviation 0·017 Å) indicates that there is no conjugation between the rings; it is suggested that intermolecular forces are responsible for the rings taking up the coplanar configuration. There are indications that steric interactions between the *ortho*-hydrogen atoms lead to displacements of these atoms from the positions they would occupy in an ideal planar molecule with 120° bond angles.

## 1. Introduction

The stereochemistry of the biphenyl molecule (Fig. 5(*a*)) has been the subject of numerous experimental and theoretical studies (Wheland, 1955) but many of the results still require clarification. It is generally believed that the molecule is planar in the solid phase and non-planar in the vapour phase (Coulson, 1958); the molecular configurations in the liquid phase and in solution are not known with certainty (see, for example, Dale, 1957; Katon & Lippincott, 1959).

Evidence that the two phenyl rings are not coplanar in the vapour phase is provided by electron-diffraction studies (Brockway & Karle, 1944; Bastianssen, 1949; Almenningen & Bastianssen, 1958) with the most recent data indicating that the rings are mutually inclined at an angle of about 42°.

The belief that the molecule is planar in the solid phase is based largely on X-ray evidence (Hengstenberg & Mark, 1929; Clark & Pickett, 1931; Dhar, 1932, 1949; Kitaigorodsky, 1946), which indicates that the crystals are monoclinic, space group $P2_1/a$, and that the unit cell contains two molecules. If this evidence is accepted then the molecules must lie on symmetry centres and the two phenyl rings in each molecule must be coplanar, or very nearly coplanar (steric interactions between the hydrogen atoms $H_2$ and $H_2'$ may possibly produce small molecular distortions which, without destroying the molecular centre of symmetry, cause deviations from perfect planarity). Only Dhar & Kitaigorodsky have attempted detailed structural analyses and their results support the view that the biphenyl molecule is planar in the solid phase. But Kitaigorodsky has not published any evidence for his results whilst Dhar's results are based on trial-and-error methods and are very inaccurate—the discrepancy factor $R$ is 43% for the only projection, [010], which he examined using accurate X-ray data.

The present study of biphenyl has been undertaken in order to examine more critically than previously the X-ray evidence for the planarity of the molecule in the crystalline phase and to obtain more accurate structural parameters. At an advanced stage of the investigation it was discovered that Dr J. Trotter was also examining the structure of biphenyl. A joint note has been published on the results obtained at this stage (Hargreaves, Rizvi & Trotter, 1961) but no attempt has been made to correlate the two investigations as the refinement procedures have been completed.

## 2. Experimental

Large, platy crystals of biphenyl were grown from ethyl alcohol by allowing the warm solution to cool down to the room temperature over a period of two days. From these plates were cut the crystal specimens used in the present study.

X-ray rotation, oscillation and Weissenberg photographs about the *a*, *b* and *c* axes, and an *h*0*l* photograph taken with a Buerger precession camera, were used to determine the space group (§ 3) and the unit-cell dimensions; sodium chloride powder lines were used as a calibrating standard in some of the Weissenberg photographs. The cell dimensions thus obtained, with estimated limits of error, are

$$a = 8{\cdot}12_4 \pm 0{\cdot}02,\ b = 5{\cdot}63_5 \pm 0{\cdot}01,\ c = 9{\cdot}51_3 \pm 0{\cdot}02\ \text{Å};$$
$$\beta = 95{\cdot}1 \pm 0{\cdot}3°.$$

It is clear that the crystal specimens examined here are similar to those for which goniometric data ($a:b:c = 1{\cdot}4428:1:1{\cdot}6448$, $\beta = 94°\,46'$) are available in the Barker Index (Porter & Spiller, 1956) and for which the crystal class is quoted as $2/m$.

With two molecules in the unit cell the calculated density (1·18 g.cm.$^{-3}$) agrees with the density measured by flotation in a mixture of bromoform and ethyl alcohol (1·19 g.cm.$^{-3}$).

Reflexions *h*0*l* and 0*kl*, recorded in zero-layer-line Weissenberg photographs using Cu $K\alpha$ radiation, provided the data from which the atomic positions were deduced: *hk*0 reflexions recorded in another Weissenberg photograph served to check the correctness of the structure thus obtained. The intensities of the reflexions were measured using the multiple-film technique and visual comparison with crystal-reflected calibration spots of known relative exposures. Crystals of rectangular cross-section, initial dimensions 0·4 × 0·4 mm. and 0·65 × 0·47 mm., were used in recording the *h0l* and *0kl* reflexions respectively; the crystals decreased in size during the exposure to X-rays in spite of attempts to reduce evaporation. No corrections were made for absorption because the absorption coefficient is small ($\mu = 6{\cdot}0$ cm.$^{-1}$) and even for the larger specimen it is estimated that the corrections would produce variations of less than 5% in the values of the structure amplitudes. Extinction errors appear to be negligible.

## 3. The space group

The X-ray photographs show that there are no systematic absences in general reflexions *hkl* and that reflexions *h0l* are present only when *h* is even; but interpretation of the observations on the *0k0* reflexions is somewhat ambiguous. Only 7 *0k0* reflexions are possible with Cu $K\alpha$ radiation and of these 020, 040 and 060 are present as strong reflexions and 010, 050 and 070 appear to be absent. A very weak 030 reflexion is observed in long exposure *0kl* Weissenberg photographs; it has been observed with more than one specimen but the intensity is so small that it has not proved possible to decide from spot shape or from Cu $K\beta$ reflexions whether it is a Renninger (1937) reflexion. A very long exposure *hk0* Weissenberg photograph shows no trace of the 030 reflexion: this suggests that it is a Renninger reflexion which is observed in the *0kl* photograph in the position which would also record the 030 reflexion.

If the odd-order *0k0* reflexions are systematically absent then the space group is $P2_1/a$, but if they are only accidentally absent the space group is $P2$ or $Pa$. It seems safe to rule out $Pa$ for two reasons. Firstly there is the goniometric evidence that the crystal class possesses a 2-fold axis (§ 2). Secondly we find that the average intensity of the even-order *0k0* reflexions is about 5 times as large as the average intensity of the *0kl* reflexions; this also strongly indicates the presence of a diad in the crystal class. The results of the present study (§ 7) show that the space group is, in fact, $P2_1/a$; nevertheless attempts have been made to solve the structure (§ 4) assuming that the space group is $P2/a$.

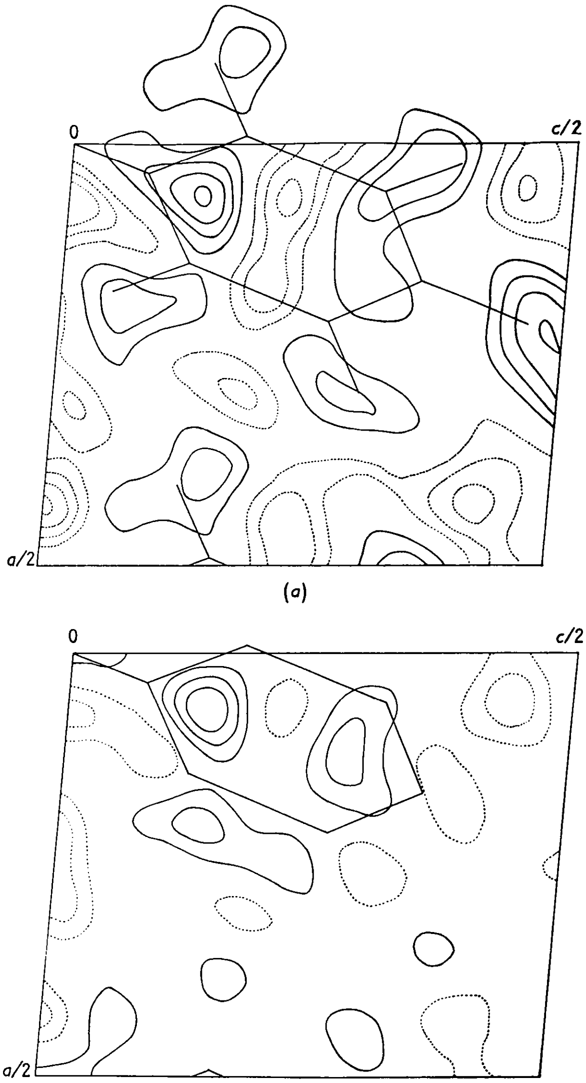
## 4. Determination of the structure

One of the objects of this study of biphenyl is to examine the possibility that the molecules in the solid phase have a non-planar configuration similar to that described by Almenningen & Bastianssen (1958) for the vapour phase. Although evidence that the space group is $P2_1/a$ suggests that the molecules are approximately planar (§ 1) it is necessary to bear in mind that the true space group may be $P2/a$ and that examples have been published (Trotter, 1958; Robertson, Shearer, Sim & Watson, 1958) of statistically-centred arrangements of non-centred molecules in space group $P2_1/a$.

A simple wire model showed that non-planar molecules, with the phenyl rings mutually inclined at an angle of about 50°, can be arranged so as to conform with the unit-cell dimensions and space group $P2/a$. This structure seemed to be very promising when it was noted that (i) the [010] projection is very similar to that determined by Dhar (§ 1); and, furthermore, the length of the molecule is perpendicular to [010] because of the diad whereas in Dhar's structure this configuration is not required by the symmetry, (ii) there are only 3 *y*-parameters for the 12 carbon atoms in the molecule; this accounts for the high average intensity of the *0k0* reflexions with *k* even (§ 3) and suggests that the symmetry axis is 2 rather than $2_1$, (iii) the molecules pack naturally midway between the glide planes so that for *0k0* reflexions with *k* odd destructive interference will occur and the reflexions should be weak or absent, as observed, (iv) the angle between the phenyl rings, which was determined from the relative intensities of the *0k0* reflexions, is similar to that found by Almenningen & Bastianssen in the vapour phase. Attempts to refine this structure—by comparing optical transforms with sections of the weighted reciprocal lattice—were made initially on the [100] projection which is substantially different from that in Dhar's structure. After failure to get a really good agreement the 'benzene peaks' in the weighted reciprocal lattice were used to estimate the orientation of a single phenyl ring (Hanson, Lipson & Taylor, 1953). Two projections were then constructed, one assuming $P2/a$ symmetry and the other $P2_1/a$ symmetry, and tested by optical transforms which indicated that the structure with symmetry $P2_1/a$ was much more likely to be correct. Attempts were made to refine the structure with symmetry $P2/a$ both by optical and Fourier methods but the discrepancy factor $R$ could not be reduced below 50%. The structure with symmetry $P2_1/a$ started with $R = 30\%$ and its satisfactory refinement (§ 5) showed that the structure with symmetry $P2/a$, which initially appeared so promising, must be abandoned. The [010] projection was deduced from a wire model constructed using the evidence provided by the [100] projection, by optical transforms and by packing considerations. At the first trial, calculations of structure amplitudes gave a discrepancy factor of only 17%.

## 5. Refinement of the structure

The [100] and [010] projections were refined by Fourier and least-squares methods. At appropriate stages individual isotropic temperature factors were introduced for the carbon atoms, and hydrogen atoms were included by assuming that they lie along the diagonals of the phenyl rings at a distance of 1·08 Å from the carbon atoms. On calculating bond lengths when $R$ had fallen to 7% for the [010] projection and 11% for the [100] projection it was disturbing to find that two chemically equivalent bonds ($C_3$–$C_4$ and $C_4$–$C_5$) differed in length by 0·12 Å. As earlier difference maps had indicated anisotropic vibrations of the carbon atoms it was decided that least-squares refinement should proceed with anisotropic temperature factors for these atoms. $R$ fell to 3·5% and 7% for the [010] and [100] projections respectively but the bond lengths ($C_3$–$C_4$) and ($C_4$–$C_5$) still differed by 0·08 Å. The discrepancy factor of 3·5% is much lower than would be expected for visually estimated intensities and this suggests that the least-squares refinement was making parameter changes which were not physically significant. Possible sources of error were false temperature factors, doubtful signs for a few small $F(0kl)$'s, overlap of hydrogen and carbon atoms in the [100] projection, errors in the measured intensities and the fact that the number of structure amplitudes available was only about twice the number of parameters being refined. To ensure that parameter changes were physically sensible refinement was therefore continued by difference syntheses using isotropic temperature factors only and omitting $3F(0kl)$'s of doubtful sign. In this way $(\varrho_o - \varrho_c)$ maps were obtained (Figs. 1(*a*) and 2(*a*)) in which only negligible shifts in the positions of the carbon atoms are indicated. Figs. 1(*b*) and 2(*b*) show the corresponding $(\varrho_o - \varrho_c)$ maps with the hydrogen atoms removed; it was assumed that the hydrogen atoms occupy positions on the diagonals of the phenyl ring although in practice there may well be substantial displacements from these positions because of steric interactions, particularly between atoms $H_2$ and $H_2'$ (§ 7). The carbon atom positions still lie on or near plateaux in Fig. 1(*b*) but in Fig. 2(*b*) some of the atoms lie on substantial slopes. Undoubtedly the reason for this is the close overlap, shown in Figs. 2(*a*) and 2(*d*), of some of the carbon atoms and hydrogen atoms from neighbouring molecules. An additional difference synthesis was therefore computed after allowing for the shifts (up to 0·02 Å) indicated in Fig. 2(*b*). The resulting $(\varrho_o - \varrho_c)$ map (Fig. 2(*c*)) gives plateaux at the carbon atom positions and was used in determining the final coordinates for the [100] projection. Fig. 2(*d*) is the corresponding $(\varrho_o - \varrho_c)$ map with the hydrogen atoms reintroduced (i.e. omitted from calculated $F$'s); it can be seen that the hydrogen atoms are represented by peaks which now lie much nearer to the calculated positions than they do in Fig. 2(*a*). It may seem somewhat arbitrary to base the final coordinates on a projection in which the hydrogen atoms have been removed when it is known that the estimated hydrogen positions are probably subject to considerable error (§ 7). Evidence that this procedure has, nevertheless, at least partially removed errors introduced by overlap is provided by the 'improved positions' of the hydrogen atoms (Fig. 2(*d*)) and by the greatly improved agreement between the $z$-coordinates derived from the [010] and [100] projections ($z_1$ and $z_2$, Table 2); before the last refinement the overall discrepancy between $z_1$ and $z_2$ was approximately $1\frac{1}{2}$ times that given by the values in Table 2. Figs. 3 and 4 show the final projections of electron density.



(*a*)

(*b*)

Fig. 1. Projections of $(\varrho_o - \varrho_c)$ along [010], (*a*) showing hydrogen atoms, (*b*) with hydrogen atoms removed. Contours are at intervals of 0·1 e.Å$^{-2}$; negative contours are broken and the zero contour is omitted.

Measured structure amplitudes are compared with those calculated from the final coordinates (§ 6) in Table 1. Hydrogen atoms were included in the calculations. The atomic scattering factors of Berghuis *et al.* (1955) for carbon and of McWeeny (1951) for hydrogen, evaluated by the method of Forsyth & Wells (1959), were used with the isotropic temperature factors $B_1$ ($h0l$ reflexions) and $B_2$ ($0kl$ reflexions) given in Table 2; mean values of $B_1$ and $B_2$ were used for the $00l$ reflexions; for all hydrogen atoms the values of $B_1$

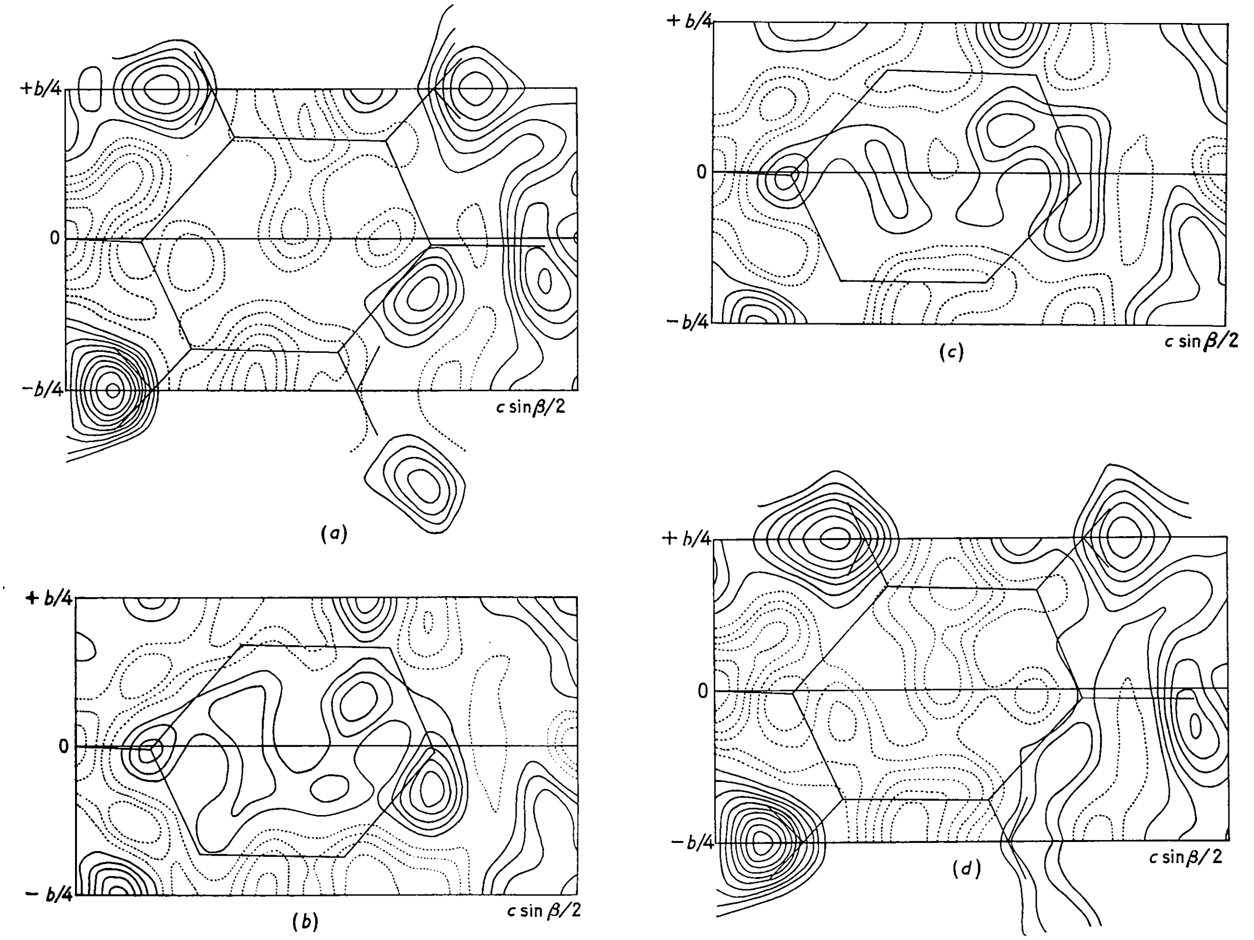


Fig. 2. Projections of ($\varrho_o - \varrho_c$) along [100], (*a*) showing hydrogen atoms, no corrections for overlap, (*b*) with hydrogen atoms removed, no corrections for overlap, (*c*) after corrections for overlap with hydrogen atoms removed and (*d*) after corrections for overlap and showing hydrogen atoms. Contours are at intervals of 0·1 e.Å$^{-2}$; negative contours are broken and the zero contour is omitted.

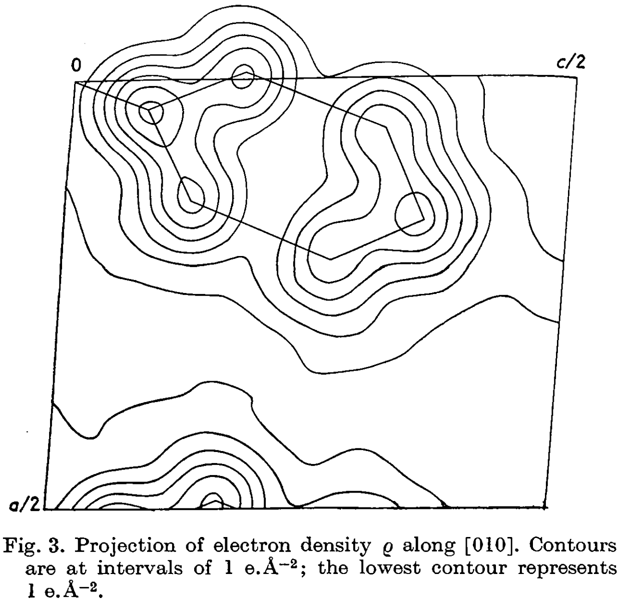


Fig. 3. Projection of electron density $\varrho$ along [010]. Contours are at intervals of 1 e.Å$^{-2}$; the lowest contour represents 1 e.Å$^{-2}$.

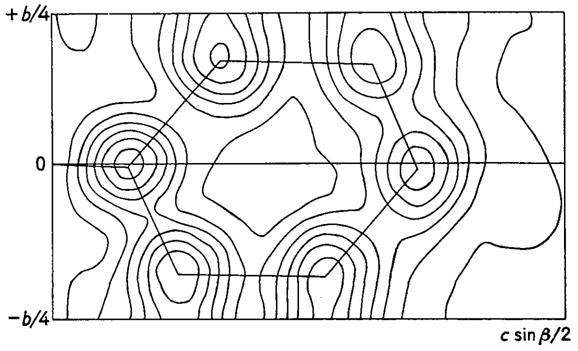


Fig. 4. Projection of electron density $\varrho$ along [100]. Contours are at intervals of 1 e.Å$^{-2}$; the lowest contour represents 1 e.Å$^{-2}$.

and $B_2$ were 7·0 and 5·5 Å$^2$ respectively. In Fig. 2(*d*) it can be seen that 4 out of the 5 hydrogen atoms in each phenyl ring overlap in projection with reflected equivalent hydrogen atoms and that two of them also overlap with carbon atoms; the fifth hydrogen atom, $H_4$, also overlaps $H_4'$ from an adjacent molecule.

Table 1. *Observed and calculated structure factors*

| $h$ | $k$ | $l$ | $\lvert F_o \rvert$ | $F_c$ |
|---|---|---|---|---|
| 0 | 0 | 1 | 20·1 | 20·3 |
| | | 2 | 32·6 | −32·4 |
| | | 3 | 8·7 | 9·1 |
| | | 4 | 21·0 | −20·5 |
| | | 5 | 19·2 | −17·3 |
| | | 6 | 2·7 | 2·0 |
| | | 7 | 1·1 | 0·8 |
| | | 8 | < 0·7 | −0·7 |
| | | 9 | 2·8 | −2·1 |
| | | 10 | 2·1 | −1·4 |
| | | 11 | 2·0 | 1·7 |
| | | 12 | 0·4 | 0·9 |
| 0 | 1 | 1 | 0·8 | 1·2 |
| | | 2 | 8·3 | 8·5 |
| | | 3 | 1·7 | 1·3 |
| | | 4 | 6·1 | 7·0 |
| | | 5 | 10·4 | 9·8 |
| | | 6 | 4·9 | −5·6 |
| | | 7 | 11·1 | −11·5 |
| | | 8 | 0·8 | −0·2 |
| | | 9 | 5·3 | 5·0 |
| | | 10 | 1·1 | 0·9 |
| | | 11 | 0·7 | 0·9 |
| | | 12 | 1·3 | 1·3 |
| 0 | 2 | 0 | 6·8 | −7·8 |
| | | 1 | 4·4 | −4·2 |
| | | 2 | 17·6 | 20·1 |
| | | 3 | 11·5 | 11·2 |
| | | 4 | 6·4 | −5·5 |
| | | 5 | 2·7 | 1·7 |
| | | 6 | 3·3 | −3·3 |
| | | 7 | 12·7 | −11·5 |
| | | 8 | 2·6 | −2·3 |
| | | 9 | 1·0 | 0·3 |
| | | 10 | 1·4 | −0·6 |
| | | 11 | 2·3 | 1·2 |
| 0 | 3 | 1 | 0·9 | −1·3 |
| | | 2 | 2·3 | −2·4 |
| | | 3 | 2·4 | 2·5 |
| | | 4 | 0·9 | −0·6 |
| | | 5 | 1·6 | −1·6 |
| | | 6 | < 0·6 | 2·4 |
| | | 7 | 1·2 | 1·0 |
| | | 8 | 1·4 | −1·0 |
| | | 9 | < 0·6 | −0·3 |
| | | 10 | 0·9 | −0·4 |
| | | 11 | < 0·3 | −0·3 |
| 0 | 4 | 0 | 4·3 | 3·3 |
| | | 1 | 2·1 | 1·0 |
| | | 2 | 5·9 | 5·4 |
| | | 3 | 3·8 | 3·7 |
| | | 4 | 3·0 | −2·7 |
| | | 5 | 0·9 | −0·8 |
| 0 | 4 | 6 | 4·4 | −3·2 |
| | | 7 | 5·3 | −5·0 |
| | | 8 | 1·0 | −0·2 |
| | | 9 | 1·0 | −0·2 |
| | | 10 | 1·1 | −0·6 |
| 0 | 5 | 1 | 1·8 | 2·3 |
| | | 2 | 1·7 | −1·9 |
| | | 3 | 0·9 | 0·1 |
| | | 4 | < 0·6 | 0·0 |
| | | 5 | 1·8 | −2·4 |
| | | 6 | 2·2 | 1·7 |
| | | 7 | 3·2 | 3·2 |
| | | 8 | 0·9 | −0·2 |
| 0 | 6 | 0 | 8·8 | 10·1 |
| | | 1 | 3·0 | 2·6 |
| | | 2 | 1·8 | −2·3 |
| | | 3 | < 0·6 | 0·0 |
| | | 4 | 2·7 | −2·3 |
| | | 5 | 2·3 | −2·5 |
| | | 6 | < 0·4 | −0·1 |
| 0 | 7 | 1 | < 0·3 | 1·1 |
| | | 2 | < 0·3 | 0·3 |
| | | 3 | < 0·3 | 0·5 |
| 2 | 0 | 0 | 16·2 | 16·0 |
| | | 1 | 19·0 | −18·8 |
| | | 2 | 7·6 | 8·4 |
| | | 3 | 17·4 | −19·0 |
| | | 4 | 23·4 | −23·0 |
| | | 5 | 3·6 | 3·6 |
| | | 6 | 8·0 | 5·8 |
| | | 7 | < 1·4 | −0·4 |
| | | 8 | 5·6 | −5·0 |
| | | 9 | 3·2 | −2·6 |
| | | 10 | < 1·2 | 1·0 |
| | | 11 | < 0·6 | 0·2 |
| 4 | 0 | 0 | 8·0 | 8·0 |
| | | 1 | 9·0 | 8·2 |
| | | 2 | 5·2 | −5·4 |
| | | 3 | 4·8 | −4·8 |
| | | 4 | < 1·2 | −0·6 |
| | | 5 | 1·8 | −2·4 |
| | | 6 | 1·0 | −1·2 |
| | | 7 | 3·0 | −3·2 |
| | | 8 | 3·0 | −2·6 |
| | | 9 | < 1·2 | 1·0 |
| | | 10 | < 0·6 | 0·4 |
| 6 | 0 | 0 | 8·6 | 8·2 |
| | | 1 | 2·2 | −1·6 |
| | | 2 | < 1·4 | 2·4 |
| | | 3 | 1·6 | −1·8 |
| | | 4 | 10·6 | −10·8 |
| | | 5 | 2·6 | −3·4 |
| 6 | 0 | 6 | < 1·4 | 0·6 |
| | | 7 | < 1·2 | −1·0 |
| | | 8 | < 0·8 | 1·4 |
| | | 9 | < 0·6 | 1·2 |
| 8 | 0 | 0 | < 1·4 | −0·6 |
| | | 1 | < 1·4 | 0·4 |
| | | 2 | < 1·4 | −1·2 |
| | | 3 | 7·4 | −7·6 |
| | | 4 | 3·0 | −3·4 |
| | | 5 | 2·2 | 1·2 |
| | | 6 | < 0·6 | 0·0 |
| 10 | 0 | 0 | 1·3 | −1·2 |
| $\bar{2}$ | 0 | 1 | 64·4 | 63·8 |
| | | 2 | 2·6 | 2·2 |
| | | 3 | 2·6 | 2·8 |
| | | 4 | 6·4 | 6·2 |
| | | 5 | 7·2 | −6·2 |
| | | 6 | < 1·2 | −0·2 |
| | | 7 | 5·0 | −5·0 |
| | | 8 | 10·0 | −10·6 |
| | | 9 | < 1·4 | −0·6 |
| | | 10 | 2·2 | 1·4 |
| | | 11 | < 0·8 | 0·0 |
| | | 12 | 1·6 | 1·6 |
| $\bar{4}$ | 0 | 1 | < 0·6 | −1·8 |
| | | 2 | < 0·8 | −2·8 |
| | | 3 | < 0·8 | 0·6 |
| | | 4 | 14·0 | 14·4 |
| | | 5 | 4·6 | 5·2 |
| | | 6 | 2·6 | −2·2 |
| | | 7 | 0·2 | 2·0 |
| | | 8 | 5·6 | −6·2 |
| | | 9 | 8·0 | −8·6 |
| | | 10 | < 0·8 | −0·2 |
| | | 11 | < 0·6 | 0·8 |
| $\bar{6}$ | 0 | 1 | 7·4 | 7·4 |
| | | 2 | 1·4 | −2·8 |
| | | 3 | 2·6 | −3·6 |
| | | 4 | < 1·4 | 1·2 |
| | | 5 | 6·6 | 7·2 |
| | | 6 | 2·6 | 2·4 |
| | | 7 | < 1·4 | −1·4 |
| | | 8 | < 1·2 | 0·0 |
| | | 9 | 2·0 | −2·6 |
| | | 10 | 2·6 | −2·8 |
| $\bar{8}$ | 0 | 1 | 3·6 | 3·8 |
| | | 2 | 2·2 | 2·0 |
| | | 3 | < 1·4 | 0·8 |
| | | 4 | 2·8 | 2·0 |
| | | 5 | 2·2 | 0·4 |
| | | 6 | < 0·8 | 1·2 |
| | | 7 | < 0·8 | 0·4 |
| $\bar{8}$ | 0 | 8 | < 0·6 | −1·2 |
| 1 | 1 | 0 | 44·2 | 52·2 |
| | 2 | 0 | 16·4 | 13·4 |
| | 3 | 0 | 7·7 | −8·4 |
| | 4 | 0 | 3·8 | −4·1 |
| | 5 | 0 | 8·2 | 8·1 |
| | 6 | 0 | < 1·3 | 2·4 |
| | 7 | 0 | 1·6 | 2·1 |
| 2 | 1 | 0 | 16·6 | 16·3 |
| | 2 | 0 | < 0·9 | 1·5 |
| | 3 | 0 | 1·2 | −0·9 |
| | 4 | 0 | 1·6 | −1·1 |
| | 5 | 0 | < 1·4 | 0·4 |
| | 6 | 0 | 2·2 | 1·9 |
| | 7 | 0 | < 0·7 | 1·4 |
| 3 | 1 | 0 | 2·1 | −2·9 |
| | 2 | 0 | 7·6 | −6·9 |
| | 3 | 0 | < 1·3 | −0·7 |
| | 4 | 0 | 2·4 | 3·3 |
| | 5 | 0 | < 1·4 | −1·5 |
| | 6 | 0 | < 1·3 | 0·0 |
| 4 | 1 | 0 | 15·8 | −14·9 |
| | 2 | 0 | 1·2 | −1·1 |
| | 3 | 0 | < 1·3 | 0·3 |
| | 4 | 0 | < 1·4 | −0·4 |
| | 5 | 0 | 1·9 | 2·0 |
| | 6 | 0 | 1·5 | 1·1 |
| 5 | 1 | 0 | 10·3 | 9·2 |
| | 2 | 0 | 4·4 | −5·2 |
| | 3 | 0 | < 1·4 | −1·4 |
| | 4 | 0 | 2·6 | 2·0 |
| | 5 | 0 | 2·2 | 3·1 |
| | 6 | 0 | < 0·9 | −0·4 |
| 6 | 1 | 0 | 1·4 | −1·2 |
| | 2 | 0 | 1·8 | 2·2 |
| | 3 | 0 | < 1·4 | −0·1 |
| | 4 | 0 | < 1·4 | 1·8 |
| | 5 | 0 | < 1·1 | 0·7 |
| 7 | 1 | 0 | 1·6 | 1·3 |
| | 2 | 0 | < 1·4 | 0·4 |
| | 3 | 0 | < 1·4 | 0·8 |
| | 4 | 0 | < 1·3 | 0·6 |
| | 5 | 0 | < 0·9 | 0·5 |
| 8 | 1 | 0 | < 1·4 | 0·3 |
| | 2 | 0 | 1·6 | −1·5 |
| | 3 | 0 | < 1·3 | 0·6 |
| | 4 | 0 | < 1·0 | −0·6 |
| 9 | 1 | 0 | 1·5 | −1·7 |
| | 2 | 0 | < 1·1 | 1·3 |
| | 3 | 0 | 1·3 | −1·8 |
| 10 | 1 | 0 | < 0·9 | 1·7 |
| | 2 | 0 | 0·9 | −0·9 |

Because of this and the low accuracy expected with visually estimated intensities no attempt has been made to determine hydrogen positions from the $(\varrho_o - \varrho_c)$ maps; the coordinates used in the structure-factor calculations were calculated geometrically, as described previously, and may be subject to considerable errors because of distortions produced by steric hindrance (§ 7). The final discrepancy factors $R$ are 8·9% for the $h0l$ reflexions, 12·3% for the $0kl$ reflexions and 14·6% for the $hk0$ reflexions. The $hk0$ reflexions were not used in the refinement of the structure and a common isotropic temperature factor $B = 4{\cdot}9$ Å$^2$ was used for all carbon atoms in calculating $F(hk0)$; the $R$-value of 14·6% for these reflexions is therefore satisfactory and confirms that the structure determined is the correct one.

## 6. Atomic coordinates: molecular dimensions

The positions of the carbon atoms deduced from the final $(\varrho_o - \varrho_c)$ maps, Figs. 1(*a*) and 2(*c*), are given by the fractional coordinates $(x, y, z)$ in Table 2; the values of the $z$-coordinates are the weighted means of the two sets of values, $z_1$ and $z_2$, deduced from Figs. 1(*a*) and 2(*c*) respectively.

Estimated standard deviations of the linear coor-

Table 2. *Atomic coordinates, temperature factors, and deviations from the mean molecular plane*

| Atoms | $x$ | $y$ | $z$ | $z_1$ | $z_2$ | $B_1$ (Å$^2$) | $B_2$ (Å$^2$) | $p$ (Å) |
|---|---|---|---|---|---|---|---|---|
| $C_1$ | 0·0355 | −0·0042 | 0·0759 | 0·0763 | 0·0745 | 4·00 | 4·00 | 0·0031 |
| $C_2$ | −0·0093 | 0·1694 | 0·1707 | 0·1716 | 0·1685 | 6·09 | 4·65 | 0·0076 |
| $C_3$ | 0·0592 | 0·1636 | 0·3130 | 0·3128 | 0·3136 | 6·72 | 5·56 | −0·0055 |
| $C_4$ | 0·1665 | −0·0161 | 0·3569 | 0·3562 | 0·3585 | 6·00 | 5·50 | 0·0053 |
| $C_5$ | 0·2119 | −0·1825 | 0·2666 | 0·2666 | 0·2666 | 6·80 | 4·42 | −0·0138 |
| $C_6$ | 0·1420 | −0·1792 | 0·1241 | 0·1240 | 0·1242 | 5·53 | 4·20 | 0·0160 |

dinates were deduced from the standard deviations in the slopes of the difference maps and the average central curvatures of the electron density of the carbon atoms: in each projection an allowance was made for the fact that the number of structure factors used in deriving the projection was not large compared with the number of parameters determined (Lipson & Cochran, 1957). Values of 0·010 and 0·015 Å were obtained for the [010] and [100] projections respectively so that, with weighted mean $z$-coordinates, the estimated standard deviations in $x$, $y$ and $z$ are

$$\sigma(x)=0{\cdot}010, \quad \sigma(y)=0{\cdot}015, \quad \sigma(z)=0{\cdot}008 \text{ Å} .$$

It is probable that overlap of the hydrogen and carbon atoms in the [100] projection accounts for the lower accuracy of this projection.

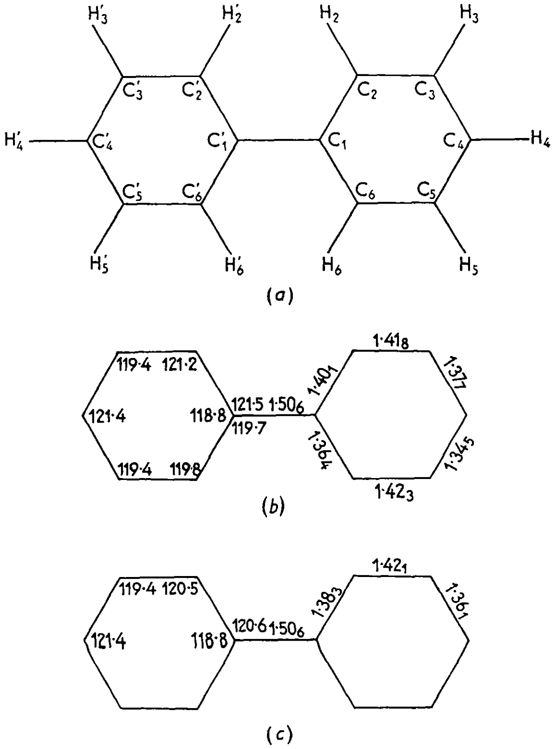


Fig. 5. Molecules of biphenyl showing (*a*) the system of numbering the atoms, which conforms with normal chemical usage and ignores the molecular centre of symmetry, (*b*) observed dimensions (Ångström units and degrees) and (*c*) mean dimensions (Ångström units and degrees).

The dimensions of the biphenyl molecule, deduced from $x$, $y$ and $z$ in Table 2, are shown in Fig. 5(*b*). The estimated standard deviations of the bond lengths are $\sigma(C_1-C_1')=0{\cdot}017$, $\sigma(C_1-C_2)=0{\cdot}017$, $\sigma(C_2-C_3)=0{\cdot}013$, $\sigma(C_3-C_4)=0{\cdot}018$, $\sigma(C_4-C_5)=0{\cdot}017$, $\sigma(C_5-C_6)=0{\cdot}013$ and $\sigma(C_6-C_1)=0{\cdot}018$ Å. The value of $\sigma(C_1-C_1')$ is of particular interest (§ 7). Since $C_1$ and $C_1'$ are related by a centre of symmetry it might be expected that $(C_1-C_1')$ will be $\sqrt{2}$ times larger than the estimated standard deviation for the other bond lengths. Fortunately the length $(C_1-C_1')$ largely depends on the most accurate coordinate of $C_1$, namely the $z$-coordinate.

Since the two phenyl rings in the molecule are coplanar to within the accuracy of our results (§ 7) it is to be expected that the biphenyl molecule will have the symmetry *mmm*. Inspection of Fig. 5(*b*) shows that the molecular dimensions do not deviate significantly (Cruickshank, 1949) from *mmm* and our final results are, therefore, probably best represented by Fig. 5(*c*) which shows the mean bond lengths and angles assuming this symmetry; the estimated standard deviations of the mean bond lengths are $\sigma(C_1-C_2)=0{\cdot}012$, $\sigma(C_2-C_3)=0{\cdot}009$ and $\sigma(C_3-C_4)=0{\cdot}012$ Å, whilst $\sigma(C_1-C_1')$ remains unchanged at 0·017 Å.

No corrections have been made for apparent atomic displacements caused by rotational oscillations of the phenyl rings (Cruickshank, 1956). The $(\varrho_o-\varrho_c)$ maps show little evidence of anisotropy in the vibrations of atom $C_1$. Moreover, since any correction for rotational oscillations will give an *increase* in the length of the bond $(C_1-C_1')$ it would only provide additional support for the conclusions drawn in § 7 from the unexpectedly great length of this bond.

## 7. Discussion

The low discrepancy factors $R$ for the three principal projections (§ 5) and the absence of substantial peaks in the final $(\varrho_o-\varrho_c)$ maps (Figs. 1(*b*) and 2(*c*)) show that the true space for biphenyl is $P2_1/a$ and that the correct structure has been determined. Much of the detail in Figs. 1(*b*) and 2(*c*) can be explained in terms of anisotropic molecular vibrations and, for Fig. 2(*c*), slightly inaccurate $B_2$ parameters: in any case the values of $(\varrho_o-\varrho_c)$ are much smaller than would be expected if the space group had been wrongly chosen or if the true structure consisted of statistically-centred arrangements of non-planar molecules in the space group $P2_1/a$. It is now clear that the structure published by Dhar (1932, 1949) is basically correct and that the discrepancy factor $R=43\%$ which he obtained (§ 1) is high only because of the low accuracy of the methods which he employed; there are errors of several degrees in the orientations which he determined for both the plane and the direction of the length of the molecule.

The symmetry centre at the centre of the molecule rules out the possibility that in the solid state the two aromatic rings are mutually inclined at an angle $\varphi \sim 40^\circ$, as observed in the vapour phase by Almenningen & Bastianssen, and indicates that the molecule must be at least approximately planar (§ 1). The planarity was tested by calculating the equation of the best plane through the 12 carbon atoms in the molecule, and thence the displacements $p$ (Table 2) of the individual atoms from this plane. The maximum value of $p$ is 0·016 Å and the root mean square value 0·010 Å. Since the estimated standard deviation in $p$ is 0·012 Å none of the displacements is significant.

The great length of the bond $(C_1-C_1')$ linking the two phenyl rings indicates that there is no conjugation between these rings. Recent estimates of the distances between trigonally-linked carbon atoms suggest that the ($sp^2$) single-bond length should be taken as 1·477 Å (Dewar & Schmeising, 1959; Cruickshank & Sparks, 1960). The observed $(C_1-C_1')$ distance of $1{\cdot}50_6$ Å, with estimated standard deviation $\sigma =$ 0·017 Å, exceeds this value by 0·029 Å, or $1{\cdot}7\sigma$, which is 'possibly significant' (Cruickshank, 1949). This suggests not only that $\pi$-bonding is completely absent but that steric repulsion between the hydrogen atoms $H_2$ and $H_2'$ and between the hydrogen atoms $H_6$ and $H_6'$ increases the separation between $C_1$ and $C_1'$ beyond the value it would have in an unstrained molecule. Similar increases, beyond theoretically estimated lengths, of approximately 0·06 Å in bishydroxydurylmethane (Chaudhuri & Hargreaves, 1956), 0·05 Å in quaterrylene (Shrivastava & Speakman, 1960) and 0·03 Å in chrysene (Burns & Iball, 1960) have also been attributed to steric interactions. The results for chrysene are of particular interest because the bond lengths have been measured very accurately (estimated standard deviations $\sim$ 0·004 Å) and because the bond $AB$ (Fig. 6), which is larger by 0·03 Å than the value calculated theoretically, is surrounded by a configuration of carbon and hydrogen atoms which is very similar to that surrounding $(C_1-C_1')$ in biphenyl. The hydrogens attached to I′ and C (Fig. 6) produce steric repulsions which are presumed to account for the stretching of $AB$ and which must be very similar to the interactions between $H_2$ and $H_2'$ and between $H_6$ and $H_6'$ in biphenyl.

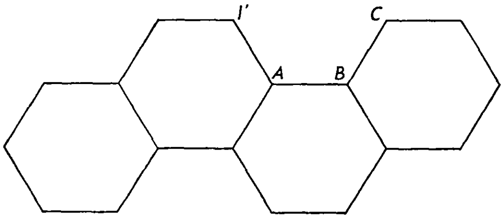


Fig. 6. Molecule of chrysene showing bond, $AB$, lengthened by steric repulsion between hydrogen atoms attached to $I'$ and $C$.

If the bond $(C_1—C_1')$ is lengthened by strong repulsions between the *ortho*-hydrogen atoms then one would also expect part of the strain resulting from the steric stress to be taken up by displacements of these atoms from the positions they would occupy (along the phenyl ring diagonals) if stress were absent; displacements out of the plane of the ring would relieve stress only if they were very considerable and therefore displacements in the plane of the ring are more likely. Discussion of the experimentally determined hydrogen positions will be restricted to the detail in Fig. 1($a$), which is the more accurate projection and free from the overlap affecting the *ortho*-hydrogens in the other projections: even so any comments must be regarded as very tentative because of the very low accuracy of the observed hydrogen positions. It can be seen that both $H_2$ and $H_6$ appear to be displaced in the directions expected, so that the separation is increased between the hydrogen atoms in contact—($H_2$ and $H_2'$) and the structurally equivalent pair ($H_6$ and $H_6'$). The distance between $H_2$ and $H_2'$, which can be deduced directly from Fig. 1($a$) since the two $y$-coordinates are almost identical, is 2·19 Å. This is approximately 0·4 Å greater than the distances obtained by placing the hydrogens on the phenyl ring diagonals but still about 0·2 Å shorter than the average value of the observed van der Waals separations between hydrogen atoms.

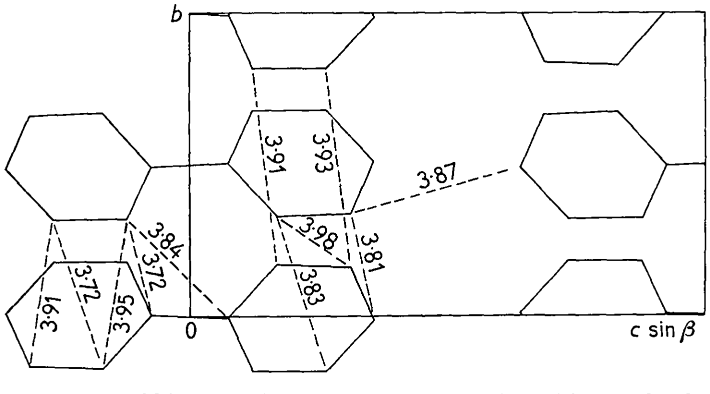


Fig. 7. The structure of biphenyl viewed along [100], showing all intermolecular distances between carbon atoms of less than 4·0 Ångström units.

The electron-diffraction measurements of Almenningen & Bastianssen (1958) on biphenyl and on related compounds (2,2′-bipyridyl and 4-4′-bipyridyl) support our observation that there is no conjugation between the phenyl rings by indicating that the non-planar configuration is adopted in the vapour phase. For biphenyl they obtain a ($C_1$–$C_1'$) distance of 1·49 Å and an angle between the rings ($\varphi \sim 42°$) corresponding to a distance of 2·35 Å between $H_2$ and $H_2'$, which can be regarded as normal. Since there is no conjugation between the phenyl rings it might be expected that the phenyl rings would also adopt a non-planar configuration in the solid phase so as to avoid strain due to steric interactions. The fact that they do not must presumably be attributed to intermolecular forces. All intermolecular distances between carbon atoms of, less than 4·0 Å are shown in Fig. 7. It will be observed that (i) the shortest distance is 3·72 Å although between CH groups in aromatic compounds shortest distances of 3·6 Å and less are common, (ii) there is a large number of intermolecular contacts at distances only slightly greater than 3·72 Å: between the 6 carbon atoms in each phenyl ring and carbon atoms in neighbouring rings there are 11 approaches in the range 3·72 to 3·98 Å and another five at distances of less than 4·08 Å. It is probable that non-planar molecules, with their lower symmetry, will not be able to pack together so as to give as many approximately equal intermolecular contacts as are obtained with planar molecules; it must be noted, of course, that the contacts actually occur through hydrogen atoms. If the resulting gain in energy is greater than the energy due to steric strain in the planar molecules, this would account for the molecules adopting a planar configuration in the solid phase and a non-planar configuration in the vapour phase.

It is interesting to note that in the solid phase of 1:3:5 triphenylbenzene (Farag, 1954) the 3 phenyl rings are twisted out of the plane of the central ring through angles of 24, 27 and 34° respectively. An important difference, however, as compared with biphenyl, is that the hydrogen atoms attached to the central ring are each acted upon in opposite directions by hydrogen atoms from two of the phenyl rings and are therefore unable to relieve stress due to steric hindrance by movements in the plane of the ring.

It is difficult to account for the observed differences in the bond lengths between atoms in the aromatic rings (Fig. 5(*c*)). Quantum-mechanical calculations based on the molecular-orbital method (Buu-Hoi *et al.*, 1947; Pullman & Pullman, 1949) have given $C_1-C_1'=1{\cdot}46$, $C_1-C_2=1{\cdot}40$, $C_2-C_3=1{\cdot}39$ and $C_3-C_4=1{\cdot}38$ Å. However, our observation that there is no conjugation between the phenyl rings suggests that all distances within the rings should be about 1·40 Å, as in the benzene molecule. The differences (Fig. 5(*c*)) between ($C_2-C_3$) and ($C_3-C_4$) are significant—unless the errors caused by molecular oscillations are unexpectedly high—and may originate from distortions produced by the steric interactions. None of the bond angles in Fig. 5(*c*) deviates significantly from 120°.

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# Structure d'une Merocyanine: $C_{10}H_{12}S_3N_2O$

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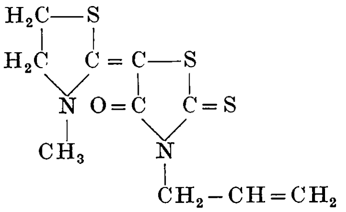
(*Reçu le* 30 *juin* 1961)

The merocyanine



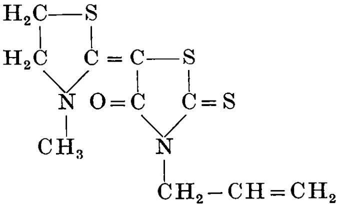
crystallizes in the orthorhombic system. Space group $P2_12_12_1$. Unit-cell dimensions:

$$a=13{\cdot}36,\ b=16{\cdot}40,\ c=5{\cdot}47\ \text{Å};\ Z=4\ .$$

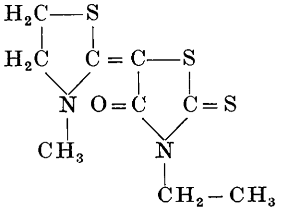
The crystal structure has been solved by the interpretation of the two- and three-dimensional sharpened Patterson function and refined by three-dimensional Fourier and least-squares methods. The rhodanine cycle is planar but in the other cycle, the two methylene carbons shows significant deviation from the general plane. The two cyclic S atoms are in trans position. The length of the $C=O$ bond (1·24 Å) shows a weak conjugation in this group. The calculations involved in this work were carried out on a WEGEMATIC 1000 computer. Details concerning the computer and the programs are given.

## Introduction

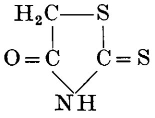
La détermination de la structure de la 2-thio-3-allyl-5-[2′-(3′-méthylthiazolidinylidène)]-thiazolidine-2,4-dione de formule



s'inscrit dans une série de recherches sur la structure moléculaire de colorants en relation avec leurs propriétés sensibilisatrices dans les processus photographiques. Une mérocyanine semblable



a fait l'objet d'une recherche parallèle dont les résultats sont publiés ailleurs (Germain *et al.*, 1961). Les structures de ces deux substances sont comparées à celle de la rhodanine.



publiée par Van der Helm *et al.* (1960).

On admet généralement que l'absorption intense

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* Chargé de recherches du Fonds National (belge) de la Recherche Scientifique.