

Crystal and Molecular Structure of 3, 3'-Dibromobenzophenone

It has become increasingly clear that in benzophenone the steric hindrance between the hydrogen atoms in the 2, 2'-positions would prevent the molecule from being coplanar. It would therefore be of great interest to get a quantitative measure of this non-coplanarity by X-ray methods. With this view the determination of the crystal structures of a series of benzophenone derivatives have been undertaken in this laboratory and the present note gives the results obtained with 3,3'-dibromobenzophenone.

The crystal belongs to the orthorhombic system with cell dimensions

$$a = 3.99, b = 11.70, \text{ and } c = 24.69 \text{ \AA.}$$

The space group is Pbcn and the unit cell contains four molecules. The C=O bond in the molecule coincides with a two fold axis of symmetry in the crystal.

Three dimensional Weissenberg data were obtained with $\text{CuK}\alpha$ radiation and the intensities were estimated visually. The structure was solved by the heavy atom method. The (y, z) coordinates of the bromine atom were determined from the Patterson projection on the (100) plane. Using the signs of a number of reflexions of the type $(0kl)$ obtained from the contribution of the bromine atom, the first Fourier map was prepared which showed distinct peaks corresponding to the light atoms. The (y, z) co-ordinates were refined by a succession of difference syntheses. The Fourier projection on (100) plane with the bromine atom removed is shown in Figure 1. An estimate of the tilt of the benzene ring was made from

the distortion it displayed on the (100) projection which gave the approximate x co-ordinate of the bromine atom. This was used for the determination of the x co-ordinate

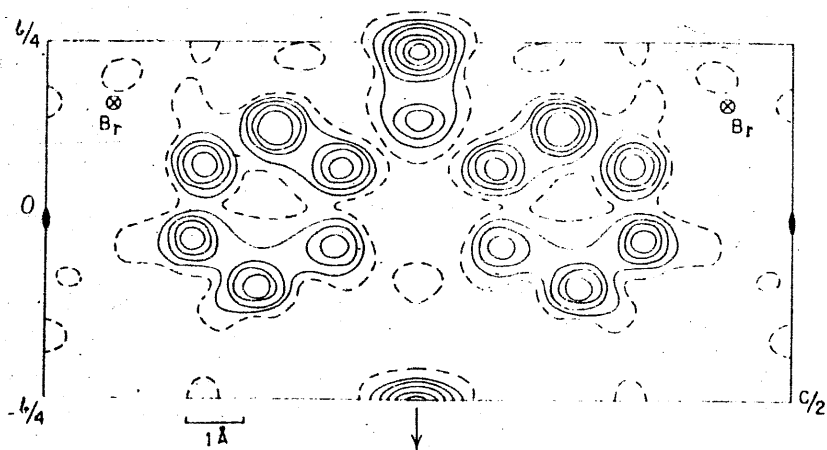


Fig. 1.—Fourier projection on the (100) plane with the Br atom removed. Contours are at arbitrary intervals. Dotted lines correspond to zero electron density.

of all the atoms by the generalized Fourier projections using the (1kl) and (2kl) reflexions. The final atomic co-ordinates are given in the Table.

Atomic co-ordinates

Atom	x/a	y/b	z/c
C ₁	0.025	0.075	0.196
C ₂	-0.100	-0.038	0.194
C ₃	-0.081	-0.092	0.142
C ₄	0.055	-0.029	0.098
C ₅	0.174	0.079	0.102
C ₆	0.158	0.138	0.151
C ₇	0.00	0.133	0.250
O	0.00	0.240	0.250
Br	0.3400	0.1573	0.0448

The R -factor for the 700 observed reflexions was 15.7%. The intramolecular distances and angles are indicated in

Figure 2. The standard deviation in the bond lengths, estimated by CRUICKSHANK'S method¹ is of the order of 0.04 Å for C—C and C—O bonds.

The angle between the 1, 4 axes of the phenyl groups is 126.2°. The equations of the planes of the benzene rings were determined by the method of least squares and it

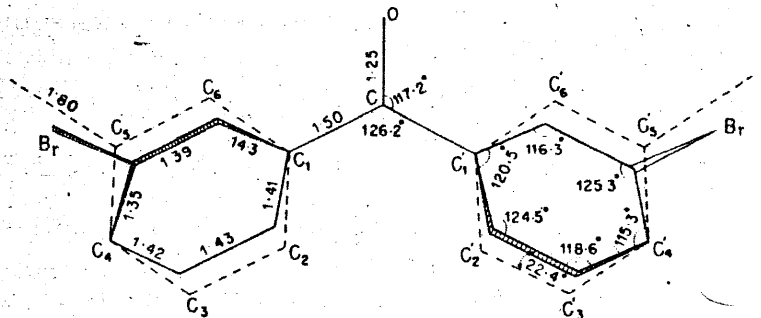
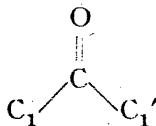


Fig. 2.—Bond lengths and bond angles for 3, 3'-dibromobenzophenone.

was found that none of the atoms was off the plane by more than 0.01 Å. The angle between the planes of the benzene rings is 39.9°; however each of the phenyl rings is twisted out of the common plane i.e., the plane containing



by an angle $\theta = 22.4^\circ$. It is estimated that the angles are accurate to $\pm 1.5^\circ$.

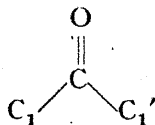
The elucidation of the stereochemistry of benzophenone derivatives by physical methods (magnetic susceptibility², dipole moment and ultraviolet spectra) was started as early as 1935, but unfortunately the substance under report has never been studied. However, the earlier workers were mostly interested in the angle between the 1, 4 axes of the two benzene rings and the values varying from 122° to 133° have been suggested. The value obtained in this determination is quite close to that computed by COOM-

¹ D. W. J. CRUICKSHANK, *Acta cryst.* 2, 65 (1949).

² K. BANERJEE and A. HAQUE, *Indian J. Phys.* 11, 87 (1938).

BER and PARTINGTON³ from dipole moment measurements for benzophenone ($125 \pm 3^\circ$). By determining the exact positions of the two iodine atoms in 4,4'-diiodobenzophenone by X-ray method, MANTHEY *et al.*⁴ have reported the angle to be 123.5° . However, the complete structure of the molecule was not solved, thus leaving the non-planarity of the molecule an open question.

In recent years the changes in the frequencies and the intensities of the ultraviolet absorption bands have been used most successfully to get an idea of the aplanarity of molecules (BRAUDE *et al.*⁵; O'SHAUGHNESS and RODEBUSH⁶; JONES⁷; REKKER and NAUTA⁸) and a series of accurate studies have been made to determine how far the various symmetrically substituted derivatives differ from the unsubstituted benzophenone. For this purpose, the investigators have to assume the tilt of the benzene ring from the common plane



and the calculated value of this angle depends on the assumptions made regarding the bond angles, bond lengths and the minimum distance of approach for the hydrogen atoms; hence the large discrepancy between the theoretical angles reported by SUTTON and COATES⁹ (28°) and JONES⁷ (15°). This angle (θ) in the present case is 22.4° and the minimum distance of approach of the $(C_2)H$ and $(C_2')H$ is of the order of 2.2 \AA . One must remember that additional intermolecular forces may come into play in a solid; but, as the distance between the

³ D. I. COOMBER and J. R. PARTINGTON, *J. chem. Soc.* 1938, 1444.

⁴ W. MANTHEY, K. PLEITH, and A. SINGEWALD, *Z. Elektrochem.* 56, 690 (1952).

⁵ E. A. BRAUDE, F. SONDEIMER, and W. F. FORBES, *Nature* 173, 117 (1954). - E. A. BRAUDE, *Exper.* 11, 457 (1955).

⁶ M. T. O'SHAUGHNESS and W. H. RODEBUSH, *J. Amer. chem. Soc.* 62, 2906 (1940).

⁷ R. NORMAN JONES, *J. Amer. chem. Soc.* 67, 2127 (1945).

⁸ R. F. REKKER and TH. W. NAUTA, *Rec. Trav. chim. Pays-Bas* 73, 969 (1954).

⁹ G. E. COATES and L. E. SUTTON, *J. chem. Soc.* 1942, 567.

atoms of neighbouring molecules is never less than 3.3 Å, one may presume that the only predominant forces are of the Van der Waals type.

It may be remarked that if the length of the bond connecting the phenyl ring to the carbonyl group becomes shorter due to substitution of electron releasing groups at the 4 position, then θ would become larger. This is perhaps the reason why in the case of 4,4'-dimethoxy benzophenone¹⁰ this angle is of the order of 30°.

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Résumé

La structure du cristal de 3,3'-dibromobenzophénone a été définie par l'emploi de données obtenues par rayons X dans trois dimensions. Les distances et les angles de liaison ont été obtenus et l'on a trouvé que deux anneaux de phényle de la molécule ne sont pas dans le même plan, l'angle compris entre eux étant de 39,9°.

¹⁰ I. L. KARLE, H. HAUPTMAN, J. KARLE, and A. B. WING, *Acta cryst.* 10, 481 (1957).
