

The Crystal and Molecular Structure of Benzoic Acid

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The crystal and molecular structure of benzoic acid (space group $P2_1/c$, 4 molecules per unit cell) has been accurately determined from a study of projections of q_o and $(q_o - q_c)$ along the a and b axes. The molecules occur as nearly planar, centrosymmetrical dimers, with hydrogen bonds (2.64 Å) between the adjacent carboxyl groups. The final difference synthesis reveals the hydrogen atoms clearly. Corrections have been made for temperature-factor variations and thermal anisotropy. The C-C bonds in the benzene ring are found to vary by 0.05 Å (total estimated standard deviation 0.017 Å), and the C-O bonds are 1.29 and 1.24 Å (total standard deviation, 0.021 Å). The benzene ring is accurately planar, but the carboxyl carbon atom and one of the oxygens are found to deviate significantly from this plane.

1. Introduction

Although the crystal structures of many simple benzene derivatives have now been examined, there are very few determinations of accuracy sufficient to reveal bond length variations from the standard values of the order that may be expected to occur in such compounds. In the ring itself quite large variations have been reported in the case of *p*-nitroaniline (Abrahams & Robertson, 1948), 1:4-dimethoxybenzene (Goodwin, Przybylska & Robertson, 1950) and other derivatives, but the accuracy is not in every case as great as can now be attained. In his recent very careful determination of the salicylic acid structure, Cochran (1953) has found the ring bonds to vary in length between 1.369 and 1.414 Å, with a standard deviation of less than 0.01 Å in the measurements. Some of these variations can be explained in terms of the probable resonance structures, but it is clearly desirable to obtain further evidence from other benzene derivatives.

Benzoic acid was among the first organic crystal structures to be examined by the X-ray method (Bragg, 1921, 1922), but a detailed study of the atomic arrangement does not appear to have been made. The hydrogen bonding present in the crystal structure has been studied by means of the deuterium isotope effect (Robertson & Ubbelohde, 1939). A small but definite expansion of the spacings of certain planes in the $(h0l)$ zone was found in these experiments, indicating the presence of fairly strong hydrogen bonds lying mainly in the (010) plane.

Our present experiments are aimed at determining the crystal and molecular structure as accurately as possible, with special reference to the role of the hydrogen atoms. For this purpose we intended carrying out a full three-dimensional analysis, but the projections obtained have proved particularly favourable for intensive refinement, and we believe that the accuracy reached in the present two-dimensional analysis is at

least sufficient for useful bond length measurements. For a more complete study of the electron distribution, a three-dimensional analysis may still be necessary, but the hydrogen atoms are very clearly revealed in the present projections.

2. Crystal data

Benzoic acid, $C_7H_6O_2$; M , 122.1; m.p. 123° C.; d , calc. 1.315, found 1.322 (Steinmetz, 1914). Monoclinic, $a = 5.52 \pm 0.02$, $b = 5.14 \pm 0.02$, $c = 21.90 \pm 0.05$ Å, $\beta = 97^\circ$. [Earlier values, $a = 5.44$, $b = 5.18$, $c = 21.6$ kX., $\beta = 97^\circ 5'$ (Bragg, 1921).] Absent spectra, $(h0l)$ when l is odd; $(0k0)$ when k is odd. Space group, $P2_1/c - C_2^2h$. Four molecules per unit cell. No molecular symmetry required. Volume of the unit cell, 617 Å³. Absorption coefficient for X-rays, $\lambda = 1.542$ Å, $\mu = 9.35$ cm.⁻¹. Total number of electrons per unit cell = $F(000) = 256$.

The crystals were obtained as fine needles with b as needle axis, and sometimes as fine plates developed on (001) . Alcohol-water mixtures and acetone-petroleum ether mixtures were the most successful solvents for crystal growing. The morphology has been described by Bodewig (1880), whose axial ratios, 1.051:1.4:208, $\beta = 97^\circ 5'$, differ somewhat from ours (1.074:1.4:260).

3. Experimental measurements

Rotation, oscillation and moving-film photographic methods were used, with copper $K\alpha$ radiation ($\lambda = 1.542$ Å). The cell dimensions were determined from rotation and equatorial layer line moving-film photographs, calibrated with superimposed NaCl powder lines. The intensity data used in the present analysis were confined to a complete survey of the $(h0l)$ and $(0kl)$ reflexions. These were estimated visually, using the multiple-film technique to correlate strong and

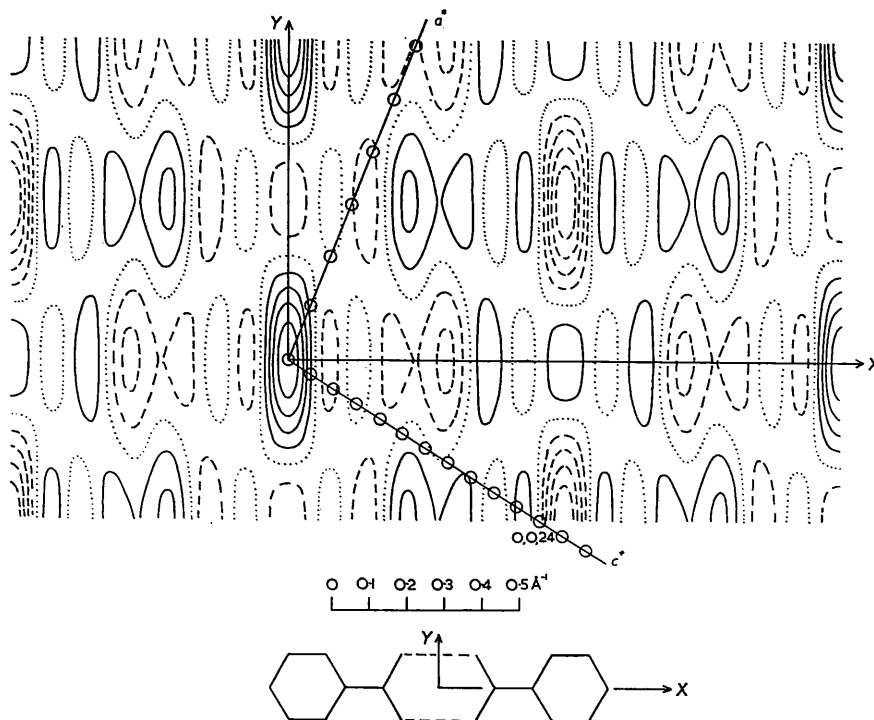


Fig. 1. Fourier transform of benzoic acid dimer, with the projections of the a^* and c^* axes. Negative contours broken, zero contour dotted.

weak reflexions (Robertson, 1943). Very small crystal specimens completely bathed in a uniform X-ray beam were employed. Care was taken to secure specimens of approximately square cross-section, about 0.2×0.2 mm. perpendicular to the rotation axis, and consequently no corrections for absorption were made. The structure factors evaluated by the usual mosaic crystal formula are given in Table 5 (F_o).

4. Structure determination

At the outset it seemed probable that the benzoic acid molecules would occur as approximately planar, centrosymmetrical dimers in the crystal, with hydrogen bonding between the adjacent carboxyl groups. On this basis, and from known bond lengths, a trial model could be set up and the problem reduced to one of finding the three parameters which define the orientation of the model relative to the crystal axes. At this stage we employed a somewhat more direct method than the usual trial-and-error structures by evaluating the Fourier transform (Knott, 1940; Klug, 1950) of such an idealized dimer with covalent bonds of 1.36 \AA throughout, and hydrogen bonds between the molecules of 2.72 \AA . As the model has a centre of symmetry, the transform is real. It was evaluated in the usual way and is plotted in Fig. 1 with respect to the axes (X, Y) whose relation to the assumed planar model is shown in the lower part of the diagram.

The orientation of the $(h0l)$ section of the reciprocal lattice on the transform was now found quite readily by trial, and this is also shown in Fig. 1. Since the space group is $P2_1/c$, the (010) projection will contain two dimers similarly oriented and separated by $c/2$, their centres coinciding with the centres of symmetry of the projection. Hence $F(h0l) = 2fT(X, Y)$, where $T(X, Y)$ is the value of the transform at the position assigned to the reciprocal-lattice point $(h0l)$, and f is a scattering factor.

The signs of the majority of the $(h0l)$ structure

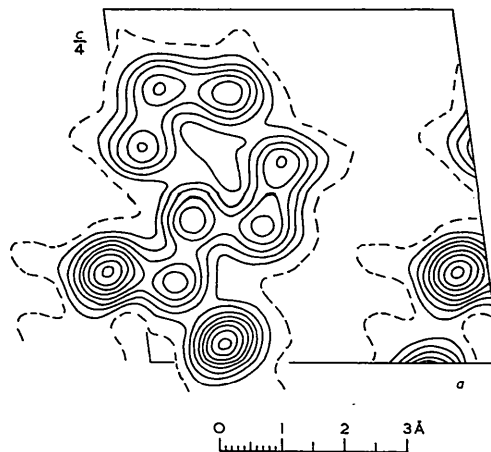


Fig. 2. Electron-density projection on (010) . Contours at intervals of $1 \text{ e.}\text{\AA}^{-2}$, the one-electron line being broken.

factors were obtained directly from the transform in this way, and were used to evaluate an electron-density projection on (010). This was found to resolve the atoms clearly and enabled the x and z coordinates to be estimated. Structure factors were then calculated and the remaining terms included in the synthesis. The final electron-density projection on (010) is shown in Fig. 2.

At this stage the percentage discrepancy $(100\Sigma|F_o - F_c| \div \Sigma F_o)$ was 15.1 for the $(h0l)$ structure factors.

5. Refinement of (010) projection and location of hydrogen atoms

Further refinement of this projection of the structure was now carried out by evaluating successive Fourier difference syntheses, with $(F_o - F_c)$ as coefficients. A study of these maps showed that the structure-factor discrepancies still remaining were due in part to the following factors:

(a) The coordinates of several atoms still required adjustment.

(b) It was not correct to assume that the constant γ in the temperature corrected scattering factor $f = f_0 \exp[-\gamma \sin^2 \theta]$ was the same for all the atoms.

(c) Atoms O_1 and C_5 showed marked thermal anisotropy, and consequently scattering factors of the form $f = f_0 \exp[-\{\alpha + \beta \sin^2(\varphi - \psi)\} \sin^2 \theta]$ should be employed for these atoms (Hughes, 1941; Cochran, 1951). In this expression α and β are constants, ψ is the angle between the direction of maximum vibration and the c axis, and $(2 \sin \theta, \varphi)$ are the polar coordinates of a point in the $(h0l)$ section of the reciprocal lattice.

(d) The contributions of the hydrogen atoms were considerable, and should be allowed for.

These factors were now dealt with in turn from a study of successive difference synthesis maps representing the function $(\rho_o - \rho_c)$, the difference between observed and calculated electron density at each point on the (010) projection. Coordinate adjustments were first made until the electron-density slope at the atomic centres became zero. Using the atomic scattering factors for carbon (valence states) listed by McWeeny (1951), the temperature factors γ were adjusted until $(\rho_o - \rho_c)$ was zero at the atomic centres. In the case of the atoms O_1 and C_5 , to which anisotropic temperature factors were applied, the values of the constants were so chosen that deviations of $(\rho_o - \rho_c)$ from zero in the regions around these atoms became as small as possible.

After these corrections had been applied, the final $(\rho_o - \rho_c)$ map was computed (Fig. 3). It represents the difference between the electron distribution existing in the crystal and that calculated for oxygen and carbon atoms only, at their appropriate positions in the unit cell. The significant peaks on this map are clearly due to the hydrogen atoms. Four of these

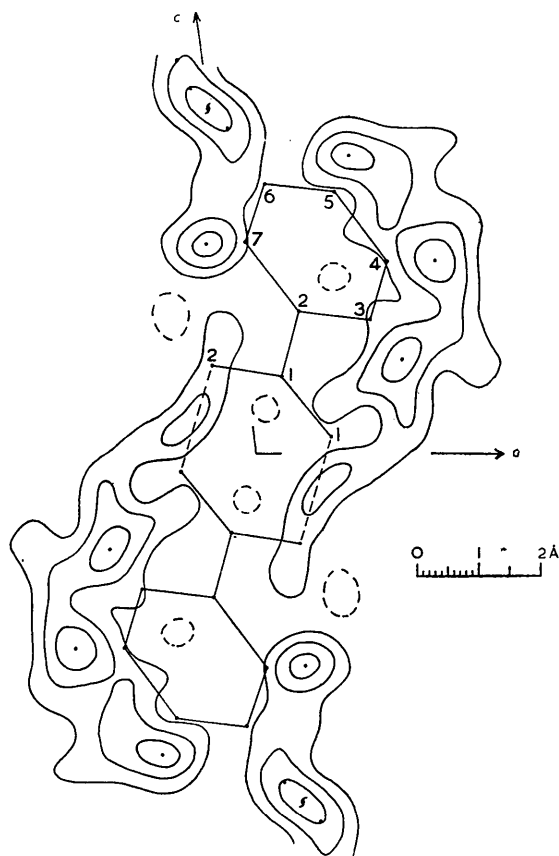


Fig. 3. Difference-synthesis projection on (010) showing electron distribution due to the hydrogen atoms in two benzoic acid molecules. Contours at intervals of $0.2 \text{ e.}\text{\AA}^{-2}$, negative contours broken and zero contour omitted.

atoms, attached to the benzene carbon atoms C_3 , C_4 , C_5 and C_7 , are well resolved, but the fifth, attached to C_6 , appears as an unresolved doublet on one of the symmetry centres (screw-axis projection). The most interesting hydrogen atom, that belonging to the carboxyl group and responsible for the hydrogen bonding which exists between the two molecules, is

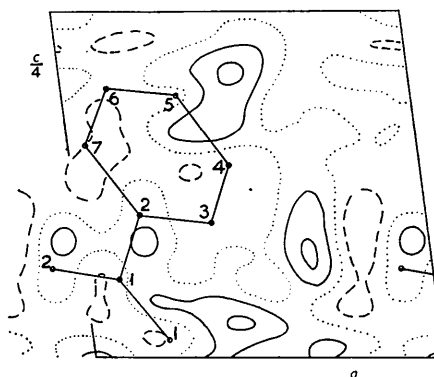


Fig. 4. Final $(F_o - F_c)$ synthesis. All atoms including hydrogen subtracted. Contour interval $0.2 \text{ e.}\text{\AA}^{-2}$, negative contours broken, zero contour dotted.

only poorly resolved and cannot be attributed with certainty to either of the oxygen atoms engaged by the hydrogen bond. It may, however, be assigned to O_2 on the basis of the C–O bond-length measurements which are discussed later.

As a check on the adequacy of the scattering factors and temperature factors employed, a difference synthesis map was prepared for a single molecule with all the atoms including hydrogen subtracted (Fig. 4). In calculating the final structure factors (F_c), which are listed in Table 5 and used in preparing this map, the benzene hydrogens were placed radially at a distance of 1.0 Å from the carbon atoms. The oxygen hydrogen was placed 1.0 Å from O_2 on the line to the oxygen of the opposite carboxyl group, and this hydrogen was given half the weight of the benzene hydrogens. The scattering curve used for hydrogen was that given by McWeeny (1951) modified by the temperature factor $\exp[-2.0 \sin^2 \theta]$. A study of Fig. 3 (which was prepared later) shows that these assumptions are not strictly accurate, and a survey of the actual hydrogen locations is given below (Table 4). Nevertheless, the general flatness of the map shown in Fig. 4 indicates that most of the outstanding features of the electron distribution have been explained. The final percentage discrepancy for the ($h0l$) structure factors, taking account of hydrogen, is 8.8. If the hydrogen atoms are not taken into account the percentage discrepancy rises to 11.8.

6. (100) projection

Approximate y coordinates for the atoms were now obtained by assuming a regular planar molecule with C–C equal to 1.39 Å and the O–H...O distances between the carboxyl groups equal to 2.64 Å. These coordinates were refined by preparing electron-density and difference synthesis maps from the ($0kl$) structure factors, giving projections on (100). The electron-density projection is shown in Fig. 5, and although all the atoms are not as well resolved as in Fig. 2, it provides useful information. In the refinement of this zone from the difference syntheses, the coordinates of the atoms and the temperature factors (values of γ) were adjusted as in the (010) projection, but no corrections for anisotropic motion were made. The final percentage discrepancy for this zone was 10.3.

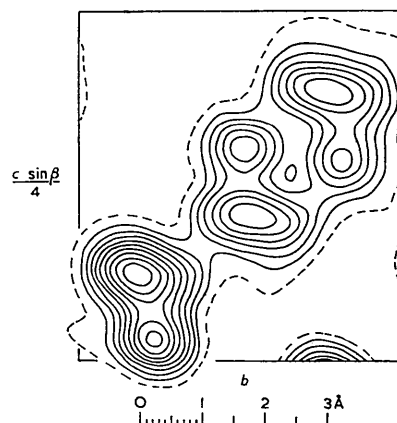


Fig. 5. Electron-density projection on (100). Contours at intervals of $1 \text{ e.}\text{\AA}^{-2}$, the one electron line being broken.

7. Coordinates, molecular dimensions and orientation

The final coordinates of the carbon and oxygen atoms are shown in Table 1, along with the temperature factors derived from the study of the two projections. The coordinates x , y and z are referred to the monoclinic crystal axes and are expressed as fractions of the axial lengths, with origin at the centre of symmetry. The coordinates X' , Y and Z' are referred to orthogonal axes a , b and c' , c' being taken perpendicular to the a and b crystal axes, so that

$$X' = X + Z \cos \beta, \quad Z' = Z \sin \beta.$$

These coordinates are expressed in Ångström units.

It is found that the coordinates of the ring atoms C_2 , C_3 , ..., C_7 can be fitted to an equation of the form

$$Y = AX' + BZ' + C.$$

A , B and C were determined by the method of least squares to be 0.8057, 0.8284 and 0.0090 respectively. The deviations, Δ , of the Y coordinates, as derived from the final difference map for the (100) projection, and as calculated by means of the above equation, are shown in Table 2.

The average deviation between the two values of Y for the ring atoms is 0.012 Å, equivalent to a perpendicular displacement from the plane of 0.008 Å. Atoms C_1 and O_2 , however, appear to depart signifi-

Table 1. *Coordinates and temperature factors*

Atom	x	y	z	X' (Å)	Y (Å)	Z' (Å)	α	β	γ_{h0l}	ψ (°)	γ_{0kl}
O_1	0.223	0.237	0.013	1.192	1.216	0.290	0.8	2.6	(2.1)	111	2.1
O_2	-0.089	0.140	0.064	-0.663	0.737	1.398	—	—	2.1	—	2.1
C_1	0.103	0.278	0.057	0.413	1.430	1.236	—	—	1.5	—	1.5
C_2	0.180	0.481	0.104	0.713	2.470	2.255	—	—	1.6	—	1.6
C_3	0.383	0.631	0.093	1.849	3.241	2.103	—	—	1.9	—	2.0
C_4	0.455	0.823	0.140	2.129	4.231	3.048	—	—	2.2	—	2.2
C_5	0.330	0.875	0.190	1.310	4.497	4.121	1.2	1.2	(1.8)	50	2.2
C_6	0.133	0.720	0.196	0.210	3.700	4.251	—	—	2.1	—	1.8
C_7	0.051	0.516	0.154	-0.128	2.653	3.338	—	—	2.0	—	2.0

Table 2. *Deviations from mean plane*

Atom	$Y_{\text{calc.}}$	$Y_{\text{obs.}}$	Δ	Displacement from plane
O ₁	1.210	1.216	-0.006	-0.004
O ₂	0.633	0.737	-0.104	-0.068
C ₁	1.366	1.430	-0.064	-0.042
C ₂	2.452	2.470	-0.018	-0.012
C ₃	3.241	3.241	0.000	0.000
C ₄	4.249	4.231	0.018	0.012
C ₅	4.478	4.497	-0.019	-0.012
C ₆	3.700	3.700	0.000	0.000
C ₇	2.671	2.653	0.018	0.012

cantly from the mean plane, their distances being 0.042 and 0.068 Å respectively.

The bond lengths and valency angles in the benzoic acid molecule are shown in Fig. 6. These were cal-

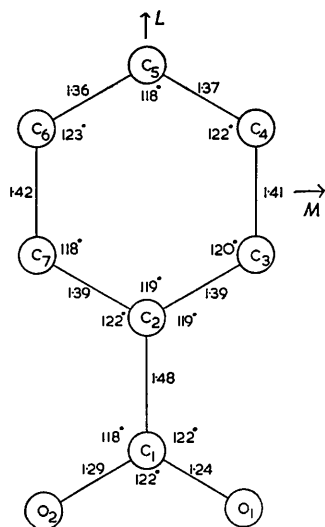


Fig. 6. Bond lengths and valency angles in benzoic acid.

culated from the coordinates in Table 1 except for the Y coordinates of the ring atoms, where the $Y_{\text{calc.}}$ values in Table 2 were employed. These do not differ significantly from the observed values, and are likely to be more reliable.

The orientation of the molecule in the crystal may be stated by giving the angles χ , ψ and ω , which the lines L , M (Fig. 6) and the plane normal N make with the crystal axes a , b and the perpendicular c' . L and M are taken to lie in the mean plane of the ring, L passing through the atoms C_2 and C_5 . These values are given in Table 3.

Table 3. *Orientation*

$\cos \chi_L = 0.2118$	$\chi_L = 77.8^\circ$
$\cos \psi_L = 0.7189$	$\psi_L = 44.0$
$\cos \omega_L = 0.6621$	$\omega_L = 48.5$
$\cos \chi_M = -0.8236$	$\chi_M = 145.5$
$\cos \psi_M = -0.2366$	$\psi_M = 103.7$
$\cos \omega_M = 0.5154$	$\omega_M = 59.0$
$\cos \chi_N = 0.5276$	$\chi_N = 58.2$
$\cos \psi_N = -0.6546$	$\psi_N = 130.9$
$\cos \omega_N = 0.5420$	$\omega_N = 57.2$

With regard to the hydrogen atoms (Fig. 3), it is not possible to make any reliable assignment of coordinates except for the four attached to the carbon atoms C_3 , C_4 , C_5 and C_7 . The estimated positions of these hydrogens are given in Table 4, the Y coor-

Table 4. *Hydrogen coordinates and bond lengths*

Atom	X' (Å)	Y (Å)	Z' (Å)
H(C_3)	2.32	1.49	3.11
H(C_4)	2.88	3.03	4.85
H(C_5)	1.53	4.71	5.14
H(C_7)	-0.74	3.32	2.16

H-C₃ = 0.79, H-C₄ = 0.96, H-C₅ = 0.91, H-C₇ = 0.79 Å.

ordinates being obtained by substituting the estimated X' and Z' values in the equation of the mean plane of the ring.

8. Estimation of accuracy

The standard deviations of the atomic coordinates, $\sigma(x)$, were estimated by the method of Cruickshank (Cruickshank, 1949, 1954; Ahmed & Cruickshank, 1953), where

$$\sigma(x) = \frac{\sigma(\partial\rho/\partial x)}{\partial^2\rho/\partial x^2} = \frac{1}{A} \frac{2\pi}{a} \left(\sum h^2 (\Delta F)^2 \right)^{\frac{1}{2}} \left| \frac{\partial^2\rho}{\partial x^2} \right|^{-1}$$

In this equation, A is the area of the cell projection, ΔF the error in the F values, and $\partial^2\rho/\partial x^2$ is the curvature at the centre of the atom. In evaluating this expression we have taken $\Delta F = |F_o - F_c|$, which includes random errors and any residual finite-series errors, although these should have been eliminated by the difference synthesis methods employed (Cochran, 1951). The curvature was estimated by assuming that the electron density, ρ_r , near the atomic centre can be written as

$$\rho_r = \rho_o \exp[-pr^2],$$

so that

$$\partial^2\rho/\partial x^2 = -2p\rho_o.$$

The constant p was evaluated by graphical plots of $\log \rho$ against r^2 .

The coordinate standard deviations obtained by these methods were:

$$\sigma(x) = \sigma(z) = 0.010 \text{ \AA}, \quad \sigma(y) = 0.014 \text{ \AA} \text{ for carbon};$$

$$\sigma(x) = \sigma(z) = 0.008 \text{ \AA}, \quad \sigma(y) = 0.010 \text{ \AA} \text{ for oxygen}.$$

From these results the standard deviation of a C-C bond is about 0.016 Å, and of a C-O bond about 0.014 Å. The standard deviation of bond angles, computed by the equation given by Ahmed & Cruickshank (1953) was found to be 0.9°. The standard deviation of electron density, given by

$$\sigma(\rho_o) = \frac{1}{A} \left(\sum (F_o - F_c)^2 \right)^{\frac{1}{2}},$$

Table 5. Observed and calculated structure factors

hkl	F_o	F_c	hkl	F_o	F_c	hkl	F_o	F_c
000	—	256	$2,0,\overline{12}$	2.1	0.7	$0,1,14$	5.0	— 4.3
100	36.0	41.3	$2,0,\overline{14}$	11.9	11.8	$0,1,15$	13.5	15.2
200	7.0	5.2	$2,0,\overline{16}$	< 2.5	— 3.3	$0,1,16$	< 1.4	2.5
300	9.7	— 11.1	$2,0,\overline{18}$	3.1	— 2.9	$0,1,17$	5.5	4.7
400	12.7	— 12.8	$2,0,\overline{20}$	5.3	5.4	$0,1,18$	11.0	— 10.4
500	3.0	— 2.7	$2,0,\overline{22}$	4.0	3.9	$0,1,19$	8.9	— 8.9
020	27.9	— 27.5	$3,0,12$	6.7	5.4	$0,1,20$	11.8	— 13.7
040	4.8	6.0	$3,0,10$	< 2.6	— 0.8	$0,1,21$	2.6	— 1.6
002	34.3	32.5	308	5.9	— 5.2	$0,1,22$	< 1.5	— 1.2
004	31.3	— 31.8	306	8.8	10.1	$0,1,23$	2.0	2.3
006	8.9	8.7	304	10.8	11.0	$0,1,24$	2.5	— 2.8
008	22.3	— 21.9	302	22.3	— 23.2	021	< 1.0	2.4
0,0,10	10.2	8.6	$30\overline{2}$	< 1.9	— 0.7	022	18.4	— 21.1
0,0,12	5.6	3.9	$30\overline{4}$	17.4	— 15.6	023	20.7	— 21.0
0,0,14	11.0	11.3	306	8.7	— 8.1	024	31.7	— 32.4
0,0,16	8.5	9.2	$30\overline{8}$	7.9	— 8.2	025	27.7	— 25.6
0,0,18	< 2.0	1.2	$3,0,\overline{10}$	6.4	— 6.2	026	11.6	— 9.2
0,0,20	11.9	11.9	$3,0,\overline{12}$	2.4	— 3.8	027	3.7	4.8
0,0,22	2.8	— 2.1	$3,0,\overline{14}$	7.4	— 8.1	028	11.1	9.1
0,0,24	9.0	— 10.9	$3,0,\overline{16}$	8.6	— 8.9	029	9.8	10.3
			$3,0,\overline{18}$	11.8	— 13.8	$0,2,10$	2.9	— 3.0
1,0,24	5.3	— 4.5	$3,0,\overline{20}$	6.7	— 8.6	$0,2,11$	4.3	5.8
1,0,22	15.3	— 16.5	$3,0,\overline{22}$	< 2.3	0.4	$0,2,12$	4.0	3.6
1,0,20	3.4	2.7	$4,0,14$	4.0	3.9	$0,2,13$	< 1.4	— 1.6
1,0,18	10.9	10.5	$4,0,12$	3.4	2.3	$0,2,14$	7.3	— 9.6
1,0,16	3.3	1.4	$4,0,10$	< 2.7	— 0.1	$0,2,15$	2.9	— 3.7
1,0,14	3.9	3.3	408	6.7	6.9	$0,2,16$	11.9	— 12.1
1,0,12	25.5	— 25.1	406	4.6	3.8	$0,2,17$	< 1.6	1.5
1,0,10	25.7	— 25.0	404	14.9	13.2	$0,2,18$	2.5	3.2
108	21.9	— 21.1	402	6.5	5.1	$0,2,19$	2.2	— 2.5
106	18.7	— 16.1	$40\overline{2}$	7.4	— 5.1	$0,2,20$	< 1.6	0.1
104	26.8	27.7	$40\overline{4}$	6.7	— 6.0	$0,2,21$	2.2	— 2.6
102	37.3	— 38.3	$40\overline{6}$	17.4	16.1	031	17.5	— 17.6
$10\overline{2}$	74.8	83.7	$40\overline{8}$	20.3	20.4	032	2.4	4.2
104	3.0	3.4	$4,0,\overline{10}$	6.5	— 7.0	033	9.8	9.7
$10\overline{6}$	6.9	8.3	$4,0,\overline{12}$	< 2.7	— 0.4	034	8.0	8.1
108	34.1	— 35.0	$4,0,\overline{14}$	< 2.7	0.8	035	3.6	2.9
$1,0,\overline{10}$	5.2	— 4.0	$4,0,\overline{16}$	5.5	— 5.6	036	5.9	4.0
$1,0,\overline{12}$	38.8	37.5	$4,0,\overline{18}$	4.6	— 4.0	037	8.7	— 8.7
$1,0,\overline{14}$	15.0	15.5	$4,0,\overline{20}$	6.5	— 7.0	038	7.6	7.7
$1,0,\overline{16}$	13.3	13.1	$50\overline{2}$	< 2.7	— 0.7	039	6.5	4.5
$1,0,\overline{18}$	8.5	10.7	$50\overline{4}$	3.0	— 3.1	$0,3,10$	3.6	2.2
$1,0,\overline{20}$	5.6	5.2	$50\overline{6}$	3.0	— 4.0	$0,3,11$	2.8	2.9
$1,0,\overline{22}$	4.2	5.1	$50\overline{8}$	21.2	19.9	$0,3,12$	2.5	3.1
$2,0,22$	2.7	— 1.9	$5,0,\overline{10}$	13.1	12.8	$0,3,13$	3.1	— 4.6
$2,0,20$	3.1	— 3.9	$6,0,\overline{10}$	5.0	5.2	$0,3,14$	3.0	4.6
$2,0,18$	2.9	4.3				$0,3,15$	< 1.6	— 2.2
$2,0,16$	< 2.7	2.0	011	11.7	— 12.9	041	< 1.5	0.5
$2,0,14$	8.8	8.5	012	20.5	19.5	042	3.4	2.6
$2,0,12$	4.6	— 5.2	013	21.8	18.0	043	< 1.5	— 0.3
$2,0,10$	34.2	— 35.0	014	79.1	— 72.7	044	3.0	4.1
208	14.0	— 15.1	015	26.5	26.5	045	5.3	3.3
206	8.6	— 9.0	016	27.6	— 27.8	046	7.7	7.5
204	16.8	— 15.4	017	11.7	— 11.7	047	< 1.6	— 0.1
202	6.7	— 3.9	018	21.1	— 18.9	048	7.7	6.6
$20\overline{2}$	18.7	— 18.3	019	12.8	— 12.4	049	3.7	— 5.7
$20\overline{4}$	36.2	— 40.0	$0,1,10$	< 1.1	— 0.4	$0,4,10$	< 1.6	1.1
$20\overline{6}$	9.5	— 8.8	$0,1,11$	7.9	— 8.3	$0,4,11$	4.8	5.3
$20\overline{8}$	4.8	— 2.4	$0,1,12$	11.4	12.2	$0,4,12$	< 1.6	— 0.5
$2,0,10$	24.9	— 25.7	$0,1,13$	< 1.3	— 0.1	$0,4,13$	2.8	4.0

was found to be $0.17 \text{ e.}\text{\AA}^{-2}$ for the $(h0l)$ zone, and $0.31 \text{ e.}\text{\AA}^{-2}$ for the $(0kl)$ zone.

9. Discussion of structure and molecular dimensions

The displacements of the carbon atoms of the benzene ring from a plane (Table 2) vary from zero to 0.012 \AA ,

and are not significant. The ring may therefore be assumed strictly planar. The displacements of the atoms C_1 and O_2 from the molecular plane are 0.042 and 0.068 \AA respectively. These displacements, though small, appear to be significant, because they are several times greater than the standard deviation of position of a carbon or oxygen atom.

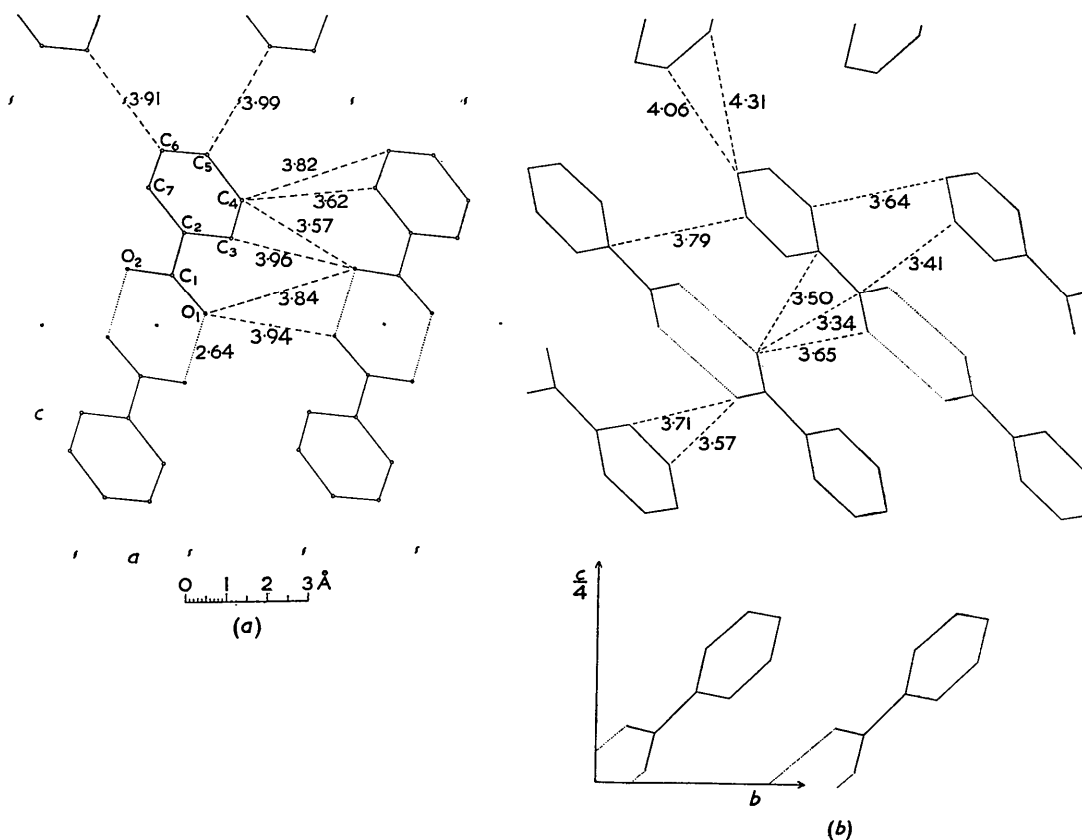


Fig. 7. Arrangement of molecules (a) in (010) projection, (b) in (100) projection.

The two C-O bonds in the carboxyl group differ in length by 0.046 Å. Since the total estimated standard deviation given by

$$\sigma^2(t) = \sigma^2(C_1O_1) + \sigma^2(C_1O_2) - 2\sigma^2(C_1) \cos \theta,$$

where θ is the angle between the bonds C_1-O_1 and C_1-O_2 , is 0.021 Å, this difference may be real. It is, however, smaller than the C-O bond differences in some carboxyl groups, e.g. salicylic acid (Cochran, 1953) and *N*-acetyl glycine (Carpenter & Donohue, 1950), where the differences are of the order of 0.10 Å. The benzoic acid difference of 0.05 Å is closer to those reported for some of the 'zwitterion' amino acids. On the basis of our measurements, however, we have assigned the hydrogen atom of the carboxyl group to O_2 . The resolution of this hydrogen atom in Fig. 3 is not good enough to confirm this assignment. This lack of resolution may indeed be connected with the nearly equal C-O distances, and could indicate a ready transfer of the hydrogen to the other oxygen across the hydrogen bond. However, this bond at 2.64 Å (see below) is not unusually short. Further discussion of these matters must await more accurate measurements.

In the benzene ring the bonds C_3-C_4 and C_6-C_7 differ from C_4-C_5 and C_5-C_6 by an average value of

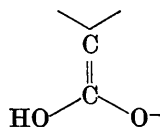
0.051 Å. Since the total estimated standard deviation (Parry, 1954), given by

$$\sigma^2(t) = \frac{1}{2}(\sigma^2(C_3C_4) + \sigma^2(C_6C_7) + \sigma^2(C_4C_5) + \sigma^2(C_5C_6)) - 2\sigma^2(C_4) \cos \theta_1 - 2\sigma^2(C_5) \cos \theta_2 - 2\sigma^2(C_6) \cos \theta_3,$$

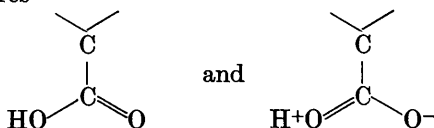
is 0.017 Å, this difference appears to be significant. It is, however, difficult to explain this difference on the basis of any reasonable structures that may be written for the benzoic acid molecule. Nor do some preliminary calculations by one of us (T.H.G.), using the molecular-orbital approximation, suggest that the bonds C_3-C_4 and C_6-C_7 should be longer than the other bonds in the ring although C_1-C_2 should be shorter than a pure single bond. These conclusions are not entirely in agreement with the X-ray results.

The bond C_2-C_1 , leading to the carboxyl group, is 1.48 Å and therefore appears to be significantly shortened from the standard single-bond value of 1.54 Å, and is even less than twice the radius, 0.75 Å, suggested as appropriate to a carbon atom hybridized in the sp^2 state (Coulson, 1948). The value found agrees closely with that observed in salicylic acid, 1.46 Å (Cochran, 1953), but is distinctly less than that in many other carboxylic acids, e.g. oxalic acid dihydrate, 1.53 Å (Ahmed & Cruickshank, 1953), α -oxalic acid, 1.56 Å (Cox, Dougill & Jeffrey, 1952) and several

of the amino acids which have recently received careful study. The shortening of this C-C bond in the benzene carboxylic acids may perhaps be correlated with an observed increase in the sum of the lengths of the two C-O bonds in these carboxyl groups. Thus, for benzoic acid this sum is 2.53 Å, and for salicylic acid 2.57 Å. For the two oxalic acids mentioned above the sum is 2.48 Å, and for L-threonine, DL-alanine, β -glycylglycine, glycyl-L-asparagine and N-acetylglycine the average value of this sum is 2.48 Å. (In the case of DL-serine, however, the value is 2.53 Å.) The examples quoted all represent determinations of high accuracy, and the results suggest that in the benzene carboxylic acids the structure



makes a considerable contribution, in addition to the structures



which are usually present.

With regard to the positions of the hydrogen atoms that are resolved in Fig. 3, the average value of the C-H bond lengths (Table 4) is 0.86 Å. Although this value is considerably less than the accepted spectroscopic value of 1.07 Å, it agrees well with the value of 0.89 Å found in salicylic acid (Cochran, 1953). These results suggest strongly that the point of estimated maximum electron density does not coincide with the position of the proton. Electron counts for the hydrogen atoms are necessarily inconclusive with the accuracy at present attained. The content of the benzene hydrogens varies from 0.7 to 1.3 electrons, so that the error is large and it is difficult to decide where to draw the boundary. The oxygen hydrogen is even less conclusive, the elongated peak in Fig. 3 having a content of about 0.9 electrons, but this, of course, overlaps the oxygen positions.

The arrangement of the molecules in the crystal and

the intermolecular approach distances are indicated in Fig. 7.

The closest approach distance occurs between the oxygen atoms of the carboxyl groups, which are related by a centre of symmetry. The O-H...O distance here is 2.64 Å, which is normal for this type of hydrogen bonding.

All other intermolecular approach distances are over 3 Å, and correspond to normal van der Waals interactions. The closest contact, 3.34 Å, occurs between C_1 of one dimer and O_1 of a dimer related to the first by a translation b .

In conclusion, one of us (G. A. S.) is indebted to the Department of Scientific and Industrial Research, and later to the Ramsay Memorial Fellowships Trust, for awards which have enabled him to take part in this work.

References

- ABRAHAMS, S. C. & ROBERTSON, J. M. (1948). *Acta Cryst.* **1**, 252.
 AHMED, F. R. & CRUICKSHANK, D. W. J. (1953). *Acta Cryst.* **6**, 385.
 BODEWIG, C. (1880). *Z. Kristallogr.* **4**, 57.
 BRAGG, W. H. (1921). *Proc. Phys. Soc.* **34**, 33.
 BRAGG, W. H. (1922). *J. Chem. Soc.* p. 2766.
 CARPENTER, G. B. & DONOHUE, J. (1950). *J. Amer. Chem. Soc.* **72**, 2315.
 COCHRAN, W. (1951). *Acta Cryst.* **4**, 81.
 COCHRAN, W. (1953). *Acta Cryst.* **6**, 260.
 COULSON, C. A. (1948). *Contribution à l'étude de la structure moléculaire*, p. 17. (Victor Henri Memorial Volume.) Liège: Desoer.
 COX, E. G., DOUGILL, M. W. & JEFFREY, G. A. (1952). *J. Chem. Soc.* p. 4854.
 CRUICKSHANK, D. W. J. (1949). *Acta Cryst.* **2**, 65.
 CRUICKSHANK, D. W. J. (1954). *Acta Cryst.* **7**, 519.
 GOODWIN, T. H., PRZYBYLSKA, M. & ROBERTSON, J. M. (1950). *Acta Cryst.* **3**, 279.
 HUGHES, E. W. (1941). *J. Amer. Chem. Soc.* **63**, 1737.
 KLUG, A. (1950). *Acta Cryst.* **3**, 176.
 KNOTT, G. (1940). *Proc. Phys. Soc. Lond.* **52**, 229.
 MCWEENY, R. (1951). *Acta Cryst.* **4**, 513.
 PARRY, G. S. (1954). *Acta Cryst.* **7**, 313.
 ROBERTSON, J. M. (1943). *J. Sci. Instrum.* **20**, 175.
 ROBERTSON, J. M. & UBBELOHDE, A. R. (1939). *Proc. Roy. Soc. A*, **170**, 222.
 STEINMETZ, H. (1914). *Z. Kristallogr.* **53**, 463.