

### 336. X-Ray Studies of Molecular Overcrowding. Part IV.<sup>1</sup> The Crystal and Molecular Structure of 2-Chloro-5-nitrobenzoic Acid.

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2-Chloro-5-nitrobenzoic acid crystallizes in the monoclinic system, space group  $P2_1/c$ , with four molecules in a unit cell of dimensions  $a = 5.86$ ,  $b = 5.13$ ,  $c = 26.65$  Å,  $\beta = 97^\circ 54'$ . The molecules occur as centrosymmetrical dimers with hydrogen bonds (2.61 Å) between adjacent carboxyl groups. The carboxyl group is rotated  $23^\circ$  and the nitro-group  $7^\circ$  out of the plane of the benzene ring.

THE molecules of *o*-chloro- and *o*-bromo-benzoic acid have been shown to be non-planar in the solid state.<sup>1,2</sup> Among more heavily substituted benzene derivatives 2-chloro-5-nitrobenzoic acid appeared to us to offer the possibility of demonstrating a relayed steric effect, for buttressing of the hydrogen atom at position 6 by the bulky 5-nitro-group could lead to the carboxyl group's being twisted further out of the benzene plane than in *o*-chlorobenzoic acid. We have therefore determined the crystal structure of 2-chloro-5-nitrobenzoic acid and refined the atomic parameters extensively by three-dimensional Fourier and least-squares methods.

TABLE I.

Final atomic co-ordinates.

(Co-ordinates  $x$ ,  $y$ , 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. Co-ordinates  $X'$ ,  $Y$ , and  $Z'$  are referred to orthogonal axes  $a$ ,  $b$ , and  $c'$  ( $c'$  being taken perpendicular to the  $a$ - and  $b$ -crystal axes) and are expressed in Å units.)

Atom	$x$	$y$	$z$	$X'$	$Y$	$Z'$
C(1) .....	-0.2551	0.1807	0.1006	-1.863	0.927	2.654
C(2) .....	-0.4479	0.0736	0.1162	-3.051	0.378	3.068
C(3) .....	-0.5264	0.1526	0.1598	-3.670	0.783	4.218
C(4) .....	-0.4142	0.3503	0.1889	-3.119	1.797	4.986
C(5) .....	-0.2209	0.4581	0.1734	-1.930	2.350	4.577
C(6) .....	-0.1431	0.3791	0.1300	-1.315	1.945	3.432
C(7) .....	-0.1520	0.0996	0.0550	-1.092	0.511	1.451
O(1) .....	-0.1858	-0.1173	0.0367	-1.223	-0.602	0.968
O(2) .....	-0.0226	0.2753	0.0384	-0.273	1.412	1.015
O(3) .....	0.0806	0.7441	0.1922	-0.232	3.817	5.075
O(4) .....	-0.1861	0.7523	0.2391	-1.966	3.859	6.312
N .....	-0.1002	0.6646	0.2034	-1.332	3.409	5.370
Cl .....	-0.6040	-0.1761	0.0822	-3.840	-0.903	2.169

The final co-ordinates of the atoms are given in Table 1; the standard deviations, calculated from the least-squares residuals in the usual way, in Table 2; and the interatomic distances and valency angles in Table 3. The arrangement of the molecules in the crystal is indicated in Fig. 1.

<sup>1</sup> Part III, Ferguson and Sim, *Acta Cryst.*, 1962, **15**, in the press.

<sup>2</sup> Ferguson and Sim, *Proc. Chem. Soc.*, 1961, 162; *Acta Cryst.*, 1961, **14**, 1262.

TABLE 2.

Standard deviations of the final atomic co-ordinates (Å).

	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$		$\sigma(x)$	$\sigma(y)$	$\sigma(z)$
C(1) .....	0.0055	0.0076	0.0054	O(1) .....	0.0042	0.0055	0.0041
C(2) .....	0.0058	0.0079	0.0058	O(2) .....	0.0044	0.0054	0.0042
C(3) .....	0.0058	0.0082	0.0057	O(3) .....	0.0045	0.0056	0.0046
C(4) .....	0.0057	0.0078	0.0058	O(4) .....	0.0044	0.0053	0.0042
C(5) .....	0.0056	0.0080	0.0055	N .....	0.0049	0.0062	0.0049
C(6) .....	0.0057	0.0078	0.0058	Cl .....	0.0015	0.0022	0.0016
C(7) .....	0.0057	0.0073	0.0058				

The plane through the carbon atoms of the benzene ring, calculated by the method of Schomaker *et al.*,<sup>3</sup> has equation

$$0.50771X' - 0.68389Y + 0.52395Z' + 0.19423 = 0.$$

The small displacements of the benzene carbon atoms from this plane (Table 4) are not significant. The displacements of the chlorine and nitrogen atoms are also not significant.

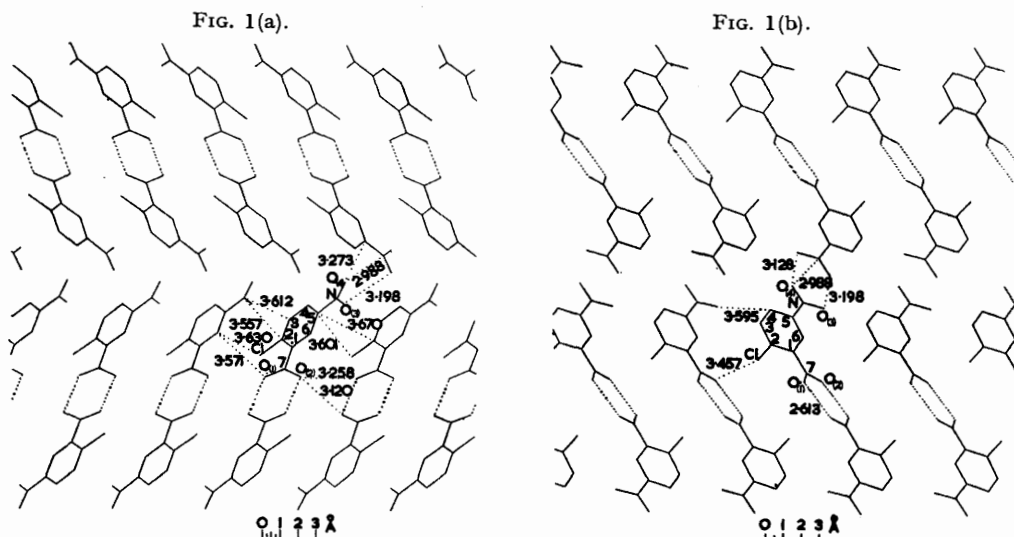


FIG. 1. The crystal structure of 2-chloro-5-nitrobenzoic acid as viewed in projection along (a) the *a*-axis and (b) the *b*-axis.

The exocyclic carbon atom C(7), on the other hand, is displaced from the benzene plane by 0.051 Å, implying an out-of-plane deflection of the exocyclic carbon-carbon bond of about 2°. This displacement, though small, is considerably greater than the estimated standard deviation of position and appears to be significant. For confirmation of this point the plane through the carbon, nitrogen, and chlorine atoms was calculated; it has equation

$$0.50083X' - 0.68361Y + 0.53090Z' + 0.14758 = 0.$$

Application of the  $\chi^2$ -test<sup>4</sup> to the displacements of the carbon, nitrogen, and chlorine atoms from this plane (Table 4) indicates that these atoms cannot all be regarded as coplanar, for  $\sum \Delta^2 = 1.28 \times 10^{-3} \text{ Å}^2$  and  $\chi^2 = \sum \Delta^2 / \sigma^2 \approx 26$ .

The atoms of the carboxyl group, C(7), O(1), O(2), and carbon atom C(1) of the benzene ring lie on the plane

$$0.72169X' - 0.35446Y + 0.59458Z' + 0.09759 = 0.$$

<sup>3</sup> Schomaker, Waser, Marsh, and Bergman, *Acta Cryst.*, 1959, **12**, 600.

<sup>4</sup> Fisher and Yates, "Statistical Tables," Oliver and Boyd, Edinburgh, 1957.

The angle between the plane of the carboxyl group and the plane of the benzene ring is  $23.0^\circ$ . The atoms of the nitro-group, N, O(3), O(4), and carbon atom C(5) of the benzene ring lie on the plane

$$0.41333X' - 0.68278Y + 0.60247Z' - 0.35560 = 0.$$

The angle between the plane of the nitro-group and the plane of the benzene ring is  $7.0^\circ$ .

The tilt of the carboxyl group to the benzene plane ( $23.0^\circ$ ) is considerably greater than that in *o*-chlorobenzoic acid ( $13.7^\circ$ ). This difference may be attributed either to intermolecular packing forces or to an intramolecular buttressing effect. It is clear that crystal forces can be important in conformation effects; biphenyl, for example, is centrosymmetrical and hence planar in the solid state,<sup>5</sup> while in the gas phase electron-diffraction studies<sup>6</sup> indicate that the two rings are inclined at about  $45^\circ$  to one another. On balance, however, we consider that intramolecular forces are of more importance in the present case. In *o*-chlorobenzoic acid it is highly probable, in view of the in-plane deflections of the

TABLE 3.  
Interatomic distances (Å) and angles.

<i>Intramolecular bonded distances</i>					
C(1)-C(2) .....	1.372	C(6)-C(1) .....	1.394	C(5)-N .....	1.452
C(2)-C(3) .....	1.368	C(1)-C(7) .....	1.489	O(3)-N .....	1.210
C(3)-C(4) .....	1.387	C(7)-O(1) .....	1.220	O(4)-N .....	1.222
C(4)-C(5) .....	1.374	C(7)-O(2) .....	1.294		
C(5)-C(6) .....	1.362	C(2)-Cl .....	1.753		
<i>Intramolecular non-bonded distances</i>					
C(7) ... Cl .....	3.173	O(2) ... C(6) .....	2.685	O(4) ... C(4) .....	2.709
O(1) ... Cl .....	2.896	O(3) ... C(6) .....	2.715	O(1) ... C(2) .....	2.951
<i>Intermolecular distances *</i>					
O(1) ... O(2) <sub>I</sub> .....	2.613	O(4) ... C(3) <sub>IV</sub> .....	3.392	C(4) ... O(3) <sub>VI</sub> .....	3.595
O(4) ... N <sub>II</sub> .....	2.988	C(7) ... O(2) <sub>I</sub> .....	3.412	C(5) ... Cl <sub>IV</sub> .....	3.601
O(2) ... O(2) <sub>III</sub> .....	3.120	Cl ... O(2) <sub>VI</sub> .....	3.457	N ... C(3) <sub>IV</sub> .....	3.612
O(4) ... O(3) <sub>II</sub> .....	3.128	Cl ... O(1) <sub>VI</sub> .....	3.472	C(6) ... Cl <sub>IV</sub> .....	3.630
O(3) ... O(4) <sub>II</sub> .....	3.198	Cl ... C(7) <sub>VI</sub> .....	3.493	N ... N <sub>II</sub> .....	3.650
O(2) ... O(1) <sub>IV</sub> .....	3.258	O(3) ... N <sub>II</sub> .....	3.509	C(5) ... C(2) <sub>IV</sub> .....	3.670
O(4) ... C(5) <sub>II</sub> .....	3.273	O(2) ... O(2) <sub>I</sub> .....	3.521	O(3) ... C(1) <sub>IV</sub> .....	3.679
O(3) ... C(3) <sub>V</sub> .....	3.315	O(3) ... C(4) <sub>II</sub> .....	3.528	N ... O(4) <sub>II</sub> .....	3.680
O(1) ... O(1) <sub>I</sub> .....	3.343	O(4) ... C(4) <sub>IV</sub> .....	3.535	O(3) ... Cl <sub>V</sub> .....	3.699
C(7) ... O(1) <sub>I</sub> .....	3.349	N ... C(2) <sub>IV</sub> .....	3.557	O(3) ... C(5) <sub>II</sub> .....	3.728
O(4) ... O(4) <sub>II</sub> .....	3.365	C(6) ... O(1) <sub>IV</sub> .....	3.571		

\* The subscripts refer to the following positions:

I	$-x, -y, -z$	IV	$x, 1+y, z$
II	$-x, \frac{1}{2}+y, \frac{1}{2}-z$	V	$1+x, 1+y, z$
III	$-x, 1-y, -z$	VI	$x-1, y, z$

*Interbond angles*

C(1) C(2) C(3)	121.8°	C(1) C(7) O(2)	114.0°
C(2) C(3) C(4)	120.2	O(1) C(7) O(2)	124.8
C(3) C(4) C(5)	118.2	C(1) C(2) Cl	121.9
C(4) C(5) C(6)	121.5	C(3) C(2) Cl	116.4
C(5) C(6) C(1)	120.6	C(4) C(5) N	119.2
C(6) C(1) C(2)	117.7	C(6) C(5) N	119.4
C(6) C(1) C(7)	116.8	C(5) N O(3)	119.2
C(2) C(1) C(7)	125.5	C(5) N O(4)	118.5
C(1) C(7) O(1)	121.3	O(3) N O(4)	122.4

exocyclic carbon-carbon and carbon-chlorine bonds, that the hydrogen atom at position 6 adjacent to the carboxyl group is displaced away from its ideal radial position. With the introduction of the bulky 5-nitro-group in-plane deflection of the hydrogen atom at position 6 is prevented and the increased H ... O(2) interaction could lead to the carboxyl

<sup>5</sup> Dhar, *Indian J. Phys.*, 1932, **7**, 43; Hargreaves, Rizvi, and Trotter, *Proc. Chem. Soc.*, 1961, 122.

<sup>6</sup> Karle and Brockway, *J. Amer. Chem. Soc.*, 1944, **66**, 1974; Bastiansen, *Acta Chem. Scand.*, 1949, **3**, 408.

group's rotating further out of the benzene plane, as is indeed observed. An identical buttressing effect can be invoked to explain the tilt ( $7^\circ$ ) of the carboxyl group in 4-chloro-3-nitrobenzoic acid,<sup>7</sup> for benzoic acid<sup>8</sup> and 2-naphthoic acid<sup>9</sup> are planar in the solid state. Similar arguments can be advanced concerning the orientations of the nitro-groups in a

TABLE 4.

Deviations (Å) of the atoms from various planes.

(a) Plane through the benzene ring atoms C(1), . . . C(6). (b) Plane through C(1), . . . C(7), N, Cl.  
(c) Plane through C(1), C(7), O(1), O(2). (d) Plane through C(5), N, O(3), O(4).

	(a)	(b)	(c)	(d)
C(1) .....	0.005	-0.010	0.003	—
C(2) .....	-0.006	-0.010	—	—
C(3) .....	0.006	0.014	—	—
C(4) .....	-0.006	0.004	—	—
C(5) .....	0.006	0.005	—	0.000
C(6) .....	-0.005	-0.018	—	—
C(7) .....	0.051	0.022	-0.009	—
O(1) .....	0.492	0.460	0.004	—
O(2) .....	-0.379	-0.416	0.003	—
O(3) .....	0.125	0.116	—	0.000
O(4) .....	-0.136	-0.124	—	0.000
N .....	0.000	0.000	—	0.001
Cl .....	-0.001	-0.007	—	—

number of molecules. Thus in *m*-dinitrobenzene,<sup>10</sup> 1-chloro-2,4-dinitrobenzene,<sup>11</sup> and 2-chloro-5-nitrobenzoic acid nitro-groups adjacent to buttressed hydrogen atoms are rotated  $11^\circ$ ,  $15^\circ$ , and  $7^\circ$ , respectively, out of the benzene plane. Nitrobenzene<sup>12</sup> and *p*-nitroaniline<sup>13</sup> are planar, as would be expected.

The in-plane displacements of the exocyclic carbon-carbon and carbon-chlorine bonds away from one another are similar to those in *o*-chlorobenzoic acid; the exocyclic valency angles C(1)-C(2)-Cl and C(2)-C(1)-C(7) are increased from the normal value of  $120^\circ$  to  $121.9^\circ$  and  $125.5^\circ$ , respectively, while the adjacent angles C(3)-C(2)-Cl and C(6)-C(1)-C(7) are decreased to  $116.4^\circ$  and  $116.8^\circ$ , respectively (Table 3).

In the carboxyl group the angle CCO considerably exceeds the angle CC(OH). This is the customary pattern for un-ionized carboxyl groups and is presumably why the conformation adopted by the molecule is that in which the carbonyl-oxygen atom of the carboxyl group is adjacent to the bulky halogen atom in the *ortho*-position. A sufficient clearance between the halogen atom and the neighbouring oxygen atom is ensured for a smaller inclination of the carboxyl group to the benzene plane than would be required by the opposite conformation with carbonyl- and hydroxyl-oxygen atoms interchanged. The preferred conformation in *o*-chlorobenzoic acid and in *o*-bromobenzoic acid is also that in which the carbonyl-oxygen atom is adjacent to the halogen atom.

The dimensions of the nitro-group do not differ significantly from those reported for nitrobenzene<sup>12</sup> and *m*-dinitrobenzene.<sup>10</sup> In each molecule the angle ONO exceeds  $120^\circ$  while the angles CNO are less than  $120^\circ$ . These angular variations in nitro- and carboxyl groups can be explained qualitatively in terms of inter-electron repulsions decreasing in the order non-bond-non-bond pairs, non-bond-bond pairs, and bond-bond pairs.

The carbon-chlorine distance of  $1.753 \text{ \AA}$  does not differ significantly from the distance

<sup>7</sup> Ferguson and Sim, unpublished results.

<sup>8</sup> Sim, Thesis, University of Glasgow, 1955.

<sup>9</sup> Trotter, *Acta Cryst.*, 1961, **14**, 101.

<sup>10</sup> Trotter, *Acta Cryst.*, 1961, **14**, 244.

<sup>11</sup> Watson, *Nature*, 1960, **188**, 1102.

<sup>12</sup> Trotter, *Acta Cryst.*, 1959, **12**, 884.

<sup>13</sup> Donohue and Trueblood, *Acta Cryst.*, 1956, **9**, 960.

of 1.737 Å in *o*-chlorobenzoic acid.<sup>2</sup> As the mean carbon-chlorine distance in halogenated aliphatic compounds is<sup>14</sup> 1.767 Å and the radius of an  $sp^2$ -hybridized carbon atom is 0.02–0.03 Å smaller than that of an  $sp^3$ -hybridized carbon atom, there appears to be little, if any, double-bond character associated with the carbon-halogen bond in 2-chloro-5-nitrobenzoic acid.

The closest intermolecular approach occurs between oxygen atoms of adjacent carboxyl groups related by a centre of symmetry. The OH...O distance here is 2.613 Å, which is normal for this type of hydrogen bonding. All other intermolecular approach distances (Fig. 1 and Table 3) correspond to normal van der Waals interactions.

## EXPERIMENTAL

*Crystal Data.*—2-Chloro-5-nitrobenzoic acid,  $C_7H_4ClNO_4$ ;  $M = 201.5$ ; m. p. 165°. Monoclinic,  $a = 5.86 \pm 0.02$ ,  $b = 5.13 \pm 0.02$ ,  $c = 26.65 \pm 0.05$  Å,  $\beta = 97^\circ 54' \pm 20'$ ,  $U = 794$  Å<sup>3</sup>,  $D_m = 1.678$ ,  $Z = 4$ ,  $D_c = 1.687$ ,  $F(000) = 408$ , space group  $P2_1/c$  ( $C_{2h}^5$ ). Absorption coefficient for X-rays ( $\lambda = 1.542$  Å),  $\mu = 42.0$  cm.<sup>-1</sup>. Crystallization from aqueous ethanol solution gave single crystals of 2-chloro-5-nitrobenzoic acid in the form of thin, narrow laths elongated along  $b$ . The most prominent face is (001).

*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 Weissenberg photographs. The space group was determined uniquely from the systematic halvings in the reflexions. The intensity data were obtained from equatorial and equi-inclination upper-layer multiple-film Weissenberg photographs. The intensities were estimated visually and were corrected for Lorentz, polarization, and the rotation factors appropriate to upper layers.<sup>15</sup> The various layers were placed on the same relative scale by comparison of common reflexions on different photographs. The absolute scale was obtained at a later stage by comparison of measured and calculated values of the structure factors. In all 1027 independent reflexions were observed (Table 7).

TABLE 5.

Progress of the least-square refinement.

Cycle	1	2	3	4	5	6	7
$R$	0.185	0.155	0.132	0.110	0.102	0.093	0.090
$\Sigma w\Delta^2$	748	532	426	356	328	288	276

TABLE 6.

Anisotropic temperature factors ( $b_{ij} \times 10^5$ ).

	$b_{11}$	$b_{22}$	$b_{33}$	$b_{23}$	$b_{13}$	$b_{12}$
C(1)	3747	6267	177	229	346	877
C(2)	4226	6153	202	63	136	491
C(3)	4235	7689	184	197	539	787
C(4)	4323	6392	193	124	570	-695
C(5)	3945	7596	172	100	275	661
C(6)	3879	6685	202	152	479	1316
C(7)	4479	4345	207	-174	563	149
O(1)	5562	6854	232	-472	777	194
O(2)	6093	5526	247	-126	1180	-350
O(3)	5570	7369	273	-276	837	-2034
O(4)	5680	6546	228	-354	556	1240
N	4611	5570	213	-48	518	-558
Cl	4241	6091	221	-188	230	-660

*Structure Analysis.*—The initial  $x$ - and  $z$ -co-ordinates of the atoms other than hydrogen were derived from the  $b$ -axis Patterson projection. Preliminary refinement of the crystal structure in the  $b$ -axis projection was then carried out by Fourier and least-squares methods; in seven rounds of calculations the value of  $R$ , the usual discrepancy factor, fell from 0.52 to 0.15 for the  $h0l$  reflexions.

<sup>14</sup> Sutton, "Tables of Interatomic Distances and Configuration in Molecules and Ions," *Chem. Soc. Spec. Publ. No. 11*, 1958.

<sup>15</sup> Tunell, *Amer. Min.*, 1939, **24**, 448.





FIG. 2(a).

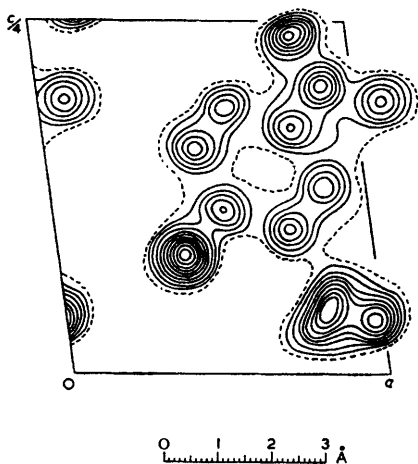


FIG. 2(b).

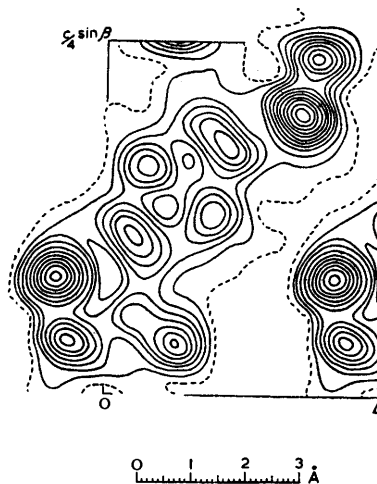


FIG. 2. Electron-density projections: (a) on (010) and (b) on (100). Contours at intervals of  $1e \text{ \AA}^{-2}$  except at the chlorine atom ( $2e \text{ \AA}^{-2}$  after the four-electron contour line). The one-electron line is broken.

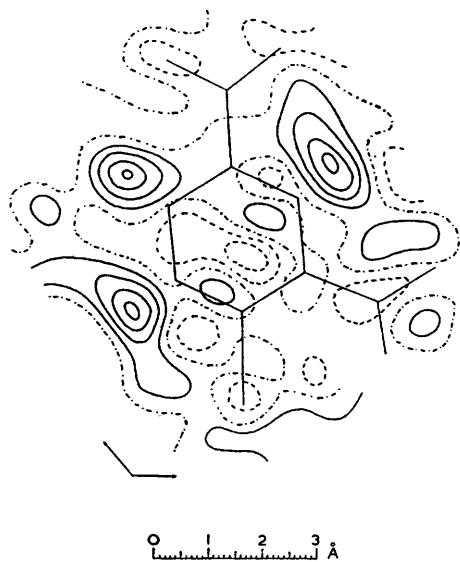


FIG. 3. Section through the three-dimensional difference electron-density distribution evaluated in the plane of the benzene ring. Contour scale:  $0.1e \text{ \AA}^{-3}$ , negative levels broken, zero contour dot-dashed.

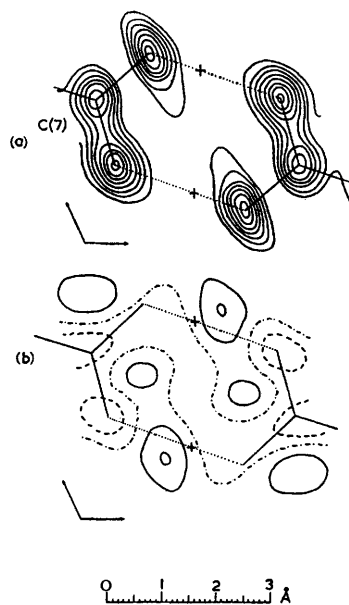


FIG. 4. Sections through (a) the three-dimensional electron-density distribution and (b) the three-dimensional difference electron-density distribution evaluated in the plane containing the oxygen atoms of the carboxyl group and the origin of the unit cell. Contour scale (a)  $1e \text{ \AA}^{-3}$ , (b)  $0.1e \text{ \AA}^{-3}$ , negative levels broken, zero contour dot-dashed.



and  $F_c$  syntheses were computed, and back-shift corrections for termination-of-series errors were applied.

At this stage allowance was made for the hydrogen atoms. Those of the benzene ring were placed radially at a distance of 1.0 Å from the carbon atoms to which they are covalently bonded, and that of the carboxyl group was placed 1.0 Å from O(2) on the line to O(1) of the opposite carboxyl group. The temperature factor  $B$  was assumed to be 4.0 Å<sup>2</sup>.

When the overall value of  $R$  had been reduced below 0.19 we proceeded to a least-squares refinement of positional and anisotropic temperature-factor parameters. The programme used was that devised by Rollett.<sup>16</sup> In the least-squares analysis 205 unobserved reflexions were included, each with a value of  $|F_o|$  equal to one-half of the minimum  $|F|$  locally observable. Hydrogen contributions were included in the structure-factor calculations, but only the parameters of the other atoms were adjusted by the programme. The course of the refinement is shown in Table 5.

The theoretical atomic scattering factors used in the structure-factor calculations were those of Berghuis *et al.* for carbon, nitrogen, and oxygen,<sup>17</sup> those of McWeeny for hydrogen,<sup>18</sup> and those of Tomiie and Stam for chlorine.<sup>19</sup> The final value for the discrepancy factor  $R$  is 0.090 over all the observed structure factors. The final atomic co-ordinates are listed in Table 1. The parameters defining the anisotropic thermal vibrations are in Table 6; they are values of  $b_{ij}$  in the equation

$$\exp(-B \sin^2\theta/\lambda^2) = 2 - (b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{23}kl + b_{13}hl)$$

The final calculated and measured values of the structure factors are shown in Table 7.

*Location of the Hydrogen Atoms.*—After completion of the three-dimensional least-squares refinement a further set of structure factors,  $F_c'$ , was computed, the hydrogen atom contributions being omitted. Fourier syntheses with coefficients  $(F_o - F_c')$  were then evaluated to represent the difference between the electron distribution existing in the crystal and that calculated for chlorine, carbon, oxygen, and nitrogen atoms only, at their appropriate positions in the unit cell and with their appropriate thermal vibrations.

The hydrogen atoms of the benzene ring show up clearly as well-resolved peaks of about 0.4 eÅ<sup>-3</sup> in the difference electron-density distribution evaluated in the plane of the benzene ring (Fig. 3). In order to minimize the effect of errors in the thermal parameters the data used in this synthesis were limited to terms with  $\sin^2\theta < 0.4$ , hydrogen-atom contributions to terms outside this range being negligible. The carbon-hydrogen bond lengths measured directly on this map are H-C(3) 0.98 Å, H-C(4) 0.96 Å, and H-C(6) 0.88 Å.

Triple  $F_o$  and  $(F_o - F_c')$  syntheses computed in the plane through the four oxygen atoms O(1), O(2), O'(1), and O'(2) and the centre of symmetry at the origin of the unit cell are shown in Fig. 4. The expected position of the carboxyl hydrogen atom, on the dotted line joining the oxygen atoms O(2) and O'(1), is indicated by a cross at 1.0 Å from O(2). On the difference map the low peak of 0.21eÅ<sup>-3</sup> situated between the oxygen atoms and to one side of the dotted line may be attributed to the hydrogen atom.

The extensive calculations were carried out on the Glasgow University DEUCE computer with programmes devised by Dr. J. S. Rollett and Dr. J. G. Sime. We are grateful to Professor J. Monteath Robertson, F.R.S., for his interest and to the Carnegie Trust for the award of a scholarship which enabled G. F. to participate in this work.

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<sup>18</sup> McWeeny, *Acta Cryst.*, 1951, **4**, 513.

<sup>19</sup> Tomiie and Stam, *Acta Cryst.*, 1958, **11**, 126.