The Crystal Structure of 2-Naphthoic Acid

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Crystals of 2-naphthoic acid are monoclinic with four molecules in a unit cell of dimensions

$$a = 30\cdot59, \quad b = 5\cdot00, \quad c = 5\cdot63 \text{ Å}, \quad \beta = 92\cdot6°,$$

space group $P2_1/n$. The structure, which has been determined from projections along the b and c axes, consists of centrosymmetrical dimers; details of the molecular geometry and dimensions, and of the intermolecular separations, have been obtained.

Introduction

The crystal structure of 2-naphthoic acid has been examined as part of a series of investigations of the structures of derivatives of naphthalene (Trotter, 1960a).

Experimental

Crystals of 2-naphthoic acid, which were obtained by crystallization from aqueous ethanol, are colourless prisms elongated along the b-axis. The density was determined by flotation in aqueous potassium iodide solution. The unit-cell dimensions and space group were determined from rotation and oscillation photographs of a crystal rotating about the b-axis, $h0l$ and $h1l$ Weissenberg films, and $hk0$ and $0kl$ precession films.

Crystal data

2-Naphthoic acid, $C_{11}H_8O_2$; $M = 172\cdot2$; m.p. $= 185$ °C. Monoclinic,

$$a = 30\cdot59 \pm 0\cdot10, \ b = 5\cdot00 \pm 0\cdot02, \ c = 5\cdot63 \pm 0\cdot02 \text{ Å},$$
$$\beta = 92\cdot6° \pm 0\cdot2°.$$

Volume of the unit cell $= 858\cdot8$ Å³.
Density, calculated (with $Z = 4$) $= 1\cdot332$, measured $= 1\cdot320$ g.cm.⁻³.
Absorption coefficients for X-rays, $\lambda = 1\cdot542$ Å,

$$\mu = 8\cdot77 \text{ cm.}^{-1}; \ \lambda = 0\cdot7107 \text{ Å}, \ \mu = 1\cdot09 \text{ cm.}^{-1}.$$

Total number of electrons per unit cell $= F(000) = 360$.
Absent spectra: $h0l$ when $(h+l)$ is odd, $0k0$ when k is odd.
Space group is uniquely determined as $P2_1/n$-C_{2h}^5.

The intensities of the $h0l$ reflexions were recorded on moving-film exposures* for a crystal rotating about the b-axis, using Cu $K\alpha$ radiation, and multiple-

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* The 200 reflexion was cut off by the beam stop, and its intensity was measured on Cu $K\alpha$ precession films of the $hk0$ zone.

film technique to correlate strong and weak reflexions. The $hk0$ reflexions were recorded on precession films with Mo $K\alpha$, using multiple exposures for intensity correlation. All the intensities were estimated visually, the range being about 8000 to 1. The same crystal was used for both zones; the cross-section normal to the b-axis was $0\cdot17 \times 0\cdot17$ mm., and no absorption corrections were applied. The structure amplitudes were derived by the usual formulae for a mosaic crystal, the absolute scale being established later by correlation with the calculated structure factors. 133 independent $h0l$ reflexions and 64 $hk0$ were observed, representing 58% and 43% respectively of the possible number observable with the radiations and experimental conditions used.

Structure analysis

[010] *projection*

In deriving an approximate trial structure it was assumed initially that the molecule was completely planar with C–C bond lengths $1\cdot40$ Å, C–O bond lengths $1\cdot25$ Å and all valency angles 120°; in addition it was assumed that the structure consisted of hydrogen-bonded dimers with O–H $\cdots$ O distance $2\cdot70$ Å. The optical transform of this trial structure was fitted to the $h0l$ weighted reciprocal lattice, and signs obtained for many of the stronger reflexions. A Fourier series was then summed using as coefficients observed structure amplitudes with the signs deduced from the optical transform. On the resulting electron-density map the individual atoms were not particularly well resolved, but the general shape of the molecule was well-defined. Coordinates for all the atoms were obtained by fitting a regular planar structure on the peaks on the map, and structure factors were calculated for all the $h0l$ reflexions, using McWeeny's (1951) scattering factors for carbon and oxygen, corrected for thermal vibration as usual, with $B = 4\cdot0$ Å² for all the atoms. The value of R, the usual discrepancy factor, was 39.9% over the observed reflexions.
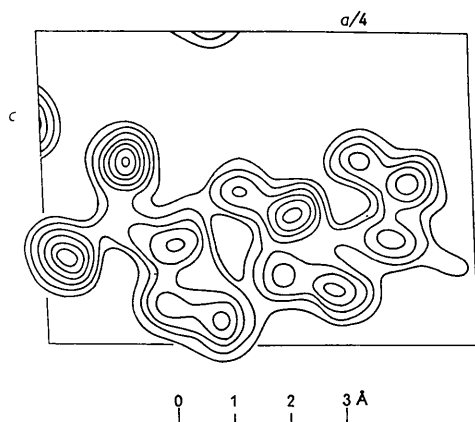
Fig. 1. Second electron-density projection along the b-axis ($R = 37\cdot4\%$), with contours at intervals of 1 e.Å^{-2}, starting at 2 e.Å^{-2}.

A second Fourier series was summed, including most of the observed reflexions—the only strong plane omitted being $\bar{5}03$, whose sign was still doubtful. The resulting electron-density map (Fig. 1) showed good resolution of all the atoms except the carboxyl carbon atom, which was poorly defined. New centres were chosen, and structure factors were recalculated. The R value was 37·4%. This was a discouragingly poor improvement in agreement, and in addition some of the agreements were so poor—particularly for $\bar{1}01$, $\bar{2}02$, $\bar{5}03$, 103, 10,0,2, 14,0,2, $\bar{1}8,0,2$—that it did not seem likely that this structure would refine.

For those reflexions for which the structure-factor agreement was particularly poor, the variation of the F_c values with change in position of the molecular centre was computed, keeping the same molecular orientation as before but neglecting any possible dimerization. All the reflexions suggested a new position for the molecular centre, only about 0·3 Å from the original position, and so all the atomic co-ordinates were changed by $\Delta x/a = 0\cdot0029$, $\Delta z/c = 0\cdot0522$. Structure factors were calculated with these new coordinates, and R was 35·8%, again not much of an improvement. A third electron-density projection was computed, and all the atoms were well-resolved, the map generally being a little better than the previous synthesis. New centres were chosen (the shifts were such that the structure now again appeared to consist of dimers) and structure factors were recalculated. R was 26·5%, so that this structure appeared to be refining satisfactorily. On reconsideration it might have been possible to proceed from the first electron-density map to the correct structure if the atoms had been placed on the peaks without attempting to keep the molecule regular.

Refinement of the positional and temperature parameters continued by computing successive $(F_o - F_c)$ syntheses, the scattering curves of Berghuis *et al.* (1955) now being used, and after two cycles the R value had dropped to 15·9% over the observed re-

flexions (at each stage F_c values were computed for many of the unobserved reflexions, and no anomalies were found). In the final difference map there were indications of hydrogen atoms and anisotropic vibrations of the carbon and oxygen atoms, but no allowance was made for these effects in the structure-factor calculations. The final values for the isotropic temperature factors were $B_{\text{carbon}} = 5\cdot1$, $B_{\text{oxygen}} = 6\cdot0$ Å^2.
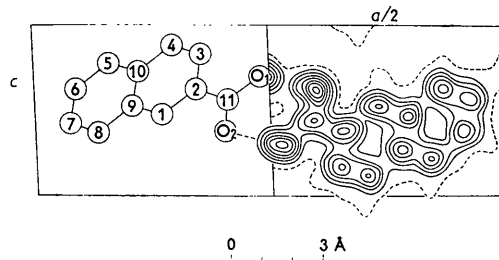

Fig. 2. Projection of the structure onto (010); and final electron-density projection along the b-axis, with contours at intervals of 1 e.Å^{-2}, one-electron line dotted.

Observed and calculated structure factors are listed in Table 4, and the final F_o synthesis is shown in Fig. 2.

[001] *projection*

Relative y-coordinates for the carbon and oxygen atoms were deduced from a consideration of the bond lengths projected on (010), and the y-coordinate of the molecular centre was then obtained by assuming that the structure consisted of centrosymmetrical dimers. Structure factors were calculated for the $hk0$ reflexions using the final temperature factors of the $h0l$ zone; the R value was 13·8% over the observed reflexions. An $(F_o - F_c)$ synthesis was computed, and
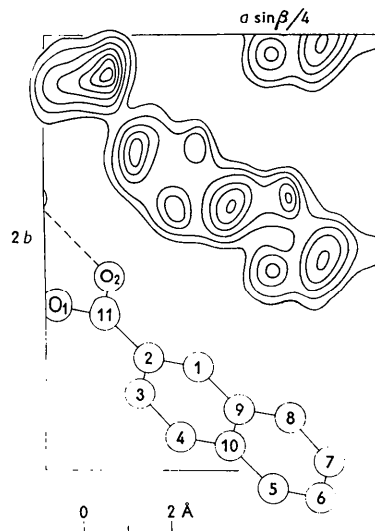

Fig. 3. Projection of the structure along [001]; and electron-density projection along the c-axis, with contours at intervals of 1 e.Å^{-2}, starting at 2 e.Å^{-2}.

the y-coordinates were changed to minimize the slopes at the atomic centres. The shifts were so small, however, that structure factors were not recalculated; the measured and calculated values at the penultimate stage are included in Table 4, and the final electron-density projection along the c-axis is shown in Fig. 3.

Coordinates and molecular dimensions

The final coordinates of the carbon and oxygen atoms, expressed as fractions of the unit-cell edges, are listed in Table 1, the numbering of the atoms being shown in Figs. 2 and 3. The coordinates of all the atoms in the molecule can be fitted to an equation of the form

$$lX' + mY + nZ' + p = 0 ,$$

where X', Y, Z' are coordinates expressed in Ångström units and referred to orthogonal axes a', b and c. The equation, determined by the method of Schomaker, Waser, Marsh & Bergman (1959), is

$$0{\cdot}4980X' + 0{\cdot}6650Y - 0{\cdot}5565Z' - 0{\cdot}0002 = 0 .$$

The deviations of the atoms from this plane, which are listed in Table 2, are not significant, so that the molecule may be taken as completely planar within the limits of experimental error.

It might be noted that the equation calculated by the usual incorrect least-squares method is

$$0{\cdot}5639X' - 0{\cdot}5074Y - 0{\cdot}6517Z' - 5{\cdot}1366 = 0 .$$

The deviations of the atoms from this plane vary from about 1–5 Å, and the plane is rotated about 72° from its correct position. These errors indicate the value of the method of Schomaker *et al.* (1959).

Table 1. *Coordinates of the atoms*

Atom	x/a	y/b	z/c
C_1	0·1157	−0·5204	0·0266
C_2	0·0771	−0·4804	−0·1261
C_3	0·0714	−0·6468	−0·3321
C_4	0·1023	−0·8488	−0·3819
C_5	0·1717	−1·0872	−0·2796
C_6	0·2065	−1·1272	−0·1261
C_7	0·2139	−0·9612	0·0764
C_8	0·1845	−0·7564	0·1364
C_9	0·1461	−0·7196	−0·0266
C_{10}	0·1400	−0·8856	−0·2242
C_{11}	0·0453	−0·2832	−0·0654
O_1	0·0084	−0·2424	−0·1961
O_2	0·0486	−0·1164	0·1265

Table 2. *Deviations from mean plane*

Atom	Deviations	Atom	Deviations
C_1	+0·04 Å	C_8	+0·01 Å
C_2	+0·03	C_9	+0·03
C_3	+0·03	C_{10}	0
C_4	+0·01	C_{11}	−0·01
C_5	+0·01		
C_6	−0·05	O_1	−0·06
C_7	−0·02	O_2	−0·01

The bond lengths and valency angles in the molecule, calculated from the coordinates of Table 1, are shown in Fig. 4. Fig. 4 also shows the hydrogen-bond distance in the dimer (2·54 Å). The distance between the oxygen atoms and the α and β' carbon atoms (C_1 and C_3) are 2·94 Å.
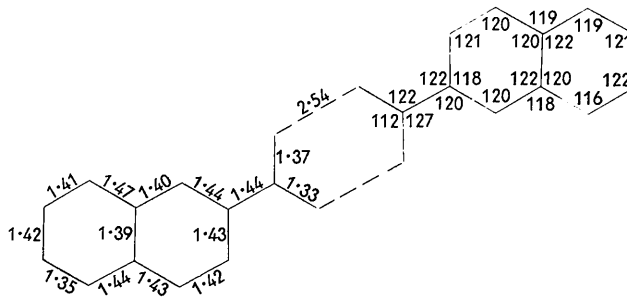

Fig. 4. Bond-lengths, valency angles and hydrogen-bond distances.

Standard deviations

The standard deviations of the atomic coordinates, calculated from Cruickshank's (1949) formulae, are $\sigma(x) = \sigma(y) = \sigma(z) = 0{\cdot}010$ Å, so that the standard deviations of the bond lengths are about 0·014 Å.

Discussion

The molecule is planar within the limits of experimental error, the root-mean-square deviation from the mean molecular plane being 0·029 Å. This might be contrasted with 1-naphthoic acid (Trotter, 1960*b*), where overcrowding in a planar model causes an 11° twisting of the carboxyl group out of the naphthalene plane. The distortion of the carboxyl group in 1-naphthoic acid (reduction of O–C–O valency angle to 110°) is, however, also observed in 2-naphthoic acid, where the corresponding valency angle is 112°.

Table 3. *Bond lengths in naphthalene and 2-naphthoic acid*

Bond	Naphthalene	2-Naphthoic acid
1– 2	1·36 Å	1·41 Å
1– 9	1·43	1·44
2– 3	1·42	1·42
9–10	1·41	1·39
C–C	—	1·44
C–O$_1$	—	1·33
C–O$_2$	—	1·37

The mean bond lengths in the molecule are compared in Table 3 with the distances in naphthalene (Abrahams, Robertson & White, 1949; Cruickshank, 1957), and there are no significant differences between corresponding aromatic bond lengths in the two molecules (except perhaps for the bond 1–2). The C(aromatic)–C(carboxyl) distance (1·44 Å) is a little shorter than the normal sp^2–sp^2 single bond distance.

The C–O distances are a little longer than the usual distances in carboxylic acids, but this may be due to small errors in the y-coordinates of the oxygen atoms. The C–O bond lengths suggest that the hydroxyl hydrogen atom is bonded to O_2.
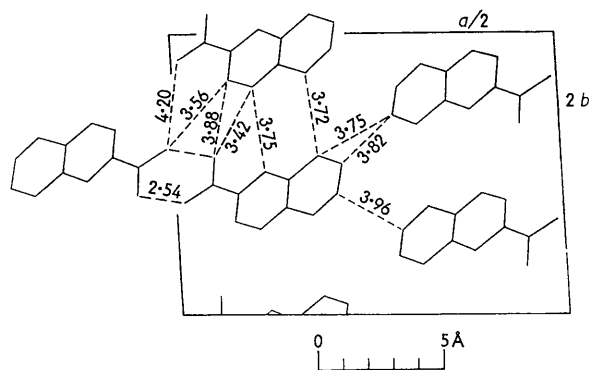

Fig. 5. Projection of the structure onto (010) showing the shorter intermolecular contacts.

Intermolecular distances

The structure consists of centrosymmetrical dimers, the O–H $\cdots$ O distance being 2·54 Å, close to the corresponding distance in 1-naphthoic acid. All other intermolecular separations correspond to normal van der Waals interactions. The shorter contacts are illustrated in Fig. 5.

Table 4. *Measured and calculated structure factors*

hkl	F_o	F_c	hkl	F_o	F_c	hkl	F_o	F_c	hkl	F_o	F_c
000	—	+360·0	$\overline{30}$,0,2	6·6	−9·0	25,0,3	8·5	−4·7	410	29	+31
200	31·8	+33·4	$\overline{24}$,0,2	3·7	+3·5	27,0,3	3·6	+3·8	510	60	+59
400	28·2	−30·2	$\overline{20}$,0,2	14·5	+8·3	$\overline{22}$,0,4	6·8	+1·7	610	62	+63
600	15·8	+14·3	$\overline{18}$,0,2	3·3	+3·2	$\overline{20}$,0,4	4·1	+3·4	810	25	+23
800	34·7	−35·4	$\overline{16}$,0,2	42·5	−39·0	$\overline{18}$,0,4	3·1	+0·5	10,1,0	18	+17
10,0,0	7·3	+6·3	$\overline{14}$,0,2	17·1	−18·5	$\overline{16}$,0,4	4·0	+5·8	11,1,0	15	−18
12,0,0	13·0	−15·9	$\overline{12}$,0,2	16·1	−20·7	$\overline{14}$,0,4	3·4	+3·5	12,1,0	8	+8
14,0,0	11·8	+20·5	$\overline{10}$,0,2	14·6	−17·1	$\overline{12}$,0,4	7·3	+8·7	13,1,0	9	−11
16,0,0	5·9	+8·4	$\overline{8}$02	3·9	−5·5	$\overline{10}$,0,4	4·8	+5·5	15,1,0	5	−8
18,0,0	11·0	+12·4	$\overline{6}$02	17·7	−17·7	$\overline{8}$04	12·4	+12·2	16,1,0	10	−12
20,0,0	11·0	+11·4	$\overline{4}$02	11·4	−8·8	$\overline{6}$04	9·3	+10·2	17,1,0	9	−8
22,0,0	7·1	+7·1	$\overline{2}$02	18·7	+12·9	$\overline{4}$04	12·8	−13·5	18,1,0	6	−5
24,0,0	4·7	+4·8	002	11·5	−7·0	$\overline{2}$04	8·1	−7·2	19,1,0	12	+18
28,0,0	14·5	+13·0	202	32·6	−32·5	004	9·6	−12·9	20,1,0	9	+11
32,0,0	11·9	−9·1	402	15·9	−15·1	204	2·8	−1·1	21,1,0	6	+9
36,0,0	3·2	−2·3	602	30·4	−30·6	404	3·5	−4·1	23,1,0	12	+11
$\overline{37}$,0,1	2·4	−1·0	10,0,2	7·3	+5·2	604	20·4	+18·9	25,1,0	5	−10
$\overline{33}$,0,1	4·7	+2·1	12,0,2	32·6	−36·2	804	25·1	+26·0	26,1,0	21	+21
$\overline{31}$,0,1	20·0	−21·5	14,0,2	3·3	+1·8	10,0,4	14·1	−20·3	27,1,0	13	−9
$\overline{27}$,0,1	7·5	+9·5	16,0,2	11·4	+15·0	12,0,4	5·0	−1·7	28,1,0	8	+3
$\overline{23}$,0,1	6·7	+10·1	18,0,2	3·6	+1·7	16,0,4	3·5	−4·9	32,1,0	4	+1
$\overline{17}$,0,1	26·5	−20·9	20,0,2	4·8	+4·5	20,0,4	5·3	−6·6	020	16	−16
$\overline{15}$,0,1	18·4	−15·0	22,0,2	5·0	−5·1	22,0,4	4·2	−0·8	120	8	+11
$\overline{13}$,0,1	18·9	−23·4	24,0,2	5·8	−3·5	24,0,4	5·5	−3·3	220	21	−21
$\overline{11}$,0,1	24·5	−24·7	26,0,2	7·9	+11·6	$\overline{25}$,0,5	6·4	−3·1	320	4	+2
$\overline{7}$01	6·7	−6·8	28,0,2	4·6	0	$\overline{23}$,0,5	7·1	−9·9	420	19	+19
$\overline{5}$01	46·9	+49·2	$\overline{33}$,0,3	3·1	−0·5	$\overline{21}$,0,5	8·5	+7·1	520	18	+18
$\overline{3}$01	68·5	−70·6	$\overline{25}$,0,3	3·4	+3·3	$\overline{19}$,0,5	4·5	+5·8	620	36	−33
$\overline{1}$01	33·2	+33·7	$\overline{19}$,0,3	11·1	+10·9	505	5·9	−9·5	720	29	+29
101	109·9	+122·6	$\overline{15}$,0,3	11·6	−13·6	705	23·6	+23·1	820	9	+4
301	20·4	+21·2	$\overline{9}$03	7·7	+7·0	905	19·3	+16·0	11,2,0	8	−11
501	26·0	+25·0	$\overline{7}$03	16·3	+15·5	15,0,5	4·2	−5·0	13,2,0	5	−7
701	16·1	−17·9	$\overline{5}$03	34·9	−36·9	19,0,5	3·1	−3·5	14,2,0	4	+1
901	1·7	−4·9	$\overline{3}$03	21·3	−23·9	$\overline{22}$,0,6	3·5	−6·4	15,2,0	7	−7
11,0,1	43·0	−44·0	$\overline{1}$03	5·1	+6·6	20,0,6	4·3	+2·2	16,2,0	6	+7
13,0,1	9·9	−2·1	103	15·6	−16·3	$\overline{8}$06	4·3	−4·7	18,2,0	4	+4
15,0,1	49·5	+44·9	303	8·5	−6·8	806	4·2	+5·1	19,2,0	5	+7
17,0,1	15·7	+12·5	503	15·2	−16·9	20,0,6	3·0	−3·4	20,2,0	9	−14
19,0,1	17·5	+17·1	703	6·6	−8·2	$\overline{9}$07	1·8	−2·9	21,2,0	5	+3
21,0,1	10·2	+10·1	903	8·1	−7·9	$\overline{7}$07	2·2	−2·9	22,2,0	18	−11
23,0,1	6·2	+5·8	11,0,3	7·8	−6·7	307	2·3	−2·1	130	14	−13
25,0,1	4·8	+7·3	15,0,3	3·2	−6·1	707	1·6	+1·6	230	6	+7
27,0,1	4·1	+0·8	17,0,3	5·2	−1·4				430	14	−14
29,0,1	3·7	−2·1	19,0,3	8·1	−7·3	110	5	+8	530	11	+9
$\overline{34}$,0,2	2·4	+3·1	21,0,3	7·3	−3·7	210	37	−35	10,3,0	15	−18
$\overline{32}$,0,2	4·3	+1·0	23,0,3	12·4	−8·6	310	34	−34	13,3,0	5	+8

Table 4. (*cont.*)

Unobserved reflexions

hkl	F_o	F_c	hkl	F_o	F_c	hkl	F_o	F_c	hkl	F_o	F_c
26,0,0	<3·9	−0·2	32,0,2	<3·5	+0·3	$\overline{1}05$	<3·9	−1·9	$\overline{5}07$	<2·0	−0·4
30,0,0	<3·9	−1·6	34,0,2	<3·1	+0·6	305	<3·9	+0·4	$\overline{3}07$	<2·1	0
34,0,0	<3·3	−0·6	36,0,2	<2·2	+0·6	11,0,5	<3·9	+0·8	$\overline{1}07$	<2·1	+0·3
38,0,0	<2·2	+0·3	$\overline{35},0,3$	<2·2	−0·3	13,0,5	<3·8	−0·1	107	<2·0	+0·5
$\overline{39},0,1$	<1·5	+0·1	$\overline{31},0,3$	<3·0	+0·7	17,0,5	<3·6	−1·1	507	<1·8	+0·4
$\overline{35},0,1$	<3·1	−0·8	$\overline{29},0,3$	<3·5	+1·2	$\overline{18},0,6$	<2·8	+0·5	710	<4	3
$\overline{29},0,1$	<3·9	−0·4	$\overline{27},0,3$	<3·8	+1·3	$\overline{16},0,6$	<3·0	+0·8	910	<4	1
$\overline{25},0,1$	<3·9	+2·3	$\overline{23},0,3$	<3·9	−0·2	$\overline{14},0,6$	<3·2	+0·8	14,1,0	<5	5
$\overline{21},0,1$	<3·5	+3·3	$\overline{21},0,3$	<3·8	−1·6	$\overline{12},0,6$	<3·3	+0·4	22,1,0	<5	4
$\overline{19},0,1$	<3·2	+1·5	$\overline{17},0,3$	<3·6	−3·3	$\overline{10},0,6$	<3·4	−0·2	24,1,0	<5	7
$\overline{9},0,1$	<2·1	−5·1	$\overline{13},0,3$	<3·3	−0·1	$\overline{6}06$	<3·5	−1·1	920	<4	8
31,0,1	<3·8	−0·9	$\overline{11},0,3$	<3·2	+3·0	$\overline{4}06$	<3·5	−1·1	10,2,0	<5	4
33,0,1	<3·3	−0·1	13,0,3	<3·4	+4·3	$\overline{2}06$	<3·6	−0·6	12,2,0	<5	9
35,0,1	<3·0	+0·4	14,0,4	<3·9	+1·0	006	<3·6	+0·1	17,2,0	<5	0
37,0,1	<2·3	+0·6	18,0,4	<3·9	−1·4	206	<3·5	+0·7	330	<5	6
$\overline{38},0,2$	<1·6	−0·4	$\overline{17},0,5$	<3·9	+1·3	406	<3·5	+1·1	630	<5	8
$\overline{36},0,2$	<2·2	−0·7	$\overline{13},0,5$	<3·9	+1·7	606	<3·4	+1·0	730	<5	1
$\overline{28},0,2$	<3·9	+1·3	$\overline{11},0,5$	<3·9	+1·5	10,0,6	<3·3	0	830	<5	6
$\overline{26},0,2$	<3·9	+2·1	$\overline{9}05$	<3·9	+0·7	12,0,6	<3·1	−0·5	930	<5	9
$\overline{22},0,2$	<3·7	+1·3	$\overline{7}05$	<3·9	−0·6	14,0,6	<2·9	−0·7	11,3,0	<5	6
802	<2·5	−6·1	$\overline{5}05$	<3·9	−1·7	16,0,6	<2·5	−0·7	12,3,0	<5	0
30,0,2	<3·7	−0·3	$\overline{3}05$	<3·9	−2·2	18,0,6	<2·0	−0·4			

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A Unified Program for Phase Determination, Type 4*P*

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The unified program for phase determination, valid for all the space groups and both the equal and unequal atom cases, is completed here for all the centrosymmetric space groups. The present paper is concerned with the space groups comprising type 4*P*, which is characterized by the noteworthy fact that the value of no phase may be arbitrarily specified, once the functional form for the structure factor has been chosen. A detailed procedure for phase determination is described.

1. Introduction

This is the seventh in a series of papers concerned with a program for phase determination initiated by us (Karle & Hauptman, 1959, hereafter referred to as 1*P*). With this paper, the application of the new probability methods, based on the Miller indices as random variables, is completed for the ninety-two centrosymmetric space groups. We are here concerned with the four space groups comprising Type 4*P* (Hauptman & Karle, 1959), *Im*3, *Ia*3, *Im*3*m* and *Ia*3*d* of the cubic system. Although these space groups are conventionally body-centered, they are referred, in