

part of a firmly bonded six-membered ring. The I_2 atoms are but loosely bonded to the sulfur atoms. The iodine molecule is thus relatively free to vibrate and the atom I_1 , being at the unbonded end of the chain, would be expected to vibrate with an even greater amplitude than that of I_2 . The high volatility of the complex, probably due to its ease of dissociation into volatile products, is also in keeping with the high observed temperature parameters for iodine. The vibrational parameters of the carbon atoms are erratic, as they often are in compounds containing ultra-heavy atoms, and are probably of little, if any, structural significance.

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The Crystal Structure of 1-Naphthoic Acid

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Crystals of 1-naphthoic acid are monoclinic with four molecules in a unit cell of dimensions

$$a = 31.12, b = 3.87, c = 6.92 \text{ \AA}, \beta = 92.2^\circ,$$

space group $P2_1/a$; all the crystals examined, however, have been twinned on (100). The structure, which consists of centrosymmetrical dimers, has been determined from projections along the b and c axes, and values of the bond lengths, valency angles, and intermolecular distances have been obtained. The strain in a planar model for the molecule is relieved by an 11° twisting of the carboxyl group out of the plane of the aromatic rings, and by valency-angle distortions.

Introduction

The crystal structure of 1-naphthoic acid has been examined as part of a series of investigations of the structures of derivatives of naphthalene (Trotter, 1960).

Experimental

Crystals of 1-naphthoic acid, which were obtained by crystallization from aqueous ethanol, are colourless plates elongated along the b -axis, with (100) developed. The density was determined by flotation in aqueous potassium iodide solution. The unit-cell dimensions and space group were determined from rotation and oscilla-

tion photographs of a crystal rotating about the b -axis, $h0l$ and $h1l$ Weissenberg films, and $hk0$ and $0kl$ precession films.

Crystal data

1-Naphthoic acid, $C_{11}H_8O_2$; $M = 172.2$; m.p. = $161^\circ C$.
 Monoclinic, $a = 31.12 \pm 0.10$, $b = 3.87 \pm 0.01$,

$$c = 6.92 \pm 0.02 \text{ \AA}, \beta = 92.2 \pm 0.2^\circ.$$

Volume of the unit cell = 832.8 \AA^3 .

Density, calculated (with $Z = 4$) = 1.373 ,
 measured = 1.380 g.cm.^{-3} .

Absorption coefficients for X-rays, $\lambda = 1.542 \text{ \AA}$,
 $\mu = 9.04 \text{ cm.}^{-1}$; $\lambda = 0.7107 \text{ \AA}$, $\mu = 1.12 \text{ cm.}^{-1}$.

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

The axial lengths correspond closely to those reported in a previous investigation (McCrone, 1953), but this previous work found the crystals to be orthorhombic. The $h0l$ Weissenberg films of all the crystals examined in the present analysis did indeed appear to exhibit orthorhombic symmetry, but examination of the positions and intensities of the reflexions indicated quite clearly that the crystals are monoclinic, but twinned on (100); the crystals used were grown chiefly from aqueous ethanol, but a few grown from aqueous acetic acid were also examined. The sizes of the two parts of a twin appeared to be generally of about the same order of magnitude.

The cell dimensions are such that there is no overlap of $h0l$ reflexions from different parts of the twinned crystal, except when $l=0$ and $l=6$; $h00$ reflexions from one part of the crystal overlap exactly the same reflexions from the other part, while $h06$ reflexions overlap exactly $-(h+2)$, 06 reflexions. Indexing of the $h0l$ Weissenberg films was therefore fairly straightforward. It was also possible, by measuring the intensities of the $h0l$ reflexions from both parts of a twinned crystal, to obtain values of the intensities for the individual $h00$ and $h06$ reflexions.

The intensities of the $h0l$ reflexions were recorded on Weissenberg exposures* for a crystal rotating about the b -axis, using Cu $K\alpha$ radiation, and multiple-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 2000 to 1. The same crystal was used for both zones; the cross-section normal to the b -axis was 0.30×0.03 mm., but no corrections for absorption 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. In the $h0l$ zone, of 280 independent reflexions observable with Cu $K\alpha$ radiation, only 108 (39%) were observed—this rather small proportion being chiefly due to the small number of higher-order reflexions of measurable intensity. In the $hk0$ zone 33 independent reflexions were observed, representing about 22% of the possible number observable with Mo $K\alpha$ and $\mu = 25^\circ$.

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 1.40 Å, C-O bond

* 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.

lengths 1.25 Å and all valency angles 120° ; no assumption was made, however, of the possible existence of hydrogen-bonded dimers in the crystal. The molecular orientation in the short b -axis projection was deduced from an examination of the $h0l$ weighted reciprocal lattice; there were six possible orientations, but three of these seemed unlikely from packing considerations and two more were eliminated since agreement between F_o and F_c for the axial reflexions was poor wherever a molecule in these orientations was placed in the unit cell. This left only one possible orientation and the position of the molecular centre was then found by computing the variation of some of the structure factors with position of the centre (Trotter, 1959); the usual curves reduce of course to straight lines for plane group $p2$. The structure derived suggested that centrosymmetrical dimers probably existed in the crystal.

Structure factors were calculated for all the $h0l$ reflexions, using McWeeny's (1951) scattering factors for carbon and oxygen, corrected for thermal vibration with $B=4.0$ Å² for all the atoms. The value of R , the usual discrepancy factor, was 39.9% over the observed reflexions. A Fourier series was then summed using as coefficients measured structure amplitudes and calculated signs. On the resulting electron-density map all the carbon and oxygen atoms were well-resolved; new atomic centres were chosen and structure factors recalculated, with B again 4.0 Å² for all the atoms. The discrepancy factor was reduced to 23.1%.

Refinement of the positional and temperature parameters continued by computing successive ($F_o - F_c$) syntheses, and after two cycles the R value had dropped to 12.7% over the observed reflexions (at each stage F_c values were computed for many of the unobserved reflexions, and no anomalies were found). The structure factors for all but the final cycle were computed on the IBM 650 at the Army Pay Ledger Unit, Ottawa, using McWeeny's (1951) scattering curves, but the final structure factors were computed on DEUCE at the University, Glasgow, where the scattering curves of Berghuis *et al.* (1955) were used, with $B_{\text{carbon}} = 3.2$, $B_{\text{oxygen}} = 4.5$ Å². In the final differ-

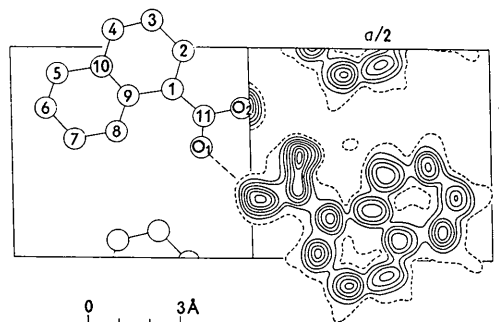


Fig. 1. Projection of the structure along [010]; and electron-density projection along the b -axis, with contours at intervals of $1 \text{ e.}\text{\AA}^{-2}$, one-electron line dotted.

ence 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.

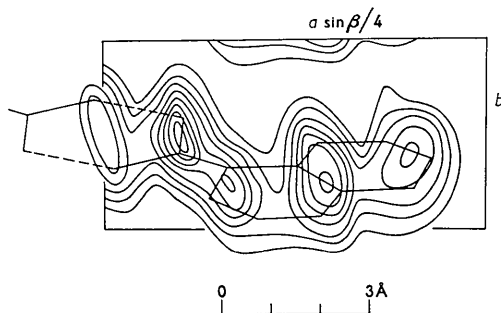


Fig. 2. Electron-density projection along [001]. Contours at intervals of $1 \text{ e.}\text{\AA}^{-2}$, starting at $2 \text{ e.}\text{\AA}^{-2}$.

Observed and calculated structure factors are listed in Table 4, and the final F_o synthesis is shown in Fig. 1.

y-Coordinates

The relative *y*-coordinates, with respect to the molecular centre, of all the atoms in the molecule were deduced from a consideration of the bond distances projected on (010), and the position of the molecule in the cell was derived by computing the variation of the F_c values for the $h10$ reflexions. Although no assumption was made about dimerization, the structure obtained did consist of centrosymmetrical dimers. Since only a few $hk0$ reflexions were observed, thorough refinement was not possible, but a difference synthesis was computed and the atoms shifted to minimize the electron-density slopes at the atomic centres. The value of R for the observed $hk0$ reflexions was 23% (4% being due to 210, where the observed value may be affected by extinction).

Observed and calculated $hk0$ structure factors are listed in Table 5, and the final F_o synthesis is shown in Fig. 2.

Coordinates and molecular dimensions

The final coordinates of the atoms, expressed as fractions of the unit-cell edges, are listed in Table 1, the numbering of the atoms being shown in Fig. 1. The coordinates of the atoms of the naphthalene nucleus 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 . l , m , n and p were determined by the method of Schomaker *et al.* (1959). The atoms of the carboxyl group can of course be fitted to a similar equation. The equations of the planes are

Naphthalene rings:

$$+0.0238X' + 0.9153Y - 0.4022Z' - 0.2826 = 0$$

Carboxyl group:

$$-0.1086X' + 0.8454Y - 0.5229Z' - 0.1831 = 0$$

The deviations of the atoms from the naphthalene plane are listed in Table 2. The angle between the naphthalene and carboxyl planes is 11.0° .

Table 1. *Coordinates of the atoms*

Atom	x/a	y/b	z/c
C ₁	0.0800	-0.176	-0.3081
C ₂	0.0677	-0.335	-0.4902
C ₃	0.0979	-0.448	-0.6335
C ₄	0.1420	-0.433	-0.5893
C ₅	0.1999	-0.286	-0.3749
C ₆	0.2135	-0.134	-0.2095
C ₇	0.1846	-0.045	-0.0607
C ₈	0.1393	-0.050	-0.0962
C ₉	0.1261	-0.167	-0.2731
C ₁₀	0.1544	-0.306	-0.4095
C ₁₁	0.0478	-0.101	-0.1783
O ₁	0.0515	+0.072	-0.0257
O ₂	0.0082	-0.176	-0.2159

Table 2. *Deviations from naphthalene plane (Å)*

Atom	Deviation	Atom	Deviation
C ₁	+0.05	C ₈	-0.03
C ₂	-0.02	C ₉	+0.04
C ₃	+0.01	C ₁₀	-0.04
C ₄	-0.01	C ₁₁	-0.09
C ₅	-0.01		
C ₆	+0.08	O ₁	+0.11
C ₇	-0.05	O ₂	-0.29

The bond lengths and valency angles in the molecule, calculated from the coordinates of Table 1, are shown in Fig. 3. Fig. 3 also shows the hydrogen-bond distance in the dimer, and the distances between those atoms which would be closer than the normal van der Waals separations in a completely planar molecule with 120° valency angles.

Standard deviations

The standard deviations of the atomic positions were calculated from Cruickshank's (1949) formulae. From the $h0l$ data the values are $\sigma(x) = \sigma(z) = 0.009 \text{ \AA}$. The *y*-coordinates have been determined with less accuracy, and although the bond lengths change only slightly with changes in *y*-coordinates, the true standard deviations of the bond lengths are probably somewhat greater than the value of 0.013 \AA suggested by $\sigma(x)$ and $\sigma(z)$.

Discussion

The deviations of the carbon atoms from the mean naphthalene plane are probably not significant (r.m.s. deviation 0.04 \AA), but the oxygen atoms lie one above and one below the aromatic plane at mean distances of about 0.20 \AA . The carboxyl group is thus twisted

about the C(aromatic)-C(carboxyl) bond, the angle between the aromatic and carboxyl planes being 11° . The strain in a completely planar model however is

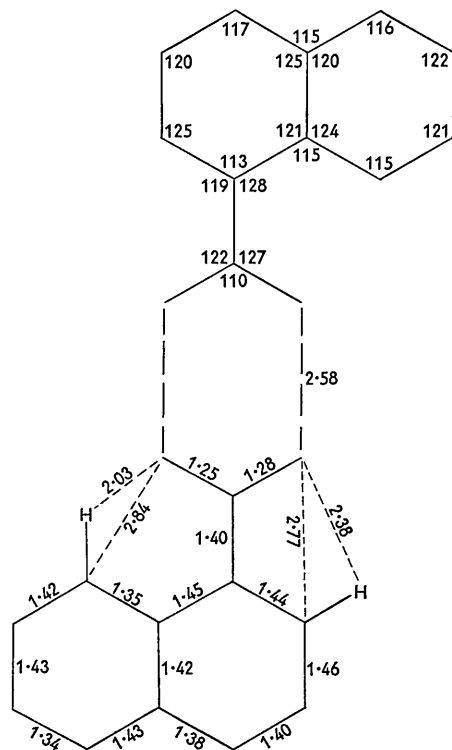


Fig. 3. Bond lengths, valency angles, hydrogen-bonded distances and intramolecular 'overcrowded' distances.

only partially relieved by these deviations from coplanarity. There is in addition a significant in-plane displacement of the C(aromatic)-C(carboxyl) bond away from the *peri* position, and a significant reduction in the O-C-O valency angle below the normal value (Fig. 3). These deviations from an ideal planar structure are sufficient to increase the separations between the oxygen atoms and neighbouring carbon and hydrogen atoms to distances which are a little less than the normal van der Waals contacts (Fig. 3).

The deviations from an ideal planar structure might be compared with the corresponding displacements in nitro derivatives. In those nitro derivatives where in-plane displacements are ineffective in reducing steric strain, such as 9,10-dinitroanthracene and nitro-mesitylene, the nitro groups are twisted about 65° out of the aromatic planes. Where in-plane displacements assist in the reduction of strain, as in 1,5-dinitronaphthalene, the angle of twist is reduced to 49° . In none of these nitro compounds are there any distortions of the nitro groups themselves. Apparently

Table 3. Bond lengths in naphthalene and 1-naphthoic acid

Bond	1-Naphthoic acid	Naphthalene
1-2	1.40 Å	1.36 Å
1-9	1.40	1.43
2-3	1.45	1.42
9-10	1.42	1.41
C-C	1.40	—
C-O ₁	1.25	—
C-O ₂	1.28	—

Table 4. Measured and calculated *hkl* structure factors

<i>hkl</i>	F_o	F_c	<i>hkl</i>	F_o	F_c	<i>hkl</i>	F_o	F_c	<i>hkl</i>	F_o	F_c
000	—	+360.0	601	75.2	+67.0	14,0,2	15.7	-15.7	$\bar{1}6,0,4$	10.3	+11.9
200	34.6	+37.7	801	3.3	-3.5	16,0,2	5.1	-2.4	$\bar{1}4,0,4$	10.9	+15.6
400	44.2	-45.1	12,0,1	41.6	-36.3	18,0,2	7.5	-7.3	804	6.3	-6.1
600	20.6	+17.3	14,0,1	40.3	-40.0	22,0,2	6.2	+11.0	404	18.3	+22.1
800	29.4	-28.7	16,0,1	39.0	+40.5	26,0,2	6.5	-10.2	204	9.3	+7.4
10,0,0	11.6	-12.0	18,0,1	21.0	+23.9	$\bar{2}8,0,3$	8.4	-9.9	004	6.8	+3.0
12,0,0	23.0	-21.6	20,0,1	17.3	+10.1	$\bar{2}4,0,3$	9.2	+10.4	204	34.9	+37.7
14,0,0	44.6	+48.8	22,0,1	21.8	+17.1	$\bar{2}0,0,3$	7.3	+10.2	404	19.4	+19.2
16,0,0	19.7	+18.4	26,0,1	6.9	+9.9	$\bar{1}6,0,3$	7.8	+5.2	604	19.4	-23.5
18,0,0	9.9	-3.4	28,0,1	8.9	+11.0	$\bar{1}2,0,3$	8.4	+5.1	10,0,4	6.0	-10.9
20,0,0	28.4	+25.6	$\bar{2}6,0,2$	7.8	+9.8	$\bar{1}0,0,3$	35.2	+32.0	16,0,4	23.0	+22.4
22,0,0	20.6	+16.6	$\bar{2}4,0,2$	54.0	-51.7	803	26.0	-29.8	18,0,4	21.7	+26.6
24,0,0	6.6	+0.7	$\bar{2}2,0,2$	11.3	-14.3	603	21.6	-26.5	20,0,4	31.8	-32.4
30,0,0	8.5	-5.6	$\bar{2}0,0,2$	22.4	+19.8	403	7.1	-4.7	$\bar{1}2,0,5$	8.9	-11.6
$\bar{3}0,0,1$	17.6	-15.7	$\bar{1}6,0,2$	17.8	+15.8	203	5.8	-11.0	005	15.4	+16.9
$\bar{2}8,0,1$	13.9	-14.1	$\bar{1}2,0,2$	3.7	+1.0	003	12.7	+12.0	205	12.3	+12.9
$\bar{2}6,0,1$	28.4	-23.7	$\bar{1}0,0,2$	66.8	-67.8	403	49.9	-47.7	405	13.1	+16.8
$\bar{2}2,0,1$	30.6	+30.0	802	60.0	-60.3	603	5.7	+2.9	805	6.6	+0.7
$\bar{1}4,0,1$	6.1	-7.4	602	4.2	+0.8	803	6.2	+7.1	18,0,5	16.4	+15.3
$\bar{1}2,0,1$	19.0	-18.2	402	39.7	-40.0	10,0,3	16.0	-15.8	20,0,5	16.8	+21.3
$\bar{1}0,0,1$	38.6	-34.0	202	40.2	-39.2	12,0,3	6.7	-5.1	806	21.5	-20.2
801	18.6	-21.9	202	15.8	+22.1	14,0,3	24.9	-25.1	606	34.8	-40.7
601	28.7	-29.1	402	8.9	-8.4	18,0,3	17.4	-16.2	406	19.0	+21.2
401	54.5	+54.4	602	5.4	-4.0	22,0,3	10.0	+12.6	206	17.0	+15.2
201	61.7	-61.5	802	26.2	-27.6	24,0,3	7.8	-9.5	806	7.8	-10.8
001	7.3	-10.9	10,0,2	25.7	-24.6	26,0,3	6.5	-3.1	407	15.0	-18.8
201	92.3	+90.8	12,0,2	14.6	-2.8	28,0,3	6.7	-7.2	10,0,7	11.7	-16.4
401	30.6	+36.9									

the distortion of the carboxyl group in 1-naphthoic acid (reduction of the O-C-O angle to 110°) allows the CO₂H group to be inclined at a much smaller angle (11°) to the aromatic plane, than the nitro groups in nitro derivatives.

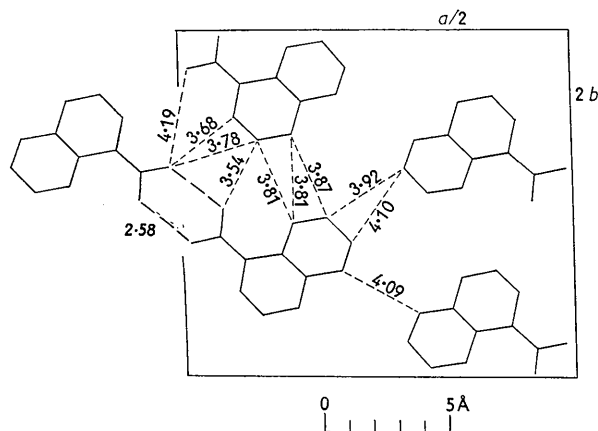


Fig. 4. Projection of the structure onto (010) showing the shorter intermolecular distances.

The mean bond lengths in the molecule are compared in Table 3 with the distances in naphthalene (Abrahams, Robertson & White, 1949; Cruickshank, 1957). The differences in the aromatic C-C distances are not significant. The C(aromatic)-C(carboxyl) distance (1.40 Å) would appear to be significantly shorter than the usual sp^2-sp^2 single bond distance, while the C-O distances are normal for carboxylic acids. The C-O distances, and small peaks corresponding to hydrogen atoms on the $h0l$ and $hk0$ difference maps, suggest that the carboxyl hydrogen atom is bonded to O₂.

Intermolecular distances

The structure consists of centrosymmetrical dimers, the O-H...O distance being 2.58 Å. All other intermolecular separations correspond to normal van der Waals interactions. The perpendicular distance between the aromatic planes of molecules related by translation b is 3.54 Å. The shorter lateral contacts are illustrated in Fig. 4.

Table 5. Measured and calculated $hk0$ structure factors

hkl	F_o	F_c	hkl	F_o	F_c
200	35	+37	510	36	+37
400	42	-45	610	5	+11
600	21	+17	710	11	-13
800	29	-29	810	6	-6
10,0,0	12	-12	910	7	-14
12,0,0	23	-22	10,1,0	<6	+6
14,0,0	45	+49	11,1,0	28	-22
16,0,0	20	+18	12,1,0	10	-8
18,0,0	10	-3	13,1,0	12	-18
20,0,0	28	+26	14,1,0	12	+3
22,0,0	21	+17	15,1,0	18	+18
24,0,0	7	+1	16,1,0	23	+35
30,0,0	9	-6	17,1,0	8	+20
110	44	+44	19,1,0	5	+1
210	70	+94	21,1,0	9	+6
310	20	+15	23,1,0	13	+18
410	16	-12	12,2,0	17	-11

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