

tioned between 50% aqueous EtOH (250 ml) and diethyl ether (500 ml) and the residue from the ether extract subjected to column chromatography on silica using hexane and EtOAc–hexane mixtures as eluants. Fractions containing (III) were concentrated *in vacuo* and the compound was crystallized from EtOAc–hexane as its EtOAc solvate: m.p. 521–523 K; [α]_D –11° (c 1.09, CHCl₃); MS *m/z*: 847.3762 [(*M* + 1)⁺, C₄₃H₅₉O₁₇ requires 847.3740]. ¹H and ¹³C NMR spectroscopic data were in accord with those previously reported (Halsall *et al.*, 1977). Mass spectra were obtained using a Kratos MS50TS spectrometer in the +FAB mode with a glycerol matrix. NMR spectra were recorded in CH₂Cl₂ on a Bruker AC360 spectrometer.

Crystal data

C ₄₃ H ₅₈ O ₁₇ ·0.355C ₄ H ₈ O ₂	Cu K α radiation
<i>M_r</i> = 878.17	λ = 1.54184 Å
Trigonal	Cell parameters from 59
P3 ₁ 2 ₁	reflections
<i>a</i> = 11.0341 (8) Å	θ = 20–22°
<i>c</i> = 62.874 (9) Å	μ = 0.852 mm ⁻¹
<i>V</i> = 6629.4 (12) Å ³	<i>T</i> = 150 (2) K
<i>Z</i> = 6	Tablet
<i>D_x</i> = 1.320 Mg m ⁻³	0.40 × 0.40 × 0.10 mm
<i>D_m</i> not measured	Colourless

Data collection

Stoe Stadi-4 four-circle diffractometer equipped with an Oxford Cryosystems low-temperature device (Cosier & Glazer, 1986)	4548 independent reflections
ω scans with learnt-profile method (Clegg, 1981)	3746 reflections with $I > 2\sigma(I)$
Absorption correction: by integration (see below)	<i>R</i> _{int} = 0.066
<i>T</i> _{min} = 0.727, <i>T</i> _{max} = 0.920	θ _{max} = 60.09°
5589 measured reflections	<i>h</i> = –9 → 10
	<i>k</i> = –11 → 11
	<i>l</i> = –33 → 70
	3 standard reflections
	frequency: 120 min
	intensity decay: <3%

Refinement

Refinement on <i>F</i> ²	$\Delta\rho$ _{max} = 0.53 e Å ⁻³
$R[F^2 > 2\sigma(F^2)] = 0.075$	$\Delta\rho$ _{min} = –0.50 e Å ⁻³
$wR(F^2) = 0.210$	Extinction correction: SHELX97
<i>S</i> = 1.043	Extinction coefficient: 0.00076 (12)
4548 reflections	Scattering factors from <i>International Tables for Crystallography</i> (Vol. C)
638 parameters	Absolute structure: Flack (1983)
H atoms: see below	Flack parameter = 0.9 (5)
$w = 1/[\sigma^2(F_o^2) + (0.1102P)^2 + 12.5558P]$	
where $P = (F_o^2 + 2F_c^2)/3$	
$(\Delta/\sigma)_{\text{max}} = 0.059$	

The approximate crystal shape was refined using *X-SHAPE* (Stoe & Cie, 1997) and symmetry-related data to give a shape bounded by eight crystal faces. This crystal shape was then used to calculate absorption corrections using *SHELXTL* (Sheldrick, 1994). Data could not be collected beyond θ _{max} = 60° because of the presence of the low-temperature device. Accordingly, the ratio of reflections to parameters is lower than would have been desired.

Data collection: *DIF4* (Stoe & Cie, 1990a). Cell refinement: *DIF4*. Data reduction: *REDU4* (Stoe & Cie, 1990b). Program(s) used to solve structure: *SHELX97* (Sheldrick, 1997). Program(s) used to refine structure: *SHELX97*. Molecular graphics: *SHELXTL* (Sheldrick, 1994). Software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1227). Services for accessing these data are described at the back of the journal.

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ortho-(1-Naphthoyl)benzoic Acid

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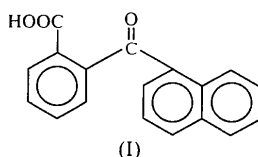
Abstract

The title acid, C₁₈H₁₂O₃, crystallized in the centrosymmetric space group *C2/c* and exhibits carboxyl group hydrogen bonding of the cyclic dimer type about a center of symmetry. The O_{donor}–O_{acceptor} distance in the hydrogen bond is 2.692 (2) Å. In addition, seven C–H groups and the three O atoms in the molecule are involved in significantly attractive C–H···O interactions

with 11 neighbors, forming a three-dimensional network. The carboxylic H atom is ordered, as are the carboxylic O atoms.

Comment

This study of *ortho*-(1-naphthoyl)benzoic acid, (I), is one of a continuing series on hydrogen bonding in aromatic carboxylic acids. The refined molecule and the numbering scheme are shown in Fig. 1. The hydrogen bonding is of the cyclic dimer type about a center of symmetry. Geometric details of the hydrogen bonding are given in Table 2, and show that the carboxylic H atom is ordered. In terms of graph-set analysis (Bernstein *et al.*, 1995), the first-level graph set is $R_2^2(8)$ and there are no higher-level graphs. This hydrogen-bonding pattern, with non-involvement of the keto oxygen atom O3, is the most commonly observed pattern in simple keto-carboxylic acids (Cote *et al.*, 1996).



As is not surprising in view of the excess of potential acceptors over O—H donors, 26 significantly attractive intermolecular C—H...O interactions [according to the criteria of Taylor & Kennard (1982), namely, $C_{\text{donor}} \cdots O_{\text{acceptor}}$ distance up to 4 Å and $C_{\text{donor}}—H—O_{\text{acceptor}}$ angle of 90° and greater] occur for each molecule in this structure. These interactions link a molecule to 11 neighbors, forming a three-dimensional network. In addition, there are four significant intramolecular C—H...O interactions. Geometric details of the strongest intermolecular C—H...O interactions [those having $H \cdots O_{\text{acceptor}}$ distances less than the sum of the corresponding Bondi (1964) van der Waals radii] are given in Table 2; a complete tabulation from the usual donor viewpoint is included in the deposited material.

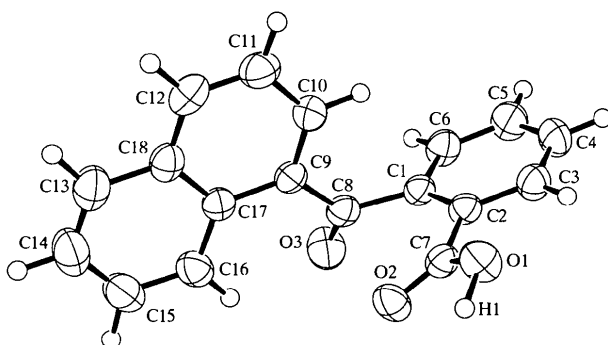


Fig. 1. ORTEPII (Johnson, 1976) plot of (I), showing the molecular numbering scheme. Displacement ellipsoids are drawn at 50% probability for all atoms except H, for which they have been set artificially small.

The most significant aspects of the molecular geometry are perhaps the values of the dihedral angles between, variously, the benzene core plane, the carboxyl group plane and the naphthyl group plane. The average deviation of the benzene core atoms from the best-fit plane describing them is 0.007 (2) Å and the maximum deviation 0.013 (2) Å. The dihedral angle between the benzene core plane and the plane of the carboxyl group (O1—C7—O2) is 20.6 (2)°. The average deviation of the naphthyl group atoms from the best-fit plane describing them is 0.006 (2) Å and the maximum deviation 0.012 (2) Å. The dihedral angle between the benzene core plane and the naphthyl group plane is 86.3 (1)°.

Bond distances and angles of special interest are given in Table 1. These data show that the carboxylic O atoms are ordered. As is apparent from Fig. 1, the largest principal axes of the carboxylic O-atom displacement tensors are almost normal to the carboxyl group planes, as expected for ordered O atoms. The remaining intramolecular distances and angles fall within normal ranges. 11 refined ring H atoms give C—H distances ranging from 0.97 (1) to 1.09 (2) Å with a mean value of 1.01 (3) Å, and U_{iso} ranging from ~ 0.05 to 0.09 Å²; the refined O—H distance appears in Table 2.

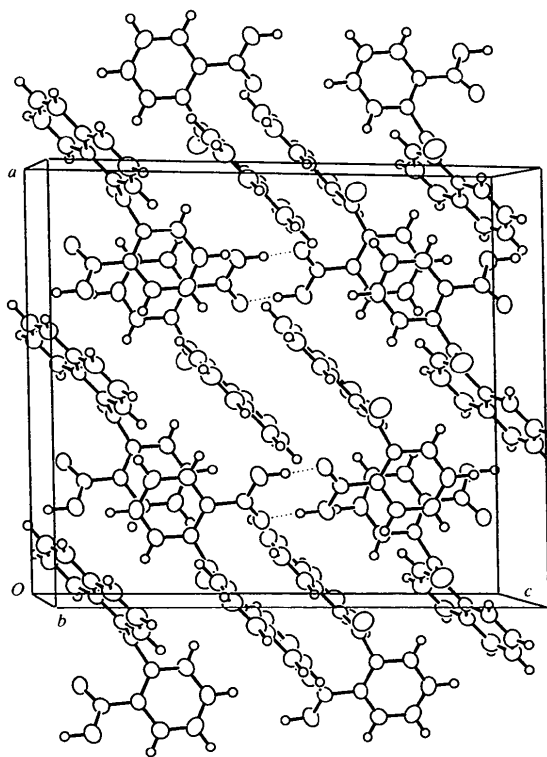


Fig. 2. ORTEPII (Johnson, 1976) packing diagram of (I). Displacement ellipsoids are drawn at 50% probability for all atoms except H, for which they have been set artificially small. Hydrogen bonds are depicted by dashed lines.

The structure comprises alternating layers along **a**: benzoic acid groups at $\sim \frac{1}{4}\mathbf{a}$ and $\frac{3}{4}\mathbf{a}$, and naphthoyl groups at $\sim 0, \frac{1}{2}\mathbf{a}$ and \mathbf{a} . The packing is shown in Fig. 2. The closest intermolecular approaches, excluding pairs of atoms in hydrogen-bonded carboxyl groups or in the tabulated C—H...O interactions, are between H1 and H13^{vi} [symmetry code: (vi) $-\frac{1}{2} + x, -\frac{1}{2} + y, z$], and are 0.06 Å less than the corresponding Bondi (1964) van der Waals radius sum. No other approach is deficient by more than 0.02 Å.

Experimental

The title acid was obtained as a colorless plate from a sample in the chemical collection of Dr M. S. Newman. This was cut several times to provide the experimental sample.

Crystal data

C ₁₈ H ₁₂ O ₃	Mo K α radiation
$M_r = 276.29$	$\lambda = 0.71073$ Å
Monoclinic	Cell parameters from 25 reflections
$C2/c$	$\theta = 12.5$ – 17.2°
$a = 17.218(2)$ Å	$\mu = 0.086$ mm ⁻¹
$b = 8.121(2)$ Å	$T = 296$ K
$c = 19.301(1)$ Å	Cut plate
$\beta = 91.264(7)^\circ$	$0.35 \times 0.35 \times 0.31$ mm
$V = 2697.9(7)$ Å ³	Colorless
$Z = 8$	
$D_x = 1.360$ Mg m ⁻³	
D_m not measured	

Data collection

Rigaku AFC-5S diffractometer	$R_{\text{int}} = 0.024$
ω scans	$\theta_{\text{max}} = 27.56^\circ$
Absorption correction: none	$h = 0 \rightarrow 22$
3459 measured reflections	$k = 0 \rightarrow 10$
3123 independent reflections	$l = -25 \rightarrow 25$
1936 reflections with $I > 2\sigma(I)$	6 standard reflections every 150 reflections intensity decay: 4.7%

Refinement

Refinement on F^2	$\Delta\rho_{\text{max}} = 0.37$ e Å ⁻³
$R(F) = 0.049$ [$I > 2\sigma(I)$]	$\Delta\rho_{\text{min}} = -0.30$ e Å ⁻³
$wR(F^2) = 0.060$	Extinction correction: Zachariassen (1963, 1968)
$S = 1.67$	Extinction coefficient: $7.2(2) \times 10^{-7}$
3123 reflections	Scattering factors from Stewart <i>et al.</i> (1965) (H) and Creagh & McAuley (1992) (C, O)
239 parameters	
All H atoms refined	
$w = 1/\sigma^2(F^2)$	
$(\Delta/\sigma)_{\text{max}} < 0.01$	

Table 1. Selected geometric parameters (Å, °)

O1—C7	1.314(2)	O3—C8	1.221(2)
O2—C7	1.227(2)		
O1—C7—O2	122.6(1)	O3—C8—C1	119.4(2)
O1—C7—C2	115.3(2)	O3—C8—C9	123.1(2)
O2—C7—C2	122.1(2)		
O3—C8—C9—C17	22.7(2)	O3—C8—C1—C6	67.9(2)

Table 2. Hydrogen-bonding geometry (Å, °)

D—H...A	D—H	H...A	D...A	D—H...A
O1—H1...O2 ⁱⁱ	1.08(2)	1.61(2)	2.692(2)	176(2)
C11—H11...O3 ⁱⁱⁱ	1.00(2)	2.59(2)	3.468(2)	147(1)
C12—H12...O1 ⁱⁱⁱⁱ	1.02(2)	2.69(2)	3.565(2)	144(1)
C13—H13...O2 ^v	1.09(2)	2.55(2)	3.592(3)	159(1)
C15—H15...O2 ^v	1.01(2)	2.55(2)	3.507(3)	158(1)

Symmetry codes: (i) $\frac{1}{2} - x, \frac{1}{2} - y, -z$; (ii) $x, 1 + y, z$; (iii) $\frac{1}{2} + x, \frac{1}{2} + y, z$; (iv) $1 - x, 1 - y, -z$; (v) $1 - x, -y, -z$.

Scan widths were $(1.50 + 0.35\text{tan}\theta)^\circ$ in ω , with a background/scan time-ratio of 0.5. The data were corrected for Lorentz and polarization effects. A linear decay correction was applied. The Laue group assignment, systematic absences and centrosymmetric intensity statistics indicated space group $C2/c$ (No. 15). Since refinement proceeded well, it was adopted. Fourier difference methods were used to locate the initial H-atom positions. The maximum effect of extinction was 15.4% of F_o for 404. The maximum positive residual peak was located ~ 0.7 Å from C1 and 0.9 Å from C8, while the maximum negative peak was located ~ 0.3 Å from C14.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *SAPI91* (Fan, 1991). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *TEXSAN* and *PLATON* (Spek, 1990).

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