

Hydrogen bonding and C—H···O interactions in 2-[1-(1-naphthyl)ethyl]benzoic acid at 150 K

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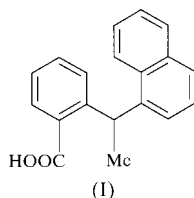
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The title acid, C₁₉H₁₆O₂, crystallized in the centrosymmetric space group *Pnna* with three molecules in the asymmetric unit (apparently the first reported instance of $Z' = 3$ in this space group). Four intermolecular hydrogen bonds have O_D···O_A distances of 2.660 (2), 2.594 (2), 2.633 (2) and 2.646 (2) Å, and angles of 177 (2), 179 (2), 175 (2) and 175 (2)°. The four hydrogen bonds form two R₂²(8) cyclic dimers, one about a twofold axis. Five leading intermolecular C—H···O interactions are present. Although first- and second-level graph sets involving these nine interactions are dominated by finite patterns, a three-dimensional network becomes evident upon analysis of higher-level graphs. A number of intramolecular C—H···O interactions are also present.

Comment

This report is one of a series on hydrogen bonding and C—H···O interactions in carboxylic acids. The title acid, (I), crystallized in the centrosymmetric space group *Pnna* with three molecules in the asymmetric unit. Four hydrogen bonds and five leading intermolecular C—H···O interactions (Taylor & Kennard, 1982; Steiner & Desiraju, 1998) are present in this structure. The geometric parameters of these are given in Table 2. The three crystallographically inequivalent molecules, shown in Fig. 1, are linked directly to five, three and three neighbors, respectively, by the tabulated interactions. The results of basic first- and second-level graph-set analysis (Bernstein *et al.*, 1995) involving these interactions, labeled *a–i* for this purpose in the order of their appearance in Table 2, are given in Table 3.



The hydrogen bonds in (I) form two R₂²(8) cyclic dimers. One of these involves one of the independent molecules and a

partner which is related by a twofold axis, while the other involves the remaining two independent molecules. Thus, although the space group includes a center of symmetry it is not involved in formation of the cyclic dimers. Since the twofold axis apposes O1 and O2 with their respective transforms, the hydrogen bonds between them must be either 'symmetric disordered' or 'symmetric centered' (terminology of Olovsson & Jönsson, 1976). Fixing H1O1 and H1O2 off the twofold axis models them as disordered. However, fixing H1O1 and H1O2 on the twofold axis would produce insignificant changes in any parameters except the O—H distances involving H1O1 and H1O2, and is an equally satisfactory model consistent with the present data. A number of such cases for short hydrogen bonds are tabulated by Olovsson & Jönsson (1976).

As expected from the presence of three independent molecules, finite graphs predominate in the first- and second-level graph sets. In the third- and fourth-level sets, however, there are, *e.g.*, three chain patterns which propagate variously along [013], [010] and [10 $\bar{1}$], thus generating a three-dimensional network of interactions. Each of these chains contains the three independent molecules and, respectively, involves interactions *efg*, *iefg* and *gcei*. Of course, the first- and second-level chains given in Table 3, which involve only one of the independent molecules and propagate along [100] and [10 $\bar{1}$], enhance the connectivity of the interaction network.

The geometric parameters of eight leading intramolecular C—H···O interactions are also given in Table 2. These interactions are quite similar for the three inequivalent molecules and doubtless participate in determining the dihedral angles of the carboxyl groups with respect to the planes of the attached benzene rings, which angles are also quite similar as they range from 24.3 (2) to 35.4 (2)°.

In (I) the maximum deviations of atoms from the best-fit planes describing the benzene and naphthalene rings are 0.013 (2) and 0.054 (2) Å, respectively. The benzene and naphthalene ring planes are nearly perpendicular in each molecule.

Selected bond distances and angles are given in Table 1. Consistent with the recognition that O—H distances in hydrogen bonds which involve symmetry elements such as centers or twofold axes can be unusually long, all distances and angles fall within normal limits. Corresponding C—C bond distances in the three independent molecules are in very good agreement: the largest of the three r.m.s. differences within 21 pairs of corresponding distances is 0.005 (2) Å, while the s.u.'s of the individual values are uniformly 0.002 Å. In (I) the closest intermolecular approaches, excluding pairs of atoms involved in the hydrogen-bonding groups or the tabulated C—H···O interactions, are between H6 and H9B^{vi} [symmetry code: (vi) $\frac{1}{2} + x, y, 1 - z$] and fall short of the corresponding Bondi (1964) van der Waals radius sum by 0.16 Å.

A search of the Cambridge Structural Database (Allen & Kennard, 1993) revealed that this structure is the first example having $Z' = 3$ in *Pnna*, and the first organic structure having $Z' > 1$ in *Pnna*. Four organometallic structures having $Z' = 1.5$

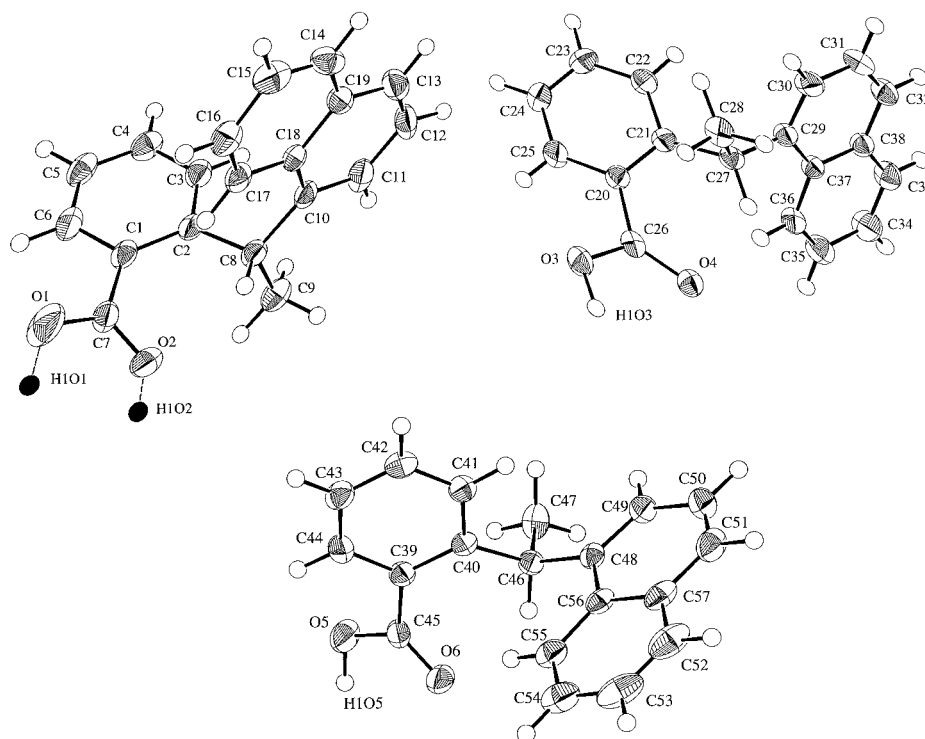


Figure 1
The three independent molecules of compound (I), showing the atom-labeling scheme, with displacement ellipsoids at the 50% probability level. Half-occupancy H atoms are shaded.

or 2 have previously been reported in this space group (Baral *et al.*, 1982; Dobrott & Lipscomb, 1962; Tang *et al.*, 1998; Yuge *et al.*, 1995).

Experimental

Compound (I) was obtained from a coarsely crystalline sample in the chemical collection of Dr M. S. Newman. An irregular hexagonal slab was cut to provide the experimental sample. A synthesis is described by Newman & Cunico (1972).

Crystal data

$C_{19}H_{16}O_2$
 $M_r = 276.33$
 Orthorhombic, $Pnna$
 $a = 16.8468$ (3) Å
 $b = 37.3753$ (7) Å
 $c = 13.8418$ (3) Å
 $V = 8715.5$ (7) Å³
 $Z = 24$
 $D_x = 1.263$ Mg m⁻³

Mo $K\alpha$ radiation
 Cell parameters from 91 848 reflections
 $\theta = 1.21$ – 27.47°
 $\mu = 0.081$ mm⁻¹
 $T = 150$ K
 Cut irregular hexagonal slab,
 colorless
 $0.31 \times 0.31 \times 0.27$ mm

Table 1

Selected geometric parameters (Å, °).

| | | | |
|------------|-------------|------------|-------------|
| O1—C7 | 1.2672 (13) | O4—C26 | 1.2239 (13) |
| O2—C7 | 1.2596 (13) | O5—C45 | 1.3200 (13) |
| O3—C26 | 1.3135 (13) | O6—C45 | 1.2240 (13) |
| O1—C7—O2 | 121.16 (12) | O4—C26—C20 | 123.97 (11) |
| O1—C7—C1 | 118.69 (11) | O5—C45—O6 | 121.35 (11) |
| O2—C7—C1 | 120.14 (11) | O5—C45—C39 | 114.50 (11) |
| O3—C26—O4 | 121.44 (11) | O6—C45—C39 | 124.13 (12) |
| O3—C26—C20 | 114.54 (11) | | |

Data collection

Nonius KappaCCD diffractometer
 ω scans with κ offsets
 91 848 measured reflections
 9954 independent reflections
 6788 reflections with $I > 2\sigma(I)$

$R_{int} = 0.046$
 $\theta_{max} = 27.47^\circ$
 $h = -21 \rightarrow 20$
 $k = -48 \rightarrow 47$
 $l = -17 \rightarrow 17$

Refinement

Refinement on F^2
 $R(F) = 0.055$
 $wR(F^2) = 0.076$
 $S = 1.67$
 9951 reflections
 624 parameters

H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma_{cs}^2 + (0.016 I)^2]$
 $(\Delta/\sigma)_{max} = 0.001$
 $\Delta\rho_{max} = 0.54$ e Å⁻³
 $\Delta\rho_{min} = -0.44$ e Å⁻³

Table 2

Geometry of hydrogen bonds and leading C—H...O interactions (Å, °).

| D—H...A | D—H | H...A | D...A | D—H...A |
|-----------------------------|----------|----------|-----------|---------|
| O1—H1O1...O1 ⁱ | 1.23 | 1.43 | 2.660 (2) | 177 (2) |
| O2—H1O2...O2 ⁱ | 1.20 | 1.40 | 2.594 (2) | 179 (2) |
| O3—H1O3...O6 | 0.99 (2) | 1.64 (2) | 2.633 (2) | 175 (2) |
| O5—H1O5...O4 | 1.07 (2) | 1.58 (2) | 2.646 (2) | 175 (2) |
| C13—H13...O5 ⁱⁱ | 0.98 | 2.52 | 3.312 (2) | 137 |
| C51—H51...O3 ⁱⁱⁱ | 0.98 | 2.64 | 3.585 (2) | 163 |
| C32—H32...O2 ^{iv} | 0.98 | 2.68 | 3.539 (2) | 147 |
| C33—H33...O2 ^{iv} | 0.98 | 2.72 | 3.570 (2) | 145 |
| C11—H11...O1 ^v | 0.98 | 2.79 | 3.536 (2) | 134 |
| C8—H8...O2 | 0.98 | 2.21 | 2.869 (2) | 123 |
| C27—H27...O4 | 0.98 | 2.24 | 2.967 (2) | 130 |
| C46—H46...O6 | 0.98 | 2.24 | 2.983 (2) | 131 |
| C25—H25...O3 | 0.98 | 2.40 | 2.730 (2) | 99 |
| C6—H6...O1 | 0.98 | 2.45 | 2.762 (2) | 98 |
| C44—H44...O5 | 0.98 | 2.47 | 2.772 (2) | 97 |
| C55—H55...O6 | 0.98 | 2.72 | 3.642 (2) | 158 |
| C36—H36...O4 | 0.98 | 2.75 | 3.698 (2) | 163 |

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

Table 3

Basic first- and second-level graph-set descriptors involving intermolecular interactions designated *a–i* in the order given in Table 2.

| | <i>a</i> | <i>b</i> | <i>c</i> | <i>d</i> | <i>e</i> | <i>f</i> | <i>g</i> | <i>h</i> | <i>i</i> |
|----------|----------|------------|----------|------------|-------------|-------------|-------------|-------------|-------------|
| <i>a</i> | <i>D</i> | $R_2^2(8)$ | None | None | $D_3^3(23)$ | None | $D_3^3(11)$ | $D_3^3(11)$ | $C_2^2(10)$ |
| <i>b</i> | | <i>D</i> | None | None | $D_3^3(23)$ | None | $D_2^2(7)$ | $D_2^2(7)$ | $C_2^2(12)$ |
| <i>c</i> | | | <i>D</i> | $R_2^2(8)$ | $D_2^2(7)$ | $R_4^4(24)$ | $D_2^2(13)$ | $D_2^2(13)$ | None |
| <i>d</i> | | | | <i>D</i> | $D_2^2(5)$ | $R_4^4(28)$ | $D_2^2(13)$ | $D_2^2(13)$ | None |
| <i>e</i> | | | | | <i>D</i> | $D_2^2(13)$ | $D_2^2(13)$ | $D_2^2(13)$ | $D_2^2(7)$ |
| <i>f</i> | | | | | | <i>D</i> | $D_2^2(13)$ | $D_2^2(13)$ | None |
| <i>g</i> | | | | | | | <i>D</i> | $R_2^1(6)$ | $D_2^2(7)$ |
| <i>h</i> | | | | | | | | <i>D</i> | $D_2^2(7)$ |
| <i>i</i> | | | | | | | | | $C(8)$ |

Difference Fourier methods were used to locate the initial H-atom positions, excepting the half-occupancy atoms H1O1 and H1O2, and all these H atoms were refined. The 45 refined C–H distances ranged from 0.93 (2) to 1.07 (2) Å, with a mean value of 0.99 (5) Å; their U_{iso} values ranged from 0.7 to 1.5 times the U_{eq} values of the attached C atoms. The 33 ring-H atoms were then made canonical, with C–H = 0.98 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. Subsequently, the half-occupancy atoms H1O1 and H1O2 were located on a difference map on a twofold axis. They were then fixed 0.1 Å off this axis, along the rays between O1 and O2 and the axis sites, to have them recognized as bonded to O1 and O2; their U_{iso} values were fixed consistent with the U_{iso} values of the refined carboxyl-H atoms.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structure: *TEXSAN* (Molecular Structure Corporation, 1992–1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *TEXSAN* and *PLATON* (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1289). Services for accessing these data are described at the back of the journal.

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