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# 2-Naphthoic Acid at 153 K

Anthony C. Blackburn, Lawrence J. Fitzgerald and Roger E. Gerkin

*Department of Chemistry, The Ohio State University, Columbus, Ohio 43210, USA. E-mail: rgerkin@magnus.acs.ohio-state.edu*

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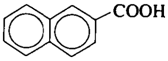
## Abstract

The structure of 2-naphthoic acid, $C_{11}H_8O_2$, has been investigated at 153 K in order to determine the degree of disorder of the carboxylic acid group for comparison with that of the room-temperature structure. Analysis of the anisotropic displacement ellipsoids of the carboxyl-O atoms demonstrated that these parameters are wholly consistent with thermal motion of the O atoms. A model with ordered carboxyl-O atoms, but with the acid-H atom refined at two sites with 0.5 occupancy at each, was found to be statistically significantly better than a model with ordered carboxyl-O atoms and an ordered acid-H atom. Thus, as in the room-temperature study, the best structural description is that the O atoms are ordered and the acid-H atom is disordered. Nonetheless, comparisons of the geometric parameters of the carboxyl groups at 296 and 153 K suggest progress toward a fully ordered structure at the lower temperature. Except for the expected slight overall contraction and the slightly altered geometry of the carboxyl group, the structure is virtually the same as at room temperature.

## Comment

On the basis of their structural study of 2-naphthoic acid, (II), at 296 K, Fitzgerald & Gerkin (1993) concluded that the carboxylic-O atoms were ordered and that the acid-H atom was disordered over two sites of 0.5 occupancy each. It was of interest to determine whether the H atom would become better ordered at our lowest feasible temperature, ~150 K.



(II)

At 153 K, the 2-naphthoic acid core-C atoms have a mean deviation from the best least-squares plane describing them of 0.003 (2) Å (identical to the room temperature value). The dihedral angle between the core plane and the plane of the carboxyl group is 2.19 (9)°, slightly larger than the 1.4 (5)° value at room temperature. Again, the small deviation of the core from planarity and the nearly planar conformation of the carboxyl group and the core occur despite intramolecular close approaches of O1 and H1 [2.45 (2) Å] and of O2 and H3 [2.51 (2) Å] which are, however, slightly larger than the corresponding values at room temperature.

For 2-naphthoic acid at room temperature, various pieces of evidence including orientations of the principal-axis components of the anisotropic displacement ellipsoids of the carboxyl-O atoms led to the conclusion that the O atoms are not statically disordered (contrary to Leiserowitz, 1976), but that the H atom is (dynamically) disordered. The present results confirm that conclusion. Firstly, the $U_{eq}$ values for O1 and O2 at low temperature, as at room temperature, are not as large as those for ring-C atoms C6 and C7, and are as large or only slightly larger than those for ring-C atoms C4, C5 and C8; thus, there is again nothing exceptional about the $U_{eq}$ values for the O atoms. Secondly, analysis of the principal components of the O-atom anisotropic displacement ellipsoids at low temperature, as at room temperature, shows (see Table 3) that their orientations are not consistent with the static disorder model of Leiserowitz (1976), as previously discussed by Fitzgerald & Gerkin (1993). Thirdly, if only thermal effects determine the values of $U_{eq}$ and if both temperatures are in the high-temperature limit for thermal displacement, the ratios $U_{eq}(296)/U_{eq}(153)$ should be equal to the ratio of the absolute temperatures, 1.93 (6) (see, for example, Dunitz, Schomaker & Trueblood, 1988). These ratios for the thirteen non-H atoms range from 1.79 to 1.89 with a mean value of 1.83 (8), the values for O1 and O2 being 1.84 and 1.85. Again, there is nothing exceptional about the O-atom behavior and the high degree of agreement for all these atoms supports the interpretation that these carboxyl-O atoms are not subject to static disorder.

As described elsewhere in this report, a model of the low-temperature structure with ordered O atoms and an acid-H atom disordered over two sites was found to be superior to a model with ordered O atoms and an ordered H atom; this result is the same as for the room temperature structure. However, as is evident from Table 4, four of the five parameters which characterize the carboxyl-group geometry have values for both the room- and low-temperature 2-naphthoic acid lying intermediate to those for acid-H-completely-disordered and acid-H-completely-ordered structures, and four of the five values for the low temperature acid lie closer to those for the H-completely ordered structure. In this sense there is progress toward acid-H-atom order by 153 K.

Geometric details of the hydrogen bonds, which are of the cyclic dimer type about a center of symmetry, are given in Table 5.

Excluding pairs of atoms involved in hydrogen bonding, the closest intermolecular approach falls short of the corresponding van der Waals radius sum (Bondi, 1964) by 0.16 Å and involves atoms O1 and H4($x$+1, $y$−1, $z$); the next-closest approaches, with deficits 0.03 Å, are

O2···H3(1−*x*, −*y*, −*z*), O2···C11(2−*x*, −*y*, −*z*) and C4···C11(*x*, 1+*y*, *z*). The pattern of close approaches to O1 and O2 by ring-H atoms matches the close approaches in the room temperature structure.

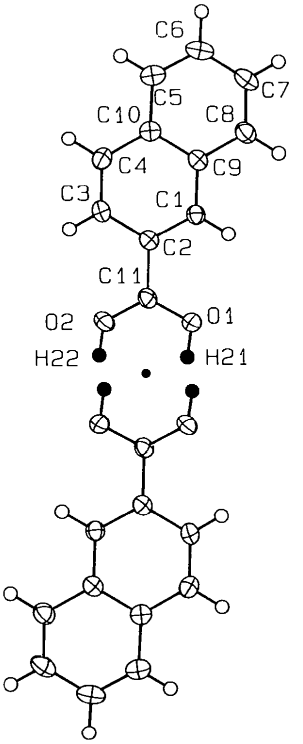


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of the 2-naphthoic acid hydrogen-bonded cyclic dimers showing our numbering scheme. Displacement ellipsoids are drawn for 50% probability for all atoms except H, for which they have been set artificially small. The center of symmetry and the half-occupancy H atoms are shown as filled circles.

## Experimental

Crystals were obtained by the slow evaporation of aqueous ethanol at room temperature.

*Crystal data*

$C_{11}H_8O_2$
$M_r$ = 172.18
Monoclinic
$P2_1/n$
$a$ = 5.580 (1) Å
$b$ = 4.916 (1) Å
$c$ = 30.174 (2) Å
$\beta$ = 91.74 (2)°
$V$ = 827.2 (5) Å$^3$
$Z$ = 4
$D_x$ = 1.382 Mg m$^{-3}$
$D_m$ not measured

Mo $K\alpha$ radiation
$\lambda$ = 0.71073 Å
Cell parameters from 25 reflections
$\theta$ = 14.2–15.1°
$\mu$ = 0.089 mm$^{-1}$
$T$ = 153 K
Plate
0.38 × 0.38 × 0.15 mm
Colorless

*Data collection*

AFC-5*S* diffractometer
$\omega$ scans
Absorption correction: none
2354 measured reflections
2140 independent reflections
1248 observed reflections [$I > 3\sigma(I)$]
$R_{\rm int}$ = 0.021
$\theta_{\rm max}$ = 27.5°

$h = 0 \rightarrow 7$
$k = 0 \rightarrow 6$
$l = -38 \rightarrow 38$
6 standard reflections monitored every 150 reflections intensity variation: ±1.7% (average maximum relative intensity)

*Refinement*

Refinement on $F$
$R$ = 0.039
$wR$ = 0.047
$S$ = 1.74
1248 reflections
155 parameters
All H-atom parameters refined
$w = \sigma_F^{-2}$
$(\Delta/\sigma)_{\rm max}$ = < 0.01

$\Delta\rho_{\rm max}$ = 0.25 e Å$^{-3}$
$\Delta\rho_{\rm min}$ = −0.18 e Å$^{-3}$
Extinction correction: Zachariasen (1963, 1968)
Extinction coefficient: 5 (4) × 10$^{-7}$
Atomic scattering factors from Stewart, Davidson & Simpson (1965) (H), and Cromer & Waber (1974) (C, O)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å$^2$)*

$$U_{\rm eq} = (1/3)\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

| | $x$ | $y$ | $z$ | $U_{\rm eq}$ |
|---|---|---|---|---|
| O1 | 1.1288 (2) | −0.3600 (3) | 0.04854 (4) | 0.0328 (4) |
| O2 | 0.7973 (3) | −0.2525 (3) | 0.00877 (4) | 0.0336 (4) |
| C1 | 1.0364 (3) | 0.0334 (4) | 0.11061 (5) | 0.0253 (5) |
| C2 | 0.8819 (3) | −0.0097 (4) | 0.07517 (5) | 0.0245 (4) |
| C3 | 0.6687 (3) | 0.1461 (4) | 0.07037 (6) | 0.0298 (5) |
| C4 | 0.6159 (3) | 0.3374 (4) | 0.10115 (6) | 0.0317 (5) |
| C5 | 0.7224 (4) | 0.5820 (4) | 0.17152 (6) | 0.0334 (5) |
| C6 | 0.8770 (4) | 0.6233 (4) | 0.20666 (6) | 0.0362 (5) |
| C7 | 1.0891 (4) | 0.4700 (4) | 0.21100 (6) | 0.0357 (5) |
| C8 | 1.1429 (4) | 0.2789 (4) | 0.18007 (6) | 0.0328 (5) |
| C9 | 0.9861 (3) | 0.2312 (4) | 0.14314 (5) | 0.0249 (5) |
| C10 | 0.7715 (3) | 0.3854 (4) | 0.13840 (5) | 0.0268 (5) |
| C11 | 0.9362 (3) | −0.2198 (4) | 0.04164 (5) | 0.0252 (4) |

Table 2. *Selected geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| C1—C2 | 1.370 (2) | C5—C10 | 1.423 (3) |
| C1—C9 | 1.416 (2) | C6—C7 | 1.406 (3) |
| C2—C3 | 1.418 (2) | C7—C8 | 1.364 (3) |
| C2—C11 | 1.484 (2) | C8—C9 | 1.415 (2) |
| C3—C4 | 1.360 (3) | C9—C10 | 1.421 (2) |
| C4—C10 | 1.419 (2) | C11—O1 | 1.288 (2) |
| C5—C6 | 1.362 (3) | C11—O2 | 1.250 (2) |
| C2—C1—C9 | 120.9 (2) | C1—C9—C8 | 121.9 (2) |
| C1—C2—C3 | 120.2 (2) | C1—C9—C10 | 118.7 (2) |
| C1—C2—C11 | 120.2 (2) | C8—C9—C10 | 119.3 (2) |
| C3—C2—C11 | 119.6 (1) | C4—C10—C5 | 122.9 (2) |
| C2—C3—C4 | 120.1 (2) | C4—C10—C9 | 119.0 (2) |
| C3—C4—C10 | 121.0 (2) | C5—C10—C9 | 118.1 (2) |
| C6—C5—C10 | 121.1 (2) | C2—C11—O1 | 116.7 (1) |
| C5—C6—C7 | 120.3 (2) | C2—C11—O2 | 119.7 (2) |
| C6—C7—C8 | 120.5 (2) | O1—C11—O2 | 123.6 (2) |
| C7—C8—C9 | 120.6 (2) | | |

Table 3. *Principal-axis components (Å² × 10⁴) and selected orientation angles (°)*

Anisotropic displacement ellipsoids of the carboxyl-O atoms and selected additional atoms in 1-naphthoic and 2-naphthoic acids at 296 K (corrected from Fitzgerald & Gerkin, 1993) and 2-naphthoic acid at 153 K (present work) are given together with selected orientation angles which specify the orientation of the ellipsoids with respect to the relevant C—O bond and the relevant O—C—O plane. Principal-axis components of the anisotropic ellipsoids for the carboxyl-C atoms and for the ring-C atoms having the largest or smallest values of $U_{eq}$ are given for comparison. Note that the principal-axis components are numbered solely in order of size, rather than by any geometric criteria.

| | | | | Angle with C—O bond | | | Angle with O—C—O plane | | |
|---|---|---|---|---|---|---|---|---|---|
| | $u_1$ | $u_2$ | $u_3$ | $u_1$ | $u_2$ | $u_3$ | $u_1$ | $u_2$ | $u_3$ |
| 1-Naphthoic acid at 296 K | | | | | | | | | |
| O1 | 1347 | 477 | 344 | 87 | 89 | 3 | 86 | 3 | 3 |
| O2 | 1205 | 385 | 367 | 86 | 6 | 86 | 85 | 3 | 4 |
| C11 | 521 | 417 | 325 | | | | | | |
| C6 | 765 | 558 | 363 | | | | | | |
| C9 | 415 | 372 | 311 | | | | | | |
| 2-Naphthoic acid at 296 K | | | | | | | | | |
| O1 | 908 | 467 | 436 | 84 | 67 | 24 | 83 | 6 | 4 |
| O2 | 912 | 580 | 368 | 82 | 74 | 18 | 73 | 17 | 3 |
| C11 | 541 | 469 | 373 | | | | | | |
| C6 | 1042 | 575 | 416 | | | | | | |
| C2 | 507 | 439 | 368 | | | | | | |
| 2-Naphthoic acid at 153 K | | | | | | | | | |
| O1 | 488 | 255 | 241 | 78 | 12 | 89 | 77 | 11 | 7 |
| O2 | 487 | 323 | 198 | 78 | 75 | 19 | 67 | 6 | 22 |
| C11 | 311 | 250 | 196 | | | | | | |
| C6 | 574 | 287 | 226 | | | | | | |
| C2 | 291 | 246 | 197 | | | | | | |

Table 4. *Bond distances and angles (Å, °) in the carboxyl groups of 1,8-naphthalenedicarboxylic acid and related compounds*

For simplicity, the atom numbering of the present report has been adopted for all acids in this table. Mean values are given for acid (I).

| Acid | C11–O1 | C11–O2 | C2–C11–O1 | C2–C11–O2 | O1–C11–O2 |
|---|---|---|---|---|---|
| (I)[a] | 1.266 (5) | 1.266 (5) | 118.3 (9) | 118.3 (9) | 123.2 (3) |
| (II), 296 K[b] | 1.274 (3) | 1.256 (3) | 117.7 (2) | 119.1 (2) | 123.1 (3) |
| (II), 153 K[c] | 1.288 (2) | 1.250 (2) | 116.7 (1) | 119.7 (2) | 123.6 (2) |
| (III)[d] | 1.312 (3) | 1.214 (3) | 114.1 (2) | 124.8 (2) | 121.1 (2) |

Notes: (*a*) 1,8-naphthalenedicarboxylic acid, carboxyl-H atoms completely disordered (Fitzgerald, Gallucci & Gerkin, 1991); (*b*) Fitzgerald & Gerkin, 1993; (*c*) this study; (*d*) 1-naphthoic acid, carboxyl-H atom completely ordered (Fitzgerald & Gerkin, 1993).

Table 5. *Hydrogen-bonding geometry (Å, °)*

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O1—H21···O2$^{i}$ | 0.89 (5) | 1.73 (5) | 2.614 (2) | 172 (4) |
| O2—H22···O1$^{i}$ | 0.88 (7) | 1.75 (7) | 2.614 (2) | 170 (6) |

Symmetry code: (i) $2 - x, -1 - y, -z$.

The intensity-data crystal of 2-naphthoic acid from the room-temperature structural study by Fitzgerald & Gerkin (1993) was employed again in the present study. A Molecular Structure Corporation low-temperature apparatus was used to achieve a temperature of 153 K, estimated to be accurate to ±2 K. Scan widths were $(1.50 + 0.35\tan\theta)^{\circ}$ in $\omega$, with a background/scan-time ratio of 0.5. The data were corrected for Lorentz and polarization effects.

The Laue group assignment, systematic absences and intensity statistics consistent with centrosymmetry indicated space group $P2_1/n$ (No. 14); since refinement proceeded well it was adopted. Fourier difference methods were used to locate the H-atom positions. Final refined values of the C—H distances ranged from 0.93 (2) to 1.00 (2) Å. The carboxylic-H atom was modelled in two ways on the basis of Fourier difference maps obtained after all other atoms (including the other H atoms) were refined. Model *A* involved one full-occupancy H atom site near O1 and model *B* involved two half-occupancy H-atom sites, designated H21 and H22, near O1 and O2. Significance testing (Hamilton, 1965) showed that Model *B* afforded significant improvement at the $\alpha = 0.005$ confidence level, and it was adopted.

The maximum effect of extinction was 2.2% of $F_o$ for 101. The maximum positive residual peak was near the midpoint of the central ring bond (C9—C10); the maximum negative peak was near the center of the unsubstituted ring.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1989). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *TEXSAN*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and least-squares-planes data have been deposited with the IUCr (Reference: BK1253). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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