Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Hydrogen bonding and C—H···*X* interactions in 3-fluoro-2-[1-(1-naphthyl)ethyl]benzoic acid

Roger E. Gerkin

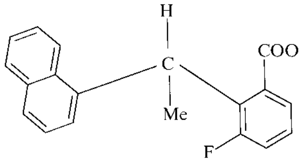
Department of Chemistry, The Ohio State University, Columbus, Ohio 43210, USA
Correspondence e-mail: gerkin@chemistry.ohio-state.edu

Received 15 February 2000
Accepted 5 April 2000

The title acid, $C_{19}H_{15}FO_2$, crystallized in the centrosymmetric space group $P\overline{1}$ with one molecule as the asymmetric unit. There is a single hydrogen bond, with an $O_D\cdots O_A$ distance of 2.632 (2) Å and an $O_D—H\cdots O_A$ angle of 177 (3)°, which forms an $R_2^2(8)$ cyclic dimer about a center of symmetry. There is a single leading intermolecular C—H···*X* interaction, with an H···F distance of 2.49 Å and a C—H···F angle of 147°. Three leading intramolecular C—H···*X* interactions appear to play a significant role in determining the orientation of the methyl and carboxyl groups.

Comment

This report on the title acid, (I), is one of a series on hydrogen bonding in carboxylic acids. It follows a report on the somewhat similar *ortho*-(1-naphthoyl)benzoic acid (Gerkin, 1998). (I) crystallized in the centrosymmetric space group $P\overline{1}$ with one molecule as the asymmetric unit. The refined molecule and the labeling scheme are shown in Fig. 1. In the carboxyl group, the O atoms are ordered, as shown by the carboxyl C—O distances (Table 1), as is the carboxylic H atom. There is a single hydrogen bond in this structure, whose geometric parameters are given in Table 2. This forms a first-level (Bernstein *et al.*, 1995) cyclic dimer, with descriptor $R_2^2(8)$, about a center of symmetry. In addition, there is a single leading intermolecular C—H···*X* interaction and three leading intramolecular C—H···*X* interactions (Taylor & Kennard, 1982; Steiner & Desiraju, 1998), whose geometric parameters are also given in Table 2. The intermolecular C—H···*X* interaction produces, at first level, a *C*(9) chain propagating along [100]. The second-level graph involving the two tabulated intermolecular interactions is a ring, $R_4^4(34)[R_2^2(8)]$. The stereodiagram, Fig. 2, shows a central molecule and the three neighbors to which it is linked directly by these two interactions. Two of the intramolecular C—H···*X* interactions involve the two carboxyl O atoms, whose distances O1—H6, O1—C6, O2—H8, O2—C8 and O2—C2 are less than the corresponding Bondi (1964) van der Waals radius sums. Significantly, a (small) counterclockwise rotation of the carboxyl group about an axis directed from C1 to C7 would reduce each of these deficits without simultaneously causing any of the carboxyl group atoms to move closer than the relevant van der Waals radius sum to any other atoms. [The closest atoms and their present distances are: H12($x-1, y-1, z$), 2.73 Å from H1 and 2.86 Å from O1; and C7($-x, 1-y, 1-z$), 3.34 Å from O2. These distances are, respectively, 0.33, 0.16 and 0.14 Å greater than the corresponding van der Waals sums.] These facts indicate that the C—H···O interactions are, in sum, attractive and significant in determining the dihedral angle between the carboxyl group plane and that of the benzene ring to which it is attached. Thus, the present situation differs from that for 2-nitrobenzaldehyde, for which an attractive C—H···O interaction was excluded (Coppens, 1964). The remaining tabulated intramolecular C—H···*X* interaction in (I) involves the methyl group C atom, C19, H19*B* and F1, and undoubtedly plays a role in determining the observed orientation of the fully refined methyl group.



(I)

The benzene ring in (I) is slightly rumpled, the maximum deviation of any of its atoms from the best-fit plane describing them being 0.026 (2) Å, while the average deviation is 0.018 (9) Å. The dihedral angle between this best-fit plane and that of the carboxyl group is 22.7 (3)°. The naphthalene ring is also slightly rumpled, the maximum deviation of any of its atoms from the best-fit plane describing them being 0.029 (2) Å, while the average deviation is 0.017 (9) Å. The dihedral angle between the planes of the benzene and naphthalene rings is 88.79 (8)°. This near-perpendicularity is apparent in Fig. 2.

Selected distances and angles are given in Table 1. For structural comparisons, two similar 3-fluoroacids are available: 3-fluorobenzoic acid itself [hereafter (II)] (Taga *et al.*, 1985)

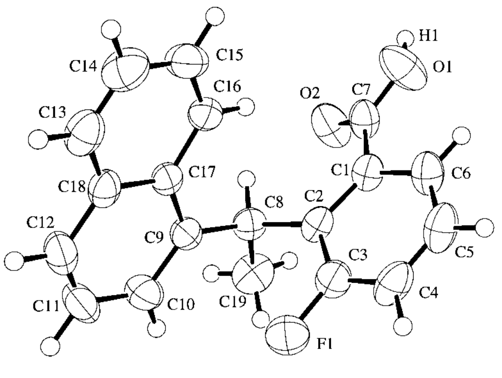


Figure 1
The structure of (I) showing the labeling scheme and displacement ellipsoids at the 50% probability level.

and potassium hydrogen 3-fluorophthalate [hereafter (III)] (Mattes & Dorau, 1986). As expected for benzene rings carrying such substituents, a significant range of benzene C—C distances and C—C—C angles is displayed by these three molecules. The range of C—C distances for the three is very similar: 1.370 (2) to 1.403 (2) in (I), 1.363 (3) to 1.389 (3) in (II) and 1.372 (7) to 1.399 (6) Å in (III). However, the values for corresponding individual bonds differ by as much as 0.021 for (I) *versus* (II) and (III), and by 0.024 Å for (II) *versus* (III). These deviations are undoubtedly due, in part, to the difference in substituents at the 2-position: a substituted ethyl group in (I), an H atom in (II) and a carboxylate ion in (III). Similarly, the most widely different interior ring angle is that at the 2-position: 114.6 (2) in (I), 118.0 (2) and 118.0 (4)° in (II) and (III). The significantly largest interior ring angle occurs at C3, the fluorine-substituted C atom, in each case, being 125.4 (2) in (I), 122.9 (2) and 123.2 (5)° in (II) and (III). The C—F bond distance in (I), 1.364 (2) Å, agrees well with the values 1.358 (3) and 1.369 (5) Å for (II) and (III), and very well with the mean value for C—F distances for monofluoroarenes tabulated by Allen *et al.* (1987), 1.363 (8) Å. Further good agreement among (I), (II) and (III) is seen for the length of the other common bond exterior to the benzene ring, namely C1—C7 (present nomenclature), whose values are 1.487 (2), 1.485 (2) and 1.483 (6) Å, respectively. All remaining distances and angles in (I) fall within normal ranges. Excluding pairs of atoms in hydrogen-bonded carboxyl groups or in the tabulated C—H···*X* interactions, the closest intermolecular approaches are between C5 and H13(x, $y - 1$, z), and are 0.14 Å less than the corresponding Bondi (1964) van der Waals radius sum.

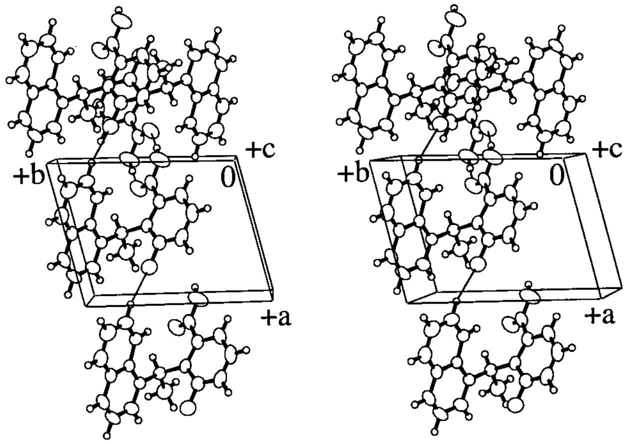


Figure 2
Stereodiagram of (I), with displacement ellipsoids at the 50% probability level. The finer interatomic lines depict the intermolecular interactions given in Table 2.

Experimental

The title acid, whose synthesis is described by Newman & Khanna (1979), was obtained from a sample in Dr M. S. Newman's chemical collection. An irregular chunk found there became the experimental sample.

Crystal data

$C_{19}H_{15}FO_2$
$M_r = 294.32$
Triclinic, $P\overline{1}$
$a = 7.5402$ (6) Å
$b = 10.4339$ (12) Å
$c = 10.8160$ (11) Å
$\alpha = 113.796$ (8)°
$\beta = 91.867$ (8)°
$\gamma = 103.108$ (9)°
$V = 750.92$ (14) Å^3

$Z = 2$
$D_x = 1.302$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 14.4$–17.5°
$\mu = 0.092$ mm^{-1}
$T = 296$ K
Irregular chunk, colorless
0.38 × 0.27 × 0.19 mm

Data collection

AFC-5*S* diffractometer
ω scans
3729 measured reflections
3464 independent reflections
1938 reflections with $I > 2\sigma_I$
$R_{\rm int} = 0.019$
$\theta_{\rm max} = 27.55°$

$h = 0 \rightarrow 9$
$k = -13 \rightarrow 13$
$l = -14 \rightarrow 14$
6 standard reflections every 150 reflections intensity decay: 1.7%

Refinement

Refinement on F^2
$R(F) = 0.050$
$wR(F^2) = 0.067$
$S = 1.70$
3464 reflections
215 parameters

H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2_{\rm cs} + (0.004I)^2]$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.33$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.32$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

F1—C3	1.364 (2)	C1—C7	1.487 (2)
O1—C7	1.302 (2)	C2—C3	1.383 (2)
O2—C7	1.2217 (19)	C3—C4	1.373 (2)
C1—C2	1.403 (2)	C4—C5	1.371 (3)
C1—C6	1.395 (2)	C5—C6	1.374 (2)
C2—C1—C6	121.05 (16)	C1—C6—C5	120.82 (18)
C1—C2—C3	114.57 (16)	O1—C7—O2	121.96 (18)
C2—C3—C4	125.43 (19)	O1—C7—C1	115.07 (18)
C3—C4—C5	118.17 (18)	O2—C7—C1	122.85 (19)
C4—C5—C6	119.73 (18)		

Table 2
Hydrogen-bonding geometry and C—H···O interactions (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O2$^{\rm i}$	1.04 (3)	1.60 (3)	2.632 (2)	177 (3)
C15—H15···F1$^{\rm ii}$	0.98	2.49	3.355 (2)	147
C8—H8···O2	0.98	2.24	2.903 (2)	124
C6—H6···O1	0.98	2.35	2.698 (2)	100
C19—H19*B*···F1	1.03 (2)	2.54 (2)	3.126 (3)	115 (2)

Symmetry codes: (i) $-x, 1 - y, 1 - z$; (ii) $x - 1, y, z$.

COOH and methyl H atoms were refined isotropically; C—H distances were in the range 0.989 (17)–1.026 (17) Å. For calculated H atoms, C—H = 0.98 Å and $U_{\rm iso} = 1.2U_{\rm eq}$ of the bonded C atom.

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: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structure: *TEXSAN*; molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *TEXSAN* and *PLATON* (Spek, 1990).

I acknowledge with pleasure my use of the departmental X-ray crystallographic facility, which is supervised by Dr J. C. Gallucci. The diffractometer system was purchased with funds provided in part by an NIH grant.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1271). Services for accessing these data are described at the back of the journal.

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans.* 2, pp. S1–19.
Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.
Coppens, P. (1964). *Acta Cryst.* **17**, 573–578.
Gerkin, R. E. (1998). *Acta Cryst.* C**54**, 1184–1186.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, TN, USA.
Mattes, R. & Dorau, A. (1986). *Z. Naturforsch. Teil B*, **41**, 808–814.
Molecular Structure Corporation (1988). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Molecular Structure Corporation (1995). *TEXSAN*. Version 1.7-2. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Newman, M. S. & Khanna, V. K. (1979). *Bull. Soc. Chim. Belg.* **88**, 871–873.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Spek, A. L. (1990). *Acta Cryst.* A**46**, C-34.
Steiner, T. & Desiraju, G. R. (1998). *J. Chem. Soc. Chem. Commun.* pp. 891–892.
Taga, T., Yamamoto, N. & Osaki, K. (1985). *Acta Cryst.* C**41**, 153–154.
Taylor, R. & Kennard, O. (1982). *J. Am. Chem. Soc.* **104**, 5063–5070.