

ORGANIC COMPOUNDS

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1,4-Dimethoxy-2-naphthoic Acid

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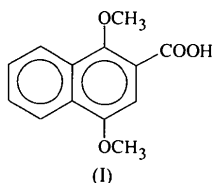
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Abstract

The title compound, $C_{13}H_{12}O_4$, crystallized in the centrosymmetric space group $P2_1/c$ and exhibits cyclic dimer hydrogen bonding about a center of symmetry. The carboxylic H atom is modeled as disordered over two half-occupancy sites. Overall, the hydrogen bonding is little affected by the methoxyl groups and is very similar to that in 2-naphthoic acid.

Comment

This is one of a series of reports on hydrogen bonding in aromatic carboxylic acids and follows our reports on two related acids: 2-naphthoic acid (Fitzgerald & Gerkin, 1993; Blackburn, Fitzgerald & Gerkin, 1996) and 5,8-dimethoxy-1-naphthoic acid (Blackburn & Gerkin, 1997). In partial accord with the suggestion of Leiserowitz (1976) that the uniformity of the carboxylic O-atom environment is conducive to carboxyl-group disordering in benzoic acids, it was determined (Fitzgerald & Gerkin, 1993) that the carboxylic O-atom environment in 2-naphthoic acid is rather uniform and, indeed, the carboxylic H atom is disordered (but the carboxylic O atoms are not, contrary to Leiserowitz). Thus, it was of interest to determine whether the methoxyl groups in 1,4-dimethoxy-2-naphthoic acid, (I), would make the carboxyl O-atom environment sufficiently less uniform to cause ordering of the carboxyl H atom.



In the title acid, the hydrogen bonding is of the cyclic dimer type about a center of symmetry, as shown in Fig. 1. The carboxylic H atom is found to be disordered (as discussed in the *Experimental* section), while the carboxylic O atoms are ordered. As expected for ordered carboxylic O atoms, the principal axes of

their displacement tensors are almost normal to the carboxyl group plane. The bond length and angle values for the carboxyl group (Table 1) are, overall, similar to those for the carboxyl group of 2-naphthoic acid as tabulated by Blackburn, Fitzgerald & Gerkin (1996).

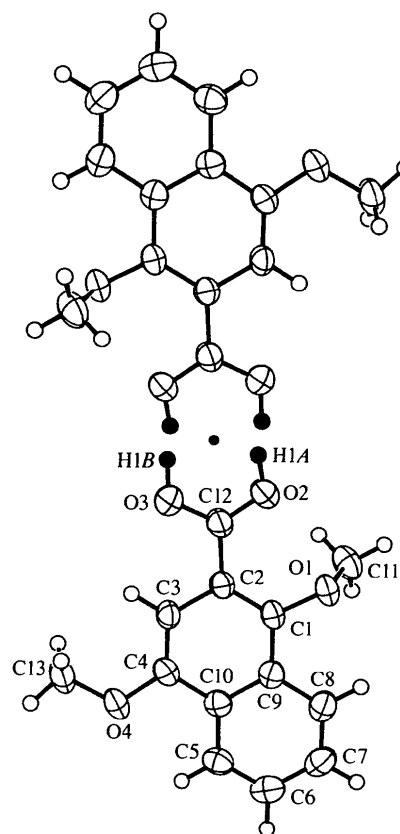


Fig. 1. ORTEP (Johnson, 1976) drawing of the 1,4-dimethoxy-2-naphthoic acid cyclic hydrogen-bonded dimer showing our numbering scheme. Displacement ellipsoids are drawn at the 50% probability level for all atoms except H atoms for which they have been set artificially small. The half-occupancy H atoms and the center of symmetry are shown as filled spheres.

The naphthalene core of the title acid is very nearly planar, the maximum deviation of a core atom from the best-fit plane describing them being 0.010 Å, the average deviation 0.005 Å, with the e.s.d. of the individual differences 0.002 Å. Further, the carboxyl group plane makes a dihedral angle of only 0.6 (3)° with the best-fit core plane and lies approximately 0.026 (2) Å from it. For comparison, in 2-naphthoic acid (Fitzgerald & Gerkin, 1993), the dihedral angle between the core plane and the carboxyl group plane is 1.4 (5)°. Methoxyl group plane C4—O4—C13 makes a dihedral angle of 2.3 (1)° with the core plane; thus, all the non-H atoms

just cited lie nearly in a plane. However, the remaining methoxyl group plane C1—O1—C11 makes a dihedral angle of 85.8 (2)° with the core plane. While the *ortho*-methoxyl group in the structure of *ortho*-methoxybenzoic acid is coplanar with the benzene ring (Parvez, 1987), the nearly perpendicular arrangement of the core plane and that of the *ortho*-methoxyl group in the title molecule is dictated by steric effects involving C8 and H8 from the unsubstituted ring, interactions which are not present in *ortho*-methoxybenzoic acid. Specifically, in the title structure, the C11···C8 separation, even though C11 lies approximately 1.16 Å out of the core plane, is 3.443 (3) Å and thus is only slightly larger than the Bondi (1964) radius sum. At the same time, one of the H atoms on C11, H11, is approximately 2.54 Å from O2, some 0.16 Å less than the corresponding Bondi radius sum. Clearly the observed configuration closely balances these two interactions involving C11, and turning C11 toward the core plane in either direction becomes increasingly unfavorable.

In the title structure, each of the methoxyl groups is intramolecularly slightly crowded by both distance and angular criteria, thus, for example, angles C3—C4—O4 [125.0 (2)°] and C2—C1—O1 [122.9 (2)°] are significantly larger than 120°. Otherwise, intramolecular distances and angles fall within normal ranges. The closest intermolecular approach, excluding pairs of atoms within directly hydrogen-bonded groups, is between a carboxyl O atom, O2, and a methyl group H atom, H12ⁱⁱ [symmetry code: (ii) 1 + x, y - 1, z], and falls short of the Bondi radius sum by 0.14 Å. No other intermolecular approach is significantly less than the corresponding Bondi sum.

Experimental

1,4-Dimethoxy-2-naphthoic acid was obtained as an orange solid from Dr M. S. Newman's chemical collection. This solid was dissolved in ethyl acetate and the solution was treated with Norit-A decolorizing carbon and filtered. Slow evaporation of the filtrate at room temperature produced colorless predominantly rod-shaped crystals, one of which was cut to provide the experimental sample.

Crystal data

C ₁₃ H ₁₂ O ₄	Mo K α radiation
$M_r = 232.24$	$\lambda = 0.71073$ Å
Monoclinic	Cell parameters from 25 reflections
$P2_1/c$	$\theta = 13.3\text{--}14.6^\circ$
$a = 3.971$ (2) Å	$\mu = 0.097$ mm ⁻¹
$b = 8.904$ (2) Å	$T = 296$ K
$c = 31.417$ (2) Å	Cut column
$\beta = 92.84$ (3)°	0.31 × 0.20 × 0.18 mm
$V = 1109.5$ (6) Å ³	Colorless
$Z = 4$	
$D_x = 1.390$ Mg m ⁻³	
D_m not measured	

Data collection

AFC-5S diffractometer	$h = 0 \rightarrow 5$
ω scans	$k = 0 \rightarrow 11$
Absorption correction: none	$l = -40 \rightarrow 40$
3118 measured reflections	6 standard reflections
2736 independent reflections	every 150 reflections
1663 reflections with $I > 0.75\sigma(I)$	intensity variation: $\pm 1.8\%$ (average maximum relative intensity)
$R_{\text{int}} = 0.020$	
$\theta_{\text{max}} = 27.5^\circ$	

Refinement

Refinement on F	Extinction correction: Zachariasen (1963, 1968)
$R = 0.059$	Extinction coefficient: $12(4) \times 10^{-7}$
$wR = 0.053$	Scattering factors from Stewart, Davidson & Simpson (1965) (H) and Cromer & Waber (1974) (C, O)
$S = 1.58$	
1663 reflections	
163 parameters	
H-atom refinement: mixed	
$w = 1/\sigma^2(F)$	
$(\Delta/\sigma)_{\text{max}} < 0.01$	
$\Delta\rho_{\text{max}} = 0.22$ e Å ⁻³	
$\Delta\rho_{\text{min}} = -0.20$ e Å ⁻³	

Table 1. Selected geometric parameters (Å, °)

C12—O2	1.247 (3)	C12—O3	1.270 (2)
C9—C1—O1	116.9 (2)	C2—C12—O2	121.2 (2)
C2—C1—O1	122.9 (2)	C2—C12—O3	117.0 (2)
C3—C4—O4	125.0 (2)	O2—C12—O3	121.8 (2)
C10—C4—O4	114.4 (2)		

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

D—H···A	D—H	H···A	D···A	D—H···A
O2—H1A···O3 [†]	0.89 (6)	1.74 (6)	2.619 (2)	167 (5)
O3—H1B···O2 [†]	0.93 (7)	1.73 (7)	2.619 (2)	159 (6)

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

[†] H1A and H1B are half-occupancy atoms.

Scan widths were $(1.40 + 0.35\tan\theta)^\circ$ in ω , with a background/scan time-ratio of 1:2. The data were corrected for Lorentz and polarization effects. The Laue group assignment, systematic absences and intensity statistics were consistent with centrosymmetry indicated space group $P2_1/c$ (No. 14) and since refinement proceeded well it was adopted. Fourier difference methods were used to locate the initial H-atom positions. In later stages of refinement, atoms H3, H5 and H6—H14 were made canonical with a C—H distance of 0.98 Å and $U_{\text{iso}} = 1.2U_{\text{eq}}$ of the attached C atom. The carboxylic H atom was refined and was modeled in two ways: as a single full-occupancy H atom and as two half-occupancy H atoms. Significance testing (Hamilton, 1965) showed that the latter model was an improvement at the $\alpha = 0.010$ confidence level and it was adopted. The maximum effect of extinction was 6.0% of F_o for 11 $\bar{3}$. The maximum positive residual peak was located near the midpoint of the C4—C10 bond; the maximum negative peak was located near the center of the substituted 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: *SHELXS86* (Sheldrick,

1985). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *TEXSAN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1333). Services for accessing these data are described at the back of the journal.

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2-Aminonicotinic Acid

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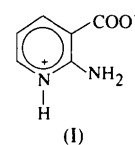
Abstract

2-Aminonicotinic acid, $C_6H_6N_2O_2$, crystallized in the centrosymmetric space group $P2_1/c$ in the zwitterionic form. Intermolecular $N-H\cdots O$ hydrogen bonds with $N\cdots O$ distances of 2.652 (2) and 2.807 (2) Å link molecules into two sets of zigzag chains propagating along the b axis. The two sets of chains are crosslinked by

$C-H\cdots O$ interactions. The dihedral angle between the planes of adjacent molecules in a chain is 9.77 (7)°. An intramolecular $N-H\cdots O$ hydrogen bond is also present.

Comment

This is one of a series of reports on hydrogen bonding in amino-substituted N-heterocyclic carboxylic acids and follows our reports on 3-aminopyrazine-2-carboxylic acid and α - and β -4-aminoquinoline-2-carboxylic acid (Dobson & Gerkin, 1996; Burd, Dobson & Gerkin, 1997). 2-Aminonicotinic acid, (I), crystallized in the centrosymmetric space group $P2_1/c$. In this structure, the molecule occurs as a zwitterion, the carboxyl proton having been transferred to the ring N atom as shown in Fig. 1, which also presents the numbering scheme.



As a consequence, cyclic carboxylic acid group hydrogen-bonded dimers are not possible. However, cyclic hydrogen-bonded dimers are formed which involve the carboxylate group O atoms as acceptors and the ring and amino N atoms as donors. Since in each of these hydrogen-bonded cycles both donors are in one molecule and both acceptors are in a second, the cycles do not occur about centers of symmetry. Since each molecule contains both functionalities, zigzag chains of cyclic hydrogen-bonded molecules can occur and do so, in this case propagating along the b axis as shown in Fig. 2. Two sets of such chains result: one set involves molecules of symmetry types 1 and 2, the

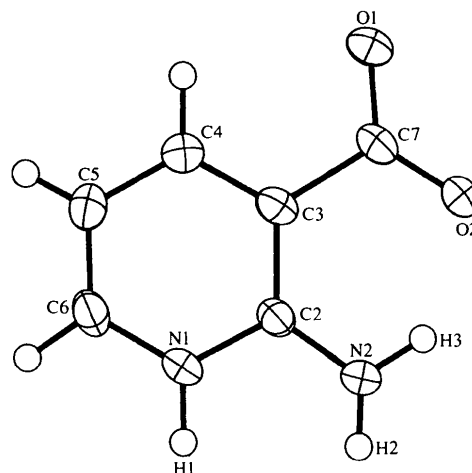


Fig. 1. *ORTEPII* (Johnson, 1976) drawing of 2-aminonicotinic acid showing our numbering scheme. Displacement ellipsoids are drawn at 50% probability for all atoms except H atoms for which they have been set artificially small.