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5,8-Dimethoxy-1-naphthoic Acid and Methyl 5,8-Dimethoxy-1-naphthoate

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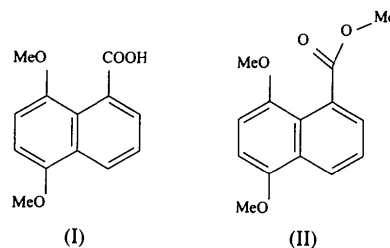
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Abstract

In 5,8-dimethoxy-1-naphthoic acid, $C_{13}H_{12}O_4$, hydrogen bonding is of the cyclic dimer type. The acid H atom is modelled as being distributed equally over two sites. In addition to the conventional hydrogen bonds, there are three significantly attractive C—H \cdots O interactions. The dihedral angle between the naphthalene core plane and the carboxyl plane is $80.0(1)^\circ$. In methyl 5,8-dimethoxy-1-naphthoate, $C_{14}H_{14}O_4$, there are no conventional hydrogen bonds but there are three significantly attractive C—H \cdots O interactions. With the exception of the C—O distances in the carboxyl groups, the molecular geometries of the acid and the ester are quite similar.

Comment

This study of 5,8-dimethoxy-1-naphthoic acid, (I), and its methyl ester, (II), was performed as part of a series of hydrogen-bonding studies of aromatic carboxylic acids. Of particular interest was the comparison of the hydrogen bonding in this acid with that in 1-naphthoic acid as previously determined by Fitzgerald & Gerkin (1993).



In the title acid, (I), the hydrogen bonding is of the cyclic dimer type as shown in Fig. 1(a). Hydrogen-bonding details are given in Table 2. [Neutron-adjusted O—H distances result in H \cdots A distances of 1.67 and 1.69 Å, and D—H \cdots A angles of 176 and 145° for the two hydrogen bonds, respectively.] The donor–acceptor distances are below average for organic O \cdots O hydrogen bonds (2.77 Å; Ceccarelli, Jeffrey & Taylor, 1981). Also as shown in Fig. 1(a), the carboxylic atoms H1 and H2 have been modelled as half-occupancy atoms.

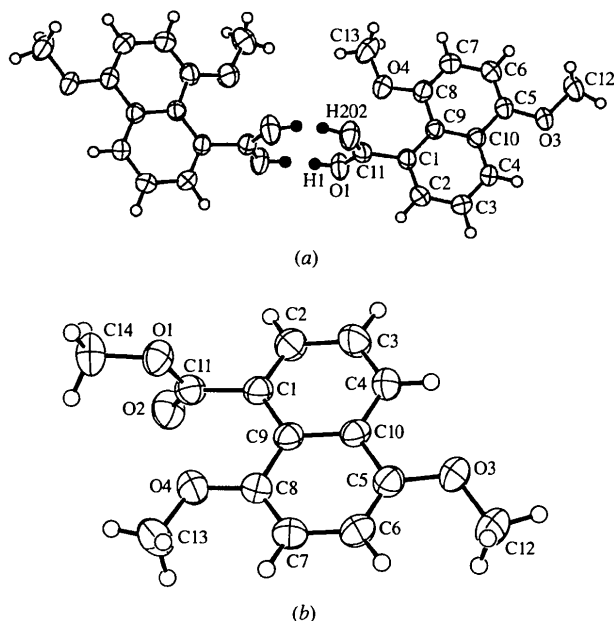


Fig. 1. ORTEPII (Johnson, 1976) drawings of (a) the cyclic hydrogen-bonded dimer of 5,8-dimethoxy-1-naphthoic acid and (b) the methyl 5,8-dimethoxy-1-naphthoate molecule with our numbering scheme. Displacement ellipsoids are drawn for 50% probability for all atoms except H for which they have been set artificially small. In (a), the four half-occupancy acid H atoms are shown as solid circles. The symmetry code relating the second molecule to the base molecule is $x, \frac{1}{2} - y, z$.

This is consistent with complete disorder of the acid H atoms *via* tunneling as seen also, for example, in 1,8-naphthalenedicarboxylic acid (Fitzgerald, Gallucci & Gerkin, 1991). This half-occupancy (disordered H) model for the carboxylic H atoms was shown by Hamilton's ratio test (Hamilton, 1965) to be superior to the full-occupancy (ordered H) model at the $\alpha = 0.01$ confidence level. Further support for this interpretation is afforded by the C—O distances in the carboxyl group [C11—O1 1.258 (2) and C11—O2 1.266 (2) Å], each of which lies well intermediate to C—O single- and double-bond distances. This result contrasts strongly with that for 1-naphthoic acid, in which the C—O bond lengths in the carboxyl group [1.312 (3) and 1.214 (3) Å] are consistent with single and double bonds, respectively, and in which the carboxylic H atom is ordered.

In the title acid, (I), the average deviation of the naphthalene core atoms from the best-fit plane describing them is 0.015 Å (maximum deviation 0.032 Å); the average e.s.d. of individual deviations from the plane is 0.002 Å. The dihedral angles between the core plane and the planes of the carboxyl group, the C5 methoxyl group (C5, O3, C12) and the C8 methoxyl group (C8, O4, C13) are 80.03 (9), 6.7 (2) and 3.3 (2)°, respectively. Thus, the methoxyl groups are roughly coplanar with the core, while the carboxyl plane lies at a substantial angle to the core plane. The substantial angle of the carboxyl group is readily rationalized in terms of non-bonded interactions between methoxyl O atom O4, which must lie near the core plane regardless of the methoxyl group dihedral angle with the core plane, and the carboxyl O atoms. If the carboxyl group were nearly coplanar with the core, one of its O atoms would lie within ~ 1.7 Å of O4 [the corresponding van der Waals radius (Bondi, 1964) sum is 3.0 Å]; in the actual configuration, the distances are 3.070 (2) and 2.912 (2) Å. This arrangement of the carboxyl group contrasts strongly with that in 1-naphthoic acid, for which the corresponding dihedral angle is 8.4 (3)°. The dihedral angles between the base molecule core plane and the core planes of the remaining three translationally inequivalent sets in this structure are 59.79 (4), 22.81 (6) and 64.85 (4)°.

In addition to the conventional hydrogen bonds discussed above, there are three C—H \cdots O interactions in (I) which are significantly attractive according to the criteria of Taylor & Kennard (1982): C2—H2R \cdots O1ⁱⁱ, C13—H13B \cdots O2ⁱⁱⁱ and C4—H4R \cdots O3 (intramolecular) [symmetry codes: (ii) $x - \frac{1}{2}, y, \frac{3}{2} - z$; (iii) $\frac{1}{2} + x, y, \frac{1}{2} - z$]. The C \cdots O distances, 3.487 (3), 3.467 (5) and 2.738 (3) Å, respectively, fall below the middle of Taylor & Kennard's prescribed distance range; the C—H \cdots O angles, 170 (2), 159 (2) and 99 (1)°, respectively, also lie in the prescribed angular range.

Excepting pairs of atoms within the carboxyl groups of a cyclic dimer and pairs of atoms which are both involved in the C—H \cdots O interactions just discussed,

the closest intermolecular approach in the title acid involves C5 and the H atom on a ring atom C6; this distance falls short of the corresponding van der Waals radius (Bondi, 1964) sum by 0.14 Å.

In the structure of (II), there are no conventional hydrogen bonds. Consistent with the criteria of Taylor & Kennard (1982), however, there are three significant C—H \cdots O attractive interactions: C2—H2 \cdots O1^{iv}, C14—H14B \cdots O2^v and C4—H4 \cdots O3 (intramolecular) [symmetry codes: (iv) $x - \frac{1}{2}, \frac{5}{2} - y, z$; (v) $-x, 2 - y, 1 - z$]. The C \cdots O distances, 3.327 (3), 3.545 (4) and 2.738 (3) Å, respectively, fall near or below the middle of Taylor & Kennard's prescribed distance range; the C—H \cdots O angles, 171 (2), 157 (2) and 100 (1)°, respectively, also lie in the prescribed angular range.

The C11—O distances found in the carboxyl group of the title ester clearly indicate a single and a double C—

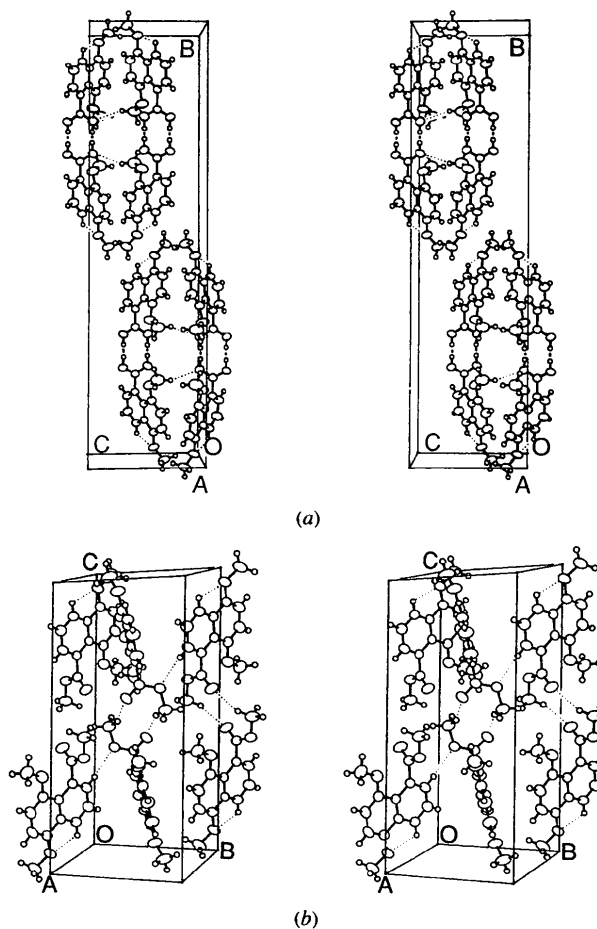


Fig. 2. Packing diagrams of (a) 5,8-dimethoxy-1-naphthoic acid and (b) methyl 5,8-dimethoxy-1-naphthoate drawn using ORTEPII (Johnson, 1976). In these diagrams, dashes indicate conventional hydrogen bonds and dotted lines indicate C—H \cdots O interactions.

O bond; C11—O1 1.333 (3) and C11—O2 1.199 (3) Å. Otherwise, the ester molecular geometry is quite similar to that of the title acid as shown by Figs. 1 and 2, and as discussed below.

In the ester, the average deviation of the naphthalene core atoms from the best-fit plane describing them is 0.007 Å (maximum deviation 0.012 Å); the average e.s.d. of the individual deviations from the plane is 0.003 Å. Thus, the naphthalene core is somewhat nearer planarity in (II). The dihedral angles between the core plane and the planes of the ester group (C11, O1, O2, C14), the C5 methoxyl group (C5, O3, C12) and the C8 methoxyl group (C8, O4, C13) are 86.41 (8), 11.5 (3) and 1.8 (2)°, respectively, quite similar to those in (I). The substantial dihedral angle between the core plane and the ester group plane is consistent with the discussion given above for the acid. The dihedral angle between the two non-parallel sets of planes in this structure is 55.32 (5)°.

Excepting the pairs of atoms both of which are involved in the C—H...O interactions described above, the closest intermolecular approach in (II) involves a ring atom, H3, and a H atom on a methoxyl C atom, C12. This distance falls short of the corresponding van der Waals radius (Bondi, 1964) sum by 0.16 Å. No other approach is significantly less than the corresponding van der Waals radius sum.

No exceptional bond distances or angles were noted.

Experimental

For compound (I), methyl 5,8-dimethoxy-1-naphthoate from Dr M. S. Newman's chemical collection was subjected to alkaline hydrolysis by heating with aqueous NaOH. Treatment of the hydrolysate with aqueous HCl produced a massive white precipitate of the title acid, (I). The precipitate was isolated by filtration, washed with water and air dried. The dried acid was dissolved in ether; evaporation of solvent from the solution at room temperature produced clear, well-faceted tablets, one of which was cut to provide the experimental sample. For compound (II), methyl 5,8-dimethoxy-1-naphthoate was obtained from Dr M. S. Newman's chemical collection as a sample mislabelled as 5,8-dimethoxy-1-naphthoic acid. A crystal from that sample was cut to provide our experimental sample. Upon data collection and analysis, it became clear that our sample was the methyl ester of the acid.

Compound (I)

Crystal data

C₁₃H₁₂O₄
M_r = 232.24
 Orthorhombic
Pnma
a = 7.227 (1) Å
b = 34.729 (2) Å
c = 9.221 (2) Å
V = 2314.3 (6) Å³
Z = 8
D_x = 1.333 Mg m⁻³
D_m not measured

Mo *K*α radiation
 λ = 0.71073 Å
 Cell parameters from 25 reflections
 θ = 14.8–15.9°
 μ = 0.093 mm⁻¹
T = 296 K
 Cut block
 0.35 × 0.31 × 0.31 mm
 Colorless

Data collection

AFC-5S diffractometer
 ω scans
 Absorption correction: none
 3114 measured reflections
 3114 independent reflections
 1675 reflections with $I > \sigma(I)$
 θ_{\max} = 27.5°

h = -9 → 0
k = 0 → 45
l = 0 → 12
 6 standard reflections
 every 150 reflections
 intensity variation: ±2.3%
 (average maximum relative intensity)

Refinement

Refinement on *F*
R = 0.049
wR = 0.036
S = 2.06
 1675 reflections
 207 parameters
 All H atoms refined
 $w = \sigma_F^{-2}$
 $(\Delta/\sigma)_{\max} < 0.01$
 $\Delta\rho_{\max} = 0.17 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.18 \text{ e } \text{Å}^{-3}$

Extinction correction:
 Zachariasen (1963, 1968)
 Extinction coefficient:
 31.2 (9) × 10⁻⁷
 Scattering factors from
 Stewart, Davidson &
 Simpson (1965) for H and
 Cromer & Waber (1974)
 for C and O atoms

Table 1. Selected geometric parameters (Å, °) for (I)

O1—C11	1.258 (2)	O4—C8	1.369 (2)
O2—C11	1.266 (2)	O4—C13	1.415 (4)
O3—C5	1.378 (2)	C1—C11	1.500 (2)
O3—C12	1.426 (3)		
C5—O3—C12	116.9 (2)	O4—C8—C7	124.7 (2)
C8—O4—C13	118.7 (2)	O4—C8—C9	114.1 (2)
C2—C1—C11	115.0 (2)	O1—C11—O2	123.8 (2)
C9—C1—C11	124.0 (2)	O1—C11—C1	119.5 (2)
O3—C5—C6	124.7 (2)	O2—C11—C1	116.4 (2)
O3—C5—C10	114.8 (2)		

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

D—H...A	D—H	H...A	D...A	D—H...A
O1—H1...O1 ⁱ	0.85 (3)	1.84 (3)	2.683 (3)	176 (3)
O2—H2...O2 ⁱ	0.93 (7)	1.77 (8)	2.600 (3)	147 (5)

Symmetry code: (i) $x, \frac{1}{2} - y, z$.

Compound (II)

Crystal data

C₁₄H₁₄O₄
M_r = 246.26
 Monoclinic
P2₁/a
a = 7.707 (2) Å
b = 8.720 (1) Å
c = 18.619 (2) Å
 β = 100.97 (1)°
V = 1228.4 (4) Å³
Z = 4
D_x = 1.331 Mg m⁻³
D_m not measured

Data collection

AFC-5S diffractometer
 ω scans
 Absorption correction: none

h = 0 → 10
k = 0 → 11
l = -24 → 23

Mo *K*α radiation
 λ = 0.71073 Å
 Cell parameters from 25 reflections
 θ = 13.0–15.0°
 μ = 0.091 mm⁻¹
T = 296 K
 Cut plate
 0.27 × 0.27 × 0.12 mm
 Colorless

3241 measured reflections
3024 independent reflections
1499 reflections with
 $I > \sigma(I)$
 $R_{\text{int}} = 0.022$
 $\theta_{\text{max}} = 27.50^\circ$

Refinement

Refinement on F^2
 $R = 0.052$
 $wR = 0.034$
 $S = 1.66$
1499 reflections
220 parameters
All H atoms refined
 $w = \sigma_F^{-2}$
 $(\Delta/\sigma)_{\text{max}} < 0.01$
 $\Delta\rho_{\text{max}} = 0.21 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.21 \text{ e } \text{\AA}^{-3}$

6 standard reflections
every 150 reflections
intensity variation: $\pm 3.0\%$
(average maximum
relative intensity)

Extinction correction:
Zachariasen (1963, 1968)
Extinction coefficient:
 $4.7(12) \times 10^{-7}$
Scattering factors from
Stewart, Davidson &
Simpson (1965) for H and
Cromer & Waber (1974)
for C and O atoms

Table 3. Selected geometric parameters (\AA , $^\circ$) for (II)

O1—C11	1.333 (3)	O3—C12	1.422 (4)
O1—C14	1.450 (3)	O4—C8	1.363 (3)
O2—C11	1.199 (3)	O4—C13	1.421 (4)
O3—C5	1.385 (3)	C1—C11	1.506 (3)
C11—O1—C14	116.3 (2)	O3—C5—C10	114.5 (2)
C5—O3—C12	117.1 (2)	O4—C8—C7	125.6 (3)
C8—O4—C13	117.8 (2)	O4—C8—C9	114.3 (2)
C2—C1—C11	115.6 (2)	O1—C11—O2	123.9 (2)
C9—C1—C11	124.2 (2)	O1—C11—C1	111.1 (2)
O3—C5—C6	124.7 (2)	O2—C11—C1	124.7 (3)

Scan widths were $(1.00 + 0.35 \tan \theta)^\circ$ in ω for (I) and $(1.40 + 0.35 \tan \theta)^\circ$ in ω for (II), with background/scan time-ratios of 0.5. 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 $Pnma$ (No. 62) for (I) and $P2_1/a$ (No. 14) for (II), and since the refinements proceeded well they were adopted. Fourier difference methods were used to locate the H-atom positions. Full-matrix least-squares refinement was performed. In (I), the maximum effect of extinction was 22.2% of F_o for 002. The maximum peak in the final difference map occurred roughly halfway between C1 and C11; the minimum peak occurred near the center of the C1—C4, C9, C10 ring. In (II), the maximum effect of extinction was 2.6% of F_o for 12 $\bar{1}$. The maximum peak in the final difference map occurred $\sim 0.8 \text{ \AA}$ from C5 and C6; the minimum peak occurred near the center of the C1—C4, C9, C10 ring.

For both compounds, 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 structures: *SHELXS86* (Sheldrick, 1985); program(s) used to refine structures: *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: BS1029). Services for accessing these data are described at the back of the journal.

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Anthracene-1-carboxylic Acid

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Abstract

The title compound, C₁₅H₁₀O₂, was found to crystallize in the centrosymmetric space group $P2_1/n$. The hydrogen bonding is of the cyclic dimer type about a center of symmetry. The carboxyl O atoms are ordered as is the carboxyl H atom. The anthracene core, while less nearly planar, shows good agreement with the anthracene cores of anthracene-9-carboxylic acid and anthracene-1,6-dicarboxylic acid. The carboxyl group plane makes a dihedral angle of 12.4 (2) $^\circ$ with the best-fit anthracene core plane.