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5,8-Dimethoxynaphthalene-1,6-dicarboxylic Acid

Roger E. Gerkin

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

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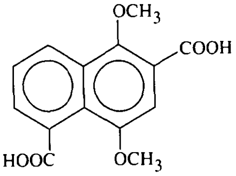
Abstract

The title compound, $C_{14}H_{12}O_6$, crystallized in the centrosymmetric space group *Pbca* but does not exhibit hydrogen bonding of the usual cyclic dimer type about a center of symmetry or otherwise. Each molecule is linked to six neighbors by eight hydrogen bonds, which leads, in this structure, to a rich pattern of chains. Of the nine patterns of chains described, six propagate along the **a** direction, while three propagate along the **c** direction. The $O_{donor}\cdots O_{acceptor}$ distances in these hydrogen bonds are 2.683 (2), 2.706 (2), 3.011 (2) and 3.218 (3) Å. In addition, each C—H group in the molecule is involved in one or more significantly attractive C—H···O interactions, while every O atom is involved in two or more. The two carboxylic H atoms are ordered, as are the carboxylic O atoms.

Comment

This study is one of a continuing series on hydrogen bonding in carboxylic acids and follows reports on two related molecules, 5,8-dimethoxy-1-naphthoic acid and 1,4-dimethoxy-2-naphthoic acid, hereafter D1NA and D2NA, respectively (Blackburn & Gerkin, 1997*a*,*b*). In 5,8-dimethoxynaphthalene-1,6-dicarboxylic acid, (I), the hydrogen bonding is not of the usual cyclic dimer type, differing in this respect from both D1NA and D2NA. The refined molecule and the numbering scheme are shown in Fig. 1. Each molecule is linked to six others by donating four, and accepting four, hydrogen bonds. Geometric details of the hydrogen bonds are given in Table 2 and show that the carboxylic H atoms are ordered. Of the O atoms, only O6 is not involved in a conventional hydrogen bond. For detailed analysis, the hydrogen bonds given in Table 2 are denoted, in the order given in the table, as *a*, *c*, *b* and *d*, respectively; thus, *a* and *b* are the two stronger hydrogen bonds, while *c* and *d* are the two weaker. Hydrogen bonds of type *a* form zigzag chains propagating in the **a** direction. Hydrogen bonds of type *b* also form zigzag chains propagating in the **a** direction. Those of type *c* form zigzag chains propagating in the **c** direction. The results of hydrogen bond graph-set analysis (Bernstein, Davis, Shimoni & Chang, 1995) for the first- and basic second-level graph sets are given in Table 3. In addition to the three chains mentioned above, there are four further chains propagating in the **a** direction and two further chains propagating in the **c** direction.



(I)

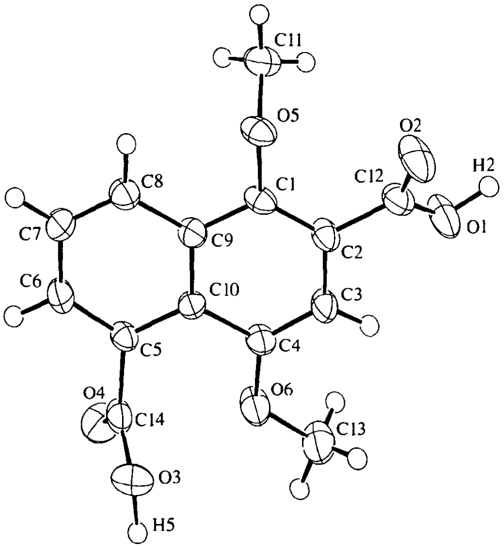


Fig. 1. *ORTEP*II (Johnson, 1976) diagram of (I) showing the molecular numbering scheme. Displacement ellipsoids are drawn at the 50% probability level for all atoms except H atoms, for which they have been set artificially small.

As is not surprising in view of the excess of potential acceptors over O—H donors, 24 significantly attractive C—H···O interactions [according to the criteria of Taylor & Kennard (1982), namely, a $C_d\cdots O_a$ distance of up to 4 Å and a C_d—H···O_a angle of 90° and greater] occur in this structure. Each C—H group is involved in one or more of these interactions, while every O atom is involved in two or more. A table providing the geometric details of these C—H···O interactions is included in the supplementary material.

The most significant aspect of the molecular geometry is perhaps the values of the dihedral angles between, variously, the naphthalene core plane, the carboxyl group planes and the methoxyl group planes. The average deviation of the naphthalene core atoms from the best-fit plane describing them is 0.034 (2) Å, the maximum deviation being 0.059 (2) Å. These deviations are approximately twice as large as the corresponding deviations in D1NA and six times as large as those in D2NA. In the title structure, the dihedral angles between the core plane and the planes of the carboxyl groups, O3—C14—O4 and O1—C12—O2, are 77.3 (1) and 31.8 (1)°, respectively. Intramolecularly speaking, the environment of the O3—C14—O4 carboxyl group is the same as that of the carboxyl group in D1NA and that of the O1—C12—O2 carboxyl group is the same as that of the carboxyl group in D2NA; the corresponding dihedral angles are 80.0 (1) for D1NA and 0.6 (3)° for D2NA. Thus, the agreement is excellent with D1NA but only moderate with D2NA, and intermolecular effects apparently force the poorer agreement for the carboxyl groups at the naphthalene β positions. The dihedral angles between the core plane and the planes of the methoxyl groups, C1—O5—C11 and C4—O6—C13, are 82.6 (2) and 5.4 (2)°, respectively. Again, intramolecularly speaking, the environment of the C1—O5—C11 methoxyl group is like that of the methoxyl group at the 1-position of D2NA, while that of the C4—O6—C13 methoxyl group is like that of the methoxyl group at the 8-position of D1NA, whose planes make dihedral angles with their core planes of 85.8 (2) and 3.3 (2)°. Thus, the agreement is excellent for both methoxyl groups. These results suggest that optimization of hydrogen bonding may be the origin of the poorer agreement noted above for the carboxyl groups at the β positions of the naphthalene cores.

Bond distances and angles of special interest are given in Table 1. These data show that the carboxylic O atoms are ordered. As is apparent from Fig. 1, the principal axes of the carboxylic O atom displacement tensors are almost normal to the carboxyl group planes, as expected for ordered O atoms. The remaining intramolecular distances and angles fall within normal ranges. Ten refined H atoms give C—H distances ranging from 0.94 (2) to 1.02 (2) Å and U_{iso} values ranging from ~0.02 to 0.11 Å^2; the two refined O—H distances appear in Table 2. The closest intermolecular approaches, excluding pairs of atoms in hydrogen-bonded carboxyl groups, are between O4 and C11$^{\text{iv}}$ [symmetry code: (iv) $\frac{1}{2}+x$, y, $-\frac{1}{2}-z$], and are 0.14 Å less than the corresponding Bondi (1964) van der Waals radius sum. No other approach is deficient by more than 0.05 Å.

Experimental

5,8-Dimethoxynaphthalene-1,6-dicarboxylic acid, obtained as a pale ecru crystalline powder from the chemical collection of Dr M. S. Newman, was dissolved in aqueous ethanol. Evaporation of the solution at room temperature produced colorless prisms, one of which was cut to provide the experimental sample.

Crystal data

$C_{14}H_{12}O_6$
$M_r = 276.25$
Orthorhombic
Pbca
$a = 18.012$ (2) Å
$b = 18.039$ (2) Å
$c = 7.579$ (1) Å
$V = 2462.6$ (6) Å^3
$Z = 8$
$D_x = 1.490$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 12.5$–$17.1°$
$\mu = 0.110$ mm^{-1}
$T = 296$ K
Cut prism
0.50 × 0.27 × 0.19 mm
Colorless

Data collection

Rigaku AFC-5*S* diffractometer
ω scans
Absorption correction: none
3255 measured reflections
3255 independent reflections
2844 reflections with $I > 0$
$\theta_{\text{max}} = 27.56°$

$h = 0 \rightarrow 23$
$k = 0 \rightarrow 23$
$l = 0 \rightarrow 9$
6 standard reflections every 150 reflections
intensity variation: ±1.2% (average maximum relative intensity)

Refinement

Refinement on F^2
$R = 0.065$
$wR = 0.059$
$S = 1.58$
2844 reflections
230 parameters
All H atoms refined
$w = 1/(\sigma_{F^2})^2$
$(\Delta/\sigma)_{\text{max}} < 0.01$
$\Delta\rho_{\text{max}} = 0.49$ e Å^{-3}
$\Delta\rho_{\text{min}} = -0.51$ e Å^{-3}

Extinction correction: Zachariasen (1963, 1968)
Extinction coefficient: 6.4 (1) × 10^{-7}
Scattering factors from Stewart, Davidson & Simpson (1965) (H) and Creagh & McAuley (1992) (C and O)

Table 1. *Selected geometric parameters (Å, °)*

O1—C12	1.330 (3)	O5—C1	1.385 (2)
O2—C12	1.210 (2)	O5—C11	1.438 (3)
O3—C14	1.327 (3)	O6—C4	1.361 (2)
O4—C14	1.204 (3)	O6—C13	1.424 (3)
C1—C2—C12	121.8 (2)	O1—C12—C2	112.1 (2)
C3—C2—C12	118.4 (2)	O2—C12—C2	126.0 (2)
C6—C5—C14	117.4 (2)	O3—C14—O4	124.2 (2)
C10—C5—C14	122.1 (2)	O3—C14—C5	111.1 (2)
O1—C12—O2	121.9 (2)	O4—C14—C5	124.4 (2)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H2···O4$^{\text{i}}$	0.99 (3)	1.72 (3)	2.706 (2)	173 (2)
O1—H2···O2$^{\text{ii}}$	0.99 (3)	3.04 (3)	3.218 (3)	91 (2)
O3—H5···O2$^{\text{iii}}$	0.97 (3)	1.82 (3)	2.683 (2)	147 (2)
O3—H5···O5$^{\text{iii}}$	0.97 (3)	2.37 (3)	3.011 (2)	123 (2)

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

Table 3. *First- and basic second-level graph set descriptors involving hydrogen bonds designated a-d as described in the text*

	a	*b*	*c*	*d*
a	$C(10)$	$C_2^2(8)$	$C_2^2(14)$	$C_2^2(10)$
b	–	$C(10)$	$C_2^2(14)$	$C_2^2(18)$
c	–	–	$C(4)$	$C_2^2(16)$
d	–	–	–	D

Scan widths were (1.50 + 0.35tanθ)° in ω, 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 centrosymmetric intensity statistics indicated space group *Pbca* (No. 61). Since refinement proceeded well, it was adopted. Fourier difference methods were used to locate the initial H-atom positions. The maximum effect of extinction was 9.3% of F_o for 002. The maximum positive residual peak was located ~1.5 Å from O2 and the maximum negative peak was located ~1.7 Å from C13.

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: *MITHRIL*84 (Gilmore, 1984). 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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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1083). Services for accessing these data are described at the back of the journal. Least-squares planes data and a list of C—H···O interactions have also been deposited.

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Hydrogen Bonding and Ring Asymmetry in (±)-*cis*-2-Phenylcyclopropanecarboxylic Acid

ROGER E. GERKIN

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

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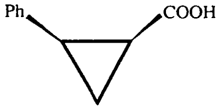
Abstract

The title compound, (±)-*cis*-2-phenylcyclopropanecarboxylic acid, $C_{10}H_{10}O_2$, crystallized in the centrosymmetric space group $P2_1/n$. The hydrogen bonding is of the cyclic dimer type about a center of symmetry; the $O_{donor}\cdots O_{acceptor}$ distance is 2.645 (2) Å. The carboxylic H atom is ordered, as are the O atoms. The cyclopropane ring is asymmetric; the values found for the asymmetry parameters are δ(COOH) = −0.045 (4) Å and δ(phenyl) = −0.027 (4) Å.

Comment

This study of (±)-*cis*-2-phenylcyclopropanecarboxylic acid, (I), is one of a continuing series on hydrogen bonding in carboxylic acids and follows a study of (+)-*trans*-(1*S*,2*S*)-2-phenylcyclopropanecarboxylic acid (Gerkin, 1997). In the title acid, hydrogen bonding is of the cyclic dimer type about a center of symmetry, as shown in Fig. 1, which also presents the adopted numbering scheme. The first-level graph set (Bernstein *et al.*, 1995) is thus $R_2^2(8)$ and there are no higher level sets. Geometric details of the hydrogen bond are given in Table 1. Data presented in Table 1 establish that the carboxylic H atom and the carboxylic O atoms are ordered.



(I)

Additional interest in the title molecule is, as for the *trans* isomer, associated with the determination of substituent-induced bond-length asymmetry in the cyclopropane ring, as discussed in detail by Allen (1980), particularly since there are few characterized structures in which sparsely substituted phenyl groups are substituents. In the present molecule, pronounced bond asymmetry in the cyclopropane ring is again observed: the bond distal to the unsubstituted ring site is longer than each of the two vicinal bonds, which

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