

atom. The average twist is similar to that found in the triphenylcarbenium cation (Gomes de Mesquita, MacGillavry & Eriks, 1965; Krebs & Paulat, 1979) and in derivatives with identical substitution on all three rings (Koh & Eriks, 1971; Andersen & Klewe, 1965).

The unit-cell dimensions of the structures reported here are quite similar, and they have a common space group. The addition of an extra 4-methoxy substituent in (2) makes very little difference to the packing of the ions in the two structures.

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2,6-Dimethoxy-3-nitrobenzoic Acid. A Hydrogen-Bonded Chain Structure

BY GAYLE M. FRANKENBACH,* DOYLE BRITTON AND MARGARET C. ETTER†‡

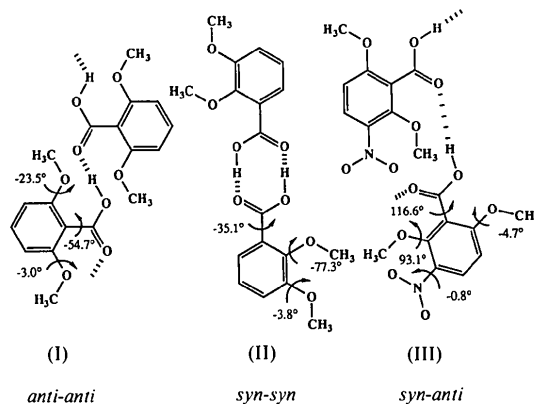
Department of Chemistry, University of Minnesota, 207 Pleasant Street SE, Minneapolis, MN 55455, USA

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Abstract. 2,6-Dimethoxy-3-nitrobenzoic acid, $C_9H_9NO_6$, $M_r = 227.18$, orthorhombic, *Pccn*, $a = 14.837$ (2), $b = 18.096$ (2), $c = 7.501$ (2) Å, $V = 2014$ (1) Å³, $Z = 8$, $D_x = 1.498$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 0.1203$ cm⁻¹, $F(000) = 944$, $T = 300$ K, $R_F = 0.061$, $wR = 0.049$ for 1301 observed reflections with $I > \sigma(I)$. Hydrogen-bonded chains rather than the typical hydrogen-bonded dimer are formed. Glide-related molecules ($x, \frac{1}{2} - y, -\frac{1}{2} + z$) are linked together in extended chains [O...O = 2.668 (2), H...O = 1.86 (4), O—H = 0.84 (3) Å, O—H...O = 160 (3)°]. The carboxyl group is in the *syn* conformation, but the lone pair of electrons acting as the hydrogen-bond acceptor is in an *anti* orientation.

Introduction. As part of an ongoing project directed at designing hydrogen-bonded chains of molecules, we sought to determine whether derivatives of 2,6-dimethoxybenzoic acid (I) would retain the unusual chain pattern manifested in the structure of (I) (Bryan & White, 1982*b*). No other

2,6-dimethoxybenzoic acid crystal structures were found in the literature, although another isomer, 2,3-dimethoxybenzoic acid (II), was found, which crystallizes in the normal acid dimer pattern, (Bryan & White, 1982*a*). In this paper, the crystal structure of 2,6-dimethoxy-3-nitrobenzoic acid (III) is reported and is shown to exist as a hydrogen-bonded chain. The carboxyl group in (III) is found to exist in the *syn* conformation, unlike the carboxyl group in (I), which exists in the *anti* conformation.



* Present address: Chemistry and Materials Science Division, Argonne National Laboratory, Argonne, IL 60349, USA.

† Author to whom correspondence may be directed.

‡ Alfred P. Sloan Fellow, 1989–1991.

Experimental. Compound (III) was purchased from Lancaster Synthesis Ltd and slowly recrystallized at room temperature from a methanol solution. A transparent rod cut to dimensions of $0.25 \times 0.55 \times 0.15$ mm was used for X-ray data collection on an automated Enraf-Nonius CAD-4 diffractometer using graphite-monochromatized Mo $K\alpha$ radiation. Lattice parameters from least-squares analysis of 25 reflections ($8 < \theta < 18^\circ$). Space group from systematic absences ($0kl: l = 2n + 1; h0l: l = 2n + 1; hk0; h + k = 2n + 1$). A total of 3760 reflections were collected at $T = 300$ K over one quadrant ($0 \leq \theta \leq 25^\circ; 0 \leq h \leq 17, 0 \leq k \leq 21, -8 \leq l \leq 8$) using variable-speed ω - 2θ scans; data were averaged to give 1775 unique independent reflections ($R_{\text{int}} = 0.026$) of which 1301 [$I > \sigma(I)$] were used for calculations. No absorption corrections were made. Change in the intensity of three check reflections was less than 2% in 11 h. Structure solved using direct methods and Fourier synthesis (B. A. Frenz & Associates Inc., 1982) then refined by full-matrix least-squares procedure to $R_F = 0.061$, $wR = 0.049$ against 1301 F_{obs} for 158 parameters; the function minimized was $\sum w(|F_o| - |F_c|)^2$, $w = 1/\sigma^2(F)$, calculated from $\sigma^2(I) = \sigma^2(I_c) + (0.05I)^2$, where $\sigma^2(I_c)$ is the standard deviation in I based on counting statistics alone. All non-H atoms were refined anisotropically. Positional parameters and isotropic thermal parameters were refined for HO; all other H atoms were refined isotropically, $S = 1.410$, max. shift/e.s.d. = 0.03. Corrections for extinction were included in the final least-squares refinement. The largest difference from zero on the final difference map was $0.28 \text{ e } \text{\AA}^{-3}$.

Discussion. The labeling scheme of (III) is given in Fig. 1; Table 1* contains the final atomic positional parameters. The hydrogen-bond chains found in the crystal structure are shown in Fig. 2. Hydrogen bonds are formed between glide-related molecules ($x, \frac{1}{2} - y, -\frac{1}{2} + z$). The hydrogen-bond geometry is $\text{O1} \cdots \text{O2} = 2.668$ (2), $\text{HO} \cdots \text{O2} = 1.86$ (4), $\text{O1} - \text{HO} = 0.84$ (3) \AA , $\text{O1} - \text{HO} \cdots \text{O2} = 160$ (3) $^\circ$. The only close contact not involving an H atom occurs between O4 and O5 [3.112 (4) \AA] on glide-related molecules in neighboring hydrogen-bonded chains.

The $\text{O} \cdots \text{O}$ hydrogen-bond distances in (I) [2.673 (5) \AA] and (III) [2.668 (2) \AA] are equivalent. The $\text{O} \cdots \text{O}$ hydrogen-bond distance for (II) [2.631 (2) \AA] is only slightly shorter, indicating that the hydrogen bonds in the dimer of (II) are not

significantly stronger than the hydrogen bonds in the chains of (I) and (III). The methoxy and nitro substituents do not participate in hydrogen bonding in (II) or (III).

Intramolecular bond distances and angles are given in Table 2. The dihedral angle between the plane of the nitro group and the benzene ring is 4.8° . The 6-methoxy group is nearly coplanar with the benzene ring [$\text{C5} - \text{C6} - \text{O6} - \text{C9} = -4.7^\circ$]. The 2-methoxy group, *ortho* to both nitro and acid groups, is rotated out of the plane of the benzene ring [$\text{C3} - \text{C2} - \text{O3} - \text{C8} = 93.1^\circ$]. Steric hindrance of the acid group with its methoxy neighbors, particularly $\text{O3} - \text{C8}$ which is in a *gauche* rather than an *anti* position with respect to the acid, is relieved by a twist of the acid group relative to the benzene ring [$\text{C2} - \text{C1} - \text{C7} - \text{O2} = 116.6^\circ$]. A large torsion angle between the plane of the acid and the benzene ring was also found in the structure of (I) (-54.7°) and another *ortho*-substituted benzoic acid, 2,4,6-trinitrobenzoic acid (78.8°) (Rheingold, Baldacchini & Grote, 1989). Hydrogen-bonded chains rather than dimers were also found in the structures of these two compounds.

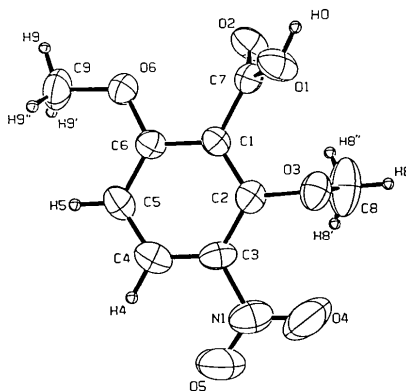


Fig. 1. An ORTEP (Johnson, 1965) drawing of 2,6-dimethoxy-3-nitrobenzoic acid (III) with atomic numbering scheme.

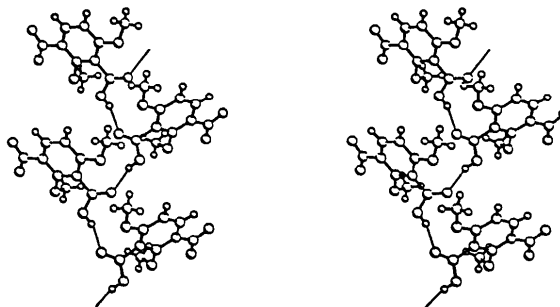


Fig. 2. A stereoview of the hydrogen-bond chains of 2,6-dimethoxy-3-nitrobenzoic acid as found in the crystal structure of (III). The chain extends along [001].

* Lists of structure factors, anisotropic thermal parameters, least-squares planes, torsion angles and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53235 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Final positional parameters with e.s.d.'s in parentheses and equivalent isotropic thermal parameters

	x	y	z	$B_{eq}(\text{\AA}^2)$
C1	0.9396 (2)	0.1275 (1)	0.0387 (3)	3.00 (6)
C2	0.8811 (2)	0.0673 (1)	0.0408 (4)	3.23 (6)
C3	0.9007 (2)	0.0089 (1)	0.1565 (4)	3.57 (6)
C4	0.9758 (2)	0.0110 (2)	0.2640 (4)	4.15 (7)
C5	1.0316 (2)	0.0711 (1)	0.2659 (4)	3.85 (7)
C6	1.0131 (2)	0.1306 (1)	0.1548 (4)	3.23 (6)
C7	0.9249 (2)	0.1889 (1)	-0.0913 (4)	3.23 (6)
O1	0.9340 (2)	0.1673 (1)	-0.2570 (2)	4.39 (5)
O2	0.9076 (1)	0.2517 (1)	-0.0496 (2)	4.44 (4)
O3	0.8095 (1)	0.0682 (1)	-0.0721 (3)	4.07 (4)
C8	0.7304 (2)	0.1027 (2)	-0.0027 (5)	7.3 (1)
N1	0.8438 (2)	-0.0569 (1)	0.1663 (4)	5.19 (6)
O4	0.7813 (2)	-0.0640 (1)	0.0691 (4)	11.96 (8)
O5	0.8608 (2)	-0.1021 (1)	0.2781 (4)	9.06 (8)
O6	1.0626 (1)	0.1926 (1)	0.1455 (3)	4.30 (5)
C9	1.1363 (2)	0.2010 (2)	0.2670 (5)	6.26 (9)

Table 2. Bond lengths (Å) and bond angles (°) with e.s.d.'s in parentheses

C1—C2	1.392 (3)	N1—O5	1.199 (3)
C1—C6	1.397 (3)	O6—C9	1.432 (3)
C1—C7	1.495 (3)	C3—N1	1.461 (3)
C2—C3	1.398 (3)	C4—C5	1.366 (3)
C2—O3	1.359 (3)	C5—C6	1.390 (3)
C3—C4	1.377 (4)	C6—O6	1.343 (3)
O1—HO	0.84 (3)	C7—O1	1.310 (3)
O3—C8	1.427 (3)	C7—O2	1.207 (3)
N1—O4	1.187 (3)		
C2—C1—C6	120.8 (2)	C1—C6—O6	115.4 (2)
C2—C1—C7	119.8 (2)	C5—C6—O6	124.8 (2)
C6—C1—C7	119.4 (2)	C1—C7—O1	112.5 (2)
C1—C2—C3	117.9 (2)	C1—C7—O2	124.2 (2)
C1—C2—O3	118.1 (2)	O1—C7—O2	123.3 (2)
C3—C2—O3	123.9 (2)	C7—O1—HO	115 (3)
C2—C3—C4	120.7 (2)	C2—O3—C8	114.8 (2)
C2—C3—N1	121.8 (3)	C3—N1—O4	120.6 (3)
C4—C3—N1	117.4 (3)	C3—N1—O5	118.0 (3)
C3—C4—C5	121.2 (2)	O4—N1—O5	121.4 (3)
C4—C5—C6	119.4 (2)	C6—O6—C9	118.2 (2)
C1—C6—C5	119.8 (2)		

Structures (I), (II) and (III) have three different hydrogen-bond patterns due to differences in the carboxylic acid conformation and the orientation of the lone pair of electrons acting as hydrogen-bond acceptors. The carboxylic acid groups in (II) and (III) are in the *syn* conformation, while the carboxylic acid in (I) is in the *anti* conformation. In (II), hydrogen bonding occurs at the *syn* lone pair of electrons giving a *syn-syn* hydrogen-bond dimer. Unlike acid dimers, carboxylic acid chains are not restricted to hydrogen bonding in this *syn-syn* mode. Hydrogen bonding in (I) and (III) occurs at the *anti* lone pair of electrons giving an *anti-anti* hydrogen bond in (I) and a *syn-anti* hydrogen bond in (III).

Mono- and dicarboxylic acids with small *R* groups such as formic acid and oxalic acid crystallize in the *syn-anti* hydrogen-bond mode (Leiserowitz, 1976). From force-field calculations, it has been shown that the *syn-anti* hydrogen-bond mode may be more stable than the *syn-syn* because each carboxylic acid is hydrogen bonded to two other acids resulting in two favorable carbonyl-carbonyl and hydroxyl-hydroxyl interactions for each acid (Hagler, Dauber & Lifson, 1979). When a benzoic acid structure is planar, the *anti* lone pair of electrons is sterically hindered. In (III), however, the carboxyl group is rotated out of planarity with the benzene ring allowing *syn-anti* hydrogen bonding to occur.

In (I), the *anti* conformation of the acid may be stabilized by an intramolecular hydrogen bond similar to that found in 2-ethoxybenzoic acid (Gopalakrishna, & Cartz, 1972). The methoxy group is coplanar with the benzene ring but the acid group is twisted 54.7° from the plane, nevertheless the O...O distance is 2.853 Å, and the O—H...O angle is 105.3°. In (III), the acid group is twisted even further from the plane (116.6°) presumably due to increased steric crowding from the tetrasubstituted pattern so no intramolecular hydrogen bond is possible.

Benzoic acids with bulky 2,6-disubstitution patterns prefer to form hydrogen-bonded chains rather than cyclic dimers. If the structure is flexible enough to allow formation of an intramolecular hydrogen bond in the chain, then the acid will have an *anti* conformation. If the acid group is locked in an unfavorable conformation so no intramolecular hydrogen bond can form, the 2,6-disubstituted acids will form *syn-anti* hydrogen-bond chains.

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