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5-Nitroisophthalic acid hydrate

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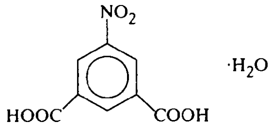
Abstract

In the title compound, $C_8H_5NO_6\cdot H_2O$, the carboxylic acid groups are coplanar with the phenyl ring, whereas the nitro group is twisted from it by 26.1 (3)°. In the crystal, the molecules are linked by O—H···O hydrogen bonds through the water molecules and by weak C—H···O hydrogen bonds involving the nitro groups, to form infinite zigzag sheets.

Comment

Crystal engineering (Desiraju, 1989) offers the opportunity to design and construct solids with a defined architecture (Goswami *et al.*, 1999) from relatively simple starting components. Co-operative non-covalent bonding interactions control the nucleation of supramolecular assemblies which grow into well defined supramolecular arrays (Duchamp & Marsh, 1969) and finally into a macroscopic aggregate, namely, a crystal. Thus, hydrogen-bonding units comprising a sequence of acceptor ($-NO_2$ or $-C{=}O$) and donor ($-NH_2$ or $-OH$) sites have been used to direct the formation of a variety of organic supramolecular entities (Whitesides *et al.*, 1991). The basic motif is an open network comprising rings of three molecules of 5AIPA (5AIPA is 5-aminoisophthalic acid) and three molecules of 5NIPA (5NIPA is 5-nitroaminoisophthalic acid) hydrogen bonded together through pairs of O—H···O and N—H···O hydrogen bonds between two carbonyl groups and between amine nitro groups. In a continuation of this general line of study, the title compound, (I), was studied by X-ray crystallography and the results are presented here.



(I)

The X-ray structure of a water-free pseudo-polymorph of 5NIPA and angular parameters for several substituents of benzene rings, including NO_2 and COOH, were calculated using regression by Colapietro *et al.* (1984). In addition, Domenicano *et al.* (1990) have performed extensive work on substituted benzene derivatives using *ab initio* molecular-orbital calculations,

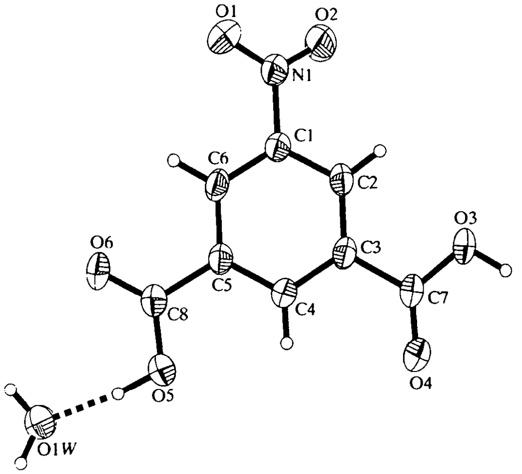


Fig. 1. The structure of (I) showing 50% probability displacement ellipsoids and the atom-numbering scheme. H atoms are drawn as circles of arbitrary radii.

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electron diffraction and comparison with other techniques.

The molecular structure of (I) is shown in Fig. 1. The experimental value [122.8 (2)°] of the internal ring angle at the *ipso* position (C2—C1—C6) in (I) agrees well with values of 122.6 (2)° for 5NIPA (calculated from X-ray data), 122.3° for 5NIPA (from molecular-orbital calculations) and 122.7 (1)° for nitrobenzene in a crystalline environment (Domenicano *et al.*, 1990). The phenyl ring and the substituted carboxylic acid groups are coplanar. The nitro group is twisted away from the phenyl plane and the average torsion angle around the N1—C1 bond is 26.1 (3)°.

In the crystal of (I), the molecules are linked by a number of O—H···O hydrogen bonds involving the water molecules and the acid groups, to form an infinite zigzag sheet-like structure (Fig. 2). The phenyl rings of adjacent sheets are stacked with their centroids 4.741 (3) Å apart, indicating the absence of π–π stacking interactions. This shows that the electronic interaction of the nitro group with the ring occurs primarily at the σ level, with limited transfer of π electrons from the ring to the substituent (Domenicano *et al.*, 1990).

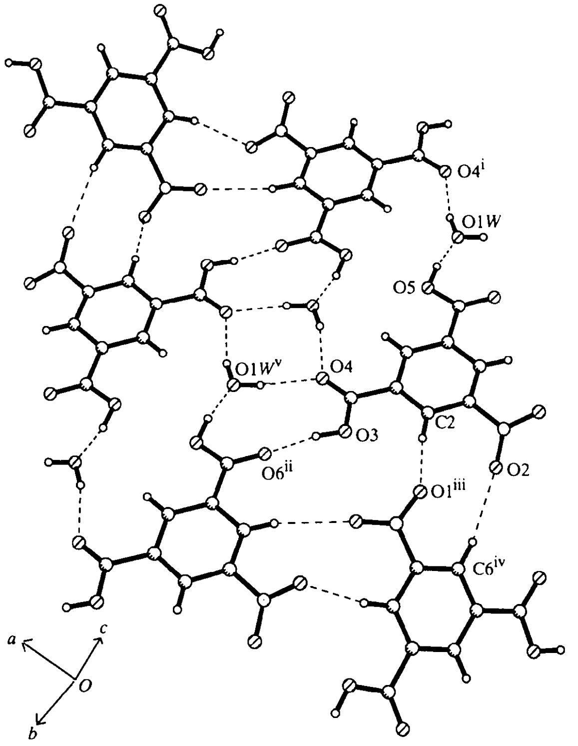

Fig. 2. A view of the hydrogen-bonding network in (I); symmetry codes are as in Table 2.

Experimental

A solution (25 ml) of concentrated nitric acid and concentrated sulfuric acid (3:2) was added dropwise to isophthalic acid (5 g, 30 mmol) at 283 K over a period of 1.5 h. The whole mixture was then heated to 333–343 K with stirring for another 1.5 h. The precipitate was filtered off, washed with ice water and dissolved in an acetone–methanol mixture. The solution was concentrated and the desired pure product was isolated by column chromatography (silica gel) using 3:1 MeOH–EtOAc (yield 4.2 g, 67%).

Crystal data

$C_8H_5NO_6{\cdot}H_2O$
$M_r = 229.15$
Orthorhombic
Pbcn
$a = 28.194\ (1)$ Å
$b = 9.5793\ (4)$ Å
$c = 6.9050\ (3)$ Å
$V = 1864.9\ (1)$ Å^3
$Z = 8$
$D_x = 1.632$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 3787 reflections
$\theta = 1.44$–$28.30°$
$\mu = 0.147$ mm^{-1}
$T = 293\ (2)$ K
Plate
0.36 × 0.26 × 0.06 mm
Colourless

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: none
11 779 measured reflections
2323 independent reflections
1446 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.073$
$\theta_{\rm max} = 28.3°$
$h = 0 \rightarrow 37$
$k = 0 \rightarrow 12$
$l = 0 \rightarrow 9$
Intensity decay: negligible

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.056$
$wR(F^2) = 0.127$
$S = 1.03$
2323 reflections
174 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0353P)^2 + 1.1634P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$

$\Delta\rho_{\rm max} = 0.29$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.20$ e Å^{-3}
Extinction correction: *SHELXTL* (Sheldrick, 1997)
Extinction coefficient: 0.0040 (7)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

O1—N1	1.220 (3)	O5—C8	1.308 (3)
O2—N1	1.223 (3)	O6—C8	1.211 (3)
O3—C7	1.316 (3)	N1—C1	1.474 (3)
O4—C7	1.206 (3)		
O1—N1—C1—C6	26.2 (3)	C2—C3—C7—O3	3.7 (4)
O2—N1—C1—C2	26.1 (3)	C6—C5—C8—O6	−1.6 (4)
C4—C3—C7—O4	4.0 (4)	C4—C5—C8—O5	−2.0 (3)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O5—H1O5···O1*W*	0.96 (4)	1.67 (4)	2.617 (3)	169 (3)
O1*W*—H1*W*1···O4^{i}	0.86 (5)	2.01 (5)	2.863 (3)	170 (4)
O3—H1O3···O6^{ii}	0.92 (4)	1.75 (4)	2.662 (2)	169 (3)
C2—H2···O1^{iii}	0.93 (3)	2.50 (3)	3.391 (3)	160 (2)
C6—H6···O2^{iv}	0.96 (2)	2.50 (2)	3.444 (3)	169 (2)
O1*W*—H2*W*1···O4^{v}	0.86 (5)	2.06 (4)	2.905 (3)	166 (4)

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

All H atoms were located from the difference Fourier map and were refined isotropically; C—H distances are in the range 0.93 (2)–0.96 (2) Å.

Data collection: *SMART* (Siemens, 1996). Cell refinement: *SAINT* (Siemens, 1996). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1301). Services for accessing these data are described at the back of the journal.

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(*E*)-1,2-Bis(3,4-dihydro-1-methoxynaphthalen-2-yl)ethylene

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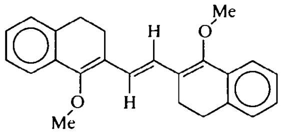
Abstract

In the structure of the title compound, $C_{24}H_{24}O_2$, one of the two types of six-membered rings is planar and the other is in a skew-boat conformation. The ethylene C═C bond distance is 1.345 (3) Å. The substituents at the ethylene are in an *E* configuration. The crystal structure consists of discrete molecules lying about inversion centres, held together by van der Waals contacts.

Comment

Reductive dimerization of carbonyl compounds with the low-valent titanium reagents developed by McMurry & Flaming (1974) has been utilized by synthetic organic chemists. Recently, we have developed a highly stereoselective method for the formation of 1,6-disubstituted 1,3,5-hexatriene derivatives. Use of the technique of reductive dimerization of carbonyl compounds with low-valent titanium reagents to produce stereoselective alkenes is of great use in the synthesis of bioactive molecules, *viz.* retinals and carotenes (Dams & Malinowski, 1982; McMurry *et al.*, 1978). The diastereomeric nature of the new double bond formed during the reaction is dependent on the reagents and reaction conditions. The stereochemistry (*i.e.* whether C1═C10 is *cis* or *trans*) of the title compound, (I), was difficult to assign from ^{1}H NMR data and so determination of the structure by X-ray crystallography was essential.



(I)

The ethylene C═C [C12═C12^i; symmetry code: (i) $2-x$, $-y$, $2-z$] bond distance of 1.345 (3) Å is slightly longer than the reported values of 1.314 (6) Å in unsubstituted ethylene (van Nes & Vos, 1977) and 1.312 Å for a Csp^2—Csp^2 distance of the *trans* type reported in the Cambridge Structural Database (Allen *et al.*, 1987), and is comparable with the value of 1.342 (3) Å for 1,1-bis(*p*-ethoxyphenyl)ethylene reported by Banerjee *et al.* (1985). In the case of polarized ethylenes, an appreciable lengthening of this bond has been reported by Adhikesavalu & Venkatesan (1981, 1982, 1983). The average C—C distance of 1.390 (3) Å within the aromatic ring (*A*) is in agreement with the value of 1.397 Å for $C_{\rm aryl}$—$C_{\rm aryl}$ distances (Allen *et al.*, 1987). The widening of the angle at C12 [125.9 (2)°] may be due to the weak intramolecular C—H···O interaction between H12*A* and O1 [C12···O1 2.809 (2) Å]. The symmetry-related molecule is in an antiperiplanar orientation, with a torsion angle of 180° through the ethylene bond.

The aromatic ring *A* is essentially planar. The total puckering amplitude Q_T (Cremer & Pople, 1975) of 0.439 (2) shows that the non-aromatic ring (*B*) adopts a skew-boat conformation, with O1 and C12 deviating

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