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Hydrogen bonding and C—H···O interactions in 3-(3-aminophthalimido)phthalic acid dihydrate

Allison J. Dobson and Roger E. Gerkin*

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

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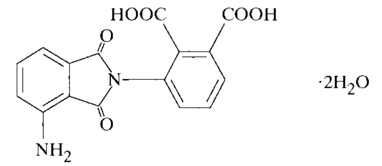
The title compound, $C_{16}H_{10}N_2O_6\cdot 2H_2O$, crystallized in the centrosymmetric triclinic space group $P\overline{1}$ with one organic molecule and two water molecules as the asymmetric unit. Eight intermolecular hydrogen bonds have donor···acceptor distances in the range 2.602 (2)–3.289 (2) Å, with angles in the range 137 (2)–177 (2)°. These generate a three-dimensional hydrogen-bond network. There is a single intramolecular hydrogen bond. There are six significant intermolecular C—H···O interactions with H···O distances in the range 2.39–2.74 Å, and C—H···O angles in the range 131–157°.

Comment

This report is one of a series on hydrogen bonding and C—H···O interactions in carboxylic acids. A definitive synthesis, isolation and characterization of 3-aminophthalic acid by Bogert & Jouard (1909) demonstrated that pure 3-aminophthalic acid is colorless, not yellow as then commonly thought, and that in aqueous solution, even at room temperature, it reacts readily to form a yellow–orange product. They characterized this product, (I), only by its melting point and by its nitrogen content, which they reported as 9.2% [for (I), the theoretical nitrogen content is 7.7%, or, if anhydrous, 8.6%]. Compound (I) was later fully characterized in the work of Fuortes & Gaetani (1962). In the present study, (I) crystallized in the centrosymmetric triclinic space group $P\overline{1}$ with one organic molecule and two water molecules as the asymmetric unit. The refined asymmetric unit and the labeling scheme are given in Fig. 1. One intramolecular and eight intermolecular hydrogen bonds and six leading intermolecular C—H···O interactions (Taylor & Kennard, 1982; Steiner & Desiraju, 1998) are present in (I). The geometric parameters of these are given in Table 2. It may be noted that the hydrogen bonds involving the amino-N atoms, H1N1 and H2N1, are the weakest of those tabulated, but they are the sole intermolecular hydrogen bonds involving these H atoms; moreover, these interactions, together with the intramolecular bond involving H1N1, undoubtedly play a significant role in determining the observed orientation of the amino group. Each acid molecule is linked directly to three neighboring acid molecules and to five neighboring water molecules by these hydrogen bonds, as shown for a central molecule in the stereodiagram (Fig. 2). The results of basic first- and second-level graph-set analysis (Bernstein *et al.*, 1995) involving the intermolecular hydrogen bonds, labeled *a–h* for this purpose in the order of their appearance in Table 2, are given in Table 3. As expected with two water molecules in the asymmetric unit in general positions, finite graphs are very prominent (26 of the 36 entries). The four chains propagate variously along [100], [010] (2) and $[01\overline{1}]$ and suffice to generate a three-dimensional network of interactions. O4 is the only O atom not involved as an acceptor of a (conventional) hydrogen bond (Table 2). Thus, it is not unexpected to find it involved in two significant C—H···O interactions (Table 2). Fig. 1 makes apparent a third-level (adf) ring, $R_3^3(11)$.



(I)

The five-membered ring is in an envelope conformation: the maximum deviation of any of the four 'body' atoms, N2, C1, C2 and C7, from the best-fit plane describing them is 0.000 (2) Å, while the 'flap' atom, C8, is 0.043 (2) Å from that plane.

Selected bond distances and angles are given in Table 1. All distances and angles fall within normal limits. For structural comparisons with (I), *N*-(*o*-nitrophenyl)phthalimide (Voliotis *et al.*, 1984) and *N*-(*o*-tolyl)phthalimide (Bocelli & Cantoni, 1989), each with one phenyl substituent *ortho* to C9, appear well suited. Taking into account that (I) is characterized at 150 K rather than at room temperature, the agreement of the geometries of the five-membered rings in these three compounds is quite satisfactory. Also, for example, the N2—C9 distance (present nomenclature) is 1.441 (2) Å in (I),

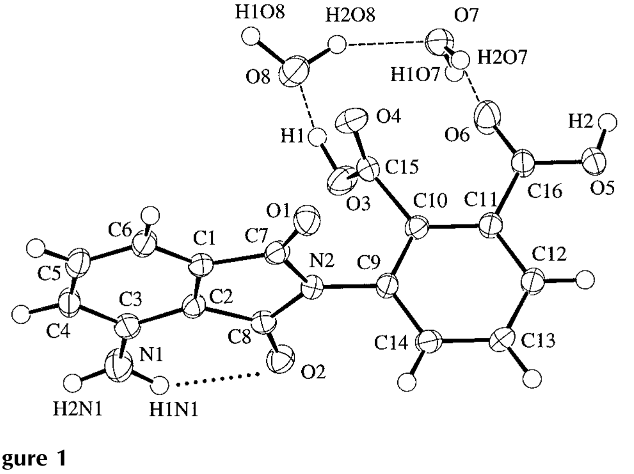


Figure 1
Displacement ellipsoids at the 50% probability level. Intermolecular hydrogen bonds within the asymmetric unit are depicted by dashed lines, the intramolecular bond by a dotted line.

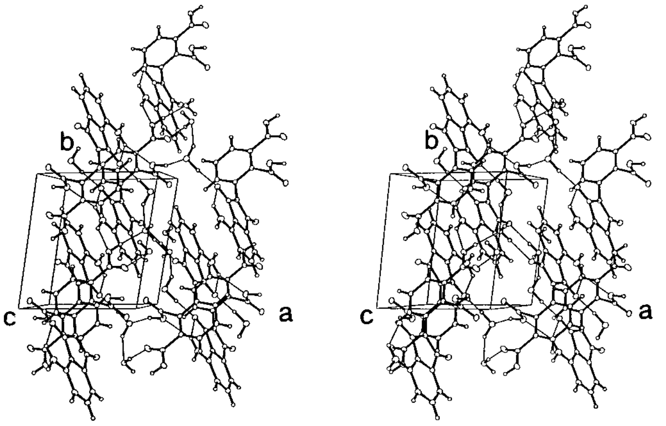


Figure 2
Stereoview of the packing, viewed nearly down the *c* axis toward the origin. Hydrogen bonds are depicted by the finer interatomic lines.

and 1.425 (3) and 1.452 (9) Å in the nitrophenyl and tolyl phthalimides, respectively. The dihedral angles between the phthalimide core plane and the phenyl-ring plane are quite different, however, being 83.5 (1), 54.0 (2) and 70.7 (2)°, respectively. In (I), the closest intermolecular approaches, excluding pairs of atoms involved in hydrogen-bonded groups or in the tabulated C—H···O interactions, are between O2 and O2^{iv} [symmetry code: (iv) $1 - x, 2 - y, 1 - z$] and fall short of the corresponding Bondi (1964) van der Waals radius sum by 0.03 Å.

Experimental

Technical grade 3-aminophthalic acid was obtained from Aldrich Chemical Company as a yellow powder. This was dissolved in water at room temperature, and the solution was filtered. Evaporation of this solution produced suitable crystals of (I) (see *Comment*).

Crystal data

$C_{16}H_{10}N_2O_6 \cdot 2H_2O$
$M_r = 362.30$
Triclinic, $P\overline{1}$
$a = 7.5608$ (2) Å
$b = 9.0632$ (2) Å
$c = 12.7245$ (3) Å
$\alpha = 69.481$ (1)°
$\beta = 82.764$ (1)°
$\gamma = 76.229$ (2)°
$V = 792.29$ (3) Å^3
$Z = 2$
$D_x = 1.519$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 20808 reflections
$\theta = 1.71$–27.50°
$\mu = 0.124$ mm^{-1}
$T = 150$ K
Uncut plate, yellow–orange (golden)
0.31 × 0.23 × 0.08 mm

Data collection

Nonius KappaCCD diffractometer
ω scans with κ offsets
20808 measured reflections
3628 independent reflections
2917 reflections with $I > 2\sigma_I$
$R_{int} = 0.037$
$\theta_{max} = 27.50°$
$h = -9 \rightarrow 9$
$k = -11 \rightarrow 11$
$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
$R(F) = 0.049$
$wR(F^2) = 0.125$
$S = 1.98$
3627 reflections
267 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2_{cs} + (0.037I)^2]$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.59$ e Å^{-3}
$\Delta\rho_{min} = -0.33$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—C7	1.217 (2)	O6—C16	1.214 (2)
O2—C8	1.213 (2)	N1—C3	1.352 (2)
O3—C15	1.323 (2)	N2—C7	1.399 (2)
O4—C15	1.200 (2)	N2—C8	1.415 (2)
O5—C16	1.318 (2)	N2—C9	1.441 (2)
C7—N2—C8	111.1 (1)	O3—C15—O4	125.1 (1)
C7—N2—C9	124.4 (1)	O3—C15—C10	111.9 (1)
C8—N2—C9	124.5 (1)	O4—C15—C10	122.8 (1)
N1—C3—C2	122.6 (2)	O5—C16—O6	122.5 (1)
N1—C3—C4	122.2 (2)	O5—C16—C11	114.9 (1)
O1—C7—N2	124.1 (1)	O6—C16—C11	122.5 (1)
O2—C8—N2	124.1 (1)		

Table 2
Hydrogen bonds and the leading intermolecular C—H···O interactions (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H1···O8	1.02 (3)	1.61 (3)	2.604 (2)	164 (2)
O8—H1O8···O2^{i}	1.09 (3)	1.68 (3)	2.764 (2)	175 (2)
O5—H2···O7^{ii}	0.86 (2)	1.75 (2)	2.602 (2)	169 (2)
O7—H2O7···O6	0.93 (2)	1.87 (2)	2.776 (2)	164 (2)
O7—H1O7···O1^{iii}	0.83 (2)	1.95 (2)	2.782 (2)	177 (2)
O8—H2O8···O7	1.00 (3)	1.98 (3)	2.884 (2)	150 (3)
N1—H1N1···O3^{iv}	0.95 (2)	2.29 (2)	3.059 (2)	137 (2)
N1—H2N1···O5^{v}	0.96 (2)	2.45 (2)	3.289 (2)	147 (2)
N1—H1N1···O2	0.95 (2)	2.41 (2)	3.077 (2)	127 (2)
C14—H14···O4^{vi}	0.98	2.39	3.118 (2)	131
C6—H6···O8^{vii}	0.98	2.48	3.408 (2)	157
C12—H12···O1^{viii}	0.98	2.55	3.285 (2)	132
C5—H5···O4^{ix}	0.98	2.57	3.363 (2)	139
C4—H4···O5^{v}	0.98	2.60	3.438 (2)	144
C13—H13···O6^{vi}	0.98	2.74	3.490 (2)	134

Symmetry codes: (i) $1 + x, y, z$; (ii) $2 - x, 3 - y, -z$; (iii) $x, 1 + y, z$; (iv) $1 - x, 2 - y, 1 - z$; (v) $x, y - 1, 1 + z$; (vi) $x - 1, y, z$; (vii) $x, y - 1, z$; (viii) $1 - x, 2 - y, -z$; (ix) $2 - x, 1 - y, 1 - z$.

Table 3
Basic first- and second-level graph-set descriptors involving interactions designated *a*–*h* in order as given in Table 2.

	a	*b*	*c*	*d*	*e*	*f*	*g*	*h*
a	*D*	$C_2^2(10)$	$D_2^2(10)$	$D_2^2(10)$	$D_2^2(11)$	$D_2^2(5)$	$D_4^4(24)$	$D_3^3(20)$
b		*D*	$D_2^2(12)$	$D_2^2(12)$	$D_2^2(9)$	$D_2^2(5)$	none	$D_3^3(18)$
c			*D*	$R_4^4(12)$	$C_2^2(11)$	$D_2^1(5)$	$D_4^4(30)$	$D_3^3(16)$
d				*D*	$C_2^2(11)$	$D_2^2(5)$	$D_4^4(30)$	$D_3^3(18)$
e					*D*	$D_2^2(5)$	$D_4^4(28)$	$D_3^3(19)$
f						*D*	none	none
g							$R_2^2(20)$	$R_4^4(18)$
h								$C(11)$

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structure: *TEXSAN* (Molecular Structure Corporation, 1995); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *TEXSAN* and *PLATON* (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1528). Services for accessing these data are described at the back of the journal.

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