

4-Iodoanilinium 3-nitrophthalate(1-): tripartite sheets built from O—H···O and N—H···O hydrogen bonds

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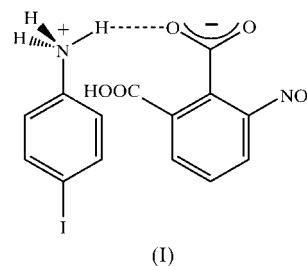
In the title compound, 4-iodoanilinium 2-carboxy-6-nitrobenzoate, $C_6H_7IN^+ \cdot C_8H_4NO_6^-$, the anions are linked by an O—H···O hydrogen bond [$H \cdots O = 1.78 \text{ \AA}$, $O \cdots O = 2.614 (3) \text{ \AA}$ and $O-H \cdots O = 171^\circ$] into $C(7)$ chains, and these chains are linked by two two-centre N—H···O hydrogen bonds [$H \cdots O = 1.86$ and 1.92 \AA , $N \cdots O = 2.700 (3)$ and $2.786 (3) \text{ \AA}$, and $N-H \cdots O = 153$ and 158°] and one three-centre N—H···(O)₂ hydrogen bond [$H \cdots O = 2.02$ and 2.41 \AA , $N \cdots O = 2.896 (3)$ and $2.789 (3) \text{ \AA}$, $N-H \cdots O = 162$ and 105° , and $O \cdots H \cdots O = 92^\circ$], thus forming sheets containing $R_2^2(6)$, $R_4^2(8)$, $R_3^3(13)$ and $R_4^4(18)$ rings.

Comment

The reaction of anilines with phthalic anhydrides under anhydrous conditions generally yields *N*-arylphthalimides, but in the presence of water, anilinium salts can be formed. We report here the molecular and supramolecular structure of the title compound, (I), in which the ionic components are linked into hydrogen-bonded sheets. Compound (I) is a salt, $IC_6H_4NH_3^+ \cdot C_6H_3(COOH)(COO)(NO_2)^-$, in which there has been complete transfer to the amine of the H atom of the carboxyl group adjacent to the nitro substituent (Fig. 1).

The nitro group is almost coplanar with the adjacent aryl ring, but the carboxylate substituent lying between the nitro group and the un-ionized carboxyl substituent is nearly orthogonal to the plane of the adjacent ring, with a dihedral angle between the C1—C6 and C2/C21/O21/O22 mean planes of $80.4 (4)^\circ$. For the un-ionized carboxyl group, the dihedral angle between the C1—C6 and C1/C11/O11/O12 planes is only $26.7 (2)^\circ$. The rotation of the carboxylate substituent on atom

C2 can be ascribed to steric congestion, which would result from three adjacent substituents if all were coplanar with the aryl ring; even so, there is evidence in the exocyclic bond angles at atoms C1 and C3 of some steric compression, as the C2—C1—C11 and C2—C3—N31 angles are both significantly larger than 120° , while the C6—C1—C11 and C4—C3—N31 angles are both much smaller than 120° (Table 1). In addition, the exocyclic C1—C11, C2—C21 and C3—N31 distances are all larger than the upper-quartile values for bonds of these types (1.491 , 1.512 and 1.476 \AA , respectively; Allen *et al.*, 1987). The C—O distances in the anion are fully consistent with the location of the H atoms as deduced from difference maps, and the O—C—O angle in the ionized carboxylate group is significantly larger than that in the un-ionized substituent.



The ions are linked by O—H···O and N—H···O hydrogen bonds into sheets. In the asymmetric unit (Fig. 1), the ions are linked by an N—H···O hydrogen bond, which can be regarded as the shorter and stronger component of a three-centre N—H···(O)₂ system (Table 2), in which the sum of the angles at H1A is 359° . The analysis and description of the supramolecular structure are most readily approached in terms of the one-dimensional substructure generated by the anions. Carboxyl atom O12 in the anion at (x, y, z) acts as a hydrogen-bond donor to carboxylate atom O22 in the anion at $(1-x, -\frac{1}{2}+y, \frac{1}{2}-z)$, so producing a $C(7)$ chain (Bernstein *et al.*, 1995) running parallel to the $[010]$ direction and generated by the 2_1 screw axis along $(\frac{1}{2}, y, \frac{1}{4})$ (Fig. 2). A second chain of

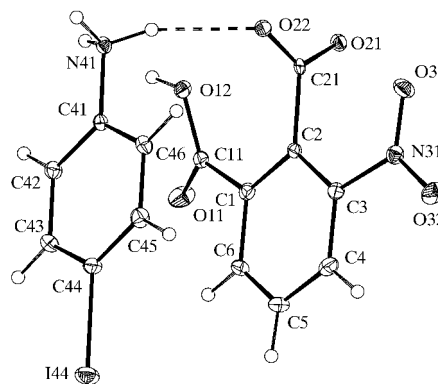


Figure 1

The independent components of compound (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

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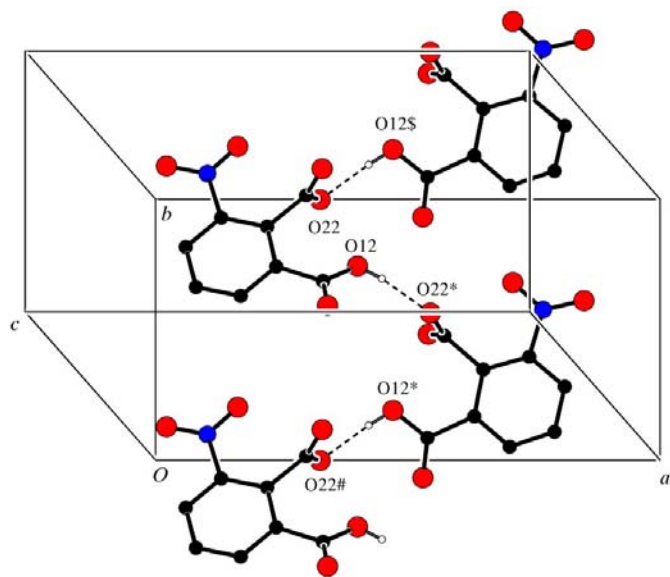


Figure 2

Part of the crystal structure of (I), showing the formation of a $C(7)$ chain of anions. For clarity, H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (*), a hash (#) or a dollar sign (\$) are at the symmetry positions $(1-x, -\frac{1}{2}+y, \frac{1}{2}-z)$, $(x, -1+y, z)$ and $(1-x, \frac{1}{2}+y, \frac{1}{2}-z)$, respectively.

this type, antiparallel to the first and related to it by inversion, is generated by the 2_1 axis along $(\frac{1}{2}, -y, \frac{3}{4})$. The $[010]$ chains are linked into sheets by the cations.

Ammonium atom N41 in the cation forms $N-H \cdots O$ hydrogen bonds to four different anions, which themselves lie in two different $[010]$ chains. Atom N41 at (x, y, z) acts as a hydrogen-bond donor, *via* atom H41A, to atom O22 in the anion at (x, y, z) and (more weakly) to atom O11 in the anion at $(1-x, \frac{1}{2}+y, \frac{1}{2}-z)$, and, *via* atom H41C, to atom O21 in the anion at $(1-x, -\frac{1}{2}+y, \frac{1}{2}-z)$. These three anions all lie in the $C(7)$ anion chain along $(\frac{1}{2}, y, \frac{1}{4})$. In addition, atom N41 at (x, y, z) acts as a donor, *via* atom H41B, to atom O21 in the anion at $(x, \frac{3}{2}-y, -\frac{1}{2}+z)$, which is a component of the anion chain along $(\frac{1}{2}, -y, -\frac{1}{4})$. Propagation by the space group of these hydrogen bonds thus links together all of the anion chains

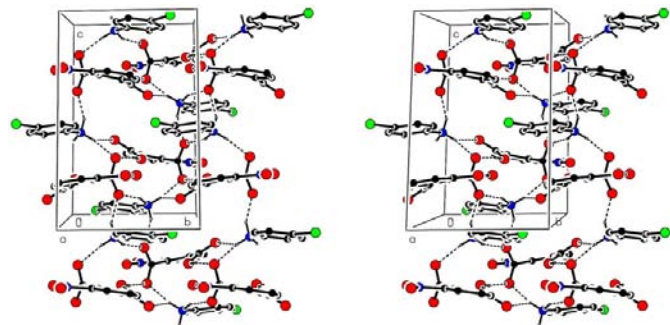


Figure 3

A stereoview of part of the crystal structure of (I), showing the formation of a (100) sheet. For clarity, H atoms bonded to C atoms have been omitted.

generated by 2_1 screw axes having $x = \frac{1}{2}$, so forming a tripartite (100) sheet in which the $-NH_3^+$, $-COOH$ and $-COO^-$ functions lie in the central layer, with the iodophenyl and nitroaryl units forming the two outer layers (Fig. 3). Note that, although the two O atoms of the ionized carboxylate group, namely O21 and O22, both act as double acceptors of hydrogen bonds, neither of the O atoms in the nitro group plays any role in the supramolecular aggregation.

The complexity of the hydrogen bonding in the (100) sheet is illustrated by the occurrence of four distinct types of ring motif within the sheet. The three-centre $N-H \cdots (O)_2$ hydrogen bond involving atom H41A represents a two-point attachment of the cation to an anion chain, producing an $R_2^2(6)$ motif (Bernstein *et al.*, 1995) that also involves atom H12 (Fig. 3). Hydrogen bonds involving atoms H41A and H41B generate centrosymmetric $R_4^4(18)$ rings, centred at $(\frac{1}{2}, 1, 0)$ and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$; hydrogen bonds involving atoms H41B and H41C generate centrosymmetric $R_4^2(8)$ rings centred at $(\frac{1}{2}, \frac{1}{2}, 0)$ and $(\frac{1}{2}, 1, \frac{1}{2})$; and hydrogen bonds involving atoms H41C and H41A generate $R_3^3(13)$ rings, which form chains of edge-fused rings along $[010]$.

There is only one contact of possible significance between adjacent (100) sheets. Atoms I44 at (x, y, z) and $(-x, -y, -z)$ are separated by 3.541 (3) Å and the $C-I \cdots I(-x, -y, -z)$ angle is 149.1 (2)°. Adopting the lower limit (1.95 Å) of the van der Waals radii for I as given by Bondi (1964), this contact appears to be very short. However, the polar flattening model (Nyburg & Faerman, 1985) developed from an extensive analysis of structures from the Cambridge Structural Database (Allen, 2002) gives a 'minor radius' for I of only 1.76 Å, indicating that the limiting $I \cdots I$ distance for near linear approaches is almost identical to the separation observed here. Hence we do not regard this $I \cdots I$ contact either as anomalously short or as having structural significance.

Experimental

Equimolar quantities of 4-iodoaniline and 3-nitrophthalic anhydride were heated together in the presence of excess water. After cooling the mixture to ambient temperature, crystallization from ethanol provided crystals of (I) suitable for single-crystal X-ray diffraction.

Crystal data

$C_6H_7IN^+ \cdot C_8H_4NO_6^-$
 $M_r = 430.15$
 Monoclinic, $P2_1/c$
 $a = 14.7434$ (5) Å
 $b = 8.1274$ (2) Å
 $c = 13.2487$ (4) Å
 $\beta = 106.7116$ (12)°
 $V = 1520.48$ (8) Å³
 $Z = 4$

$D_x = 1.879$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 3460 reflections
 $\theta = 3.1$ – 27.5°
 $\mu = 2.14$ mm⁻¹
 $T = 120$ (2) K
 Block, colourless
 $0.32 \times 0.20 \times 0.18$ mm

Data collection

Nonius KappaCCD diffractometer
 φ scans, and ω scans with κ offsets
 Absorption correction: multi-scan (DENZO-SMN; Otwinowski & Minor, 1997)
 $T_{\min} = 0.532$, $T_{\max} = 0.678$
 17 530 measured reflections

3460 independent reflections
 2898 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.051$
 $\theta_{\text{max}} = 27.5^\circ$
 $h = -19 \rightarrow 19$
 $k = -10 \rightarrow 10$
 $l = -17 \rightarrow 17$

Table 1

Selected geometric parameters (Å, °).

C1—C11	1.509 (4)	C2—C21	1.530 (3)
C11—O11	1.205 (3)	C21—O21	1.252 (3)
C11—O12	1.322 (3)	C21—O22	1.259 (3)
C3—N31	1.483 (3)		
C6—C1—C2	120.5 (2)	C2—C3—C4	123.8 (2)
C2—C1—C11	124.7 (2)	C2—C3—N31	120.3 (2)
C6—C1—C11	114.8 (2)	C4—C3—N31	115.7 (2)
C1—C2—C3	116.0 (2)	O11—C11—O12	123.8 (3)
C1—C2—C21	120.8 (2)	O21—C21—O22	126.2 (2)
C3—C2—C21	123.2 (2)		
C2—C1—C11—O11	155.1 (3)	C2—C3—N31—O31	2.5 (4)
C1—C2—C21—O21	−78.9 (3)		

Table 2

Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O12—H12 \cdots O22 ⁱ	0.84	1.78	2.614 (3)	171
N41—H41A \cdots O22	0.91	2.02	2.896 (3)	162
N41—H41A \cdots O11 ⁱⁱ	0.91	2.41	2.789 (3)	105
N41—H41B \cdots O21 ⁱⁱⁱ	0.91	1.86	2.700 (3)	153
N41—H41C \cdots O21 ⁱ	0.91	1.92	2.786 (3)	158

Symmetry codes: (i) $1-x, y-\frac{1}{2}, \frac{1}{2}-z$; (ii) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$; (iii) $x, \frac{3}{2}-y, z-\frac{1}{2}$.**Refinement**

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.029$
 $wR(F^2) = 0.068$
 $S = 1.03$
 3460 reflections
 210 parameters
 H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0247P)^2 + 2.0308P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 1.11 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.75 \text{ e } \text{Å}^{-3}$

Crystals of (I) are monoclinic and the space group $P2_1/c$ was assigned uniquely from the systematic absences. All H atoms were

located from difference maps and were subsequently treated as riding atoms, with C—H distances of 0.95 Å, N—H distances of 0.91 Å and O—H distances of 0.84 Å.

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1653). Services for accessing these data are described at the back of the journal.

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