

3-Iodoanilinium 2-carboxy-6-nitrobenzoate: a three-dimensional framework built from O—H···O and N—H···O hydrogen bonds and a two-centre iodo–nitro interaction

Christopher Glidewell,^{a*} John N. Low,^b Janet M. S. Skale^b and James L. Wardell^c

^aSchool of Chemistry, University of St Andrews, Fife KY16 9ST, Scotland,

^bDepartment of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen AB24 3UE, Scotland, and ^cInstituto de Química, Departamento de Química Inorgânica, Universidade Federal do Rio de Janeiro, 21945-970 Rio de Janeiro, RJ, Brazil

Correspondence e-mail: cg@st-andrews.ac.uk

Received 22 February 2005

Accepted 24 February 2005

Online 18 March 2005

In the title compound, $C_6H_7IN^+ \cdot C_8H_4NO_6^-$, the anions are linked by a single type of O—H···O hydrogen bond into $C(7)$ chains, and these chains are linked *via* three independent N—H···O hydrogen bonds into sheets. The sheets, in turn, are linked by a two-centre iodo–nitro interaction into a single three-dimensional framework.

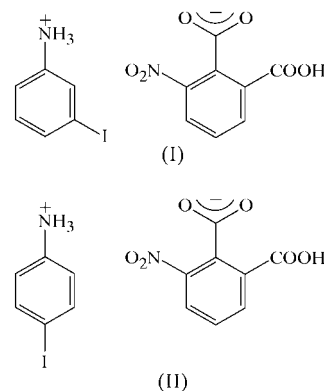
Comment

We report here the molecular and supramolecular structure of the title compound, (I), and compare it with the isomeric 4-iodoanilinium 2-carboxy-6-nitrobenzoate, (II) (Glidewell *et al.*, 2003). Compound (I) is a salt; the H atoms are all fully ordered, and the C—O distances (Table 1) in both the unionized carboxyl group and the anionic carboxylate group are fully consistent with the H-atom locations found from difference maps. Of the three adjacent substituents in the anion, the central carboxylate group is nearly orthogonal to the ring, while the two outer substituents show much smaller rotations about the exocyclic bonds away from planarity, as shown by the key torsion angles (Table 1); these observations can be ascribed to steric congestion.

The supramolecular structure of (I) (Fig. 1) contains hydrogen-bonded sheets, which are linked into a continuous three-dimensional framework structure by a two-centre iodo–nitro interaction. The formation of the hydrogen-bonded sheet is most readily analysed in terms of the low-dimensional substructures from which it is generated.

The anions are linked by a single O—H···O hydrogen bond (Table 2) to form chains running parallel to the [010] direction. Carboxyl atom O12 in the anion at (x, y, z) acts as a hydrogen-

bond donor to carboxylate atom O21 in the anion at $(1 - x, \frac{1}{2} + y, \frac{3}{2} - z)$, so forming a $C(7)$ chain (Bernstein *et al.*, 1995) of anions generated by the 2_1 screw axis along $(\frac{1}{2}, y, \frac{3}{4})$ (Fig. 2). A second anion chain, antiparallel to the first and related to it by inversion, is generated by the 2_1 screw axis along $(\frac{1}{2}, -y, \frac{1}{4})$, and these chains are linked by N—H···O hydrogen bonds into (100) sheets.



Anilinium atom N41 acts as a hydrogen-bond donor, *via* H41A, to carboxylate atom O22 within the asymmetric unit (Fig. 3); in addition, atom N41 in the cation at (x, y, z) acts as a donor, *via* H41B, to carboxylate atom O21 in the anion at $(x, \frac{3}{2} - y, -\frac{1}{2} + z)$. Propagation of these two N—H···O hydrogen bonds then produces a $C_2^2(6)$ chain running parallel to the [001] direction and generated by the *c*-glide plane at $y = \frac{3}{4}$ (Fig. 3). Since the anions at (x, y, z) and $(x, \frac{3}{2} - y, -\frac{1}{2} + z)$ form parts, respectively, of the anion chains along $(\frac{1}{2}, y, \frac{3}{4})$ and $(\frac{1}{2}, -y, \frac{1}{4})$, these three hydrogen bonds, one O—H···O and two N—H···O, suffice to form a (100) sheet. In the third N—H···O hydrogen bond, atom N41 in the cation at (x, y, z) acts as a donor, *via* H41C, to carboxylate atom O22 in the anion at $(1 - x, 1 - y, 1 - z)$, so generating a centrosymmetric $R_4^2(8)$ ring (Fig. 4), which serves further to reinforce the sheet. It is

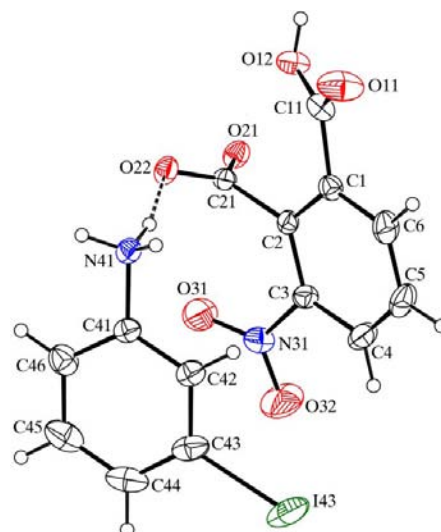


Figure 1
The independent components of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

notable that the O atoms of the nitro group play no part in the hydrogen bonding.

Just a single (100) sheet passes through each unit cell and it is tripartite in form, with a central polar layer containing the hydrogen bonds linking the $-\text{NH}_3^+$, $-\text{COO}^-$ and $-\text{COOH}$ units, and with two outer layers containing the iodophenyl and nitrophenyl units. The location of both the iodo and the nitro substituents on the outer faces of this tripartite layer allows the formation of iodo–nitro interactions, which link adjacent sheets.

Atom I43 in the cation at (x, y, z) lies in the (100) sheet centred at $x = \frac{1}{2}$; this atom forms a two-centre iodo–nitro

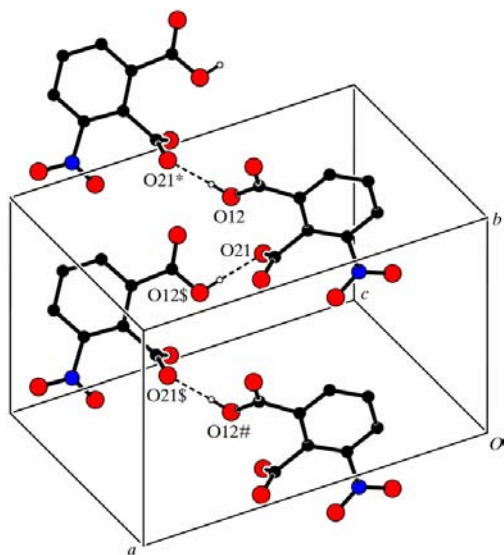


Figure 2

Part of the crystal structure of (I), showing the formation of a hydrogen-bonded $C(7)$ chain of anions along [010]. 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 $(1 - x, \frac{1}{2} + y, \frac{3}{2} - z)$, $(x, -1 + y, z)$ and $(1 - x, -\frac{1}{2} + y, \frac{3}{2} - z)$, respectively.

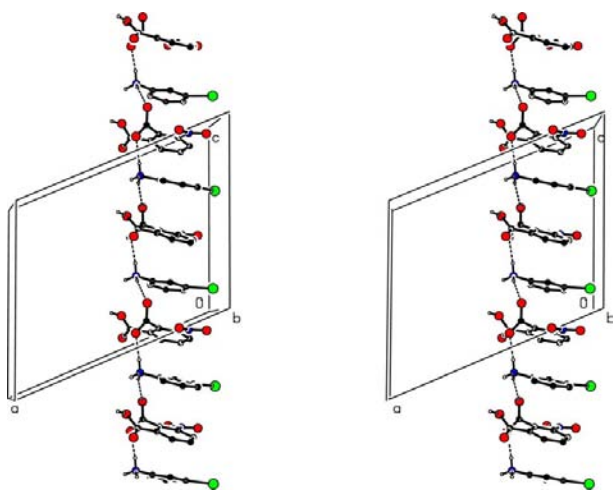


Figure 3

A stereoview of part of the crystal structure of (I), showing the formation of a hydrogen-bonded $C(6)$ chain along [001]. For clarity, H atoms bonded to C atoms have been omitted.

interaction with nitro atom O32 in the anion at $(-x, \frac{1}{2} + y, \frac{1}{2} - z)$ [$\text{I} \cdots \text{O}^{\text{iv}} = 3.423(4) \text{ \AA}$, $\text{C}-\text{I} \cdots \text{O}^{\text{iv}} = 166.1(2)^\circ$ and $\text{I} \cdots \text{O}^{\text{iv}} - \text{N}^{\text{iv}} = 141.4(3)^\circ$; symmetry code: (iv) $-x, \frac{1}{2} + y, \frac{1}{2} - z$], so producing a $C_2^2(12)$ chain (Bernstein *et al.*, 1995; Starbuck *et al.*, 1999) running parallel to the [010] direction (Fig. 5). The anion at $(-x, \frac{1}{2} + y, \frac{1}{2} - z)$ forms part of the (100) sheet centred at $x = -\frac{1}{2}$, and propagation by inversion of this iodo–nitro interaction thus links each sheet to the two adjacent sheets, hence forming a single three-dimensional framework structure.

The only possible π – π stacking interaction in the structure of (I) is, at best, a weak one and, in any event, it lies within the hydrogen-bonded sheet. The aryl rings of the anion at (x, y, z) and the cation at $(x, \frac{3}{2} - y, \frac{1}{2} + z)$ have a ring-centroid separation of $3.760(2) \text{ \AA}$; in addition, the dihedral angle between the ring planes is $8.4(2)^\circ$ and the interplanar spacing is *ca* 3.65 \AA , corresponding to a centroid offset of *ca* 0.88 \AA .

The supramolecular structure of (I) may be compared with that of its isomer (II). In (II), the anions again form $C(7)$

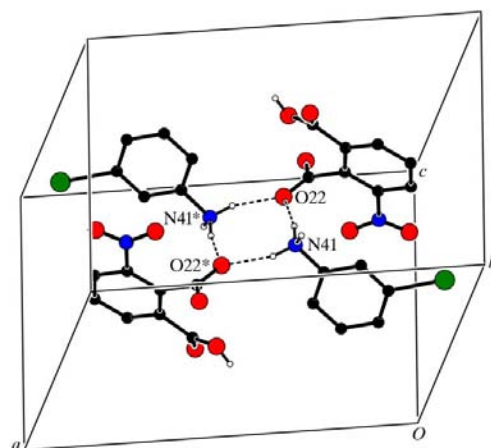


Figure 4

Part of the crystal structure of (I), showing the formation of a hydrogen-bonded $R(8)$ ring. For clarity, H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (*) are at the symmetry position $(1 - x, 1 - y, 1 - z)$.

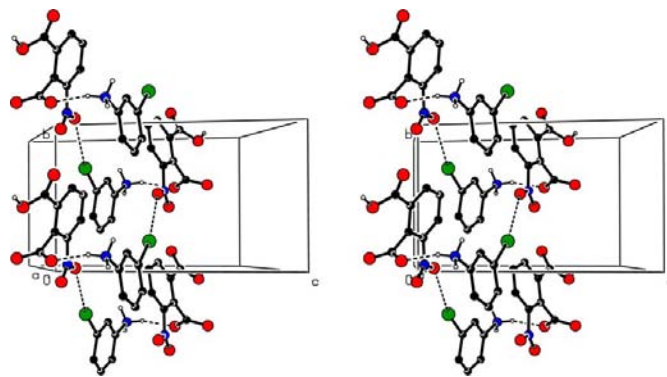


Figure 5

A stereoview of part of the crystal structure of (I), showing the [010] chain generated by the iodo–nitro interaction. For clarity, H atoms bonded to C atoms have been omitted.

chains generated by a 2_1 screw axis, but the linking of these chains by the cations into sheets differs in detail from that in (I); in particular, there are no centrosymmetric motifs in (II). Moreover, there are no iodo–nitro interactions in (II) and no significant direction-specific interactions between adjacent hydrogen-bonded sheets.

Experimental

A mixture of 3-iodoaniline and 3-nitrophthalic acid (5 mmol of each) in methanol (20 ml) was heated under reflux for 30 min and then cooled. The solid that formed slowly was collected and recrystallized from acetone (m.p. 460–461 K).

Crystal data

$C_8H_7IN^+ \cdot C_8H_4NO_6^-$
 $M_r = 430.15$
 Monoclinic, $P2_1/c$
 $a = 16.0068$ (10) Å
 $b = 7.8616$ (5) Å
 $c = 13.5718$ (9) Å
 $\beta = 113.3770$ (10)°
 $V = 1567.67$ (17) Å³
 $Z = 4$

$D_x = 1.823$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 3603 reflections
 $\theta = 2.8$ – 27.5 °
 $\mu = 2.08$ mm⁻¹
 $T = 291$ (2) K
 Plate, colourless
 $0.50 \times 0.10 \times 0.08$ mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer
 φ - ω scans
 Absorption correction: multi-scan (SADABS; Bruker, 2000)
 $T_{\min} = 0.424$, $T_{\max} = 0.852$
 11 173 measured reflections

3603 independent reflections
 2253 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.037$
 $\theta_{\text{max}} = 27.5$ °
 $h = -13 \rightarrow 20$
 $k = -10 \rightarrow 10$
 $l = -17 \rightarrow 17$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.043$
 $wR(F^2) = 0.113$
 $S = 0.95$
 3603 reflections
 210 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0656P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.89$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.95$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

C11–O11	1.214 (4)	C21–O21	1.253 (4)
C11–O12	1.302 (4)	C21–O22	1.245 (4)
C2–C1–C11–O11	157.3 (4)	C2–C3–N31–O31	–13.4 (5)
C1–C2–C21–O21	104.2 (4)		

Table 2

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O12–H12 \cdots O21 ⁱ	0.82	1.75	2.570 (3)	176
N41–H41A \cdots O22	0.89	1.88	2.745 (4)	164
N41–H41B \cdots O21 ⁱⁱ	0.89	2.23	3.052 (4)	153
N41–H41C \cdots O22 ⁱⁱⁱ	0.89	1.91	2.747 (4)	156

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

For compound (I), the space group $P2_1/c$ was uniquely assigned from the systematic absences. All H atoms were located from difference maps and then treated as riding atoms [$C-H = 0.93$ Å and $U_{\text{iso}}(H) = 1.2U_{\text{eq}}(C,N)$ or $1.5U_{\text{eq}}(O)$].

Data collection: SMART (Bruker, 1998); cell refinement: SAINT (Bruker, 2000); data reduction: SAINT; 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).

X-ray data were collected at the University of Aberdeen; the University is thanked for funding the purchase of the Bruker SMART diffractometer. JNL thanks NCR Self-Service, Dundee, for grants which have provided computing facilities for this work. JLW thanks CNPq and FAPERJ for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1819). Services for accessing these data are described at the back of the journal.

References

- Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
 Bruker (1998). SMART. Version 5.0. Bruker AXS Inc., Madison, Wisconsin, USA.
 Bruker (2000). SADABS (Version 2.03) and SAINT (Version 6.02a). Bruker AXS Inc., Madison, Wisconsin, USA.
 Ferguson, G. (1999). PRPKAPPA. University of Guelph, Canada.
 Glidewell, C., Low, J. N., Skakle, J. M. S. & Wardell, J. L. (2003). *Acta Cryst. C* **59**, o509–o511.
 Sheldrick, G. M. (1997). SHELXS97 and SHELXL97. University of Göttingen, Germany.
 Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
 Starbuck, J., Norman, N. C. & Orpen, A. G. (1999). *New J. Chem.* **23**, 969–972.