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A second crystal polymorph of anilinium picrate

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Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.005 Å
R factor = 0.053
wR factor = 0.209
Data-to-parameter ratio = 14.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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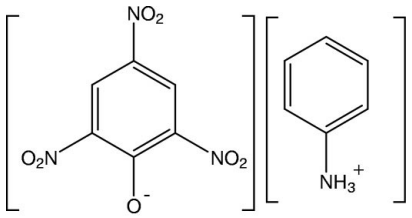
The crystal structure of a second monoclinic polymorph of anilinium picrate ($C_6H_8N^+\cdot C_6H_2N_3O_7^-$) shows a three-dimensional hydrogen-bonded polymer with strong primary interspecies interactions involving the proximal phenolate and adjacent nitro group O-atom acceptors and separate anilinium H-atom donors in two cyclic $R_1^2(6)$ associations. Other nitro-O–anilinium-H hydrogen bonds together with heteromolecular π–π interactions are also present.

Comment

As a continuing project involving the systematization of the hydrogen-bonding modes in charge-transfer compounds of 3,5-dinitrosalicylic acid (DNSA) with Lewis bases, the crystal structures of more than 40 such compounds have been reported by our group. These include compounds with aliphatic amines (Smith *et al.*, 2002), monocyclic aromatic amines (Smith, Lynch *et al.*, 1995, 1996; Smith *et al.*, 2003; Smith, Wermuth, Healy & White, 2004*a*), and polycyclic hetero-aromatic and aromatic aliphatic amines (Smith, Wermuth, Healy & White, 2004*b*). In a series that includes seven compounds of DNSA with the aniline-type amines (Smith, Wermuth, Healy & White, 2004*a*), anilinium 3,5-dinitrosalicylate was synthesized and characterized. A minor morphologically different yellow–brown crystal, which was manually isolated from the product, was initially thought to be a monoclinic polymorph of the yellow triclinic DNSA compound. However, this compound has now been crystallographically characterized as a second polymorph of anilinium picrate, $C_6H_8N^+\cdot C_6H_2N_3O_7^-$, (I). The structure of the first monoclinic polymorph (polymorph 1) has been reported previously (Takayanagi *et al.*, 1996) [comparative cell parameters a = 11.882 (2) Å, b = 16.112 (2) Å, c = 7.652 (1) Å, β = 93.23 (1)° and space group $P2_1/c$]. This unit cell is significantly different from that of (I). A crystallographic study of anilinium picrate was also reported by Hertel & Schneider (1931). Crystalline picrates have commonly been used in the preparation of amine derivatives in qualitative organic chemistry (Shriner *et al.*, 1980), and the crystal structures of a large number of such compounds with biological base molecules are known [with serotonin (a monohydrate) (Thewalt & Bugg, 1972), guanine (Bugg & Thewalt, 1975), tryptamine and DL-tryptophane (Gartland *et al.*, 1974), acetylcholine (Frydenvang *et al.*, 1988), imidazole (Soriano-García *et al.*, 1990), L-proline (Jin *et al.*, 2003), L-valine (Anitha *et al.*, 2004*a*), and β-alanine (Anitha *et al.*, 2004*b*)]. Neutral adduct compounds having heteromolecular π–π interactions are also common [with naphthalene (1/1) (Banerjee & Brown, 1985), anthranilic acid (2/1) (In *et al.*, 1997), benzene (1/1) (Takayanagi *et al.*, 1991), phenanthrene (1/1) (Goto, Takaya-

nagi *et al.*, 1992*a*), 1,4-naphthoquinone (1/1) (Goto, Toubai *et al.*, 1992) and 4,6,8-trimethylazulene (1/1) (Näther *et al.*, 1997)]. Among the proton- transfer examples, π–π interactions have only been found in the picrates of isoquinoline (Goto, Takayanagi *et al.*, 1992*b*), *N*-methylaniline and *m*-phenylenediamine (Takayanagi *et al.*, 1996) but not with polymorph 1 or quinoline (Goto, Takayanagi *et al.*, 1992*b*).



(I)

In the structure of (I) (Fig. 1), proton transfer from the phenolic group of picric acid to the primary amine group of aniline occurs. This behaviour is similar to that of the DNSA compound, except that the proton is derived from the carboxylic acid group. This transfer might be expected to occur in both, considering the relative acid strengths of picric acid and DNSA (pK_a = 0.29 and 2.2, respectively). The picrate anion species has different conformational and dimensional features from those of the chemically analogous DNSA anion, particularly about the proximal groups at C1, C2 and C6. In all proton-transfer compounds with DNSA, the phenolic H atom is retained and participates in an intramolecular *S*(6) hydrogen-bonding interaction with the carboxyl O atom, which is absent in the picrates. This hydrogen bond essentially maintains coplanarity of the carboxyl group and the benzene ring. In DNSA compounds, this interaction also results in a relatively short O(phenol)···O(carboxyl) separation [2.447 (2) Å in anilinium 3,5-dinitrosalicylate is typical], which is significantly less than the values of 2.696 (4) and 2.694 (4) Å found in (I) for the O1···O21 and O1···O62 separations. The torsion angles associated with the *ortho*-related nitro groups in (I) (C1—C2—N2—O22 and C1—C6—N6—O61) are −146.4 (4) and −161.2 (3)°, respectively. In this respect, (I) differs significantly from polymorph 1, in which the equivalent angles are −142 and 60°, with O(phenol)···O(nitro) separations of 2.76 and 2.88 Å. It has been found that in the DNSA compounds, the analogous proximal *ortho*-related nitro group, which is commonly involved in hydrogen-bonding interactions, suffers more from rotation out of the molecular plane than the *para*-related nitro group (Smith *et al.*, 2003). This situation is also found in (I), where the non-interactive nitro group at atom C4 is essentially coplanar with the ring [torsion angle C3—C4—N4—O42 = 175.4 (4)° *cf.* 170° in polymorph 1]. Another definitive feature of the picrate anion is the equality of the N—O and C—N bond lengths [1.214 (4)–1.227 (5) Å and 1.450 (4)–1.457 (4) Å, respectively]. In the DNSA anion, the C—O distances are unequal and the aromatic ring C—C(carboxyl) bond distance is longer [typically 1.231 (3), 1.280 (3) and 1.509 (3) Å, respectively, in anilinium DNSA].

In (I), two of the hydrogen donor atoms of the aminium groups are involved in separate but similar three-centred $R_1^2(6)$ cyclic intermolecular hydrogen-bonding interactions with the phenolate O-atom and adjacent nitro O-atom acceptors of the two picrate residues [N11—H11*B*···O1^{i}/O21^{i} = 2.909 (5)/3.037 (5) Å and N11—H11*C*···O1^{ii}/O62^{ii} = 2.704 (4)/2.771 (4) Å; symmetry codes: (i) $x, \frac{1}{2}-y, \frac{1}{2}+z$; (ii) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$; Fig. 2]. This hydrogen bonding is the same as that found in polymorph 1, the only variation being in the asymmetry of the associations compared with the symmetry found in (I). This duplex association in both polymorphs differs significantly from that found in anilinium DNSA, where the oxygen acceptors of the proximal phenolic and nitro O atoms give only one $R_1^2(6)$ association, the carboxyl O atom being directly linked to an aminium H atom in a single bridging mode. In (I), there is also a direct but weaker interaction between the third aminium H atom and nitro atom O61, extending the structure across the *c* cell direction while the

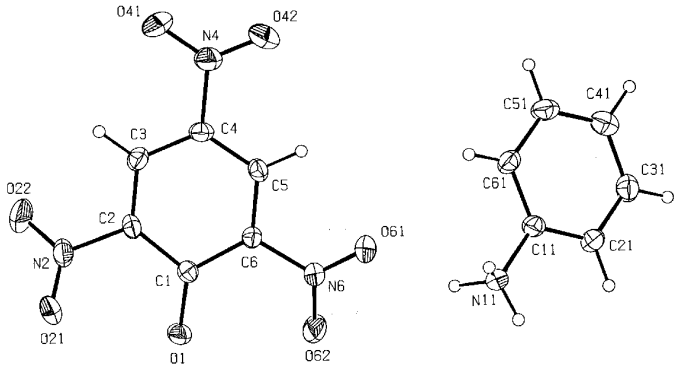


Figure 1
The molecular configuration and atom-numbering scheme for the picrate anion and the anilinium cation in (I). Non-H atoms are shown as 30% probability displacement ellipsoids.

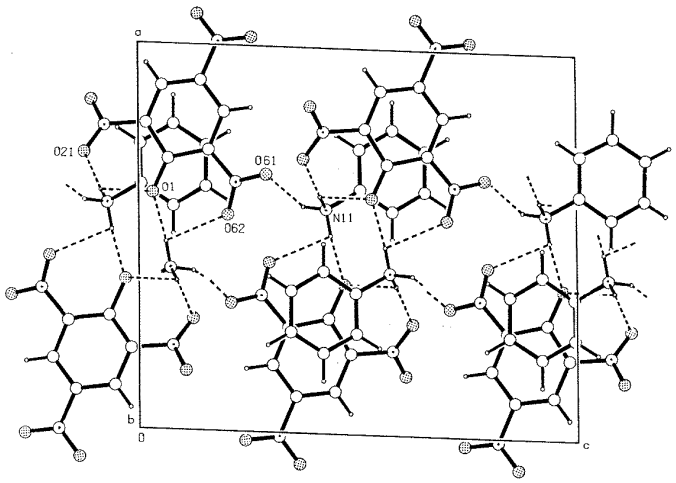


Figure 2
The packing of (I) in the unit cell, viewed down *b*, showing hydrogen-bonding associations as broken lines and partial superposition of anion and cation species.

cation and anion species give partial ring superposition down the *b* cell direction [the shortest ring centroid separation is 3.73 (1) Å, indicative of some π–π interaction]. Although this structural feature is absent in polymorph 1, it is not uncommon among both aromatic neutral and proton-transfer compounds of picric acid (Herbstein & Kaftory, 1975; Banerjee & Brown, 1985; Yamaguchi *et al.*, 1988; Näther *et al.*, 1997; Goto, Takayanagi *et al.*, 1992*a*; Takayanagi *et al.*, 1996), although it has been found only in those DNSA compounds with the polycyclic hetero-aromatic bases quinoline, 2,2′-bipyridine and 1,10-phenanthroline (Smith, Wermuth, Healy & White, 2004*b*) and with adenosine (Smith, Wermuth & Healy, 2004). The result in (I) is a three-dimensional hydrogen-bonded polymer structure, which is significantly different from that found in the first crystal polymorph of anilinium picrate (Takayanagi *et al.*, 1996). The difference may be the result of solvent choice; polymorph 1 was obtained with diethyl ether, while (I) was obtained with 50% ethanol/water.

Experimental

Compound (I) was isolated as a very minor morphologically different crystal from the synthesis of anilinium 3,5-dinitrosalicylate (Smith, Wermuth, Healy & White, 2004*a*) by heating under reflux, for 10 min, 1 mmol quantities of aniline and 3,5-dinitrosalicylic acid (DNSA) in 50% ethanol/water (50 ml). After concentration to *ca* 30 ml, partial room-temperature evaporation of the hot- filtered solution gave short yellow–brown prisms of (I) (m.p. 452.1–454.5 K, decomposed) among the yellow plates of the major DNSA component. The literature melting point for anilinium picrate is 453 K (decomposed) (Rikovski, 1949; Rappoport, 1967). The isolation of an adventitious crystal of (I) in this preparation appears to have resulted by formation from picric acid, presumably present in the commercial DNSA.

Crystal data

$C_6H_8N^+\cdot C_6H_2N_3O_7^-$
M_r = 322.24
Monoclinic, $P2_1/c$
a = 13.064 (7) Å
b = 7.1007 (17) Å
c = 14.863 (8) Å
β = 92.96 (3)°
V = 1376.9 (11) Å^3
Z = 4
D_x = 1.554 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 13.0–17.0°
μ = 0.13 mm^{-1}
T = 298 (2) K
Block, yellow–brown
0.40 × 0.34 × 0.30 mm

Data collection

Rigaku AFC 7*R* diffractometer
ω–2θ scans
Absorption correction: none
3420 measured reflections
3160 independent reflections
1417 reflections with $I > 2\sigma(I)$
R_{int} = 0.023
θ_{max} = 27.5°
$h = -16 \rightarrow 16$
$k = -9 \rightarrow 0$
$l = -7 \rightarrow 19$
3 standard reflections
frequency: 150 min
intensity decay: 0.6%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.053
$wR(F^2)$ = 0.209
S = 0.92
3160 reflections
221 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.1P)^2 + 1.0338P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.023
$\Delta\rho_{max}$ = 0.24 e Å^{-3}
$\Delta\rho_{min}$ = −0.27 e Å^{-3}

Table 1
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N11—H11A···O61	0.95 (6)	2.01 (6)	2.881 (5)	152 (6)
N11—H11B···O1^{i}	0.97 (6)	2.38 (5)	2.909 (5)	114 (3)
N11—H11B···O21^{i}	0.97 (6)	2.09 (5)	3.037 (5)	167 (5)
N11—H11C···O1^{ii}	0.92 (7)	1.79 (7)	2.704 (4)	169 (6)
N11—H11C···O62^{ii}	0.92 (7)	2.40 (6)	2.771 (4)	104 (4)
C5—H5···O22^{iii}	0.95	2.47	3.135 (5)	127
C31—H31···O62^{iv}	0.95	2.56	3.394 (5)	146

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

H atoms of the anilinium group were located by difference methods and their positional and isotropic displacement parameters were refined. Other H atoms were included in the refinement at calculated positions (C—H = 0.95 Å) as riding atoms, with U_{iso}(H) values fixed at 1.2U_{eq}(C).

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1999); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN for Windows* (Molecular Structure Corporation, 1999); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON for Windows* (Spek, 1999); software used to prepare material for publication: *PLATON for Windows*.

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