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The 1:1 proton-transfer compound of benzylamine with 3,5-dinitrosalicylic acid

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The crystal structure of the proton-transfer compound from the reaction of 3,5-dinitrosalicylic acid (DNSA) with benzylamine (BA), *viz.* benzylammonium 3,5-dinitrosalicylate, $C_7H_{10}N^+ \cdot C_7H_3N_2O_7^-$, shows a hydrogen-bonded polymer in which the protonated primary amine group of benzylamine gives a total of six inter-species interactions with O atoms of the DNSA anions. In addition, there are unusual centrosymmetric interactions between the carboxylate groups of the DNSA anions.

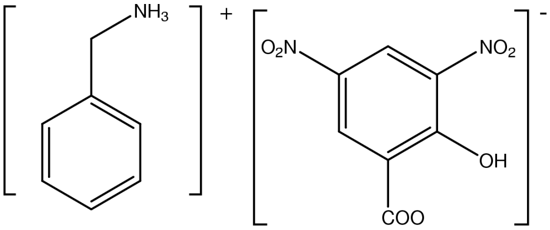
Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.006 Å
R factor = 0.056
wR factor = 0.217
Data-to-parameter ratio = 14.6

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

Comment

3,5-Dinitrosalicylic acid (DNSA) has proved to be the best of the nitro-substituted aromatic carboxylic acids for the construction of stable hydrogen-bonded cocrystalline solids. As well as giving a number of neutral crystalline polymorphic solvate systems (Smith *et al.*, 1995; Kumar *et al.*, 1999), a total of 20 proton-transfer compounds with both aromatic and aliphatic amines have been synthesized and characterized crystallographically (Smith *et al.*, 2001, 2002). With the exception of the 1:2 adduct with 4-aminobenzoic acid (Smith *et al.*, 1995), all of these are 1:1 compounds. To investigate the effect of the presence of an aromatic substituent group on the interactive behaviour of the primary amine moiety in reactions with DNSA, the mixed aromatic substituted aliphatic amine benzylamine (BA) was investigated. This resulted in crystals of the title compound, benzylammonium 3,5-dinitrosalicylate, $(BA)^+(DNSA)^-$, (I).



(I)

The structure determination of (I) has shown that the primary amine group of benzylamine is protonated (Fig. 1), giving a hydrogen-bonded network polymer in which all three H atoms are involved in six associations (all three-centre) with DNSA O-atom acceptors [carboxylate (O71 and O72), phenolate (O2) and nitro (O31 and O32): N···O 2.823 (6)–3.239 (7) Å] (Table 1). The usual intramolecular hydrogen bond is found between the phenolic O atom and the *anti*-related H atom on the carboxyl group [O72—H72···O2 2.483 (6) Å], compared with the mean of 2.46 Å for the current series (Smith *et al.*, 2002). An unusual centrosymmetric intermolecular association is also found between the carboxylate groups of the DNSA anions [O72—H72···O72^i 2.814 (6) Å and O—H···O^i 101 (5)°: symmetry code: (i) $2-x$, $2-y$, $1-z$]. The centrosymmetric stacks of DNSA anions forming down the *a*-cell direction are linked into polymer sheets by parallel rows of BA cations (Fig. 2). As found with other examples of these DNSA salts, significant π–π interaction between the DNSA anions in the stacks is in evidence.

Experimental

The synthesis of the title compound, (I), was carried out by heating under reflux for 10 min, using 1 mmol quantities of 3,5-dinitrosalicylic acid and benzylamine in 50 ml of 80% ethanol/water. After concentration to *ca* 30 ml, partial room-temperature evaporation of the hot-filtered solution gave crystals suitable for X-ray crystallography.

Crystal data

$(C_7H_{10}N)^+\cdot(C_7H_3N_2O_7)^-$	$Z = 2$
$M_r = 335.27$	$D_x = 1.505$ Mg m^{-3}
Triclinic, $P\overline{1}$	Mo $K\alpha$ radiation
$a = 10.953$ (15) Å	Cell parameters from 25 reflections
$b = 11.450$ (8) Å	$\theta = 12.6$–$17.1°$
$c = 7.118$ (4) Å	$\mu = 0.12$ mm^{-1}
$\alpha = 94.56$ (5)°	$T = 295$ (2) K
$\beta = 105.61$ (7)°	Block, yellow
$\gamma = 117.61$ (6)°	0.30 × 0.25 × 0.20 mm
$V = 739.7$ (14) Å^3	

Data collection

Rigaku AFC-7*R* diffractometer	$\theta_{max} = 27.5°$
ω–2θ scans	$h = -14 \rightarrow 6$
Absorption correction: none	$k = -13 \rightarrow 14$
3872 measured reflections	$l = -8 \rightarrow 9$
3406 independent reflections	3 standard reflections every 150 reflections
1708 reflections with $I > 2\sigma(I)$	intensity decay: 1.2%
$R_{int} = 0.027$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.1P)^2 + 1.0302P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.056$	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2) = 0.217$	$\Delta\rho_{max} = 0.23$ e Å^{-3}
$S = 0.88$	$\Delta\rho_{min} = -0.22$ e Å^{-3}
3406 reflections	
234 parameters	
H atoms treated by a mixture of independent and constrained refinement	

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

D—H···A	D—H	H···A	D···A	D—H···A
O72—H72···O2	0.96 (7)	1.57 (8)	2.483 (6)	158 (7)
O72—H72···O72^i	0.96 (7)	2.47 (7)	2.814 (6)	101 (5)
N81—H811···O71^{ii}	0.99 (5)	1.96 (6)	2.912 (7)	160 (6)
N81—H811···O72^{ii}	0.99 (5)	2.54 (6)	3.031 (7)	110 (4)
N81—H812···O2^{iii}	1.00 (5)	1.85 (5)	2.823 (6)	164 (5)
N81—H812···O31^{iii}	1.00 (5)	2.51 (6)	3.081 (7)	116 (4)
N81—H813···O31	0.90 (7)	2.39 (7)	3.239 (7)	158 (4)
N81—H813···O32	0.90 (7)	2.47 (6)	3.125 (7)	130 (5)
C71—H712···O52^{iv}	0.96	2.58	3.530 (7)	172

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

H atoms involved in hydrogen-bonding interactions (H72, H811, H812 and H813) were located by difference syntheses and their positional and isotropic displacement parameters were refined. Others H atoms were included in the refinement as riding models. For refined H atoms, the N—H range is 0.90 (7)–1.00 (5) Å; the intramolecular O—H distance in the DNSA anion is 0.96 (7) Å.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1999); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (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: *TEXSAN*.

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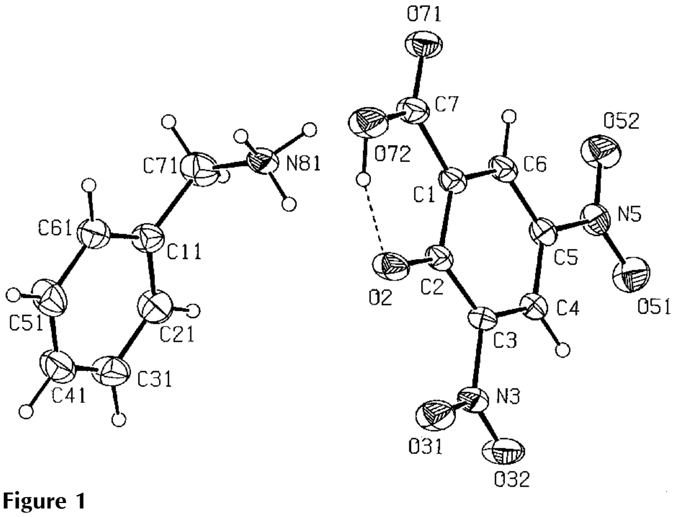

Figure 1
The molecular configuration and atom-labelling scheme for the individual anion and cation species in (I), with non-H atoms shown as 30% probability ellipsoids (Spek, 1999).

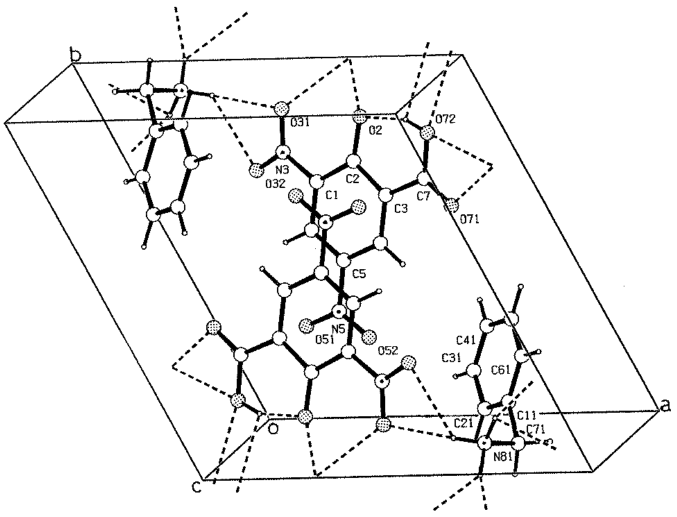

Figure 2
Perspective view of the packing in the unit cell, viewed down *c*, showing hydrogen-bonding associations as broken lines.

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