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

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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.

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, C7H10N⁺·C7H3N2O7⁻, 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.

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).

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 centrosym-
metric intermolecular association is also found between the carboxylate groups of the DNSA ions [O72—H72···O72 2.814 (6) Å and O—H···O 101 (5)°: symmetry code: (i) 2—x, 2—y, 1—z]. The centrosymmetric stacks of DNA 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 DNA salts, significant π–π interaction between the DNA 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-dinitro salicylic 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**

(C7H10N)+·(C7H3N2O7)−

M = 335.27

Triclinic, P T

a = 10.953 (15) Å

b = 11.450 (8) Å

c = 7.118 (4) Å

α = 94.56 (5)°

β = 105.61 (7)°

γ = 117.61 (6)°

V = 739.7 (14) Å³

Z = 2

D = 1.505 Mg m⁻³

Cell parameters from 25 reflections

θ = 12.6–17.1°

μ = 0.12 mm⁻¹

T = 295 (2) K

Block, yellow

0.30 × 0.25 × 0.20 mm

**Data collection**

Rigaku AFC7R diffractometer

ω-2θ scans

Absorption correction: none

3872 measured reflections

3406 independent reflections

1709 reflections with I > 2σ(I)

Rint = 0.027

**Refinement**

Reefinement on F²

R[F² > 2σ(F²)] = 0.056

wR(F²) = 0.217

S = 0.88

3406 reflections

234 parameters

H atoms treated by a mixture of independent and constrained refinement

w = 1/[σ²(Fo)² + (0.1P)² + 0.0001P]

where P = (Fo)² + 2Fe²/3

(Δ/σ)max < 0.001

Δρmax = 0.23 e Å⁻³

Δρmin = −0.22 e Å⁻³

**Table 1**

Hydrogen-bonding geometry (Å, °).

<table>
<thead>
<tr>
<th>D—H···A</th>
<th>D—H</th>
<th>H···A</th>
<th>D···A</th>
<th>D—H···A</th>
</tr>
</thead>
<tbody>
<tr>
<td>O72—H72···O2</td>
<td>0.96 (7)</td>
<td>1.57 (8)</td>
<td>2.483 (6)</td>
<td>158 (7)</td>
</tr>
<tr>
<td>O72—H72···O72</td>
<td>0.96 (7)</td>
<td>2.47 (7)</td>
<td>2.814 (6)</td>
<td>101 (5)</td>
</tr>
<tr>
<td>N81—H811···O71</td>
<td>0.99 (5)</td>
<td>1.96 (6)</td>
<td>2.912 (7)</td>
<td>160 (6)</td>
</tr>
<tr>
<td>N81—H811···O72</td>
<td>0.99 (5)</td>
<td>2.54 (6)</td>
<td>3.031 (7)</td>
<td>110 (4)</td>
</tr>
<tr>
<td>N81—H812···O31</td>
<td>1.00 (5)</td>
<td>1.85 (5)</td>
<td>2.823 (6)</td>
<td>164 (5)</td>
</tr>
<tr>
<td>N81—H812···O31</td>
<td>1.00 (5)</td>
<td>2.51 (6)</td>
<td>3.081 (7)</td>
<td>116 (4)</td>
</tr>
<tr>
<td>N81—H813···O31</td>
<td>0.90 (7)</td>
<td>2.39 (7)</td>
<td>3.239 (7)</td>
<td>158 (4)</td>
</tr>
<tr>
<td>N81—H813···O32</td>
<td>0.90 (7)</td>
<td>2.47 (6)</td>
<td>3.125 (7)</td>
<td>130 (5)</td>
</tr>
<tr>
<td>C71—H712···O52</td>
<td>0.96</td>
<td>2.58</td>
<td>3.530 (7)</td>
<td>172</td>
</tr>
</tbody>
</table>

Symmetry codes: (i) 2—x, 2—y, 1—z; (ii) x—1, y, z—1; (iii) 1—x, 2—y, 1; (iv) 2—x, 2—y, 1—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 0.94 (7)–1.00 (5) Å; the intramolecular O—H distance in the DNSA anion is 0.96 (7) Å.

Data collection: *MSC/AFC Diffractor Control Software* (Molecular Structure Corporation, 1999); cell refinement: *MSC/AFC Diffractor Control Software*, data reduction: *TEXSAN* (Molecular Structure Corporation, 1999); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* for Windows (Spek, 1999); software used to prepare material for publication: *TEXSAN*.

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References