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

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.002 Å
R factor = 0.037
wR factor = 0.098
Data-to-parameter ratio = 12.2

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

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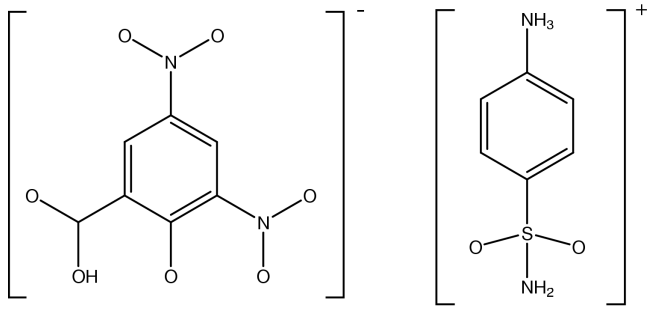
The crystal structure of the proton-transfer compound from the reaction of 3,5-dinitrosalicylic acid (DNSA) with sulfanilamide (ABSA), *i.e.* 4-sulfonamidoanilinium 3,5-dinitrosalicylate, $C_6H_9N_2O_2S^+\cdot C_7H_3N_2O_7^-$, shows an extensively hydrogen-bonded polymeric structure in which the protonated amino group of sulfanilamide together with the amide group give a total of eight intermolecular interactions with most of the O atoms of the DNSA anions [N···O 2.822 (2)–3.172 (2) Å], together with both of the sulfonate O atoms of adjacent ABSA cations [N···O 2.867 (2) and 3.090 (2) Å].

Comment

3,5-Dinitrosalicylic acid (DNSA) provides one of the best chemical synthons for the construction of hydrogen-bonded structural motifs. The acid has provided examples of polymorphism in which associations with solvent molecules such as water (two examples), dioxane (four examples) and *tert*-butyl alcohol (one example) give a variety of hydrogen-bonded molecular assemblies (Smith *et al.*, 1995; Kumar *et al.*, 1999). The low pK_a of the acid (2.18) also means that with Lewis bases, protonation of the hetero-N atom usually occurs, giving further promotion of hydrogen bonding. We have synthesized and determined the structures of the proton-transfer compounds with the isomeric aminobenzoic acids (Smith *et al.*, 1995), *viz*. 3-amino-1*H*-1,2,4-triazole (Smith *et al.*, 1996), 8-aminoquinoline (Smith, Wermuth, Bott *et al.*, 2001), 8-hydroxyquinoline (Smith, Wermuth & White, 2001), guanidine (Smith *et al.*, 2001*a*) and 8-quinolylurea (Smith *et al.*, 2001*b*). All of these are 1:1 except for the 1:2 adduct with 4-aminobenzoic acid.



(I)

In a continuation of the study of the nature of the interactions of DNSA with Lewis bases, reaction with sulfanilamide (4-aminobenzenesulfonamide, ABSA), gave large yellow crystals of the title compound [$(ABSA)^+(DNSA)^-$], (I). The structure determination has shown that the amine group of sulfanilamide is protonated (Fig. 1), subsequently giving an

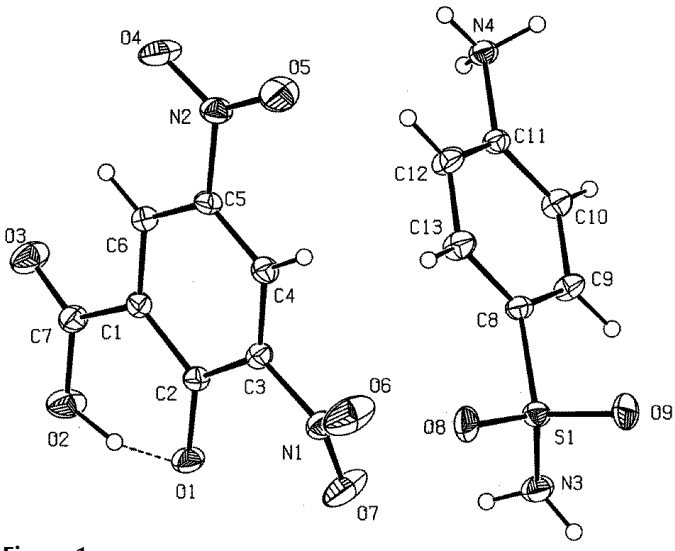


Figure 1
The molecular configuration and atom-numbering scheme for (I) with atoms shown as 30% probability ellipsoids.

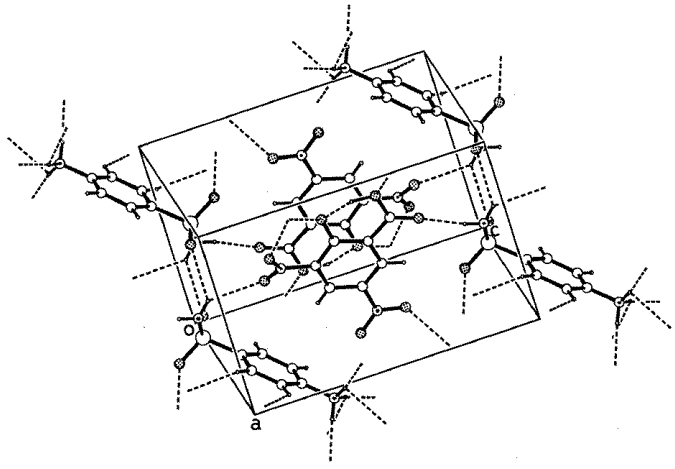


Figure 2
Packing in the unit cell, showing hydrogen-bonding associations as broken lines.

extensively hydrogen-bonded network polymer in which all ABSA H atoms are involved in a total of eight associations [five to the protonated amine (two three-centred); three to the amide (one three-centred)], with DNSA oxygen acceptors or sulfonate O atoms of other ABSA molecules.

The sulfanilamide cations form centrosymmetric hydrogen-bonded cyclic dimers through the sulfonamide groups [N4—H4*C*···O9 2.867 (2) Å; symmetry code: $-x, 2-y, 2-z$] (Fig. 2). These dimers are linked by weak hydrogen bonds [C10—H10···O8 3.171 (2) Å; symmetry code: $1-x, y, z$] to form infinite chains extending along the *a* axis of the cell. Hydrogen bonds between the protonated amine groups and sulfanilamide O atoms [N3—H3*A*···O8 3.090 (2) Å; symmetry code: $1-x, 1-y, 2-z$] form a two-dimensional network parallel to (001). The 3,5-dinitrosalicylate anions are stacked down the *a* cell direction and are linked peripherally to the ABSA framework sheets by N—H···O hydrogen bonds (Table 1).

The usual intramolecular hydrogen bonding is found between the phenolic O atom and the *anti*-related H atom on the carboxyl group [O2—H1···O1 2.462 (2) Å], comparing closely with the mean for the current series (2.461 Å). This arrangement with the H atom located on the carboxyl O atom rather than the phenolic O atom is found in 75% of the known proton-transfer compounds of DNSA with Lewis bases (Smith, Bott, Wermuth *et al.*, 2001).

Experimental

The synthesis of the title compound was carried out by heating, under reflux for 10 min, 1 mmol quantities of 3,5-dinitrosalicylic acid and sulfanilamide (4-aminobenzenesulfonamide) in 30 ml of 80% ethanol/water. Crystals were obtained after partial room-temperature evaporation of the solvent.

Crystal data

$C_7H_3N_2O_7^+\cdot C_6H_9N_2O_2S^-$
M_r = 400.33
Triclinic, $P\overline{1}$
a = 7.0167 (9) Å
b = 9.137 (1) Å
c = 12.430 (1) Å
α = 90.77 (1)°
β = 99.736 (9)°
γ = 95.70 (1)°
V = 781.17 (15) Å^3
Z = 2
D_x = 1.702 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 12–15°
μ = 0.27 mm^{-1}
T = 293 (2) K
Prismatic, yellow
0.35 × 0.25 × 0.20 mm

Data collection

Nonius CAD-4 diffractometer
ω–2θ scans
3867 measured reflections
3575 independent reflections
3080 reflections with $I > 2\sigma(I)$
R_{int} = 0.010
θ_{max} = 27.5°
$h = 0 \rightarrow 9$
$k = -11 \rightarrow 11$
$l = -16 \rightarrow 15$
3 standard reflections
frequency: 160 min
intensity decay: 5.0%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.098
S = 1.05
3575 reflections
293 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0482P)^2 + 0.3779P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.006
$\Delta\rho_{max}$ = 0.39 e Å^{-3}
$\Delta\rho_{min}$ = −0.35 e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.008 (2)

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

D—H···A	D—H	H···A	D···A	D—H···A
O2—H1···O1	1.03 (4)	1.48 (4)	2.462 (2)	157 (3)
N3—H3*A*···O6^{i}	0.82 (3)	2.53 (2)	3.172 (2)	137 (2)
N3—H3*A*···O8^{ii}	0.82 (3)	2.46 (3)	3.090 (2)	135 (2)
N3—H3*B*···O3	0.84 (3)	2.10 (3)	2.934 (2)	170 (3)
N4—H4*A*···O1^{iii}	0.91 (3)	1.93 (3)	2.822 (2)	166 (3)
N4—H4*A*···O7^{iii}	0.91 (3)	2.41 (3)	2.870 (2)	111.2 (19)
N4—H4*B*···O2^{iv}	0.93 (3)	2.01 (3)	2.926 (2)	172 (2)
N4—H4*B*···O4^{v}	0.93 (3)	2.51 (3)	2.880 (2)	104 (2)
N4—H4*C*···O9^{v}	0.89 (2)	1.97 (2)	2.867 (2)	176 (2)
C4—H4···O5	0.88 (3)	2.42 (3)	2.711 (2)	100.0 (18)
C9—H9···O7^{vi}	0.94 (2)	2.57 (2)	3.414 (2)	150.6 (16)
C10—H10···O8^{vii}	0.96 (2)	2.43 (2)	3.171 (2)	133.5 (16)
C13—H13···O8	0.89 (2)	2.53 (2)	2.896 (2)	105.3 (15)

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

H atoms were located from a difference map and both positional and isotropic displacement parameters were refined. For H atoms: C—H range 0.88 (2)–0.96 (2) Å; N—H range 0.81 (3)–0.93 (3) Å, and the intramolecular O—H distance is 1.03 (4) Å.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *PROCESS DATA* (Gable *et al.*, 1994); 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).

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