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The 1:1 proton-transfer complex of 3,5-dinitrosalicylic acid with (8-quinolinyl)urea

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Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.002 Å
R factor = 0.045
wR factor = 0.125
Data-to-parameter ratio = 13.9

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

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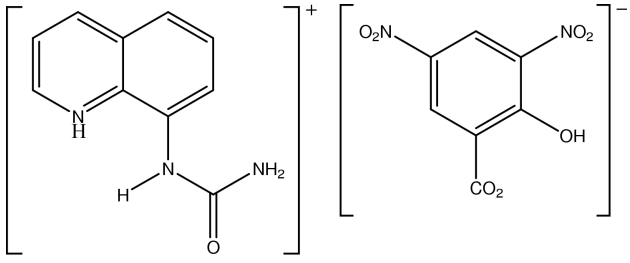
In the crystal structure of the proton-transfer complex of (8-quinolinyl)urea (QUR) with 3,5-dinitrosalicylic acid (DNSA), 8-ureidoquinolinium 3,5-dinitrosalicylate, $[(QUR)^+(DNSA)^-]$ or $C_{10}H_{10}N_3O^+\cdot C_7H_3N_2O_7^-$, the hetero–N atom of QUR is protonated and, together with all urea protons, is involved in extensive hydrogen-bonding associations which result in a three-dimensional network polymer [N···O 2.711–3.251 (2) Å]. In addition, the quinolinium proton is involved in an intramolecular hydrogen bond with a urea–N atom [N—N 2.841 (2) Å] and within the DNSA anions a short intramolecular O(carboxyl)···O(hydroxy) hydrogen bond is also present [O···O 2.492 (2) Å].

Comment

The nitro-substituted aromatic acid 3,5-dinitrosalicylic acid (DNSA) has proved a very useful compound for structure formation, giving a number of complexes which acquire stable crystalline lattices through hydrogen-bonding associations. These compounds may be either neutral or ionic, the latter involving proton transfer to a Lewis base acceptor. In addition, association may involve π–π interactions through the aromatic ring and its interactive nitro substituents, although



(I)

the majority of reported examples primarily interact *via* the carboxylate group, the *ortho*-related hydroxy group, and, to a lesser extent, the nitro groups. Issa and co-workers have categorized a large number of examples using IR spectroscopy (Hindawey *et al.*, 1980; Issa *et al.*, 1980, 1981), while those characterized to date by our group using X-ray diffraction are the compounds with 3-amino-1*H*-1,2,4-triazole (Smith *et al.*, 1995), 8-aminoquinoline (Smith, Wermuth, Bott *et al.*, 2001), 8-hydroxyquinoline (Smith, Wermuth & White, 2001), guanidine (Smith, Bott & Wermuth, 2001) and the isomeric aminobenzoic acids (Smith *et al.*, 1995). In the case of the compound with 4-aminobenzoic acid, the only example is a 1:2

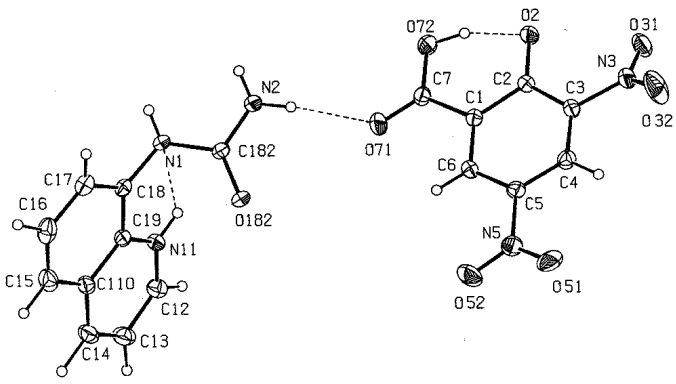


Figure 1
The (8-quinolinyl)urea cation and the 3,5-dinitrosalicylate anion in the structure of [QUR$^+$][DNSA$^-$]. Non-H atoms are shown as 30% probability ellipsoids.

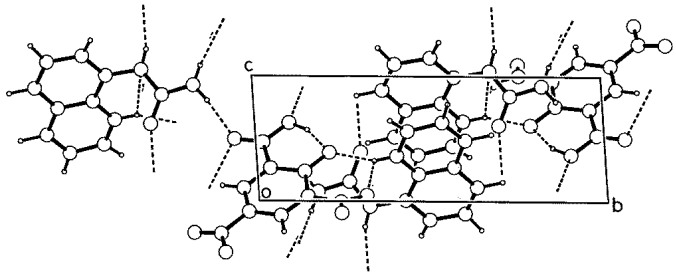


Figure 2
The hydrogen-bonding scheme (hydrogen bonds shown as broken lines) viewed down the *a* axis of the crystal.

adduct. Neutral compounds are less common but the 1:1 adducts with urea (Smith, Baldry *et al.*, 1997), 1,1-diethylurea (Smith *et al.*, 2000), and a series of polymorphic solvates with dioxane (1:1) (two) and (2:1) (two) (Kumar *et al.*, 1999) have been characterized. A series of four polymorphs is also known for the hydrates [all (1:1)] (Smith *et al.*, 1995; Kumar *et al.*, 1999)].

Taking into account the potential for proton transfer and the associative nature of the urea molecule, we expected the structure of the product of the interaction of the unsymmetrically substituted urea, 8-quinolinylurea (QUR) with DNSA, the (1:1) proton-transfer complex [(QUR)$^+$(DNSA)$^-$], to be of considerable interest. QUR is also known for its biological effects, such as cytotoxicity or mutagenic properties (Pagani *et al.*, 1983: Smith, Hansch & Morton, 1997).

The structure (Fig. 1) shows that the hetero–N atom of QUR is protonated and gives strong intermolecular hydrogen-bonding associations with a hydroxyl O atom [N11$\cdots$O2^{i} 2.711 (2) Å; symmetry code: (i) $1-x, -y, 1-z$] and a nitro–O atom of the same DNSA anion [N11$\cdots$O31^{i} 2.837 (2) Å]. Completing a four-centre association about the quinolinium proton is an intramolecular hydrogen bond to the first urea–N atom [N11—H11$\cdots$N1 2.841 (2) Å]. The urea residue is twisted out of the plane of the quinolinyl ring [torsion angles: C17—C18—N1—C182 115.2 (2)°; C18—N1—C182—N2 −167.3 (2)°]. All available hydrogen-bonding sites on the urea residue are utilized [N1$\cdots$O182 2.800 (2) Å; N2$\cdots$O71 2.981 (2) Å; N2$\cdots$O71 3.251 (2) Å; N2$\cdots$O72 3.101 (2) Å], giving a three-dimensional network polymer (Fig. 2). A number of C—H$\cdots$O associations (Table 1) add to the stability of the structure.

The intramolecular hydrogen bond between the carboxylate group and the *ortho*-related hydroxyl group is dimensionally similar to those found in all of the complexes and adducts of DNSA [O72—O2 2.492 (2) Å; range 2.409–2.464 Å]. The type of intramolecular bond found here places this compound in a minor category within the series of those compounds in which the hydroxyl proton is *anti*-located adjacent to the carboxyl oxygen within the hydrogen bond, rather than being on the hydroxyl oxygen (this type of hydrogen bond was also reported in the proton-transfer compounds with 3-amino-1*H*-1,2,4-triazole, 3-aminobenzoic acid and 4-aminobenzoic acid).

Experimental

Synthesis was carried out by initially mixing together equimolar quantities (1 mmol) of 3,5-dinitrosalicylic acid and (8-quinolinyl)urea at which stage reaction was observed as a colour change to orange-yellow. 50 ml of 80% ethanol/water were added to the product and the mixture was heated with stirring until the volume was reduced to *ca* 40 ml. Crystals were obtained after partial room temperature evaporation of the filtered solution.

Crystal data

$C_{10}H_{10}N_3O^+\cdot C_7H_3N_2O_7^-$
$M_r = 415.32$
Triclinic, $P\overline{1}$
$a = 13.061$ (2) Å
$b = 13.898$ (2) Å
$c = 4.8910$ (17) Å
$\alpha = 93.33$ (2)°
$\beta = 93.21$ (2)°
$\gamma = 101.764$ (14)°
$V = 865.6$ (4) Å^3
$Z = 2$
$D_x = 1.594$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 12.6$–17.7°
$\mu = 0.13$ mm^{-1}
$T = 295$ (2) K
Blocky prism, yellow
0.45 × 0.42 × 0.20 mm

Data collection

Rigaku AFC-7*R* diffractometer
ω–2θ scans
4728 measured reflections
3980 independent reflections
3117 reflections with $I > 2\sigma(I)$
$R_{int} = 0.058$
$\theta_{max} = 27.5°$
$h = -16 \rightarrow 16$
$k = -18 \rightarrow 18$
$l = -6 \rightarrow 2$
3 standard reflections every 150 reflections
intensity decay: 1.4%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.125$
$S = 1.04$
3980 reflections
287 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0527P)^2 + 0.3656P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.30$ e Å^{-3}
$\Delta\rho_{min} = -0.20$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.024 (4)

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O182^{i}	0.83 (2)	2.00 (2)	2.800 (2)	162 (2)
N11—H11···N1	0.89 (2)	2.54 (2)	2.841 (2)	100.3 (17)
N11—H11···O2^{ii}	0.89 (2)	1.89 (2)	2.7111 (19)	152.7 (17)
N11—H11···O31^{ii}	0.89 (2)	2.48 (2)	2.837 (2)	104.4 (17)
N2—H21···O71	0.88 (2)	2.10 (2)	2.981 (2)	173 (2)
N2—H22···O71^{i}	0.83 (3)	2.58 (3)	3.251 (2)	139 (2)
N2—H22···O72^{iii}	0.83 (3)	2.41 (3)	3.101 (2)	142 (2)
O72—H72···O2	0.93 (3)	1.60 (3)	2.492 (2)	161 (3)
C4—H4···O51^{iv}	0.989	2.57	3.547 (3)	171
C12—H12···O31^{v}	0.92	2.37	3.201 (3)	150
C13—H13···O31^{vi}	1.00	2.47	3.326 (3)	144
C14—H14···O52^{vii}	1.06	2.52	3.347 (3)	135
C15—H15···O52^{viii}	1.02	2.60	3.168 (3)	115

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

The positional parameters only for those atoms which are involved in hydrogen bonding (H1, H11, H21, H22 and H72; located by difference methods) were refined. All other H atoms were placed in calculated positions and included in the refinement in the riding-model approximation.

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

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