Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

Guanidinium 3,5-dinitrosalicylate

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Received 18 May 2001
Accepted 21 June 2001
Online 29 June 2001

The crystal structure determination of guanidinium 3,5-dinitrosalicylate, $(GU)^+(DNSA)^-$, $CH_6N_3^+\cdot C_7H_3N_2O_7^-$, has revealed a three-dimensional network polymer comprising hydrogen-bonded cyclic A—B hetero-dimer units [O···N 2.914 and 2.924 (3) Å] linked through peripheral hydrogen bonds between guanidinium H atoms and O atoms (carboxylate, phenolic and nitro) of the DNSA anions [N···O 2.844–3.166 (3) Å].

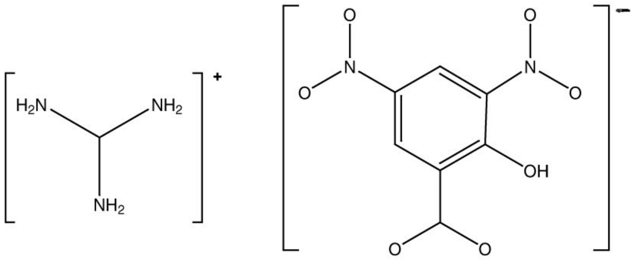
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.040
wR factor = 0.133
Data-to-parameter ratio = 10.1

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

Comment

The nitro-substituted aromatic acid 3,5-dinitrosalicylic acid (DNSA) has proven potential for formation of proton-transfer compounds, particularly because of its acid strength (pK_a = 2.18), its interactive *ortho*-related phenolic substituent group together with the nitro substituents which have potential for both π–π interactions as well as hydrogen-bonding interactions. A large number of both neutral and proton-transfer compounds of Lewis bases with DNSA, together with their IR spectra have been reported (Hindawey *et al.*, 1980; Issa *et al.*, 1981), while the crystal structures of both the parent acid as the monohydrate DNSA.H_2O (Smith *et al.*, 1995) and several of its adducts are also known: with urea [(DNSA)(UR)] (Smith *et al.*, 1997); with the isomeric aminobenzoic acids (Smith *et al.*, 1995): 2-aminobenzoic acid [$(2\text{-ABA})^+(DNSA)^-$], 3-aminobenzoic acid [$(3\text{-ABA})^+(DNSA)^-$] and 4-aminobenzoic acid [$(4\text{-ABA})(4\text{-ABA})^+(DNSA)^-$]; with 3-amino-1*H*-1,2,4-triazole [$(3\text{-AT})^+(DNSA)^-$] (Smith *et al.*, 1996), with 8-aminoquinoline [$(8\text{-AQ})^+(DNSA)^-$] (Smith, Wermuth, Bott *et al.*, 2001), and with 8-quinolinol [$(8\text{-HQ})^+(DNSA)^-$] (Smith, Wermuth & White, 2001). In all of these, the hydrogen-bonded interactions following proton transfer are extensive giving stable high melting point solids.



(I)

Reported here is the 1:1 proton-transfer compound, (I), of guanidine (GU) with DNSA [$(GU)^+(DNSA)^-$] in which the primary hydrogen-bonding interaction is between both O atoms of the carboxylate group of DNSA and H atoms of two

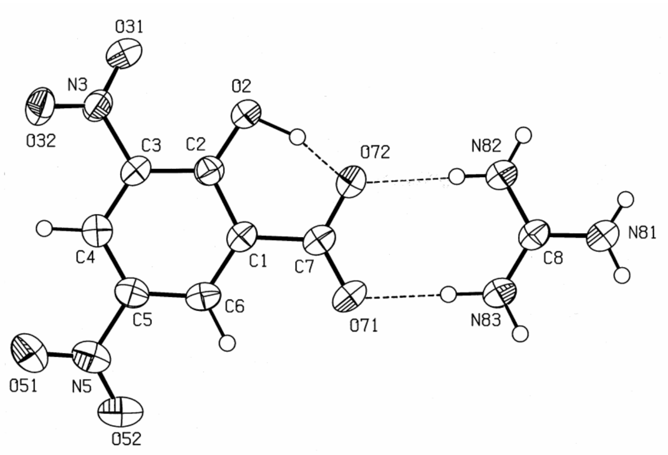


Figure 1
The molecular configuration and atom-numbering scheme for the hydrogen-bonded guanidinium cation and 3,5-dinitrosalicylate anion dimer units in [GU$^+$][DNSA$^-$]. Atoms are shown as 50% probability ellipsoids.

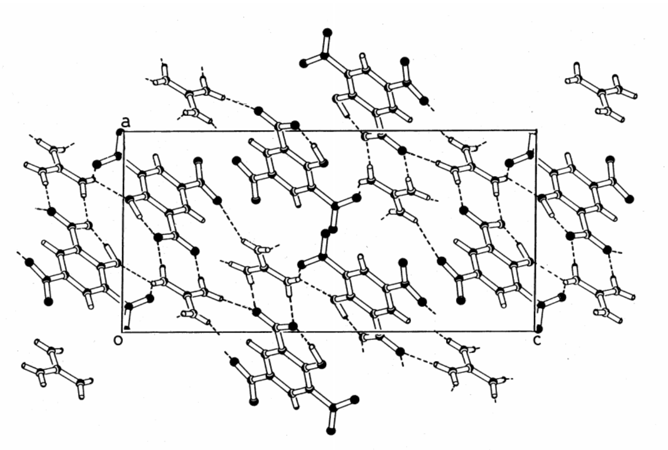


Figure 2
The hydrogen-bonding scheme (shown as broken lines) viewed down the *b*-cell direction.

of the amine groups of GU [O71···H832—N83 2.914 (3) Å and O···H—N 178 (2)°; O72···H821—N82 2.924 (3) Å and O···H—N 179 (2)°]. This forms a cyclic eight-membered ring [graph-set $R_2^2(8)$; Etter, 1990] (Fig. 1). The second proton on N82 gives secondary three-centre interactions with the DNSA substituent groups, one to the phenol oxygen [N82—H822···O2 2.904 (3) Å and N—H···O 142 (2)°; symmetry code: $1 - x$, $2 - y$, $2 - z$] and one to a nitro oxygen [N82—H822···O31 3.070 (3) Å and N—H···O, 143 (2)°; symmetry code: $1 - x, 2 - y, 2 - z$]. Oxygen O31 is also linked to one of the protons on N81 [O31···H811—N81 2.972 (3) Å and O···H—N 149 (2)°; symmetry code: $1 - x$, $2 - y$, $2 - z$]. The other proton on N81 is also linked to a nitro oxygen [N81—H812···O52 3.166 (3) Å and N—H···O 146 (2)°; symmetry code: $\frac{1}{2} - x$, $\frac{3}{2} + y$, $\frac{3}{2} - z$)], while the second proton on N83 gives a peripheral link to an adjacent carboxyl group [N83—H831···O71 2.844 (3) Å and N—H···O 156 (2)°; symmetry code: $\frac{1}{2} - x$, $\frac{1}{2} + y$, $\frac{3}{2} - z$]. This results in a network polymer (Fig. 2). The phenolic proton participates in an intramolecular hydrogen bond with the carboxylic acid oxygen [O2—H2···O72 2.415 (3) Å and O—H···O 164 (2)°]. This is similar to the situation found for salicylic acid (O···O 2.640 Å; Sundaralingam & Jensen, 1965), and for 3,5-dinitrosalicylic acid (O···O 2.566 Å; Smith *et al.*, 1995). Although this distance is shorter than for these acids, it is comparable with the values for the other known Lewis-base compounds with DNSA (range 2.452–2.460 Å; Smith *et al.*, 1995).

Experimental

The synthesis of the title compound was carried out by refluxing equimolar quantities (1 mmol) of 3,5-dinitrosalicylic acid and guanidine in 20 ml of 50% aqueous ethanol for 15 min at 350 K. Crystals were obtained by room-temperature evaporation of the solvent.

Crystal data

$CH_6N_3^+\cdot C_7H_3N_2O_7^-$
M_r = 287.19
Monoclinic, $P2_1/n$
a = 9.806 (3) Å
b = 5.928 (3) Å
c = 19.933 (2) Å
β = 90.696 (16)°
V = 1158.6 (7) Å^3
Z = 4

D_x = 1.647 Mg m^{-3}
Mo Kα radiation
Cell parameters from 25 reflections
θ = 18.0–20.0°
μ = 0.15 mm^{-1}
T = 293 (2) K
Prism, yellow
0.50 × 0.35 × 0.20 mm

Data collection

Rigaku AFC-7*R* diffractometer
ω–2θ scans
2172 measured reflections
2046 independent reflections
1307 reflections with $I > 2\sigma(I)$
R_{int} = 0.024
θ_{max} = 25.1°

$h = 0 \rightarrow 11$
$k = 0 \rightarrow 7$
$l = -23 \rightarrow 23$
3 standard reflections every 150 reflections
intensity decay: 0.1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.134$
S = 1.05
2046 reflections
203 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.069P)^2 + 0.2414P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.20 e Å^{-3}
$\Delta\rho_{min}$ = −0.26 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.020 (3)

The positional parameters for only the atoms involved in intermolecular hydrogen bonding (H2, H811, H812, H821,H822, H831 and H832) were refined. All other H atoms were constrained in the refinement.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1996); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN for Windows* (Molecular Structure Corporation, 1997–1999); program(s) used to solve structure: *SAPI*91 (Fan, 1991); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); software used to prepare material for publication: *TEXSAN for Windows* and *PLATON for Windows* (Spek, 1999).

The authors acknowledge financial support from The Centre for Instrumental and Developmental Chemistry (Queensland University of Technology) and the Australian Research Council. Dr Peter Healy is thanked for collection of X-ray diffraction data.

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