Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Diethylaminium 3,5-dinitrosalicylate at 130 K

Graham Smith,[a]* Urs D. Wermuth[a] and Jonathan M. White[b]

[a]School of Physical and Chemical Sciences, Queensland University of Technology, GPO Box 2434, Brisbane 4001, Australia, and [b]School of Chemistry, University of Melbourne, Parkville 3052, Australia

Correspondence e-mail: g.smith@qut.edu.au

Key indicators

Single-crystal X-ray study
T = 130 K
Mean σ(C–C) = 0.004 Å
R factor = 0.065
wR factor = 0.195
Data-to-parameter ratio = 11.7

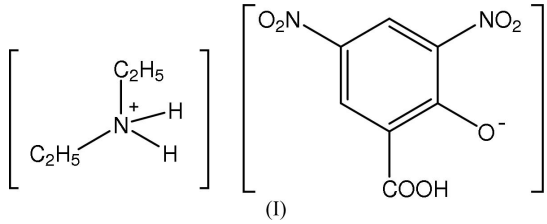
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 5 May 2005
Accepted 12 May 2005
Online 21 May 2005

The low-temperature (130 K) crystal structure of the 1:1 proton-transfer compound of 3,5-dinitrosalicylic acid (DNSA) with diethylamine, *viz*. diethylaminium 3,5-dinitrosalicylate, $C_4H_{12}N^+\cdot C_7H_3N_2O_7^-$, shows the presence of conformationally extended diethylaminium cations in which both H atoms of the aminium centres participate in three-centre hydrogen-bonding associations [one $R_1^2(4)$ and the other $R_1^2(6)$] with carboxyl, phenol and nitro O-atom acceptors of two separate DNSA anion species [N···O = 2.813 (3)–3.320 (3) Å]. These result in 12-membered cyclic $R_6^4(12)$ associations linking the two sets of hetero-species into discrete centrosymmetric tetramers which have no significant peripheral extensions.

Comment

3,5-Dinitrosalicylic acid (DNSA) is a sufficiently strong acid (pK_a 2.2) to protonate most amines and only in rare examples with very weak bases does protonation not occur, *e.g.* with phenazine (pK_a 1.2) (Kumar *et al.*, 2002). The phenazine compound is analogous to the DNSA adducts formed with compounds such as urea (Smith *et al.*, 1997), 1,1-diethylurea (Smith *et al.*, 2000), and the pseudopolymorphic set of solvates, namely two monohydrates (Smith *et al.*, 1995; Kumar *et al.*, 1999), four dioxinates and a *tert*-butyl alcoholate (Kumar *et al.*, 1999). We have previously reported the crystal structures of a number of proton-transfer compounds of DNSA with Lewis bases (Smith *et al.*, 1995, 2002, 2003). Among these compounds, those with primary amines particularly result in alkylaminium or anilinium cations which often give hydrogen-bonding interactions with up to six acceptor atoms, *e.g.* with methylamine 1:1 (Smith *et al.*, 2002) and aniline (Smith *et al.*, 2003). As expected, the number of hydrogen-bonding interactions increases, proceeding from tertiary to primary amine types, with π–π interactions insignificant in the self-assembly process, occurring only occasionally among heteroaromatic types.



(I)

Compound (I) is the 1:1 proton-transfer compound of DNSA with diethylamine (DEA; pK_a = 11.0) (Fig. 1). Each of the H atoms on the aminium-N of the DEA cation participates in three-centre hydrogen-bonding interactions with DNSA

O-acceptors from two separate DNSA anions (Fig. 2). The first is an $R_1^2(6)$ association involving the phenolic and nitro groups (N11—H11*A*···O2 and N11—H11*A*···O31) and the second is an asymmetric $R_1^2(4)$ association with the two carboxylate O atoms of an inversion-related DNSA anion [N11—H11*B*···O71^{i} and N11—H11*B*···O72^{i}; symmetry code: (i) $1-x, -y, 1-z$]. This creates discrete centrosymmetric hetero-tetramer units with cyclic interstitial $R_6^4(12)$-linked centres. The ethyl groups of the DEA cations adopt extended conformations which place them above and below the plane of the tetramer units. The ethyl groups are also ordered, unlike those found in the cations in the low-temperature structure of triethylaminium 3,5-dinitrosalicylate (Smith *et al.*, 2002). There are no significant peripheral extensions of the tetramer units through hydrogen bonding (Table 1).

The usual intramolecular hydrogen bond is found between the phenolic and carboxylate groups of the DNSA anion (O72—H72···O2), with the H atom located on the carboxylate O atom. The carboxyl group is therefore essentially coplanar with the benzene ring [C2—C1—C7—O71 176.6 (3)°], as are the two nitro substituent groups [C2—C3—N3—O32 172.3 (2)° and C4—C5—N5—O52 179.0 (2)°].

Experimental

The title compound was synthesized by heating 1 mmol quantities of 3,5-dinitrosalicylic acid (DNSA) and diethylamine (DEA) in 80% ethanol–water (50 ml) for 10 min under reflux. After concentration to *ca* 30 ml, partial room-temperature evaporation of the hot-filtered solution gave yellow crystals of (I) (m.p. 431.8–433.6 K).

Crystal data

$C_4H_{12}N^+\cdot C_7H_3N_2O_7^-$
$M_r = 301.26$
Triclinic, $P\overline{1}$
$a = 7.329$ (3) Å
$b = 10.168$ (5) Å
$c = 10.660$ (5) Å
$\alpha = 67.126$ (5)°
$\beta = 80.663$ (8)°
$\gamma = 71.700$ (8)°
$V = 694.1$ (5) Å^3
$Z = 2$
$D_x = 1.441$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1831 reflections
$\theta = 2.3$–27.5°
$\mu = 0.12$ mm^{-1}
$T = 130$ (2) K
Block, yellow
0.40 × 0.40 × 0.35 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: none
3502 measured reflections
2395 independent reflections
1886 reflections with $F^2 > 2\sigma(F^2)$
$R_{int} = 0.071$
$\theta_{max} = 25.0°$
$h = -6 \rightarrow 8$
$k = -8 \rightarrow 12$
$l = -11 \rightarrow 12$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.065$
$wR(F^2) = 0.195$
$S = 1.04$
2395 reflections
204 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.119P)^2 + 0.1544P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.46$ e Å^{-3}
$\Delta\rho_{min} = -0.32$ e Å^{-3}

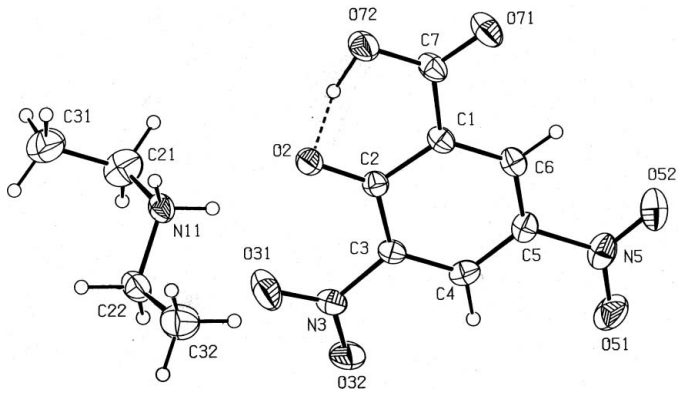


Figure 1
The molecular configuration and atom-numbering scheme for the DEA cation–DNSA anion pair in (I). Atoms are shown as 30% probability displacement ellipsoids. The dashed line indicates a hydrogen bond.

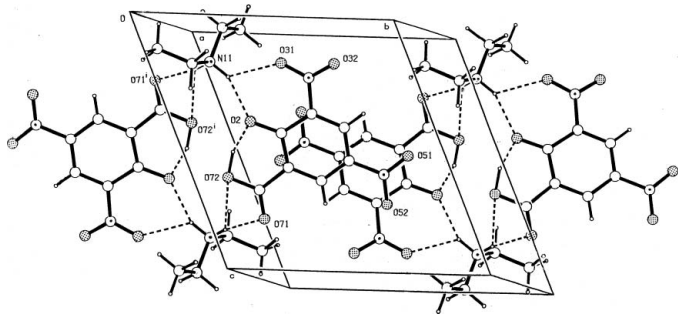


Figure 2
A perspective view of the packing in the unit cell of (I), viewed approximately down the *a* axis direction, showing hydrogen-bonding associations as broken lines.

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

D—H···A	D—H	H···A	D···A	D—H···A
O72—H72···O2	1.05 (4)	1.47 (4)	2.489 (3)	161 (4)
N11—H11*A*···O2	0.92 (4)	1.96 (4)	2.813 (3)	154 (4)
N11—H11*A*···O31	0.92 (4)	2.40 (4)	2.986 (3)	122 (3)
N11—H11*B*···O71^{i}	0.92 (5)	1.96 (5)	2.871 (3)	169 (4)
N11—H11*B*···O72^{i}	0.92 (5)	2.60 (4)	3.320 (3)	136 (4)
C22—H22*A*···O31	0.99	2.55	3.099 (4)	115
C22—H22*B*···O71^{ii}	0.99	2.54	3.469 (4)	156

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

H atoms involved in hydrogen-bonding interactions (H11*A*, H11*B* and H72) were located by difference methods and their positional and isotropic displacement parameters were refined. Other H atoms were included in the refinement in calculated positions [C—H(aromatic) = 0.92 Å and C—H(aliphatic) = 0.95 or 0.99 Å], using the riding-model approximation, with U_{iso}(H) fixed at $1.2U_{eq}$(C). The methyl groups were allowed to rotate but not tip.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Bruker, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *PLATON*.

The authors acknowledge financial support from the School of Physical and Chemical Sciences of the Queensland University of Technology and the University of Melbourne.

References

Bruker (1997). *SHELXTL*. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (1999). *SAINT*. Version 6.02. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2000). *SMART*. Version 5.55. Bruker AXS Inc., Madison, Wisconsin, USA.
Kumar, V. S. S., Kuduva, S. S. & Desiraju, G. R. (1999). *J. Chem. Soc. Perkin Trans. 2*, pp. 1069–1073.
Kumar, V. S. S., Kuduva, S. S. & Desiraju, G. R. (2002). *Acta Cryst.* E**58**, o865–o866.
Smith, G., Baldry, K. A., Byriel, K. A. & Kennard, C. H. L. (1997). *Aust. J. Chem.* **50**, 727–736.
Smith, G., Coyne, M. G. & White, J. M. (2000). *Aust. J. Chem.* **53**, 203–208.
Smith, G., Lynch, D. E., Byriel, K. A. & Kennard, C. H. L. (1995). *Aust. J. Chem.* **48**, 1133–1149.
Smith, G., Wermuth, U. D., Bott, R. C., Healy, P. C. & White, J. M. (2002). *Aust. J. Chem.* **55**, 349–356.
Smith, G., Wermuth, U. D., Healy, P. C. & White, J. M. (2003). *Aust. J. Chem.* **56**, 707–713.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.