organic papers

1,4-Diazabicyclo[2.2.2]octanium bis(3,5-dinitro-benzoate) monohydrate

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The title compound, $C_6H_{14}N_2^{2+} \cdot 2C_7H_3N_2O_6^- \cdot H_2O$, is a monohydrate of a 1:2 hydrate adduct of 1,4-diazabicyclo[2.2.2]-octane (DABCO) and 3,5-dinitrobenzoic acid. The $(DABCOH_2)^{2+}$ cation adopts the role of a donor in intermolecular N—H···O hydrogen bonding, while both the 3,5-dinitrobenzoate anions act as multiple acceptors of N—H···O, O—H···O and C—H···O hydrogen bonds. These hydrogen bonds result in the formation of a three-dimensional network.

Comment

Interactions of organic acids with amine bases in the solid phase have been of interest due to their hydrogen-bonding interactions (Coupar *et al.*, 1997; Sobczyk *et al.*, 2000) and their important role in biological systems (Blow, 1976). Among the organic acids, 3,5-dinitrobenzoic acid is of interest since it readily forms the 3,5-dinitrobenzoate anion when co-crystallized with amine bases by transferring a proton. This proton transfer leads to the formation of salt-like adducts consisting of 3,5-dinitrobenzoate anions and amine-based cations in which the 3,5-dinitobenzoate anion is expected to act as a multiple acceptor of hydrogen bonds *via* nitro and carboxylate groups.

Owing to this interest, we have investigated recently the interaction between 3,5-dinitrobenzoic acid with several amine bases such as 2,4′-bipyridine (Chantrapromma *et al.*, 2002*a*), quinuclidine (Chantrapromma,Usman, Fun, Poh & Karalai, 2004) and hexamethylenetetramine (Fun *et al.*, 2003; Chantrapromma, Usman & Fun, 2004). The proton transfer process occurs in these adducts and the adduct of 3,5-dinitrobenzoic acid with hexamethylenetetramine undergoes a phase transition (Fun *et al.*, 2003). In our ongoing systematic studies on the interactions between 3,5-dinitrobenzoic acid and amine bases, the title compound, (I), was prepared.

(I)
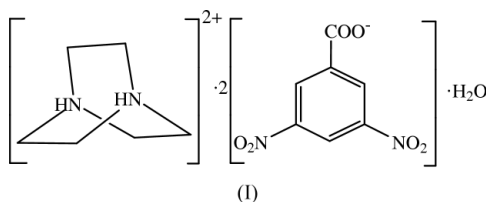
The asymmetric unit of (I) (Fig. 1) comprises one 1,4-di-azabicyclo[2.2.2]octanium dication, $[HN(CH_2CH_2)_3NH]^{2+}$ or $(DABCOH_2)^{2+}$, two 3,5-dinitrobenzote anions and one water molecule. Each molecule of 3,5-dinitrobenzoic acid has transferred a proton from its carboxyl group to an N atom of
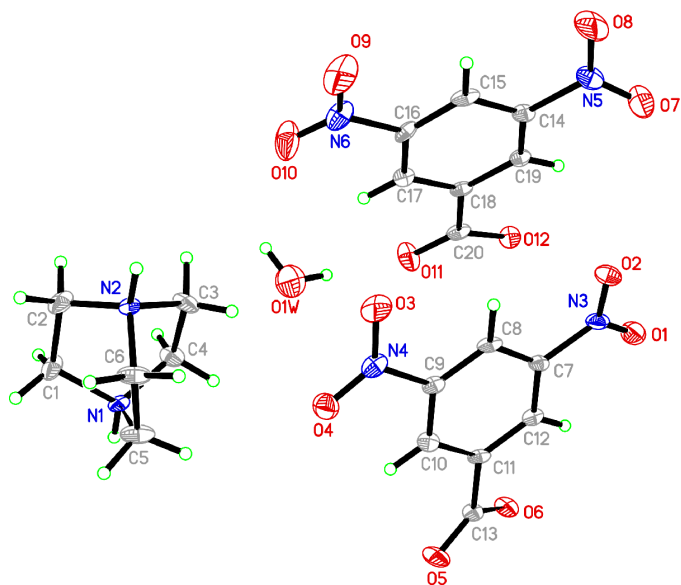
Figure 1
The asymmetric unit of the title compound, showing 50% probability displacement ellipsoids and the atomic numbering scheme.

Figure 2
Packing diagram of the title compound, viewed down the c axis, illustrating the intermolecular hydrogen bonds (dashed lines).

DABCO which, together with the water molecule, has resulted in the asymmetric unit being a hydrated salt.

This protonation process is accompanied by an increase in the N—C bond distances around these N atoms [average N—C bond distance is 1.492 (4) Å]. These N—C bond distances agree with the mean value of 1.502 (15) Å reported for C—N⁺ bonds by Allen *et al.* (1987). The protonated N—C bonds in the doubly protonated (DABCOH₂)²⁺ are comparable with the protonated N—C bond in the singly protonated (DABCOH)⁺ cation (Chantrapromma *et al.*, 2002*b*; Ferguson *et al.*, 1997).

The N—C—C—N—C—C six-membered rings of the (DABCOH₂)²⁺ cation adopt a slightly twisted boat conformation with puckering parameters (Cremer & Pople, 1975) Q = 0.827 (3) Å, θ = 89.9 (2)° and φ = 348.4 (2)° for the N1/C1/C2/N2/C3/C4 ring, Q = 0.832 (3) Å, θ = 90.1 (2)° and φ = 191.6 (2)° for the N1/C1/C2/N2/C6/C5 ring, and Q = 0.825 (3) Å, θ = 89.7 (2)° and φ = 348.3 (2)° for the N1/C4/C3/N2/C6/C5 ring. The bond lengths and angles within the two symmetry-independent 3,5-dinitrobenzoate anions are comparable and both molecules are nearly planar. The geometric parameters in the 3,5-dinitrobenzoate anion are also comparable with the corresponding values in its adducts with quinuclidine (Chantrapromma, Usman, Fun, Poh & Karalai, 2004).

In the crystal structure of (I) (Fig. 2), the (DABCOH₂)²⁺ cation and 3,5-dinitrobenzoate anions are linked by intermolecular N—H···O hydrogen bonds (Table 2), with the (DABCOH₂)²⁺ cation acting as a donor. The carboxylate O atoms act as acceptors of intermolecular O—H···O hydrogen bonds with the water molecules. In addition to the electrostatic, N—H···O and O—H···O interactions, the crystal structure is also stabilized by C—H···O interactions (Table 2). These interactions link the ions and water molecules into a three-dimensional network.
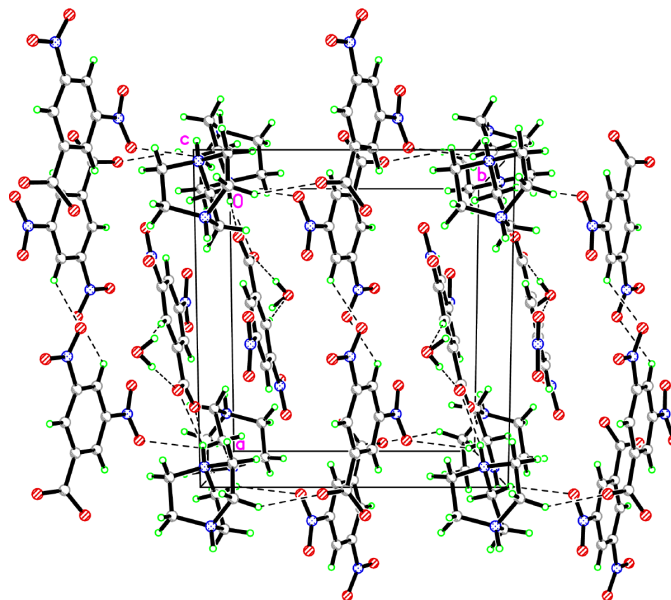
Experimental

Equimolar amounts of 1,4-diazabicyclo[2.2.2]octane (0.34 g, 3 mmol) and 3,5-dinitrobenzoic acid (0.64 g, 3 mmol) were mixed and dissolved in ethanol (50 ml), with addition of 4 ml of distilled water, and the mixture was warmed to the temperature range 328–333 K until a clear solution was obtained. The solution was then filtered and the filtrate was left to evaporate slowly in air. Colorless single crystals, suitable for X-ray diffraction studies, were obtained from the solution after a few days [m.p. 547–548 K (decomposition)].

Crystal data

C₆H₁₄N₂²⁺·2C₇H₃N₂O₆⁻·H₂O	D_x = 1.600 Mg m⁻³
M_r = 554.44	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 10514
a = 11.6505 (5) Å	reflections
b = 10.4942 (5) Å	θ = 2.7–25.0°
c = 19.4752 (9) Å	μ = 0.14 mm⁻¹
β = 104.799 (1)°	T = 183 (2) K
V = 2302.10 (18) Å³	Block, colorless
Z = 4	0.44 × 0.32 × 0.16 mm

Data collection

Bruker SMART CCD area-detector	2527 reflections with $I > 2\sigma(I)$
ω scans	R_{int} = 0.076
Absorption correction: multi-scan	θ_{max} = 25.0°
(*SADABS*; Sheldrick, 1996)	$h = -13 \rightarrow 13$
T_{min} = 0.943, T_{max} = 0.979	$k = -12 \rightarrow 12$
10 514 measured reflections	$l = -20 \rightarrow 23$
3987 independent reflections	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o{}^2) + (0.0309P)^2]$
$R[F^2 > 2\sigma(F^2)]$ = 0.053	where $P = (F_o{}^2 + 2F_c{}^2)/3$
$wR(F^2)$ = 0.128	$(\Delta/\sigma)_{max} < 0.001$
S = 0.94	$\Delta\rho_{max}$ = 0.38 e Å⁻³
3987 reflections	$\Delta\rho_{min}$ = −0.44 e Å⁻³
367 parameters	Extinction correction: *SHELXTL*
H atoms treated by a mixture of	Extinction coefficient: 0.0103 (11)
independent and constrained	
refinement	

Table 1
Selected geometric parameters (Å, °).

O5—C13	1.238 (3)	N2—C6	1.488 (4)
O6—C13	1.286 (3)	N2—C2	1.490 (3)
O11—C20	1.234 (3)	N3—C7	1.473 (3)
O12—C20	1.283 (3)	N4—C9	1.482 (3)
N1—C4	1.491 (3)	N5—C14	1.473 (4)
N1—C5	1.497 (3)	N6—C16	1.482 (3)
N1—C1	1.497 (3)	C11—C13	1.521 (4)
N2—C3	1.487 (3)	C18—C20	1.529 (4)
O5—C13—O6	125.6 (3)	O11—C20—O12	125.4 (3)
O6—C13—C11	114.3 (2)	O12—C20—C18	115.7 (2)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1N1$\cdots$O11[i]	0.94 (1)	2.56 (2)	3.119 (3)	118 (2)
N1—H1N1$\cdots$O12[i]	0.94 (1)	1.72 (2)	2.658 (3)	174 (3)
N2—H1N2$\cdots$O6[ii]	0.94 (1)	1.63 (3)	2.566 (3)	174 (4)
O1W—H1W1$\cdots$O5[iii]	0.90 (1)	1.97 (3)	2.823 (3)	156 (3)
O1W—H2W1$\cdots$O11	0.91 (1)	1.95 (3)	2.839 (3)	168 (3)
C1—H1B$\cdots$O1[iv]	0.99	2.50	3.332 (4)	141
C3—H3A$\cdots$O4	0.99	2.60	3.409 (3)	139
C3—H3B$\cdots$O5[iii]	0.99	2.43	3.306 (4)	148
C6—H6B$\cdots$O2[v]	0.99	2.51	3.397 (4)	149
C6—H6B$\cdots$O7[v]	0.99	2.54	3.189 (4)	123
C8—H8$\cdots$O3[v]	0.95	2.49	3.264 (3)	138
C17—H17$\cdots$O1W	0.95	2.41	3.315 (4)	160

Symmetry codes: (i) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; (ii) $x-1, y, z$; (iii) $\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$; (iv) $x-\frac{1}{2}, \frac{3}{2}-y, \frac{1}{2}+z$; (v) $-x, 2-y, -z$.

H atoms of the water molecule and the H atoms attached to atoms N1 and N2 were located in a difference map. They were refined isotropically with the O—H and H$\cdots$H distances restrained to 0.89 (1) and 1.39 (1) Å, respectively, and with N—H = 0.93 (1) Å. The remaining H atoms were positioned geometrically (C—H = 0.95–0.99 Å) and allowed to ride on their parent C atoms, with U_{iso}(H) = $1.2U_{eq}$(C).

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2003).

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