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Key indicators

Single-crystal X-ray study
T = 100 K
Mean $\sigma(\text{C}-\text{C}) = 0.001 \text{ \AA}$
R factor = 0.028
wR factor = 0.073
Data-to-parameter ratio = 11.6

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

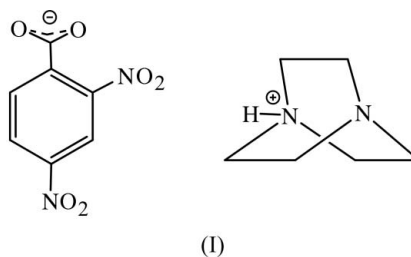
4-Aza-1-azoniabicyclo[2.2.2]octane 2,4-dinitrobenzoate

In the title compound, $\text{C}_6\text{H}_{13}\text{N}_2^+ \cdot \text{C}_7\text{H}_3\text{N}_2\text{O}_6^-$, the 1-azonia-4-azabicyclo[2.2.2]octane cation acts as a donor in intermolecular $\text{N}-\text{H} \cdots \text{O}$ hydrogen bonds. Beside the electrostatic interactions, the crystal structure is also stabilized by $\text{C}-\text{H} \cdots \text{O}$ hydrogen bonds to give a three-dimensional molecular network.

Received 6 September 2006
Accepted 15 September 2006

Comment

Interactions between phenols or organic acids with amine bases in the solid phase are widely used to study hydrogen bonds since the two components are generally linked by intramolecular or intermolecular $\text{O}-\text{H} \cdots \text{O}$, $\text{O}-\text{H} \cdots \text{N}$ or $\text{N}-\text{H} \cdots$ hydrogen bonds (Desiraju, 1995; Chantrapromma *et al.*, 2006). As part of our ongoing studies of hydrogen-bonded interactions and phase transitions due to hydrogen-bonding (Usman *et al.*, 2001; Fun *et al.*, 2003; How *et al.*, 2005), we have investigated the interaction between 2,4-dinitrobenzoic acid and several amine bases, such as hexamethylenetetraminium (Rosli *et al.*, 2006a) and 2-methylquinolinium (Rosli *et al.*, 2006b). In this paper, we present another compound, (I), in which protonation has occurred, resulting in an organic salt.



In the crystal structure of (I), all bond lengths and angles show normal values (Allen *et al.*, 1987). The carboxylate and neighbouring nitro group are twisted away from the plane of the benzene ring, with dihedral angles of $46.33 (5)^\circ$ for $\text{O}2-\text{N}1-\text{O}2$, $14.93 (7)^\circ$ for $\text{O}3-\text{N}2-\text{O}4$ and $56.6 (1)^\circ$ for $\text{O}5-\text{C}7-\text{O}6$. The dihedral angle between the planes of the adjacent carboxylate and nitro groups is $51.99 (10)^\circ$. The 1-azonia-4-azabicyclo[2.2.2]octane cation, $(\text{DABCO})^+$, is made up of three four-atom planes having atoms N3 and N4 in common, with the following puckering parameters (Cremer & Pople, 1975): $Q = 0.805 (1) \text{ \AA}$, $\theta = 90.6 (1)^\circ$ and $\varphi = 183.00 (7)^\circ$ for the N3/C8/C9/N4/C11/C10 ring, $Q = 0.814 (1) \text{ \AA}$, $\theta = 89.0 (1)^\circ$ and $\varphi = 357.37 (7)^\circ$ for the N3/C8/C9/N4/C13/C12 ring, and $Q = 0.804 (1) \text{ \AA}$, $\theta = 91.1 (1)^\circ$ and $\varphi = 183.15 (8)^\circ$ for the N3/C10/C11/N4/C13/C12 ring.

In the crystal structure of (I), the $(\text{DABCO})^+$ cation and 2,4-dinitrobenzoate anions are linked by intermolecular $\text{N}3-$

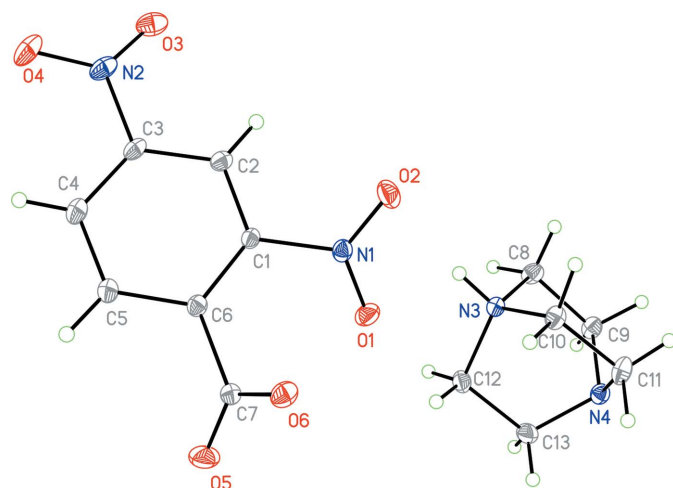


Figure 1
The asymmetric unit of (I), showing 50% probability displacement ellipsoids and the atomic numbering.

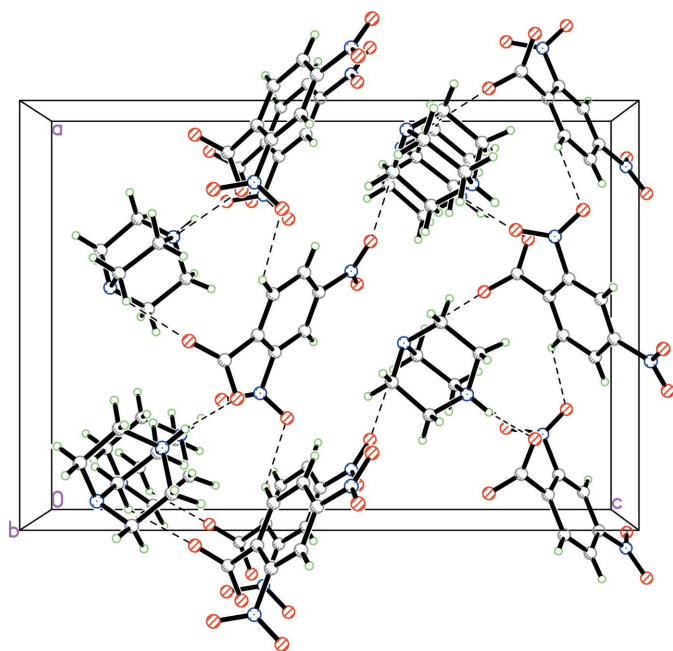


Figure 2
The crystal packing of (I) viewed down the *b* axis. Hydrogen bonds are shown as dashed lines.

H1N3...O6ⁱ hydrogen bonds (Table 1). The crystal structure is also stabilized by C—H...O interactions (Table 1), forming a three-dimensional network

Experimental

Equimolar amounts of triethylenediamine (0.23 g, 2 mmol) and 2,4-dinitrobenzoic acid (0.43 g, 2 mmol) were thoroughly mixed and dissolved in acetone (45 ml) with addition of 1 ml of distilled water. The mixture was warmed up to the temperature range 313–318 K until a clear solution was obtained. The solution was filtered and the filtrate was left to evaporate slowly in air. Pale-yellow block-shaped

single crystals suitable for X-ray diffraction studies were obtained from the solution after a few days (m.p. 470–472 K).

Crystal data

C₆H₁₃N₂⁺·C₇H₃N₂O₆[−]
M_r = 324.30
 Orthorhombic, *Pna*2₁
a = 12.7934 (2) Å
b = 5.9310 (1) Å
c = 18.4255 (3) Å
V = 1398.08 (4) Å³

Z = 4
D_x = 1.541 Mg m^{−3}
 Mo Kα radiation
 μ = 0.12 mm^{−1}
T = 100.0 (1) K
 Block, pale yellow
 0.78 × 0.49 × 0.32 mm

Data collection

Bruker SMART APEX2 CCD area-detector diffractometer
 ω scans
 Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
T_{min} = 0.866, *T_{max}* = 0.961

22351 measured reflections
 3163 independent reflections
 3059 reflections with *I* > 2σ(*I*)
R_{int} = 0.031
 θ_{max} = 35.0°

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.028
wR(*F*²) = 0.074
S = 1.05
 3163 reflections
 272 parameters
 Only H-atom coordinates refined

$w = 1/[\sigma^2(F_o^2) + (0.0531P)^2 + 0.0611P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 (Δ/σ)_{max} = 0.001
 Δρ_{max} = 0.38 e Å^{−3}
 Δρ_{min} = −0.20 e Å^{−3}

Table 1

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N3—H1N3...O6 ⁱ	0.88 (2)	1.85 (2)	2.6870 (11)	158 (2)
C5—H5...O2 ⁱⁱ	0.94 (2)	2.50 (2)	3.2375 (12)	135 (2)
C9—H9A...O4 ⁱⁱⁱ	0.96 (2)	2.52 (2)	3.3304 (14)	142 (1)
C9—H9B...O5 ^{iv}	1.02 (2)	2.44 (2)	3.2999 (13)	142 (2)

Symmetry codes: (i) *x*, *y* + 1, *z*; (ii) *x* − ½, −*y* + ½, *z*; (iii) −*x* + 1, −*y* + 2, *z* − ½; (iv) *x* + ½, −*y* + ½, *z*.

All H atoms were located in a difference Fourier map and refined isotropically. In the absence of significant anomalous scattering effects, Friedel pairs were merged.

Data collection: *APEX2* (Bruker, 2005); cell refinement: *APEX2*; data reduction: *SAINT* (Bruker, 2005); program(s) used to solve structure: *SHELXTL* (Sheldrick, 1998); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*, *PARST* (Nardelli, 1995) and *PLATON* (Spek, 2003).

The authors thank the Malaysian Government and Universiti Sains Malaysia for the Scientific Advancement Grant Allocation (SAGA) grant No. 304/PFIZIK/653003/A118. SC also thanks Prince of Songkla University for partial financial support.

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