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1,4-Diazabicyclo[2.2.2]octanium 2,4-dinitrophenolate

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Key indicators

Single-crystal X-ray study
T = 203 K
Mean σ(C–C) = 0.003 Å
R factor = 0.054
wR factor = 0.131
Data-to-parameter ratio = 12.6

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

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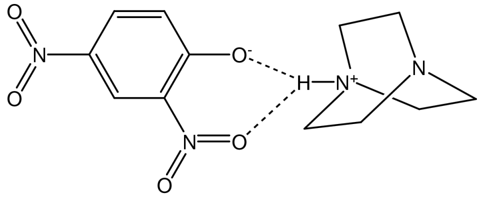
In the title salt, $C_6H_{13}N_2^+\cdot C_6H_3N_2O_5^-$, the cation acts as a donor for the bifurcated intermolecular N—H···O hydrogen bonding interactions with the O atoms of the phenolate and one of the nitro groups of the 2,4-dinitrophenolate. The crystal packing structure is built from molecular ribbons of 2,4-dinitrophenolates parallel to the *c* axis, with the cation linking them by four intermolecular C—H···O hydrogen bonds.

Comment

In the crystal structures of the adducts of 2,4-dinitrophenol (DNP) with relatively strong amine bases, such as diamines [*N*,*N*-dimethylethylenediamine (Chantrapromma *et al.*, 2002) and piperazine (Usman *et al.*, 2001)] or a tertiary amine [hexamethylenetetramine (Usman *et al.*, 2001)], DNP transfers an H atom to the amines forming a DNP$^-$ anion and acts as a multiple acceptor of N—H···O hydrogen bonds involving the nitro and phenolate groups. In a continuation of our systematic studies on the hydrogen-bonding motifs in the adducts of DNP with diamine bases, we have prepared and structurally characterized a 1:1 adduct of 1,4-diazabicyclo[2.2.2]octane $N(CH_2CH_2)_3N$, (DABCO), with DNP. DABCO is also a relatively strong basic diamine which readily forms the $[N(CH_2CH_2)_3NH]^+$ cation with phenols, *e.g.* 1,1,1-tris(4-hydroxyphenyl)ethane (Ferguson *et al.*, 1997); it also forms the $[HN(CH_2CH_2)_3NH]^{2+}$ dication with stronger acids, such as 3,5-dinitrobenzoic acid (Burchell *et al.*, 2001) and phenylphosphonic acid (Ferguson *et al.*, 1998), where the unprotonated N is active in an O—H···N interaction and N—H bonds are involved in N—H···O hydrogen bonds.



(I)

The asymmetric unit (Fig. 1) comprises of one molecule each of DNP and DABCO, in which DNP transfers an H atom from the hydroxy group to the DABCO making them an ionic pair, *viz.* the 2,4-dinitrophenolate (DNP$^-$) anion and 1,4-diazabicyclo[2.2.2]octanium $[N(CH_2CH_2)_3NH]^+$ (DABCOH$^+$) cation.

The H atom transferred to atom N1 was located from a difference map and was freely refined. The DABCOH$^+$ cation N1—C1, N1—C3, and N1—C5 bond distances [1.502 (2),

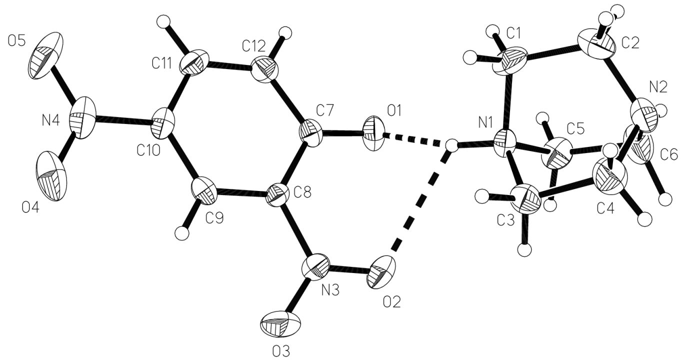


Figure 1
The structure of the title adduct showing 50% probability displacement ellipsoids and the atom-numbering scheme.

1.496 (2) and 1.492 (2) Å] are elongated compared with the unprotonated N2—C2, N2—C4 and N2—C6 [1.456 (3), 1.455 (3) and 1.465 (3) Å]. A similar feature in the DABCOH$^+$ cation was observed by Ferguson *et al.* (1997). The bond lengths and angles in DNP$^-$ are comparable with the corresponding values in its adduct with hexamethylenetetramine or piperazine, irrespective of the fact that both nitro groups of the DNP$^-$ in the title adduct are less twisted around their N—C bonds.

In the title adduct, the N—C—C—N—C—C six-membered rings of the DABCOH$^+$ cation adopt almost a boat conformation with puckering parameters (Cremer & Pople, 1975) Q = 0.816 (2) Å, θ = 90.4 (1) and φ = 7.8 (2)° for N1/C1/C2/N2/C4/C3, Q = 0.799 (2) Å, θ = 88.4 (1) and φ = 7.2 (2)° for N1/C1/C2/N2/C6/C5, and Q = 0.813 (2) Å, θ = 91.4 (1) and φ = 8.0 (2)° for N1/C3/C4/N2/C6/C5.

Within the asymmetric unit (Fig. 1), the DABCOH$^+$ and DNP$^-$ ions are linked by intermolecular N1—H11N···O1 and N1—H11N···O2 hydrogen bonds, with the DABCOH$^+$ cation acting as a hydrogen donor in this bifurcated system. DNP$^-$ acts as a multiple acceptor of hydrogen bonds and the DNP$^-$ anions are packed into molecular ribbons along the *c* axis, with DABCOH$^+$ linking DNP$^-$ anions into layers by C5—H5*B*···O3$^{\rm iii}$. DABCOH$^+$ also interconnects DNP$^-$ anions in adjacent layers by C2—H2*A*···O1$^{\rm ii}$, C1—H1*A*···O4$^{\rm i}$ and C3—H3*A*···O5$^{\rm i}$ hydrogen bonds into a three-dimensional molecular network. Fig. 2 shows the packing diagram of the title adduct viewed down the *b* axis, and indicates the intermolecular hydrogen bonds.

Experimental

The title adduct, (I), was prepared by mixing thoroughly equimolar amounts of 1,4-diazabicyclo[2.2.2]octane (0.56 g, 5 mmol) and 2,4-dinitrophenol. The mixture was dissolved in 40 ml of ethanol with addition of 3 ml of distilled water, and was warmed up to the temperature range of 328–333 K until a clear solution was obtained. The solution was then filtered and the filtrate was left to evaporate slowly in air. Yellow single crystals, suitable for X-ray diffraction studies, were obtained from the solution after a few days.

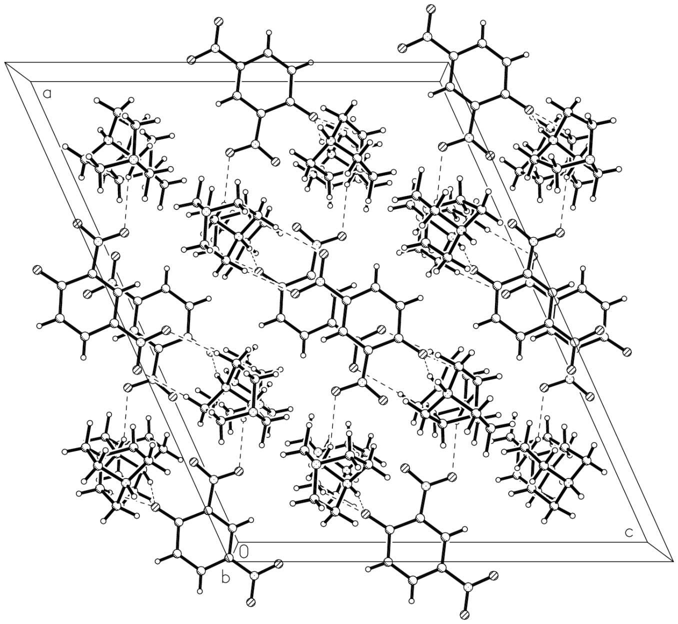


Figure 2
Packing diagram of the title adduct viewed down the *b* axis, showing the hydrogen-bond network.

Crystal data

$C_6H_{13}N_2^+ \cdot C_6H_3N_2O_5^-$
M_r = 296.29
Monoclinic, $C2/c$
a = 23.6934 (4) Å
b = 6.4529 (2) Å
c = 19.1830 (5) Å
β = 114.247 (1)°
V = 2674.2 (1) Å^3
Z = 8
D_x = 1.472 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4593 reflections
θ = 3.3–28.3°
μ = 0.12 mm^{-1}
T = 203 (2) K
Block, yellow
0.38 × 0.32 × 0.18 mm

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{\rm min}$ = 0.957, $T_{\rm max}$ = 0.979
7527 measured reflections
3218 independent reflections
1908 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.074
$\theta_{\rm max}$ = 28.3°
$h = -31 \rightarrow 22$
$k = -8 \rightarrow 8$
$l = -23 \rightarrow 25$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.054
$wR(F^2)$ = 0.131
S = 0.83
3218 reflections
255 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2)]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max}$ = 0.31 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.29 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0057 (7)

Table 1
Selected geometric parameters (Å, °).

C2—C1	1.528 (3)	C6—C5	1.538 (3)
C4—C3	1.534 (3)		
O3—N3—C8—C9	8.9 (2)	O5—N4—C10—C11	−1.2 (2)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H11N···O1	1.00 (3)	1.70 (3)	2.676 (2)	166 (2)
N1—H11N···O2	1.00 (3)	2.60 (2)	3.187 (2)	118 (2)
C1—H1*A*···O4^{i}	1.03 (3)	2.45 (3)	3.442 (3)	160 (2)
C2—H2*A*···O1^{ii}	1.06 (3)	2.55 (3)	3.490 (3)	147 (2)
C3—H3*A*···O5^{i}	1.00 (3)	2.47 (3)	3.461 (3)	172 (2)
C5—H5*B*···O3^{iii}	1.02 (2)	2.47 (3)	3.366 (3)	146 (2)

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

Several of the H atoms, especially those involved in hydrogen bonds, were located from difference maps and were isotropically refined. The other H atoms were geometrically fixed, with ideal bond lengths and angles, to their attached parent C atoms and were treated as riding atoms.

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, PARST* (Nardelli, 1995) and *PLATON* (Spek, 1990).

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