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The 1:2 adduct *N*,*N*-dimethylethylenediamine-1,4-diium bis(2,4-dinitrophenolate)

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Key indicators

Single-crystal X-ray study
T = 183 K
Mean σ(C–C) = 0.005 Å
R factor = 0.058
wR factor = 0.138
Data-to-parameter ratio = 11.3

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

In the title salt, $C_4H_{14}N_2^{2+}\cdot 2C_6H_3N_2O_5^-$, the dication acts as a hydrogen donor with all its N—H bonds involved in hydrogen bonds to the O atoms of the phenolate and nitro groups, and with six of its eight C—H bonds involved in interactions with the O atoms of the nitro groups of the surrounding 2,4-dinitrophenolates. The packing structure is stabilized by these hydrogen-bonding interactions.

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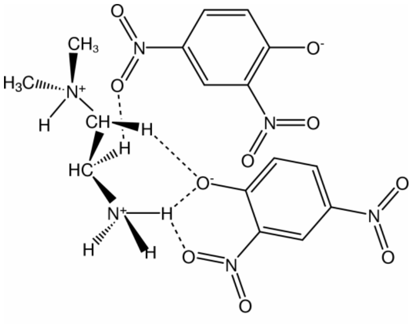
Comment

In general, relatively strong phenolic acids cocrystallize with relatively strong base amines, forming salts in which there is an H-atom transfer from the phenols to amines. The amine–phenol ratio varies depending on the proton acceptance ability of the amine. For instance, 2,4-dinitrophenol (DNP) forms the DNP⁻ anion and acts as a multiple acceptor of N—H···O hydrogen bonds involving the NO_2 and O^- groups in its adducts with hexamethylenetetramine or piperazine (Usman *et al.*, 2001, 2002). In these adducts, the hexamethylenetetramine and piperazine are present as cation and dication, crystallizing with one and two DNP⁻, respectively. In our continuing systematic studies on the hydrogen-bonding motifs in the adducts of these relatively strong base amines, we have prepared and structurally characterized a 1:2 adduct of *N*,*N*-dimethylethylenediamine (DMED) with DNP. The DMED has an N—C—C—N linkage, which is a common feature of relatively strong base diamines, such as hexamethylenetetramine and piperazine. In DMED, the amine groups are tertiary and primary and capable, particularly when protonated, of acting as donors in N—H···O hydrogen bonds.



(I)

The title adduct, (I), is an ionic salt, in which both DNP molecules transfer an H atom from the hydroxy group to the DMED moiety to form 2,4-dinitrophenolate (DNP⁻) anions and a *N*,*N*-dimethylethylenediamine-1,4-diium ($DMED^{2+}$) dication.

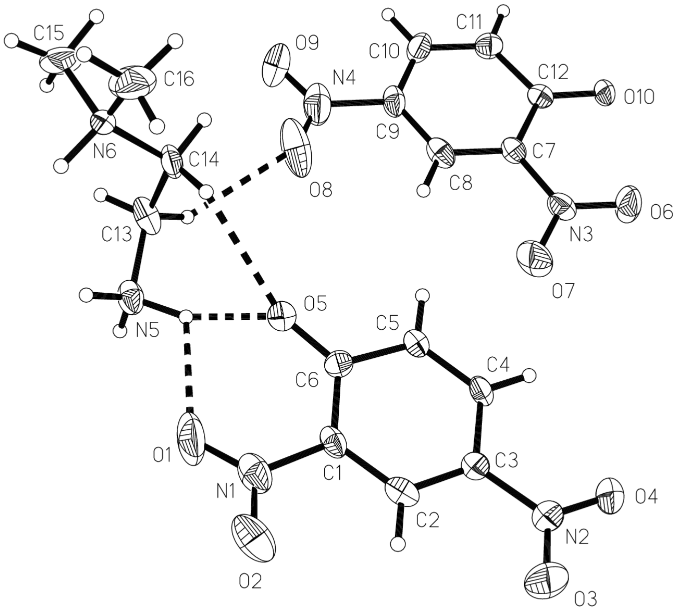


Figure 1
The structure of the title salt showing 50% probability displacement ellipsoids and the atom-numbering scheme.

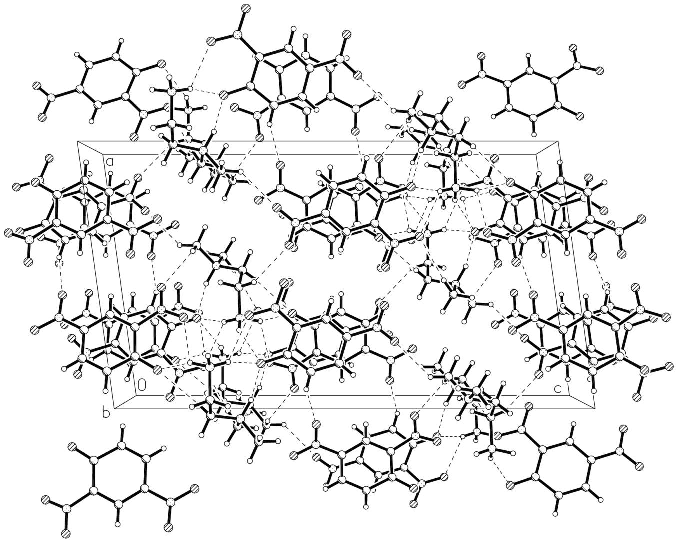


Figure 2
Packing diagram of the title salt viewed down the *b* axis, showing the hydrogen-bond network.

In addition to the fact that the transferred H atoms were located explicitly at both tertiary and primary amines (N6 and N5) from difference maps and were freely refined, the H-atom transfer process is also supported by the observation that the C—N bond distances within DMED^{2+} are in the 1.477 (5) to 1.494 (5) Å range, within acceptable values for C—N$^+$ bonds (Allen *et al.*, 1987). These C—N bond distances within DMED^{2+} are longer than those in unprotonated DMED [1.429 (7)–1.437 (7) Å; Ferguson *et al.*, 1990].

As observed in the DNP$^-$ adducts with hexamethylenetetramine or piperazine, the H-atom transfer process also affects the π-electron delocalization in DNP$^-$ resulting in slight variations in the N—O, C—N and C—O bond distances of the functional groups (Table 1). In the title adduct, both the DNP$^-$ anions are nearly planar with their nitro groups slightly twisted around their N—C bonds.

In the asymmetric unit (Fig. 1), the DMED^{2+} is interconnected by a bifurcated system of N5—H5B···O1 and N5—H5B···O5 hydrogen bonds; there is also a C14—H14A···O5 hydrogen bond to one DNP$^-$ and a C13—H13B···O8 to another DNP$^-$. The DNP$^-$ anions in adjacent ionic pairs are linked by C11—H11···O3$^{\rm iii}$. The ionic complexes are also interconnected by another four intermolecular N—H···O hydrogen bonds and another four C—H···O hydrogen bonds (Table 2) into a three-dimensional molecular network. Fig. 2 shows the packing diagram of the title salt viewed down the *b* axis, and indicates the intermolecular hydrogen-bonding interactions, which stabilize the packing structure.

Experimental

N,N-Dimethylethylenediamine (0.88 g, 10 mmol) was added to a solution of equimolar 2,4-dinitrophenol in 40 ml ethanol. The mixture was stirred while it was warmed up to the temperature range 323–328 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.

Crystal data

$C_4H_{14}N_2^{+}\cdot 2C_6H_3N_2O_5^{-}$
M_r = 456.38
Monoclinic, $P2_1/n$
a = 12.3777 (3) Å
b = 7.3596 (2) Å
c = 22.0064 (1) Å
β = 97.886 (2)°
V = 1985.71 (7) Å^3
Z = 4

D_x = 1.527 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3306 reflections
θ = 2.9–28.3°
μ = 0.13 mm^{-1}
T = 183 (2) K
Block, yellow
0.28 × 0.28 × 0.10 mm

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\rm min}$ = 0.965, $T_{\rm max}$ = 0.987
9040 measured reflections

3427 independent reflections
1790 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.093
$\theta_{\rm max}$ = 25.0°
$h = -14 \rightarrow 14$
$k = -8 \rightarrow 8$
$l = -26 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.058
$wR(F^2)$ = 0.138
S = 0.87
3427 reflections
304 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0449P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max}$ = 0.25 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.29 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0120 (13)

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Table 1
Selected geometric parameters (Å, °).

O1—N1	1.225 (4)	O6—N3	1.224 (3)
O2—N1	1.235 (4)	O7—N3	1.237 (3)
O3—N2	1.232 (3)	O8—N4	1.229 (4)
O4—N2	1.242 (3)	O9—N4	1.225 (4)
O5—C6	1.258 (4)	O10—C12	1.284 (3)
O2—N1—C1—C2	10.2 (5)	O7—N3—C7—C8	6.4 (4)
O3—N2—C3—C2	−6.9 (5)	O8—N4—C9—C8	8.9 (5)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N5—H5*A*···O6$^{\rm i}$	0.97 (4)	2.29 (4)	2.889 (4)	119 (3)
N5—H5*A*···O10$^{\rm i}$	0.97 (4)	1.83 (4)	2.771 (4)	162 (3)
N5—H5*B*···O1	0.96	2.28	2.985 (4)	129
N5—H5*B*···O5	0.96	1.78	2.636 (4)	147
N5—H5*C*···O10$^{\rm ii}$	0.96 (4)	2.17 (4)	3.024 (3)	147 (3)
N6—H6···O10$^{\rm i}$	1.01 (4)	1.72 (4)	2.708 (3)	166 (3)
C11—H11···O3$^{\rm iii}$	0.93	2.41	3.249 (5)	150
C13—H13*B*···O8	0.97	2.39	3.195 (5)	140
C14—H14*A*···O5	0.97	2.50	3.163 (4)	125
C14—H14*B*···O4$^{\rm iv}$	0.97	2.59	3.462 (4)	150
C15—H15*A*···O9$^{\rm v}$	0.96	2.33	3.039 (5)	130
C15—H15*B*···O2$^{\rm vi}$	0.96	2.41	3.127 (5)	131
C16—H16*A*···O6$^{\rm iv}$	0.96	2.41	3.320 (5)	159

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

The H atoms attached to N5 and N6 were located from difference Fourier maps and were isotropically refined, while those attached to their parent C atoms were geometrically fixed with C—H = 0.93–0.97 Å 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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References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans.* 2, pp. S1–19.

Ferguson, G., Lough, A. J., Sheehan, J. P. & Spalding, T. R. (1990). *Acta Cryst.* C**46**, 2390–2392.

Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.

Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.

Sheldrick, G. M. (1997). *SHELXTL*. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.

Siemens (1996). *SMART* and *SAINT*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Spek, A. L. (1990). *Acta Cryst.* A**46**, C-34.

Usman, A., Chantrapromma, S. & Fun, H.-K. (2001). *Acta Cryst.* C**57**, 1443–1446.

Usman, A., Chantrapromma, S., Fun, H.-K., Poh, B.-L., Karalai, C. (2002). *Acta Cryst.* C**58**. In the press.

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