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Ammonium 1,3,4,6-tetranitro-2,5-diazapentalene

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Key indicators

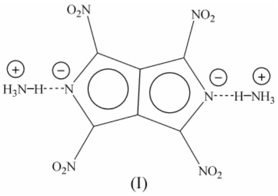
Single-crystal X-ray study
T = 294 K
Mean σ(C–C) = 0.002 Å
R factor = 0.031
wR factor = 0.085
Data-to-parameter ratio = 10.1

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

The structure of the ammonium salt of the dianion of 1,3,4,6-tetranitro-2,5-diazapentalene is reported, *viz.* $2NH_4^+\cdot C_6N_6O_8^{2-}$. Only three atoms of the central 2,5-diazapentalene skeleton are unique, as the anion possesses 2/*m* symmetry. The ammonium cation forms strong hydrogen bonds to the aza N and nitro O atoms, forming a sheet in the *ac* plane.

Comment

The structure of the potassium salt of the dianion of 1,3,4,6-tetranitro-2,5-diazapentalene has been published (Butcher *et al.*, 2003). We report here the structure, (I), of the ammonium salt of the same dianion.



(I)

The structure consists of two ammonium cations and one 1,3,4,6-tetranitro-2,5-diazapentalene dianion. Only three atoms of the central 2,5-diazapentalene skeleton are unique, as the anion possesses 2/*m* symmetry. The ammonium cation forms strong hydrogen bonds to the aza N and nitro O atoms, forming a sheet in the *ac* plane. Within experimental error, the diazapentalene moiety is planar (mean deviation 0.003 Å), with atom O1 (which forms weaker out-of-plane hydrogen bonds to adjoining anions) having the largest deviation [0.245 (2) Å]. A comparison of the metrical parameters of the diazapentalene anion with those of the corresponding neutral and cationic moieties shows that, as in the previous example (Butcher *et al.*, 2003), the largest changes occur in the bond distances to the aza N atom [N1—C2 = 1.3364 (16) Å compared with average values of 1.3765 and 1.3885 Å found for the neutral (Closs *et al.*, 1988) and cationic (Virnekaes *et al.*, 2001) moieties, respectively]. Due to the shortening of the C—N bonds in the five-membered rings there is a corresponding increase in the exocyclic angle (C2—C1—C2′) to the extremely large value of 151.18 (17)°, the same as was seen in the previous example (Butcher *et al.*, 2003). If both rings are coplanar (as they are in the present instance) and regular, their internal rings angles would be 108°, leading one to expect a value of 144° for the exocyclic angle [360 − (2 × 108)°].

Both the ammonium and potassium salts of 1,3,4,6-tetranitro-2,5-diazapentalene are isostructural since they crystallize in the same space group with similar cell constants and with the anions having the same site symmetry.

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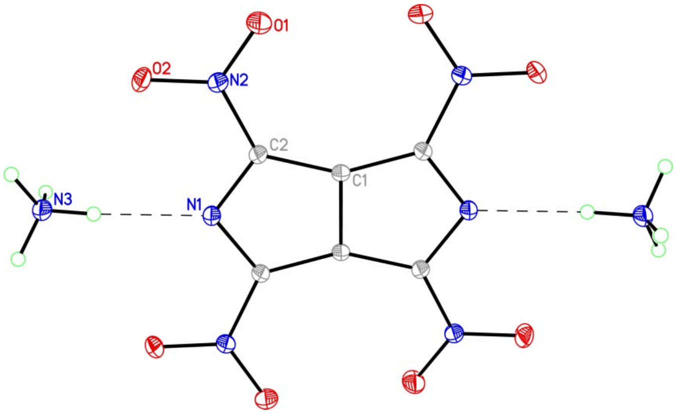

Figure 1
View of the molecule of (I), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 20% probability level.

Experimental

Crystals suitable for X-ray crystallography were supplied by Dr Jeffrey C. Bottaro, Menlo Park, California. Details of the synthesis will be published elsewhere.

Crystal data

$2H_4N^+ \cdot C_6N_6O_8{}^{2-}$
$M_r = 320.20$
Monoclinic, $C2/m$
$a = 12.1938$ (3) Å
$b = 9.8825$ (2) Å
$c = 5.2130$ (1) Å
$\beta = 112.294$ (1)°
$V = 581.24$ (2) Å^3
$Z = 2$
$D_x = 1.830$ Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 1485 reflections
$\theta = 11.9$–$133.9°$
$\mu = 1.50$ mm^{-1}
$T = 294$ (2) K
Prism, red
0.10 × 0.04 × 0.03 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: by integration (Wuensch & Prewett, 1965)
$T_{\min} = 0.874$, $T_{\max} = 0.959$
2066 measured reflections
545 independent reflections
474 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.045$
$\theta_{\max} = 66.8°$
$h = -14 \rightarrow 14$
$k = -11 \rightarrow 11$
$l = -6 \rightarrow 5$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.085$
$S = 1.07$
545 reflections
54 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0494P)^2 + 0.1754P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.24$ e Å^{-3}
$\Delta\rho_{\min} = -0.16$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—N2	1.2295 (16)	N2—C2	1.4202 (17)
O2—N2	1.2379 (16)	C1—C2	1.4217 (14)
N1—C2	1.3364 (16)		
C2—N1—C2$^{\rm i}$	106.23 (15)	C2—C1—C1$^{\rm iii}$	104.41 (9)
O1—N2—O2	121.81 (11)	N1—C2—N2	116.74 (12)
O1—N2—C2	119.72 (11)	N1—C2—C1	112.47 (12)
O2—N2—C2	118.45 (11)	N2—C2—C1	130.67 (13)
C2—C1—C2$^{\rm ii}$	151.18 (17)		

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

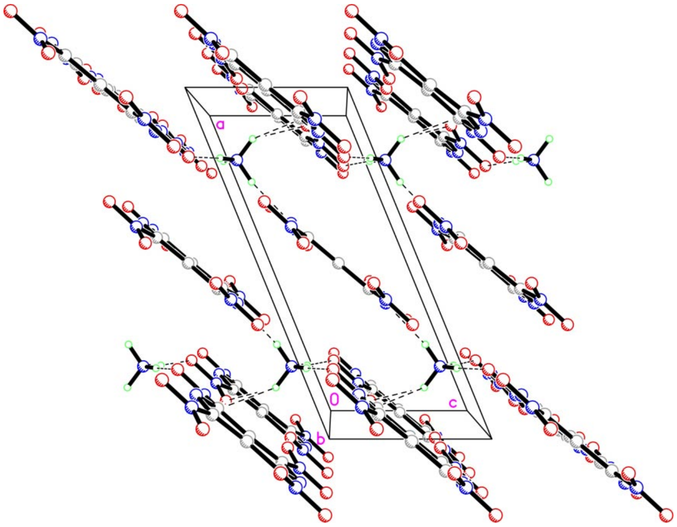

Figure 2
The molecular packing of (I), viewed in the *ac* plane, showing the sheets of planar anions linked by hydrogen bonds from the ammonium cations.

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

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3A···O1$^{\rm iv}$	0.93	2.53	3.197 (2)	129
N3—H3B···N1	0.93	2.01	2.925 (2)	170
N3—H3C···O2$^{\rm v}$	0.93	2.02	2.9412 (14)	172

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

For the ammonium salt, the three unique H atoms attached to the N were observed in a difference Fourier map and were then idealized by refining with a riding model and N—H distance of 0.93 Å. The $U_{\rm iso}$ for the H atoms were 1.5 times the $U_{\rm eq}$ value of the atom to which they were attached.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2001); 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*.

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