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

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Key indicators
Single-crystal X-ray study
T = 93 K
Mean σ(C–C) = 0.002 Å
R factor = 0.024
wR factor = 0.063
Data-to-parameter ratio = 12.9

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

The structure of the potassium salt of the dianion of 1,3,4,6-tetranitro-2,5-diazapentalene is reported, *viz*. $2\,K^+\cdot C_6N_6O_8^{2-}$. Only three atoms of the central 2,5-diazapentalene skeleton are unique, as the anion possesses $2/m$ symmetry. The potassium cation is nine-coordinate, forming K—O and K—N bonds to five different 1,3,4,6-tetranitro-2,5-diazapentalene anions.

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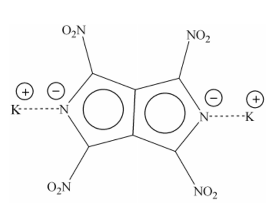
Comment

Pentalene is a thermally unstable compound belonging to the class of destabilized antiaromatic π-systems (Randic, 1977; Gutman *et al.*, 1977). Stabilization of the pentalene system can be achieved by steric shielding (Hafner & Süss, 1973) or by the introduction of donor groups in the 1, 3, 4, and 6 positions and acceptor groups in the 2 and 5 positions (Gais & Hafner, 1974). According to molecular orbital (MO) calculations (Jartín *et al.*, 2002; Gutman *et al.*, 1977), 2,5-diazapentalene is expected to be non-aromatic, while 1,3,4,6-tetradonor-2,5-diacceptor-substituted pentalenes should exhibit aromatic stabilization and a delocalized π-bonding system, as well as being strong bases and readily forming dicationic 2,5-diazapentalene derivatives (Closs & Gompper, 1987; Closs *et al.*, 1988). The structures of one example of both of these types have been reported, *viz*. a sterically hindered neutral 1,3,4,6-tetrakis(dimethylamino)-2,5-diazapentalene (Closs *et al.*, 1988) and a cationic 1,4-bis(dimethylamino)-3,6-bis(iodo)-2,5-diazapentalene triiodide (Virnekaes *et al.*, 2001). However, it is well known that the introduction of nitro groups into organic molecules markedly increases their acidity. For instance, the pK_a of phenol is 9.89 while that of picric acid (2,4,6-trinitrophenol) is 0.38 (Dean, 1999). Hence the 1,3,4,6-tetranitro-2,5-diazapentalene moiety is a strong acid and readily forms dianionic salts.



(I)

We report here the structure of the potassium salt of the dianion of 1,3,4,6-tetranitro-2,5-diazapentalene, (I). The structure consists of two potassium 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 potassium cation is nine-coordinate, forming K—O and K—N bonds to five different

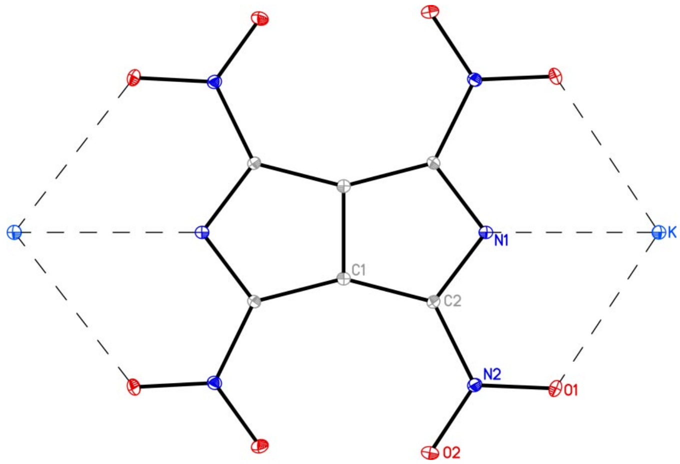


Figure 1
View of the molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 20% probability level.

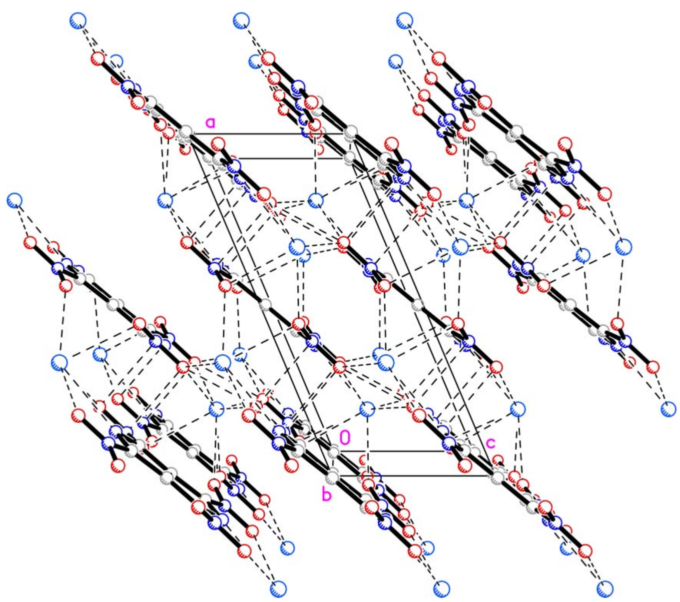


Figure 2
The molecular packing of (I), viewed along the *b* axis.

1,3,4,6-tetranitro-2,5-diazapentalene anions, at bond distances ranging from 2.8214 (15) to 3.0458 (11) Å and bond angles ranging from 53.446 (19) to 148.33 (3)°. Within experimental error, the diazapentalene moiety is planar (mean deviation 0.003 Å) with atom O2 having the largest deviation [0.282 (2) Å]. A comparison of the metrical parameters of the diazapentalene anion with those of the corresponding neutral and cationic moieties shows that the largest changes occur in the bond distances to the aza nitrogen [N1—C2 = 1.3384 (15) 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 151.13 (17)°. If both rings are coplanar (as they are in the present instance) and regular, their internal ring angles would be 108°, leading one to expect a value of 144° for the exocyclic angle [360 − (2 × 108)°].

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

$2K^+\cdot C_6N_6O_8^{2-}$
M_r = 362.32
Monoclinic, $C2/m$
a = 11.7540 (15) Å
b = 9.6390 (13) Å
c = 5.1732 (7) Å
β = 112.946 (2)°
V = 539.73 (12) Å^3
Z = 2
D_x = 2.229 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2017 reflections
θ = 5.7–58.2°
μ = 0.94 mm^{-1}
T = 93 (2) K
Plate, orange
0.25 × 0.10 × 0.05 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)
T_{min} = 0.684, T_{max} = 0.928
2152 measured reflections
699 independent reflections
665 reflections with $I > 2\sigma(I)$
R_{int} = 0.031
θ_{max} = 28.2°
$h = -15 \rightarrow 15$
$k = -11 \rightarrow 12$
$l = -6 \rightarrow 6$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.024
$wR(F^2)$ = 0.063
S = 1.13
699 reflections
54 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0318P)^2 + 0.526P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.36 e Å^{-3}
$\Delta\rho_{min}$ = −0.27 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

K—N1	2.8214 (15)	O2—N2	1.2371 (15)
K—O1^{i}	2.8477 (10)	N1—C2	1.3384 (15)
K—O2^{ii}	2.8600 (11)	N2—C2	1.4169 (15)
K—O1	2.9945 (10)	C1—C1^{iv}	1.426 (3)
K—O2^{iii}	3.0458 (11)	C1—C2	1.4274 (12)
O1—N2	1.2461 (14)		
C2—N1—C2^{v}	105.97 (14)	C2—C1—C2^{vi}	151.13 (17)
O2—N2—O1	121.83 (11)	N1—C2—N2	116.65 (10)
O2—N2—C2	119.59 (10)	N1—C2—C1	112.58 (12)
O1—N2—C2	118.57 (10)	N2—C2—C1	130.64 (12)
C1^{iv}—C1—C2	104.43 (8)		

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

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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