Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

1,3,4-Trinitro-7,8-diazapentalene

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Key indicators

Single-crystal X-ray study
T = 93 K
Mean σ(C–C) = 0.006 Å
R factor = 0.048
wR factor = 0.110
Data-to-parameter ratio = 5.5

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

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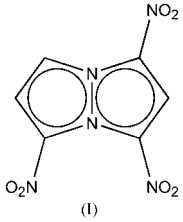
The structure of 1,3,4-trinitro-7,8-diazapentalene, $C_6H_3N_5O_6$, is reported. In this molecule, while the 7,8-diazapentalene skeleton is planar, the nitro groups are twisted with respect to and deviate from this plane. The metrical parameters of the monosubstituted and disubstituted five-membered rings differ.

Received 4 August 2003
Accepted 9 September 2003
Online 23 October 2003

Comment

Pentalene, C_8H_6, is a thermally unstable bicyclic compound belonging to the class of destabilized antiaromatic π-systems (Randic, 1977; Gutman *et al.*, 1977) and has fascinated synthetic as well as theoretical organic chemists for more than four decades (Lindner, 1985). Introduction of N atoms into the pentalene skeleton will drastically alter the electronic nature of this moiety. Many neutral polyazapentalene derivatives are stable and some have been structurally characterized, with a maximum substitution of six of the eight atoms by nitrogen (2-methyl-5-phenyl-1,2,3,4,5,6-hexaazapentalene; Jones *et al.*, 1993). According to molecular orbital calculations (Jartín *et al.*, 2002; Gutman *et al.*, 1977), 2,5-diazapentalene is expected to be non-aromatic, while 2,5-diacceptor- and/or 1,3,4,6-tetradonor-substituted 2,5-diazapentalenes 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, 1989).



(I)

Anionic forms of 2,5-diazapentalene are stabilized by nitro substitution. 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-tetrakis(nitro)-2,5-diazapentalene moiety is a strong acid and readily forms dianionic salts. The structure of the potassium and ammonium salts of this anion have been published previously (Butcher *et al.*, 2003*a*,*b*).

7,8-Diazapentalenes appear to behave very differently from 2,5-diazapentalenes. The 1-nitro- (Butcher *et al.*, 2003*c*), 1,3,4-trinitro-, and 1,3,4,6-tetrakis-7,8-diazapentalene (Butcher *et al.*, 2003*d*) moieties are all planar, stable, neutral species. One

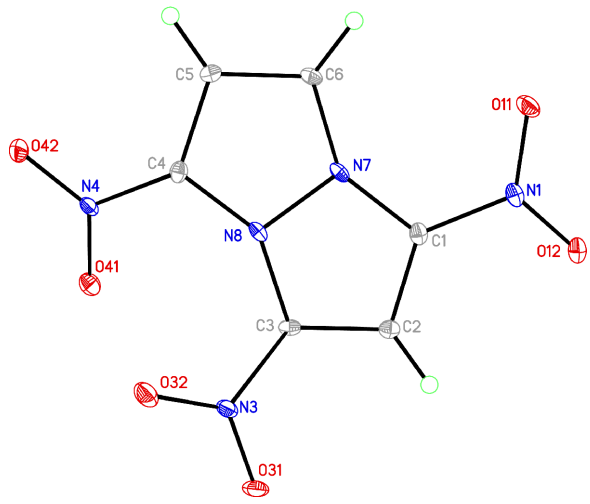


Figure 1
View of the molecule of 1,3,4-trinitro-7,8-diazapentalene, showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 20% probability level.

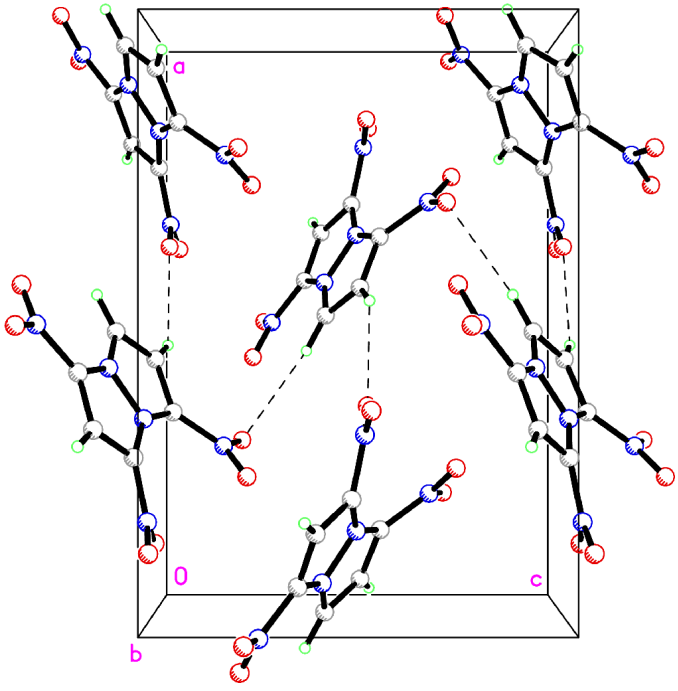


Figure 2
The molecular packing of 1,3,4-trinitro-7,8-diazapentalene, viewed down the *b* axis

cannot make meaningful comparisons of the metrical parameters of the ring systems of 2,5- and 7,8-diazapentalenes as the former are charged species and the latter neutral. However, in the monosubstituted 1,3,4-trinitro-7,8-diazapentalene derivative, (I), the effect of the nitro substituent could be detected in the changes induced in the metrical parameters of the substituted *versus* unsubstituted rings (Butcher *et al.*, 2003*c*). In 1,3,4-trinitro-7,8-diazapentalene, one ring has two nitro substituents and the other has only one. This asymmetric substitution also has effects on the ring metrical parameters. In the disubstituted ring the C—N and C—C bond lengths are all equivalent [N7—C1 = 1.379 (5) Å and N8—C3 = 1.382 (4) Å; C1—C2 = 1.375 (5) Å and C2—C3 = 1.375 (5) Å]. However, in the monosubstituted ring, the C—N (bridgehead) distances are considerably shorter [C4—N8 = 1.358 (4) Å and N7—C6 = 1.358 (4) Å], and for the C atom to which the single nitro substituent is attached the C—C bond is longer [C4—C5 = 1.407 (5) Å and C5—C6 1.370 (5) Å].

In contrast to 1-nitro-7–8-diazapentalene (Butcher *et al.*, 2003*c*), in 1,3,4-trinitro-7,8-diazapentalene the nitro groups are substantially twisted with respect to and deviate from the 7,8-diazapentalene plane. This twist and deviation is larger for the sterically hindered 3- and 4-nitro groups [twist angles of 24.6 (7) and 17.8 (6)°; angles between planes of 30.3 (4) and 25.4 (6)°], than for the 1-nitro group [twist angle of 12.4 (7), angle between planes of 12.7 (7)°]. As in the monosubstituted derivative, there is some perturbation in the metrical parameters of the nitro groups themselves. A search of the Cambridge Structural Database (*CONQUEST* Version 1.4 in CSD Version 5.23; Allen, 2002) gave 10 453 examples of nitro groups attached to C atoms. From Table 1 it can be seen that in the present structure the C—N distances [C1—N1 = 1.428 (5) Å, C3—N3 = 1.418 (5) Å, and C4—N4 = 1.419 (5) Å] are shorter than the CSD average of 1.462 (33) Å. Similar differences occur in the other metrical parameters of the nitro group (average N—O = 1.229 (3) Å and CSD average = 1.219 (28); average O—N—O angle = 125.2 (1)° and CSD average = 123.41 (3)°).

If these systems contained two fused coplanar regular pentagons, all internal ring angles would be 108°, leading one to expect a value of 144° for the exocyclic angle [360° − 2(108°)]. In the pentalene, 2,5-diazapentalene, and 7,8-diazapentalene systems there is considerable variation in this angle. In the two pentalene derivatives these angles are 144 (1) and 144.9 (6)°, *i.e.* within experimental error of the expected value. In the 7,8-diazapentalene series these angles have similar values [143.1 (1), 144.8 (3), and 144.0 (6)°, for the 1-nitro, 1,3,4-trinitro, and 1,3,4,6-tetranitro derivatives, respectively], in contrast to the 2,5-diazapentalene derivatives (Butcher *et al.*, 2003*a*,*b*), where these angles are much larger at 151.18 (17)°.

The packing is shown in Fig. 2, and features an interpenetrating network of molecules linked by C—H···O hydrogen bonds.

Experimental

Crystals suitable for X-ray crystallography were supplied by Dr Jeffrey C. Bottaro, Menlo Park, California.

Crystal data

$C_6H_3N_5O_6$
M_r = 241.13
Orthorhombic, $Pc2_1b$
a = 7.0098 (15) Å
b = 9.363 (2) Å
c = 13.344 (3) Å
V = 875.8 (3) Å^3
Z = 4
D_x = 1.829 Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 2958 reflections
θ = 5.8–50.6°
μ = 0.17 mm^{-1}
T = 93 (2) K
Chunk, red
0.35 × 0.22 × 0.13 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1999)
T_{min} = 0.190, T_{max} = 0.981
4530 measured reflections
851 independent reflections
795 reflections with $I > 2\sigma(I)$
R_{int} = 0.102
θ_{max} = 25.4°
$h = -8 \rightarrow 8$
$k = -11 \rightarrow 10$
$l = -16 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.048
$wR(F^2)$ = 0.110
S = 1.18
851 reflections
155 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0594P)^2 + 0.2676P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.28 e Å^{-3}
$\Delta\rho_{min}$ = −0.34 e Å^{-3}
Extinction correction: *SHELXTL*
Extinction coefficient: 0.006 (4)

Table 1
Selected geometric parameters (Å, °).

C1—C2	1.375 (6)	N3—O32	1.236 (5)
C1—N7	1.379 (6)	C4—N8	1.359 (5)
C1—N1	1.428 (6)	C4—C5	1.407 (6)
N1—O12	1.225 (5)	C4—N4	1.417 (6)
N1—O11	1.234 (5)	N4—O41	1.226 (5)
C2—C3	1.375 (6)	N4—O42	1.227 (5)
C3—N8	1.381 (5)	C5—C6	1.369 (7)
C3—N3	1.418 (6)	C6—N7	1.355 (5)
N3—O31	1.228 (5)	N7—N8	1.380 (5)
C2—C1—N7	110.7 (4)	N8—C4—N4	121.3 (4)
C2—C1—N1	128.8 (4)	C5—C4—N4	127.5 (4)
N7—C1—N1	120.4 (4)	O41—N4—O42	125.3 (4)
O12—N1—O11	125.3 (4)	O41—N4—C4	117.6 (4)
O12—N1—C1	117.4 (4)	O42—N4—C4	117.0 (4)
O11—N1—C1	117.3 (4)	C6—C5—C4	106.7 (4)
C3—C2—C1	105.5 (4)	N7—C6—C5	108.3 (4)
C2—C3—N8	109.6 (4)	C6—N7—C1	144.3 (4)
C2—C3—N3	126.2 (4)	C6—N7—N8	109.5 (3)
N8—C3—N3	121.7 (4)	C1—N7—N8	106.2 (3)
O31—N3—O32	124.8 (3)	C4—N8—N7	106.9 (3)
O31—N3—C3	116.7 (3)	C4—N8—C3	145.2 (4)
O32—N3—C3	118.5 (3)	N7—N8—C3	107.8 (3)
N8—C4—C5	108.5 (4)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2*A*···O42^{i}	0.95	2.47	3.280 (5)	143
C5—H5*A*···O32^{ii}	0.95	2.56	3.275 (5)	132

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

All H atoms were fixed in calculated positions, with C—H = 0.93 Å, and with isotropic displacement parameters fixed at 1.2 times that of the atom to which they were attached. In an orthorhombic system, the software controlling the diffractometer automatically chooses the cell axes in order of increasing size, *i.e.* $a < b < c$. The reduced data file thus matches this. If the conventional setting was chosen then the indices for the structure factor file would not match the indices for the raw file.

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*.

The authors acknowledge the financial support from the Office of Naval Research, Mechanics Division. RJB acknowledges the ASEE/Navy Summer Faculty Research Program for support during the summer of 2003.

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