

## 1-Nitro-7,8-diazapentalene

Ray J. Butcher,<sup>a</sup> Jeffrey C. Bottaro<sup>b</sup> and R. Gilardi<sup>c\*</sup><sup>a</sup>Department of Chemistry, Howard University, 525 College Street NW, Washington, DC 20059, USA, <sup>b</sup>SRI International, Menlo Park, California 94025, USA, and <sup>c</sup>Laboratory for the Structure of Matter, Naval Research Laboratory, Washington, DC 20375, USA

Correspondence e-mail: gilardi@nrl.navy.mil

## Key indicators

Single-crystal X-ray study

T = 296 K

Mean  $\sigma(\text{C}-\text{C}) = 0.004 \text{ \AA}$ 

R factor = 0.034

wR factor = 0.093

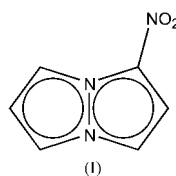
Data-to-parameter ratio = 6.8

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

The structure of 1-nitro-7,8-diazapentalene,  $\text{C}_6\text{H}_5\text{N}_3\text{O}_2$ , is reported. This is a planar molecule, in which the metrical parameters of the two five-membered rings are substantially altered by the effect of the 1-nitro substituent. Additionally, the parameters of the nitro group itself are also perturbed.

## Comment

Pentalene,  $\text{C}_8\text{H}_6$ , which is a thermally unstable bicyclic compound belonging to the class of destabilized antiaromatic  $\pi$ -systems (Radic, 1977; Gutman *et al.*, 1977), has fascinated synthetic as well as theoretical organic chemists for more than four decades (Lindner, 1985). Stabilization of the pentalene system can be achieved by steric shielding (Hafner & Süß, 1973) or by the introduction of acceptor groups in the 2- and 5-positions and/or donor groups in the 1-, 3-, 4-, and 6-positions (Gais & Hafner, 1974; Closs *et al.*, 1989). Some substituted examples of neutral pentalenes have been synthesized (Hafner & Süß, 1973; Hafner & Suda, 1976) and both the parent molecule (Bally *et al.*, 1997) and its derivatives (Hafner & Süß, 1973; Bischoff *et al.*, 1978; Falchi *et al.*, 1998; Bussotti *et al.*, 2001) have been spectroscopically characterized. In addition, the structures of two derivatives have been determined (Kitschke & Lindner, 1977). The dianion of pentalene is aromatic, and hence stable, and has been used as a ligand in organometallic chemistry (Cloke, 2001).

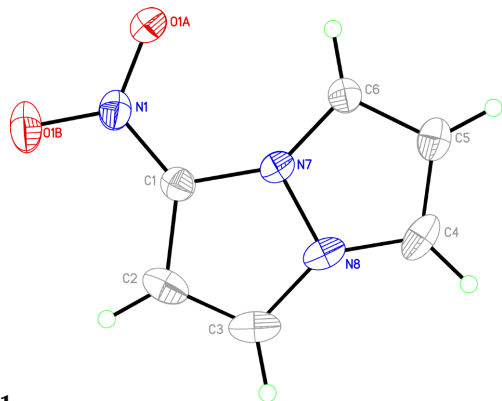


Introduction of N atoms into the pentalene skeleton drastically alters the electronic nature of this moiety. Many neutral polyazapentalene derivatives are stable and some have been structurally characterized, with a maximum substitution of six of the eight atoms by nitrogen (2-methyl-5-phenyl-1,2,3,4,5,6-hexaazapentalene, Jones *et al.*, 1993). According to molecular orbital calculations (Jartín *et al.*, 2002; Gutman *et al.*, 1977), 2,5-diazapentalene is expected to be nonaromatic but 1,3,4,6-tetradonor-2,5-diacceptor-substituted 2,5-diazapentalenes should exhibit aromatic stabilization and a delocalized  $\pi$ -bonding system. They are also strong bases and readily form dicationic 2,5-diazapentalene derivatives (Closs & Gompper, 1987; Closs *et al.*, 1988). The structure of one example of each of these types has been reported, *viz.* a sterically hindered neutral 1,3,4,6-tetra(dimethylamino)-2,5-diazapentalene

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**Figure 1**

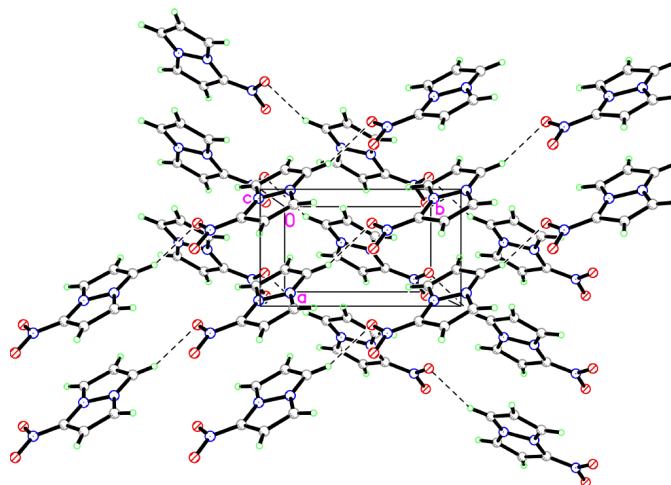
View of the molecule of 1-nitro-7,8-diazapentalene, showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 20% probability level.

(Closs *et al.*, 1988) and a cationic 1,4-bis(dimethylamino)-3,6-diiodo-2,5-diazapentalene triiodide (Virnekaes *et al.*, 2001).

Anionic forms of 2,5-diazapentalene can be formed 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-tetranitro-2,5-diazapentalene moiety is a strong acid and readily forms dianionic salts. The structures 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, 1,3,4-trinitro- (Butcher *et al.*, 2003*c*), and 1,3,4,6-tetranitro-7,8-diazapentalene (Butcher *et al.*, 2003*d*) moieties are all stable neutral species containing planar 7,8-diazapentalene skeletons (average deviation from the 7,8-diazapentalene planes being 0.004, 0.016, and 0.009 Å for the 1-nitro, 1,3,4-trinitro, and 1,3,4,6-tetranitro derivatives, respectively). One cannot make meaningful comparisons of the metrical parameters of the ring systems of 2,5- and 7,8-diazapentalenes (containing nitro substituents) as the former are charged species and the latter neutral. However, in the monosubstituted 1-nitro-7,8-diazapentalene derivative, (I), the effect of the nitro substituent can be detected in the changes induced in the metrical parameters of the substituted *versus* unsubstituted rings. These effects manifest themselves in a lengthening of both the C–C and C–N bonds involving the C atom to which the nitro group is attached [C1–C2 = 1.415 (3) Å and C1–N7 = 1.387 (2) Å *versus* C5–C6 = 1.372 (3) Å and C6–N7 = 1.356 (2) Å] along with a shortening of the other C–C bond in the five-membered ring [C2–C3 = 1.351 (4) Å and C4–C5 = 1.363 (3) Å *versus* C5–C6 = 1.372 (3) Å], as shown in Table 1.

In 1-nitro-7,8-diazapentalene, the nitro group is only slightly twisted (average nitro torsion angle =  $1.0^\circ$ ) and slightly out of the 7,8-diazapentalene plane [angle between the planes =  $3.0(3)^\circ$ ]. In addition, while nitro substitution perturbs the metrical parameters of the five-membered ring, the metrical parameters of the nitro group are also substantially altered from the norm. A search of the Cambridge



**Figure 2**

The molecular packing of 1-nitro-7,8-diazapentalene, viewed down the *c* axis

Structural Database (Conquest Version 1.4 in CSD Version 5.23; Allen, 2002) gave 10 453 examples of nitro groups attached to C atoms. In the present structure, the C–N distance of 1.341 (2) Å is substantially shorter than the CSD average of 1.462 (33) Å. Similar differences occur in the other metrical parameters of the nitro group [N–O = 1.257 (2) and 1.261 (2) Å, CSD average = 1.219 (28)°; O–N–O angle =  $121.9(2)^\circ$ , CSD average =  $123.41(3)^\circ$ ].

Lastly, in systems containing two fused regular coplanar regular pentagons, their internal ring angles would be  $108^\circ$ , leading one to expect a value of  $144^\circ$  for the exocyclic angle [ $360^\circ - 2(108^\circ)$ ]. 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  $144.9(6)^\circ$ , *i.e.* within experimental error of the expected value. In the 2,5-diazapentalene derivatives, these angles, on average, are much larger at  $151.18(17)^\circ$  (Butcher *et al.*, 2003*a,b*), while in 1-nitro-7,8-diazapentalene, these values average  $143.1(1)^\circ$ , which is even less than the expected value.

The packing is shown in Fig. 2, and features an alternating herring-bone arrangement of ribbons of molecules, in the [110] and  $[\bar{1}10]$  directions, linked by head-to-tail C–H...O hydrogen bonds.

## Experimental

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

### Crystal data

$C_6H_5N_3O_2$   
 $M_r = 151.13$   
 Orthorhombic,  $P2_12_12_1$   
 $a = 4.02130(10)$  Å  
 $b = 6.91200(10)$  Å  
 $c = 23.0998(3)$  Å  
 $V = 642.06(2)$  Å<sup>3</sup>  
 $Z = 4$   
 $D_x = 1.563$  Mg m<sup>-3</sup>

Cu  $K\alpha$  radiation  
 Cell parameters from 2865 reflections  
 $\theta = 7.7$ – $133.5^\circ$   
 $\mu = 1.04$  mm<sup>-1</sup>  
 $T = 296(2)$  K  
 Plate, orange  
 $0.36 \times 0.20 \times 0.02$  mm

## Data collection

Bruker SMART CCD area-detector diffractometer	686 independent reflections
$\varphi$ and $\omega$ scans	659 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Sheldrick, 1999)	$R_{\text{int}} = 0.036$
$T_{\text{min}} = 0.790$ , $T_{\text{max}} = 0.980$	$\theta_{\text{max}} = 66.9^\circ$
2994 measured reflections	$h = -4 \rightarrow 4$
	$k = -8 \rightarrow 8$
	$l = -27 \rightarrow 27$

## Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0526P)^2 + 0.0922P]$
$R[F^2 > 2\sigma(F^2)] = 0.035$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.093$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.06$	$\Delta\rho_{\text{max}} = 0.11 \text{ e } \text{\AA}^{-3}$
686 reflections	$\Delta\rho_{\text{min}} = -0.13 \text{ e } \text{\AA}^{-3}$
101 parameters	Extinction correction: <i>SHELXL97</i>
H-atom parameters constrained	Extinction coefficient: 0.020 (11)

Table 1

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

C1—N1	1.341 (3)	C3—N8	1.392 (3)
C1—N7	1.386 (3)	C4—N8	1.349 (3)
C1—C2	1.415 (3)	C4—C5	1.364 (4)
N1—O1B	1.258 (2)	C5—C6	1.372 (3)
N1—O1A	1.262 (2)	C6—N7	1.355 (3)
C2—C3	1.350 (4)	N7—N8	1.360 (2)
N1—C1—N7	120.63 (19)	C4—C5—C6	108.2 (2)
N1—C1—C2	132.7 (2)	N7—C6—C5	107.5 (2)
N7—C1—C2	106.7 (2)	C6—N7—N8	108.00 (18)
O1B—N1—O1A	121.9 (2)	C6—N7—C1	143.24 (19)
O1B—N1—C1	119.8 (2)	N8—N7—C1	108.74 (18)
O1A—N1—C1	118.33 (19)	C4—N8—N7	108.9 (2)
C3—C2—C1	107.8 (2)	C4—N8—C3	143.1 (2)
C2—C3—N8	108.9 (2)	N7—N8—C3	107.9 (2)
N8—C4—C5	107.4 (2)		

Table 2

Hydrogen-bonding geometry ( $\text{\AA}$ ,  $^\circ$ ).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
C4—H4A $\cdots$ O1A <sup>i</sup>	0.93	2.41	3.288 (3)	158
C2—H2A $\cdots$ O1B <sup>ii</sup>	0.93	2.34	3.143 (3)	145

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

All H atoms were fixed in calculated positions with C—H = 0.93  $\text{\AA}$  and with isotropic displacement parameters fixed at 1.2 times that of the atom to which they were attached.

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