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2,4,6-Trinitro-2,4,6,8-tetraazabicyclo[3.3.0]-octan-7-one

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Key indicators

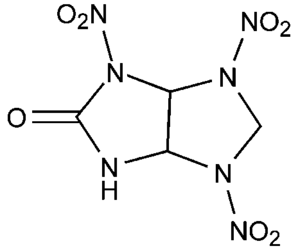
Single-crystal X-ray study
T = 94 K
Mean σ(C–C) = 0.002 Å
R factor = 0.035
wR factor = 0.087
Data-to-parameter ratio = 10.9

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

The structure of 2,4,6-trinitro-2,4,6,8-tetraazabicyclo[3.3.0]-octan-7-one, $C_4H_5N_7O_7$, is reported. The molecule contains two unsymmetrically substituted planar fused five-membered rings with a *cis* junction between them.

Comment

The title compound, (I), contains two fused five-membered rings which are unsymmetrically substituted. One ring contains two nitramine groups, while the other contains a single nitramine and a keto group. A search of the April 2004 release of the Cambridge Structural Database (CSD; Allen, 2002) for the 2,4,6,8-tetraazabicyclo[3.3.0]octane skeleton gave 32 hits, of which 20 contained the 2,4,6,8-tetraazabicyclo[3.3.0]octan-3,7-dione moiety, six contained 2,4,6,8-tetraazabicyclo[3.3.0]octane (glycoluril) derivatives and four contained 3,3,7,7-tetrakis(trifluoromethyl) substituents. In addition, there was one structure each of 2,4,6,8-tetraazabicyclo[3.3.0]octan-3-one-7-thione and 2,4,6,8-tetraazabicyclo[3.3.0]octan-3,7-dinitramine. There are no previous examples of a structure containing the unsymmetrically substituted 2,4,6,8-tetraazabicyclo[3.3.0]octan-7-one skeleton. Thus it is of interest to compare the effects that these substituent patterns have on the two five-membered rings.



(I)

Fig. 1 shows the structure of (I) and the atom-numbering scheme. For the purposes of the present discussion, the two five-membered rings will be labeled *A* (that containing the 2- and 4-aza N atoms) and *B* (that containing the 6- and 8-aza N atoms). Even though ring *A* is symmetrically substituted, the two aza N atoms are in very different environments, with one pyramidal and the other planar: the sum of the angles subtended at N2 is 359.2°, and that at N4 is 344.8°. This is in marked contrast with the situation in ring *B*, where the substituents on the aza N atoms are very different, yet both are essentially planar: the sums of the angles subtended at N6 and N8 are 357.5 and 355.5°, respectively.

Ignoring substituents, the two rings are almost planar [for rings *A* and *B*, the average deviations from planarity are

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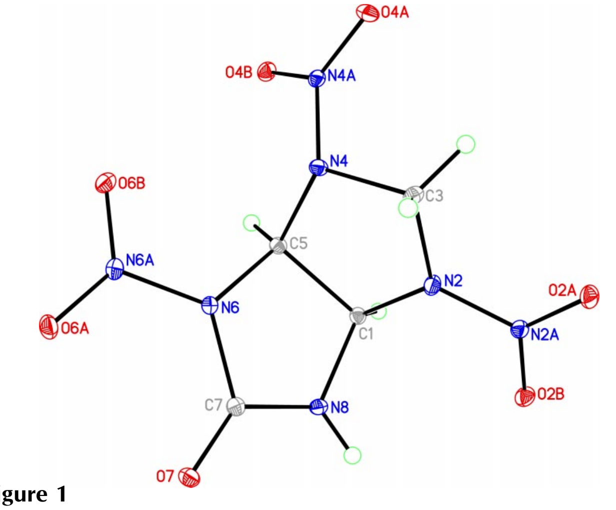

Figure 1
A view of the molecule of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 20% probability level and H atoms are shown as small spheres of arbitrary radii.

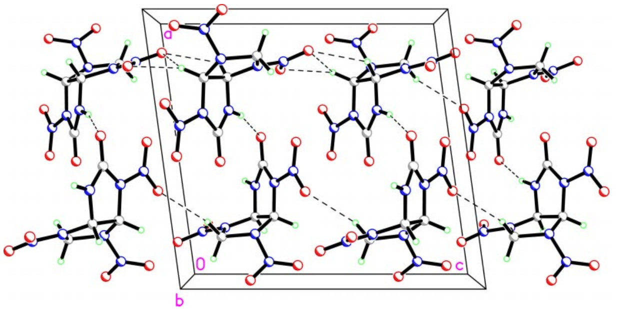

Figure 2
A view of the structure of (I) down the *b* axis, showing the packing arrangement and the intermolecular interactions (dashed lines).

0.072 (1) and 0.065 (1) Å, respectively]. In ring *A*, the largest deviation from planarity is for the pyramidal aza atom N4, which is 0.24 Å from a plane fit (to within 0.02 Å) to the other four atoms of the ring. The dihedral angle between the two ring planes is 68.83 (6)°. The nitramine metrical parameters (Table 1) are similar to those observed in related compounds containing the 2,4,6,8-tetraazabicyclo[3.3.0]octane skeleton (Boileau *et al.*, 1985, 1988; Flippen-Anderson *et al.*, 1990; George *et al.*, 1992; Gilardi *et al.*, 1992; Gilardi, George & Evans, 2002; Gilardi, Flippen-Anderson & Evans, 2002; Butcher *et al.*, 2004).

Fig. 2 illustrates the hydrogen-bonding interactions in (I), and details of their geometry are given in Table 2. The H atom attached to the amine N atom takes part in strong intermolecular hydrogen-bonding interactions to the keto O atom of an adjacent moiety. In addition, there are several weaker C—H intermolecular hydrogen-bonding interactions with adjoining nitro O atoms. As is usual in crystals containing nitro groups, there are several short intermolecular O···O contacts, the shortest of which is 2.890 (2) Å. A very short intermolecular O···N distance of 2.808 (2) Å is also present; this is a quasi-perpendicular approach between a peripheral O atom and the central N atom of two neighboring nitramine groups. Short contacts fitting this pattern are not uncommon involving the highly polar nitramine group, but this contact is unusually short. A search of the April 2004 release of the CSD revealed only six shorter O···N contacts of this type (Flippen-Anderson *et al.*, 1990; George & Gilardi, 1989; Nielsen *et al.*, 1998; Vedachalam *et al.*, 1991; Gilardi, Flippen-Anderson & Evans, 2002). There is also a rather short $O_{nitro}\cdots C_{carbonyl}$ contact of 3.055 (2) Å which is also quasi-perpendicular, in this case to the carbonyl plane.

The structure has recently been determined (Butcher *et al.*, 2004) of the related compound, 2,5,7-trinitro-2,5,7,9-tetraazabicyclo[4.3.0]nonan-8-one, (II). Both this and (I) contain the same substituents attached to fused tetraaza ring systems {2,5,7,9-tetraazabicyclo[4.3.0]nonane in (II) and 2,4,6,8-tetraazabicyclo[3.3.0]octane in the case of (I)}, so it is of interest to compare their similarities and differences. Of the four aza N atoms in (I), three are approximately planar while the fourth is pyramidal, whereas in (II), two aza N atoms are planar and two are only slightly pyramidal (one of each type in each ring). In both cases, the fused rings have adopted a *cis* conformation, but while the two five-membered rings in the 2,4,6,8-tetraazabicyclo[3.3.0]octane skeleton are planar (but not coplanar), in the 2,5,7,9-tetraazabicyclo[4.3.0]nonane derivative the six-membered ring has adopted a nonplanar twisted-boat conformation. While both crystal structures show similar intermolecular contacts, in (II) there is a very short $O_{nitro}\cdots C_{carbonyl}$ contact and a conventional $O_{nitro}\cdots N_{nitro}$ contact, while in (I) there is a very short $O_{nitro}\cdots N_{nitro}$ contact and a conventional $O_{nitro}\cdots C_{carbonyl}$ contact.

Experimental

A sample of (I) was synthesized and crystallized by Clifford L. Coon of the Lawrence Livermore National Laboratory, using methods described by Pagoria *et al.* (1996).

Crystal data

$C_4H_5N_7O_7$
$M_r = 263.15$
Monoclinic, $P2_1/c$
$a = 11.3962\ (12)$ Å
$b = 6.4089\ (7)$ Å
$c = 12.3267\ (13)$ Å
$\beta = 97.786\ (2)^\circ$
$V = 892.01\ (16)$ Å^3
$Z = 4$

$D_x = 1.959$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4730 reflections
$\theta = 2.6$–26.4°
$\mu = 0.19$ mm^{-1}
$T = 94\ (2)$ K
Faceted brick, colorless
0.38 × 0.28 × 0.26 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: by integration (Wuensch & Prewitt, 1965)
$T_{min} = 0.935$, $T_{max} = 0.957$
5880 measured reflections

1816 independent reflections
1662 reflections with $I > 2\sigma(I)$
$R_{int} = 0.039$
$\theta_{max} = 26.4^\circ$
$h = -14 \rightarrow 14$
$k = -8 \rightarrow 7$
$l = -14 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.087$
$S = 1.09$
1816 reflections
166 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0408P)^2 + 0.4733P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.35$ e Å^{-3}
$\Delta\rho_{min} = -0.21$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C1—N8	1.4339 (19)	N4*A*—O4*B*	1.2098 (17)
C1—N2	1.4596 (19)	N4*A*—O4*A*	1.2281 (16)
C1—C5	1.544 (2)	O4*A*—N4*A*$^{\rm ii}$	2.8075 (17)
N2—N2*A*	1.3358 (18)	C5—N6	1.4588 (18)
N2—C3	1.457 (2)	N6—N6*A*	1.3922 (17)
N2*A*—O2*A*	1.2268 (17)	N6—C7	1.4285 (19)
N2*A*—O2*B*	1.2324 (18)	N6*A*—O6*A*	1.2155 (16)
O2*A*—O4*B*$^{\rm i}$	2.8898 (16)	N6*A*—O6*B*	1.2158 (17)
C3—N4	1.4695 (18)	C7—O7	1.2046 (18)
N4—N4*A*	1.3987 (17)	C7—N8	1.350 (2)
N4—C5	1.4539 (18)		
N8—C1—N2	113.15 (12)	O4*B*—N4*A*—N4	118.60 (12)
N8—C1—C5	104.57 (11)	O4*A*—N4*A*—N4	115.21 (12)
N2—C1—C5	100.57 (11)	N4—C5—N6	111.27 (12)
N2*A*—N2—C3	122.00 (12)	N4—C5—C1	106.54 (11)
N2*A*—N2—C1	120.31 (12)	N6—C5—C1	100.64 (11)
C3—N2—C1	117.44 (12)	N6*A*—N6—C7	124.85 (12)
O2*A*—N2*A*—O2*B*	126.11 (13)	N6*A*—N6—C5	119.10 (12)
O2*A*—N2*A*—N2	117.15 (13)	C7—N6—C5	113.53 (12)
O2*B*—N2*A*—N2	116.73 (12)	O6*A*—N6*A*—O6*B*	127.54 (13)
N2*A*—O2*A*—O4*B*$^{\rm i}$	138.27 (10)	O6*A*—N6*A*—N6	117.77 (12)
N2—C3—N4	100.37 (11)	O6*B*—N6*A*—N6	114.68 (12)
N4*A*—N4—C5	116.31 (11)	O7—C7—N8	128.53 (15)
N4*A*—N4—C3	116.26 (11)	O7—C7—N6	126.62 (14)
C5—N4—C3	112.22 (12)	N8—C7—N6	104.84 (12)
O4*B*—N4*A*—O4*A*	126.07 (13)	C7—N8—C1	114.02 (13)

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

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C1—H1···O2*A*$^{\rm i}$	1.00	2.51	3.1902 (18)	125
C1—H1···O4*A*$^{\rm ii}$	1.00	2.56	3.0407 (18)	110
C3—H3*A*···O4*A*	0.99	2.30	2.6637 (19)	100
C3—H3*B*···O6*B*$^{\rm iii}$	0.99	2.45	3.3028 (19)	144
C5—H5···O2*A*$^{\rm i}$	1.00	2.56	3.2572 (19)	127
C5—H5···O2*B*$^{\rm i}$	1.00	2.29	3.2478 (18)	159
C5—H5···O4*B*	1.00	2.23	2.6547 (18)	104
N8—H8···O7$^{\rm iv}$	0.87 (2)	2.06 (2)	2.8940 (18)	161.9 (17)

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

The amino H atom was located in a difference map and its *xyz* coordinates were included in the refinement. H atoms attached to tertiary C atoms were fixed at a C—H distance of 1.00 Å, while H atoms attached to methylene C atoms were fixed at a C—H distance of 0.99 Å. In both cases the geometries were optimized. All H atoms were treated as riding, with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C,N).

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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