Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

2,5,7-Trinitro-2,5,7,9-tetraazabicyclo[4.3.0]-nonan-8-one

Ray J. Butcher,[a] Robin Evans[b] and R. Gilardi[b]*

[a]Department of Chemistry, Howard University, 525 College Street NW, Washington, DC 20059, USA, and [b]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 = 93 K
Mean σ(C–C) = 0.003 Å
R factor = 0.050
wR factor = 0.108
Data-to-parameter ratio = 11.1

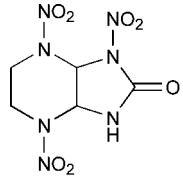
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 13 July 2004
Accepted 15 July 2004
Online 24 July 2004

The structure of the title compound, $C_5H_7N_7O_7$, contains fused five- and six-membered rings in a flattened envelope and a twist-boat conformation, respectively, with a *cis* junction between the two heterocyclic rings.

Comment

The title compound, 2,5,7-trinitro-2,5,7,9-tetraazabicyclo-[4.3.0]nonan-8-one, (I), is one of a family of compounds containing the tetraazabicyclo[4.3.0]nonane ring system synthesized by Pagoria *et al.* (1996) and Koppes *et al.* (1987) as possible precursors to energetic materials. The structures of some derivatives of this ring system have already been reported (Flippen-Anderson *et al.*, 1990; George *et al.*, 1992). In all cases, these molecules have similar conformations, in that the five-membered ring is a flattened envelope and the six-membered ring is in a twist-boat conformation. There is a *cis* junction between the two heterocyclic rings. Each of the rings contains both a planar and a slightly pyramidal N atom. The sum of the angles subtended at N2 and N7 are 352.3 and 351.2°, respectively. The geometrical parameters of the nitro groups are similar to those observed in related compounds (Flippen-Anderson *et al.*, 1990; George *et al.*, 1992; Gilardi, George & Evans, 2002; Gilardi, Flippen-Anderson & Evans, 2002).



(I)

The amine H atom takes part in a strong intermolecular hydrogen-bonding interaction with the keto O atom of an adjacent molecule. In addition, there are several weaker C—H intermolecular hydrogen-bonding interactions with adjoining nitro O atoms. As is usual in compounds containing the nitro group, there are several short intermolecular O···O contacts, the shortest of which is 2.867 (2) Å. A short intermolecular nitro–nitro O···N contact [2.874 (3) Å] is also displayed. This is not all that uncommon in crystal structures containing the highly polar nitramine group. Shorter O···N contacts of this type have been previously observed (Flippen-Anderson *et al.*, 1990; Gilardi, Flippen-Anderson & Evans, 2002) and occur in more than 20 other structures in Version 5.25 of the Cambridge Structural Database (CSD; April 2004 update; Allen, 2002). There is also a very short nitro–carbonyl O···C contact of 2.746 (3) Å; this approach is approximately

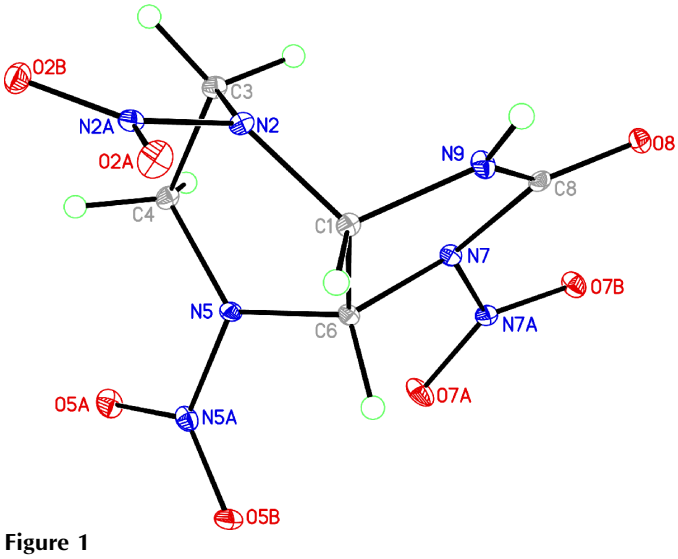


Figure 1
A displacement ellipsoid plot of the title compound, with ellipsoids drawn at the 20% probability level.

perpendicular to the carbonyl plane. Only a few nitro–carbonyl contacts less than 2.8 Å have been reported in the CSD. Excluding organometallic structures, there are six reports, the shortest contact being 2.76 Å in the dipeptide ALA–ASN (Konopelski *et al.*, 1999).

Experimental

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

Crystal data

$C_5H_7N_7O_7$
M_r = 277.18
Monoclinic, $C2/c$
a = 23.607 (3) Å
b = 6.7381 (8) Å
c = 12.7583 (16) Å
β = 110.215 (2)°
V = 1904.4 (4) Å^3
Z = 8
D_x = 1.933 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5019 reflections
θ = 3.3–26.4°
μ = 0.18 mm^{-1}
T = 93 (2) K
Thick plate, colorless
0.56 × 0.26 × 0.14 mm

Data collection

Bruker SMART CCD diffractometer
φ and ω scans
Absorption correction: by integration (Wuensch & Prewitt, 1965)
T_{min} = 0.907, T_{max} = 0.970
6356 measured reflections
1946 independent reflections
1751 reflections with $I > 2\sigma(I)$
R_{int} = 0.058
θ_{max} = 26.4°
$h = -29 \rightarrow 13$
$k = -8 \rightarrow 8$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.050
$wR(F^2)$ = 0.108
S = 1.25
1946 reflections
176 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0286P)^2 + 4.4051P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.30 e Å^{-3}
$\Delta\rho_{min}$ = −0.29 e Å^{-3}

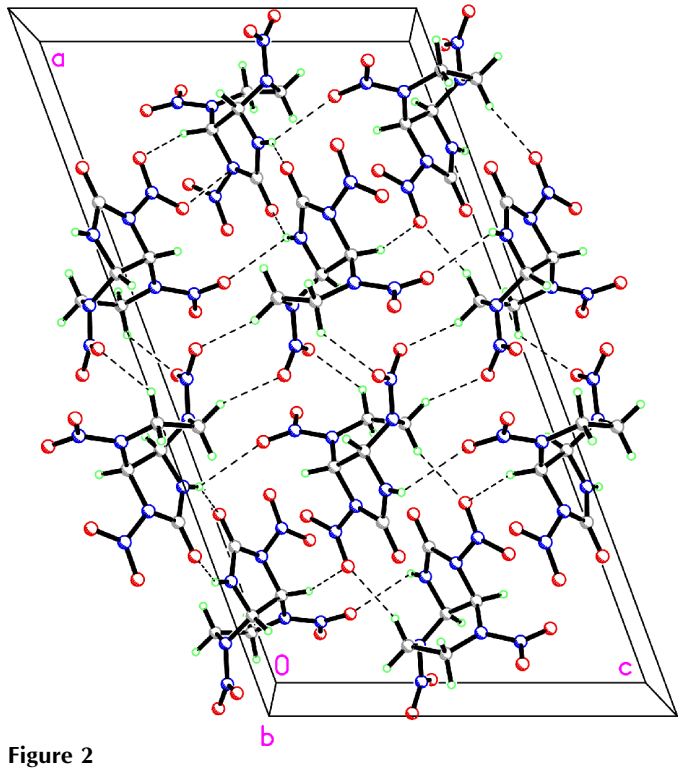


Figure 2
A view down the b axis, showing the packing arrangement of the title compound and the intermolecular interactions (dashed lines).

Table 1
Selected geometric parameters (Å, °).

O8—C8	1.193 (3)	N5—N5*A*	1.363 (3)
O2*A*—N2*A*	1.221 (3)	N5—C6	1.413 (3)
O2*B*—N2*A*	1.210 (3)	N5—C4	1.450 (3)
O5*A*—N5*A*	1.215 (3)	N7—N7*A*	1.362 (3)
O5*B*—N5*A*	1.212 (3)	N7—C8	1.427 (3)
O7*A*—N7*A*	1.213 (2)	N7—C6	1.472 (3)
O7*B*—N7*A*	1.197 (2)	N9—C8	1.330 (3)
N2—N2*A*	1.361 (3)	N9—C1	1.431 (3)
N2—C1	1.439 (3)	C1—C6	1.541 (3)
N2—C3	1.451 (3)	C3—C4	1.504 (3)
N2*A*—N2—C1	117.02 (17)	O7*B*—N7*A*—O7*A*	125.6 (2)
N2*A*—N2—C3	118.40 (18)	O7*B*—N7*A*—N7	119.43 (18)
C1—N2—C3	116.92 (18)	O7*A*—N7*A*—N7	114.89 (18)
O2*B*—N2*A*—O2*A*	124.93 (19)	C8—N9—C1	115.90 (19)
O2*B*—N2*A*—N2	118.43 (19)	N9—C1—N2	112.10 (18)
O2*A*—N2*A*—N2	116.58 (18)	N9—C1—C6	102.45 (17)
N5*A*—N5—C6	118.80 (18)	N2—C1—C6	110.56 (17)
N5*A*—N5—C4	117.18 (18)	N2—C3—C4	111.21 (18)
C6—N5—C4	123.48 (17)	N5—C4—C3	108.04 (18)
O5*B*—N5*A*—O5*A*	125.97 (19)	N5—C6—N7	113.63 (18)
O5*B*—N5*A*—N5	118.51 (19)	N5—C6—C1	111.60 (18)
O5*A*—N5*A*—N5	115.50 (19)	N7—C6—C1	100.73 (16)
N7*A*—N7—C8	122.16 (17)	O8—C8—N9	129.3 (2)
N7*A*—N7—C6	117.86 (17)	O8—C8—N7	125.9 (2)
C8—N7—C6	111.15 (17)	N9—C8—N7	104.78 (18)

Table 2
Contact distances (Å).

O2*A*···N5*A*^{i}	2.874 (3)	O7*A*···C8^{ii}	2.746 (3)

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

Table 3
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N9—H9···O8^{iii}	0.79 (3)	2.22 (3)	2.931 (3)	149 (3)
N9—H9···O5B^{iv}	0.79 (3)	2.53 (3)	3.073 (3)	127 (3)
C3—H3A···O7B^{v}	0.99	2.25	3.186 (3)	157
C3—H3B···O2B^{vi}	0.99	2.52	3.234 (3)	129
C1—H1A···O2A	1.00	2.22	2.642 (3)	103
C6—H6A···O5B	1.00	2.21	2.648 (3)	105
C6—H6A···O7B^{vii}	1.00	2.43	3.305 (3)	146
C4—H4A···O2A^{viii}	0.99	2.57	3.170 (3)	119

Symmetry codes: (iii) $\frac{1}{2}-x,\frac{1}{2}-y,1-z$; (iv) $x,-y,\frac{1}{2}+z$; (v) $\frac{1}{2}-x,-\frac{1}{2}-y,1-z$; (vi) $1-x,y,\frac{3}{2}-z$; (vii) $\frac{1}{2}-x,\frac{1}{2}+y,\frac{1}{2}-z$; (viii) $1-x,-y,1-z$.

The H atom bonded to N9 was refined freely with an isotropic displacement parameter. The C—H distance for H atoms attached to tertiary C atoms was fixed at 1.00 Å, while that for H atoms attached to methylene C atoms was fixed at 0.99 Å. In both cases, the geometries were optimized and the H atoms refined as riding, with $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT*; data reduction: *SAINT* (Sheldrick, 1999); 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/ONR program for a 2004 Summer Faculty Fellowship.

References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Bruker (2001). *SMART* (Version 5.624) and *SAINT* (Version 6.04). Bruker AXS Inc., Madison, Wisconsin, USA.
Flippen-Anderson, J. L., George, C. & Gilardi, R. (1990). *Acta Cryst.* C**46**, 1122–1125.
George, C., Gilardi, R. & Flippen-Anderson, J. L. (1992). *Acta Cryst.* C**48**, 1527–1528.
Gilardi, R., Flippen-Anderson, J. L. & Evans, R. (2002). *Acta Cryst.* E**58**, o972–o974.
Gilardi, R., George, C. & Evans, R. (2002). *Acta Cryst.* E**58**, o969–o971.
Konopelski, J. P., Wei, Y. & Olmstead, M. M. (1999). *J. Org. Chem.* **64**, 5148–5151.
Koppes, W. M., Chaykovsky, M., Adolph, H. G., Gilardi, R. & George, C. (1987). *J. Org. Chem.* **52**, 1113–1119.
Pagoria, P. F., Mitchell, A. R., Schmidt, R. D., Coon, C. L. & Jessop, E. S. (1996). *Am. Chem. Soc. Symp. Ser.* **623**, 151–164.
Sheldrick, G. M. (1997). *SHELXTL.* Version 5.10. Bruker AXS Inc., Madison Wisconsin, USA.
Sheldrick, G. M. (1999). *SAINT*. Version 6.02. Bruker AXS Inc., Madison Wisconsin, USA.
Wuensch, B. & Prewitt, C. (1965). *Z. Kristallogr.* **122**, 24–59.