Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

6,8-Dinitro-2,4-dioxa-6,8-diazabicyclo[3.3.0]octan-3-one

Richard D. Gilardi[a]* and Ray J. Butcher[b]

[a]Laboratory for the Structure of Matter, Naval Research Laboratory, Washington, DC 20375-5341, USA, and [b]Department of Chemistry, Howard University, 525 College Street, NW, Washington DC 20059, USA

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

Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.002 Å
R factor = 0.033
wR factor = 0.092
Data-to-parameter ratio = 10.2

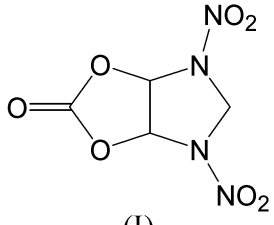
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 23 July 2001
Accepted 22 August 2001
Online 31 August 2001

The title compound, $C_4H_4N_4O_7$, is a bicyclic carbonate ester of 1,3-dinitroimidazolidine-4,5-diol. It contains only C, H, N, and O, and has a remarkably high density of 1.953 Mg m^{-3}, one of the top 12 densities in the CHNO realm. Such high densities are usually only observed in strained polycyclic ring compounds such as the nitrocubanes and hexanitrohexaaza-isowurtzitane.

Comment

The title compound, 6,8-dinitro-2,4-dioxa-6,8-diazabicyclo-[3.3.0]octan-3-one, (I), contains only C, H, N, and O, and has a remarkably high density of 1.953 Mg m^{-3}. This value is one of the top 12 in the CHNO realm [based on the results of a search of Version 5.2 (April 2001) of the Cambridge Structural Database (Allen *et al.*, 1991) using *ConQuest* (CCDC, 2001)]. The synthesis of new energetic CHNO compounds that have high densities is a prime goal in the field of energetic compounds. Such high densities are usually only observed in strained polycyclic ring compounds such as the nitrocubanes (Zhang *et al.*, 2000; Lukin *et al.*, 1997; Lukin *et al.*, 1996) and hexanitrohexaazaisowurtzitane (Nielsen *et al.*, 1998) or in a few planar molecules linked by inter- and intramolecular hydrogen bonding (Gilardi & Butcher, 2001) that can stack in parallel layers.



(I)

In the present instance, the central core of the molecule contains no double bonds and consists of a cyclic carbonate ring fused to an imidazolidine ring. The molecule is not planar but is folded about the C1*A*—C1*B* ring junction (the angle between the carbonate and imidazolidine rings is 61.3°). It is thus related to another dense energetic cyclic carbonate, 4,5-bis(fluorodinitromethyl)-1,3-dioxolan-2-one (Ammon & Bhattacharjee, 1984). Metrical parameters for the cyclic carbonate ring are within the normal range observed for such compounds (Allen *et al.*, 1991). However, the metrical parameters of the imidazolidine ring are affected by nitration of the N atoms. This nitration results in a shortening of the two C—N distances [C1*A*—N6 1.443 (2) and C1*B*—N8 1.440 (2)

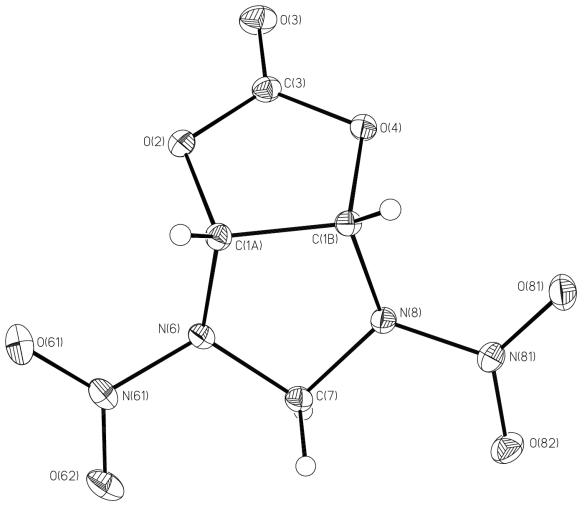


Figure 1
View of 6,8-diaza-6,8-dinitro-2,4-dioxabicyclo[3.3.0]octan-3-one. Displacement ellipsoids are drawn at the 20% level; H atoms are shown as small circles of arbitrary radii.

versus 1.466 Å], an increase in the C—N—C angles (115.4 *versus* 108.7°) and a corresponding decrease in the N—C—N angle (99.4 *versus* 103.6°).

Experimental

Crystals of the title compound were supplied by Dr Michael Chaykovsky, Naval Surface Warfare Center - White Oak, Silver Spring, MD.

Crystal data

$C_4H_4N_4O_7$
M_r = 220.11
Orthorhombic, $P2_12_12_1$
a = 6.7249 (5) Å
b = 9.979 (2) Å
c = 11.1574 (10) Å
V = 748.74 (19) Å^3
Z = 4
D_x = 1.953 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 69 reflections
θ = 7.9–43.5°
μ = 0.19 mm^{-1}
T = 293 (2) K
Octahedron, colorless
0.36 × 0.28 × 0.24 mm

Data collection

Bruker $P4$ diffractometer
$2\theta/\omega$ scans
Absorption correction: by integration (Wuensch & Prewitt, 1965)
T_{min} = 0.627, T_{max} = 0.689
1568 measured reflections
1568 independent reflections
1371 reflections with $I > 2\sigma(I)$
θ_{max} = 32.5°
$h = 0 \rightarrow 10$
$k = 0 \rightarrow 15$
$l = 0 \rightarrow 16$
3 standard reflections
every 97 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.092
S = 1.07
1568 reflections
153 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0565P)^2 + 0.0240P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.30 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}
Extinction correction: *SHELXL*
Extinction coefficient: 0.024 (6)

Crystal and reflection data were obtained using standard procedures (Butcher *et al.*, 1995).

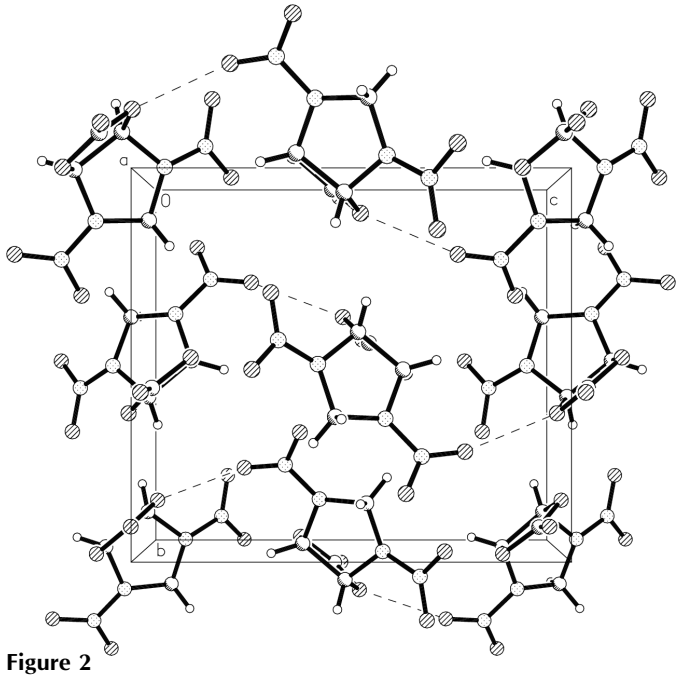


Figure 2
Packing diagram of 6,8-diaza-6,8-dinitro-2,4-dioxabicyclo[3.3.0]-octan-3-one. A recurrent short (2.88 Å) distance between a nitro-O atom and a ring-O atom is indicated by dashed lines.

Data collection: *XSCANS* (Siemens, 1994); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Sheldrick, 1997*a*); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*b*); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*b*); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

The authors wish to acknowledge the financial support from the Office of Naval Research, Mechanics Division. RJB wishes to acknowledge the ASEE/Navy Summer Faculty Research Program for support during the summer of 2001.

References

Allen, F. H., Davies, J. E., Galloy, J. J., Johnson, O., Kennard, O., Macrae, C. F., Mitchell, E. M., Mitchell, G. F., Smith, J. M. & Watson, D. G. (1991). *J. Chem. Inf. Comput. Sci.* **31**, 187–204.
Ammon, H. L. & Bhattacharjee, S. K. (1984). *Acta Cryst.* C**40**, 487–490.
Butcher, R. J., Bashir-Hashemi, A. & Gilardi, R. D. (1995). *J. Chem. Crystallogr.* **25**, 661–670.
CCDC (2001). *ConQuest*. Version 2.1. Cambridge Crystallographic Data Centre, Cambridge, England.
Gilardi, R. D. & Butcher, R. J. (2001). *Acta Cryst.* E**57**, o657–o658.
Lukin, K. A., Li, J., Gilardi, R. & Eaton, P. E. (1996). *Angew. Chem. Int. Ed. Engl.* **36**, 864–866.
Lukin, K. A., Li, J., Eaton, P. E., Kanomata, N., Hain, J., Punzalan, E. & Gilardi, R. (1997). *J. Am. Chem. Soc.* **119**, 9591–9602.
Nielsen, A. T., Chafin, A. P., Christian, S. L., Moore, D. W., Nadler, M. P., Nissan, R. A., Vanderah, D. J., Gilardi, R. George, C. F. & Flippen-Anderson, J. L. (1998). *Tetrahedron*, **64**, 11793–11812.
Sheldrick, G. M. (1997*a*). *SHELXTL*. Version 5.10. Bruker AXS, Madison, Wisconsin, USA.
Sheldrick, G. M. (1997*b*). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.
Siemens (1994). *XSCANS*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Wuensch, B. & Prewitt, C. (1965). *Z. Kristallogr.* **122**, 24–59.
Zhang, M.-X., Eaton, P. E. & Gilardi, R. (2000). *Angew. Chem. Int. Ed. Engl.* **39**, 401–414.