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2,5-Dinitro-7,9-dioxa-2,5-diazabicyclo[4.3.0]nonan-8-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) = 0.007 Å
Disorder in main residue
R factor = 0.045
wR factor = 0.111
Data-to-parameter ratio = 6.4

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

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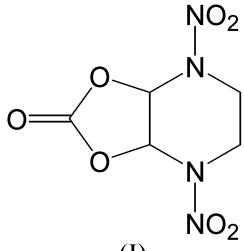
The title compound, $C_5H_6N_4O_7$, is a cyclic carbonate ester of 1,4-piperazine-2,3-diol. It contains only C, H, N, and O atoms, and has a high density of 1.828 Mg m^{-3}.

Comment

The title compound, 2,5-diaza-2,5-dinitro-7,9-dioxabicyclo-[4.3.0]nonan-8-one, (I), crystallizes in the orthorhombic space group $Pna2_1$, contains only C, H, N, and O, and has a density of 1.828 Mg m^{-3}. The central core of the molecule contains no double bonds and consists of a cyclic carbonate ring fused to a piperazine ring. The molecule is not planar but is folded about the C1—C6 ring junction (the angle between the carbonate and piperazine rings is 61.8°). It is thus related to the other dense energetic cyclic carbonates, 6,8-diaza-6,8-dinitro-2,4-dioxabicyclo[3.3.0]octan-3-one (Gilardi & Butcher, 2001), and 4,5-bis(fluorodinitromethyl)-1,3-dioxolan-2-one (Ammon & Bhattacharjee, 1984). The synthesis of new energetic CHNO compounds that have high densities is a prime goal in the



(I)

field of energetic compounds. However, 2,5-diaza-2,5-dinitro-7,9-dioxabicyclo[4.3.0]nonan-8-one has a much lower density than 6,8-diaza-6,8-dinitro-2,4-dioxabicyclo[3.3.0]octan-3-one (1.828 *versus* 1.953 Mg m^{-3}). One factor which contributes to this is the conformational flexibility of the –NCH_2CH_2N– backbone of the piperazine ring, which is disordered over two conformations with occupancies of 0.60:0.40 (2). Metrical parameters for the cyclic carbonate ring are within the normal range observed for such compounds (as summarized in the Cambridge Structural Database; Allen *et al.*, 1991). However, the metrical parameters of the piperazine ring are affected by the nitration of the N atoms, and the disorder of the ethylene backbone, and the fusion of the cyclic carbonate ring. The major differences are found in the C1—N2 and C6—N5 bond lengths which, at 1.416 (5) Å, are considerably shortened from the expected value of 1.464 Å (Allen *et al.*, 1991).

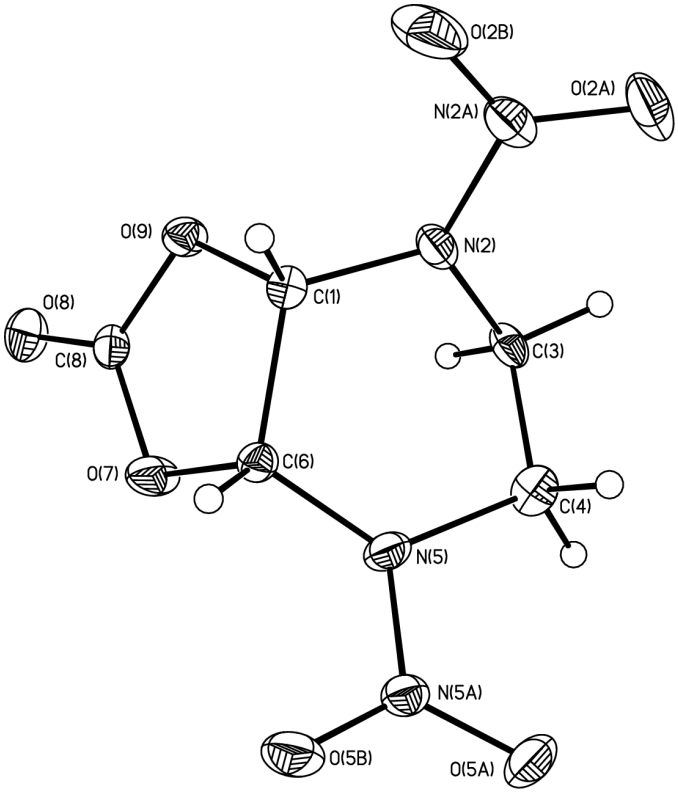


Figure 1
View of 2,5-dinitro-7,9-dioxa-2,5-diazabicyclo[4.3.0]nonan-8-one. Displacement ellipsoids are at the 20% probability level and H atoms are drawn as small circles of arbitrary radii.

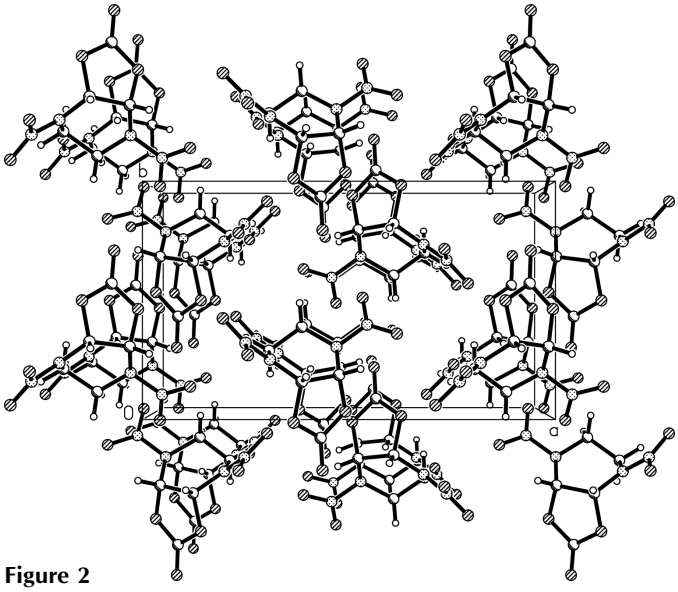


Figure 2
Packing diagram of 2,5-dinitro-7,9-dioxa-2,5-diazabicyclo[4.3.0]nonan-8-one.

Experimental

Crystals of the title compound were supplied by Dr Michael Chaykovsky, Naval Surface Warfare Center – White Oak, Silver Spring, MD. Crystal and reflection data were obtained using standard procedures (Butcher *et al.*, 1995).

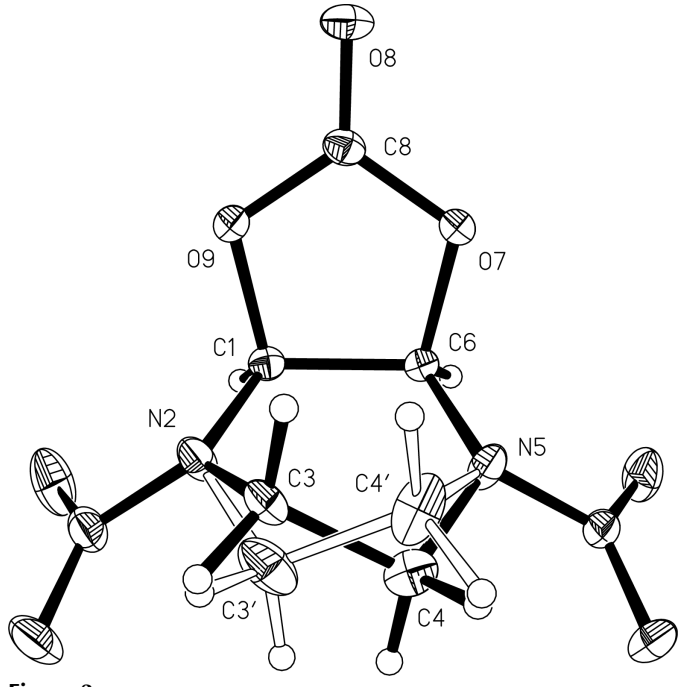


Figure 3
A side view of the disordered diazacyclohexane ring of the title molecule, with displacement ellipsoids at the 20% level. There is a 60:40 (2) ratio between the occupancies of the C3—C4 and the C3′—C4′ segments.

Crystal data

$C_5H_6N_4O_7$
M_r = 234.14
Orthorhombic, $Pna2_1$
a = 14.609 (2) Å
b = 8.4266 (12) Å
c = 6.9097 (8) Å
V = 850.61 (19) Å^3
Z = 4
D_x = 1.828 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 44 reflections
θ = 2.8–17.0°
μ = 0.17 mm^{-1}
T = 293 (2) K
Plate, colorless
0.45 × 0.39 × 0.03 mm

Data collection

Bruker $P4$ diffractometer
$2\theta/\omega$ scans
Absorption correction: by integration (Wuensch & Prewitt, 1965)
T_{min} = 0.947, T_{max} = 0.992
1049 measured reflections
1049 independent reflections
805 reflections with $I > 2\sigma(I)$
θ_{max} = 27.5°
$h = 0 \rightarrow 18$
$k = 0 \rightarrow 10$
$l = 0 \rightarrow 8$
3 standard reflections
every 97 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.111
S = 1.04
1049 reflections
165 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0470P)^2 + 0.4504P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.24 e Å^{-3}
$\Delta\rho_{min}$ = −0.19 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.025 (6)

The ethylene (–NCH_2CH_2N–) backbone of the piperazine ring was found to be disordered over two conformations. Using the *SHELXTL* refinement package, the disordered ethylene segments of the two conformers shown in Fig. 3 were constrained to be equivalent in their bond distances and angles, while their occupancies refined to convergence at 0.596 (16) and 0.404 (16). H atoms were found in

difference maps, except for those in the disordered segment, where they were generated to be in ideal tetrahedral positions. All H atoms were constrained in the refinement to ideal positions, with C—H distances of 0.97 or 0.98 Å, and angles as close to 109.5° as possible. Each was assigned a U_{iso} value equal to $1.2U_{eq}$ of the attached C atom.

Data collection: *XSCANS* (Siemens, 1994); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Sheldrick, 1997*a*); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*b*); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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