organic papers

cis-2,4,6,8-Tetranitro-1H,5H-2,4,6,8-tetraaza-bicyclo[3.3.0]octane, the energetic compound 'bicyclo-HMX'

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The title compound, $C_4H_6N_8O_8$, represents the energetic molecule commonly called 'bicyclo-HMX'. It was synthesized because it was expected to be denser than the powerful energetic material HMX, and thus exhibit improved energetic performance. X-ray diffraction analysis showed that this molecule was actually slightly less dense than HMX.
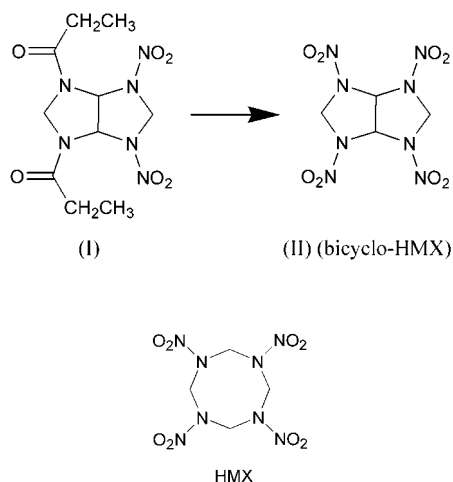
Comment

The title compound, (II), was synthesized from the dipropionyl precursor, (I), with the use of powerful and quite dangerous new nitrolysis agents (Pagoria et al., 1996; Gilardi et al., 2002). This synthesis succeeded only after several more direct synthetic routes from simpler precursors had failed, leading often to the decomposition of the tetraaza ring system.

Molecule (II) (Fig. 1) was a target material for several US Department of Defense and Department of Energy laboratories because of its close resemblance to HMX, which is one of the most powerful energetic compounds in explosive and propellant formulations used by the military. The density of (II) was expected to be slightly greater than HMX since it contains fewer H atoms, and its heat of formation was expected to be slightly greater due to added ring strain. However, its density, found in this X-ray analysis to be 1.86 Mg m^{-3}, is slightly less than that of β-HMX (1.91 Mg m^{-3}). Since the detonation pressure and velocity of an explosive are closely correlated with the density, this slight difference was enough to make the calculated properties of (II) equivalent to, but no better than, HMX as an energetic material, despite the added strain of the five-membered ring closures. It is difficult to explain a slight difference in density, but the rigid butterfly shape of the ring system in (II) may have
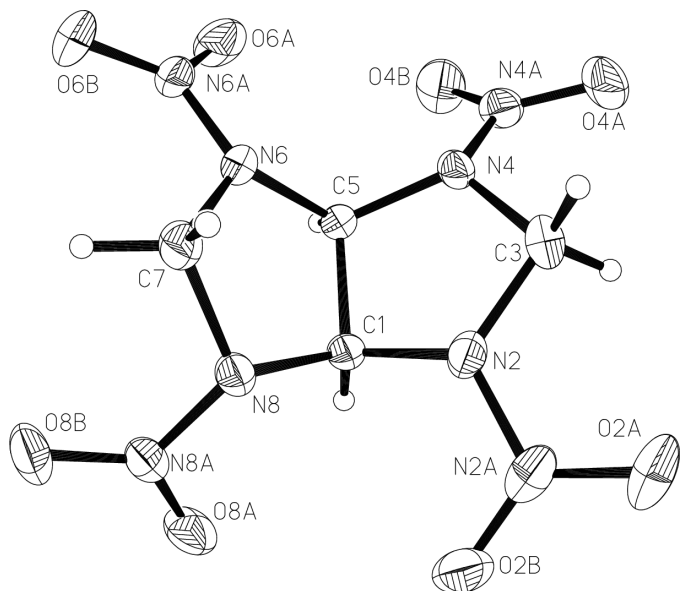
Figure 1
A view of the title compound, bicyclo-HMX, with 50% probability displacement ellipsoids.

Figure 2
A view, down the *b* axis, of the packing of the title compound.

led to inefficient packing. There are three short intermolecular distances, shown as dashed lines in Fig. 2, found in the crystal; N8A···O6A^i [symmetry code: (i) $1 - x$, $y - \frac{1}{2}$, $1 - z$] has a distance of 2.843 (4) Å, which is slightly less than van der Waals distance (3.07 Å) and two intermolecular C—H···O hydrogen bonds (Table 1), at H···O 2.43 and 2.53 Å *versus* the van der Waals distance of 2.72 Å (Rowland & Taylor, 1996). The crystal structure of the precursor molecule, (I), is reported in the preceding article (Gilardi *et al.*, 2002).

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).
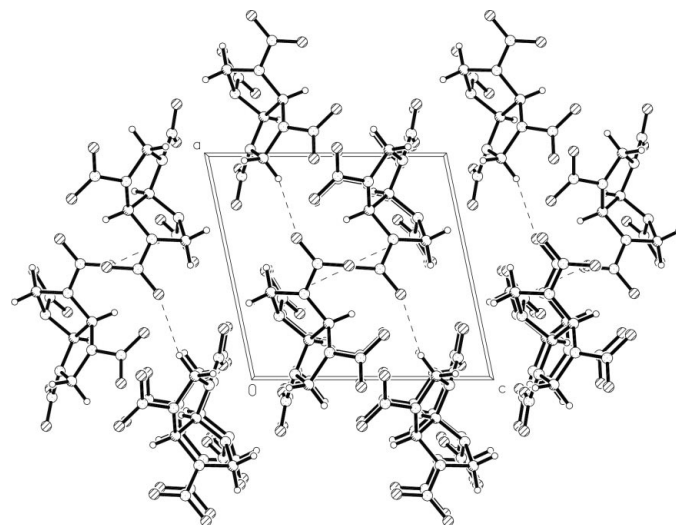
Crystal data

$C_4H_6N_8O_8$	$D_x = 1.861$ Mg m^{-3}
$M_r = 294.17$	Cu $K\alpha$ radiation
Monoclinic, $P2_1$	Cell parameters from 2531
$a = 8.5979$ (2) Å	reflections
$b = 6.9495$ (2) Å	$\theta = 5.0–66.8°$
$c = 8.9726$ (2) Å	$\mu = 1.60$ mm^{-1}
$\beta = 101.783$ (2)°	$T = 294$ (2) K
$V = 524.83$ (2) Å^3	Rectangular prism, colorless
$Z = 2$	$0.60 \times 0.14 \times 0.10$ mm

Data collection

Bruker 6K CCD area detector diffractometer	1442 independent reflections
	1400 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.027$
Absorption correction: multi-scan (*SADABS*; Bruker, 2001).	$\theta_{max} = 66.7°$
$T_{min} = 0.384$, $T_{max} = 0.853$	$h = -9 \rightarrow 9$
2607 measured reflections	$k = -6 \rightarrow 7$
	$l = -9 \rightarrow 10$

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} = 0.007$
$R[F^2 > 2\sigma(F^2)] = 0.036$	$\Delta\rho_{max} = 0.22$ e Å^{-3}
$wR(F^2) = 0.091$	$\Delta\rho_{min} = -0.23$ e Å^{-3}
$S = 1.15$	Extinction correction: *SHELXL*97
1442 reflections	Extinction coefficient: 0.077 (4)
182 parameters	Absolute structure: Flack (1983),
H-atom parameters constrained	484 Friedel pairs
$w = 1/[\sigma^2(F_o^2) + (0.0562P)^2$	Flack parameter = 0.1 (3)
$+ 0.0158P]$	
where $P = (F_o^2 + 2F_c^2)/3$	

Table 1
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C1—H1A···O8A	0.98	2.25	2.661 (3)	104
C7—H7A···O8B	0.97	2.25	2.671 (3)	105
C5—H5A···O6A^i	0.98	2.53	3.017 (3)	111
C3—H3B···O6B^{ii}	0.97	2.43	3.357 (3)	160

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

H atoms were placed at ideal (Sheldrick, 1997) tetrahedral positions and allowed to ride on their bonded neighbors during the refinement, with periodic re-idealization. The H-atom displacement parameters were set to be isotropic, with a value equal to 1.2 times the U_{eq} value of the neighboring C atom.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2001); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1997); software used to prepare material for publication: *SHELXTL*.

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