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# *cis*-2,4-Dinitro-6,8-dipropionyl-1*H*,5*H*-2,4,6,8-tetraazabicyclo[3.3.0]octane, a precursor of the energetic compound 'bicyclo-HMX'

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**Key indicators**

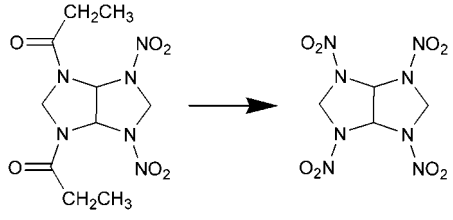
Single-crystal X-ray study
$T$ = 295 K
Mean $\sigma$(C–C) = 0.004 Å
Disorder in main residue
$R$ factor = 0.051
$wR$ factor = 0.139
Data-to-parameter ratio = 11.0

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

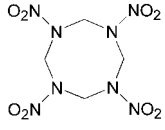
The title compound, $C_{10}H_{16}N_6O_6$, belongs to a family of compounds that contain the tetraazabicyclo[3.3.0]octane ring system, and served as the precursor to the energetic material known as 'bicyclo-HMX'. Both five-membered rings have envelope conformations, with methylene C atoms displaced from the respective $C_2N_2$ planes towards the *endo* side of the bicyclic system by 0.466 (3) and 0.315 (4) Å for the dinitro- and dipropionyl-substituted rings, respectively. The dihedral angle formed by the $C_2N_2$ planes is 118.1 (1)°.

## Comment

The title compound, (I), is one of a family of many compounds containing the tetraazabicyclo[3.3.0]octane ring system, synthesized by Pagoria *et al.* (1996) and Koppes *et al.* (1987) as possible energetic materials or precursors to energetic materials. Compound (I) was the only precursor found that was successfully nitrolyzed to the target material known as 'bicyclo-HMX', (II). This fully nitro-substituted product proved to be energetically equivalent to, but no better than HMX, a widely used component in explosive and propellant formulations. The crystal structure of (II) is reported in the article following this (Gilardi *et al.*, 2002). Crystal structure analyses of several other derivatives of this ring system were reported by Koppes *et al.* (1987).




(I) (II) (bicyclo-HMX)




HMX

The bicyclic system in molecule (I) (Fig. 1) adopts a butterfly shape, with both five-membered rings having envelope conformations, best seen in Fig. 2. The methylene atoms C3 and C7 are displaced from the C1/C5/N2/N4 and C1/C5/N6/N8 planes by 0.466 (3) and 0.315 (4) Å, respectively; in both cases, they deviate towards the *endo* side of the bicyclic system. The dihedral angle measured between the two

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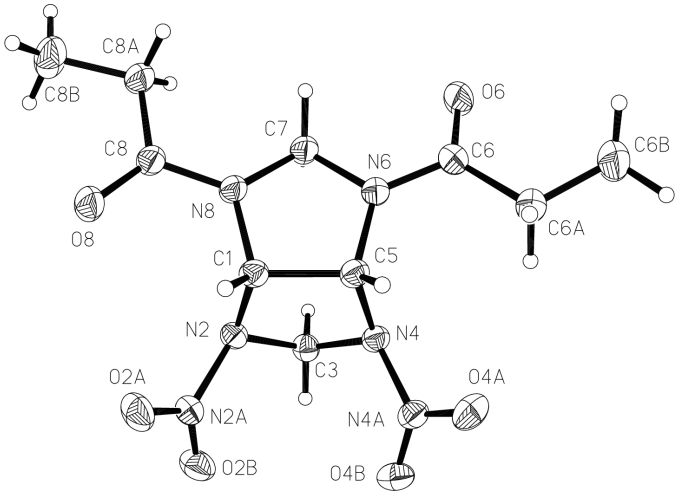


**Figure 1**
A view of the title compound, (I), with 25% probability atomic displacement ellipsoids; only the major component of the disordered C6—C6*A*—C6*B* chain is shown. Both components of the disorder are shown in Fig. 2.

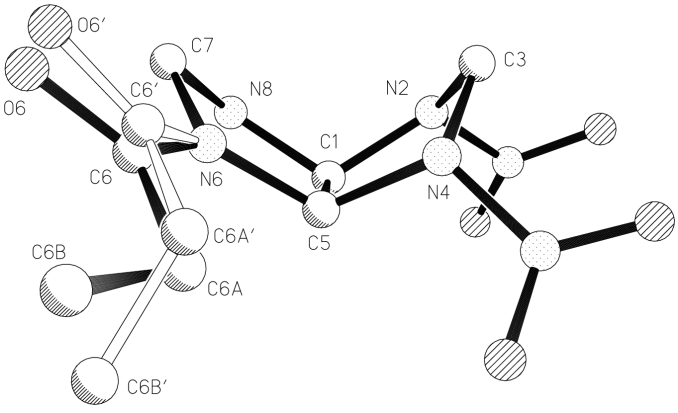


**Figure 2**
A view showing the *cis*-junction cleft between the two rings of the title compound. The disordered model of the C6 propionyl group is also shown. The conformer with dark bonds refined to an occupancy of 0.79 (1); the occupancies of both forms were constrained to add to 1. The propionyl group on N8 has been omitted for clarity.

four-atom planes is 118.1 (1)°. The carbonyl groups of the two propionyl substituents are oriented in opposite directions relative to the C1—C5 bridgehead, with torsion angles C5—N6—C6—O6 and C1—N8—C8—O8 of 173.0 (5) and 1.5 (4)°, respectively. A similar reversal of direction has always been seen in the three earlier reports of diketo substitution on a ring of this same ring system. Such a fragment occurred twice in *cis*-2,4,6,8-tetraacetyl-1*H*,5*H*-2,4,6,8-tetraazabicyclo[3.3.0]-octane (Koppes *et al.*, 1987) and once in *cis*-6,8-diacetyl-2,4-dinitro-1*H*,5*H*-2,4,6,8-tetraazabicyclo[3.3.0]octane (Gilardi *et al.*, 1992). The propionyl carbonyls and their attached atoms are roughly in the plane of the ring to which they are attached. In contrast, the two nitro substituents are bent far back from

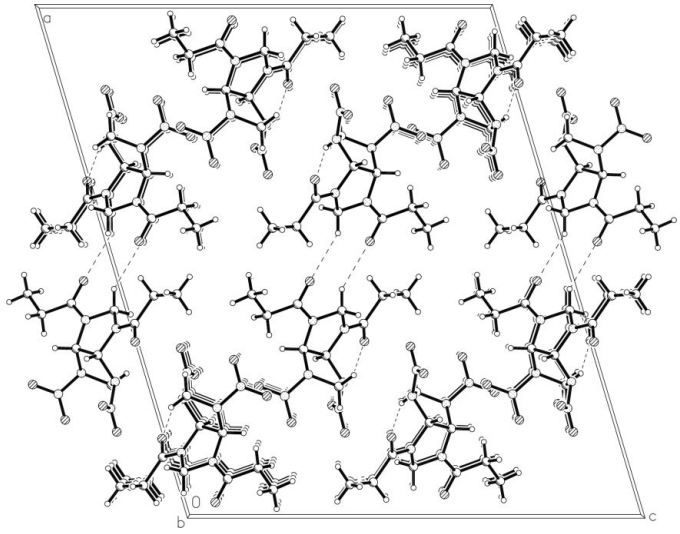


**Figure 3**
A view of the packing of the title compound down the *b* axis.

their adjacent ring, deviating towards the *exo* side of the ring system (Fig. 2). A measure of this bend is given by the dihedral angle between the plane through the $NNO_2$ segment and the plane through the adjacent C—N—C segment of the ring. This dihedral angle is 41.0 (1)° for the nitro group on N2 and is 42.8 (2)° for the nitro group on N4. The four N atoms of the ring system are thus nearly planar in the one ring, and are highly pyramidalized in the other. (In the absence of any nitro twist, the out-of-plane dihedral angle would be 54.7° for a 'tetrahedral' nitro-substituted N atom.) Nitramines are noted for the flexibility of their amine N atom; Gilardi & Karle (1991) reported that a range of 0–59° had been observed for the 'bend angles' between the N—N bond and the adjacent C—N—C plane, a measure very similar to the dihedral angles reported here.

There is only one short intermolecular contact found in the crystal (see Fig. 3): the O8···H3$A^{i}$ distance of 2.34 Å [symmetry code: (i) $x$, $y-1$, $z$] is considerably less than the van der Waals distance of 2.72 Å (Rowland & Taylor, 1996).

## 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*

$C_{10}H_{16}N_6O_6$
$M_r$ = 316.29
Monoclinic, $C2/c$
$a$ = 23.8006 (4) Å
$b$ = 6.1611 (1) Å
$c$ = 20.2972 (4) Å
$\beta$ = 106.539 (1)°
$V$ = 2853.20 (9) Å$^3$
$Z$ = 8
$D_x$ = 1.473 Mg m$^{-3}$
Cu $K\alpha$ radiation
Cell parameters from 5104 reflections
$\theta$ = 3.9–67.0°
$\mu$ = 1.06 mm$^{-1}$
$T$ = 295 (2) K
Plate, colorless
0.28 × 0.11 × 0.03 mm

*Data collection*

Bruker 6K CCD area-detector diffractometer
$\varphi$ and $\omega$ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)
$T_{min} = 0.744$, $T_{max} = 0.969$
7129 measured reflections
2410 independent reflections
2178 reflections with $I > 2\sigma(I)$
$R_{int} = 0.032$
$\theta_{max} = 67.0°$
$h = -27 \rightarrow 25$
$k = -7 \rightarrow 6$
$l = -23 \rightarrow 23$

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.051$
$wR(F^2) = 0.139$
$S = 1.08$
2410 reflections
219 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0533P)^2 + 4.0092P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.003$
$\Delta\rho_{max} = 0.22$ e Å$^{-3}$
$\Delta\rho_{min} = -0.22$ e Å$^{-3}$
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0046 (3)

The appearance of large difference peaks near the propionyl substituent on N6 prompted the use of a disordered model involving two conformations. The occupancies of the two forms were constrained to add to 1.0, and refined to a 79 (1):21(1) ratio. All atoms in the disordered substituent were 'split' into two images, even if there was no separate difference peak. The bond distances and angles of the two images, from N6 outwards along the propionyl chains, were strongly restrained to be equal, or nearly so (aiming toward a specified s.u. of 0.001 Å for the differences). Thus the added refinement parameters were essentially just the torsion angles of the minor conformer and the occupation ratio. Atoms in the low-occupancy form have primed labels. 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. Methyl H atoms were allowed to torsion about the C—$CH_3$ bond, except for the methyl group in the low-occupancy (21%) form of the propionyl on N6, which was fixed at a staggered location. The H-atom displacement parameters were specified to be isotropic, with a value equal to 1.5 times the $U_{eq}$ value of the C atom for methyl groups, and equal to 1.2 times the $U_{eq}$ value of the neighboring bonded atom for all other groups.

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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