

## 1,2,3,4,5,7-Hexanitrocubane

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## Key indicators

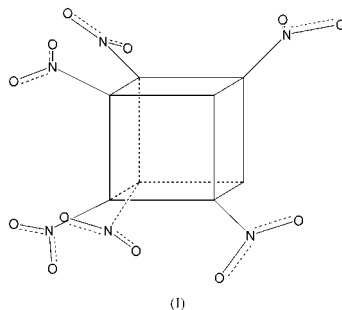
Single-crystal X-ray study  
 $T = 295$  K  
Mean  $\sigma(\text{C}-\text{C}) = 0.002$  Å  
Disorder in main residue  
 $R$  factor = 0.046  
 $wR$  factor = 0.136  
Data-to-parameter ratio = 10.5

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

The hexanitrocubane structure,  $\text{C}_8\text{H}_2\text{N}_6\text{O}_{12}$ , reported herein, is one of the last in the series of nitrocubanes, ranging from mono- to octanitrocubane. In this molecule, the H atoms participate in short hydrogen-bonding contacts to the nitro O atoms in adjoining molecules [ $2.50$  (1) Å], thus linking molecules into a two-dimensional sheet in the  $bc$  plane. In addition, the  $\text{O} \cdots \text{O}$  contacts in hexanitrocubane are shorter than van der Waals contact distances. The shortest of these [ $2.766$  (3) Å] involve the O atoms of one of the attached nitro groups. These contacts involve molecules in an extended two-dimensional sheet parallel to the  $ab$  plane.

## Comment

Nitrocubanes have long been sought after as powerful, shock-insensitive, high-density explosives (Eaton, 1992). In these compounds are combined the energy associated with the highly strained cubane skeleton (Eaton, 1992) with that associated with polynitrated compounds. One of the more interesting stories in organic synthesis in recent years has been the long (*ca* 20 years) development of methods (Eaton *et al.*, 2000) to make octanitrocubane (Zhang *et al.*, 2000), the 'holy grail' of the energetic materials community. Theoretical predictions (Alster *et al.*, 1981) had indicated that this compound would have one of the highest densities observed in compounds containing only C, H, N and O. In this search, the structures of 1,4-dinitro (Eaton *et al.*, 1984), 1,3,5-trinitro (Eaton *et al.*, 1993), 1,3,5,7-tetranitro- (Eaton *et al.*, 1993), 1,2,3,5,7-pentanitro- (Lukin *et al.*, 1997), 1,2,3,4,5,6,8-heptanitro- (Zhang *et al.*, 2000), and 1,2,3,4,5,6,7,8-octanitrocubane (Zhang *et al.*, 2000) have been reported. However, to date the structure of the simplest member of this series, nitrocubane, is only now being reported (Butcher & Gilardi, 2002).

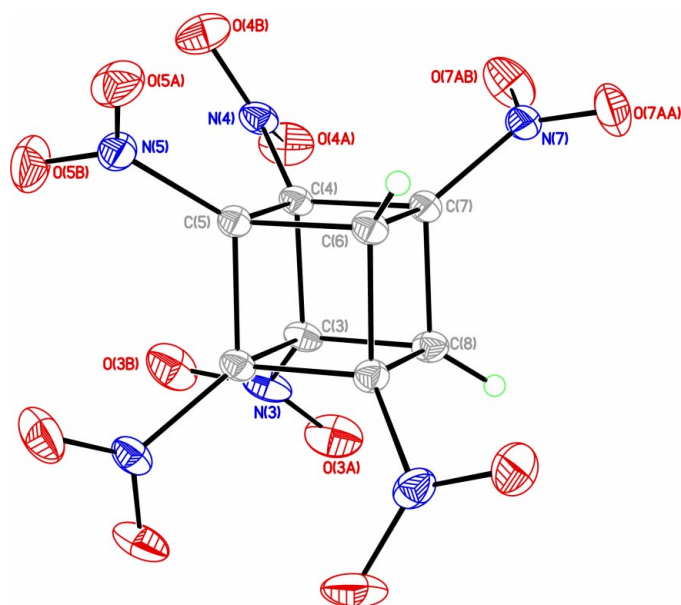


The structure of 1,2,3,4,5,7-hexanitrocubane, (I), is reported herein; previously the structure of its acetonitrile solvate had been reported (Lukin *et al.*, 1997). Pure hexanitrocubane crystallizes in the orthorhombic space group  $Pnma$  with four

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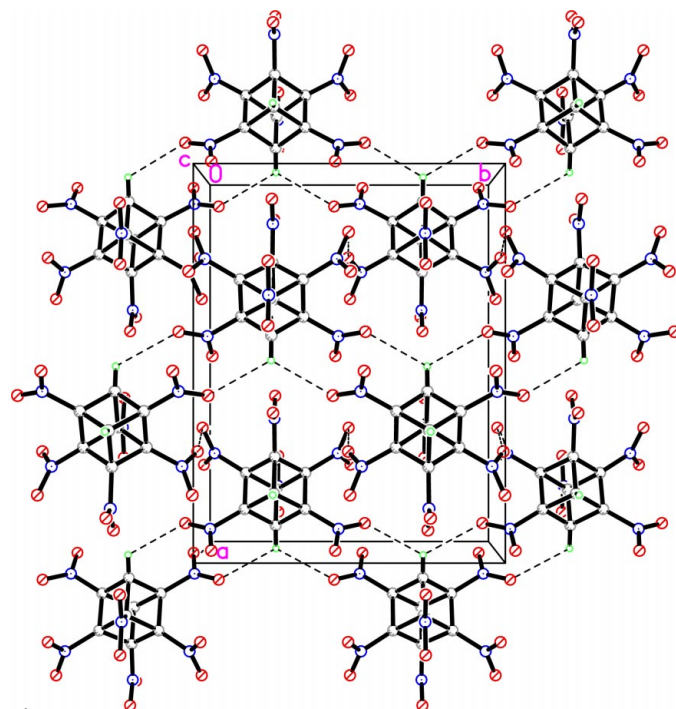
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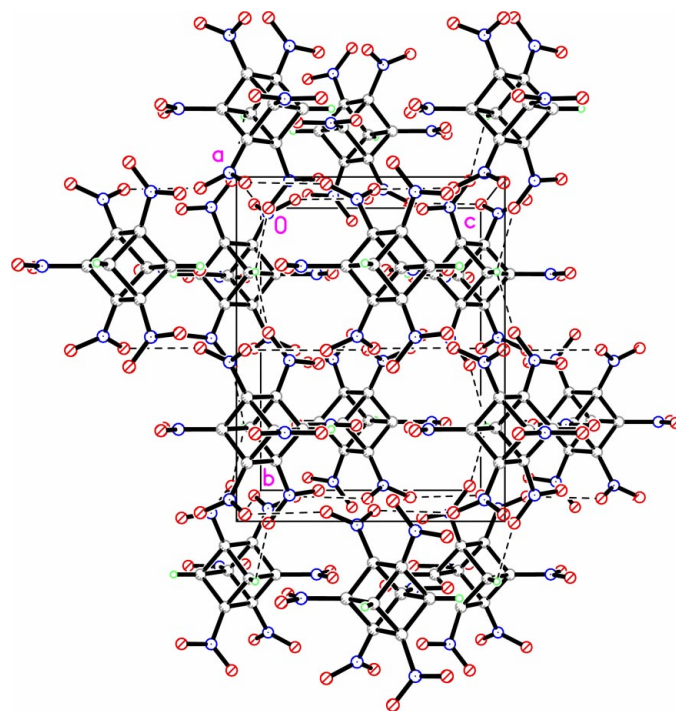
**Figure 1**  
Displacement ellipsoid plot (50% probability level) of the title molecule, showing the atomic labeling scheme.

molecules in the unit cell and thus the molecule has crystallographically imposed mirror symmetry passing through atoms C3, N3, O3A, O3B, C5, N5, O5A, O5B, C6, H6, C8, and H8. Positions C4A and C7A, generated by the mirror plane, correspond to positions C2 and C1 in the conventional cubane numbering scheme. In hexanitrocubane, the C—C bond lengths average 1.565 (6) Å, which is somewhat longer than the average found in all cubane structures, but well within the normal range (Butcher *et al.*, 1995). The nitro O atoms attached to N7 are disordered over two positions, with occupancies of 0.600 (4) and 0.400 (4), which is not unusual for such moieties. As the number of nitro substituents increase, H atoms attached to the cubane skeleton become increasingly acidic (Lukin *et al.*, 1997), and thus participate in stronger hydrogen-bonding interactions than is commonly observed for hydrocarbon H atoms. In this instance, H6 participates in short hydrogen-bonding contacts to O7AB in two adjoining molecules (2.501 Å), thus linking molecules into a two-dimensional sheet in the *ab* plane, as shown in Fig. 2. In addition, just as is the case in pentanitrocubane (Lukin *et al.*, 1997), heptanitrocubane (Zhang *et al.*, 2000), and octanitrocubane (Zhang *et al.*, 2000), several O···O contacts in hexanitrocubane are shorter than the van der Waals contact distance of 3.04 Å (Rowland & Taylor, 1996). The shortest of these, 2.766 Å, involve the O atoms of the nitro group attached to C4. In hexanitrocubane, the nitro groups attached to C4 (and C4A which is related to C4 by the crystallographic mirror plane) are the only nitro groups that are *ortho* to three other nitro groups. These contacts are between the molecules that lie in an extended two-dimensional sheet parallel to the *bc* plane, as shown in Fig. 3.

Density is of critical importance to the performance of an explosive. The overall packing in hexanitrocubane described above leads to a density of 1.931 Mg m<sup>-3</sup> at 294 K. While this



**Figure 2**  
The molecules of (I) linking into a two-dimensional sheet in the *ab* plane through short hydrogen-bonding contacts to C7 in adjoining molecules.



**Figure 3**  
Short O···O contacts from the C4 nitro group linking up molecules in an extended two-dimensional sheet parallel to the *bc* plane.

is less than that observed for pentanitrocubane (1.959 Mg m<sup>-3</sup>; Lukin *et al.*, 1997), heptanitrocubane (2.028 Mg m<sup>-3</sup>; Zhang *et al.*, 2000), and octanitrocubane (1.979 Mg m<sup>-3</sup>; Zhang *et al.*, 2000), this is still an impressive value for a compound containing only C, H, N, and O, and is

much higher than the value previously observed for its acetonitrile solvate ( $1.676 \text{ Mg m}^{-3}$ ; Lukin *et al.*, 1997). The metrical parameters found for this unsolvated structure of hexanitrocubane are very similar to those found for the acetonitrile solvate (Lukin *et al.*, 1997).

## Experimental

The preparation of hexanitrobenzene has been reported previously (Lukin *et al.*, 1997). Solvent-free crystals were grown by slow evaporation from a mixed  $\text{HNO}_3/\text{H}_2\text{SO}_4$  solution at 313 K.

### Crystal data

$\text{C}_8\text{H}_2\text{N}_6\text{O}_{12}$	Mo $K\alpha$ radiation
$M_r = 374.16$	Cell parameters from 4545 reflections
Orthorhombic, $Pnma$	$\theta = 2.8\text{--}28.3^\circ$
$a = 13.936 (2) \text{ \AA}$	$\mu = 0.19 \text{ mm}^{-1}$
$b = 10.8870 (19) \text{ \AA}$	$T = 295 (2) \text{ K}$
$c = 8.4833 (14) \text{ \AA}$	Plate, orange
$V = 1287.1 (4) \text{ \AA}^3$	$0.74 \times 0.29 \times 0.11 \text{ mm}$
$Z = 4$	
$D_x = 1.931 \text{ Mg m}^{-3}$	

### Data collection

Bruker P4/CCD diffractometer	1202 reflections with $I > 2\sigma(I)$
$\omega$ scans	$R_{\text{int}} = 0.026$
Absorption correction: multi-scan (Bruker, 2001)	$\theta_{\text{max}} = 28.3^\circ$
$T_{\text{min}} = 0.819$ , $T_{\text{max}} = 0.962$	$h = -18 \rightarrow 18$
9511 measured reflections	$k = -14 \rightarrow 14$
1655 independent reflections	$l = -11 \rightarrow 9$

### Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0747P)^2 + 0.3718P]$
$R[F^2 > 2\sigma(F^2)] = 0.046$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.136$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.03$	$\Delta\rho_{\text{max}} = 0.35 \text{ e \AA}^{-3}$
1655 reflections	$\Delta\rho_{\text{min}} = -0.24 \text{ e \AA}^{-3}$
157 parameters	
All H-atom parameters refined	

All H atoms were initially located in a difference Fourier map and refined isotropically. The nitro O atoms attached to N7 are disordered over two positions, with occupancies of 0.600 (4) and 0.400 (4), as is commonly found for such moieties.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2001); 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*.

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