Acta Crystallographica Section C
**Crystal Structure
Communications**
ISSN 0108-2701

4,10-Dinitro-2,6,8,12-tetraoxa-4,10-diazaisowurtzitane (TEX): a nitramine with an exceptionally high density

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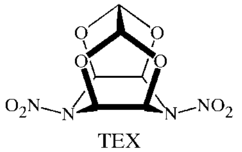
Received 19 July 2002
Accepted 14 August 2002
Online 31 August 2002

The title compound (systematic name: 4,10-dinitro-2,6,8,12-tetraoxa-4,10-diazatetracyclo[5.5.0.$0^{3,11}$.$0^{5,9}$]dodecane), $C_6H_6N_4O_8$, exhibits the highest density among known *N*-nitramines, due to its close-packed crystal structure. It may be regarded as consisting of a distorted hexagonal close-packed lattice formed by the isowurtzitane cages, with the nitro groups occupying the free space between the cages.

Comment

4,10-Dinitro-2,6,8,12-tetraoxa-4,10-diazaisowurtzitane, hereinafter TEX, is an insensitive highly energetic material which was first described by Ramakrishnan and co-workers in 1990 (Ramakrishnan *et al.*, 1990). It displays the highest density recorded for a nitramine and therefore a very high detonation velocity (7470 m s^{-1}), according to both Jacob *et al.* (2000), Li *et al.* (2001) and Klapötke & Ang (2001), while its sensitivity towards shock, impact or friction is extremely low, as mentioned by Vagenknecht (2000) and Zeman (1999) [*cf.* also Klapötke *et al.* (1999)]. These and other features make TEX a highly interesting model compound for the investigation of explosion processes.



TEX

A recently published X-ray structure of TEX (Yu *et al.*, 1996) did not provide any information about the crystal lattice (such as lattice constants, space group, atom positions in the unit cell *etc.*). Since the density of an explosive compound is closely related to its explosion properties, we were prompted to investigate closely the crystal lattice of TEX in order to find an explanation for its extraordinarily high density. The molecule shows a cage structure composed of three C_2 units, which are linked by four O atoms, and by two N atoms bearing nitro groups (Fig. 1).

The seven-membered rings put a strain on the cage and thus increase the energy content of the molecule. A part of the explosive power of TEX is derived from this cage strain. The extraordinarily high density of TEX may be explained by the compactness of the molecule, which can be described, except for the nitro groups, as nearly spherical (Fig. 1). Atoms N11 and N31 are coordinated, as expected, in a planar manner [both angle sums are 359.9 (4)°]. There is significant deviation from planarity in the coordination of atoms N1 and N3, with an angle sum of 343.2 (3)° for N1 and 351.2 (4)° for N3. Atoms C1–C4 deviate only slightly from the planes defined by the respective nitro groups. The N—N bond length appears in both cases (N1—N11 and N3—N31) to be shorter (1.40–1.41 Å) than a single N—N bond (1.48 Å), but much longer than a double bond (1.20 Å). The C1—C2 and C3—C4 bond distances [both 1.56 (2) Å] are slightly shorter than that of C5—C6 [1.58 (1) Å]. A possible reason for this difference is the fact that both the C1—C2 and C3—C4 bonds connect a

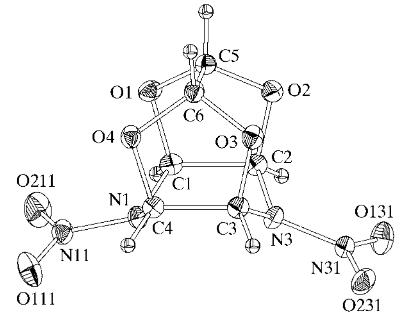


Figure 1
A view of the molecule of TEX showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

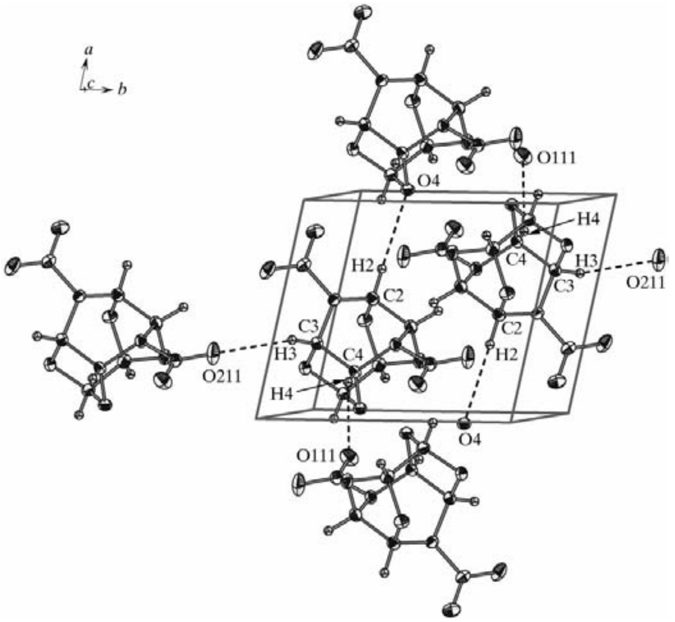


Figure 2
Close O···H contacts in the crystal structure of TEX, forming a three-dimensional network.

five-membered and a seven-membered ring and are thus less strained than the C5—C6 bond, which connects two seven-membered rings. The Pitzer strain destabilizes the seven-membered rings to a higher degree than the five-membered rings.

TEX crystallizes in a structure that is remarkably similar to a distorted hexagonal close packing of spheres. The crystal lattice of TEX contains molecules in two different orientations (Fig. 2). Within the structure, the shortest distances between molecule cages are O1···O4$^{\rm i}$ [2.8773 (15) Å], O111···O111$^{\rm ii}$ [2.999 (2) Å] and C6···O1$^{\rm i}$ [2.9974 (18) Å], all of which are significantly shorter than the sum of the van der Waals radii (3.0 Å for O···O and 3.2 Å for C···O; Holleman *et al.*, 1995) [symmetry codes: (i) $-x, 1-y, 1-z$; (ii) $-x, 1-y, -z$].

Relatively short distances are observed for H2···O4, H3···O211 and H4···O111 (Table 2 and Fig. 2). However, due to the comparatively long H···O distances and C—H···O angles deviating significantly from linearity, we may assume that the contacts cannot be regarded as bonding.

Experimental

The title compound was synthesized as described by Ramakrishnan *et al.* (1990). Crystallization by slow evaporation from a saturated solution of TEX in acetone afforded colourless crystals suitable for X-ray analysis.

Crystal data

$C_6H_6N_4O_8$
$M_r = 262.15$
Triclinic, $P\bar{1}$
$a = 6.8360\ (12)$ Å
$b = 7.6404\ (14)$ Å
$c = 8.7765\ (16)$ Å
$\alpha = 82.37\ (2)^\circ$
$\beta = 75.05\ (2)^\circ$
$\gamma = 79.46\ (2)^\circ$
$V = 433.64\ (14)$ Å^3
$Z = 2$
$D_x = 2.008\ (1)$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3304 reflections
$\theta = 2.4$–27.9°
$\mu = 0.19$ mm^{-1}
$T = 200\ (2)$ K
Prismatic, colourless
0.27 × 0.27 × 0.20 mm

Data collection

Stoe IPDS diffractometer
φ scans
Absorption correction: numerical (*X-RED*; Stoe & Cie, 1997)
$T_{\rm min} = 0.958$, $T_{\rm max} = 0.971$
3698 measured reflections
1911 independent reflections
1555 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.023$
$\theta_{\rm max} = 28.1^\circ$
$h = -8 \rightarrow 9$
$k = -10 \rightarrow 10$
$l = -11 \rightarrow 10$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.099$
$S = 1.05$
1911 reflections
187 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0684P)^2 + 0.0238P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.25$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.25$ e Å^{-3}

Data collection: *EXPOSE* in *IPDS* (Stoe & Cie, 1997); cell refinement: *CELL* in *IPDS*; data reduction: *INTEGRATE* in *IPDS*; program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1996).

The authors thank Dr H. Piotrowski for the X-ray data and Dr B. Krumm for his experience in the synthesis of TEX, and also Ludwig-Maximilias University, Munich, for financial support.

Table 1
Selected geometric parameters (Å, °).

N1—N11	1.4162 (16)	N31—O131	1.2128 (19)
N1—C1	1.450 (2)	N31—O231	1.2247 (18)
N1—C4	1.4672 (18)	C3—O3	1.4214 (17)
N11—O211	1.2139 (19)	C3—C4	1.5574 (19)
N11—O111	1.218 (2)	C4—O4	1.4196 (17)
C1—O1	1.4222 (17)	O1—C5	1.4222 (16)
C1—C2	1.5628 (19)	O2—C5	1.4174 (17)
C2—O2	1.4243 (17)	O3—C6	1.4162 (17)
C2—N3	1.4480 (19)	O4—C6	1.4215 (17)
N3—N31	1.3962 (16)	C5—C6	1.577 (2)
N3—C3	1.4476 (19)		
N11—N1—C1	114.58 (11)	N31—N3—C3	117.11 (12)
N11—N1—C4	113.14 (12)	N31—N3—C2	117.67 (12)
C1—N1—C4	115.51 (11)	C3—N3—C2	116.42 (11)
O211—N11—N1	117.19 (14)	O131—N31—N3	117.40 (13)
O111—N11—N1	116.79 (12)	O231—N31—N3	117.07 (13)
C1—N1—N11—O211	12.66 (18)	C2—N3—N31—O131	−14.90 (18)
C4—N1—N11—O111	−36.20 (17)	C3—N3—N31—O231	21.39 (17)

Table 2
Hydrogen-bond and short-contact geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2···O4$^{\rm i}$	0.95 (2)	2.49 (2)	3.439 (2)	174.9 (14)
C3—H3···O211$^{\rm ii}$	0.956 (16)	2.394 (16)	3.192 (2)	140.5 (14)
C4—H4···O231$^{\rm iii}$	0.976 (18)	2.546 (16)	3.238 (2)	127.9 (14)
C4—H4···O111$^{\rm iv}$	0.976 (18)	2.49 (2)	3.240 (2)	133.4 (14)
C6—H6···O3$^{\rm v}$	0.953 (19)	2.559 (18)	3.365 (2)	142.7 (12)

Symmetry codes: (i) $1+x, y, z$; (ii) $x, y-1, z$; (iii) $1-x, -y, -z$; (iv) $-x, 1-y, -z$; (v) $-x, -y, 1-z$.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1130). A packing diagram is also available. Services for accessing these data are described at the back of the journal.

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Acta Cryst. (2002). C**58**, o580–o581 Konstantin Karaghiosoff *et al.* • $C_6H_6N_4O_8$ **o581**