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A High-Density Thermally Stable Explosive: Octahydro-2,5-bis(nitroimino)-imidazo[4,5-*d*]imidazole

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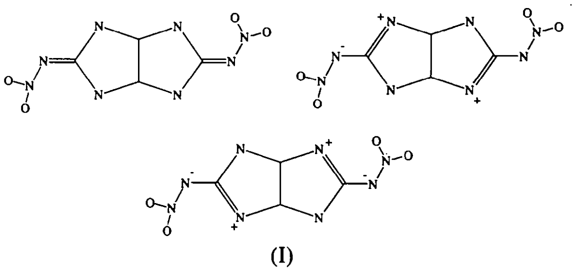
Abstract

The title compound, $C_4H_6N_8O_4$, has a calculated crystal density of 1.84 Mg m^{-3}. It lies on a crystallographic twofold axis passing through the midpoint of the C4—C4^i bond [symmetry code: (i) $-x, -y, z$]. The five-membered ring has a flattened envelope conformation with C4 lying 0.17 Å out of the plane of the other four atoms. The geometry at one of the ring N atoms (N1) is planar and that at the other (N3) is slightly pyramidal. There is a *cis* junction between the fused five-membered rings (H—C—C—H = −13.1°) with a dihedral angle of 62.7° between the ring planes. The hydrogen-bonding system contains one intra-intermolecular bifurcated bond and one linear intermolecular bond.

Comment

The title compound, (I), is a nitramine explosive with unusually high thermal stability since it decomposes without melting at 599 K (Kony & Dagley, 1994). The predicted density for this compound (assuming all the N—H protons are hydrogen bonded) is 1.84 Mg m^{-3} (Cichra, Holden & Dickinson, 1980), which is in agreement with the calculated crystal density.



(I)

This X-ray structure analysis (Fig. 1) was performed to compare the structural features of (I) with those found for other energetic molecules containing N—H bonds and nitro groups. The bond lengths around C2 indicate that the double bond is delocalized, giving rise to three possible resonance forms (shown above). The X-ray results show that for (I) there are three unique N—H···O hydrogen bonds. H1 is the donor in a bifurcated bond, comprising an intramolecular bond to O2*B* and an intermolecular bond to O2*A*′ (N1—H1 = 0.940, N1···O2*B* = 2.621, H1···O2*B* = 2.075, N1···O2*A*′ = 2.863, H1···O2*A*′ = 2.015 Å, N1—H1···O2*B* = 115.4, N1—H1···O2*A*′ = 149.1 and O2*B*···H1···O2*A*′ = 88.4°), while H3 is the donor atom in a single linear intermolecular hydrogen bond to a second symmetry-related O2*A* (N3—H3 = 0.927, N3···O2*A*″ = 2.899, H3···O2*A*″ = 1.975 Å and N3—H3···O2*A*″ = 174.6°). In all, each molecule participates in ten hydrogen bonds which link it to eight neighboring molecules (Fig. 2).

2-Nitroiminoimidazolidine, the monocyclic analogue of (I) (Nordenson, 1981) shows a similar pattern of intra- and intermolecular hydrogen bonding. However, it differs from this structure in that the linear bond is an N—H···N interaction rather than an N—H···O interaction and, as a result, one of the two nitro O atoms does not participate in any hydrogen bonds. Similar hydrogen bonding was also found in the high-melting compounds nitroguanidine (Bryden, Burkardt, Hughes

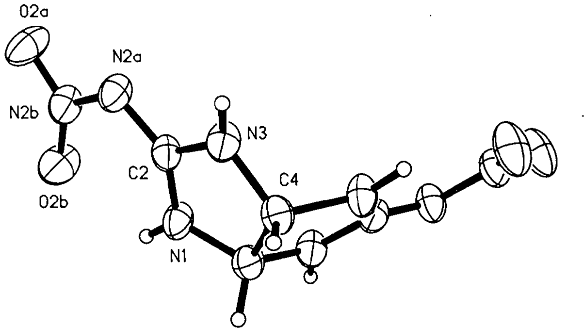


Fig. 1. Structure of (I) showing 20% probability displacement ellipsoids.

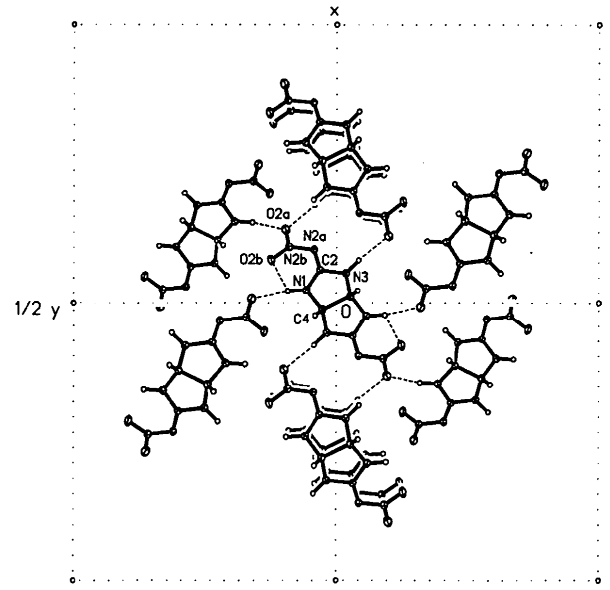


Fig. 2. Packing diagram for (I). The molecules are shown looking down the c axis surrounded by the nearest neighbors with which it forms hydrogen bonds.

& Donohue, 1956; Choi, 1981) and 1,3,5-triamino-2,4,6-trinitrobenzene (Cady & Larson, 1965), as well as in 2,4,6-trinitrophenylhydrazine (Flippen-Anderson & Dudis, 1989) and in several *para*-nitroanilines reported by Butcher, Gilardi, Flippen-Anderson & George (1992).

Experimental

The compound was prepared from the hydrochloride salt of octahydro-5-imino-2-nitroiminoimidazo[4,5-*d*]imidazole using the nitration procedure of Kony & Dagley (1994).

Crystal data

$C_4H_6N_8O_4$
$M_r = 230.17$
Orthorhombic
$Fdd2$
$a = 14.402$ (2) Å
$b = 27.795$ (4) Å
$c = 4.152$ (1) Å
$V = 1662.1$ (5) Å^3
$Z = 8$
$D_x = 1.840$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.54178$ Å
Cell parameters from 25 reflections
$\theta = 32.85\text{-}42.25°$
$\mu = 1.37$ mm^{-1}
$T = 295$ (2) K
Rod
0.60 × 0.22 × 0.22 mm
Colorless

Data collection

Siemens $R3m/V$ four-circle diffractometer
Wykoff scans
Absorption correction: none
398 measured reflections
380 independent reflections
363 observed reflections [$I > 2\sigma(I)$]
$R_{\text{int}} = 0.0129$

$\theta_{\text{max}} = 62.48°$
$h = 0 \rightarrow 16$
$k = 0 \rightarrow 31$
$l = 0 \rightarrow 4$
3 standard reflections monitored every 97 reflections
intensity variation: constant during data collection

Refinement

Refinement on F^2
$R(F) = 0.0455$
$wR(F^2) = 0.1279$
$S = 1.147$
380 reflections
83 parameters
Only coordinates of H atoms refined
Calculated weights
$w = 1/[\sigma^2(F_o^2) + (0.0948P)^2 + 1.2707P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = 0.015$
$\Delta\rho_{\text{max}} = 0.234$ e Å^{-3}
$\Delta\rho_{\text{min}} = -0.228$ e Å^{-3}
Extinction correction: *SHELXL* (Sheldrick, 1994)
Extinction coefficient: 0.0031 (7)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2, 6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\text{eq}} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
N1	0.0458 (2)	0.0558 (1)	0.6473 (11)	0.037 (1)
C2	0.1161 (2)	0.0298 (1)	0.5277 (12)	0.032 (1)
N2*A*	0.1892 (2)	0.0416 (1)	0.3456 (10)	0.038 (1)
N2*B*	0.2001 (2)	0.0883 (1)	0.2734 (11)	0.040 (1)
O2*A*	0.2642 (2)	0.0962 (1)	0.0754 (11)	0.055 (1)
O2*B*	0.1523 (2)	0.1212 (1)	0.3840 (12)	0.056 (1)
N3	0.1047 (2)	−0.0170 (1)	0.5934 (10)	0.037 (1)
C4	0.0235 (3)	−0.0251 (1)	0.7968 (12)	0.034 (1)

Table 2. *Selected geometric parameters* (Å, °)

N1—C2	1.336 (5)	N2*B*—O2*B*	1.234 (4)
N1—C4$^{\text{i}}$	1.451 (5)	N2*B*—O2*A*	1.255 (5)
C2—N2*A*	1.337 (5)	N3—C4	1.459 (5)
C2—N3	1.342 (5)	C4—C4$^{\text{i}}$	1.553 (8)
N2*A*—N2*B*	1.342 (5)		
C2—N1—C4$^{\text{i}}$	111.4 (3)	O2*B*—N2*B*—N2*A*	124.7 (4)
N1—C2—N2*A*	132.5 (4)	O2*A*—N2*B*—N2*A*	113.6 (3)
N1—C2—N3	110.7 (3)	C2—N3—C4	111.4 (3)
N2*A*—C2—N3	116.6 (3)	N1$^{\text{i}}$—C4—N3	113.2 (4)
C2—N2*A*—N2*B*	117.0 (3)	N1$^{\text{i}}$—C4—C4$^{\text{i}}$	103.1 (3)
O2*B*—N2*B*—O2*A*	121.6 (3)	N3—C4—C4$^{\text{i}}$	102.2 (3)

Symmetry code: (i) $-x, -y, z$.

Data collection, cell refinement, data reduction, structure solution and molecular graphics: *SHELXTL-Plus* (Sheldrick, 1992). Structure refinement and software used to prepare material for publication: *SHELXL* (Sheldrick, 1994).

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: BK1017). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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2,2′-Dimethoxybibenzyl

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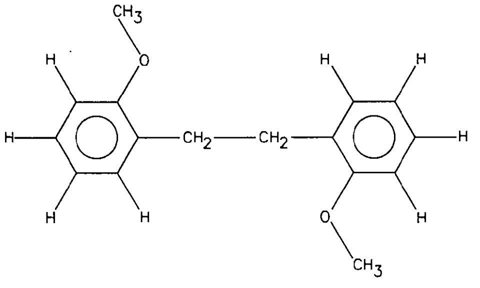
Abstract

The 2′,2′-dimethoxybibenzyl molecule, $C_{16}H_{18}O_2$, has the midpoint of the —CH_2—CH_2— bond on an inversion centre. Each benzene ring deviates slightly from planarity, shows marked angular distortion and is inclined at 81.5 (1)° to the plane of the C(Ar)—CH_2—CH_2— moiety.

Comment

There are only two structures similar to that of the title compound, (I), in the Cambridge Structural Database (1993): dibenzyl (Cruickshank, 1949) and 4,4′-dimethylbibenzyl (Brown, 1954). The structures are similar in that, in each case, the centre of the molecule coincides with a crystallographic centre of symmetry. Both structures have large *R* factors (15% and 18%, respectively) so that no real comparison with bond lengths and angles can be made, except to say that the current structural details are in broad agreement with those found from the earlier studies.



(I)

The benzene ring is not planar at a 3σ level, the deviations of some of the ring atoms from the ring mean plane being as large as 6σ. The ring also shows a range of angle values which reflect angular distortion due to the ring substituents (Domenicano & Hargittai, 1992). Initially, we were surprised to find a value of 115.28 (10)° for the angle C1—C2—O2, but a search of the April 1993 release of the Cambridge Structural Database for the *o*-$C_6H_4(OMe)CH_2$ fragment yielded ten 'hits' for which the mean value of the C—C—O angle was 115.2° (range 112.0–118.8°). Similarly, the mean values of the torsion angles CH_2—C—C—O and C—C—O—CH_3 are 1.7 and 172.6°, respectively. It would appear that the geometry reported here for the title molecule is entirely in accord with that reported in all previous examples.

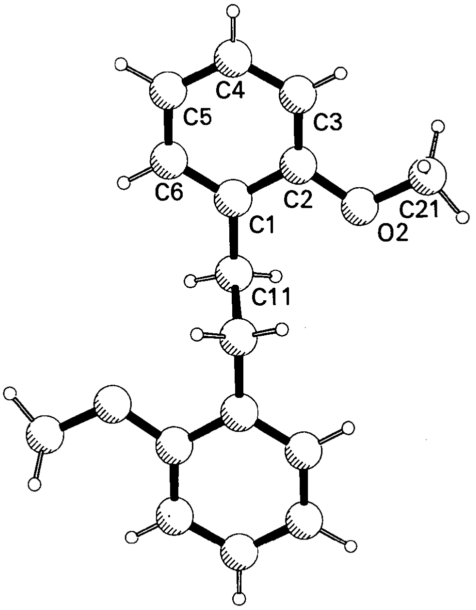


Fig. 1. View of the title molecule.

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