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Exceeding the oxygen content of liquid oxygen: bis(2,2,2-trinitroethyl) carbonate

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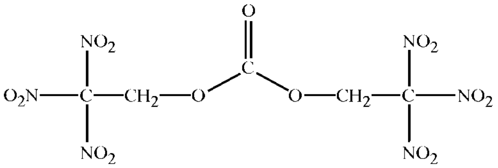
Bis(2,2,2-trinitroethyl) carbonate, $C_5H_4N_6O_{15}$, is an oxygen-rich compound (61.83% of molecular weight) of interest with respect to energetic materials. The molecule adopts an *s–cis–s–cis* conformation of the carbonate group. Intra- as well as intermolecular C—H···O and dipolar nitro-group interactions account for its exceptionally high density of 1.975 Mg m^{-3}. As a consequence of the relationship between structure and crystal density, this polymorph contains available oxygen in amounts even superior to liquid oxygen.

Comment

To date, many new polynitro aliphatic compounds have been discovered. These compounds, which often are derivatives of trinitromethane, contain available oxygen in amounts never before attained in solid explosive compounds. We are determining the structures of a number of high-crystal-density polynitro compounds as a preliminary step in an investigation of the relationships between structure and crystal density in energetic substances. Density is a critical parameter in the prediction of explosive performance parameters, such as velocity of detonation or detonation pressure.

The structure of the valuable compound bis(2,2,2-trinitroethyl) carbonate, (I), in the solid state has not previously been investigated. We have found that (I) at 100 K has an exceptionally high density of 1.975 Mg m^{-3}, which is significantly higher than the reported value of 1.88 Mg m^{-3} (Hill, 1956). The asymmetric unit of (I) (Fig. 1) consists of one bis(2,2,2-trinitroethyl) carbonate molecule. The geometry in both trinitroethyl groups is very similar, with a propeller-type orientation of the nitro groups (C_3) bonded to the β-C atoms, the conformation of the substituents of the α- and β-C atoms being staggered. The bond lengths of the trinitroethyl units show unusual values in that the C—N bonds joining the three nitro groups to the β-C atom (Table 1) are significantly longer than the normal C—N bond distance of 1.47 Å (Shannon, 1976); the N—C—N bond angles are smaller than the tetrahedral value, whereas the corresponding N—C—C angles are greater (Table 1), as was similarly observed in the structure determinations of bis(2,2,2-trinitroethyl)urea (Lind, 1970) and 2,2,2-trinitroethanol (Göbel & Klapötke, 2007).



(I)

Early investigations into the structural properties of (I) using IR spectroscopy (Hall, 1968) could not settle the question of the molecular geometry adopted by the carbonate, *s–cis–s–cis*, *s–cis–s–trans* or *s–trans–s–trans* conformations all being possible for organic carbonates. Short intramolecular C—H···O contacts are present (Table 2), associated with the *s–cis–s–cis* conformation. The bond lengths and angles of the carbonate unit (Table 1) may be considered normal in comparison with the Cambridge Structural Database results (Allen, 2002). The extended structure of (I) involves intermolecular C—H···O hydrogen bonding (Table 2). The resulting bifurcated hydrogen bonding is displayed in Fig. 2.

Short intermolecular O···O distances with values substantially less than 3.04 Å, *i.e.* the sum of the van der Waals radii for O (1.52 Å; Bondi, 1964), are observed as a consequence of noncovalent dipolar nitro-group interactions. Dipolar nitro-group interactions were accepted for N···O contacts shorter than 3.17 Å. This value was chosen as the sum of the van der Waals radii of nitrogen and oxygen (Bondi, 1964) plus a tolerance value of 0.1 Å. Given these values, three dipolar nitro-group contacts were identified. These interactions were found for the N1/O4/O5 nitro group interacting with the N6/O14/O15 nitro group, for N2/O6/O7 interacting with N3/O8/O9, and finally for N6/O14/O15 interacting with N4/O10/O11 and N5/O12/O13, leading to O···O distances of 2.8317 (11) [O4···O7^{ii}; symmetry code: (ii) $-x + \frac{3}{2}$, $y - \frac{1}{2}$, z], 2.8626 (12) [O5···O14^{iii}; symmetry code: (iii) $-x + \frac{3}{2}$, $-y$, $z - \frac{1}{2}$] and

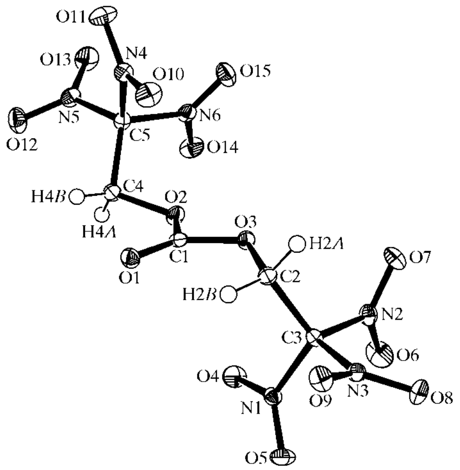


Figure 1
The asymmetric unit of (I), together with the atomic numbering scheme. Displacement ellipsoids are shown at the 50% probability level.

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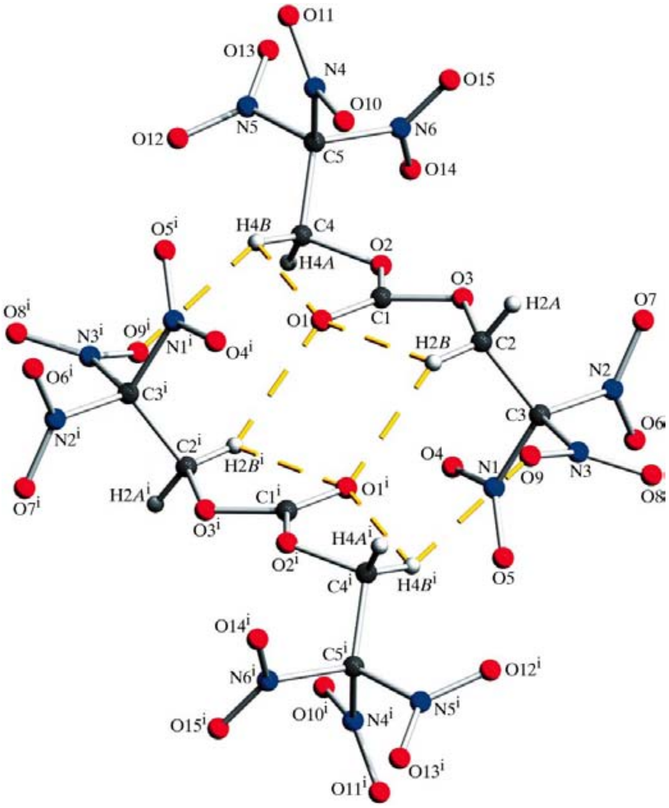

Figure 2
A centrosymmetric dimer containing two bis(2,2,2-trinitroethyl) carbonate molecules. The bifurcated hydrogen bonding is indicated by dashed lines. [Symmetry code: (i) $-x + 1$, $-y$, $-z + 1$.]

2.8381 (12) Å [O14$\cdots$O12^{iv}; symmetry code: (iv) $x + \frac{1}{2}$, y, $-z + \frac{3}{2}$], respectively. The corresponding values for the N$\cdots$O contacts are 3.0125 (11) (O4$\cdots$N3^{ii}), 2.9935 (12) (O5$\cdots$N6^{iii}) and 3.1045 (12) Å (O14$\cdots$N4^{iv}), respectively.

The high oxygen content of (I), together with the intermolecular contacts (dipolar nitro-group interactions and hydrogen bonding) yield a high-crystal-density polymorph that displays an oxygen content of 1.221 Mg m^{-3}, higher than the value of 1.140 Mg m^{-3} (Holleman, 1995) in liquid oxygen at 90 K.

Experimental

Caution: Bis(2,2,2-trinitroethyl) carbonate is an energetic material. Proper protective measures [safety glasses, face shields, leather coat, earthing (equipment and person), Kevlar gloves and ear protectors] should be used when handling this material. Bis(2,2,2-trinitroethyl) carbonate (Hill, 1956) was prepared from the reaction of trinitroethanol with phosgene (Hall, 1968). The crystal growth was accomplished by concentration of a saturated CHCl$_3$ solution at ambient temperature, yielding colourless single crystals.

Crystal data

$C_5H_4N_6O_{15}$
$M_r = 388.14$
Orthorhombic, *Pbca*
$a = 10.8828$ (2) Å
$b = 11.4746$ (2) Å
$c = 20.9073$ (4) Å
$V = 2610.81$ (8) Å^3
$Z = 8$
Mo $K\alpha$ radiation
$\mu = 0.20$ mm^{-1}
$T = 100$ (1) K
0.18 × 0.17 × 0.03 mm

Data collection

Oxford Diffraction Xcalibur3 CCD diffractometer
12846 measured reflections
3795 independent reflections
2765 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.025$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.027$
$wR(F^2) = 0.068$
$S = 0.99$
3795 reflections
251 parameters
All H-atom parameters refined
$\Delta\rho_{\rm max} = 0.38$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.24$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C1—O1	1.1915 (12)	C3—N1	1.5238 (13)
C1—O3	1.3399 (12)	C4—O2	1.4294 (13)
C1—O2	1.3451 (12)	C5—N5	1.5131 (13)
C2—O3	1.4255 (12)	C5—N4	1.5262 (14)
C3—N3	1.5201 (13)	C5—N6	1.5271 (13)
C3—N2	1.5214 (13)		
O1—C1—O3	127.57 (10)	N5—C5—C4	112.25 (8)
O1—C1—O2	126.98 (9)	N5—C5—N4	107.55 (8)
O3—C1—O2	105.46 (8)	C4—C5—N4	113.26 (8)
C2—C3—N3	110.72 (8)	N5—C5—N6	107.57 (8)
C2—C3—N2	112.73 (8)	C4—C5—N6	109.88 (8)
N3—C3—N2	107.22 (8)	N4—C5—N6	105.99 (8)
C2—C3—N1	113.01 (8)	C1—O2—C4	116.48 (8)
N3—C3—N1	106.17 (8)	C1—O3—C2	116.39 (8)
N2—C3—N1	106.59 (8)		
O1—C1—O2—C4	17.35 (15)	O1—C1—O3—C2	9.22 (15)
O3—C1—O2—C4	−162.59 (8)	O2—C1—O3—C2	−170.84 (8)
C5—C4—O2—C1	118.99 (9)	C3—C2—O3—C1	117.22 (9)

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

D—H$\cdots$$A$	D—H	H$\cdots$$A$	$D\cdots A$	D—H$\cdots$$A$
C2—H2$B\cdots$O1^{i}	0.923 (13)	2.448 (12)	3.2598 (13)	146.7 (10)
C4—H4$B\cdots$O9^{i}	0.966 (13)	2.651 (13)	3.4532 (13)	140.7 (9)
C4—H4$B\cdots$O1	0.966 (13)	2.359 (12)	2.7392 (13)	102.8 (8)
C2—H2$B\cdots$O1	0.923 (13)	2.330 (12)	2.7261 (13)	105.5 (8)

Symmetry code: (i) $-x + 1$, $-y$, $-z + 1$.

H atoms were directly located in difference maps and then refined freely, giving a range of C—H distances of 0.923 (13)–0.966 (13) Å.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2006); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *DIAMOND* (Brandenburg & Putz, 2005); software used to prepare material for publication: *PLATON* (Spek, 2003), *SHELXL97*, *ORTEP-3*, *DIAMOND* and *publCIF* (Westrip, 2008).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3179). Services for accessing these data are described at the back of the journal.

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