organic compounds

2,2,2-Trinitroethanol

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2,2,2-Trinitroethanol, $C_2H_3N_3O_7$, at 100 (2) K has $Z' = 2$ in the space group $P2_1/c$. The structure displays intramolecular O—H···O hydrogen bonds, as well as intermolecular O—H···O and C—H···O hydrogen bonding; the O—H···O hydrogen bonds, forming $R_4^4(8)$ rings, and dipolar nitro–nitro interactions account for the high density of 1.839 Mg m^{-3}.

Comment

2,2,2-Trinitroethanol, (I), with three nitro groups bonded to the same C atom, is a valuable intermediate in the preparation of energetic materials. However, the structure of (I) in the solid state has not been investigated. Only a hypothesis about the intra- and intermolecular hydrogen bonding, based on IR spectroscopy data, has been made (Ungnade & Kissinger, 1963). Our X-ray investigation shows intra- and intermolecular O—H···O hydrogen bonding, as well as nonclassical C—H···O hydrogen bonding.

$$(O_2N)_3C—CH_2OH$$
$$(I)$$
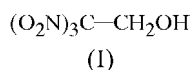
The asymmetric unit of (I) (Fig. 1) consists of two crystallographically independent trinitroethanol molecules. These two molecules display a very similar molecular geometry with a propeller-type orientation of the nitro groups (D_3) bonded to the β-C atom. In both molecules, the conformation of the substituents of the α- and β-C atoms is found to be staggered, and intramolecular O—H···O hydrogen bonding does occur (O1—H1···O3 and O8—H8···O13). The C—N bonds joining the three nitro groups to the β-C atom [range 1.5150 (18)–1.5197 (18) Å; Table 1] are significantly longer than the normal C—N bond distance of 1.47 Å (Shannon, 1976), as was observed previously in the determination of the crystal structure of N,N'-bis(β,β,β-trinitroethyl)urea (Lind, 1970). A comparison of the geometrical trends for the bonding of the three nitro groups to one C atom in (I) with those in N,N'-bis(β,β,β-trinitroethyl)urea reported by Lind again shows good agreement, taking into account that the measurement of Lind was undertaken at 296 K, whereas our experiment was run at 100 K. The independent N—C—N angles are smaller [range 105.90 (10)–108.43 (10)°] than the tetrahedral value,

whereas the corresponding N—C—C angles are greater [range 110.18 (11)–113.42 (12)°] than the tetrahedral value. The three independent nitro groups of each molecule are identical in structure within the limits of error and display common N—O distances [range 1.2079 (18)–1.2181 (18) Å], O—N—O angles [range 126.96 (14)–127.91 (15)°] and O—N—C angles [range 113.63 (12)–118.64 (12)°]. In turn, the arrangement of the C—N and N—O bonds is coplanar, the sum of the three bond angles around one N atom being 360° within the limits of error.

The extended structure of (I) involves secondary interactions in terms of intermolecular O—H···O hydrogen bonding, intermolecular C—H···O hydrogen bonding and dipolar nitro-group interactions. Circular O—H···O hydrogen bonding between the hydroxyl groups of four trinitroethanol molecules results in four-membered homodromic rings (O1—H1···O8—H8···O1^i—H1^i···O8^i—H8^i; symmetry code as in Table 2). The structure that can be observed along the crystallographic a axis shows a stacking of these rings. Every ring is surrounded by four neighbouring rings, whereby two of the four molecules of trinitroethanol that form such a ring inter-
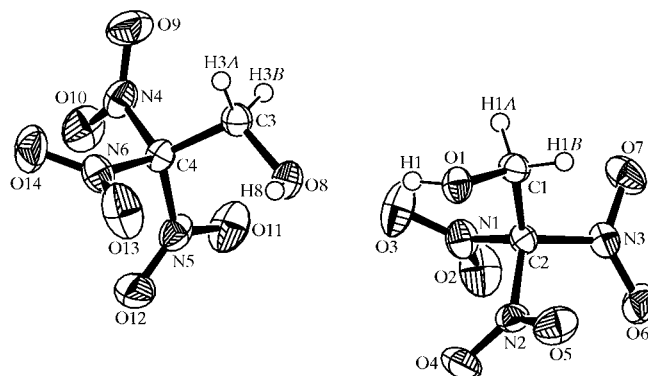

Figure 1
The asymmetric unit of trinitroethanol, together with the atom-numbering scheme. Displacement ellipsoids are shown at the 50% probability level.
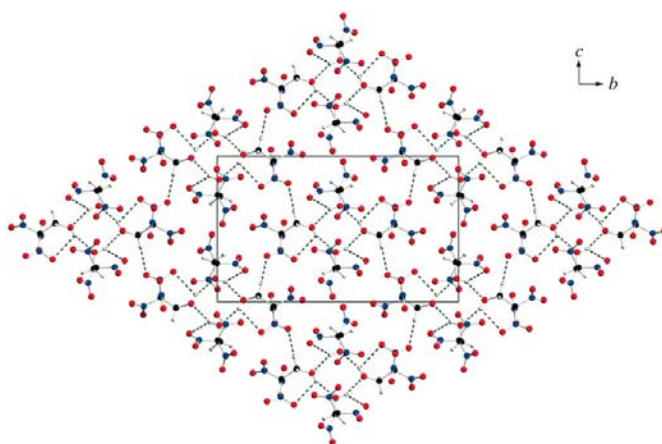

Figure 2
A representation of the structure of trinitroethanol, viewed along the a axis. Hydrogen bonding is indicated by dashed lines.

connect the central ring to the surrounding rings *via* C3—H3*B*···O14^{ii} hydrogen bonding (Table 2 and Fig. 2). The close approach of O atoms found in the extended structure of (I) suggests the possibility of dipolar nitro-group interactions, in analogy to a variety of noncovalent interactions, such as halogen···O$_{nitro}$ (Allen *et al.*, 1997), halogen···O=C (Lommerse *et al.*, 1996) and carbonyl interactions (Allen *et al.*, 1998). Short intermolecular O···O distances with values substantially less than 3.04 Å, the sum of the van der Waals radii for O (1.52 Å; Bondi, 1964), were investigated to that effect. Dipolar nitro-group interactions were accepted for N···O contacts shorter than 3.17 Å. The value of 3.17 Å 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, two dipolar nitro-group contacts were identified. Those two interactions were found for the N2/O4/O5 nitro group interacting with the N5/O11/O12 nitro group in one case and with itself in the other, leading to O···O distances of 2.8519 (18) [O5^{iii}···O12; symmetry code: (iii) −*x* + 1, −*y* + 1, −*z* + 1] and 2.8251 (15) Å (O4···O4^{iii}). The corresponding values for the N···O contacts are 3.1184 (17) (O5···N5^{iii}) and 3.1234 (16) Å (O4···N2^{iii}). Fig. 3 displays the symmetric interaction of the two N2/O4/O5 nitro groups.
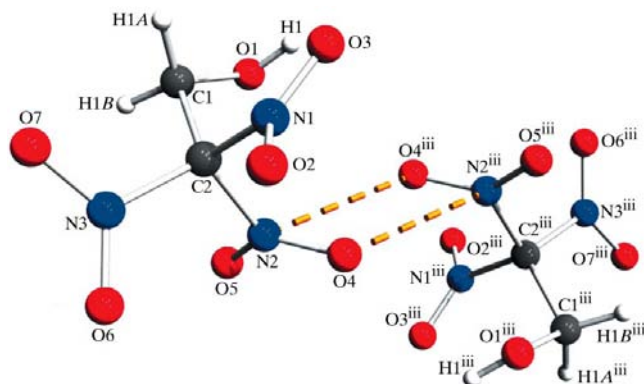

Figure 3
The interaction of the N2 and O4 atoms [O···N^{iii} = 3.1234 (16) Å] obviously brings the O atoms into close proximity [O4···O4^{iii} = 2.8251 (15) Å]. [Symmetry code: (iii) −*x* + 1, −*y* + 1, −*z* + 1.]

Experimental

Caution: Trinitroethanol 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. Trinitroethanol (Marans & Zelinski, 1950) was prepared from the reaction of trinitromethane with formaldehyde (Feuer & Kucera, 1960). Multinuclear NMR spectroscopy data confirm the structure of the compound. ^{1}H NMR (acetone-d_6): δ 5.17 (2H, *d*, ^3J = 5.6 Hz), 6.32 (1H, *t*, ^3J = 5.6 Hz); ^{13}C NMR (acetone-d_6): δ 63.1 (*d*, –CH$_2$), 127.5 [*bs*, –C(NO$_2$)$_3$]; ^{14}N NMR (acetone-d_6, nitromethane): δ −30.8 (–NO$_2$). The crystal growth was accomplished by sublimation of the solid at 298 K applying static low pressure (0.1 mbar), yielding colourless single crystals of rectangular habit.

Crystal data

C$_2$H$_3$N$_3$O$_7$	V = 1308.14 (11) Å^3
M_r = 181.07	Z = 8
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
a = 6.1242 (4) Å	μ = 0.19 mm^{-1}
b = 18.8223 (7) Å	T = 100 (2) K
c = 11.7466 (4) Å	0.44 × 0.19 × 0.10 mm
β = 104.962 (3)°	

Data collection

Oxford Diffraction Xcalibur3 CCD diffractometer	2566 independent reflections
	2345 reflections with $I > 2\sigma(I)$
13153 measured reflections	R_{int} = 0.030

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.037	241 parameters
$wR(F^2)$ = 0.092	All H-atom parameters refined
S = 1.13	$\Delta\rho_{max}$ = 0.21 e Å^{-3}
2566 reflections	$\Delta\rho_{min}$ = −0.18 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C2—N1	1.5197 (18)	N2—O5	1.2141 (17)
C2—N2	1.5155 (17)	N3—O6	1.2094 (17)
C2—N3	1.5159 (17)	N3—O7	1.2168 (16)
C4—N4	1.5177 (18)	N4—O9	1.2103 (18)
C4—N5	1.5188 (19)	N4—O10	1.2181 (18)
C4—N6	1.5150 (18)	N5—O11	1.2128 (18)
N1—O2	1.2094 (18)	N5—O12	1.2093 (19)
N1—O3	1.2130 (18)	N6—O13	1.2113 (18)
N2—O4	1.2107 (16)	N6—O14	1.2079 (18)
N1—C2—N2	106.24 (11)	O9—N4—O10	127.04 (14)
N1—C2—N3	105.90 (10)	O11—N5—O12	127.91 (15)
N2—C2—N3	108.43 (10)	O13—N6—O14	126.96 (14)
N4—C4—N5	105.94 (11)	O2—N1—C2	117.80 (13)
N4—C4—N6	106.44 (11)	O3—N1—C2	115.20 (12)
N5—C4—N6	107.81 (11)	O4—N2—C2	117.80 (12)
N1—C2—C1	113.42 (12)	O5—N2—C2	114.40 (12)
N2—C2—C1	110.18 (11)	O6—N3—C2	118.64 (12)
N3—C2—C1	112.35 (11)	O7—N3—C2	113.63 (12)
N4—C4—C3	111.98 (12)	O9—N4—C4	115.51 (13)
N5—C4—C3	112.24 (11)	O10—N4—C4	117.45 (13)
N6—C4—C3	112.04 (11)	O11—N5—C4	113.80 (13)
O2—N1—O3	126.98 (14)	O12—N5—C4	118.27 (13)
O4—N2—O5	127.78 (13)	O13—N6—C4	115.13 (13)
O6—N3—O7	127.73 (13)	O14—N6—C4	117.90 (13)

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O3	0.81 (2)	2.55 (2)	2.9948 (17)	116.2 (16)
O1—H1···O8	0.81 (2)	2.11 (2)	2.8431 (15)	150.2 (19)
O8—H8···O13	0.804 (18)	2.572 (17)	2.9444 (17)	109.9 (14)
O8—H8···O1^i	0.804 (18)	2.089 (19)	2.8512 (15)	158.3 (16)
C3—H3*B*···O14^{ii}	0.953 (17)	2.385 (17)	3.3304 (19)	171.0 (13)

Symmetry codes: (i) −*x* + 2, −*y* + 1, −*z* + 1; (ii) *x*, −*y* + $\frac{1}{2}$, *z* + $\frac{1}{2}$.

H atoms were directly located in the crystallographic study using difference Fourier maps. All H-atom parameters were then refined, giving O—H distances of 0.804 (18) and 0.81 (2) Å, and C—H distances in the range 0.942 (18)–0.981 (17) 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*

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(Farrugia, 1997) and *DIAMOND* (Brandenburg & Putz, 2005); software used to prepare material for publication: *PLATON* (Spek, 2003), *SHELXL97*, *ORTEP-3*, *DIAMOND* and *publCIF* (Westrip, 2007).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3132). Services for accessing these data are described at the back of the journal.

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