

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

Bis(2,2-dinitropropyl)formal

 Fei Liu,^a Huajun Dai,^a Zhong Huang,^b Yonggang Liu^b and Xingming Kou^{a*}
^aCollege of Chemistry, Sichuan University, Chengdu 610064, People's Republic of China, and ^bChina Academy of Engineering Physics, Mianyang 621900, People's Republic of China

Correspondence e-mail: kouxm@scu.edu.cn

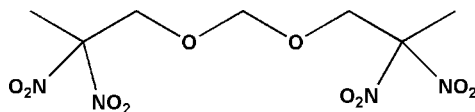
Received 11 March 2009; accepted 23 March 2009

 Key indicators: single-crystal X-ray study; $T = 291$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.046; wR factor = 0.138; data-to-parameter ratio = 12.8.

The complete molecule of the title compound [systematic name: bis(2,2-dinitropropoxy)methane], $\text{C}_7\text{H}_{12}\text{N}_4\text{O}_{10}$, which was synthesized by the condensation reaction between 2,2-dinitropropanol and paraformaldehyde in methylene chloride, is generated by crystallographic twofold symmetry with one C atom lying on the rotation axis. In the crystal structure, molecules are linked into chains running parallel to the b axis by intermolecular $\text{C}-\text{H}\cdots\text{O}$ hydrogen-bond interactions, generating rings of graph-set motif $R_2^2(14)$.

Related literature

For the applications and chemistry of the title compound, see: Garver *et al.* (1985); Hamilton & Wardle (1995); Adolph (1991); Hamilton & Wardle (1997). For graph-set motifs, see: Bernstein (1995).



Experimental

Crystal data

 $\text{C}_7\text{H}_{12}\text{N}_4\text{O}_{10}$
 $M_r = 312.21$

 Monoclinic, $C2/c$
 $a = 23.330$ (3) Å

 $b = 6.207$ (3) Å

 $c = 10.009$ (6) Å

 $\beta = 109.60$ (3)°

 $V = 1365.6$ (11) Å³
 $Z = 4$

 Mo $K\alpha$ radiation

 $\mu = 0.14$ mm⁻¹
 $T = 291$ K

 $0.48 \times 0.44 \times 0.28$ mm

Data collection

Enraf–Nonius CAD-4

diffractometer

Absorption correction: none

1404 measured reflections

1255 independent reflections

 863 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.008$

3 standard reflections

every 100 reflections

intensity decay: 1.5%

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.046$
 $wR(F^2) = 0.138$
 $S = 1.09$

1255 reflections

98 parameters

H-atom parameters constrained

 $\Delta\rho_{\text{max}} = 0.18$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.17$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{C1}-\text{H1A}\cdots\text{O4}^{\text{i}}$	0.97	2.59	3.509 (3)	158
$\text{C1}-\text{H1B}\cdots\text{O4}^{\text{ii}}$	0.97	2.59	3.509 (3)	158

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

Data collection: *DIFRAC* (Gabe & White, 1993); cell refinement: *DIFRAC*; data reduction: *NRCVAX* (Gabe *et al.*, 1989); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

The authors thank Mr Zhi-Hua Mao of Sichuan University for the X-ray data collection.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: RZ2302).

References

- Adolph, H. G. (1991). US Patent No. 4 997 499.
 Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
 Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
 Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.
 Gabe, E. J. & White, P. S. (1993). *DIFRAC*. American Crystallographic Association, Pittsburgh meeting. Abstract PA 104.
 Garver, L. C., Grakauskas, V. & Baum, K. (1985). *J. Org. Chem.* **50**, 1699–1702.
 Hamilton, R. S. & Wardle, R. B. (1995). US Patent No. 5 449 835.
 Hamilton, R. S. & Wardle, R. B. (1997). US Patent No. 5 648 556.
 Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.

supporting information

Acta Cryst. (2009). E65, o903 [doi:10.1107/S1600536809010642]

Bis(2,2-dinitropropyl)formal

Fei Liu, Huajun Dai, Zhong Huang, Yonggang Liu and Xingming Kou

S1. Comment

The title compound is an important energetic material used in propellant and explosive formulations (Garver *et al.* 1985; Hamilton & Wardle, 1995). It was also combined with liquid bis(2,2-dinitropropyl)acetal (BDNPA) to prepare the BDNPF/A energetic plasticizer (Adolph, 1991; Hamilton & Wardle, 1997). Here we report the crystal structure of the title compound.

The molecule of the title compound (Fig. 1), has crystallographically imposed two-fold symmetry. The average of N—O bond length is 1.204 (3) Å. The dihedral angle formed by the planes through the nitro group is 74.3 (2)°. The O(1)—C(2)—C(3)—N(1), O(5)—N(2)—C(3)—C(4) and O(4)—N(2)—C(3)—C(4) torsion angles are 172.59 (17), -176.2 (2) and 5.6 (3) ° respectively. In the crystal structure, the molecules are linked into chains running parallel to the *b* axis by intermolecular C—H···O hydrogen interactions (Table 1) generating rings of graph set motif $R^2_2(14)$.

S2. Experimental

The title compound was synthesized by reacting 2,2-dinitropropanol (6.0 g) with paraformaldehyde (0.6 g) in the presence of concentrated sulfuric acid as catalyst in methylene chloride below 5°C. Single crystals suitable for X-ray analysis were obtained by slow evaporation of a diethyl ether/mineral ether (1:6 v/v) solution.

S3. Refinement

All non-H atoms were refined with anisotropic atomic displacement parameters. All H atoms were positioned geometrically and refined using a riding model, with C—H = 0.96–0.97 Å and with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$ or $1.5 U_{\text{eq}}(\text{C})$ for methyl H atoms.

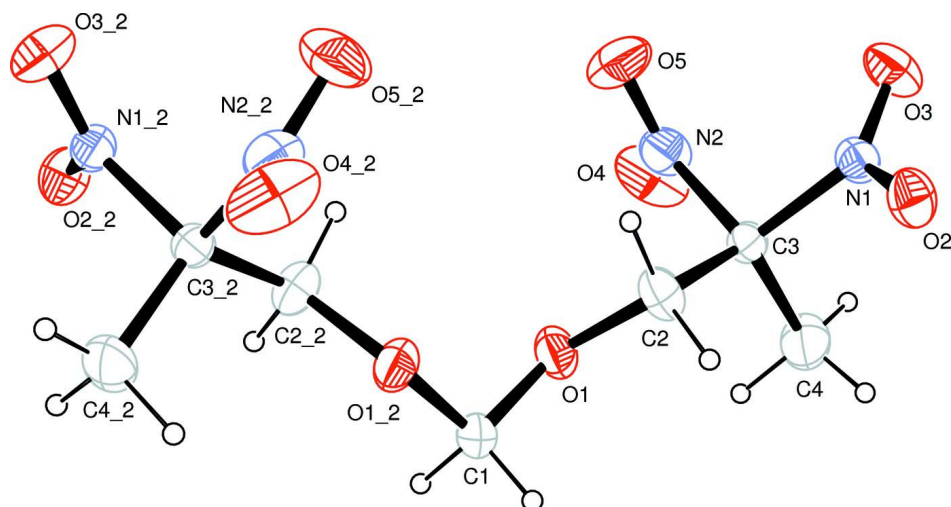


Figure 1

The molecular structure of the title compound, with displacement ellipsoids drawn at the 30% probability level. Atoms labelled with the suffix 2 are generated by the symmetry operator (1-x, y, 1/2-z).

Bis(2,2-dinitropropoxy)methane

Crystal data

$C_7H_{12}N_4O_{10}$
 $M_r = 312.21$
 Monoclinic, $C2/c$
 Hall symbol: -C 2yc
 $a = 23.330$ (3) Å
 $b = 6.207$ (3) Å
 $c = 10.009$ (6) Å
 $\beta = 109.60$ (3)°
 $V = 1365.6$ (11) Å³
 $Z = 4$

$F(000) = 648$
 $D_x = 1.519$ Mg m⁻³
 Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
 Cell parameters from 23 reflections
 $\theta = 5.2$ – 8.7 °
 $\mu = 0.14$ mm⁻¹
 $T = 291$ K
 Block, colourless
 $0.48 \times 0.44 \times 0.28$ mm

Data collection

Enraf–Nonius CAD-4
 diffractometer
 Radiation source: fine-focus sealed tube
 Graphite monochromator
 $\omega/2\theta$ scans
 1404 measured reflections
 1255 independent reflections
 863 reflections with $I > 2\sigma(I)$

$R_{int} = 0.008$
 $\theta_{max} = 25.5$ °, $\theta_{min} = 1.9$ °
 $h = -28 \rightarrow 20$
 $k = 0 \rightarrow 7$
 $l = -12 \rightarrow 12$
 3 standard reflections every 100 reflections
 intensity decay: 1.5%

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.046$
 $wR(F^2) = 0.138$
 $S = 1.09$
 1255 reflections
 98 parameters
 0 restraints

Primary atom site location: structure-invariant
 direct methods
 Secondary atom site location: difference Fourier
 map
 Hydrogen site location: inferred from
 neighbouring sites
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0654P)^2 + 0.7176P]$
 where $P = (F_o^2 + 2F_c^2)/3$

$$(\Delta/\sigma)_{\max} < 0.001$$

$$\Delta\rho_{\max} = 0.18 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.17 \text{ e } \text{\AA}^{-3}$$

Extinction correction: *SHELXL97* (Sheldrick, 2008), $F_c^* = kFc[1 + 0.001x Fc^2 \lambda^3 / \sin(2\theta)]^{-1/4}$
 Extinction coefficient: 0.032 (3)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
O1	0.54239 (7)	0.5416 (3)	0.21472 (18)	0.0661 (6)	
O2	0.68680 (8)	0.8202 (3)	0.51558 (17)	0.0706 (6)	
O3	0.70016 (9)	1.0217 (3)	0.3547 (2)	0.0854 (7)	
O4	0.60961 (13)	0.8225 (4)	0.0432 (2)	0.1153 (10)	
O5	0.57606 (12)	1.0244 (4)	0.1735 (3)	0.1154 (9)	
N1	0.67637 (8)	0.8730 (3)	0.3932 (2)	0.0538 (5)	
N2	0.60412 (11)	0.8729 (4)	0.1542 (2)	0.0702 (7)	
C1	0.5000	0.4161 (6)	0.2500	0.0721 (11)	
H1A	0.5211	0.3241	0.3297	0.087*	0.50
H1B	0.4789	0.3241	0.1703	0.087*	0.50
C2	0.58346 (10)	0.6513 (4)	0.3320 (2)	0.0619 (7)	
H2A	0.5991	0.5550	0.4124	0.074*	
H2B	0.5636	0.7721	0.3596	0.074*	
C3	0.63384 (9)	0.7279 (3)	0.2821 (2)	0.0470 (6)	
C4	0.67114 (13)	0.5524 (5)	0.2509 (4)	0.0887 (10)	
H4A	0.7000	0.6135	0.2122	0.133*	
H4B	0.6450	0.4542	0.1835	0.133*	
H4C	0.6924	0.4765	0.3368	0.133*	

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0497 (9)	0.0705 (11)	0.0702 (11)	-0.0102 (8)	0.0098 (8)	-0.0145 (8)
O2	0.0670 (11)	0.0859 (12)	0.0506 (10)	-0.0086 (9)	0.0086 (7)	-0.0062 (9)
O3	0.0912 (13)	0.0750 (13)	0.0901 (14)	-0.0353 (11)	0.0306 (11)	-0.0070 (10)
O4	0.179 (3)	0.1115 (18)	0.0553 (12)	-0.0540 (17)	0.0396 (14)	-0.0049 (12)
O5	0.1221 (19)	0.0748 (14)	0.127 (2)	0.0347 (14)	0.0122 (15)	0.0233 (13)
N1	0.0481 (10)	0.0533 (11)	0.0610 (12)	-0.0045 (9)	0.0193 (9)	-0.0076 (9)
N2	0.0834 (15)	0.0650 (14)	0.0552 (13)	-0.0133 (12)	0.0137 (11)	0.0046 (11)
C1	0.0401 (16)	0.0499 (18)	0.114 (3)	0.000	0.0094 (17)	0.000
C2	0.0580 (13)	0.0718 (15)	0.0523 (13)	-0.0174 (12)	0.0138 (10)	-0.0065 (11)
C3	0.0464 (11)	0.0457 (11)	0.0454 (11)	0.0006 (9)	0.0107 (9)	-0.0038 (9)

C4	0.0676 (16)	0.0807 (19)	0.108 (2)	0.0146 (14)	0.0159 (15)	-0.0383 (18)
----	-------------	-------------	-----------	-------------	-------------	--------------

Geometric parameters (Å, °)

O1—C1	1.394 (3)	C1—H1A	0.9700
O1—C2	1.416 (3)	C1—H1B	0.9700
O2—N1	1.211 (2)	C2—C3	1.500 (3)
O3—N1	1.205 (2)	C2—H2A	0.9700
O4—N2	1.202 (3)	C2—H2B	0.9700
O5—N2	1.198 (3)	C3—C4	1.491 (3)
N1—C3	1.514 (3)	C4—H4A	0.9600
N2—C3	1.528 (3)	C4—H4B	0.9600
C1—O1 ⁱ	1.394 (3)	C4—H4C	0.9600
C1—O1—C2	113.52 (16)	O1—C2—H2B	110.7
O3—N1—O2	124.98 (19)	C3—C2—H2B	110.7
O3—N1—C3	118.63 (19)	H2A—C2—H2B	108.8
O2—N1—C3	116.20 (18)	C4—C3—C2	114.6 (2)
O5—N2—O4	126.0 (3)	C4—C3—N1	107.70 (18)
O5—N2—C3	116.5 (2)	C2—C3—N1	109.75 (17)
O4—N2—C3	117.5 (2)	C4—C3—N2	112.8 (2)
O1—C1—O1 ⁱ	112.1 (3)	C2—C3—N2	106.23 (18)
O1—C1—H1A	109.2	N1—C3—N2	105.44 (18)
O1 ⁱ —C1—H1A	109.2	C3—C4—H4A	109.5
O1—C1—H1B	109.2	C3—C4—H4B	109.5
O1 ⁱ —C1—H1B	109.2	H4A—C4—H4B	109.5
H1A—C1—H1B	107.9	C3—C4—H4C	109.5
O1—C2—C3	105.36 (18)	H4A—C4—H4C	109.5
O1—C2—H2A	110.7	H4B—C4—H4C	109.5
C3—C2—H2A	110.7		
C2—O1—C1—O1 ⁱ	70.17 (16)	O3—N1—C3—N2	-31.8 (3)
C1—O1—C2—C3	165.8 (2)	O2—N1—C3—N2	152.91 (19)
O1—C2—C3—C4	-66.1 (3)	O5—N2—C3—C4	-176.2 (2)
O1—C2—C3—N1	172.59 (17)	O4—N2—C3—C4	5.6 (3)
O1—C2—C3—N2	59.1 (2)	O5—N2—C3—C2	57.6 (3)
O3—N1—C3—C4	88.8 (3)	O4—N2—C3—C2	-120.7 (2)
O2—N1—C3—C4	-86.4 (3)	O5—N2—C3—N1	-58.9 (3)
O3—N1—C3—C2	-145.9 (2)	O4—N2—C3—N1	122.9 (2)
O2—N1—C3—C2	38.9 (3)		

Symmetry code: (i) $-x+1, y, -z+1/2$.*Hydrogen-bond geometry (Å, °)*

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
C1—H1A \cdots O4 ⁱⁱ	0.97	2.59	3.509 (3)	158

C1—H1B···O4 ⁱⁱⁱ	0.97	2.59	3.509 (3)	158
----------------------------	------	------	-----------	-----

Symmetry codes: (ii) $x, -y+1, z+1/2$; (iii) $-x+1, -y+1, -z$.