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# Bis(2,2-dinitropropyl)formal

**Fei Liu,[a] Huajun Dai,[a] Zhong Huang,[b] Yonggang Liu[b] and Xingming Kou[a]***

[a]College of Chemistry, Sichuan University, Chengdu 610064, People's Republic of China, and [b]China Academy of Engineering Physics, Mianyang 621900, People's Republic of China
Correspondence e-mail: kouxm@scu.edu.cn

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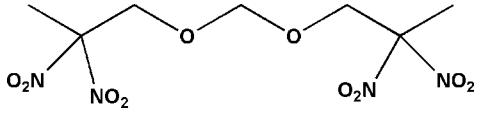
Key indicators: single-crystal X-ray study; $T$ = 291 K; mean $\sigma$(C–C) = 0.004 Å; $R$ factor = 0.046; $wR$ factor = 0.138; data-to-parameter ratio = 12.8.

The complete molecule of the title compound [systematic name: bis(2,2-dinitropropoxy)methane], $C_7H_{12}N_4O_{10}$, 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 C—H···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

$C_7H_{12}N_4O_{10}$
$M_r$ = 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) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 0.14 mm$^{-1}$
$T$ = 291 K
0.48 × 0.44 × 0.28 mm

### Data collection

Enraf–Nonius CAD-4 diffractometer
Absorption correction: none
1404 measured reflections
1255 independent reflections
863 reflections with $I > 2\sigma(I)$
$R_{int}$ = 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
$\Delta\rho_{max}$ = 0.18 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.17 e Å$^{-3}$

**Table 1**
Hydrogen-bond geometry (Å, °).

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| C1—H1$A$···O4$^{i}$ | 0.97 | 2.59 | 3.509 (3) | 158 |
| C1—H1$B$···O4$^{ii}$ | 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*.

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

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# supplementary materials

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# Bis(2,2-dinitropropyl)formal

**F. Liu, H. Dai, Z. Huang, Y. Liu and X. Kou**

## 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 $R^2_2(14)$.

## 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.

## 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 $U_{iso}$(H) = 1.2 $U_{eq}$(C) or 1.5 $U_{eq}$(C) for methyl H atoms.

## Figures

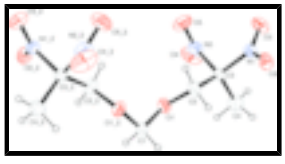


Fig. 1. The molecular structure of the title compound, with displacement ellipsoids drawn at the 30% probability level. Atoms labelled with the suffix 2 are generated by the symmetry operator (1-x, y, 1/2-z).

## Bis(2,2-dinitropropoxy)methane

*Crystal data*

| | |
|---|---|
| $C_7H_{12}N_4O_{10}$ | $F_{000}$ = 648 |
| $M_r$ = 312.21 | $D_x$ = 1.519 Mg m$^{-3}$ |
| Monoclinic, *C*2/*c* | Mo *K*α radiation<br>λ = 0.71073 Å |

| | |
|---|---|
| Hall symbol: -C 2yc | Cell parameters from 23 reflections |
| $a$ = 23.330 (3) Å | θ = 5.2–8.7º |
| $b$ = 6.207 (3) Å | μ = 0.14 $mm^{-1}$ |
| $c$ = 10.009 (6) Å | $T$ = 291 K |
| β = 109.60 (3)º | Block, colourless |
| $V$ = 1365.6 (11) $Å^3$ | 0.48 × 0.44 × 0.28 mm |
| $Z$ = 4 | |

*Data collection*

| | |
|---|---|
| Enraf–Nonius CAD-4 diffractometer | $R_{int}$ = 0.008 |
| Radiation source: fine-focus sealed tube | $\theta_{max}$ = 25.5º |
| Monochromator: graphite | $\theta_{min}$ = 1.9º |
| $T$ = 291 K | $h$ = −28→20 |
| ω/2θ scans | $k$ = 0→7 |
| Absorption correction: none | $l$ = −12→12 |
| 1404 measured reflections | 3 standard reflections |
| 1255 independent reflections | every 100 reflections |
| 863 reflections with $I > 2\sigma(I)$ | intensity decay: 1.5% |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Hydrogen site location: inferred from neighbouring sites |
| Least-squares matrix: full | H-atom parameters constrained |
| $R[F^2 > 2\sigma(F^2)]$ = 0.046 | $w = 1/[\sigma^2(F_o^2) + (0.0654P)^2 + 0.7176P]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| $wR(F^2)$ = 0.138 | $(\Delta/\sigma)_{max} < 0.001$ |
| $S$ = 1.09 | $\Delta\rho_{max}$ = 0.18 e $Å^{-3}$ |
| 1255 reflections | $\Delta\rho_{min}$ = −0.17 e $Å^{-3}$ |
| 98 parameters | Extinction correction: SHELXL97 (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$ |
| Primary atom site location: structure-invariant direct methods | Extinction coefficient: 0.032 (3) |
| Secondary atom site location: difference Fourier map | |

*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 (Å$^2$)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ | 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 (Å$^2$)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| 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) | | |

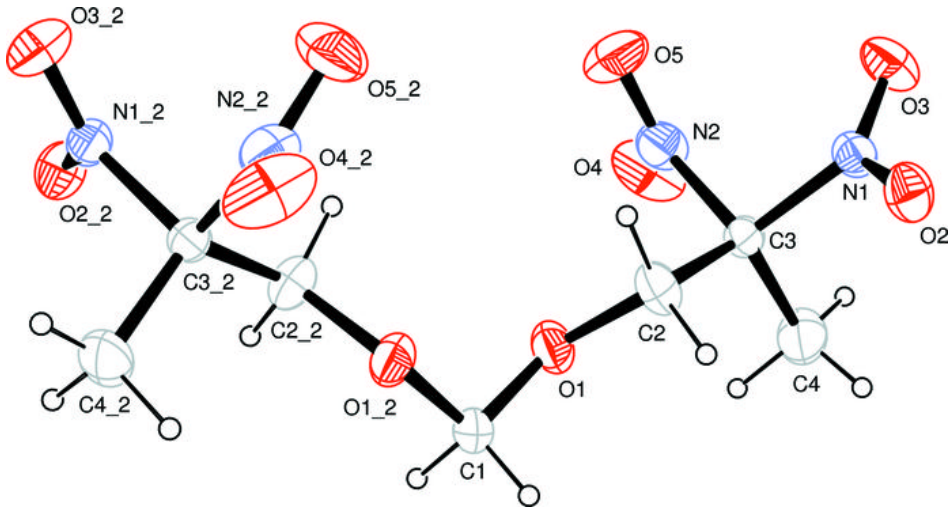
Symmetry codes: (i) −*x*+1, *y*, −*z*+1/2.

*Hydrogen-bond geometry (Å, °)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| C1—H1A···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*.

**Fig. 1**


O3_2
N1_2
N2_2
O5_2
O4_2
O2_2
C3_2
C2_2
C4_2
O1_2
C1
O1
C2
O5
N2
O4
O3
N1
O2
C3
C4