

Acta Crystallographica Section E

## Structure Reports

Online

ISSN 1600-5368

## (Methylenedinitrilo)tetraacetonitrile

Xiang-Hua Song, Mei-Li Feng, Kai Wang, Yu-Feng Li and Hong-Jun Zhu\*

Department of Applied Chemistry, College of Science, Nanjing University of Technology, Nanjing 210009, People's Republic of China

Correspondence e-mail: zhu hj@njut.edu.cn

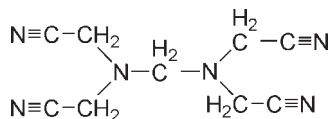
Received 20 January 2010; accepted 3 March 2010

Key indicators: single-crystal X-ray study;  $T = 293$  K; mean  $\sigma(\text{C}-\text{C}) = 0.003$  Å;  $R$  factor = 0.047;  $wR$  factor = 0.143; data-to-parameter ratio = 14.5.

The molecular structure of the title compound,  $\text{C}_9\text{H}_{10}\text{N}_6$ , exhibits four cyanomethyl groups around a central  $\text{N}-\text{CH}_2-\text{N}$  unit. In the crystal structure, molecules are connected *via* intermolecular  $\text{C}-\text{H}\cdots\text{N}$  hydrogen bonds, forming a three-dimensional network.

## Related literature

For bond-length data, see: Allen *et al.* (1987). For the synthetic procedure, see: W. R. Grace & Co. (1969). For the use of the title compound in the synthesis of *N*-(phosphonomethyl) iminodiacetic acid, see: Obeso Caceres & Urcelay del Pozo (1991).



## Experimental

## Crystal data

$\text{C}_9\text{H}_{10}\text{N}_6$   
 $M_r = 202.23$   
 Monoclinic,  $P2_1/n$   
 $a = 6.743$  (1) Å  
 $b = 15.984$  (3) Å

$c = 10.610$  (2) Å  
 $\beta = 105.88$  (3)°  
 $V = 1099.9$  (4) Å<sup>3</sup>  
 $Z = 4$   
 Mo  $K\alpha$  radiation

$\mu = 0.08$  mm<sup>-1</sup>  
 $T = 293$  K

0.30 × 0.20 × 0.10 mm

## Data collection

Enraf–Nonius CAD-4 diffractometer  
 Absorption correction:  $\psi$  scan (North *et al.*, 1968)  
 $T_{\min} = 0.976$ ,  $T_{\max} = 0.992$   
 2167 measured reflections

1991 independent reflections  
 1396 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.016$   
 3 standard reflections every 200 reflections  
 intensity decay: 1%

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.047$   
 $wR(F^2) = 0.143$   
 $S = 1.00$   
 1991 reflections

137 parameters  
 H-atom parameters constrained  
 $\Delta\rho_{\text{max}} = 0.13$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.14$  e Å<sup>-3</sup>

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{C}2-\text{H}2B\cdots\text{N}4^i$	0.97	2.56	3.409 (3)	146
$\text{C}4-\text{H}4B\cdots\text{N}3^{ii}$	0.97	2.58	3.432 (3)	147

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

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

The authors thank the Center of Testing and Analysis, Nanjing University, for support.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IM2179).

## References

- Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.  
 Enraf–Nonius (1994). *CAD-4 Software*. Enraf–Nonius, Delft, The Netherlands.  
 Harms, K. & Wocadlo, S. (1995). *XCAD4*. University of Marburg, Germany.  
 North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst. A* **24**, 351–359.  
 Obeso Caceres, R. M. & Urcelay del Pozo, M. I. (1991). ES Patent No. 2018746.  
 Sheldrick, G. M. (2008). *Acta Cryst. A* **64**, 112–122.  
 W. R. Grace & Co. (1969). GB Patent No. 1167693.

**supplementary materials**

*Acta Cryst.* (2010). E66, o785 [ doi:10.1107/S160053681000824X ]

## (Methylenedinitrilo)tetraacetonitrile

X.-H. Song, M.-L. Feng, K. Wang, Y.-F. Li and H.-J. Zhu

### Comment

The title compound, {[Bis-cyanomethyl-amino)-methyl]cyanomethyl-amino}-acetonitrile is an important intermediate for the synthesis of *N*-(Phosphonomethyl) iminodiacetic acid (Obeso Caceres & Urcelay del Pozo, 1991), which can be used to synthesize glyphosphates. Herein we report the crystal structure of the title compound, (I).

The molecular structure of (I) is shown in Fig. 1, bond lengths and angles are within normal ranges (Allen *et al.*, 1987).

In the crystal of the title compound molecules are connected *via* intermolecular C—H $\cdots$ N hydrogen bonds to form a three dimensional network.

### Experimental

The title compound, (I) was synthesized according to a literature method (W.R. Grace & Co., 1969). Crystals were obtained by dissolving compound (I) (1.5 g) in methanol (25 ml) and evaporating the solvent slowly at room temperature for about 8 d.

### Refinement

H atoms were positioned geometrically, with C—H = 0.97 Å and constrained to ride on their parent atoms, with  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ .

### Figures

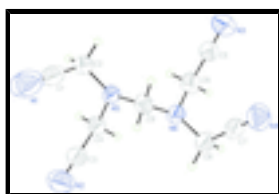


Fig. 1. Molecular structure of the title compound showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

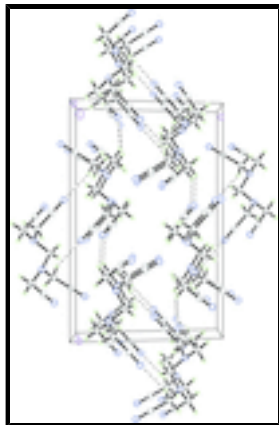


Fig. 2. Packing diagram for (I). C—H...N hydrogen bonds are shown as dashed lines.

**(Methylenedinitrilo)tetraacetonitrile**

*Crystal data*

$C_9H_{10}N_6$

$M_r = 202.23$

Monoclinic,  $P2_1/n$

Hall symbol:  $-P\ 2_1n$

$a = 6.743\ (1)\ \text{\AA}$

$b = 15.984\ (3)\ \text{\AA}$

$c = 10.610\ (2)\ \text{\AA}$

$\beta = 105.88\ (3)^\circ$

$V = 1099.9\ (4)\ \text{\AA}^3$

$Z = 4$

$F(000) = 424$

$D_x = 1.221\ \text{Mg m}^{-3}$

Mo  $K\alpha$  radiation,  $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 25 reflections

$\theta = 10\text{--}13^\circ$

$\mu = 0.08\ \text{mm}^{-1}$

$T = 293\ \text{K}$

Block, colorless

$0.30 \times 0.20 \times 0.10\ \text{mm}$

*Data collection*

Enraf–Nonius CAD-4  
diffractometer

Radiation source: fine-focus sealed tube  
graphite

$\omega/2\theta$  scans

Absorption correction:  $\psi$  scan  
(North *et al.*, 1968)

$T_{\min} = 0.976$ ,  $T_{\max} = 0.992$

2167 measured reflections

1991 independent reflections

1396 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.016$

$\theta_{\max} = 25.3^\circ$ ,  $\theta_{\min} = 2.4^\circ$

$h = 0 \rightarrow 8$

$k = 0 \rightarrow 19$

$l = -12 \rightarrow 12$

3 standard reflections every 200 reflections

intensity decay: 1%

*Refinement*

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.047$

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$wR(F^2) = 0.143$	$w = 1/[\sigma^2(F_o^2) + (0.085P)^2]$
$S = 1.00$	where $P = (F_o^2 + 2F_c^2)/3$
1991 reflections	$(\Delta/\sigma)_{\max} < 0.001$
137 parameters	$\Delta\rho_{\max} = 0.13 \text{ e } \text{Å}^{-3}$
0 restraints	$\Delta\rho_{\min} = -0.14 \text{ e } \text{Å}^{-3}$
Primary atom site location: structure-invariant direct methods	Extinction correction: SHELXL97 (Sheldrick, 2008), $F_c^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$ Extinction coefficient: 0.112 (10)

### Special details

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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 ( $\text{Å}^2$ )

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	-0.0963 (3)	0.70909 (15)	0.4827 (2)	0.0615 (6)
N1	-0.0281 (3)	0.67348 (19)	0.5772 (2)	0.1033 (9)
C2	-0.1891 (3)	0.75550 (13)	0.3610 (2)	0.0500 (5)
H2A	-0.2811	0.7179	0.3005	0.060*
H2B	-0.2727	0.8002	0.3813	0.060*
N2	0.3724 (3)	0.66055 (14)	0.3957 (2)	0.0783 (7)
C3	0.2363 (3)	0.69176 (13)	0.3233 (2)	0.0528 (6)
N3	-0.2530 (3)	1.06022 (13)	0.3005 (2)	0.0812 (7)
C4	0.0600 (3)	0.73457 (12)	0.23192 (19)	0.0472 (5)
H4A	0.1101	0.7652	0.1679	0.057*
H4B	-0.0362	0.6926	0.1851	0.057*
N4	0.3020 (3)	1.08661 (11)	0.45391 (19)	0.0650 (6)
N5	-0.0489 (2)	0.79180 (9)	0.29447 (15)	0.0444 (4)
C5	-0.1757 (3)	1.01621 (13)	0.2444 (2)	0.0563 (6)
N6	0.1060 (2)	0.91629 (9)	0.25246 (15)	0.0451 (4)
C6	-0.0768 (3)	0.95691 (13)	0.1736 (2)	0.0560 (6)
H6A	-0.1765	0.9142	0.1338	0.067*
H6B	-0.0411	0.9868	0.1032	0.067*
C7	0.2980 (3)	1.03432 (12)	0.3814 (2)	0.0480 (5)
C8	0.2920 (3)	0.96600 (12)	0.2853 (2)	0.0555 (6)
H8A	0.3094	0.9905	0.2053	0.067*
H8B	0.4083	0.9292	0.3202	0.067*
C9	0.0716 (3)	0.86329 (11)	0.35568 (18)	0.0457 (5)

## supplementary materials

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H9A	0.2025	0.8449	0.4129	0.055*
H9B	-0.0018	0.8941	0.4076	0.055*

### Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C1	0.0474 (12)	0.0761 (15)	0.0674 (15)	0.0003 (11)	0.0266 (11)	0.0082 (13)
N1	0.0719 (15)	0.150 (2)	0.0938 (17)	0.0147 (15)	0.0319 (13)	0.0500 (17)
C2	0.0450 (11)	0.0465 (11)	0.0627 (12)	0.0006 (9)	0.0219 (10)	0.0000 (9)
N2	0.0670 (13)	0.0839 (15)	0.0872 (15)	0.0192 (12)	0.0263 (12)	0.0043 (12)
C3	0.0534 (13)	0.0451 (11)	0.0675 (13)	0.0022 (10)	0.0292 (11)	-0.0072 (10)
N3	0.0713 (14)	0.0637 (13)	0.1181 (18)	0.0208 (11)	0.0419 (13)	0.0157 (12)
C4	0.0527 (11)	0.0397 (10)	0.0530 (11)	-0.0015 (9)	0.0210 (10)	-0.0084 (9)
N4	0.0758 (13)	0.0522 (11)	0.0720 (12)	-0.0069 (10)	0.0287 (10)	-0.0107 (10)
N5	0.0462 (9)	0.0358 (8)	0.0559 (9)	-0.0021 (7)	0.0218 (8)	-0.0058 (7)
C5	0.0470 (12)	0.0459 (12)	0.0764 (15)	0.0039 (10)	0.0176 (11)	0.0155 (11)
N6	0.0438 (9)	0.0388 (8)	0.0552 (9)	-0.0052 (7)	0.0176 (7)	-0.0047 (7)
C6	0.0596 (13)	0.0518 (12)	0.0559 (12)	-0.0032 (10)	0.0148 (10)	0.0026 (10)
C7	0.0479 (12)	0.0408 (11)	0.0590 (12)	-0.0067 (9)	0.0210 (10)	-0.0010 (9)
C8	0.0529 (13)	0.0479 (11)	0.0733 (14)	-0.0092 (10)	0.0303 (11)	-0.0149 (10)
C9	0.0514 (11)	0.0352 (10)	0.0510 (11)	0.0026 (9)	0.0151 (9)	-0.0056 (8)

### Geometric parameters ( $\text{\AA}$ , $^\circ$ )

C1—N1	1.135 (3)	N5—C9	1.449 (2)
C1—C2	1.472 (3)	C5—C6	1.478 (3)
C2—N5	1.447 (2)	N6—C6	1.441 (2)
C2—H2A	0.9700	N6—C8	1.445 (2)
C2—H2B	0.9700	N6—C9	1.452 (2)
N2—C3	1.138 (3)	C6—H6A	0.9700
C3—C4	1.480 (3)	C6—H6B	0.9700
N3—C5	1.136 (3)	C7—C8	1.487 (3)
C4—N5	1.443 (2)	C8—H8A	0.9700
C4—H4A	0.9700	C8—H8B	0.9700
C4—H4B	0.9700	C9—H9A	0.9700
N4—C7	1.132 (2)	C9—H9B	0.9700
N1—C1—C2	178.7 (2)	C8—N6—C9	116.50 (16)
N5—C2—C1	116.91 (16)	N6—C6—C5	115.26 (17)
N5—C2—H2A	108.1	N6—C6—H6A	108.5
C1—C2—H2A	108.1	C5—C6—H6A	108.5
N5—C2—H2B	108.1	N6—C6—H6B	108.5
C1—C2—H2B	108.1	C5—C6—H6B	108.5
H2A—C2—H2B	107.3	H6A—C6—H6B	107.5
N2—C3—C4	178.2 (2)	N4—C7—C8	179.6 (2)
N5—C4—C3	114.24 (16)	N6—C8—C7	115.34 (16)
N5—C4—H4A	108.7	N6—C8—H8A	108.4
C3—C4—H4A	108.7	C7—C8—H8A	108.4
N5—C4—H4B	108.7	N6—C8—H8B	108.4

C3—C4—H4B	108.7	C7—C8—H8B	108.4
H4A—C4—H4B	107.6	H8A—C8—H8B	107.5
C4—N5—C2	116.91 (15)	N5—C9—N6	107.91 (14)
C4—N5—C9	114.36 (14)	N5—C9—H9A	110.1
C2—N5—C9	117.30 (15)	N6—C9—H9A	110.1
N3—C5—C6	178.4 (2)	N5—C9—H9B	110.1
C6—N6—C8	116.11 (16)	N6—C9—H9B	110.1
C6—N6—C9	114.43 (15)	H9A—C9—H9B	108.4
N1—C1—C2—N5	160 (12)	N3—C5—C6—N6	-68 (9)
N2—C3—C4—N5	-26 (7)	C6—N6—C8—C7	71.1 (2)
C3—C4—N5—C2	-77.5 (2)	C9—N6—C8—C7	-68.2 (2)
C3—C4—N5—C9	65.1 (2)	N4—C7—C8—N6	-92 (32)
C1—C2—N5—C4	70.3 (2)	C4—N5—C9—N6	69.05 (19)
C1—C2—N5—C9	-71.2 (2)	C2—N5—C9—N6	-148.50 (16)
C8—N6—C6—C5	-77.2 (2)	C6—N6—C9—N5	68.47 (19)
C9—N6—C6—C5	63.0 (2)	C8—N6—C9—N5	-151.47 (15)

*Hydrogen-bond geometry (Å, °)*

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
C2—H2B...N4 <sup>i</sup>	0.97	2.56	3.409 (3)	146.
C4—H4B...N3 <sup>ii</sup>	0.97	2.58	3.432 (3)	147.

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

Fig. 1

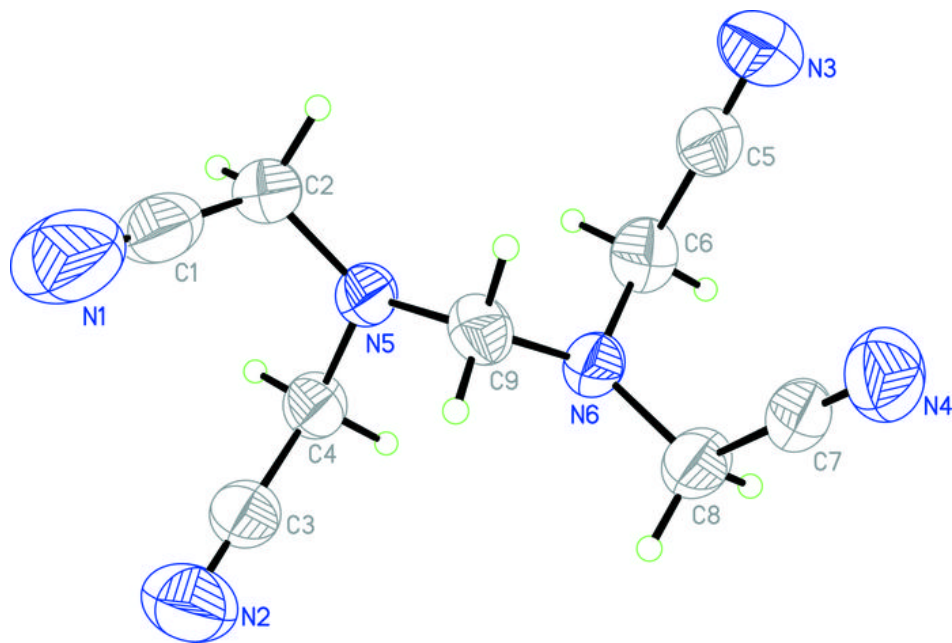




Fig. 2

