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# (Methylenedinitrilo)tetraacetonitrile

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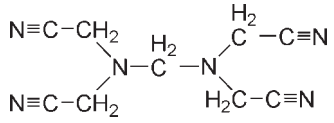
Key indicators: single-crystal X-ray study; $T$ = 293 K; mean $\sigma$(C–C) = 0.003 Å; $R$ factor = 0.047; $wR$ factor = 0.143; data-to-parameter ratio = 14.5.

The molecular structure of the title compound, $C_9H_{10}N_6$, exhibits four cyanomethyl groups around a central N—$CH_2$—N unit. In the crystal structure, molecules are connected *via* intermolecular C—H···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*

$C_9H_{10}N_6$
$M_r$ = 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$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 0.08 mm$^{-1}$
$T$ = 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 $I > 2\sigma(I)$
$R_{int}$ = 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
$\Delta\rho_{max}$ = 0.13 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.14 e Å$^{-3}$

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| C2—H2$B$···N4$^{i}$ | 0.97 | 2.56 | 3.409 (3) | 146 |
| C4—H4$B$···N3$^{ii}$ | 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*.

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

## References

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# supporting information

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## (Methylenedinitrilo)tetraacetonitrile

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

### S1. Comment

The tittle 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···N hydrogen bonds to form a three dimensional network.

### S2. 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.

### S3. Refinement

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

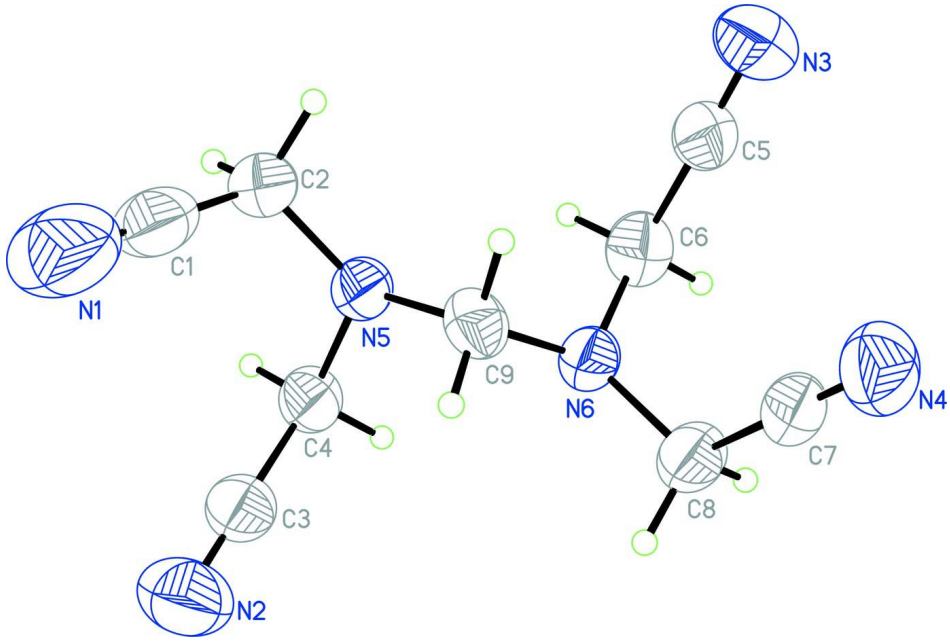


**Figure 1**

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

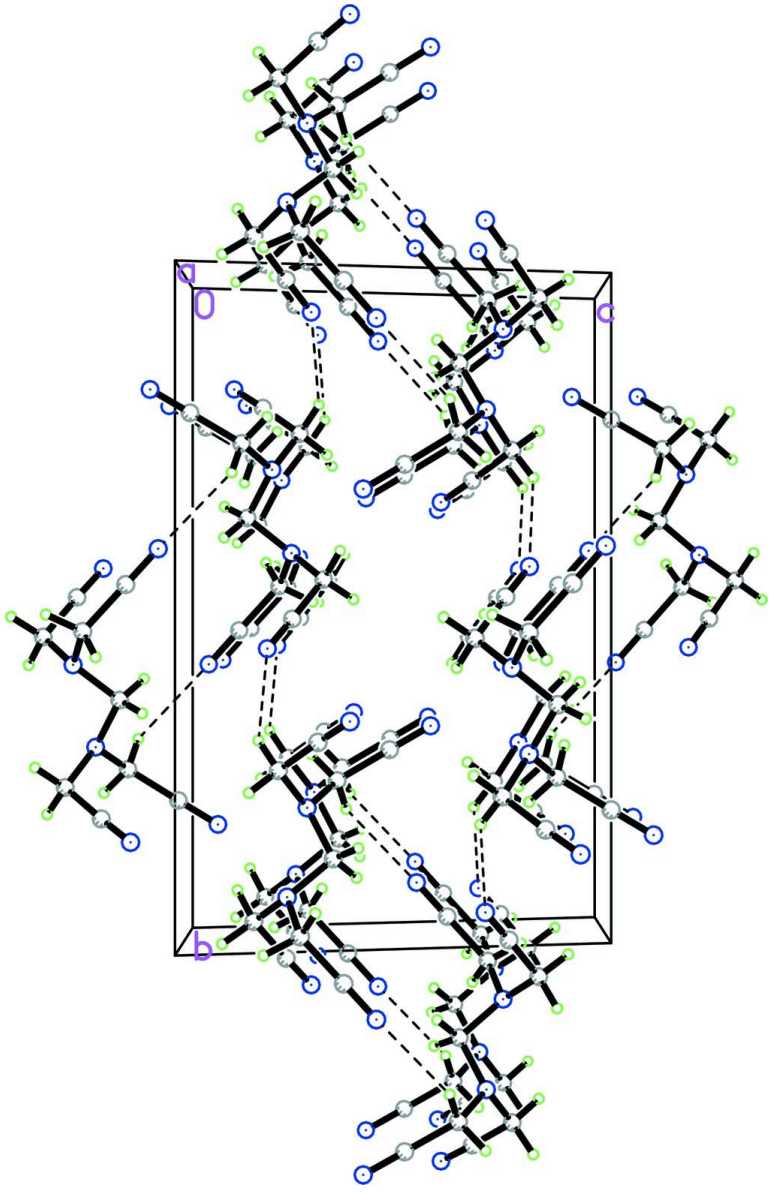


**Figure 2**

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 2yn
$a = 6.743$ (1) Å
$b = 15.984$ (3) Å
$c = 10.610$ (2) Å
$\beta = 105.88$ (3)°
$V = 1099.9$ (4) Å$^3$
$Z = 4$

$F(000) = 424$
$D_x = 1.221$ Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 10$–13°
$\mu = 0.08$ mm$^{-1}$
$T = 293$ K
Block, colorless
0.30 × 0.20 × 0.10 mm

*Data collection*

Enraf–Nonius CAD-4 diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
$\omega/2\theta$ 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 $I > 2\sigma(I)$
$R_{int}$ = 0.016
$\theta_{max}$ = 25.3°, $\theta_{min}$ = 2.4°
$h$ = 0→8
$k$ = 0→19
$l$ = −12→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
$wR(F^2)$ = 0.143
$S$ = 1.00
1991 reflections
137 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
$w = 1/[\sigma^2(F_o^2) + (0.085P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.13 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.14 e Å$^{-3}$
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
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 (Å$^2$)*

| | $x$ | $y$ | $z$ | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| 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) |
| H9A | 0.2025 | 0.8449 | 0.4129 | 0.055* |
| H9B | −0.0018 | 0.8941 | 0.4076 | 0.055* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| 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 (Å, º)*

| | | | |
|---|---|---|---|
| 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, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| C2—H2*B*···N4$^{i}$ | 0.97 | 2.56 | 3.409 (3) | 146 |
| C4—H4*B*···N3$^{ii}$ | 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.