

A low-temperature redetermination of
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A low-temperature redetermination of metaldehyde (systematic name: 2,4,6,8-tetramethyl-1,3,5,7-tetroxocane), $(\text{CH}_3\text{-CHO})_4$ or $\text{C}_8\text{H}_{16}\text{O}_4$, is reported, 69 years after the original determination [Pauling & Carpenter (1936). *J. Am. Chem. Soc.* **58**, 1274–1278]. Metaldehyde crystallizes in the space group *I4*. The asymmetric unit contains one quarter of a molecule and the complete molecule is generated by the fourfold rotation axis.

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Key indicators

Single-crystal X-ray study

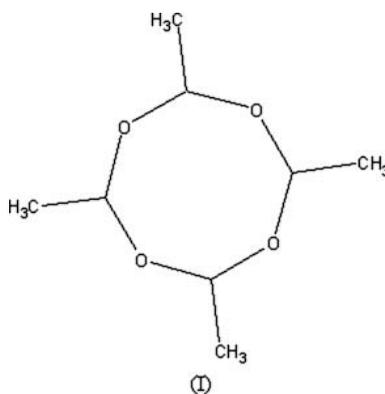
 $T = 150\text{ K}$ Mean $\sigma(\text{C-C}) = 0.002\text{ \AA}$ R factor = 0.029 wR factor = 0.073

Data-to-parameter ratio = 7.0

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

Comment

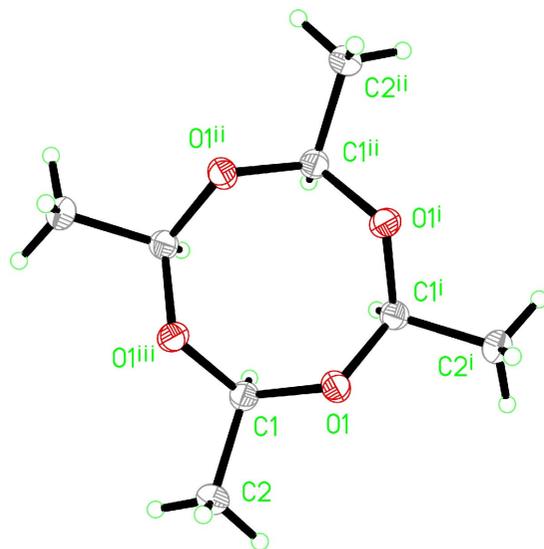
The structure of metaldehyde, or 2,4,6,8-tetramethyl-1,3,5,7-tetroxocane, (I), was first reported by Pauling & Carpenter (1936), using photographic methods. In the intervening 69 years, no further single-crystal determination of this compound has been deposited with the Cambridge Structural Database (Version of February 2005; Allen, 2002). We now report a low-temperature redetermination of this structure using a modern area-detector-equipped diffractometer, with all H-atom positions determined from the electron-density map.



Crystals of metaldehyde were grown by chance while attempting a recrystallization of 5-fluorocytosine from acetaldehyde. Under the conditions of the recrystallization experiment, four acetaldehyde molecules cyclized to form metaldehyde and this subsequently crystallized from solution.

The crystals grew as long needles. Attempts to cut a crystal perpendicular to the axis of the needle led to the shattering of the entire crystal. Therefore, a large complete needle was mounted, with no attempt made to reduce its size. This crystal measured approximately 1.25 mm in the direction of the long axis of the needle.

Metaldehyde (Fig. 1) comprises a tetramer of CH_3CHO units, with only one unit present in the asymmetric unit. The fourfold rotation axis generates the complete molecule and

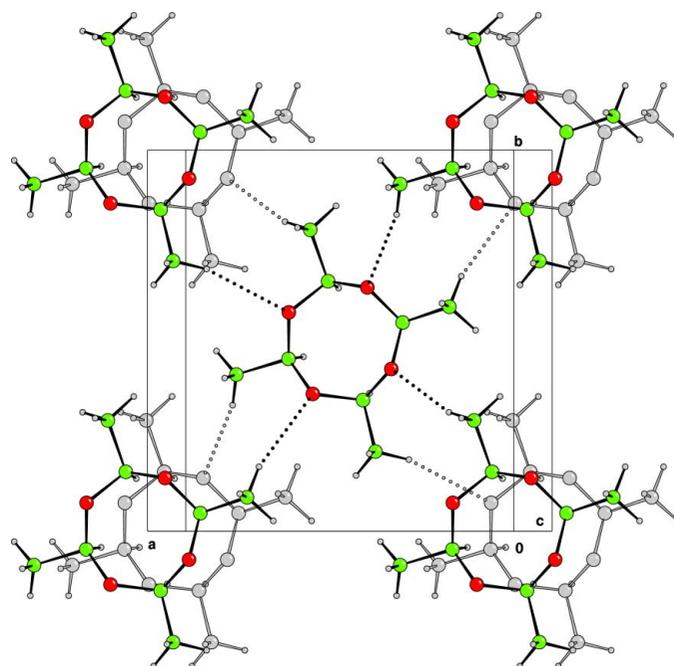

Figure 1

A single molecule of the title compound. Displacement ellipsoids are drawn at the 50% probability level. H atoms are drawn as spheres of arbitrary radii. [Symmetry codes: (i) $1 - y, 1 + x, z$; (ii) $-x, 2 - y, z$; (iii) $y - 1, 1 - x, z$.]

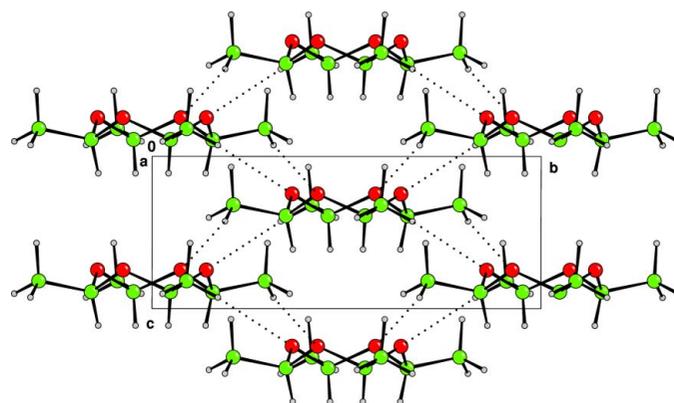
two molecules are present in the unit cell. There are no conventional strong hydrogen bonds in the structure, due to the lack of a hydrogen-bond donor. One weak $C2-H2 \cdots O1^{iv}$ hydrogen-bond interaction is present within the accepted range for $C-H \cdots O$ bonds (Desiraju, 1996) [$C2 \cdots O1 = 3.631(2) \text{ \AA}$ and $C2-H2 \cdots O1^{iv} = 164(2)^\circ$; symmetry code: (iv) $\frac{3}{2} - y, \frac{1}{2} + x, z - \frac{1}{2}$].

The molecule in the body-centred position of the unit cell forms four $C-H \cdots O$ bonds, one to each of the four molecules located at the unit-cell vertices with $z = 0$. It also forms four $O \cdots H-C$ bonds, one to each of the four molecules at the vertices of the unit cell with $z = 1$ (Fig. 2). The overall motif is a three-dimensional hydrogen-bonded network (Fig. 3). The molecules stack directly upon one another to form columns, parallel to the c axis. As described in the original paper (Pauling & Carpenter, 1936), there may be electrostatic interactions between the adjacent members of the column, as each molecule has a partially negatively charged face (comprising the four O atoms in the ring), and a partially positively charged face (comprising the four H atoms bonded to the C atoms in the ring). The distance between the plane of the four O1 atoms in one molecule and the plane of the four C1 atoms in the adjacent molecule in the column is 3.51 \AA .

The largest geometrical difference between this redetermination and the original structure is in the bond angles about C1. In the original determination, the angles about C1 were constrained to the tetrahedral bond angle, whereas in the structure reported here, these angles deviate by up to 2.5° from the tetrahedral angle [$C2-C1-O1 = 106.9(1)^\circ$, $C2-C1-O1^{iii} = 106.7(1)^\circ$ and $O1-C1-O1^{iii} = 112.0(1)^\circ$; symmetry code: (iii) $y - 1, 1 - x, z$]. These deviations may be due to changes in the molecular conformation with temperature, rather than the use of constraints in the original report.


Figure 2

A view inclined to the c axis, showing the $C-H \cdots O$ hydrogen bonding as dotted lines. The grey molecules are one unit cell lower than the coloured molecules. The central molecule bonds to the four molecules in the upper plane and the four in the lower plane.


Figure 3

View along the a axis, showing the $C-H \cdots O$ hydrogen-bonded network. Hydrogen bonds are shown as dotted lines.

Experimental

Metaldehyde crystals were produced from an attempt to recrystallize 5-fluorocytosine from acetaldehyde by solvent evaporation at 278 K .

Crystal data

$C_8H_{16}O_4$
 $M_r = 176.21$
 Tetragonal, $I4$
 $a = 10.4974(10) \text{ \AA}$
 $c = 4.0967(7) \text{ \AA}$
 $V = 451.44(10) \text{ \AA}^3$
 $Z = 2$
 $D_x = 1.296 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation
 Cell parameters from 1875 reflections
 $\theta = 2.7\text{--}28.3^\circ$
 $\mu = 0.10 \text{ mm}^{-1}$
 $T = 150(2) \text{ K}$
 Needle, colourless
 $1.24 \times 0.39 \times 0.22 \text{ mm}$

Data collection

Bruker SMART APEX diffractometer	314 independent reflections
ω rotation with narrow-frame scans	312 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$R_{\text{int}} = 0.017$
$T_{\text{min}} = 0.883$, $T_{\text{max}} = 0.978$	$\theta_{\text{max}} = 28.3^\circ$
1953 measured reflections	$h = -13 \rightarrow 13$
	$k = -13 \rightarrow 13$
	$l = -5 \rightarrow 5$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0515P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.029$	$+ 0.1168P]$
$wR(F^2) = 0.073$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.08$	$(\Delta/\sigma)_{\text{max}} < 0.001$
314 reflections	$\Delta\rho_{\text{max}} = 0.17 \text{ e } \text{\AA}^{-3}$
45 parameters	$\Delta\rho_{\text{min}} = -0.18 \text{ e } \text{\AA}^{-3}$
All H-atom parameters refined	Extinction correction: <i>SHELXL97</i>
	Extinction coefficient: 0.103 (18)

The quoted transmission factors result from correction for incomplete irradiation of the long needle crystal as well as absorption effects. All H atoms were located in a difference map and were refined isotropically; the range of C–H bond lengths is 0.94 (2)–1.00 (3) Å. Friedel pairs were merged as no significant anomalous scattering effects were observed.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINTE* (Bruker, 1998); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *CAMERON* (Watkin *et al.*, 1996); software used to prepare material for publication: *SHELXL97*.

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