A low-temperature redetermination of metaldehyde

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Key indicators

Single-crystal X-ray study

T = 150 K

Mean σ(C–C) = 0.002 Å

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.

A low-temperature redetermination of metaldehyde (systematic name: 2,4,6,8-tetramethyl-1,3,5,7-tetroxocane), $(CH_3–CHO)_4$ or $C_8H_{16}O_4$, 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.

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.

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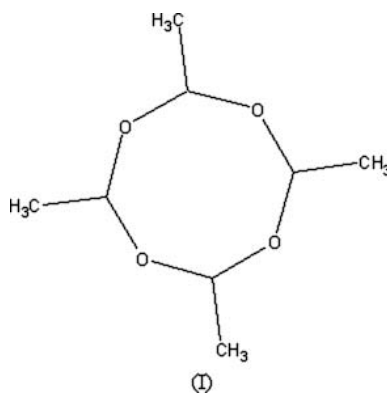
Crystals of metaldehyde were grown by chance while attempting a recrystallization of 5-fluorocytosine from acetaldehyde. Under the conditions of the recrystallization experiment, four acetaldehyde molecules cyclized to form metaldehyde and this subsequently crystallized from solution.

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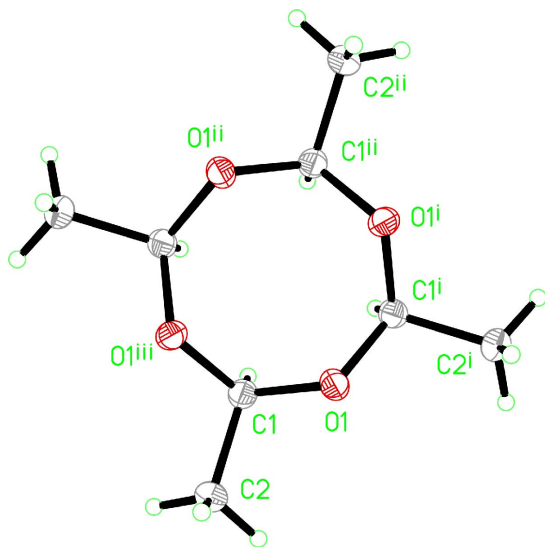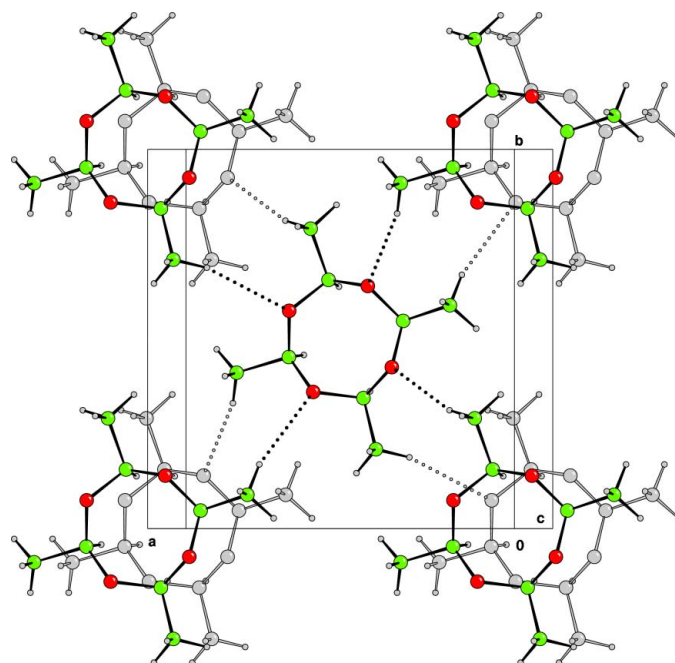
Figure 1
A single molecule of the title compound. Displacement ellipsoids are drawn at the 50% probability level. H atoms are drawn as spheres of arbitrary radii. [Symmetry codes: (i) $1 - y, 1 + x, z$; (ii) $-x, 2 - y, z$; (iii) $y - 1, 1 - x, z$.]

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.

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) Å 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 Å.

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.
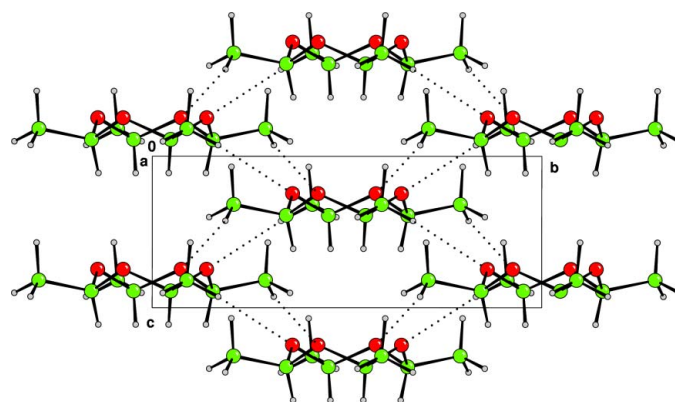
Experimental

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

Crystal data

$C_8H_{16}O_4$	Mo $K\alpha$ radiation
$M_r = 176.21$	Cell parameters from 1875
Tetragonal, $I4$	reflections
$a = 10.4974 (10)$ Å	$\theta = 2.7–28.3^\circ$
$c = 4.0967 (7)$ Å	$\mu = 0.10$ mm^{-1}
$V = 451.44 (10)$ Å^3	$T = 150 (2)$ K
$Z = 2$	Needle, colourless
$D_x = 1.296$ Mg m^{-3}	$1.24 \times 0.39 \times 0.22$ mm

Data collection

Bruker SMART APEX
 diffractometer
ω rotation with narrow-frame scans
Absorption correction: multi-scan
 (*SADABS*; Sheldrick, 1996)
 $T_{min} = 0.883$, $T_{max} = 0.978$
1953 measured reflections

314 independent reflections
312 reflections with $I > 2\sigma(I)$
$R_{int} = 0.017$
$\theta_{max} = 28.3°$
$h = -13 \rightarrow 13$
$k = -13 \rightarrow 13$
$l = -5 \rightarrow 5$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.073$
$S = 1.08$
314 reflections
45 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0515P)^2$
 $+ 0.1168P]$
 where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.17$ e Å^{-3}
$\Delta\rho_{min} = -0.18$ e Å^{-3}
Extinction correction: *SHELXL97*
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: *SAINT* (Bruker, 1998); data reduction: *SAINT*; 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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2,4,6,8-tetramethyl-1,3,5,7-tetroxocane

Crystal data

$C_8H_{16}O_4$	$D_x = 1.296$ Mg m^{-3}
$M_r = 176.21$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Tetragonal, $I4$	Cell parameters from 1875 reflections
Hall symbol: I 4	$\theta = 2.7$–28.3°
$a = 10.4974$ (10) Å	$\mu = 0.10$ mm^{-1}
$c = 4.0967$ (7) Å	$T = 150$ K
$V = 451.44$ (10) Å^3	Needle, colourless
$Z = 2$	$1.24 \times 0.39 \times 0.22$ mm
$F(000) = 192$	

Data collection

Bruker SMART APEX diffractometer	1953 measured reflections
Radiation source: fine-focus sealed tube	314 independent reflections
Graphite monochromator	312 reflections with $I > 2\sigma(I)$
ω rotation with narrow frames scans	$R_{int} = 0.017$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$\theta_{max} = 28.3°$, $\theta_{min} = 2.7°$
$T_{min} = 0.883$, $T_{max} = 0.978$	$h = -13 \rightarrow 13$
	$k = -13 \rightarrow 13$
	$l = -5 \rightarrow 5$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.029$	All H-atom parameters refined
$wR(F^2) = 0.073$	$w = 1/[\sigma^2(F_o^2) + (0.0515P)^2 + 0.1168P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.08$	
314 reflections	$(\Delta/\sigma)_{max} < 0.001$
45 parameters	$\Delta\rho_{max} = 0.17$ e Å^{-3}
1 restraint	$\Delta\rho_{min} = -0.18$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: SHELXL97, $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
	Extinction coefficient: 0.103 (18)

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	$U_{iso}*/U_{eq}$
O1	0.13979 (8)	1.07448 (8)	1.0388 (2)	0.0199 (3)
C1	0.15579 (11)	0.95252 (11)	0.8957 (4)	0.0187 (3)
H1	0.1373 (19)	0.9582 (17)	0.672 (6)	0.019 (4)*
C2	0.29095 (11)	0.91096 (13)	0.9674 (5)	0.0247 (4)
H2	0.310 (2)	0.831 (2)	0.861 (6)	0.035 (5)*
H3	0.352 (2)	0.974 (2)	0.885 (8)	0.041 (6)*
H4	0.298 (2)	0.903 (2)	1.211 (7)	0.036 (6)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0201 (4)	0.0173 (5)	0.0222 (5)	0.0022 (3)	−0.0029 (4)	−0.0015 (4)
C1	0.0182 (6)	0.0177 (5)	0.0201 (6)	−0.0005 (4)	0.0019 (5)	−0.0009 (5)
C2	0.0184 (6)	0.0225 (6)	0.0333 (8)	0.0021 (4)	0.0016 (6)	−0.0010 (6)

Geometric parameters (Å, º)

O1—C1	1.4181 (15)	C1—H1	0.94 (2)
O1—C1^i	1.4181 (15)	C2—H2	0.96 (2)
C1—O1^{ii}	1.4181 (15)	C2—H3	0.98 (2)
C1—C2	1.5132 (17)	C2—H4	1.00 (3)
C1—O1—C1^i	116.97 (13)	C1—C2—H2	111.1 (13)
O1—C1—O1^{ii}	112.01 (12)	C1—C2—H3	110.9 (14)
O1—C1—C2	106.92 (10)	H2—C2—H3	107 (2)
O1^{ii}—C1—C2	106.68 (10)	C1—C2—H4	106.4 (13)
O1—C1—H1	108.8 (12)	H2—C2—H4	111 (2)
O1^{ii}—C1—H1	108.8 (11)	H3—C2—H4	111 (2)
C2—C1—H1	113.7 (13)		
C1^i—O1—C1—O1^{ii}	−90.06 (16)	C1^i—O1—C1—C2	153.41 (10)

Symmetry codes: (i) −y+1, x+1, z; (ii) y−1, −x+1, z.