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), (CH₃–CHO)₄ or C₈H₁₆O₄, 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, (1), 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 CH₃CHO units, with only one unit present in the asymmetric unit. The fourfold rotation axis generates the complete molecule and
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/C1/C1/C1O1iv hydrogen-bond interaction is present within the accepted range for C—H/C1/C1/C1O bonds (Desiraju, 1996) [C2—C1/C1/C1O1 = 3.631 (2) Å and C2—H2/C1/C1/C1O1iv = 164 (2)°; symmetry code: (iv) $\frac{1}{2} - y, \frac{1}{2} + x, z$].

The molecule in the body-centred position of the unit cell forms four C—H/C1/C1/C1O bonds, one to each of the four molecules located at the unit-cell vertices with $z = 0$. It also forms four O/C1/C1/C1H—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)°, C2—C1—O1iii = 106.7 (1)° and O1—C1—O1iii = 112.0 (1)°; 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**

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_8H_{16}O_4$</td>
<td></td>
</tr>
<tr>
<td>$M_r$</td>
<td>176.21</td>
</tr>
<tr>
<td>Tetragonal, $I4$</td>
<td></td>
</tr>
<tr>
<td>$a = 10.4974$ (10) Å</td>
<td></td>
</tr>
<tr>
<td>$c = 4.0967$ (7) Å</td>
<td></td>
</tr>
<tr>
<td>$V = 451.44$ (10) Å³</td>
<td></td>
</tr>
<tr>
<td>$Z = 2$</td>
<td></td>
</tr>
<tr>
<td>$D_x = 1.296$ Mg m⁻³</td>
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</tbody>
</table>

**Mo Kα radiation**

<table>
<thead>
<tr>
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<th>Value</th>
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<tbody>
<tr>
<td>Cell parameters from 1875 reflections</td>
<td></td>
</tr>
<tr>
<td>$\theta = 2.7$–28.3°</td>
<td></td>
</tr>
<tr>
<td>$\mu = 0.10$ mm⁻¹</td>
<td></td>
</tr>
<tr>
<td>$T = 150$ (2) K</td>
<td></td>
</tr>
<tr>
<td>Needle, colourless</td>
<td></td>
</tr>
<tr>
<td>$1.24 \times 0.39 \times 0.22$ mm</td>
<td></td>
</tr>
</tbody>
</table>
**Data collection**

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

**Refinement**

Refinement on \(F^2\)
\(\text{weight} = \frac{1}{[\sigma(F)^2 + (0.0515P)^2]^{1/2}}\)
where \(P = (\text{Fo}^2 + 2\text{Fc}^2)/3\)
\((\Delta \sigma)_{\text{max}} < 0.001\)
\(\Delta \rho_{\text{max}} = 0.17 e \text{Å}^{-3}\)
\(\Delta \rho_{\text{min}} = -0.18 e \text{Å}^{-3}\)

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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**References**


