

n-Octadecane: A Correction and Refinement of the Structure given by Hayashida

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Owing to a mis-indexing of the $Ok\bar{l}$ zone, the triclinic cell proposed by Hayashida (*J. Phys. Soc. Japan* (1962), 17, 306) for octadecane, $C_{18}H_{38}$, is not correct: nor therefore is the structure proposed by him. The error has been corrected and the structure refined from Hayashida's $h0l$ and $Ok\bar{l}$ data. Even after correction, the structure showed some minor anomalies. These we believe are due to inaccuracies in Hayashida's triclinic cell parameters. Good results are obtained using the cell originally proposed by Müller & Lonsdale (*Acta Cryst.* (1948), 1, 127), suitably transformed to suit the axial system used by Hayashida, namely, $a = 4.285$, $b = 4.820$, $c = 24.898$ Å, $\alpha = 85.150^\circ$, $\beta = 67.8^\circ$ and $\gamma = 72.70^\circ$. Space group $P\bar{1}$.

If sufficiently pure, the straight chain alkanes C_nH_{2n+2} with n even ($6 < n < 26$) crystallize in the triclinic system (a hexagonal form is exhibited near the m.p.), whereas those with n odd ($11 < n < 43$) are orthorhombic (Broadhurst, 1962). A representative structure of the n odd has been given for $C_{23}H_{48}$ by Smith (1953). For so simple a molecule the structure analysis of octadecane has had a chequered history.

The first single-crystal examination of $C_{18}H_{38}$ seems to have been that of Müller & Lonsdale (1948), hereafter M & L. They determined the six parameters for the triclinic cell (I, Table 1), showing it to contain one molecule. Kitaigorodsky & Mnyukh (1959) obtained from Lonsdale $h0l$ and $Ok\bar{l}$ intensity data which had apparently been recorded but not referred to in the 1948 paper with Müller. From these intensity data, Kitaigorodsky & Mnyukh proposed an approximate structure in $P\bar{1}$. The results were expressed in the form of the angles made by the molecular long axis with the z axis of the cell and the positions of the atoms in the subcell. Atomic coordinates were not explicitly given and although two somewhat poorly resolved Fourier projections were published no observed or calculated structure factors were given. It is clear that any structural inferences drawn from Kitaigorodsky & Mnyukh's work would of necessity be very approximate.

Hayashida (1962) published a paper on the crystal structure of octadecane based on photometrically measured intensity data from the $h0l$ and $Ok\bar{l}$ zones. (In addition, hhl data were said to have been collected but these were not published). The cell constants given by Hayashida differed from those given by M & L (Table 1) but, according to him, 'agreed well... after a transformation of axes'. Hayashida also claimed that his cell volume agreed with that given by M & L which it manifestly did not, M & L giving explicitly 454.4 Å³ Hayashida giving 398.1 Å³. (This is in any

case wrong; the cell given by Hayashida would have a volume 436.2 Å³.) Hayashida made no reference to the work of Kitaigorodsky & Mnyukh.

In 1970, Crissman, Passaglia, Eby & Colson measured the positions of the powder lines of the next triclinic n -even homologue, eicosane, $C_{20}H_{42}$. They showed, as might be expected, that five of the six cell parameters were virtually identical to those given by M & L for octadecane (II, Table 1). The c repeat is longer by 2.45 Å to accommodate the two extra methylene groups. In a footnote, Crissman *et al.* remarked that for $C_{18}H_{38}$ neither $d(001)$ nor the cell volume given by Hayashida agreed with those given by M & L.

We first became concerned about the structure of $C_{18}H_{38}$ published by Hayashida when we discovered that the triclinic cell would not yield the same Delauney reduced cell as that given by M & L (already reduced). We also found that the atomic coordinates given by Hayashida gave C-C bond lengths alternating between 1.38 and 1.70 Å. That there was a discrepancy between the cells given by M & L and by Hayashida was also noted by an Editor of *Structure Reports* (1962) in which the β angle given by Hayashida is changed to its supplement. We found that this modified cell does indeed reduce reasonably well to the cell given by M & L but the atomic coordinates are still wrong.

We have traced the error to Hayashida's faulty assignment of the γ cell angle, which in turn seems to have arisen from a misindexing of the $Ok\bar{l}$ reflexions as $Ok\bar{l}$. (We have confirmed this on a precession photograph of $C_{20}H_{42}$). Unfortunately γ was not consistently mis-assigned. Thus the $h0l$ projection has the correct $\pi-\beta^*$ angle (II, Table 2) between x and z axes. Both $Ok\bar{l}$ projections [Hayashida (1962), Figs. 1(b) and 3] have the correct $\pi-\alpha^*$ angle between axes but the former has γ running in the wrong direction. In contrast the $hk0$ projection has quite the wrong angle between axes. It has been calculated from the erroneous γ instead of from its supplement.

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temperature factors for carbon in Table 4 and derived hydrogen coordinates in Table 5.

Table 5. *Derived hydrogen fractional coordinates, $\times 10^3$ (x and y), $\times 10^4$ (z)*

	x	y	z
H2(1)	243	419	-4498
H2(2)	-20	-66	-3847
H2(3)	220	371	-3459
H2(4)	-54	-104	-2801
H2(5)	203	324	-2416
H2(6)	-87	-145	-1756
H2(7)	178	277	-1373
H2(8)	-123	-187	-709
H2(9)	157	229	-337
H3(1)	-188	396	-4263
H3(2)	412	-46	-4085
H3(3)	-214	356	-3223
H3(4)	382	-94	-3043
H3(5)	-235	321	-2180
H3(6)	351	-143	-1994
H3(7)	-261	277	-1139
H3(8)	318	-193	-950
H3(9)	-286	240	-100
H1(1)	153	145	-4784

The calculated bond lengths and angles were reasonably good but showed some alternation in magnitude along the molecular chain. We have now traced this to what we believe to be the inaccurate cell parameters used by Hayashida. Table 1 shows that the cell parameters given by M & L for $C_{18}H_{38}$ and those given by Crissman *et al.* (1970) for $C_{20}H_{42}$ agree better with each other (apart from β) than with the parameters obtained from Hayashida's cell after reduction. Accordingly, we have used the M & L parameters transformed to the system used by Hayashida (V, Table 1). Use of cell parameters removed the apparent alternation in bond lengths and angles along the chain. The results, which are of unknown accuracy, but probably of order 0.05 Å and 2° are given in Table 6.

Table 6. *C-C bond lengths and C-C-C angles*

C(1)-C(2)	1.49 Å	C(1)-C(2)-C(3)	114.9°
C(2)-C(3)	1.50	C(2)-C(3)-C(4)	115.5
C(3)-C(4)	1.50	C(3)-C(4)-C(5)	115.6
C(4)-C(5)	1.52	C(4)-C(5)-C(6)	115.0
C(5)-C(6)	1.51	C(5)-C(6)-C(7)	115.0
C(6)-C(7)	1.51	C(6)-C(7)-C(8)	114.8
C(7)-C(8)	1.51	C(7)-C(8)-C(9)	114.3
C(8)-C(9)	1.52	C(8)-C(9)-C(9')	114.2
C(9)-C(9')	1.52		

The C-C bonds are somewhat shorter and the C-C-C angles somewhat larger than those found in n-alkanes generally. The lower members, whose structures are more accurately known, give typically 1.533 (6) Å and 112.1 (3)° (for pentane, see Mathisen, Norman & Pedersen, 1967). The results obtained here may well be due to the marked librational motion of the carbon atoms in planes normal to the chain axis. This is well illustrated by the ORTEP plot Fig. 1 which shows a

steady increase in size of the thermal ellipsoids as one moves outwards from the centre of the molecule. This would have the well known effect of bringing the mean positions of the carbon atoms inwards towards the chain axis thus shortening the C-C bonds and widening the C-C-C angles.

Packing

The shortest non-bonded contacts are all H...H. Fig. 2 shows the central parts of the molecules in z projection and, because the molecules are parallel to each other, the diagram is typical of those for any other sets of carbon atoms along the chain. (The only change is a movement away from the origin of coordinates because the molecular axis is not parallel to the z axis.)

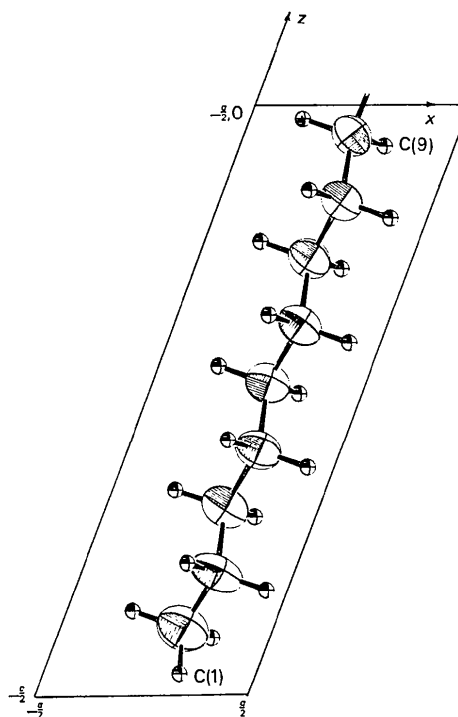


Fig. 1. ORTEP plot of half-molecule in y projection.

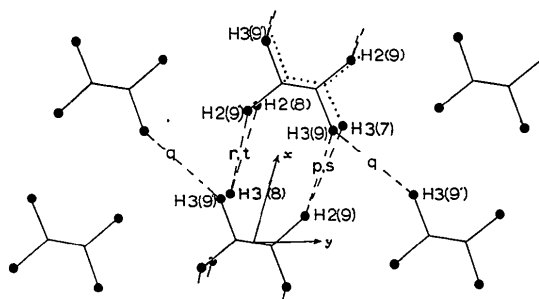


Fig. 2. Close contacts illustrated for molecular centre in z projection.

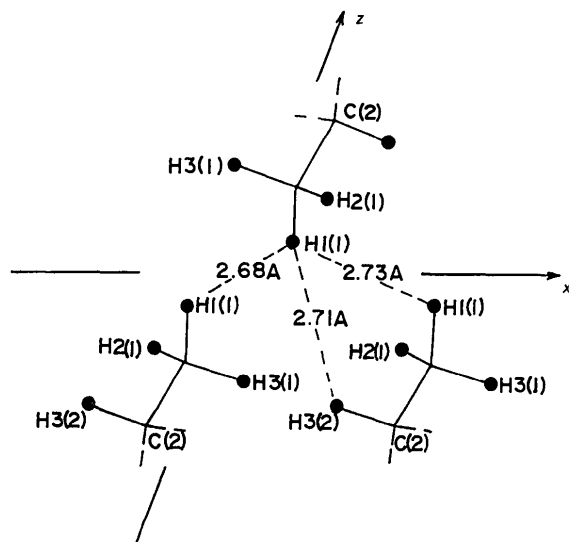


Fig. 3. Close contacts at ends of molecules (y projection).

The centre of symmetry at the molecular midpoint is between atoms C(9) and C(9'), Fig. 2. The shortest H...H distances between adjacent chains are of five kinds and are very closely similar in length. Atom H2(9) lies $p=2.68$ Å from H3(9) and $s=2.60$ Å from H3(7). The distances p and s for the whole chain range between 2.67₈ and 2.68₄ Å and 2.57 and 2.61 Å respectively. Because of the centre of symmetry at the molecular midpoint H2(7'), H2(9') are related in the same way. However, if we move down the chain towards C(1),

the hydrogen atoms lying beneath H2(9') and H3(9') are all attached to even-numbered carbon atoms. These hydrogen atoms show similar non-bonded distances to those on neighbouring chains. Thus distance r , typified by H2(8)–H3(8), is 2.69 Å and t , typified by H2(8)–H3(9'), is 2.64 Å. The distances r range between 2.68 and 2.69 Å, distances t between 2.62 and 2.64 Å.

The fifth type of close contact between adjacent chains is q , typified by H3(9)–H3(9'), 2.59 Å. These q distances range between the latter value and 2.69 Å.

There are three types of H...H contact between the ends of the chains. Two of these of length 2.68 and 2.73 Å are between H1(1) terminal hydrogen atoms and the other of length 2.71 Å is between H1(1) of one chain and H3(2) of another (Fig. 3).

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A Neutron Diffraction Study of the Anisotropic Thermal Expansion of β -Uranyl Dihydroxide

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Neutron diffraction powder patterns were taken to obtain positional parameters for all the atoms in β - $\text{UO}_2(\text{OH})_2$ at six temperatures from 21 to 260°C. The results confirm that the strongly anisotropic thermal expansion of this material is caused by the rotation of oxygen octahedra in the structure. These octahedra also undergo temperature-induced shape changes, which may be attributed to the effects of hydrogen bonding in the structure.

Introduction

In a previous publication (Bannister & Taylor, 1970), it was shown that the thermal expansion of β - $\text{UO}_2(\text{OH})_2$ is anisotropic, with a large contraction in a , a large expansion in b and a smaller cyclic change in c . The anisotropy reaches a saturation level at 260°C. It was

proposed that the effect is caused by a rotation of the U–O(2) (hydroxyl oxygen) bonds about [110], their inclination to that direction being unchanged. At saturation, the O(2) atoms reach their maximum possible intrusion into holes in the structure, and the O(2) plane of the oxygen octahedra surrounding each uranium atom has its maximum tilt with respect to the (001)