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A Twinned Structure for *n*-Tetracosane

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Abstract

A platy specimen of *n*-$C_{24}H_{50}$ grown from *n*-dodecane has been found to be a twin. Bragg reflections from the two twins overlap extensively and a cyclic procedure was used to correct the observed intensities for mutual overlapping. The resulting data could only be refined isotropically to $R = 0.23$, but the molecule is not overly distorted. The crystal structure is isostructural with other even triclinic, $P\bar{1}$ *n*-alkanes.

Introduction

The crystal structures of the *n*-alkanes with an even number of C atoms from C_6H_{14} to $C_{22}H_{46}$ are known with considerable certainty (Nyburg & Gerson, 1992; Heyding, Russell, Varty & St-Cyr, 1990). They are isostructural, triclinic, $P\bar{1}$, with one molecule per unit cell. Their cell dimensions fit well with those predicted from the $C_{18}H_{38}$ structure (Nyburg & Lüth, 1972) by Nyburg & Potworowski (1973) (N & P). Up to $C_{22}H_{46}$ no polymorphs have been reported. Above $C_{22}H_{46}$ the structures become less certain. While lattice parameters consistent with those predicted have been reported for $C_{24}H_{50}$ and $C_{26}H_{54}$ (Heyding, Russell, Varty & St-Cyr, 1990) powder patterns have also been reported which yield ambiguous results (Gerson, Roberts & Sherwood, 1991). The cell dimensions predicted for $C_{28}H_{58}$ (N & P) from the monoclinc $C_{36}H_{74}$ structure (Shearer & Vand, 1956) have been confirmed (Gerson, Roberts & Sherwood, 1991). An orthorhombic polytypic modification of this structure has also been reported (Boistelle, Simon & Pèpe, 1976).

We felt it desirable to attempt the crystal structure analysis of $C_{24}H_{50}$. In the event we were frustrated by our inability to grow a single crystal. The best crystals we could grow were twinned. Bragg reflections from the two twins overlap badly and only an approximate crystal structure could be established. However, $C_{24}H_{50}$ does appear to belong to the isostructural series of triclinic even *n*-alkanes.

Experimental

A flat plate (1 × 0.6 × 0.3 mm) of $C_{24}H_{50}$ (Aldrich Chemical Company Ltd) giving well-defined extinctions on rotation in cross-polarized light was cut from an agglomeration grown in *n*-dodecane ($C_{12}H_{26}$) by slow cooling from 303 to 298 K.

On a $0kl$ precession photograph, the $00l$ reflections were clearly resolved. Their spacing $c^* = 0.033$ Å^{-1}, agrees well with $c^* = 0.0331$ Å^{-1} from the predicted cell (N & P): $a = 4.285$, $b = 4.82$, $c = 32.50$ Å, $\alpha = 86.43$, $\beta = 68.71$, $\gamma = 72.7°$.

The $01l$ row, by contrast, had less-well resolved reflections and exhibited one striking anomaly: two prominent reflections with a separation of $1.65c^*$ along z^* (Fig. 1). This can be explained as due to twinning. First, we assume the $0kl$ planes from the two twins, $t1$ and $t2$ are coplanar. Second, we assume that the two z^* axes are collinear or nearly so. If the N & P cell is assumed, the $01l$ reflections with anomalous separation can be indexed as 01,13 from one twin and $0\bar{1}$,12 from the other (Fig. 1). Their separation along z^* calculates as $1.66c^*$ as required, and allows an unambiguous assignment of the x^* axes to be made. A consequence of this mutual

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orientation of the two axial systems is that for a fixed *h* and *k* the *hkl* row of one twin and the $\overline{hkl}$ row of the other are closely collinear and, because of the small magnitude of c^*, there will be extensive overlapping of reflections.

Examination of the *hk*0 precession photograph of one twin showed that it was not a single crystal; some reflections showed up to six closely spaced contributions. This added considerably to the difficulty of obtaining good orientation matrices on the diffractometer. An *hk*0 photograph of the other twin was not taken. A schematic view of the possible crystal composition is shown in Fig. 2.

The sample was transferred to a Picker four-circle diffractometer where, despite considerable overlap of the reflections from the two twins, two orientation matrices could be obtained. Ni-filtered Cu $K\alpha$ was used to determine the positions of 16 reflections from each twin, $39.8 < 2\theta < 79.0°$. The resulting least-squares unit cells are: *t*1, $a = 4.282$ (6), $b = 4.828$ (6), $c = 32.56$ (2) Å, $\alpha = 86.20$ (8), $\beta = 68.83$ (9), $\gamma = 72.3$ (1)°; *t*2, $a = 4.289$ (7), $b = 4.82$ (1), $c = 32.54$ (2) Å, $\alpha = 86.19$ (9), $\beta = 68.55$ (8), $\gamma = 72.2$ (2)°. They are both close to the N & P prediction (see above). In a few cases a strong reflection from a twin was free from overlap and a θ–2θ scan showed the half width to be about 0.4°.

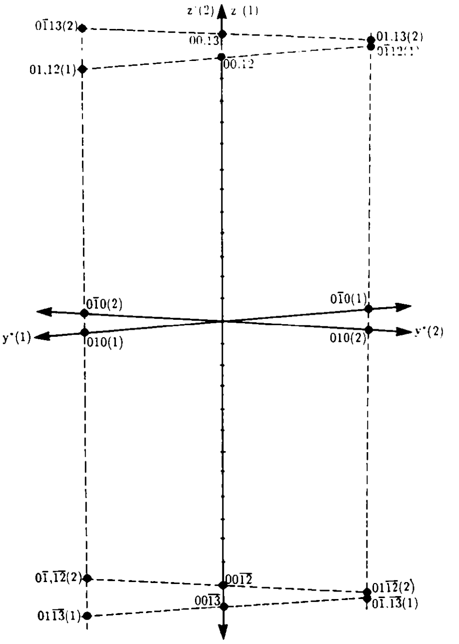

Fig. 1. Layout of some reflections on the precession photo of the 0*kl* plane. The z^* axes of the two twins are collinear. The $0\bar{1},\overline{12}$ reflection of *t*2 is separated from the $01,\overline{13}$ reflection of *t*1 by $1.66c^*$. This can be calculated from $c^* + [2b^*\sin(\alpha^* - 90°)/c^*]$.

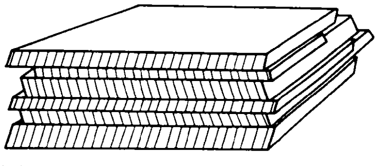

Fig. 2. Possible composition of the crystal. Hatching indicates the two twin components.

Using the two orientation matrices, two sets of data were collected in the range $5 < 2\theta < 90°$, each reflection being scanned over 3° in θ–2θ scan mode at 3° min^{-1} with 1.5 min of background counts at each end. The intensity of a standard reflection was measured every 25 reflections and showed no significant decay for either twin. The index ranges were *h*, 0 to 3, *k*, $\bar{3}$ to 4 and *l*, $\overline{26}$ to 27. 945 reflections were measured for both *t*1 and *t*2 of which 345 and 415 respectively were significant $[I > 2.5\sigma(I)]$ after the correction for overlap in cycle 4. Friedel-related reflections were not measured.

For the first cycle of data refinement the relative masses of the two twins were not required. Not unexpectedly, if the data set for either twin was not corrected for overlap from the other, no crystal structure result could be obtained.

To make overlap corrections it is necessary to establish the form of the reflection profile. We made no attempt to decompose the reflection profile into separate parts, $I_{\text{rel}}(hkl)$, thermal-diffuse scattering and general background. Virtually all reflections of the lesser *t*1 suffer from overlap from *t*2. However, in many cases, the overlap is highly asymmetric, being confined to largely one end of the θ–2θ profile. Several functions were examined in an attempt to match the profile. The one found to give the best fit was that used for powder data of the form (Hall, Veeraraghavan, Rubin & Winchell, 1977)

$$n(2\theta') = a(hkl)[1 + c(2\theta'/w)^2]^m \qquad (1)$$

where $n(2\theta')$ is counts deg^{-1}, $2\theta'$ is measured from the Bragg 2θ where the counts deg^{-1} is $a(hkl)$, w is the full width (°) of the profile between $2\theta'$ values at which $n(2\theta')$ is $a(hkl)/2$, and m and c are constant for all reflections. c is related to m *via*

$$c = 4(2^{1/m} - 1).$$

The best fit to the asymmetrically overlapped reflections of *t*2 and *t*1 yielded $w = 0.80°$ and $m = 1.22$.

We also examined ω profiles of a few reflections. Equation (1) did not fit these at all well. These ω scans commonly exhibited several subsidiary maxima due, no doubt, to the fragmentary nature of the twin components.

Overlap correction

From the diffractometer orientation matrices of *t*1 and *t*2 the distance *d*1 in *r* space (Fig. 3) between reflections from one twin to any reflection of the other can be calculated. Reflections separated by *d*1

> 0.033 Å^{-1} were deemed not to overlap. The exact nature of this overlap depends upon the two components of $d1$, $d2$ and $d3$ (Fig. 3), normal to and along the θ–2θ scan line in r space.

In order to use (1) to apply corrections for overlap we need the $a(hkl)$ values of the overlapping reflections. These can be obtained by dividing the θ–2θ scan count by the area under the curve of (1) between $2\theta'$ of ± 1.5° with $a(hkl)$ set to unity. We found this latter integral by graphical summation to be 1.02 counts. Knowing $a(hkl)$, $d2$ and $d3$ it is possible to calculate the counts which an overlapping reflection contributes to both the θ–2θ scan and to the backgrounds of any specified reflection of the other twin. Where subtraction of the counts resulted in a negative intensity, this intensity was set equal to one count so that it would be preserved as a very weak reflection in the least-squares refinement.

Clearly the above procedure, applied in the first cycle (see Fig. 4), is grossly inaccurate because the majority of reflections which cause overlapping are themselves overlapped and hence their $a(hkl)$ values derived by the above method are all in error to a lesser or greater extent.

First cycle of refinement

Corrections for overlapping of $t2$ by $t1$ were made as described. The resulting corrected $t2$ intensity data were subject to scaling and reduction and the E values used to generate eight $P\bar{1}$ phase sets using *SOLVER* (Gabe, Le Page, Charland, Lee & White, 1989). The E maps fell into two classes of four each. One class showed a disordered chain of atoms, the second had a clearly resolved chain of atoms closely isostructural to those of the other triclinic *n*-even alkanes. In view of the close agreement with the cell expected we chose the latter structure for further refinement.

The phase assignment in this class was used for the C-atom coordinates with isotropic thermal factors $u = 0.06$, the average of those found in $C_{20}H_{42}$ (Nyburg & Gerson, 1992). H atoms were added with isotropic factors $u = 0.10$. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). Carbon positions and thermal factors were refined by least squares, giving a final unweighted residual of 0.32. Refinement of all the parameters in all the cycles was based on F values.

Second and subsequent cycles

The molecular model obtained from least squares had a somewhat irregular geometry. It was replaced, using the best-fitting program *BMFIT* (Yuen & Nyburg, 1979) by an idealized model having C—C, 1.519 Å, C—C—C, 113.37° and C—H 1.0 Å. One isotropic thermal factor $u = 0.073$ (the average from

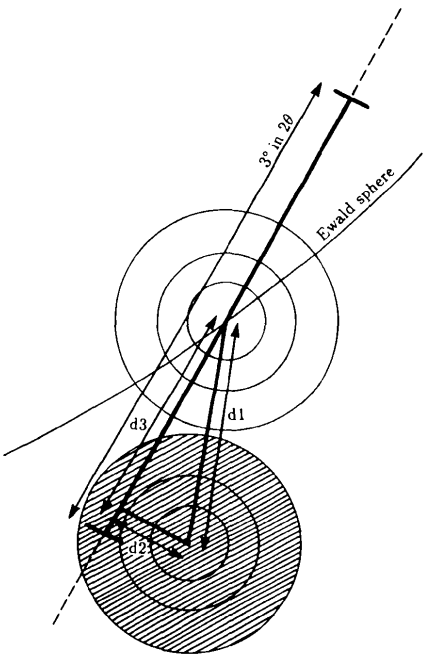

Fig. 3. The overlap of a reflection (hatched) on the 3° 2θ scan of another reflection (not hatched), in reciprocal space. $d1$ is the distance between the centers of the two reflections. $d2$ and $d3$ are the components of $d1$ normal and parallel to the 2θ scan trajectory.

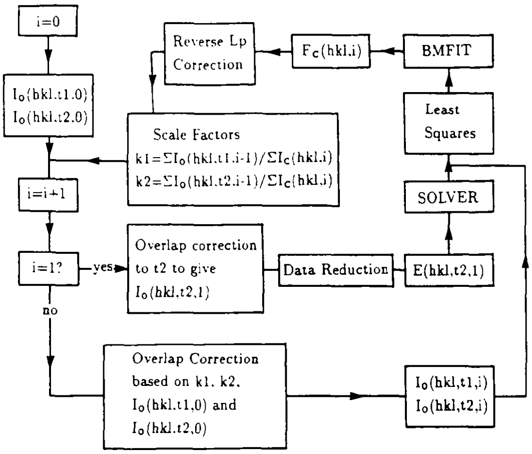

Fig. 4. A flow chart of the procedure undertaken to correct the data sets of both twins for overlap. i is the number of cycles carried out. $I_o(hkl,t1,i)$ and $I_o(hkl,t2,i)$ indicate the data sets for $t1$ and $t2$, respectively, after i cycles. Cycle 0 is the situation where the data are uncorrected for overlap. $E(hkl,t2,1)$ indicates the E values generated for $t2$ during cycle 1. *SOLVER* generates phase sets from these E values. Least squares refines the model against the corrected data. An idealized molecule is fitted to the refined model using *BMFIT* to produce a model for the next cycle. $F_c(hkl,i)$ are the calculated scattering factors. Lp is the Lorentz–polarization correction. $I_c(hkl,i)$ are the reflection intensities calculated from the model.

Table 1. *The progress of each cycle*

S is the goodness of fit. BMF is the sum of the deviations squared (Å^2) between the idealized molecule and the refined model.

	Twin 1				Twin 2				Mass ratio
Cycle	*R*	*wR*	*S*	BMF	*R*	*wR*	*S*	BMF	*t*1:*t*2
1					0.32	0.33	28	0.75	
2	0.30	0.38	30	1.51	0.25	0.24	22	0.67	1:1.47
3	0.31	0.38	31	1.41	0.25	0.23	22	0.71	1:1.74
4	0.28	0.31	25	1.31	0.23	0.19	17	0.63	1:1.74

the last cycle) was applied to all C atoms. The H-atom thermal factor was 1.2 times those for carbon, $u = 0.09$.

To apply intensity-overlap corrections based on a molecular model it is necessary to know the scale factors relating the observed to calculated intensities for both twins. These were obtained from $k = \sum I_o(hkl)/\sum I_c(hkl)$ for both twins, $I_o(hkl)$ being uncorrected for overlap. The *k* values of the two twins give their mass ratio which, at this stage, calculated as $t1{:}t2 = 1{:}1.47$.

Subsequent cycles were run in the same manner except that *k* factors were based on overlap-corrected observed intensities.

There was no significant change in the molecular model obtained after four cycles of refinement. Table 1 summarizes the progress at the end of each cycle.

Although the final residual, 0.23, is poor by conventional structure-analysis standards, nevertheless the molecular model obtained is not greatly distorted (Fig. 5). In addition the sum of squares of the deviations of the C atoms from an idealized model is quite small, 0.63 Å^2. The bond lengths of the final refined structure of *t*2 vary from 1.44 to 1.67 Å with an average of 1.54 (6) Å. The bond angles vary from 102 to 118° with the average being 112 (5)°. The final average temperature factor for the carbons was $U = 0.07$ Å^2. The diad relationship between the orientation of the unit cells of the two twins is shown in Fig. 6.*

We noted a few quite poor agreements between F_o and F_c, in particular for *t*1 01$\bar{2}$, $F_o - F_c = 32.17$, 106, $F_o - F_c = 44.64$, 11$\bar{8}$, $F_o - F_c = 48.08$ and *t*2 $\bar{1}1\bar{6}$, $F_o - F_c = 15.36$, 11$\bar{8}$, $F_o - F_c = 26.08$, 02,11, $F_o - F_c = 18.79$. We did 2θ profiles of these reflections of *t*2 and found the interfering reflections for *t*1 were neither of the calculated intensity, nor in the calculated position. We attribute this to the multiple structure of the twins. Having only one orientation

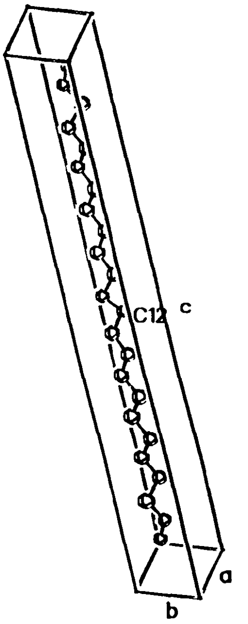

Fig. 5. *ORTEP* plot (Johnson, 1965) of the $C_{24}H_{50}$ molecule of *t*2 at cycle 4.

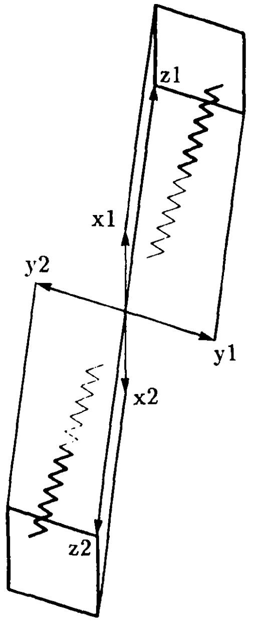

Fig. 6. The relationship in orientation of the unit cells of the two twins in *z** projection.

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* Lists of atomic fractional coordinates of the final idealized $C_{24}H_{50}$ structure, the corresponding structure factors and the experimentally observed structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55241 (8 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

matrix for each of the twins is insufficient to completely define the overlapping. The Renninger effect did not appear to be the cause of these spurious reflections.

Discussion

It is not clear whether $C_{24}H_{50}$ is particularly prone to twinning; twins of $C_{28}H_{58}$ (Aquilano, 1977; Boistelle & Aquilano, 1977) and also of $C_{33}H_{68}$ (Piesczek, Strobl & Malzahn, 1974) have been reported. For $n > 24$ one is entering the range where even alkanes change their mode of packing from triclinic to monoclinic and othorhombic. The reported existence of a polytypic monoclinic modification of $C_{28}H_{58}$ (Boistelle, Simon & Pèpe, 1976), with adjacent layers of molecules related by a diad axes normal to the basal plane, may be a related phenomenon.

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