

potential has effective threefold symmetry, with a barrier near 20 kJ mol^{-1} .

To be sure, the poor quality of the ADPs in these structures limits the precision of the barrier heights calculated from them, and the arbitrary choices in disorder-model refinement limit the precision of the energy differences calculated from non-bonded potentials. Nevertheless we are encouraged by the complementary and consistent results from potential-energy calculations and from ADP analysis to continue looking at crystal structures containing librating, possibly rigid groups that are chemically but not crystallographically equivalent. We plan to study (1) and related molecules using low-temperature solid-state ^{13}C NMR, and plan also to make variable-temperature crystal structure analyses of other compounds with *tert*-butyl and similar substituents.

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X-ray Powder Diffraction Studies of Alkanes: Unit-Cell Parameters of the Homologous Series $\text{C}_{18}\text{H}_{38}$ to $\text{C}_{28}\text{H}_{58}$

BY A. R. GERSON, K. J. ROBERTS* AND J. N. SHERWOOD

Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow G1 1XL, Scotland

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Abstract

Synchrotron radiation high-resolution powder diffraction has been applied to determination of the unit-cell parameters of *n*-alkanes in the range $\text{C}_{18}\text{H}_{38}$ to $\text{C}_{28}\text{H}_{58}$. The data confirm the previously reported results for $\text{C}_{18}\text{H}_{38}$, $\text{C}_{20}\text{H}_{42}$, $\text{C}_{23}\text{H}_{48}$ and $\text{C}_{25}\text{H}_{52}$. With the exception of $\text{C}_{24}\text{H}_{50}$ and $\text{C}_{26}\text{H}_{54}$, these data support the predictions made for the other homologues in this series by Nyburg & Potworowski [*Acta Cryst.* (1973), **B29**, 349–352] *i.e.* $\text{C}_{18}\text{H}_{38}$, $\text{C}_{20}\text{H}_{42}$ and $\text{C}_{22}\text{H}_{46}$ – triclinic unit cells ($Z = 1$), $\text{C}_{28}\text{H}_{58}$ – monoclinic unit cell ($Z = 2$), and $\text{C}_{19}\text{H}_{40}$, $\text{C}_{21}\text{H}_{44}$, $\text{C}_{23}\text{H}_{48}$, $\text{C}_{25}\text{H}_{52}$ and $\text{C}_{27}\text{H}_{56}$ – orthorhombic unit cells ($Z = 4$). In contrast, $\text{C}_{24}\text{H}_{50}$ and $\text{C}_{26}\text{H}_{54}$ are found to have lattice parameters consistent with a triclinic (pseudo-monoclinic) unit cell containing two molecules possibly arranged in a polytypic conformation of two

triclinic ($Z = 1$) unit cells related by a pseudo-twofold axis.

1. Introduction

The structures of *n*-alkanes ($\text{C}_n\text{H}_{2n+2}$) in the range $10 < n < 36$ are of fundamental and technological importance. The first structural studies on the *n*-alkanes are probably due to Müller (1928, 1930, 1932). Lattice parameters have been measured for $\text{C}_{18}\text{H}_{38}$ (Müller & Lonsdale, 1948), $\text{C}_{20}\text{H}_{42}$ (Crissman, Passaglia, Eby & Colson, 1970), $\text{C}_{23}\text{H}_{46}$ (Retief, Engel & Boonstra, 1985*a,b*) and $\text{C}_{25}\text{H}_{52}$ (Retief *et al.*, 1985*a,b*). Full structures have been determined for $\text{C}_{18}\text{H}_{38}$ ($Z = 1$, $P\bar{1}$) (Nyburg & Lüth, 1972) and for the monoclinic ($Z = 2$, $P2_1/a$) (Scheerer & Vand, 1956) and orthorhombic ($Z = 4$, $Pca2_1$) (Teare, 1959) polymorphs of $\text{C}_{36}\text{H}_{74}$. These three structures are shown schematically in Fig. 1. Nyburg & Potworowski (1973) predicted the lattice parameters of *n*-alkanes in the range $n = 6$ –40.

* Also at SERC Daresbury Laboratory, Warrington, WA4 4AD, England.

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Lüth, Nyburg, Robinson & Scott (1972) proposed the following overall scheme for the expected crystal structures of the *n*-alkanes: *n* even, $12 < n < 28$ – triclinic, $Z = 1$, $P\bar{1}$; *n* even, $n > 26$ – monoclinic, $Z = 2$, $P2_1/a$; *n* odd, $12 < n < 40$ – orthorhombic, $Z = 4$, $Pca2_1$. These predictions have yet to be extensively verified experimentally.

Polytypism is also well known in these materials and orthorhombic polytypic structures (based on a monoclinic subcell) for $C_{28}H_{58}$ and $C_{36}H_{74}$ ($Pbca$, $Z = 4$) (Boistelle, Simon & Pépe, 1976) and $C_{36}H_{74}$ ($Pca2_1$, $Z = 4$) (Teare, 1959) have also been reported. It is likely (Teare, 1959; Smith, 1953; Müller, 1930) that these polymorphs are due to the presence of impurities within the sample or to solvent effects.

Determination of these structures using single-crystal X-ray methods can be difficult since these materials crystallize in the form of plates which are typically only a few hundred μm thick. They also tend to twin readily across the close-packed (00 l) planes. Powder diffraction provides a potential solution to this problem. The combination of large unit cells and low crystal symmetry produces a high density of diffraction lines in the powder patterns. *Ab initio* indexing of such patterns requires the high-quality data which is obtained by using the synchrotron radiation parallel-beam powder diffraction technique. Previously when these high-quality data were not available it was common (*e.g.* Hoffman & Decker, 1952; Broadhurst, 1962) to base the phase analysis on the (00 l) reflections, owing to the difficulties associated with the unambiguous indexing of reflections of, for example, the ($hk0$) type. This method of identification can be problematic since the lattice spacings of the (00 l) type are very similar in all the known polymorphs.

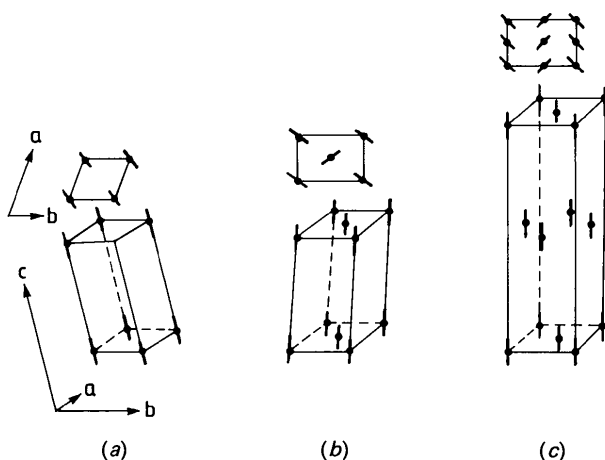


Fig. 1. A schematic representation of the molecular arrangements as found in (a) triclinic $C_{18}H_{38}$ ($P\bar{1}$), (b) monoclinic $C_{36}H_{74}$ ($P2_1/a$) and (c) orthorhombic $C_{36}H_{74}$ ($Pbc2_1$).

Synchrotron radiation techniques can provide excellent angular resolution together with an almost total elimination of sample misalignment and beam-focussing errors (Hart & Parrish, 1986) and enable extremely high-quality powder diffraction patterns to be obtained.

In this paper we report the unit-cell parameters determined from synchrotron X-ray powder diffraction patterns of the *n*-alkanes in the range $C_{18}H_{38}$ to $C_{28}H_{58}$.

2. Unit-cell conventions for *n*-alkanes

2.1. Triclinic unit cells of even *n*-alkanes

The most convenient choice of axes for the comparisons to be made here is that used by Nyburg & Lüth (1972) in the structural refinement of $C_{18}H_{38}$ and by Nyburg & Potworowski (1973) in the predictions of the lattice parameters of the other even *n*-alkanes. In this, which we call axial choice (1), the *c*-parameter direction is as nearly parallel as possible to the long axes of the *n*-alkane molecules, and the *a* and *b* parameters change very little from one *n*-alkane to the next. A different axial choice (2) is used by Norman & Mathison (1961*a,b*) to describe the structures of C_6H_{14} and C_8H_{18} and by Mathison, Norman & Pedersen (1967) for the structures of C_5H_{12} and C_8H_{18} . A more conventional choice for a triclinic unit cell, with α and β as close to 90° as possible, choice (3), was used by Müller & Lonsdale (1948) for $C_{18}H_{38}$ and by Crissman *et al.* (1970) for $C_{20}H_{42}$. The program *ITO* (Visser, 1969) used here, yields this choice. $\mathbf{a}_2, \mathbf{b}_2, \mathbf{c}_2$ of choice (2) or $\mathbf{a}_3, \mathbf{b}_3, \mathbf{c}_3$ of choice (3) may be transformed to $\mathbf{a}_1, \mathbf{b}_1, \mathbf{c}_1$ of choice (1) as follows:

$$\begin{pmatrix} \mathbf{a}_1 \\ \mathbf{b}_1 \\ \mathbf{c}_1 \end{pmatrix} = \begin{pmatrix} 1 & 0 & 1 \\ 0 & 1 & 0 \\ -1 & 0 & 1 \end{pmatrix} \begin{pmatrix} \mathbf{a}_2 \\ \mathbf{b}_2 \\ \mathbf{c}_2 \end{pmatrix} = \begin{pmatrix} -1 & 0 & 1 \\ 0 & 1 & 0 \\ -2 & 0 & 1 \end{pmatrix} \begin{pmatrix} \mathbf{a}_3 \\ \mathbf{b}_3 \\ \mathbf{c}_3 \end{pmatrix}.$$

The lattice parameters of the even *n*-alkanes from C_6H_{14} up to and including $C_{24}H_{50}$ were predicted by Nyburg & Potworowski to be isostructural with $C_{18}H_{38}$ (triclinic, $Z = 1$). The structure of $C_{26}H_{54}$ (Hoffman & Decker, 1952; Broadhurst, 1962) was predicted either to conform to this pattern or to be similar to the monoclinic or orthorhombic ($Pca2_1$) form of $C_{36}H_{74}$.

2.2. Even *n*-alkane monoclinic unit cells

The refinement of Schearer & Vand (1956) showed that the *n*-alkane chains in the monoclinic form of $C_{36}H_{74}$ were aligned approximately parallel to the *z* axis in a unit cell of choice (4) axial system. This axial system is used for monoclinic unit cells in this

paper. The transformation from a choice (3) monoclinic axial system (β being set as close as possible to 90°) as output by Visser's indexing program (1969) to a choice (4) monoclinic unit cell is:

$$\begin{pmatrix} \mathbf{a}_4 \\ \mathbf{b}_4 \\ \mathbf{c}_4 \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ -3 & 0 & 1 \end{pmatrix} \begin{pmatrix} \mathbf{a}_3 \\ \mathbf{b}_3 \\ \mathbf{c}_3 \end{pmatrix}.$$

2.3. Orthorhombic unit cells of odd *n*-alkanes

The unit cells of odd *n*-alkanes have been predicted (Nyburg & Potworowski, 1973) to be of similar dimensions (except for the *c* parameter) to those of C₂₃H₄₈, C₂₅H₅₂ and the orthorhombic form of C₃₆H₇₄. Since we have interchanged Teare's (1959) *a* and *b* axes, the space group in *Pbc*2₁.

3. Experimental

All samples were obtained from Aldrich and had a stated purity of at least 99%. Powder samples were prepared by recrystallization twice from *n*-dodecane (C₁₂H₂₆) at room temperature followed by grinding. A particle size of approximately 0.05 mm was achieved.

X-ray powder diffraction spectra were recorded on the high-resolution powder diffractometers on stations 8.3 and 9.1 (Pattison, Cernik & Clark, 1988) at Daresbury Laboratory. The wavelength was selected by a channel cut silicon (111) monochromator and was approximately 1.5 Å. The wavelength and zero point were calibrated from the first five peaks observed for a Si (NBS 640b) standard. The wavelength was determined to ±0.001 Å and the zero point to ±0.01° in 2θ. The resolution obtained on both stations gave a peak half-width of 0.05° in 2θ. All spectra were recorded over the range 2θ = 2–100°.

4. Data analysis

The powder diffraction patterns were indexed using *ITO*, a computer program devised by Visser (1969) specifically optimized for the indexing of low-symmetry powder patterns. In no case was the type of unit cell initially stipulated.

Using the program the degree of fit of the diffraction pattern to a set of lattice parameters is assessed by the number of peaks indexed from the first 20 peaks observed and a figure of merit. A peak was considered indexed if the difference between the observed position and a calculated position was less than 0.03°. In all cases the figure of merit was greater than 4, and more than 18 out of the first 20 peaks were indexed.

For triclinic unit cells the unambiguous indexing of peaks at high diffraction angles is not possible due to extremely high peak densities. The number of peak positions used as data for each sample is given in Table 1; the maximum number accepted by the program is 40. (For C₁₈H₃₈ 854 peaks are predicted in the 2θ range 0–100°.) In all cases the unit-cell parameters were refined with *ITO* against the input data until no further change occurred, and then further refined using the program *REFCEL* from the Daresbury Laboratory Powder Diffraction Library to give the values in Table 1. The data for this program consisted of the index and position for all unambiguously indexed peaks as well as the wavelength and zero point.

5. Results

Lattice parameters, standard deviations and unit-cell volumes are given in Table 1. All unit-cell parameters reported fulfil the criteria for order of merit and numbers of peaks indexed stated above. An example of the high quality of powder diffraction obtained is given in Fig. 2. Fig. 3 shows a comparison of the (00*l*) peaks for the even alkanes in the range studied.

5.1. Confirmation of previously measured unit cell

The unit cells determined for C₁₈H₃₈ and C₂₀H₄₂ agree with previous measurements [C₁₈H₃₈ (Müller & Lonsdale, 1948), C₂₀H₄₂ (Crissman *et al.*, 1970)] and predictions (Nyburg & Potworowski, 1973). The unit cells obtained for the odd *n*-alkanes (C₂₃H₄₈ and C₂₅H₅₂) also agree with those previously recorded [C₂₃H₄₈ (Smith, 1953), C₂₅H₅₂ (Retief *et al.*, 1985*a,b*)] and also with the unit cells predicted by Nyburg & Potworowski (1973).

5.2. Lattice parameters not previously measured

5.2.1. *Odd n-alkanes* (C₁₉H₄₀, C₂₁H₄₄, C₂₇H₅₆). The unit cells determined for C₁₉H₄₀, C₂₁H₄₄ and C₂₇H₅₆ agree with the orthorhombic (*Z* = 4) lattice parameters predicted by Nyburg & Potworowski (1973).

5.2.2. *Even n-alkanes* (C₂₂H₄₆, C₂₄H₅₀, C₂₆H₅₄, C₂₈H₆₀). The unit cell determined for C₂₂H₄₆ agrees with the parameters extrapolated from those of C₁₈H₃₈ (Nyburg & Potworowski, 1973) and is triclinic with *a*, *b*, α and γ nearly equal to those of C₁₈H₃₈ but with a longer *c* parameter. The unit cells of C₂₄H₅₀ and C₂₆H₅₄ do not agree with the lattice parameters predicted and are discussed further below. However, the unit cell found for C₂₈H₅₈ does agree with the unit cell predicted by Nyburg & Potworowski (1973) from the monoclinic form of C₃₆H₇₄, the only difference being in the length of the *c* parameter.

Table 1. Unit-cell parameters of *n*-alkanes from C₁₈H₃₈ to C₂₈H₅₈ with *e.s.d.*'s below

No. of C atoms ^a	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	α (°)	β (°)	γ (°)	<i>V</i> (Å ³)	<i>z</i>	Figure of merit	No. of peak positions ^b
Choice (1) axial system										
18	4.293	4.826	24.823	85.115	67.785	72.540	454	1	132	40
	0.001	0.001	0.004	0.004	0.02	0.02				
20	4.282	4.818	27.412	85.586	68.279	72.607	501	1	109	40
	0.0003	0.0004	0.001	0.005	0.008	0.006				
22	4.289	4.823	29.544	86.237	70.661	72.097	548	1	37	39
	0.0003	0.0004	0.0001	0.007	0.007	0.01				
24	5.275	7.671	33.022	83.580	66.793	82.739	1219	2	35	40
	0.0002	0.0004	0.002	0.03	0.02	0.01				
26	5.261	7.675	35.284	83.642	68.365	83.011	1312	2	12	32
	0.003	0.005	0.001	0.05	0.05	0.07				
Choice (3) axial system										
24	4.272	4.810	60.589	91.341	90.737	107.300	1188	2	47	40
	0.0006	0.0006	0.004	0.01	0.01	0.01				
26	4.270	4.813	65.447	91.189	89.488	107.351	1283	2	45	32
	0.003	0.0006	0.005	0.03	0.10	0.01				
Choice (4) axial system										
28	5.577	7.421	38.254	90.000	119.684	90.000	1389	2	47	29
	0.004	0.004	0.006		0.03					
Orthorhombic axial system										
19	4.975	7.458	51.999	90.000	90.000	90.000	1929	4	12	37
	0.001	0.001	0.007							
21	4.970	7.463	57.089	90.000	90.000	90.000	2118	4	51	39
	0.0006	0.0009	0.005							
23	4.968	7.441	62.369	90.000	90.000	90.000	2301	4	16	40
	0.002	0.004	0.02							
25	4.962	7.442	67.240	90.000	90.000	90.000	2483	4	17	39
	0.001	0.002	0.005							
27	4.953	7.455	72.588	90.000	90.000	90.000	2680	4	6	35
	0.002	0.003	0.02							

Notes: (a) the number of C atoms per alkane chain; (b) the number of peak positions used as data.

It was not possible to unambiguously index the diffraction patterns for C₂₄H₅₀ and C₂₆H₅₄ due to the profusion of peaks present. The diffraction patterns did indicate that both C₂₄H₅₀ and C₂₆H₅₄ had low-symmetry structures which were likely to be very similar. It was possible however to grow a single crystal of C₂₄H₅₀ and it was from X-ray analysis of this crystal that the lattice parameters for C₂₄H₅₀ were initially identified (Nyburg, 1990). Subsequently these lattice parameters were confirmed from the

powder diffraction data for C₂₄H₅₀ and similar lattice parameters identified for C₂₆H₅₄.

The unit cells determined for C₂₄H₅₀ and C₂₆H₅₄ are triclinic with a *c* parameter indicating a two-layer structure. The systematic absence (00*l*): *l* = 2*n* + 1 is present in the powder diffraction patterns and suggests a pseudo-monoclinic molecular conformation. The similarity of the *a* and *b* parameters for the unit

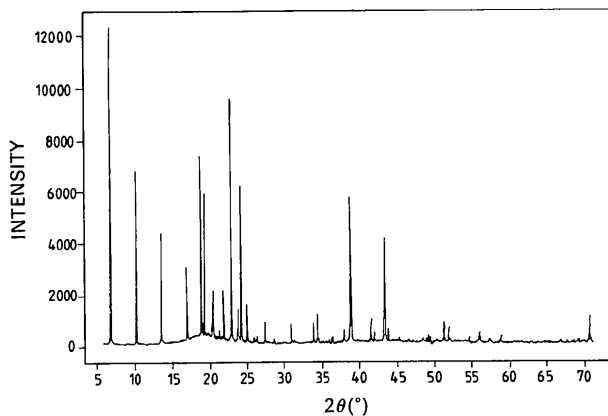


Fig. 2. Powder diffraction pattern of C₁₈H₃₈. Intensity is given as counts per 2 s.

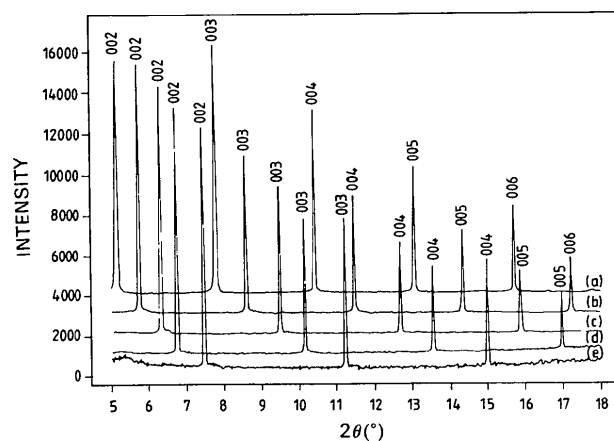


Fig. 3. Long lattice spacing (00*l*, *l* = 2–5) peaks: (a) C₂₆H₅₄, (b) C₂₄H₅₀, (c) C₂₂H₄₆, (d) C₂₀H₄₂ and (e) C₁₈H₃₈. Intensity is given as counts per 2 s.

cells of C₂₄H₅₀ and C₂₆H₅₄ with the unit cells for the shorter even alkanes (C₁₈H₃₈, C₂₀H₄₂ and C₂₂H₄₆) and the observation of α and β being near 90° suggests a polytypic structure containing two layers of triclinic ($Z=1$) 'type' unit cells related by a pseudo-twofold axis nearly perpendicular to the (00l) plane. This analysis is also substantiated by the similarity of γ for C₂₄H₅₀ and C₂₆H₅₄ to the value (180 - γ) for the shorter even *n*-alkanes.

These results emphasize the necessity of obtaining good-quality powder diffraction data over a wide range of 2θ in order to reliably identify such low-symmetry phases. Much of the confusion in the literature surrounding identification of alkane phases results either from impure samples or poor-quality data. High-resolution powder diffraction using a synchrotron source now provides an available technique capable of resolving the phase structure of the *n*-alkanes and other related low-symmetry materials.

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Conformational Analysis of Rotational Barriers in *N*-Arylpyrrolidin-2-ones

BY D. G. BILLING, J. C. A. BOEYENS,* L. DENNER, K. E. DU PLOOY, G. C. LONG AND J. P. MICHAEL
Department of Chemistry, University of the Witwatersrand, PO Wits, 2050 Johannesburg, South Africa

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Abstract

The structures of *N*-phenylpyrrolidin-2-one and the three isomeric *N*-tolylpyrrolidin-2-ones have been studied by single-crystal X-ray diffraction, as a basis for the conformational analysis of the barrier to rotation around the single bond between the rings. Force-field simulation of the molecular structure is consistent with a rotational barrier of 7 kJ mol⁻¹. Crystal data: *N*-phenylpyrrolidin-2-one, orthorhombic, *Pbca*, $a = 14.114$ (3), $b = 6.879$ (4), $c = 17.386$ (5) Å, $R = 0.059$ for 1110 unique reflections [$F_o \geq 4\sigma(F_o)$]; *N*-(2-methylphenyl)pyrrolidin-2-one,

orthorhombic, *Pbca*, $a = 16.999$ (4), $b = 16.411$ (2), $c = 7.008$ (2) Å, $R = 0.077$ for 1479 unique reflections [$F_o \geq 4\sigma(F_o)$]; *N*-(3-methylphenyl)pyrrolidin-2-one, monoclinic, *P2₁/c*, $a = 10.411$ (2), $b = 7.645$ (2), $c = 12.782$ (1) Å, $\beta = 110.32$ (1)°, $R = 0.065$ for 1641 unique reflections [$F_o \geq 4\sigma(F_o)$]; *N*-(4-methylphenyl)pyrrolidin-2-one, orthorhombic, *P2₁2₁2₁*, $a = 7.668$ (2), $b = 10.804$ (2), $c = 11.456$ (1) Å, $R = 0.054$ for 1155 unique reflections [$F_o \geq 4\sigma(F_o)$].

Introduction

Elementary theory predicts that bonds of even order produce sterically rigid structures whereas those of

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* Author for correspondence.