Lattice Parameters of Solid Solutions of Long-Chain n-Alkanes

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Abstract
Crystal lattice parameters of mixtures of the normal alkanes \( n-C_{23}H_{48} \) and \( n-C_{25}H_{52} \) have been determined by X-ray powder diffractometry. The c-axis length increases nearly monotonically with increasing \( C_{25}H_{52} \) content. \( a \) and \( b \) are larger for the mixtures than for the pure substances with maximum values at 15% \( n-C_{25}H_{52} \). The small but significant increases in \( a \) of 0.6% and \( b \) of 0.9% have not been previously reported.

Introduction
n-Alkanes crystallize in unit cells with one very long axis (c axis) to accommodate the long molecule. The ability of the molecules to form solid solutions with others with slightly different chain lengths has been extensively studied. Diffraction studies have been undertaken by, amongst others, Piper, Chibnall, Hopkins, Pollard, Smith & Williams (1931), Barbezat-Debreuil (1958), Kitaigorodskii & Mnyukh (1959) and reviewed by Mnyukh (1960). The variation of the 'long spacing', i.e. the (001) interplanar spacing, was determined as a function of composition.

The solid solutions are orthorhombic as are pure n-alkanes with an odd number of carbon atoms in the chain. Even-numbered n-alkanes have triclinic or monoclinic space groups (cf. Broadhurst, 1962; Nyburg & Potworowski, 1973).

We report here a diffraction study of solid solutions of \( n \)-tricosane \( (C_{23}H_{48}) \) and \( n \)-pentacosane \( (C_{25}H_{52}) \) in which the variation with composition of the \( a \) and \( b \) lattice parameters in addition to \( c \) is determined. The odd–odd mixture was chosen in order to have a continuous series of solid solutions over the whole range of compositions. An experimental procedure was developed for these substances based upon the use of an internal Si standard and the correction of the line centroids for instrumental aberrations. The procedure is described in the preceding paper (Retief, Engel & Boonstra, 1985) where it is applied to the two pure substances. The application of the method to Fischer–Tropsch waxes is described by Retief & le Roux (1983).

Experimental
Weighed amounts of \( n \)-tricosane and \( n \)-pentacosane (99% pure, Humphrey Chemical Co., North Haven) were mixed, melted in a stream of warm air and allowed to cool, while being stirred until the sample had solidified. The sample was ground, mixed with 5% Si powder and the diffractogram recorded using a Philips PW1050 vertical goniometer and Co Kα radiation. The peak centroid positions were determined and corrected as described by Retief, Engel & Boonstra (1985).

Results and discussion
The corrected centroid positions \( 2\theta_0 \) of nine reflections for each mixture are given in Table 1.* Lattice parameters (Table 1) were calculated from these by least-squares refinement and the differences between observed and calculated values of \( 2\theta \) are given in each case to indicate the precision of the procedure. The c axis is the direction in which the disorder (presence of chains of different length) is evidenced. The 001 reflection profiles are generally broader, and the broadening increases more rapidly with increasing \( l \) for the

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mixtures especially for compositions between 10 and 50% of the longer component. For these samples the weak 0.0.14 reflection was omitted. This broadening can be considered to be due to paracrystalline distortion (see Phaovibul, Cackovic, Laboda-Cackovic & Hosemann, 1973) in the end-group region of the chains as a result of the difference in chain length. While this broadening will not be considered further here, it is noted that the distortion is greatest for compositions between 10 and 90% of the longer component.

The variation of the lattice parameters with composition is illustrated in Fig. 1. Starting with pure C23H52 (abbreviated to C23) the c axis increases in length with increasing C25 content quite sharply at first. Above about 80% C25 c is virtually constant, decreasing slightly towards 100% C25. Replacing a small fraction of the molecules in the pure substance with shorter molecules thus leaves the c axis virtually unchanged while replacement with longer molecules causes a marked increase in c (see Mnyukh, 1960). Piper et al. (1931) reported similar behavior of the mixture of C29 with C31.

Mixing causes an increase in both a and b, the increase being more rapid on addition of longer molecules to the pure substance than on addition of shorter molecules. a has a flat maximum at about 17% C25 while b shows a very marked maximum in this region. The X-ray density D (Fig. 1) calculated from composition and lattice parameters exhibits a flat minimum for the 33% C25 mixture. Referred to the pure C23 sample there is a decrease of 2.3% in density of which 1.2% is due to ‘excess’ increase in c, but 0.6 and 0.5% respectively are due to the expansion of a and b. Thus the effect of packing difficulties in mixtures on a and b is by no means negligible compared to the well-established effect on c. The curve shows a slight subsidiary minimum at 17% C25 associated with the anomalous behavior of b.

Bonsor & Bloor (1977) have reported the variation of measured bulk density of C21–C23 mixtures with composition. One would expect similar behavior in the two systems as both are mixtures of odd n-alkanes differing in chain length by two carbon atoms. Their measurements do indeed show a similar reduction in density in the mixtures. There is, however, a much more marked minimum at 24% longer-chain content. A further difference is in the density of the pure C23 component common to both systems studied. Our X-ray density is 936 kg m−3 and their (measured) density 869 kg m−3. Their densities refer to an average value for crystalline and amorphous components and would thus be expected to be lower than X-ray densities. Air bubbles trapped in the samples would further lower the bulk density. It is possible that the large b value at 17% C25 indicates that the energy advantage on crystallization is not so great at this composition and that the amorphous fraction is larger, resulting in the very low bulk density observed by Bonsor & Bloor (1977). They have interpreted the decrease in density as due to the presence of voids in the crystalline phase.

The phase diagram of the C23–C25 binary system was determined using differential scanning calorimetry. Fig. 1 (curves T and H) shows the temperature and enthalpy of the solid–solid transition to the hexagonal high-temperature phase. The curves have the same general shape as the density curve. These quantities are thus generally low for the range of compositions where the molecular packing is inefficient (low density) and the crystallinity is poor (broad peaks). Mazee (1960) has determined thermodynamic parameters for the C21–C23 system.

Variations in the axial lengths a and b have been reported as a function of temperature (Kavesh & Schultz, 1969) and as a function of chain branching (Walter & Reding, 1956; Preedy, 1973). In both cases b is reported to increase much more strongly than a. A change in a and b due to admixture of a second component has not been reported before. The maximum change determined here is 0.6% in a and 0.7% in b if the sharp peak at 15% C25 is excluded and 0.9% in b if the peak is included. The effect of the admixture disturbing the correct registry of the end group of the chains thus appears to influence a and b approxi-
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The difference of 0.012 Å in $b$ between pure C23 and pure C25 is considered to be significant but is probably due to impurity, to which the axial lengths are clearly very sensitive. From the graph it is estimated that the addition of 1–2% of a longer-chain molecule would produce this difference.

The observed variation of $a$ and $b$ with composition is difficult to interpret. The accommodation of chains of different lengths in unit cells with the observed $c$-axis length suggests the occurrence of voids where a small fraction of shorter molecules is present (>80% C25) as the $c$ axis is not shortened in this range. Where a small fraction of longer molecules is present (<20% C25) they could protrude into the next unit cell or could display kinks, i.e. a distortion of the regular zig-zag of the carbon chain to decrease the overall length of the molecule. [Phaoivibul et al. (1973) and Strobl, Ewen, Fischer & Piesczek (1974) explain the defect structure of paraffins postulating kinks.] The kinks may occur near the end of the chain causing a progressive increase with C25 content in the thickness of a rather disordered end-group layer between the regular stacks of parallel chains. Both protrusions and kinks could be expected to increase $a$ and $b$. $a$ and $b$ increase less markedly in the >80% C25 range but it is not clear why they should increase there at all.

It might be expected that at 50% C25 long and short molecules could pair off to pack more optimally with a lower value of $c$. No evidence of such an effect is observed.

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