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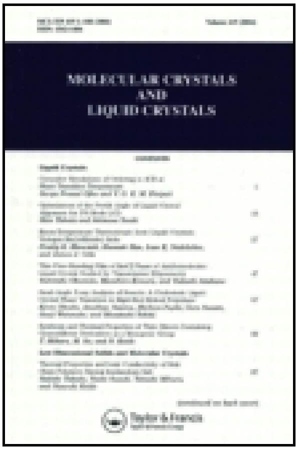

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Crystallographic and Calorimetric Phase Studies of the n-Eicosane, $C_{20}H_{42}$: n-Docosane, $C_{22}H_{46}$ System

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Crystallographic and Calorimetric Phase Studies of the n-Eicosane, $C_{20}H_{42}$: n-Docosane, $C_{22}H_{46}$ System

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The *n*-eicosane, $C_{20}H_{42}$: *n*-docosane, $C_{22}H_{46}$ system has been studied by X-ray crystallographic and calorimetric techniques. The phase diagram exhibits no less than six distinct solid phases. The two terminal solid solutions, γ_1 and γ_2 are triclinic in keeping with the pure components. An orthorhombic phase, β_0, exists at all compositions just below the solidus and has a centered (*C* or *F*) lattice. The structure of the low temperature orthorhombic phases β_1, β_2 (indistinguishable on the basis of powder photographs) has been determined from a single crystal X-ray analysis. The most probable space group of these phases is $Bb2_1m$, the mirror planes required of the molecules perpendicular to their length being obtained by disordering.

INTRODUCTION

Over the last forty years a substantial amount of information has been gathered concerning the crystallography and phase equilibria of the normal alkanes (for

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brevity simply called alkanes in this paper), n-$C_n H_{2n+2}$ (hereafter C_n), particularly those with melting points above room temperature ($n > 17$). Early studies on these alkanes were bedevilled by the presence of small amounts of impurities, and many phase equilibrium studies were prompted by efforts to understand the effect of impurities, particulary other homologs, on the crystallography and other physical properties of the pure components.

The earliest crystallograpic study of an alkane was by Müller [1] in 1928; single crystals of C_{29} were grown from solution, and rotation and oscillation X-ray photographs were used to determine the lattice parameters and space group (*Pnam*). In two later papers[2,3] he reported that at room temperature C_{20} existed in a low symmetry form, but became orthorhomic below the melting point. C_{24} was found to have two distinct orthorhomic structures with a well defined transition at 40°C. Also, on the basis of lattice parameters, all the alkanes from C_{21} to C_{27} appeared to become hexagonal below their melting point. In 1948 however, Mazee[4] reported a triclinic to monoclinic transition in C_{24} at 42°C which casts doubt on the purity of Müller's sample.

In 1962 Broadhurst [5] reviewed the existing literature on the alkanes and concluded that almost all the known alkanes could be placed in one of three structural groups with triclinic, monoclinic or orthorhombic symmetry, the exceptions being those with short chains. The dependence of crystal structure on carbon number is shown below:

Odd carbon alkanes:

i) $n \geqslant 11$, orthorhombic, *Pbcm* or *Pbnm*

Even carbon alkanes:

ii) $6 \leqslant n \leqslant 26$, triclinic $P\bar{1}$

iii) $n \geqslant 26$, monoclinic, $P2_1/a$

iv) The even alkanes $n \geqslant 26$ also exhibit an orthorhombic form, $Pbc2_1$, almost certainly caused by impurities[6,7,8].

In each of the four cases above a typical structure is known in some detail, e.g. (i) C_{23},[6] (ii) C_{18}[9,10] (iii) C_{36} [11] and (iv) C_{36}.[12] In all these structures the alkanes crystallize with the carbon backbones flat and fully extended and with their long molecular axes parallel; thus their unit cells have one long cell dimension traditionally labelled *c*. Both the monoclinic and orthorhombic structures can be described in terms of a common orthorhombic sub-cell. However the different molecular symmetries of odd and even carbon alkanes result in different arrangements of the end groups of the chains. The triclinic structure has a different sub-cell. Because of the close relationship of the structures within each group, knowledge of the cell dimensions of a single member enables the structures of the other members of the group to be predicted.[13]

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In addition to these structures many of the alkanes both odd ($9 < n < 43$) and even ($22 < n < 42$) are reported to exhibit a hexagonal phase just below the melting point.[3-5, 14-16]

Crystallographic studies of mixtures of alkanes were first made by Piper *et al.*[17] in 1931: they examined the low order X-ray reflections at small scattering angles and thus obtained accurate measurements of the long spacings, *d*(001) in monoclinic and triclinic and *d*(002) in orthorhombic structures. They found marked discontinuities when C_{28} was added to C_{26}, and when C_{27} or C_{29} was added to C_{28}; less marked discontinuities were observed with C_{29}, C_{31} mixtures. They suspected that these discontinuities were related to a change in the tilt of the molecules with respect to the (001) plane, an explanation now considered to be correct. An alternative suggestion by Mnyukh[18] involving void formation has not been generally accepted.

Ubbelohde[19] noted similar changes in long spacings determined from powder photographs when C_{18} was added to C_{16} but these were not sudden, the crystal structure of C_{16} being gradually replaced by a new phase between 2.2 and 16.0 mole percent of C_{18}. Measurements of long spacings therefore became a useful basis for checking purity.

Apart from X-ray diffraction there have been numerous calorimetric studies both of pure alkanes and of their mixtures.[20-23] Most of the studies of binary systems indicate complete solid solubility at the solidus temperature but wide varieties of behaviour have been found at lower temperatures. Since these studies were made without parallel X-ray diffraction measurements, the assignment of crystal structures to the observed phases is absent or speculative.

In this paper we present an analysis of the cell dimensions and possible structures of the phases, as well as the equilibria between the phases, found in the C_{20}/C_{22} system.

We have been unable to find a detailed phase diagram for C_{20}/C_{22}. Our results however are in general accord with but somewhat more complex than the phase diagram for C_{16}/C_{18} published by Mazee.[20]

MATERIALS

The specimens of eicosane (n-$C_{20}H_{42}$) and docosane (n-$C_{22}H_{46}$) used in these investigations were supplied by Imperial Oil Limited. The eicosane was stated to be 98.1% pure and had a measured melting point of 36.4°C and the docosane melted at 43.6°C: Broadhurst[5] quotes 36.6°C and 44.0°C respectively as the melting points of these alkanes. To avoid possible oxidation they were stored at 0°C under nitrogen.

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CALORIMETRIC MEASUREMENTS

Binary mixtures covering the whole range of compositions in steps of about 5% were prepared in 200 mg batches by melting weighed amounts of the two components under dry nitrogen in sealed pyrex ampoules. The melts were thoroughly mixed by shaking and then quenched into iced brine: after quenching, the samples were held at room temperature for a week and at −16°C for a further six weeks to facilitate equilibration by solid state diffusion.

The calorimetric measurements were made with a Rigaku-Denki DTA-TGA calorimeter. Samples weighing from 10 to 15 mg were heated from −40°C to just above the liquidus at a rate of 2.5°C min^{-1} : preliminary tests had shown that the observed transformation temperatures were independent of heating rate for rates of this order. In all twenty-one binary mixtures and the pure components were studied calorimetrically, two or three samples of each composition being examined.

Figure 1 illustrates a typical DTA curve from this system; the smaller peak from 15–20°C corresponds to a phase change in the solid while the larger peak corresponds to melting, the solidus temperature for this sample being about 37°C. All compositions showed a phase change prior to melting: the temperatures at which the phase change started and finished as well as the solidus and liquidus temperatures for each composition are shown in Figure 2.

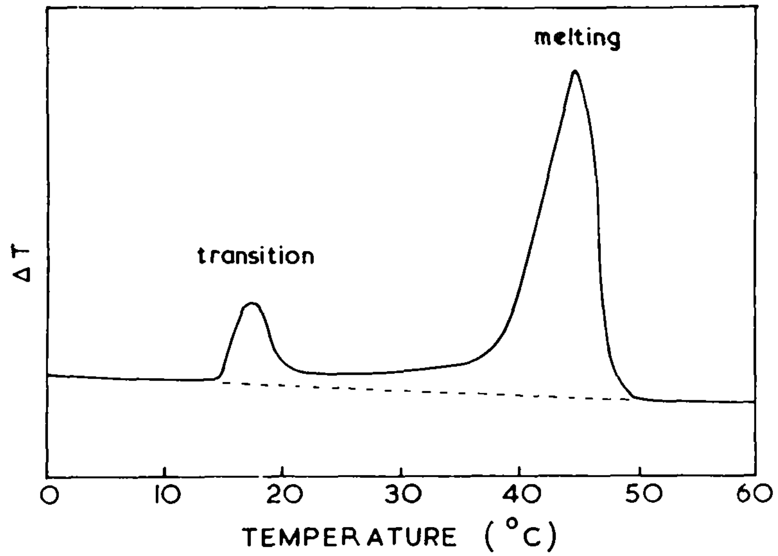

FIGURE 1. DTA curve for C_{20} : 25% C_{22}. Peaks at about 17° and 45°C (indicated temperatures) correspond to the $\beta \rightarrow \beta_0$ solid phase transition and melting respectively. Note the high specific heat of the β_0 phase between 20° and 37°C.

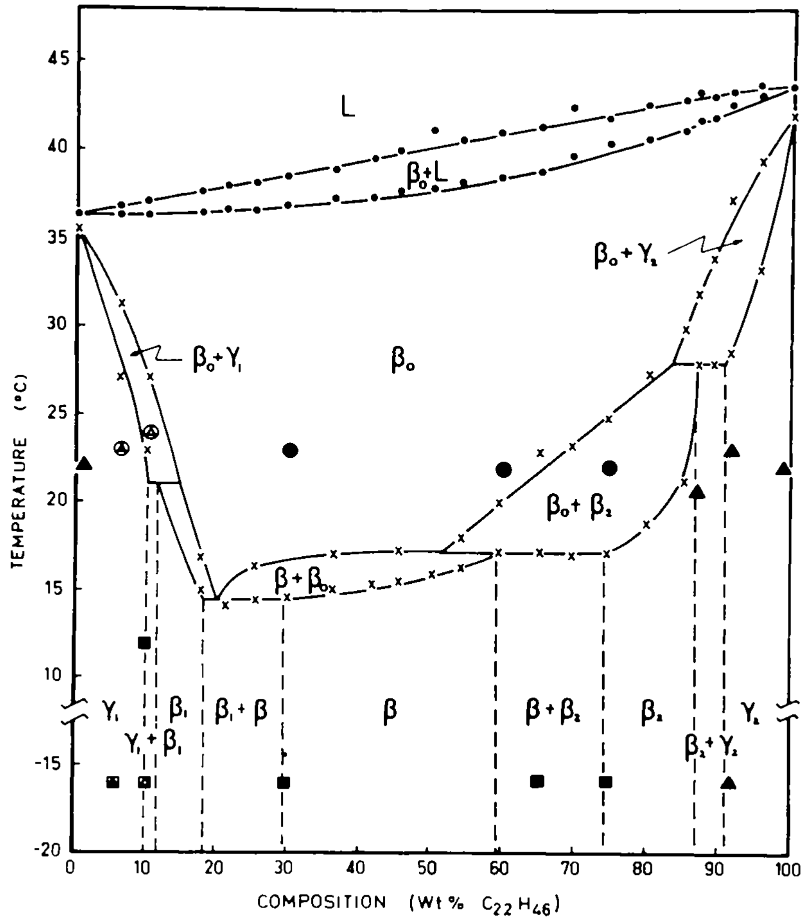

FIGURE 2 Phase diagram of C_{20} : C_{22} system. Calorimetric points indicated by *x* (phase change) and • melting. Phases identified by X-ray diffraction are shown thus: △, ▲ triclinic; □, ■ low temperature orthorhombic; ○, ● high temperature orthorhombic. (In compound symbols the filled symbol indicates the major phase.)

X-RAY POWDER DIFFRACTION

To facilitate the interpretation of Figure 2 powder photographs of some of the calorimetric samples were taken at room temperature (22–24°C) and at −15°C, using a Guinier-Hägg focussing camera with thoria as an internal standard. Three distinct crystal structures were identified, one being triclinic (C_{20} and C_{22} have essentially the same structure, but different *c*-dimensions) and two orthorhombic. The conditions under which these structures were found are shown,

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TABLE I

Lattice Parameters in the C_{20} : C_{22} System

Composition (mole % C_{22})	Temperature (°C)	Phase	*a* (Å)	*b* (Å)	*c* (Å)
pure C_{20}	24	$^a\gamma$	4.279	4.818	25.55
			(α = 91.03°	β = 93.40°	γ = 107.40°)
9.2	24	β_O	5.025	7.626	55.46
	-15	$^b\beta$	4.965	7.375	55.34
28.1	24	β_O	5.025	7.657	~57.46
	-15	$^b\beta$	4.971	7.392	56.58
57.7	24	β_O	5.023	7.646	58.63
73.2	22	β_O	5.030	7.622	58.76
	24	$^b\beta$	4.992	7.469	58.77
	-15	$^b\beta$	4.972	7.377	59.20

[a] Crissman *et al.*(24) give a = 4.281(1)b = 4.820(1), c = 25.52(1)Å, α = 91.18(2)°, β = 93.52(2)°, γ = 107.35(2)°

[b] β includes the low temperature phases labelled β_1 and β_2 in Fig. 2.

together with the calorimetric data, in Figure 2. Because of the long *c*-dimension in all these structures, unambiguous indexing of all the lines in the powder photographs was not possible so that, on this basis alone, only very limited conclusions as to the space groups occurring could be drawn. However, enough lines could be indexed definitely to enable the lattice parameters of the phases to be determined accurately: the values found are listed in Table 1.

LONG SPACINGS

Long spacings were determined from powder photographs and also from single crystal precession photographs. The compositions of the single crystals were determined by vapour phase chromatography, while the powders were assumed to have the same composition of the corresponding bulk mixtures. The results of these measurements are presented in Figure 3, and show clearly the discontinuities in spacing towards the two extremes of composition. Comparison of Figures 2 and 3 shows that these discontinuities are associated with the change from a triclinic (γ_1 or γ_2) to an orthorhombic (β_0) structure. It should be noted that the orthorhombic cell is based on two layers of molecules, so that in this structure the inter-layer periodicity is just half the *c* parameter.

Broadhurst [5] has given the dependence of *d* on *n* for triclinic alkanes as

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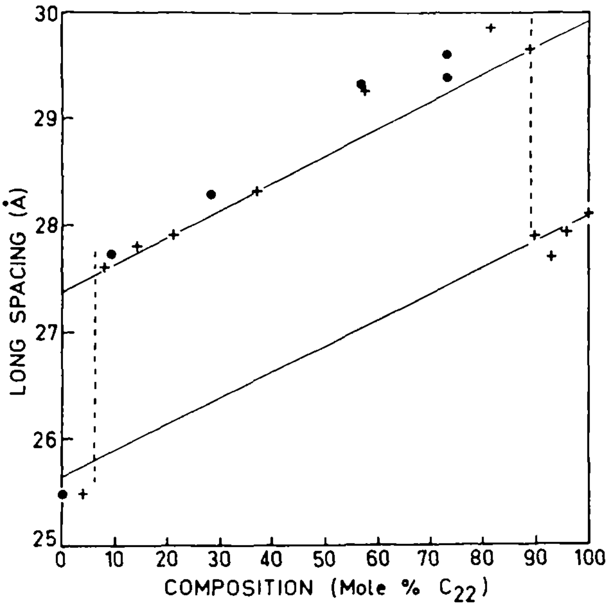

FIGURE 3 Crystal long spacings in C_{20} : C_{22} system. + single crystal and ● powder diffraction data (Table 1). Theoretical values shown by lines derived from Broadhurst's expressions for dependence of long spacing on carbon number.

$d(001) = (1.219n + 1.28)$ Å, and for orthorhombic alkanes as $d(002) = (1.270n + 1.98)$ Å. In the absence of voids we would expect the long spacings in binary mixtures to be given by linear interpolation between the values for the pure components. The d spacings calculated from Broadhurst's formulae using linear interpolation are indicated in Figure 3; the observed values lie close to the calculated lines for both the triclinic and orthorhombic phases suggesting that there is little void formation, except perhaps at the C_{22} rich end of β_0.

Taken in conjunction with the constancy of the other lattice parameters across each phase, the variation of the d spacing with composition implies that within a phase the angle of tilt of the molecules to the (001) plane remains constant (90° in orthorhombic and about 72° in triclinic phases).

X-RAY SINGLE CRYSTAL STUDIES

Single crystals of the pure components and of some binary mixtures were grown by cooling well mixed melts of known composition sealed in glass bottles at 0.1°C h^{-1} in a large thermostatically controlled oil bath from above the liquidus to that temperature at which the first platy crystalline fragments appeared. The

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temperature was then kept constant for 24 h or so until these crystals had grown to a few millimeters in maximum dimension. The glass bottle was removed from the oil bath, the contents allowed to solidify at room temperature, and the bottle carefully broken: the relatively large platy crystals first formed were teased from the polycrystalline mass with dissecting needles. The crystals were checked between crossed polaroids and those showing the most uniform extinction were mounted for examination by X-ray diffraction using a precession camera with unfiltered copper radiation.

The temperature at which crystals first appeared from a mixed melt gave the liquidus temperature of the bulk, while the composition of the first crystals to form, determined after X-ray examination by vapour phase chromatography, gave a corresponding point on the solidus. The solidus and liquidus lines determined in this way were in good agreement with those established by calorimetry, and with a rather rudimentary phase diagram given by Kieras *et al.*[23]

TRICLINIC CRYSTALS (γ PHASE)

Crystals of both the pure components were examined by Weissenberg and precession techniques. The lattice parameters for C_{20} agreed with those of Crissman *et al.*[24] and with our values determined independently from powder photographs.

The triclinic C_{20} and C_{22} phases are known to be isostructural with triclinic C_{18}.[10, 13]

ORTHORHOMBIC CRYSTALS – LOW TEMPERATURE (β) PHASE

Only one composition, C_{20} : 25% C_{22}, in the β phase field yielded sufficiently good single crystals for a partial structure determination: even these crystals had many subgrains. Precession photographs of the $0k\ell$, $h0\ell$, $hk0$, $1k\ell$, $h1\ell$ and $hh\ell$ sections were taken with the specimen cooled to 10°C by a stream of cold nitrogen. Figure 4 shows typical photographs of one of these crystals and illustrates how the long c dimension causes poor resolution of certain reflections. Reflections $hk\ell$ were observed only if $h + \ell = 2n$; for $0k\ell$ reflections there was an additional condition $k = 2n$.

Certain reflections in the $hk0$ section (110, 120, 130, 310) appeared to violate the restriction $h + \ell = 2n$. However, in the $h1\ell$ section 310 was absent while 311 was strong and 111 so strong that we could not tell whether 110 was present or not. We have taken it to be absent. Reflections 120 and 121 fall in the "blind" region of the $1k\ell$ section, while 130 and 131 were not resolved. It is probable therefore that the apparent $hk0$ reflections with h odd were really $hk1$,

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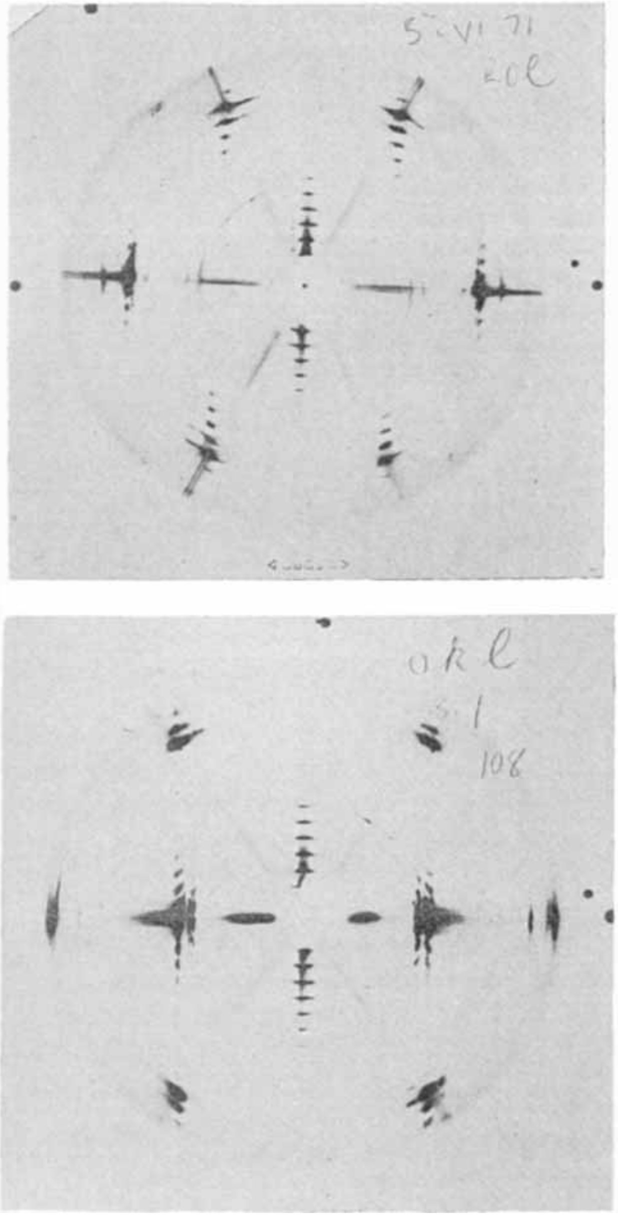

FIGURE 4 Precession photographs of C_{20}: 25% C_{22} at 10°C. Upper: *h0ℓ*, lower, *0kℓ*.

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breaking through into the adjacent section because of the short c^*-axis and appreciable angular spread of the crystal sub-grains. There are only four space groups which satisfy the reflection conditions above: $Bb2_1m$, $Bb2b$, $Bbm2$ and $Bba2$.

The lattice parameters for this mixed crystal are $a = 4.99$ Å, $b = 7{\cdot}47$ Å and $c = 56.26$ Å. The a and b parameters are so similar to those reported for polyethylene,[25] C_{23},[6] orthorhombic C_{36}[12] and for the subcell in monoclinic C_{36}[11] that it must be concluded that the basic chain packing in the mixed crystal is the same as that in these other structures. The basic layer is one in which molecules in the two orientations related by a b glide have their long axes normal to the plane of the layer; from the length of the c-axis it is clear that the unit cell consists of two such layers.

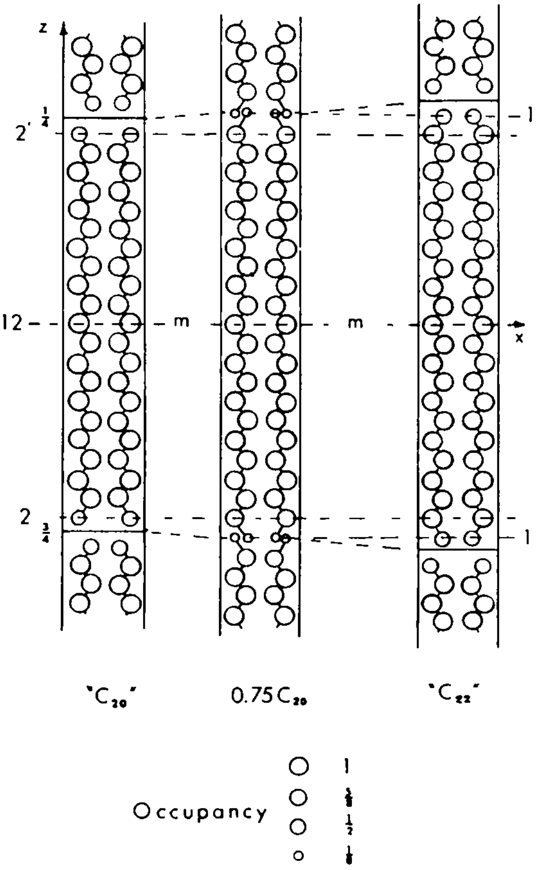

FIGURE 5. Diagramatic representation of disorder of C_{20} : 25% C_{22}. β phase in y-projection.

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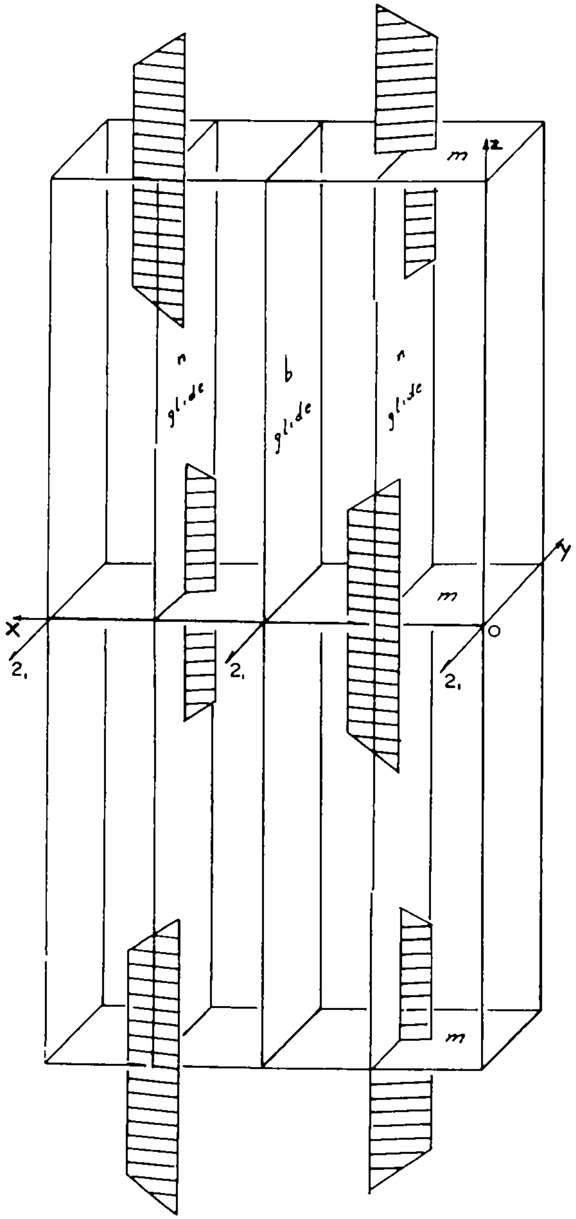

FIGURE 6 Packing and symmetry in $Bb2_1m$. Each disordered molecule represented by rhombus.

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Of the four space groups mentioned above the last two must be rejected as inconsistent with the basic layer, while the second does not lead to a feasible structure with two layers. The remaining space group, $Bb2_1m$, leads to a physically reasonable structure only for those alkanes with mirror symmetry normal to the long axis, i.e. for the odd carbon alkanes; however such symmetry could arise in the even carbon alkanes as a result of disorder.

The model we have taken is illustrated in Figures 5 and 6. It is most easily explained by considering the structures pure C_{20} and C_{22} would have if they had crystallized as β phases. These hypothetical structures, "C_{20}" and "C_{22}", are on the left and right sides of Figure 5. The carbon atom sites are numbered 1 through 12 (which lies on the mirror plane) thence 11′ through 1′. In "C_{20}" the molecules are envisaged as lying equally in one of two sets of sites, 2 through 3′ and 3 through 2′ (the 1,1′ sites are vacant). Hence the occupancies are $\frac{1}{2}$ at sites 2 and 2′ and unity elsewhere. Analogously for "C_{22}" where the occupancies at sites 1 and 1′ are $\frac{1}{2}$ and unity elsewhere. For the 0.75 C_{20} solid solution the site occupancies are suitably averaged, namely at sites 1 and 1′, 0.75 (0) + 0.25 ($\frac{1}{2}$) = $\frac{1}{8}$ and at sites 2 and 2′, 0.75 ($\frac{1}{2}$) + 0.25(1) = $\frac{5}{8}$.

The fractional group coordinates (i.e. fractional coordinates relative to the centre of gravity of the molecule) used were those given by Teare,[12] adjusted only to take account of the shorter *c*-dimension. Packing considerations require the molecular axes to be midway between the *b* glide planes with group 12 on the mirror plane. The atomic co-ordinates used are listed in Table 2.

Structure factors were calculated using this model for all the accessible reflections. The precession photographs were not suitable for accurate intensity measurements, so that the comparison of observed and calculated intensities was limited to the approximate relative strengths, and the absences both accidental and systematic, of the Bragg reflections. At this level of accuracy the agreement between observed and calculated intensities was excellent (Table 3).

TABLE 2

Fractional Co-ordinates[a] of Atoms Used in Calculation of Structure Factors for C_{20} : 25% C_{22}
($n = 1,\ldots 6$)

Atom	x	y	z
C ($2n$)	0.186	-0.039	0.02267 ($2n-12$)
H_1 ($2n$)	0.206	-0.181	
H_2 ($2n$)	-0.024	-0.008	
C ($2n-1$)	0.314	0.039	0.02267 ($2n-13$)
H_1 ($2n-1$)	0.294	0.181	
H_2 ($2n-1$)	0.524	0.008	

[a] Relative to an origin at $b2_1\,m$

TABLE 3

Comparison of Calculated Structure Factors and Observed Intensities (qualitative) for C_{20} : 25% C_{22} at 10° C

h k ℓ	*F* calc	*I* obs	*h k* ℓ	*F* calc	*I* obs	*h k* ℓ	*F* calc	*I* obs
0 0 2	48	s	17	17	vw	5	12	vw
4	44	s	19	30	w	7	7	vw
6	38	ms	21	84	m	9	3	vw
8	31	m	23	84	s	11	2	vw
10	23	m	25	22	vw	13	4	vw
12	16	w	27	10	no	15	6	vw
14	10	vw				17	11	vw
16	5	no	1 1 1	233	vs	19	20	vw
18	3	no	3	71	s	21	57	m
20	1	no	5	35	ms	23	59	s
22	1	no	7	19	w			
24	1	no	9	9	vw	2 0 0	169	vs
26	1	no	11	3	no	2	13	m
28	3	no	13	3	no	4	12	w
30	5	no	15	6	no	6	10	vw
			17	10	w	8	9	vw
0 2 0	326	vs	19	17	m	10	7	no
2	24	s	21	48	ms	12	5	no
4	22	m	23	48	s	14	3	no
6	19	w	25	12	vw	16	2	no
8	17	w	27	6	no	18	1	no
10	13	vw	29	3	no	20	1	vw
12	11	vw						
14	9	vw	1 2 1	46	ms	2 1 0	55	w
16	9	vw	3	14	-	2	4	vw
18	8	vw	5	7	–	4	4	vw
20	6	w	7	4	–	6	4	no
22	117	s	9	2	–	8	4	no
24	11	m	11	2	–	10	5	no
26	8	vw	13	4	vw	12	6	no
			15	6	vw	14	7	no
1 0 1	1	no	17	11	vw	16	7	no
3	1	no	19	19	w	18	7	no
5	1	no	21	53	s	20	5	no
7	1	no	23	55	s	22	106	m
9	1	no	25	15	vw	24	10	w
11	3	no				26	7	vw
13	6	vw	1 3 1	81	s			
15	10	vw	3	25	m			

vs = very strong, s = strong, ms = moderately strong, m = moderate, w = weak, vw = very weak, no = not observed.

Reflections marked (-) were not accessible in the sections photographed.

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We have also considered whether the observed intensities might be explained by a structure similar to that found by Teare for C_{36}, which has the space group $Pbc2_1$. This space group is inconsistent with the reflection condition $h + \ell = 2n$ but the closely related $Pbn2_1$ appeared worth examination. In $Pbn2_1$ no disorder is necessary and the y co-ordinate of the group origin can be varied. With a suitable choice of this y co-ordinate the condition $h + \ell = 2n$ for general reflections could be approximately satisfied for low orders of ℓ, but for large ℓ there was a parity change to $h + \ell = 2n + 1$ which was inconsistent with the experimental data. A structure based on $Pbn2_1$ is therefore not acceptable.

On the basis of the evidence above we conclude that the low temperature form of C_{20}: 25% C_{22} is orthorhombic, space group $Bb2_1m$ with a = 4.99 Å, b = 7.467 Å, c = 56.26 Å and Z = 4. The structure is disordered with molecules occupying either of two orientations related by a 180° rotation about, and 1.275 Å translation along the molecular long axis. It should perhaps be stressed that, except for the terminal groups, the methylene groups occupy identical positions in the unit cell for each of the two orientations: the packing of the molecules within the layer is therefore undisturbed by the disorder (see Figure 7(A)).

Smith[26] mentions single crystal studies of two compositions in the C_{24} : C_{26} system. Both crystals had the space group $Pbnm$, which implies disorder by virtue of the mirror plane, with a = 4.963 Å and b = 7.486 Å. The c-axes were very long 137.2 and 202.0 Å the cells containing 8 and 12 molecules respectively. We have found no evidence in the C_{20} : C_{22} system for such large unit cells.

ORTHORHOMBIC CRYSTALS – HIGH TEMPERATURE FORM (β_0 PHASE)

When the crystals described above (C_{20} : 25% C_{22}) were warmed to room temperature, a phase change occurred. Because of the disruptive nature of this change (the low temperature structure was studied first) the high temperature photographs were not very satisfactory. A reasonable $hk0$ section photograph was obtained which showed only those reflections for which $h + k = 2n$, implying that the z-projection is centred. In view of the likelihood of the $hk0$ section including $hk1$ reflections also, it is probable that the condition $h + k = 2n$ applies to general reflections. This is confirmed by powder photographs on which all the observed reflexious satisfied $h + k = 2n$, indicating that the structure is C-centered.

The kinetics of the $\beta \rightleftharpoons \beta_0$ transition were examined by setting up a crystal of about C_{20} : 50% C_{22} (but not exactly known composition) on a diffractometer. The crystal and counter were set to record peak intensity from the 121 reflection and the dependence of intensity on temperature examined. As noted above,

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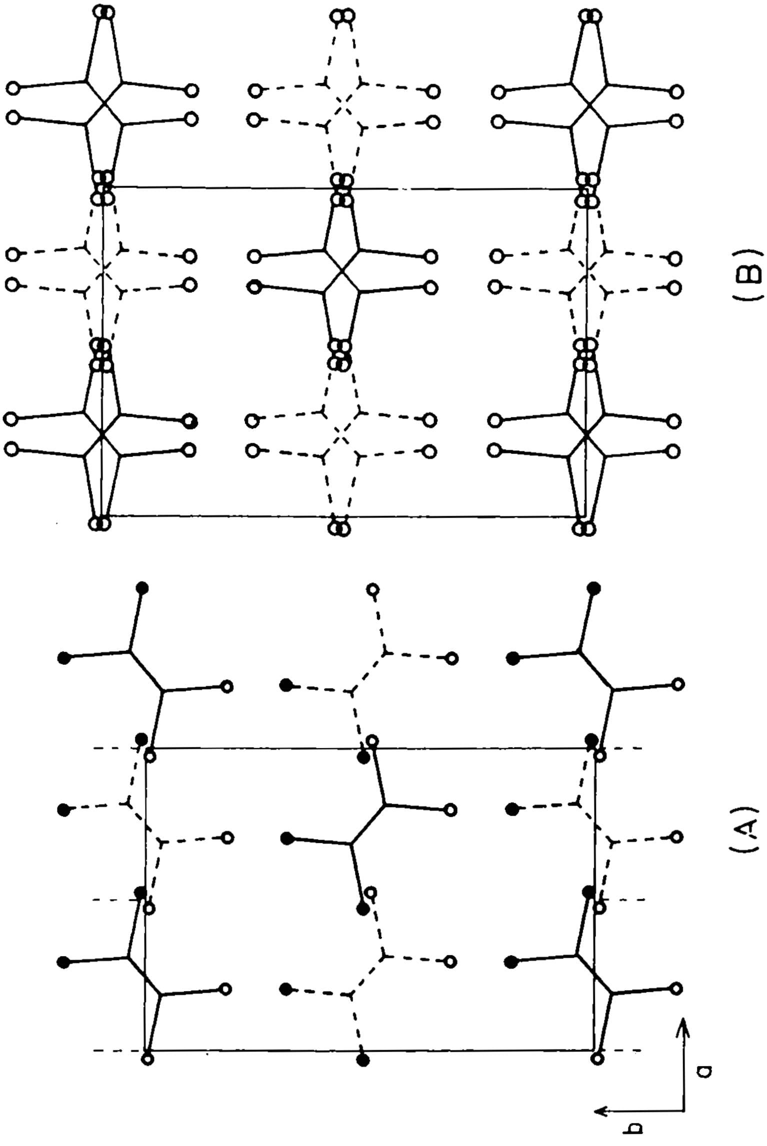

FIGURE 7 *hk*0 projections (idealized) of (A)β, and (B) β_0 phases.

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the β_0 phase appears to be *C*-centered so the 121 disappears on warming the β phase through the transition temperature.

Counting-rate meter traces in arbitrary intensity units are given in Figure 8 (A and B) for heating and cooling. The hysteresis should be noted. The crystal could be taken only twice round the heating-cooling cycle because of marked reduction in intensity from 121 with each additional cycle.

The phase change is also associated with a marked increase in the *a* and *b* lattice parameters to 5.025 Å and 7.637 Å, the area of the (*ab*) plane being 38.38 Å compared with 37.28 Å for the low temperature form, an increase of nearly 3%. This is very similar to the parameter change in C_{21} reported by Mazee[4]

The simplest model which would result in a *C*-centered structure is one in which each molecule in the basic alkane layer occupies one of two positions related by a mirror plane parallel to and midway between the *b* glide planes (Figure 7(B)). Such disorder would of course result in some dilation of the (*ab*) plane. Alternatively, there could be fourfold disorder based on the two molecular orientations just mentioned, together with two more derived from these by 180° rotation about the chain axis. This fourfold disorder could be regarded as a precursor to free rotation of the molecules and, in view of the continuous-transition to at least a pseudohexagonal structure as temperature is increased, is considered more likely than the twofold disorder.

There is virtually no change in the *c* parameter in passing from the low temperature to the high temperature orthorhombic structure so that this latter structure is clearly based on two layers in the unit cell. The space group corre-

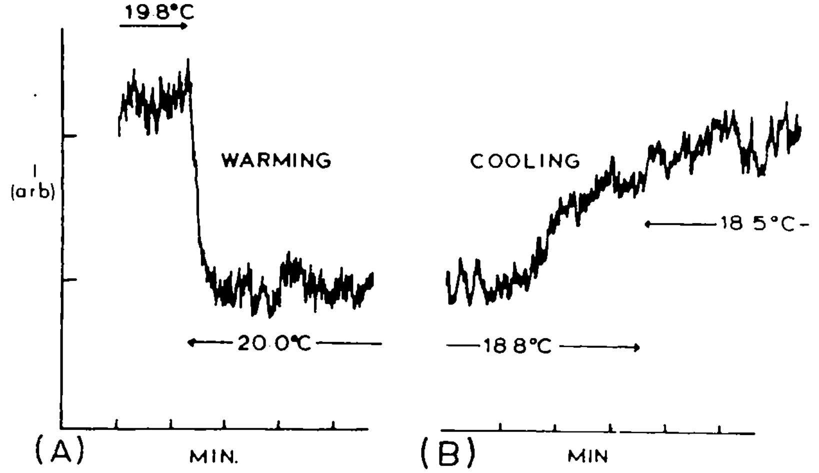

FIGURE 8 Heating-cooling counting-rate meter traces for the $\beta_0 \rightleftarrows \beta$ transition. (121 reflection, CuKα radiation).

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sponding to fourfold disorder of the low temperature orthorhombic structure is *Fmmm*, which is not inconsistent with our limited X-ray data for the β_0 phase.

THE HEXAGONAL PHASE

As mentioned earlier there have been numerous reports of a hexagonal phase just below the melting point for many pure alkanes. Some of these reports are based solely on calorimetric evidence [5, 16] and it seems probable that the transition observed calorimetrically was in fact that from triclinic or monoclinic (even alkanes) to high temperature orthorhombic, or from low temperature orthorhombic (odd alkanes and impure even alkanes) to high temperature orthorhombic. The work described in this paper provides definite evidence that both $\gamma \rightarrow \beta_0$ and $\beta \rightarrow \beta_0$ transitions do occur (see Figure 2) and are associated with an enthalpy of transformation of about 2 kcal mole.$^{-1}$

In an attempt to obtain calorimetric evidence for a hexagonal phase in the C_{20} : C_{22} system we examined a number of samples of nominal composition C_{20} : 25% C_{22} using a Perkin-Elmer DSC-1B scanning calorimeter, which is more sensitive than the Rigaku-Denki instrument used for most of this work. This composition was selected as the $\beta \rightarrow \beta_0$ transition is sharp and complete some 20°C below the onset of melting; also single crystal precession photographs indicated that the structure was at least pseudohexagonal (in the sense that d(200) = d(110) by 33°C, some 4°C before melting. No evidence for any first order transition between the $\beta \rightarrow \beta_0$ transition and melting could be found, and a transition as small as 25 cal mole^{-1} should have been detected; however it was noted that the specific heat in this temperature range was anomalously high, indicated by the large displacement of the DTA curve from the base line in this region, suggesting that thermal motion increases rapidly and continuously prior to melting. Figure 1 is the DTA curve for this composition.

X-ray evidence for a hexagonal phase has relied chiefly on powder photographs [3, 14] which do not distinguish readily between a truly hexagonal structure and an orthorhombic structure with a fortuitous relation $b = a\sqrt{3}$. Larsson [27] reports a single crystal X-ray examination of C_{19} (m.pt. 32.0° where $a = 4.79$, $a\sqrt{3} = b = 8.30$A. However the lattice he ascribes is *F*-centered orthorhombic, which, as he points out, lacks the sixfold symmetry required of a hexagonal lattice. He states also that 'the distribution of reflection intensities is in general agreement with theoretical predictions for rotating chains by Vainshtein'. [28] These results are in accord with ours to the extent that our data for the β_0 phase are consistent with *F*-centering and with limited, if not full rotational disorder. Müller [3] contrasts the sharp change of lattice parameters at 40° – 41°C in C_{24} (the $\beta \rightarrow \beta_0$ transition) with the continuous change thereafter to a hexagonal ratio for a: b.

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At this stage therefore the status of the hexagonal phase is ambiguous. It seems certain that the transition to a hexagonal phase, if it occurs, is not first order and that calorimetric data which appears to contradict this refers to transitions to the disordered orthorhombic phase (β_0). More evidence, e.g. single crystal Laue photographs taken at different temperatures, is needed to distinguish clearly between the hexagonal and pseudohexagonal alternatives.

It is perhaps worth noting that a continuous transition from a two layer alkane structure with the space group *Fmmm* (a possibility for β_0) to a hexagonal structure is formally impossible as the relative positions of adjacent layers are completely determined, and different, in the two structures. If the β_0 phase had the space group *Cmcm*, and there were two crystallographically independent molecules each with weight $\frac{1}{2}$ in the cell (*Fmmm* can be regarded as a limiting case of this), then continuous transition to a hexagonal phase would appear feasible as this orthorhombic space group allows a degree of freedom in the relationship between adjacent layers.

EQUILIBRATION KINETICS IN THE SOLID PHASE

Two methods of preparing samples for powder diffraction from the bulk mixtures used in the calorimetry were tried: in one the waxy materials were simply smeared onto the aluminium foil supports, while in the other the specimens were melted and allowed to solidify. The methods produced characteristic differences in the diffraction patterns; the "premelted" specimens showed much stronger 00ℓ reflections, five or six orders being visible compared with one or two at most in the smeared samples, an effect previously noted by Müller.[2] In two phase regions of the equilibrium diagram the proportions of the two phases were often noticeably different, the premelted samples invariably showing a higher proportion of the β_0 phase than did the smeared samples.

These variations were studied in some detail in C_{20} : 10% C_{22}. At room temperature a smeared sample showed both β_0 and γ_1 phases, with a slight preponderance of the γ_1: the premelted sample initially appeared to be entirely β_0 and remained so for at least a week. After three weeks though, weak lines corresponding to the γ_1 phase were visible in the pattern and these increased in strength in succeeding weeks until after two months the smeared and premelted samples were indistinguishable.

Comparable changes were observed in C_{20} : 90% C_{22}, though in this case premelted samples were initially two phase, $\beta_0 + \gamma_2$, but became single phase, γ_2 only, within three months: smeared samples were single phase, γ_2 at all times. The changes were quite reversible and both "smeared" and "melted and aged" specimens could be restored to the premelted condition by melting and solidification: this rules out chemical changes, e.g. oxidation, as a possible cause of the changes.

A simple explanation of these changes is not apparent; that observed in C_{20} : 10% C_{22} is consistent with the segregation of a quenched metastable homogeneous mixture into two phases in equilibrium, but the change in C_{20} : 90% C_{22} cannot be explained in this way. One thing is certain however, that samples prepared by cooling binary melts are not, in general, stable phases at room temperature. The relatively slow nature of the changes occurring on annealing at room temperature, compared to the rapid $\gamma \rightarrow \beta_0$ and $\beta \rightarrow \beta_0$ transitions observed by calorimetry, suggests that solid state diffusion, notoriously slow in molecular crystals, is the rate controlling process for the changes.

In view of these very sluggish changes the phase diagram of Figure 2 which is based largely on transitions which occur rapidly should only be regarded as an approximation to the true equilibrium situation.

DISCUSSION AND CONCLUSIONS

The combined results of calorimetry and X-ray diffraction indicate that there are no less than six distinct solid phases in the C_{20} : C_{22} system, the regions of stability of which are shown in Figure 2. The two terminal solid solutions, γ_1 and γ_2, are triclinic and have crystal structures which differ essentially only in the lengths of their c dimensions. A high temperature phase, β_0, exists at all compositions just below the solidus temperature and this has a centred (either C or F) orthorhombic structure, which it is suggested, arises from fourfold rotational disorder of the molecules about their long axes. This disorder would account for the relatively large a and b parameters, 5.023 Å and 7.636 Å respectively compared with 4.970 Å and 7.478 Å for ordered alkanes, and also for the relatively high symmetry implied by the centred structure.

The low temperature phases, β_1, β_2, and β_2, are not distinguishable on the basis of powder X-ray diffraction, so that on the diffraction evidence alone the whole region from 12% to 87% C_{22} below about 15°C could be described as a single orthorhombic phase. However the well defined eutectoid in the vicinity of 20% C_{22} and peritectoid at about 65% C_{22} imply that there are in fact three distinct phases rather than one. It is worth noting that Smith,[26] working with mixed single crystals of C_{24} : C_{26} has established the existence of at least two distinct low temperature orthorhombic phases in that system. Single crystal techniques are of course much more suitable than powder diffraction for studying subtle changes in structure, but we have not yet been able to prepare a suitable range of mixed single crystals in this system. Taken at face value, the phase diagrams of Kieras *et al.*[23] for C_{20} : C_{22}, and Mazee[21] for C_{22} : C_{24}

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indicate complete solubility (and therefore a triclinic structure if the components were pure) at low temperatures as well as high: however these diagrams were determined calorimetrically and, without diffraction studies to indicate structural changes, fine detail could well be overlooked.

The similarity of the *a* and *b* parameters of the low temperature orthorhombic phases with those for polyethylene,[26] the odd-carbon alkanes[1, 4, 6] and C_{36}[11, 12] indicates that all these phases have a common packing of the methylene chains, structural differences arising only from the packing of the end groups between adjacent layers. Only one structure in this system, that of C_{20} : 25% C_{22}, was determined and that only partially: consideration of the systematically absent X-ray reflections and of the possible packing of layers of alkanes molecules indicates $Bb2_1m$ as the most probable space group. This space group in turn implies a disordered structure with an average molecule occupying one of two positions related by 180° rotation about, and 1.275 Å (half the alternate carbon spacing) along the molecular long axis, to satisfy the space group symmetry. The space group *Pbnm* quoted by Smith for C_{24}: C_{26} likewise implies a disordered structure.

We have been unable to establish unambiguously the presence of a hexagonal phase in this system. There is some X-ray evidence for at least a pseudo hexagonal phase just below the solidus temperature, but calorimetric studies do not indicate any first order phase change in this temperature range. Further work on this question is needed.

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