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Structure and molecular disorder in three modifications of a binary $C_{23}H_{48}$ - $C_{24}H_{50}$ paraffin

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Résumé. — La dépendance en température des intensités des réflexions (00 l) de la paraffine binaire ($C_{23}H_{48}$ -25 % $C_{24}H_{50}$) a été déterminée afin d'en déduire des paramètres structuraux liés aux mouvements moléculaires et aux défauts intramoléculaires. La grande distance réticulaire a également été déterminée en fonction de la température. On compare tous ces résultats avec la variation en température du rapport des deux petits paramètres de réseau. La corrélation très nette entre tous ces résultats expérimentaux permet de caractériser assez bien les structures moléculaires et leurs changements lors des transitions de phase dans l'état solide.

Abstract. — The temperature dependence of the intensities of the (00 l) X-ray reflections from a binary paraffin ($C_{23}H_{48}$ -25 % $C_{24}H_{50}$) was determined, in order to obtain structural parameters related to the molecular disorder and intramolecular defects. The long lattice spacing was also determined as a function of temperature. All these results are compared with the temperature dependence of the ratio of the two short lattice parameters. The clear correlation of all of these experimental results provides a close characterization of the molecular structures and their changes at the various solid state phase transitions.

1. Introduction.

Odd-numbered paraffins C_nH_{2n+2} with $n = 23$ and 25 exhibit two solid state phase transitions [1, 2]. At low temperatures the stable phase has a well ordered crystalline structure (C phase) (primitive orthorhombic lattice). At higher temperatures two « rotator » phases were observed below the liquidus. The low temperature rotator phase, R_I , has a face-centred orthorhombic lattice and the high temperature phase, R_{II} , an hexagonal lattice [2]. In these three phases all the molecular axes are parallel and the molecules form a layered structure. The molecular axes are perpendicular to the stacking planes of the layers.

The $C \rightarrow R_I$ and $R_I \rightarrow R_{II}$ transitions are characterized by increments on the orientational disorder of the molecules around their long axis and by well-defined lateral displacement of the layers [1, 2]. Recent inves-

tigations in odd-numbered compounds established that, in addition, longitudinal molecular displacements and conformational intramolecular defects play an important rôle in the phase transitions of paraffins [3].

Studies of the temperature dependence of the intensities of the (00 l) X-ray small angle diffraction peaks of odd-numbered pure paraffins [3] indicate a clear increase of the amplitude of the longitudinal molecular displacements and of the fraction of intramolecular defects at the $C \rightarrow R_I$ transition temperature. The amplitude of the motion increases with temperature and the fraction of molecules with conformational defects remains constant in the temperature domain of stability of the two rotatory phases [3]. No evidence of the phase transition $R_I \rightarrow R_{II}$ was found in these studies. The $R_I \rightarrow R_{II}$ phase transition was first detected by differential thermal analysis as a weak effect (1) and also, by determining the

temperature variation of the short lattice parameters, a and b [1]. The ratio a/b has a value of about 1.5 just above the $C \rightarrow R_I$ transition temperature; it increases continuously up to about $\sqrt{3}$ at the $R_I \rightarrow R_{II}$ transition and it remains constant and equal to $\sqrt{3}$ up to the melting temperature (1). The constant value of the a/b ratio ($a/b = \sqrt{3}$) allows us to characterize the structure of rotator II phase as an hexagonal structure. The long spacing (layer thickness) in pure odd-numbered paraffins was found to be constant within the whole temperature range of R_I and R_{II} and no discontinuity has been detected at the $R_I \rightarrow R_{II}$ transition temperature.

From a recent determination of the phase diagram of the binary $C_{23}H_{48}$ - $C_{24}H_{50}$ system [4], it was concluded that: a) the rotator phases R_I and R_{II} , which were previously observed in pure $C_{23}H_{48}$, are present up to 90 % of $C_{24}H_{50}$, and b) the temperature domain of stability of the rotator phases increases with $C_{24}H_{50}$ content, reaching a maximum near the center of the equilibrium diagram.

This paper is devoted to the study of the molecular arrangement, displacements and conformational defects in a binary paraffin as a function of temperature. Since the temperature domain of stability of the rotator phase is wider in binary $C_{23}H_{48}$ - $C_{24}H_{50}$, we expect to provide a more detailed description of the molecular structure of these phases than that previously reported for the pure $C_{23}H_{48}$ and $C_{25}H_{52}$ compounds [3].

2. Experimental

The compounds $C_{23}H_{48}$ and $C_{24}H_{50}$ were purchased from Fluka and their purity grade were 99 % and > 98 %, respectively. The binary sample (75 % $C_{23}H_{48}$ -25 % $C_{24}H_{50}$) was prepared by mixing the weighed amounts of the components in the liquid state, shaking and pouring it into the sample holder. The polycrystalline plate-shaped sample was placed into a specially designed water-heated cell to keep it at constant temperature during the X-ray diffraction measurements.

The structure study was carried out by means of the small-angle X-ray diffraction technique. The experiments were performed at the small-angle scattering station of the synchrotron radiation facility at LURE. The X-ray beam was monochromatized and focussed by means of a bent germanium crystal. The X-ray wavelength used was $\lambda = 1.590 \text{ \AA}$. The high intensity of the source allowed us to obtain the diagrams using pin-hole collimation and counting times of about 200 sec. The intensity measurements of the X-ray reflections were carried out by means of an Elphyse position sensitive detector. The integral intensities of the (00 l) diffraction peaks were determined after subtracting the continuous background from the total intensity by the standard method. Figure 1 shows three small-angle X-ray diffraction patterns as obtained from a multichannel analyser. In figure 1 only one

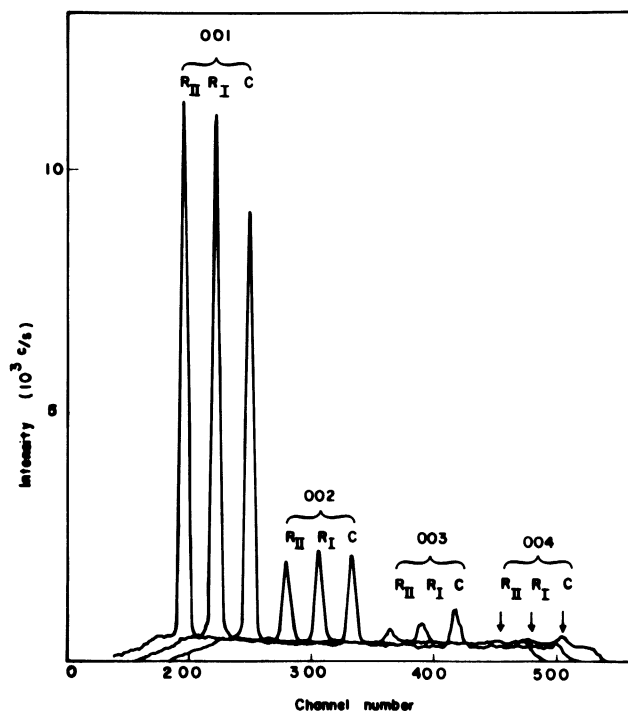


Fig. 1. — Three small angle X-ray diffraction patterns at several temperatures : R_{II} : 46.4 C (rotator II phase), R_I : 39.4 C (rotator I phase) and C : 35.8 C (crystal phase). The patterns are laterally displaced for clarity.

pattern of each solid state phase was plotted. The experimental intensity associated with each (00 l) reflection (Fig. 1) was multiplied by l^2 (Lorentz factor) before further analysis. Polarization and absorption effects on diffraction intensities are negligible at small angles. All of the X-ray diffraction patterns corresponding to different temperatures were normalized in order to compensate for the continuous decrease of intensity of the synchrotron radiation beam. The direct X-ray beam was monitored by means of an ionization chamber.

The disorder parameters were derived from the small-angle diffraction experimental patterns of polycrystalline paraffine samples by means of a method developed by Strobl *et al.* [5] and already applied to pure paraffins [3, 5]. The (00 l) X-ray intensities of a layered structure are related to the average value $\eta(z)$ of the electron density in planes parallel to the layer interface at a distance z from it. For an analysis of the low angle (00 l) reflections, the electron density can be taken as a constant in the inner part of the molecule. The shape of the electron density function within the « void » region of the interface between neighbouring molecules, can be described by the difference $\Delta\eta(z)$ which is shown in figure 2. The « voids » are in fact depleted regions with low but non-vanishing electronic density due to the methyl terminal groups.

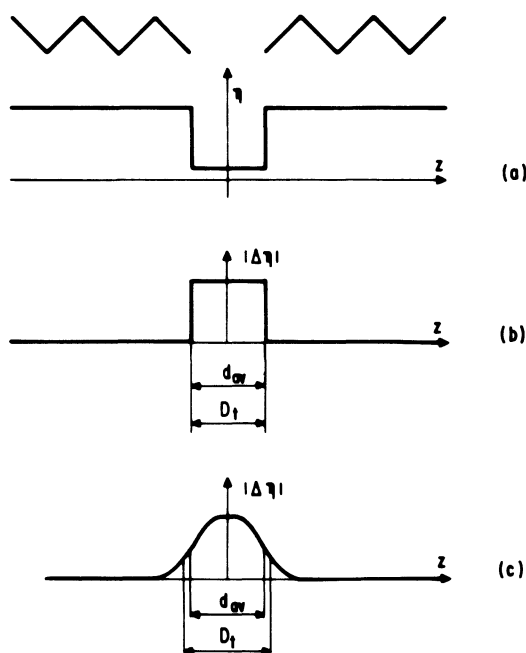


Fig. 2. — Schematic electron density function (a) and difference function (b) corresponding to a perfect stacking of defect-free molecules without longitudinal displacements. The same system with molecular longitudinal displacements yields difference functions as that represented in (c). Two neighbouring paraffin molecules are schematically shown (top).

In short, the Strobl *et al.* method [5] relates the integral of the $\Delta\eta(z)$ function with the extrapolated value to zero angle, $I(0)$, of the low angle intensities I_{00l} by

$$[I(0)]^{1/2} = \kappa = \int \Delta\eta(z) dz.$$

The extrapolation is done by means of even 4th or 6th order polynomials. The slope of the polynomials at zero angle provides the second moment, σ^2 , of the difference function $\Delta\eta(z)$. From the value of the parameter κ , the average distance between the neighbouring molecules, d_{av} , can be derived. A parameter D_t , related to σ by $D_t = \sqrt{12} \sigma$, is useful to characterize the shape of the void profile. It is equal to d_{av} in the case of a rectangular void profile (perfect stacking of identical molecules). Longitudinal displacements of the molecules and/or heterogeneities in molecular length lead to $D_t > d_{av}$. A more detailed description of the method can be found in previous papers [3, 5].

In order to determine the d_{av} parameter in absolute units, the X-ray reflection intensities should also be measured on an absolute scale. Since our measurements were performed on a relative scale, we obtained a parameter which is proportional to the average distance between molecular ends. We remark that in our earlier work on pure paraffins [3] we were able to obtain d_{av} in absolute units by assuming a rectan-

gular interlayer void profile for the crystalline phase. This assumption is not a reasonable approximation for binary paraffins and consequently cannot be used here.

3. Discussion.

The intensities of the corrected and normalized (00l) small-angle X-ray reflections were fitted by 4th degree polynomials for each temperature. From the extrapolated values of the polynomials and their slopes, towards zero angle, the d_{av} and D_t parameters were determined by means of the Strobl *et al.* method [5]. The long spacings, L , were obtained from the values of the angular positions of the (00l) reflections. All of these parameters are plotted as a function of temperature in figure 3. This figure also includes the plots of the a/b ratio, of the two short lattice parameters which were deduced from a previous study [4] by interpolation between the experimental values at two different concentrations (70 and 80 % $C_{24}H_{50}$). The D_t parameters are also represented in figure 3. Since the D_t parameters are subjected to a high inaccuracy within the temperature domain of the crystalline phase [3, 5], they were only plotted for the rotator phases.

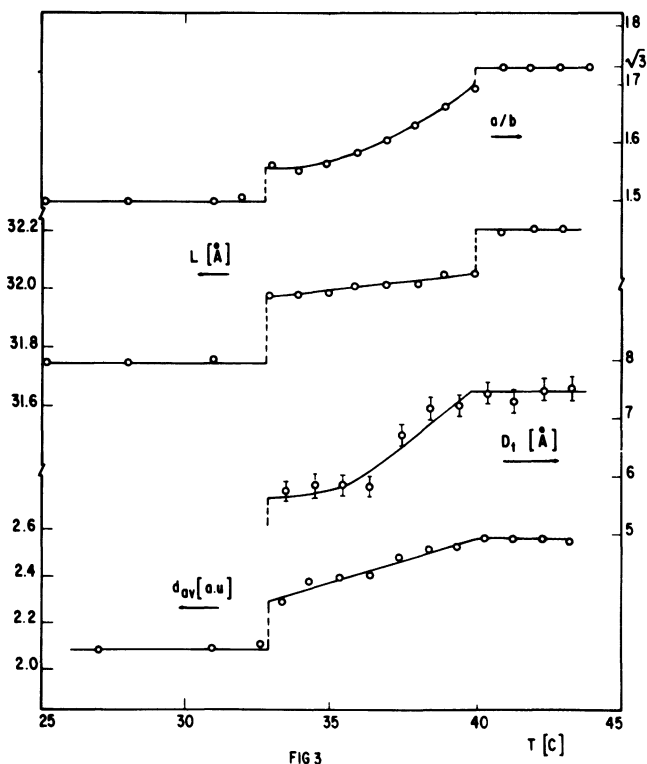


Fig. 3. — Structural parameter determined from small-angle diffraction data as a function of temperature : ratio of the short lattice parameters (a/b), long spacing or layer thickness (L), parameter proportional to the mean square root of the thickness of voids between layers (D_t) and mean distance between molecular terminal group or mean void thickness (d_{av}).

The temperature dependence of the a/b ratio exhibits the same features as those of previously studied odd-numbered paraffins [1]. The increase of a/b from 1.52 up to approximately 1.73 for the binary system, within the temperature domain of stability of the R_I phase, can also be attributed to the increase of the orientational oscillation amplitude of the molecules around their long axes. The constancy of $(a/b) = \sqrt{3}$ within the temperature domain of stability of the R_{II} phase corresponds to an hexagonal lattice. The hexagonal symmetry is a consequence of the « free » rotation of the molecules around their long axes. Earlier evidences of free molecular rotation in the rotator phase of paraffins have been obtained from neutron scattering experiments on $C_{23}H_{48}$ [6].

The D_l parameter increases with the mean amplitude of the molecular longitudinal displacement. Its temperature dependence is similar to that of the a/b ratio. D_l increases with temperature within the R_I phase up to the $R_I \rightarrow R_{II}$ transition temperature and remains constant within the temperature domain of stability of the R_{II} phase.

The d_{av} and L parameters also increase with temperature in the R_I phase and are constant in the R_{II} phase. In addition, a clear discontinuity of the long spacing, L , was detected at the $R_I \rightarrow R_{II}$ transition temperature.

From the close correlation between the temperature dependence of a/b and D_l , a correlation between the angular oscillation and the longitudinal displacement of the molecules can be inferred. This means that the increase in amplitude of the angular oscillation of the molecules with temperature is accompanied by an increase in the average of the molecular longitudinal displacements. This correlation is expected since the increase in amplitude of the angular oscillation of the molecules around their long axes produces a lateral expansion. Consequently, the weaker van der Waals lateral molecular interactions lead to a larger longitudinal displacive freedom. At the $R_I \rightarrow R_{II}$ transition temperature the amplitude of the angular oscillations reaches its maximum (molecular rotation starts) and, consequently, the amplitude of the longitudinal displacements also reaches an upper limit. Within the temperature domain of stability of R_{II} no appreciable variation occurs in either of the amplitudes.

The increase in amplitude of the oscillations and longitudinal displacements of the molecules with temperature is also correlated with the temperature dependence of the d_{av} parameter. The fraction of molecules with simple conformational defects (kinks) is proportional to $d_{av} - d_s$, d_s being the mean thickness of the inter-layer voids in a defect free crystal [3, 5]. Assuming $d_s = d_{av}$ in the crystalline phase, we can conclude that above the $C \rightarrow R_I$ transition temperature, a fraction of the molecules has kink defects. The fraction of molecules with kinks increases with temperature and reaches a maximum at the $R_I \rightarrow R_{II}$ transition temperature. Thus the formation of kink

defects in the paraffin molecules seems to be enhanced by the orientational and displacive molecular disorders.

The temperature dependence of the long spacing, L , can be explained by a variation of the interpenetration of the molecular terminal groups. This interpenetration is facilitated for the well oriented and less disordered molecules of the crystalline phase. A greater degree of interpenetration corresponds to a lower long spacing. Within R_I the increase in amplitude of the molecular angular oscillations is accompanied by a continuous decrease of the layer interpenetration and, consequently, by an increase in L . The free rotation state of the molecules in the R_{II} phase leads to a still lower degree of interpenetration and to a higher and temperature independent long spacing.

4. Conclusions.

This experimental X-ray diffraction study of a binary $C_{23}H_{48}$ - $C_{24}H_{50}$ system furnishes the temperature dependence of lattice and disorder parameters. They have a clearly correlated behaviour which enables us to characterize the overall average structure and molecular disorder of the three solid state modifications. In the crystal phase the amplitudes of the molecular angular oscillations and longitudinal displacements are low and essentially temperature independent. The rotator I phase exhibits molecular angular oscillations and longitudinal displacements of high amplitude. These amplitudes as well as the fraction of molecules with kinks increase continuously with temperature. A consequent continuous decrease of the degree of molecular interpenetration occurs. In rotator II phase all the parameters characterizing the different structural features reach an extreme and constant value. These parameters exhibit clear discontinuities at the $C \rightarrow R_I$ transition temperature. The long spacing and the a/b ratio present additional discontinuities at the $R_I \rightarrow R_{II}$ transition temperature. This evidence corroborates the observed correlation between the amplitude of the molecular angular oscillation and degree of molecular interpenetration.

The variations in layer thickness, L , and average distance between molecules, d_{av} , within the temperature domain of stability of the rotator phases, was not found in the previous studies of pure paraffins [3]. The observed saturation effect on D_l at the $R_I \rightarrow R_{II}$ transition temperature of the binary system (Fig. 3) also constitutes a new result. As was pointed out in previous sections, the temperature domain of stability of the rotator phases of the pure $C_{23}H_{50}$ compound is narrower than that of the $C_{23}H_{48}$ -25 % $C_{24}H_{50}$ binary system. We think that the structural features of this binary system must also be found in the single-component $C_{23}H_{48}$ and $C_{25}H_{52}$ paraffins by subjecting the samples to a more precise temperature control.

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