MOLECULAR DISORDER IN EVEN-NUMBERED PARAFFINS

by

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Abstract

Conformational and displacive molecular defects in even-num bered paraffins $C_n H_{2n+2}$, with $22 \leq n \leq 28$, are studied as a function of the temperature by means of X-ray small-angle diffraction. Intramolecular defects (kinks) are formed in the rotator (high tem perature) phase at the crystal-rotator transition. The amplitude of the molecular longitudinal motion in the rotator phase increases with molecular length, as it was also found in previous studies of odd-numbered paraffins. This amplitude is temperature independ ent in rotator phases of even paraffins with $22 \leq n \leq 26$. The voids between molecular layers in the crystalline phase of even paraffins are narrower than in that of odd paraffins. This indicates a closer packing of layers in systems in which molecules are tilted. Structures of the high temperature hexagonal rotator phases of odd and even paraffins exhibit a minor but significant difference which has been associated with different interactions between molecular ends.

Key-Words: Paraffins; Alkaries; Molecular disorders.

INTRODUCTION

Previous wide angle X-ray diffraction studies lead to a con sistent average atomic structure model of even-numbered paraffins[1,2]. In the low temperature crystalline phase the molecules stack together forming a layered structure with the long molecular axes tilted with respect to the normal to the layer planes. The paraffins with a number of carbon atoms $n < 26$ crystallize in a triclinic lattice. For $n > 26$ the lattice is monoclinic. A coexistence of monoclinic and triclinic phases is observed for $n = 26$. All even-numbered paraffins with $n \geq 22$ present an intermediate phase at temperatures between the crystal and the liquid. This mesophase is called "rotator" phase because of the high degree of orientational disorder of the molecules. The lattices associated with the rotator phase in paraffins with $n \leq 26$ and $n = 28$ are hexagonal and monoclinic, respectively.

The temperature dependence of the small angle-X-ray diffrac tion patterns from odd-numbered paraffins (3) showed clear evidences of the existence of "rigid body" longitudinal molecular displacements and, also, of conformational intramolecular defects (kinks) in the rotator phase. The magnitude of molecular disorders increases both, with temperature and molecular length. These disorders show a correlated behaviour. The displacement disorder and formation of kink defects are also correlated with the orientational molecular disorder, as it has been inferred from previous wide and small angle X-ray diffraction (3,4,5) and neutron (6) studies.

This work is devoted to the study of molecular disorders in even-numbered paraffins with $22 \leq n \leq 28$ by means of the low angle

diffraction technique (long spacing 00ℓ Bragg reflections). These disorders have been studied as functions of temperature and molecular length and compared with a similar previous study of odd-numbered paraffins (3). Paraffins with n=23 and 25 exhibit two rotator phases at increasing temperatures named rotator I (quasi-hexagonal) and rotator II (hexagonal). Odd numbered paraffins with n=19 and 21 present only one R_1 mesophase (3).

SAMPLES AND METHODS

The samples of the several paraffins C_nH_{2n+2} with n=22, 24, 26 and 28 were purchased from Fluka with the purity grades of 98%, 99%, 99% and 98%, respectively. The X-ray small angle diffraction patterns from the various paraffins were obtained by using synchrotron radiation produced by the DCI positron storage ring at LURE (Orsay, Université Paris-Sud). An elastically bent germanium monochromator was used to obtain a focussed monochromatic beam with $\lambda=1.60$Å. The cross-section of the beam was kept small enough to allow us to consider it as "point-like" (pin-hole collimation). The intensity associated with the low angle (00ℓ) Bragg reflections, I_ℓ, were measured by means of an Elphyse position sensitive detector (7).

The samples were held at constant temperature within ±0.5 C during the diffraction experiments, by using a specially designed camera heated by a circulating water device.

The knowledge of the extrapolated values towards zero angle of the intensities of the (00ℓ) Bragg reflections and the decay of those intensities, with increasing ℓ, allow us to determine

structure parameters which are related to the function $\eta(z)$, which represents the projection of the electronic density on a direction perpendicular to the molecular stacking layers (3,8). Assuming $\eta(z)$ as a constant equal to η_c within the molecule, the difference $\Delta\eta(z) = \eta(z) - \eta_c$ is non-vanishing only in the depleted region between the molecular layers (interlayers voids), as it is shown in Fig. 1.

Two parameters related to the function $\Delta\eta(z)$ have been determined from the intensities of the (00ℓ) peaks of the small-angle diffraction patterns. They are a) the moment of zero order κ and b) the second moment σ^2 of the difference function $\Delta\eta(z)$, which are associated with the electronic density profile in the interlayer voids. These parameters can be obtained directly from the structure function $B_\ell = \int \Delta\eta(z) \exp[2\pi i(\ell/L)z] dz$ by means of the following expressions (3.8):

$$\kappa = B_\ell \quad (s \to 0) \tag{1}$$

and

$$\sigma^2 = -\frac{1}{8\pi^2} \frac{d^2 B^2}{ds^2} \quad (s \to 0) \tag{2}$$

were s represents the modulus of the diffraction vector. If the X-ray diffraction intensities at small angles, I_ℓ, are known in absolute scale, we can obtain B_ℓ directly by

$$B_\ell = (I_\ell)^{1/2} \tag{3}$$

By combining equation 1 and 3 a relationship between the extrapolated intensity towards zero angle $I(0)$, and the average value

of the distance between the ends of consecutive molecules, d_{av} can be obtained:

$$I(0) = [\eta_c d_{av} - \varepsilon/d_s]^2 \qquad (4)$$

were ε is the electronic density within the depleted zone (inter-layer voids) and $d_s = L_k \cos\psi$, L being the long lattice spacing, L_k the length of the molecules in its more extended conformation $(L_k = (n-1)\ 1.273\ \text{Å})$, and ψ the molecular tilting angle. The parameter d_{av} is equal to d_s in the case of a perfect crystal (3,8).

In order to determined d_{av} for the rotator phases from measurements of X-ray diffraction intensities in relative scale, we should find the ratio between the intensities $[I(0)]_C$ and $[I(0)]_R$, corresponding to crystal and rotator phases, respectively. This ratio is equal to (3.8):

$$\frac{[I(0)]_R}{[I(0)]_C} = \left\{ \frac{(\eta_c d_{av} - \varepsilon/d_s)_R}{(\eta_c d_{av} - \varepsilon/d_s)_C} \right\}^2 \qquad (5)$$

Being $\eta_c d_{av} \gg \varepsilon/ds$, $(d_{av})_R$ can be obtained by the approximate expression

$$(d_{av})_R = \left\{ \frac{[I(0)]_R}{[I(0)]_C} \right\}^{1/2} (d_{av})_C \qquad (6)$$

The deviation of the d_{av} values determined by means of equation 6, from those of equation 5, is not greater than 2%. The average parameter $(d_{av})_C$ can be calculated by assuming the structure of the crystalline phase as defect free (3). In this case

$$(d_{av})_C = d_s = (L - L_k \cos\psi)_C \tag{7}$$

The quotient between the extrapolated intensities is determined from experiments in relative scale after normalization of the extrapolated intensities to equivalent sample thickness and incident beam intensity. For the cyrstalline (orthorhombic) phase of odd paraffins with $n \leq 25$ the tilting is known ($\psi = 0$). Hence the calcuation of $(d_{av})_C$ is possible from eq. 7 and, furtherly, equation 6 yields $(d_{av})_R$.

Detailed structural data of the crystalline phase of even paraffin are not available. Consequently the tilting angle ψ is not known with an accuracy high enough to permit the use of equation 7 to determine $(d_{av})_C$. Therefore we used in this case an alternative procedure. In order to deduce $(d_{av})_C$ for even paraffins we determined the ratio of the extrapolated intensities $I(0)$ corresponding to one odd and one even paraffin ($C_{23}H_{48}$ and $C_{24}H_{50}$). The parameter (d_{av}) of the even paraffin was determined by an equation similar to equation 6:

$$(d_{av})_{even} = \left\{ \frac{[I(0)]_{even}}{[I(0)]_{odd}} \right\}^{1/2} (d_{av})_{odd} \tag{8}$$

the parameter $(d_{av})_{odd}$ was taken as the average of the d_{av} values corresponding to several odd paraffins with orthorhombic structure (3).

The extrapolation to zero angle of the low angle diffraction intensities I_ℓ has been performed by approximating the experimental values of the integral of the (00ℓ) diffraction peaks by a fourth degree polynomial, as described in an earlier paper (3). Be

cause of the pinhole collimation used in our measurements, the ex

perimental intensities were only corrected for the Lorentz fac-

tor and normalized to equivalent sample thickness and intensity

of the incident X-ray beam.

In order to determine the second moment σ^2, measurements in

absolute scale are not necessary. It is often useful to determine

another parameter $D_t = \sqrt{12}\,\sigma$, which is equal to d_{av} in case of ab-

sence of molecular defects (perfect crystal) (3). The accuracy of

the experimental results is generally not high enough to permit

the determination of D_t with reasonable precision for the crys-

talline phase (3,8). Therefore the D_t parameter has only been here

determined for the rotator phases of the several studied paraf-

fins. From the D_t values it is possible to calculate the mean

square amplitude of the longitudinal displacements of the mole-

cules (3). Qualitatively, an increase in D_t ($D_t \geq d_{av}$) is associa

ted with an increase in molecular displacement amplitude. $D_t = d_{av}$

results in case of absence of longitudinal displacements and in-

tramolecular defects.

EXPERIMENTAL RESULTS

Several diffraction patterns which include the (00ℓ) reflec

tions from paraffin $C_{24}H_{50}$, at temperatures below and above the

crystal-rotator transition are plotted in Fig. 2. The plots cor-

responding to several temperatures do not show differences within

the domain of stability of each phase. A sharp increase in in-

tensity of the two lowest order peaks at the transition tempera-

ture was observed for every studied paraffin. The diffraction peaks

have also shown a more rapid decay in intensity, for increasing orders of reflection, in rotator phase than in crystalline phase.

From the several set of diffraction patterns corresponding to the different even-paraffins, the extrapolated I(0) values have been determined as a function of temperature, as explained in the preceeding section.

By substituting in equation 8 the experimental value of the ratio $[I(0)_{24}/[I(0)]_{23}$ and $(d_{av})_{odd} = 1.95$ Å (average value for $19 \leq n \leq 25$), the thickness of the interlayer molecular voids $(d_{av})_{even}$ of the triclinic even paraffins has been estimated. The result was $(d_{av})_{even} = 1.25$ Å, which is significantly lower than that of odd paraffins.

The average thickness of voids d_{av} of every even paraffins, are represented in Fig. 3 as a function of temperature. The value $(d_{av})_C$ was assumed to be the same for all the studied even paraffins in crystalline state. That is a good approximation for $C_{22}H_{46}$, $C_{24}H_{50}$ and $C_{26}H_{14}$ (having all off them the same triclinic lattice), but it is only a rough estimate for the monoclinic structure of the crystalline phase of $(C_{28}H_{58})$. We did not find significant variation in d_{av} within the temperature domain of stability of the rotator phases. Only one experimental value of d_{av} has been determined for the rotator phase of $C_{22}H_{46}$ because of the narrow temperature domain of stability of this phase.

The experimental values of the displacement parameter D_t are also represented in Fig. 3 for the rotator phase of every paraffin. We notice that D_t can be considered as temperature independent for $C_{22}H_{46}$, $C_{24}H_{50}$ and $C_{26}H_{54}$. In contrast the parameter D_t cor

responding to $C_{28}H_{58}$ increases with temperature.

DISCUSSION

The sharp discontinuity in thickness of the interlayer voids at the transition temperature is mainly due, as in odd paraffins, to the formation of intramolecular defects (kinks) in the rotator phases. Molecules with kinks, being shorter than defect-free molecules, cause an increase in the average distance between molecular ends. The constant value of d_{av} within the whole domain of stability of rotator phase indicates that the formation of kinks occurs essentially at the transition temperature.

The constancy of D_t for $C_{22}H_{46}$, $C_{24}H_{50}$ and $C_{26}H_{54}$ within the temperature stability domain of the hexagonal rotator phase, implies that the significant variations in longitudinal molecular displacement are associated with major changes in the mean molecular structure which occur at the transition temperature. The singular behaviour of $C_{28}H_{58}$, which exhibits a clear variation in D_t within the domain of stability of the monoclinic rotator phase, can be explained as a consequence of a variation in molecular tilting angle.

Average values of the d_{av} parameter are represented in Fig. 4 for the crystalline and rotator phases as a function of the molecular length. This figure also includes the parameter d_{av} corresponding to odd-numbered paraffins. The measured value of $(d_{av})_{even}$ = 1.25 Å for the crystalline phase, which is significantly lower than $(d_{av})_{odd}$ = 1.95 Å, can be easily understood since in crystalline phases of even and odd paraffins the molecules are tilted

and non tilted, respectively. The tilting of the molecules in even paraffins allows a closer packing of the molecular ends and, furthermore, the narrowing of the interlayer voids.

The average parameter d_{av} for the rotator phase of even paraffins presents a roughly a linear dependence on molecular length. We have established from phase diagram determined in a previous work (9), that the hexagonal rotator II phase of even paraffins is of the same nature than that of rotator II of odd paraffins. Both have been assumed as composed by freely rotating molecules (6). The results showed in Fig. 4 put in evidence a weak but significant structural difference for even and odd paraffins, which may be explained as a consequence related to slight variations in in teraction between molecular ends. The plot of Fig. 4 suggests that molecules in the rotator phase behave to some extent as in crystalline phases, in the sense that molecules ends interpenetrate more in even than in odd paraffins.

In order to check independently the statement related to the packing differences in rotator phases of even and odd paraffins, we plotted in Fig. 5 the long lattice spacing L as a function of the molecular length. We can see that the long spacings of odd and ever paraffins lie on different straight line. The lower spacing in even paraffins, is consistent with the lower value of d_{av} shown in Fig. 4. The magnitude $\Delta L \cong 0.2 \overset{\circ}{A}$ (Fig. 5) is smaller than $\Delta d_{av} =$ $= 0.6 \overset{\circ}{A}$, but this difference may be a consequence of the approximations and experimental errors involved in the determination of d_{av} (equation 8) and/or the intrinsic low accuracy in the determination of the long spacing L from the angular position of the small angle (00ℓ) reflections. We plotted in Fig. 6 the average

parameter D_t as a function of the molecular length of the studied paraffins. In the same figure we also present the maximal D_t values (3) corresponding to $C_{23}H_{48}$, $C_{25}H_{52}$ and $C_{27}H_{56}$, which are associated with the rotator II phase for $n=23$ and 25 (4) and with the rotator IV phase for $n=27$ (2). Since paraffins $C_{19}H_{40}$ and $C_{21}H_{44}$ melt before reaching the free rotator (R_{II}) phase, their associated D_t values correspond to the quasi-hexagonal rotator phase (4). It is apparent in Fig. 6 that the D_t values lies in the same straight line for even and odd paraffin with $n \gtrsim 22$. This suggest that the features of the longitudinal molecular motion are similar in the rotator II phases of odd and even paraffins. The lower molecular displacement for $C_{19}H_{40}$ and $C_{21}H_{44}$ is expected since the intermolecular interaction in the quasi-hexagonal rotator I phase is stronger than in the free-rotator (R_{II}) phase.

CONCLUSIONS

Several even-numbered paraffins exhibit a layered high temperature rotator phase in which the molecules are perpendicular $(C_{22}H_{46}, C_{24}H_{50}$ and $C_{26}H_{54})$ or tilted $(C_{28}H_{58})$ with respect to the stacking planes. In the rotator phase two kinds of disorder have been detected (conformational and displacive) in addition to the previously studied orientational one.

The sharp increase in thickness of the interlayer voids at the transition temperature indicates that molecules in rotator II phase contain conformational defects (kinks) which are formed at the transition temperature.

Comparison of the dependence of the thickness of interlayer voids on molecular length for even and odd paraffins (Fig. 4) suggests the existence of a different correlation between molecules and packing of molecular ends, in crystalline and also in rotator phases. This different correlation does not lead to significant differences in the longitudinal displacements of the molecules, as it can be inferred from the data in Fig. 6.

The rather unexpected result concerning the finding of slight but clearly different features in rotator II phases of odd and even paraffins seems to be conclusive since it has been inferred from two independent measurements (Fig. 4 and 5). This implies that the molecules keep particular features associated with their eveness or oddness even in the hexagonal rotator II phase. This conclusion supports the idea that molecules in rotator II phase of even paraffins behave like quasi-free rotators and not like rigorously free rotators as it has been assumed in the past.

FIGURE CAPTIONS

Fig. 1 - Schematic profiles of the $\eta(z)$ and $\Delta\eta(z)$ functions:

  a) Paraffin molecules and projection of their electronic density on a direction perpendicular to the stacking plans, $\eta(z)$. The electronic density variations at an atomic scale are not shown since they are not relevant for small-angle diffraction analysis.

  b) Difference $\Delta\eta(z)$ function for a perfect layered struc ture (molecules with neither intramolecular defects nor longitudinal displacements).

  c) $\Delta\eta(z)$ associated with a system composed by defect free molecules with longitudinal displacements.

  d) $\Delta\eta(z)$ for a system of molecules with longitudinal mo- viments and kink defects.

Fig. 2 - (00ℓ) x-ray reflection diagrams corresponding to $C_{24}H_{50}$, at several temperaturs (C): a) 42.0, b) 46.0, c) 49.0, d)59.5, e) 50.0, f) 50.5, g) 51.0.

Fig. 3 - Disorder parameters of the several even paraffins as func tions of temperature ($\blacktriangle:D_t$, $\bullet$; d_{av}). The arrows indicate the d_s value obtained by eq. 8.

Fig. 4 - Average distance d_{av} of even-numbered paraffins corre- sponding to the crystalline ($\triangle$), and rotator (o) phases. The empty symbols, corresponding to odd paraffins, have been extracted form ref. 3 for comparison.

Fig. 5 - Long spacing L as a function of molecular length. The plot ted parameters have been determined in previous studies (1,4).

Fig. 6 - Disorder D_t parameter corresponding to rotator I phase for n=19 and 21, rotator II for 22$\leq$n$\leq$26 and rotator IV for n=27 and 28. The values for odd paraffins are those of ref. 3.
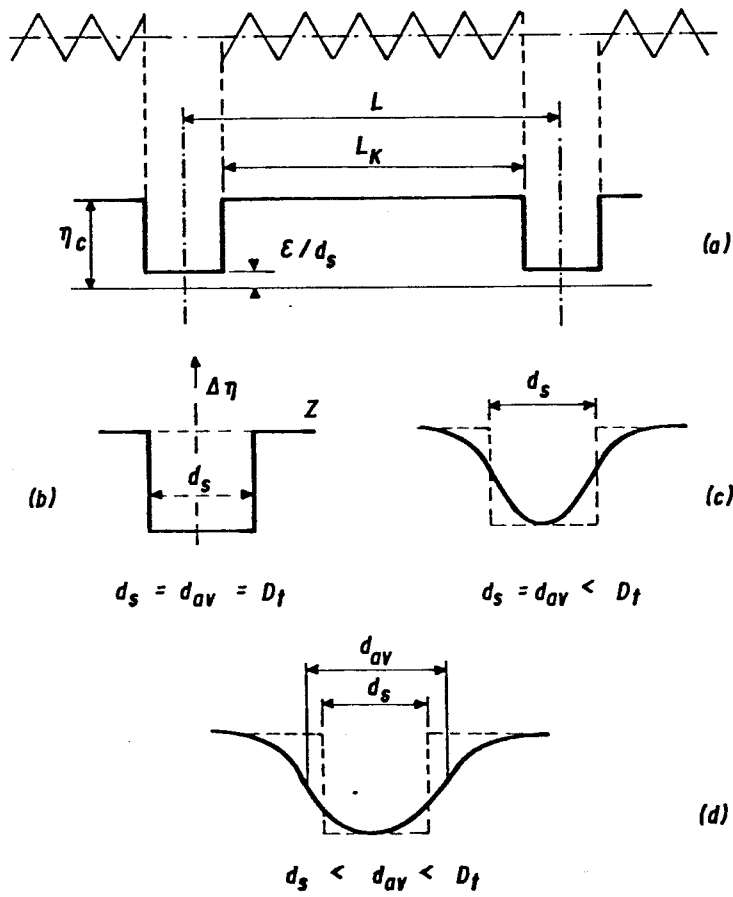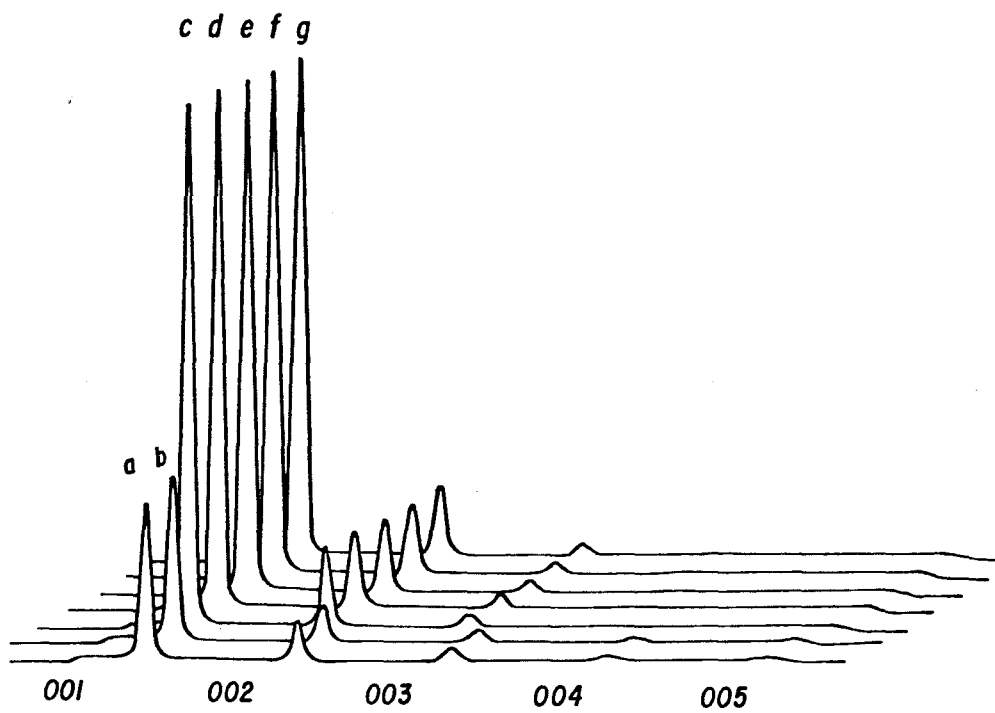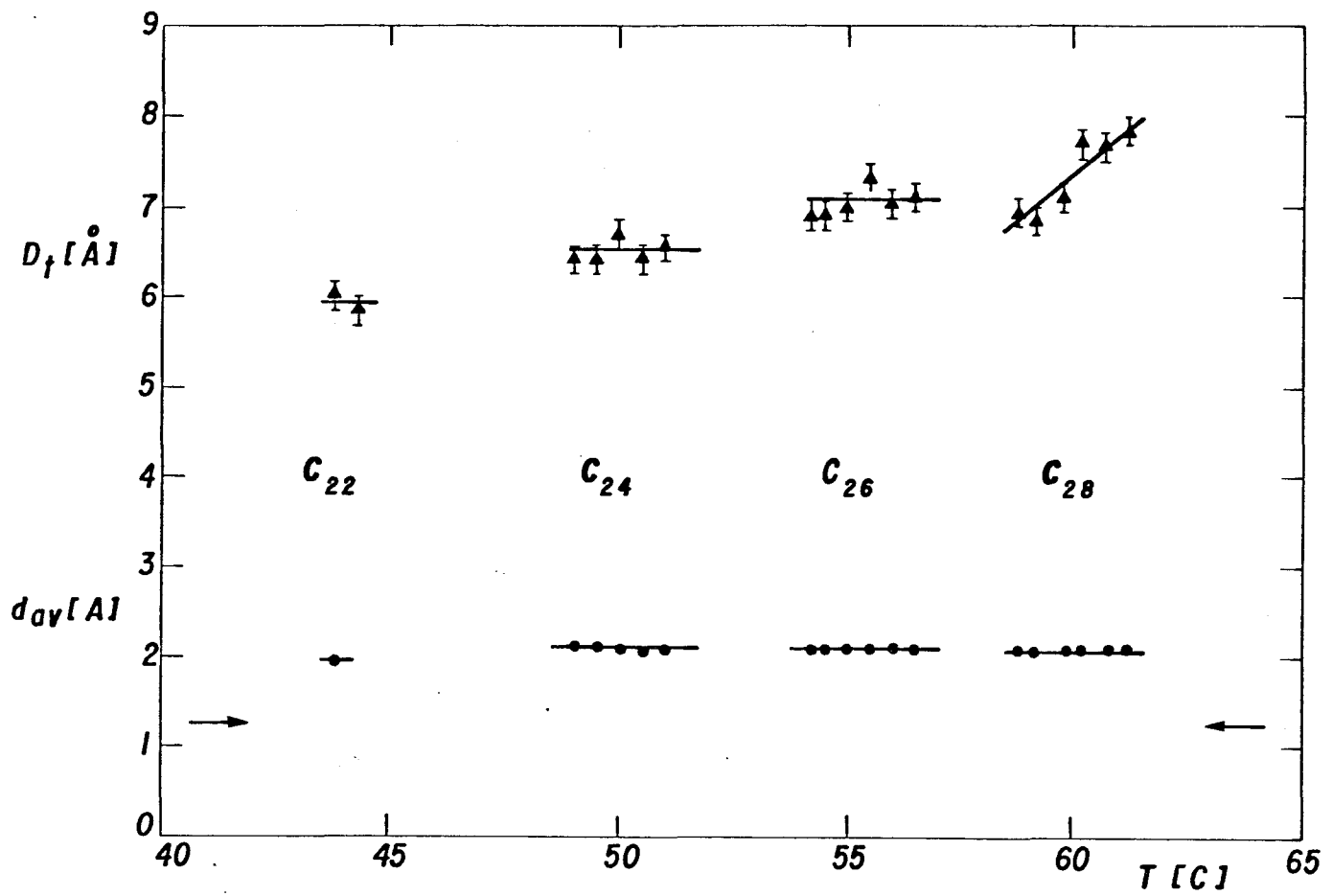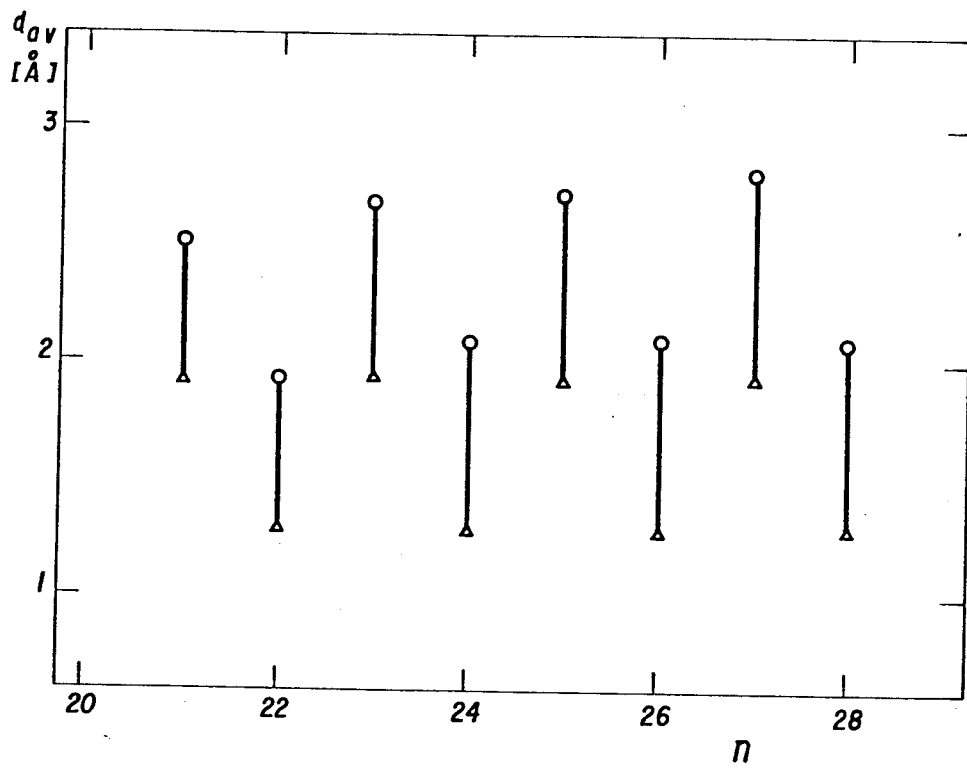
FIGURE 1

FIGURE 2
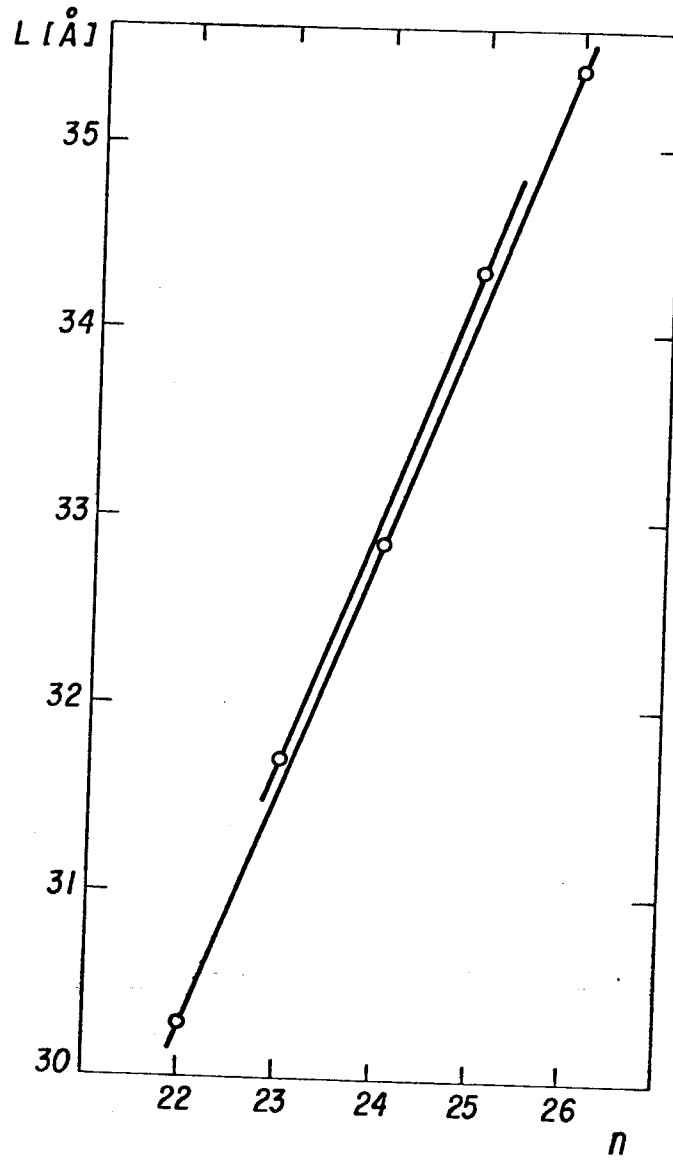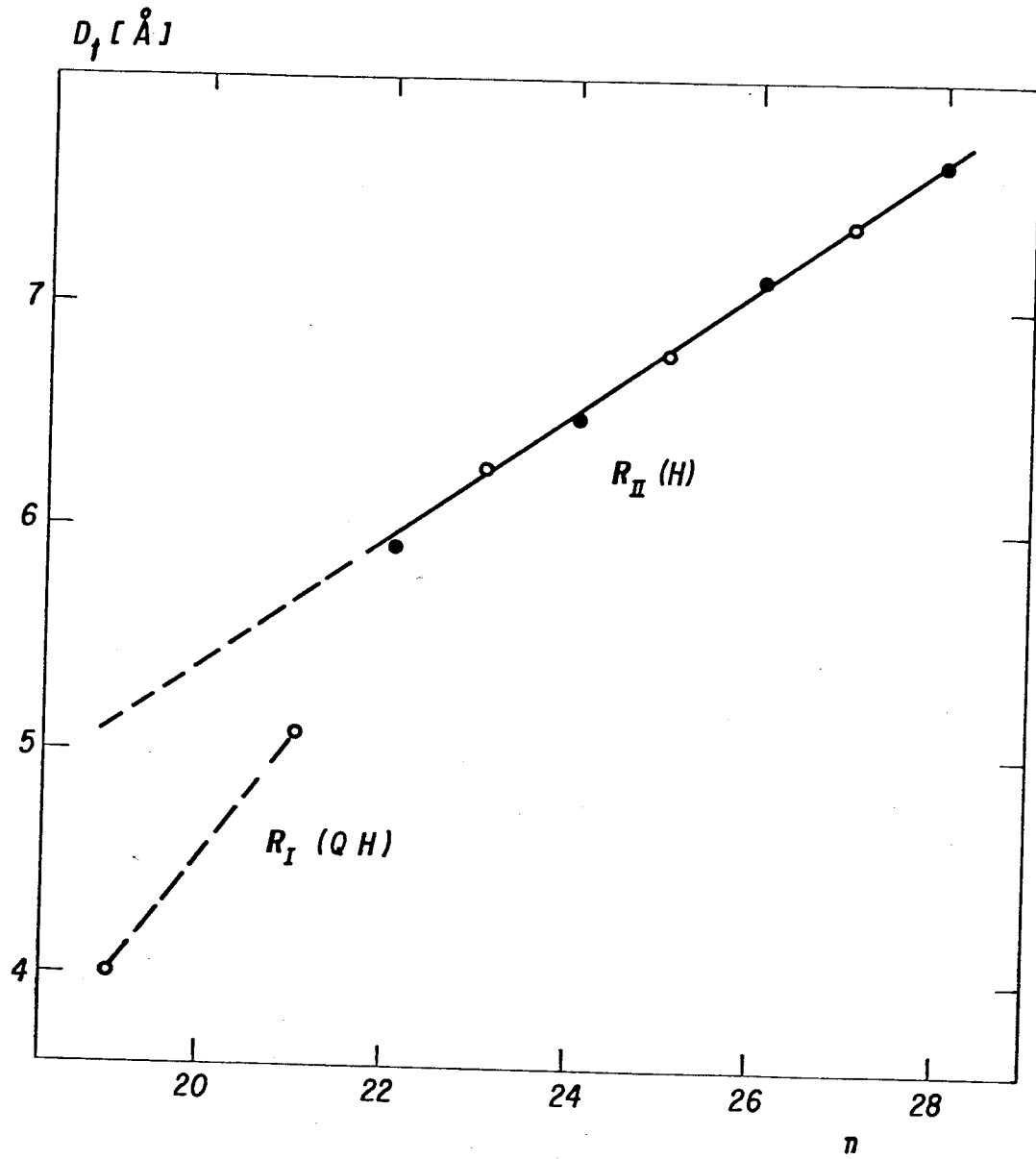
FIGURE 3

FIGURE 4

FIGURE 5

FIGURE 6

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