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X-Ray Studies of Liquid Crystals VIII: A Study of the Temperature Dependence of the Directly Observed Parameters of the Skewed Cybotactic Nematic Phase of Some Bis-(4′-n-Alkoxybenzal) -2-Chloro-1,4-Phenylenediamines

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X-Ray Studies of Liquid Crystals VIII:† A Study of the Temperature Dependence of the Directly Observed Parameters of the Skewed Cybotactic Nematic Phase of Some Bis-(4′-n-Alkoxybenzal)-2-Chloro-1,4-Phenylenediamines‡

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By X-ray diffraction, one can determine the average tilt angle, the average layer thickness, the average intermolecular distance, and the intensities of the inner and outer rings of the skewed cybotactic nematic phase, all independently of each other. We have investigated the behavior of these parameters as a function of temperature in the presence of a magnetic field for the C_6, C_8, C_{10} and C_{12} members of the bis-(4′-*n*-alkoxybenzal)-2-chloro-1,4-phenylenediamine series.

INTRODUCTION

A skewed cybotactic nematic is defined[1] as a nematic phase wherein a large part of the molecules are in groups (known as cybotactic groups) in which the centers of gravity of the molecules lie in well defined planes and the long axes of the molecules make, on an average, a rather large angle with the normal to these planes. X-ray diffraction photographs of well aligned samples in this phase show that the outer ring splits up into two crescents and the inner ring into four spots. The direction in which the

† The previous paper in the series is the one in Ref. 5.

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maxima of the outer ring are formed is perpendicular to the mean direction of the molecules, and for the inner ring these directions are perpendicular to the mean directions of the planes of four sets of cybotatic groups.[1]

From such a pattern one can determine[1,2] very easily the average tilt angle (τ, the average angle between the molecular long axis and the normal to the plane), the average layer thickness (d), the average intermolecular distance (D, the average distance between the long axes of adjacent parallel molecules), and the average intensities of the inner and outer ring maxima (I_i and I_o, respectively). We have made a study of the temperature dependence in the presence of a magnetic field of these directly observed parameters for the skewed cybotactic nematic (N_{SC}) phases of the hexyl, octyl, decyl and dodecyl members of the bis-(4′-*n*-alkoxybenzal)-2-chloro-1,4-phenylenediamine series.

The study has been done because of conflicting results for the temperature dependence of some of these parameters reported by Chistyakov and Chaikowsky,[2] De Vries,[1] McMillan,[3] Usha Deniz *et al.*,[4] and De Vries and Qadri.[5] The tilt angle is almost constant in Refs. 2 and 4 but decreases significantly in Refs. 1 and 5. Moreover, the intensity of the inner ring is found to decrease monotonically in Ref. 3 but shows a slower decrease at low temperatures in Ref. 5.

EXPERIMENTAL PROCEDURE AND DATA ANALYSIS

X-ray diffraction photographs were taken, with a flat plate camera,[1] of samples in glass capillaries (0.9 mm in diameter) using Ni-filtered Cu radiation. The temperature of the sample was determined by using a calibrated thermometer[6] and the sample-to-film distance was determined by using a precalibrated compound (calibrated with aluminum powder).[6]

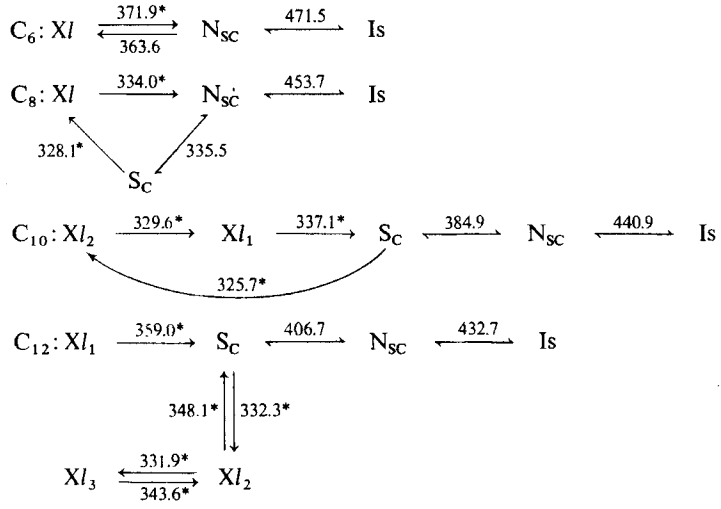
The sample was first heated into the isotropic phase (Is) and a magnetic field of about 5 K Gauss was applied parallel to the capillary axis. After the magnetic field had stabilized (about 30 min.), the sample was allowed to cool naturally to just above the smectic C (S_C) to nematic (N_{SC}) transition temperature (crystalline to N_{SC} transition temperature in the case of the hexyloxy homolog). After the temperature had stabilized, the magnetic field was lowered to about 1 K Gauss (because stronger fields had a noticeable effect on the operation of the X-ray tube) and the X-ray tube was switched on. Photographs were taken at various constant temperatures, increasing the temperature each time, until the compound had gone well into the isotropic phase (three photographs were taken in the isotropic phase for each sample), all the while maintaining the magnetic field. The exposure time for each photograph was 20 min. (25 min. for the hexyloxy homolog due to the weakness of the pattern) and all photographs for each compound were taken in one continuous series (only allowing time for the

temperature to stabilize each time at its new value) to minimize decomposition of the sample. The N_{SC}–Is transition temperature was determined before and after the experiment to check on any decomposition that might have occurred during the experiment and was found to remain constant within 1°C. Thus, there has been no significant decomposition.

All the photographs were analyzed on a digital densitometer[5,7] and all the calculations were done on the numerical data thus obtained.

The position of each of the four maxima of the inner ring was determined as the average position of the center of gravity determined for at least five different intensity contours.[5] From the position of these four maxima, the average tilt angle (τ) and the average layer spacing (d) were determined. The intensity of the inner ring was determined as the average of the five highest intensities in each of the four maxima. The two crescents of the outer ring were found to be a part of an ellipse (the long axis coincided with the direction in which the two crescents were formed) and the maximum distance between the two crescents was used to calculate the average intermolecular distance (D). For each crescent, the average maximum intensity was determined by making a scan along a radius through the center of the crescent, averaging all data within a 5° wide section centered around this radius. The intensity of the outer ring was taken as the average of these two maximum intensities. D and d were both obtained from data corrected for ellipticity on account of the geometry of our experimental set-up.[7]

All the compounds used were custom synthesized for us by Dr. M. E. Neubert and co-workers.[8] The following phase transitions were noted:



All temperatures in K.

* These temperatures reported to us by Dr. M. E. Neubert.

RESULTS

The temperature dependence of the intensity of the inner ring I_i is shown in Figure 1. The intensity of the hexyloxy homolog has been corrected for the different exposure time. The steepness of I_i and its maximum value are seen to increase with homolog number. For the C_6 and C_8 members, I_i appears to become more or less temperature independent at high temperatures, but for the C_{10} and C_{12} members this is not so. We interpret this as indicating the possibility of the existence of some cybotactic groups even in the isotropic phase. This is supported by our calculations of d (the layer spacing) in the isotropic phase.[9] Our results have failed to show a saturation effect in the low temperature region as reported in Ref. 5, but indicate rather that the intensity does decrease monotonically as mentioned in Ref. 3.

Figure 2 shows the temperature dependence of the intensity of the outer ring I_o. (The intensity of the hexyloxy homolog has been corrected for the different exposure time.) The results again do not show the saturation effect in the low temperature region,[5] except for the C_{12} homolog. There is far more scatter of the intensity data for the outer ring than for the inner ring because the outer rings were so weak on our photographs. This is a consequence of the fact that short exposure times were necessary to avoid saturating the films at the inner maxima (for C_8, C_{10}, C_{12}) and to minimize sample decomposition.

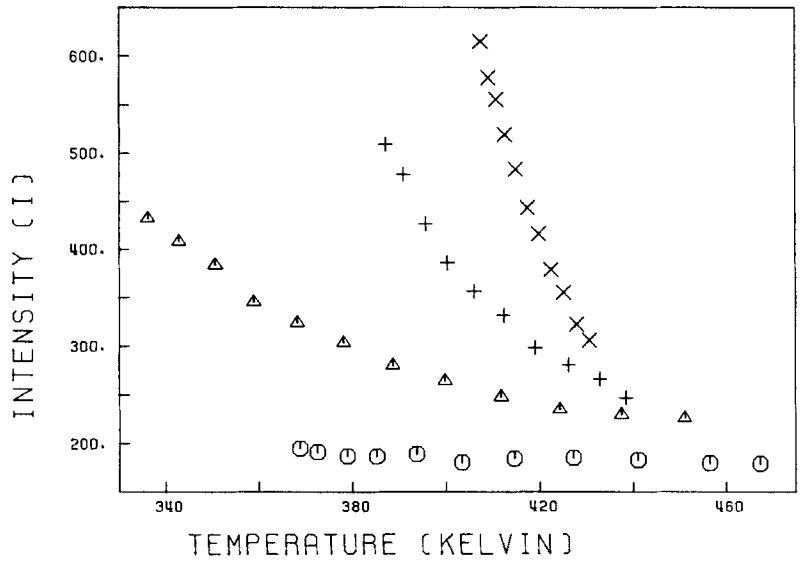


FIGURE 1 Plot of intensity of inner ring against temperature. ⏀: C_6 homolog, △: C_8 homolog, +: C_{10} homolog and ×: C_{12} homolog.

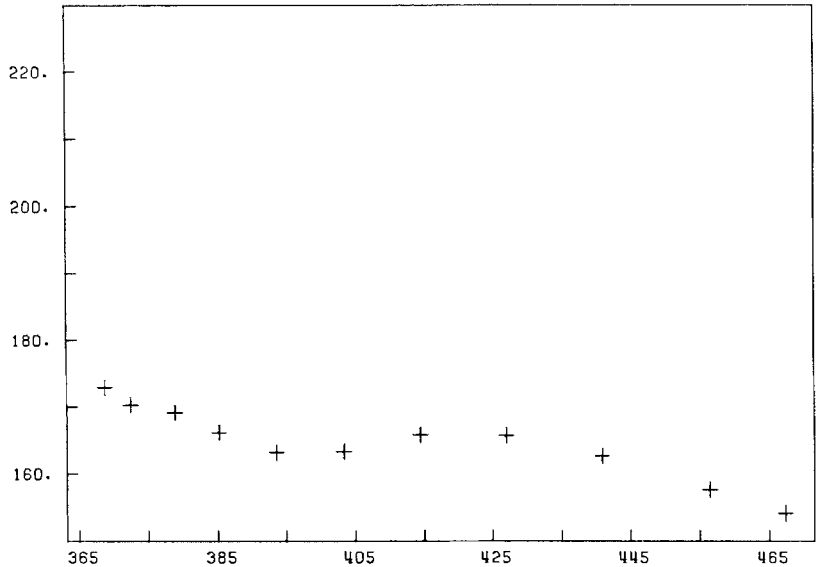
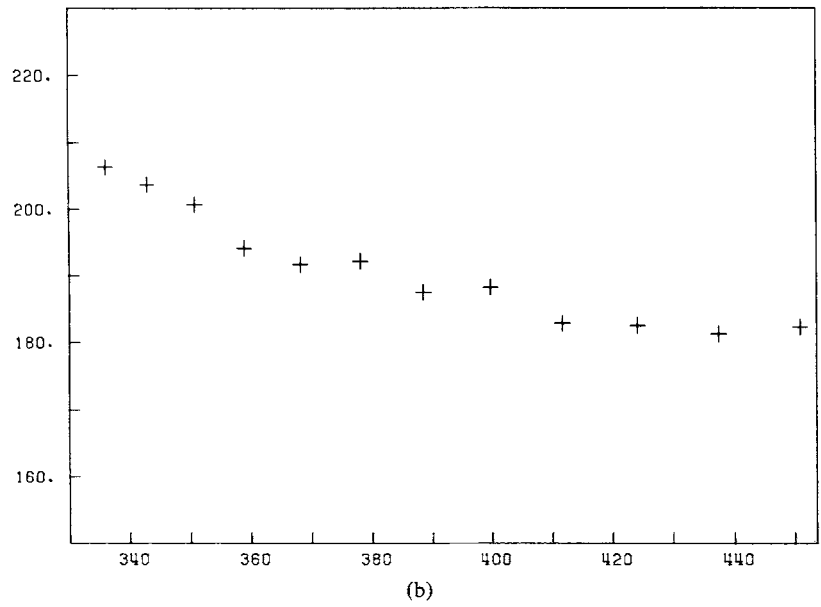
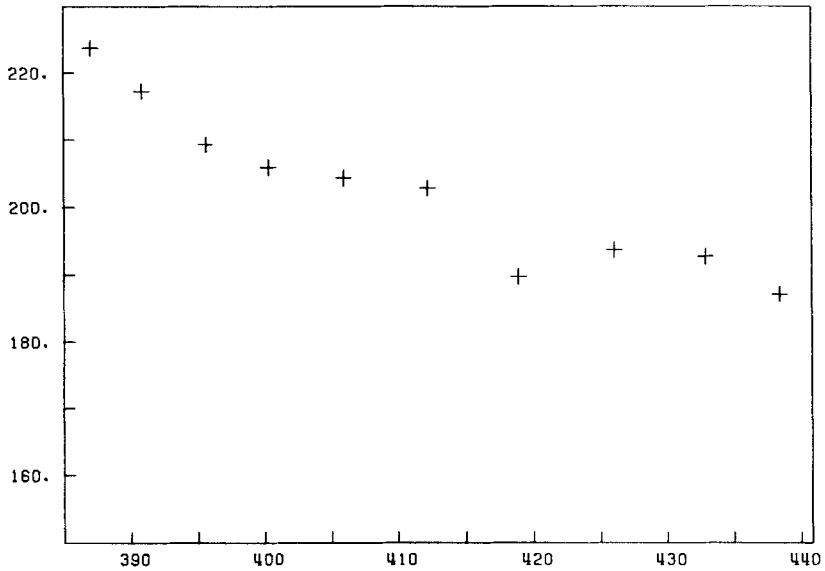
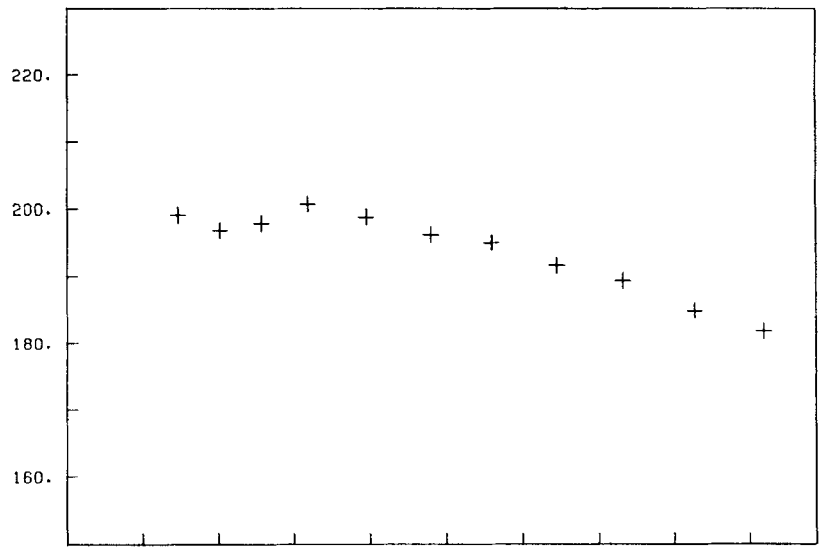


FIGURE 2 Plot of intensity of outer ring against temperature (a) C_6 homolog, (b) C_8 homolog, (c) C_{10} homolog, and (d) C_{12} homolog.





(c)



(d)

The temperature dependence of the average intermolecular distance (D) and the average layer spacing (d) (both in angstroms) are shown in Figures 3 and 4 respectively, and some numerical data are given in Table I. It is clear from the data in Table I (columns 3 and 4) that d increases significantly

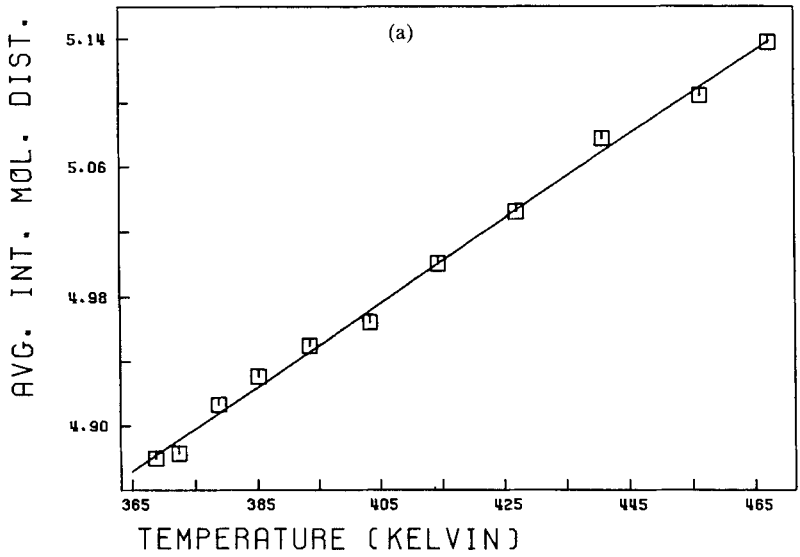
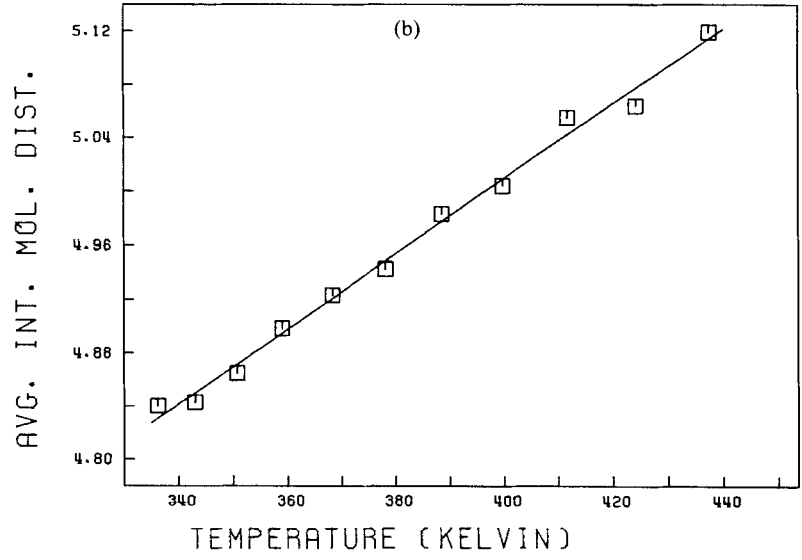
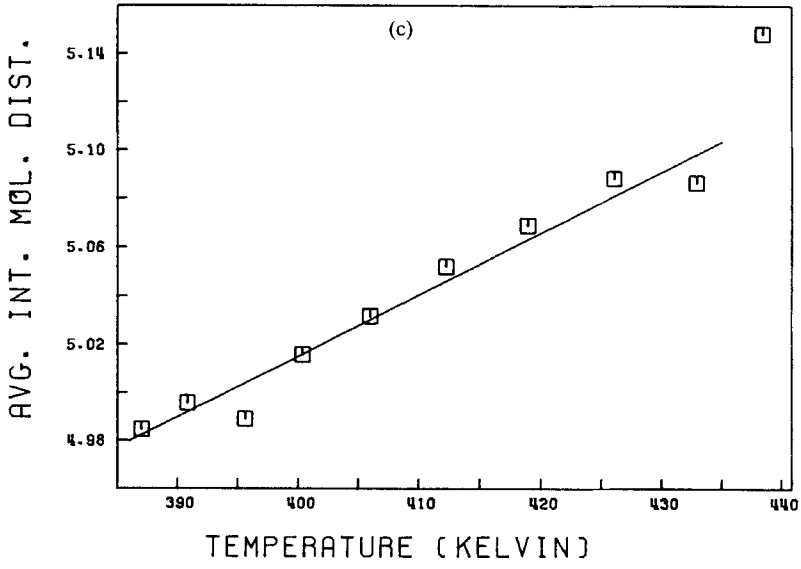


FIGURE 3 Average intermolecular distance as a function of temperature. (a) C_6 homolog, (b) C_8 homolog, (c) C_{10} homolog, and (d) C_{12} homolog. Straight line is the linear least-squares fit.





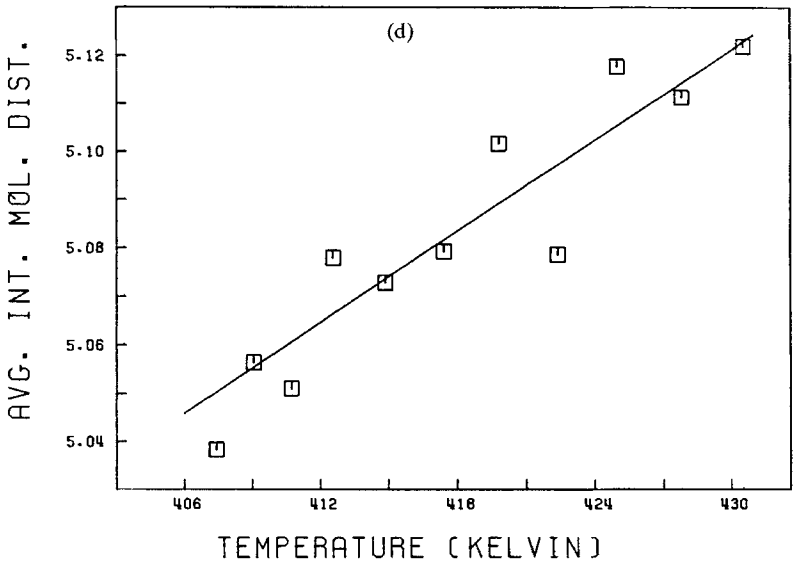


TABLE I

Some numerical data

Homolog	d at T_{SN}^{b} (Å)	d at 420 K (Å)	D at 420 K (Å)	σ^{a} (10^{-2} Å)	$\Delta D/\Delta T$ (10^{-3} Å/K)
C_6	24.05	26.54	5.015 ± 0.003	0.6	2.60 ± 0.05
C_8	27.04	30.30	5.066 ± 0.005	0.9	2.80 ± 0.08
C_{10}	32.16	33.92	5.066 ± 0.004	0.9	2.53 ± 0.19
C_{12}	36.32	37.46	5.090 ± 0.003	1.1	3.14 ± 0.19

[a] Average standard deviation of the data points.

[b] T_{SN} is the S_C to N_{SC} transition temperature. (X_l to N_{SC} transition temperature for the hexyloxy homolog).

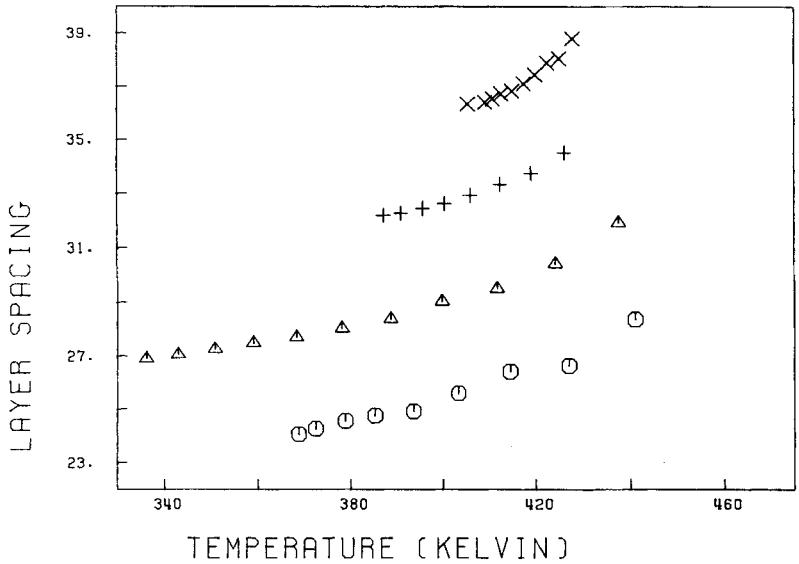


FIGURE 4 Layer spacing against temperature. ①: C_6 homolog, △: C_8 homolog, +: C_{10} homolog and ×: C_{12} homolog.

with the length of the alkyl chains[1,2,4] (n) but that the changes in D are rather small, in agreement with data reported earlier.[1,4] Nevertheless, there appears to be some increase of D with n, in particular on going from $n = 6$ to $n = 8$. Assuming a linear relationship between D and n, we find the average change of D between even homologs to be .022 ± .007 Å. This represents a much smaller increase per carbon atom than reported by De Vries[11] for some isotropic phases.

For each compound the variation of D with T (Figure 3) could be very well represented by a straight line (as for the isotropic and smectic phases of

other compounds).[6,11] The slopes of these lines are given in Table I. They are essentially equal, with an average value of $2.66 \pm 0.04 \times 10^{-3}$ Å/K. (This value is little different from the value of 2.5×10^{-3} found earlier as the average for five isotropic phases).[10,11] The average standard deviations (σ) of the individual data points are also given in Table I. The average over the four homologs is 0.008 Å which is rather large compared to the value of 0.003 Å obtained in another study.[7] The reason for this is probably the low intensity of the outer diffraction maxima.

The temperature dependence of d (Figure 4) is clearly not linear. For all homologs $\Delta d/\Delta t$ appears to increase with temperature, but this is most evident for the highest homolog. For this compound (C_{12}), $\Delta d/\Delta t$ approaches zero at low temperatures. It is interesting, in this regard, to compare Figure 4 with Figure 1; in Figure 1 the slope of the curve for the C_{12} homolog is *highest* at low temperatures. It thus appears that the changes in d and I_i do not derive from the same cause, at least not at the lower temperatures. The probable error in the data points in Figure 4, estimated from the changes in d with changes in the number of points used in determining the centers of the maxima, is about 0.1% (0.6% in the hexyloxy homolog due to the diffuseness of the four maxima in the inner ring). As is evident from Figure 4, the layer spacing increases with homolog number.

In Figure 5, we see the temperature dependence of the tilt angle τ (represented by the triangles). Also shown is the behavior of the "tilt angle"

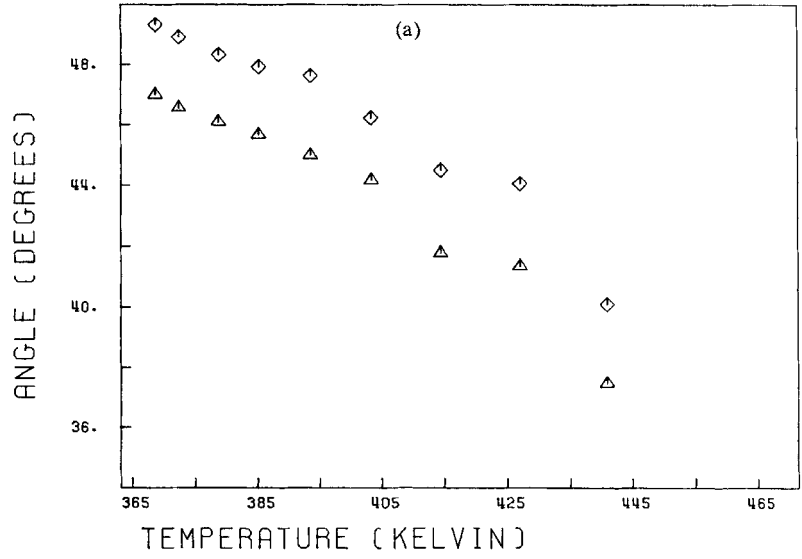
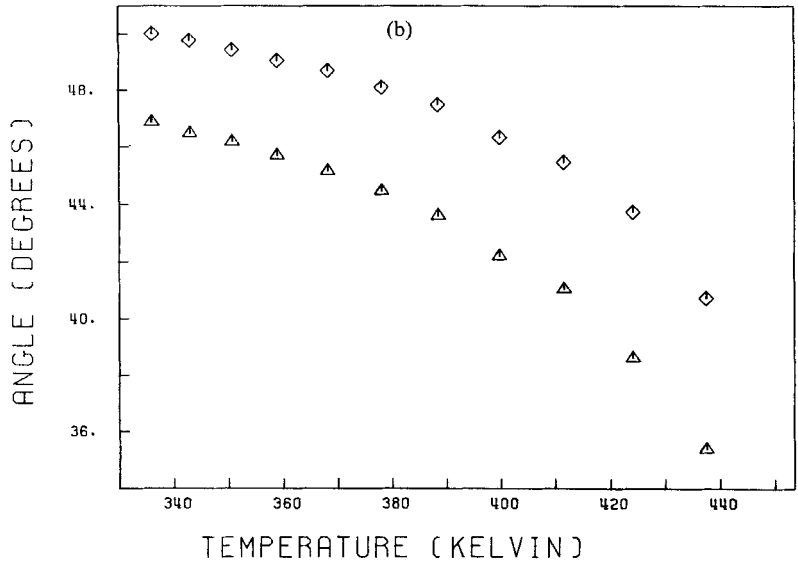
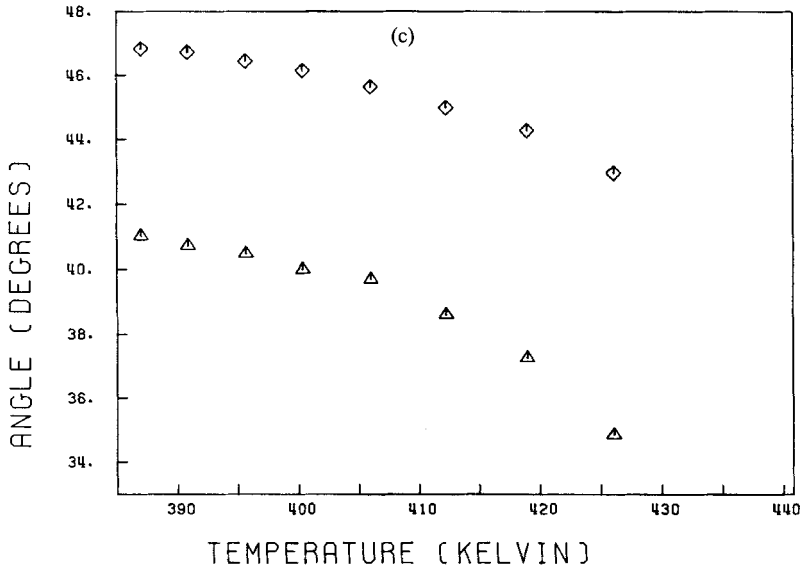
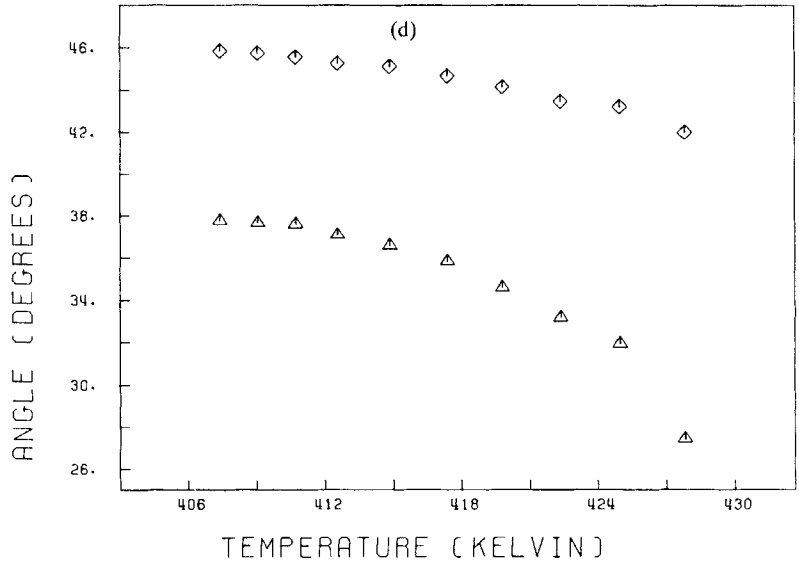


FIGURE 5 Angles against temperature. △: Observed tilt angle τ, ◇: calculated tilt angle $\cos^{-1}(d/l(T))$. (a) C_6 homolog, (b) C_8 homolog, (c) C_{10} homolog, and (d) C_{12} homolog.







which can be calculated from the layer thickness d and the molecular length $l(T)$, $\cos^{-1}[d/l(T)]$, with $l(T)$ defined as in Ref. 10. It is evident that both τ and $\cos^{-1}[d/l(T)]$ decrease monotonically with increasing temperature. The behavior of $|\Delta\tau/\Delta t|$ appears to be similar to that noted above for $\Delta d/\Delta t$. Thus, the changes in d and τ appear to derive primarily from the same cause. The difference between $\cos^{-1}[d/l(T)]$ and τ increases with temperature (except, maybe, for the C_6 homolog) and also with homolog number. The probable error in τ varies from about 0.5% at low temperatures to about 4% at high temperatures.

Two further comments should be made about Figure 5. First, for each compound the last 1 or 2 data points are missing, because at temperatures close to the N–Is point the maxima become so diffuse that their positions can no longer be determined. Second, for the more diffuse maxima there is a strong correlation between the experimental errors in $\cos^{-1}[d/l(T)]$ and in τ; this is particularly evident for the C_6 homolog (Figure 5a) which has very weak (Figure 1) and diffuse inner maxima.

CONCLUSIONS

From our data, we conclude that the intensities of the inner and outer rings decrease monotonically and do not show saturation at the lower temperature end. These results differ from those reported in Ref. 5. This might be a consequence of not using a magnetic field in the other study. The layer

spacing and the directly measured tilt angle τ, however, do level off toward lower temperatures. The tilt angle was observed to decrease monotonically with temperature by about 10 degrees. The calculated tilt angle also decreases monotonically but very slowly when compared to τ.

Acknowledgements

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