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WHY THE MOLECULES ARE TILTED IN ALL SMECTIC A PHASES, AND HOW THE LAYER THICKNESS CAN BE USED TO MEASURE ORIENTATIONAL DISORDER*

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ABSTRACT - Even though the average molecular direction in smectic A phases is perpendicular to the smectic planes, most molecules in these phases have rather large tilt angles because the orientational order parameter S in all smectic A phases is significantly less than unity. This molecular tilt inherent to all A phases accounts for the observed differences between layer thickness d and molecular length ℓ of four quite different compounds, without any need for assuming additional tilt, interdigitation, or kinking of chains. From the differences between d and ℓ, S values from 0.78 to 0.84 are obtained, which yield average molecular tilt angles from 20° to 17°. It is predicted that all smectic A phases with monomolecular layers will follow the same pattern. The concept of "inherent tilt" should apply to all orthogonal smectic phases, thermotropic as well as lyotropic.

Introduction

Since about 1970[1-4] the general understanding has been that whereas the molecules are perpendicular to the smectic planes in smectic A phases, they are tilted in smectic C phases. These models imply that in smectic A phases the thickness of the smectic layer should be about the same as the length of the molecule, but that in smectic C phases the layer thickness should be less. This indeed appeared to be the case[5-6] although it was noted[7] that even in smectic A phases the layer thickness d was about 1.7 Å less than the length ℓ of the molecule in the planar all-trans conformation (we exclude bimolecular layers from our present discussion). De Vries[5] explained this by assuming that there was a slight

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interpenetration of the ends of the molecules of adjacent layers.

Diele, Brand, and Sackmann,[8] however, reported data indicating that for a number of smectic *A* phases the differences between d and ℓ were significantly greater than those reported by De Vries.[7] They suggested that the most probable explanation for these large differences was a kinking of the aliphatic end-chains of the molecules. On the basis of the same d data of Diele et al., however, De Vries[9] argued that in these *A* phases the molecules were tilted, as in *C* phases, but without long-range order in the *direction* of tilt. De Vries reported later[10] data confirming the data of Diele et al.[8] for one of the compounds they had investigated, and De Vries, Ekachai, and Spielberg[11] found similar results for a new compound. De Jeu and De Poorter[12] reported another compound for which d in the smectic *A* phase was much less than ℓ, and adopted the explanation given by De Vries.[9] Wulf[13] developed a theory for the corresponding *A*-*C* phase transition. Doucet and Levelut[14] obtained similar data on yet another compound, but explained their results by assuming kinks in the aliphatic end-chains (the explanation preferred by Diele et al.[8]) rather than a tilted arrangement of the molecule. Leadbetter[15,16] and Leadbetter and Richardson[17] appear to have been the only ones to recognize that the orientational order parameter S should have an influence on d and should cause d to be less than it would have been without orientational disorder. But even they do not appear to have given a clear indication of how this influence of S should be taken into account.

Outline

In this paper we now propose the following general procedure for the comparison of d and ℓ values for smectic *A* phases: (1) First correct the calculated ℓ values for thermal expansion, to obtain "$\ell(T)$". (2) Next calculate from $\ell(T)$ the "d_{calc}" that would be expected on the basis of S. (3) Compare d_{obs} and d_{calc} to see if there are any significant differences.

We will also show that for our data on four quite different compounds, even though there appeared to be significant differences between d_{obs} and ℓ, there are no significant differences between d_{obs} and d_{calc}. This means that for these four compounds there are no indications of any significant interpenetration, kinking, or additional tilt (i.e., tilt beyond the inherent tilt due to S), contradicting earlier conclusions.[5,7,8,10]

Assuming that there are indeed no significant factors influencing $\underline{d}$ apart from thermal expansion and orientational disorder, we then proceed to calculate $\underline{S}$ from $\underline{d}_{obs}$ and $\ell(T)$. We find very reasonable values, and an indication that for our data $\underline{S}$ seems to be influenced more by the temperature of the measurement than by the nature of the compound.

Correction for Thermal Expansion

As far as we know, all comparisons in the literature of $\underline{d}$ data with $\underline{\ell}$ data have overlooked one important point: The $\underline{d}$'s are measured at various temperatures generally significantly above room temperature, but the $\underline{\ell}$'s are calculated from data (bond lengths, bond angles, and Van der Waals radii) obtained in general at room temperature (298°K). Because of this, a direct comparison of $\underline{d}$ and $\underline{\ell}$ is improper, and either one or the other should first be corrected to bring the two data sets to the same temperature. We have chosen to correct our $\underline{\ell}$ values for thermal expansion to the temperatures at which the $\underline{d}$'s are measured.

To do this, one obviously needs a value for the linear expansion coefficient of $\underline{\ell}$ in the smectic phase, but it is not so obvious how one can obtain this value. For the time being we have decided that the best currently available data are the linear expansion coefficients for the intermolecular distance $\underline{D}$ in the isotropic phases of various liquid crystals. For both $\underline{D}$ and $\underline{\ell}$ the contacts between adjacent molecules are mainly Van der Waals contacts involving hydrogen atoms, and as a first approximation we will assume that in both cases the thermal expansion can be treated as an increase in the Van der Waals radius of hydrogen. If this is correct, the thermal expansion should be the same for different compounds, and the data indicate that $\Delta D/\Delta T$ is indeed roughly independent of the material studied. The best data available to us are those in reference 7, Table 2. Leaving out the value for PeBEA because it appears somewhat anomalous, we obtain from these data an average of $\Delta D/\Delta T = 2.5 \times 10^{-3}$ Å/°K. We have taken this value as the magnitude of $\Delta\ell/\Delta T$ for all compounds studied, and calculated the molecular length $\underline{\ell}$ at the temperature $\underline{T}$ as $\ell(T) = \ell + (\Delta\ell/\Delta T) \times (T-298°)$, where $\underline{\ell}$ is the calculated molecular length[5] at room temperature.

Molecular Tilt Caused by Orientational Disorder

The basic characteristic of liquid crystal phases with elongated molecules is that the long axes of neighboring molecules are approximately parallel to each other. The degree of parallelism is given by the orientational order parameter $S = 1/2\langle 3\cos^2\theta - 1\rangle$, where θ is the angle between the molecular long axis and the average direction of these long axes. S values given in the literature[18-22] for smectic A phases vary considerably, but 0.8 appears to be a reasonable average value to use as a first approximation.

We will assume that the probability distribution for the direction of the molecular long axis, θ, is given by $P(\theta) = c \sin\theta \exp\{f(T) \cos^2\theta\}$. The $\cos^2\theta$ dependency follows a suggestion by Leadbetter and Richardson[17] based on the Maier-Saupe model for the distribution in nematic phases,[23] and c is a normalization constant. The function f(T) is also obtained from Maier and Saupe's paper, and is given by $(aS)/(TV^2)$, where a is a constant, S the orientational order parameter, T the absolute temperature, and V the molar volume. With this formula, S = 0.8 gives $f(T) = 8.24$ and this yields the probability distribution for θ given in Fig. 1, with $\theta_{max} = 14.2°$ and $\langle\theta\rangle = 19.3°$. Since θ is the molecular tilt angle, this means that the average molecular tilt angle in

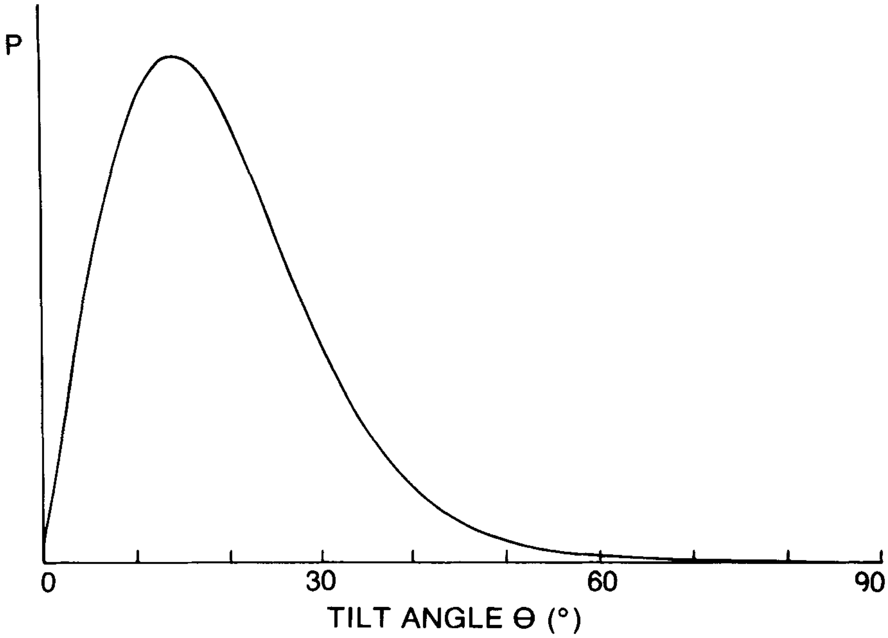

FIGURE 1. Probability distribution for the tilt angle θ, calculated for S = 0.80.

any smectic A phase is quite large.[a] Therefore, this tilt should[b] be taken into account in any model for a smectic *A* phase.

Average tilt angles as large as those indicated in the preceding paragraph will have a significant influence on the thickness of the smectic layers. This influence will have to be taken into account before any comparisons are made between d and ℓ. Thus, all discussions on the differences between d and ℓ that did not take S into consideration, such as the ones referred to in the Introduction, have been premature.

The effect of S on the smectic layer thickness d can be calculated as follows. With molecules of length ℓ and a tilt angle θ, the layer thickness d at a temperature T will be $d = \ell(T)\cos\theta$. Using the probability function $P(\theta)$ with $f(T) = 8.24$ (i.e., taking $S = 0.80$; see above), one obtains the probability distribution for $\cos\theta$ given in Fig. 2, with a

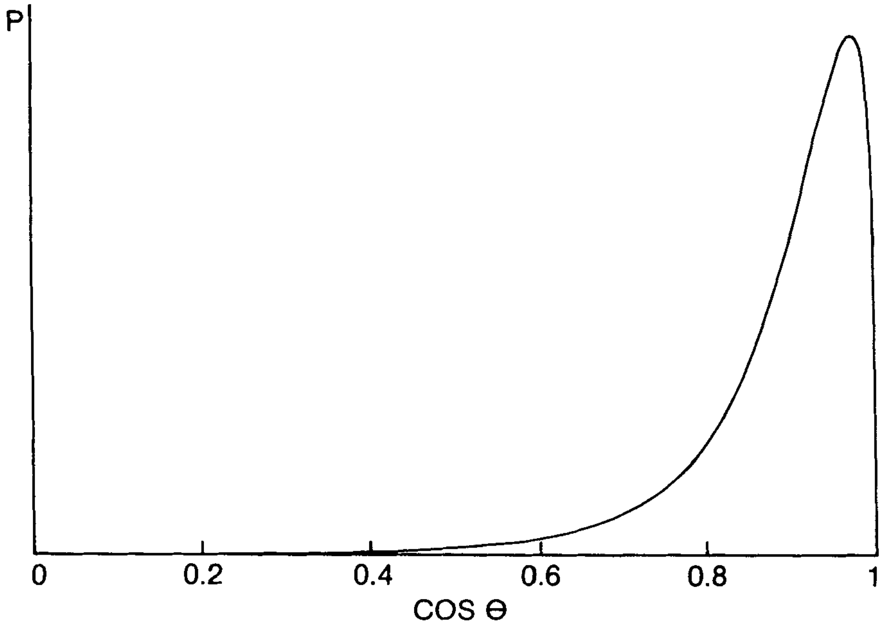

FIGURE 2. Probability distribution for $\cos\theta$, calculated for $S = 0.80$.

maximum at 0.969 and an average value of 0.927. The average d value obtained from this <cosθ> incorporates the influence of S. We will call it the calculated layer thickness, d_{calc}.

No Interpenetration, Kinking, or Additional Tilt

In Table I we have listed the d values for four smectic A phases studied at the Liquid Crystal Institute, together with the calculated molecular lengths ℓ at room temperature (planar all-trans conformation, standard bond-lengths and angles, Van der Waals radius for hydrogen), and the corresponding values of d_{calc} (using $S = 0.80$). It may be seen that whereas $\ell - d_{obs}$ is always positive and rather large, $d_{calc} - d_{obs}$ is much smaller and not constant in sign. In fact, considering that we used for S a rather arbitrarily assigned average value, these differences between d_{calc} and d_{obs} are not significant. This leads to two conclusions. (1) For the compounds listed in Table I the effects of thermal expansion and orientational disorder can account completely for the differences between d_{obs} and ℓ, without any need for assuming additional tilt, interdigitation of the molecules of adjacent layers, or kinking of the aliphatic end-chains, contrary to earlier conclusions.[5,7,8,10] (2) If we make the assumption that S does indeed account completely for the differences between d_{obs} and $\ell(T)$, then these differences provide us with a new method of measuring S.

Determination of S

Table II gives the S value (S_{exp}) obtained by requiring d_{calc} to be equal to d_{obs}, i.e., taking $\langle\cos\theta\rangle = d_{obs}/\ell(T)$.

TABLE II

Determination of S

Compound	T(°K)	S_{exp}	S_{calc}	$S_{calc} - S_{exp}$
HpBEA	333.7	0.840	0.829	-.011
EEB	349.1	0.791	0.814	+.023
HABP	366.2	0.809	0.797	-.012
PDBC	384.3	0.778	0.779	+.001

TABLE I

Data on Smectic A Phases, Taking $\underline{S}$ = 0.80

Compound[*]	Reference	$\underline{T}$ (°K)	$\underline{d}_{obs}$ (Å)	$\underline{\ell}$ (Å)	$\underline{\ell}-\underline{d}_{obs}$ (Å)	$\underline{d}_{calc}$ (Å)	$\underline{d}_{calc}-\underline{d}_{obs}$ (Å)
EEB	5	349.1	20.06[†]	21.6	+1.5	20.14	+0.1
HpBEA	7	333.7	23.85[†]	25.2	+1.4	23.45	-0.4
HABP	7	366.2	25.57[†]	27.3	+1.7	25.47	-0.1
PDBC	10	384.3	34.41	37.27	+2.9	34.75	+0.3

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[*] For the meaning of the abbreviations see the references.

[†] The data reported earlier had to be slightly corrected (+0.59%) because of a calibration error.

All four values appear very reasonable, in particular in comparison with the estimated average value of 0.80 used above. The differences among the values are not large, but a comparison with the T data shows that there might be a correlation between S_{exp} and T, with larger T giving smaller S, as would be expected. Postulating a linear relationship between S_{exp} and T, we determined the constants for this relationship ($\Delta S/\Delta T = -9.8 \times 10^{-4} (°K)^{-1}$, $S(298°K) = 0.864$), and from these and the T values we obtained the S_{calc} values given in Table II. The agreement between S_{exp} and S_{calc} is indeed quite good. No definite conclusions can be drawn from these data, but they do suggest that S_{exp} seems to be influenced more by the temperature of the measurement[c] than by the nature of the compound.

Smectic A Model

Leadbetter[15] has pointed out that, although the absolute magnitudes of the differences between ℓ and d_{obs} vary considerably for different compounds, their relative magnitudes are fairly similar.[d] For this reason we believe that an analysis of accurate data on *any* smectic *A* phase with monomolecular layers will give results similar to the ones presented in this paper. Thus, we come to the following general model for the smectic *A* phase: The molecules are extended, with no appreciable kinking or interpenetration. The average direction of the long axis is perpendicular to the smectic planes, but the long axes of individual molecules can make quite large angles with the plane normal; the average angle is about 19°. This "tilt" is a simple consequence of the imperfect parallel alignment of the molecules inherent to the smectic *A* phase. There is no long-range order in the direction of tilt. The layer thickness is not constant, but fluctuates as a function of the local average tilt angle. This results in a rather poor definition of the smectic layer spacing, and hence a rapid decrease in intensity of the higher-order reflections from the smectic layers, as observed by many investigators. These large variations in local tilt angle and layer thickness also explain why it is possible to mix smectic *A* phases with molecules of different lengths and to obtain an experimental thickness that is a linear function of the composition of the mixture.[24]

Optical modeling studies of smectic structures[25] have already shown that a structure as described above does indeed give the x-ray diffraction pattern of a smectic *A* phase (see Ref. 25, Figure 4f). A rough two-dimensional model of the molecular arrangement in such a structure is also given in that paper (same Figure).

The concept of smectic A phases as "orthogonal" and smectic C phases as "tilted" thus appears to make sense only if applied to the average direction of the molecular long axis, not to the molecular long axes themselves.

The conclusion that the molecules are tilted in smectic A phases extends, of course, also to the other "orthogonal" phases, as smectic B and E, and also to lyotropic lamellar phases and biological membranes.

Footnotes

a. One might argue that the value of $\langle\theta\rangle$ depends on the function used for $P(\theta)$. It turns out, however, that a variety of $P(\theta)$ functions give essentially the same $\langle\theta\rangle$ for a given S.

b. This appears to have been done in the incoherent neutron scattering calculations in reference 17.

c. All T values are temperatures roughly in the middle of the smectic A ranges.

d. There appear to be a few exceptions, but explanations for these anomalous cases will be found in due time, we trust.

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