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Molecular Conformation and Orientation in Some Smectic C Phases

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X-ray diffraction measurements are reported on two types of smectic C phases. First, an example of a compound showing very small variation in layer spacing through the smectic A and C phases was studied. It is concluded that the results are consistent with the normal second-order behaviour in which the tilt angle in the smectic C phase is zero at the A to C transition, but in this case only reaches about 10 ° at lower temperatures because of the small temperature range of the C phase.

Second, a homologous series of 4-alkyloxycinnamic acids was studied and some measurements were also made on 4-hexadecyloxybenzoic acid. The cinnamic acid results have been analysed to give information about the gross average molecular conformation in the smectic C phase. This conformation is similar to that determined earlier for the 4-alkyloxybenzoic acids in both crystal and smectic C phases. Direct measurements of the tilt angle from the symmetry of the diffraction patterns show that the appropriate long axis of the molecule is the vector joining the two ends of the markedly non-linear molecule. The implications of these results for the fast molecular rotations known to occur in smectic C phases are briefly discussed.

INTRODUCTION

Smectic C (S_C) phases have a finite tilt angle, θ, between the wave normal of the smectic density wave and the director. The magnitude of the tilt angle will depend somewhat on how the director is defined and measured, but for our present purposes we take this to be the average

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direction of some "long axis" of the molecules which may be defined operationally according to the experiment in question.

It is well known that there are different kinds of behaviour for the temperature dependence of θ according to which phase occurs above the S_C phase. The most widely studied S_C phases are those formed on cooling from smectic A (S_A) phases. These S_A to S_C transitions appear to be second order with $\theta = 0$ at the transition temperature and progressively increasing on cooling.[1-6] TBBA has been perhaps the most extensively studied example where optical, e.s.r., n.m.r, and X-ray measurements of θ are all in agreement. X-ray measurements can give values for θ in two different ways: firstly, from the observed symmetry of the diffraction pattern from an aligned sample and, secondly, from the layer spacing d and the effective molecular length, l, when $\theta = \cos^{-1}(d/l)$. In some cases (e.g. TBBA) l appears to be just the actual molecular length for the most fully extended conformation and then, in the S_A phase, $d = l$. More usually, however, in the S_A phase $d < l$ for the most extended conformation because of thermal fluctuations of the long axes and/or conformational changes in the molecules themselves, and the choice of l for evaluating θ in the S_C phase requires some care. A number of cases have been reported[7-10] where $d < l$ in which d is said to be constant throughout the S_A and S_C phases, suggesting the existence of a different type of S_A to S_C transition but, because of the small range of existence of the S_C phase and the correspondingly small tilt angles, the latter are difficult to measure accurately from d-spacing measurements of conventional accuracy (*ca* 1%).

A second common type of S_C behaviour is found following a nematic (N) to S_C transition. Here, S_C-like fluctuations (cybotactic groups) are usually present in the N phase, having a tilt angle similar to that found in the S_C phase at the transition.[11] The temperature dependence of θ is always weak in these cases. Following earlier work in the 4-alkyloxybenzoic acid series,[12,13] we report here similar X-ray measurements on a series of 4-alkyloxycinnamic acid S_C phases having N to S_C (or isotropic to S_C) behaviour. Analysis of the data leads to positive information on the gross molecular conformations and the tilts of the molecules relative to the layers.

Similar behaviour, in which θ is only weakly temperature dependent, is found below the direct transition from isotropic liquid to S_C and data on one such system have been obtained. Finally, it is interesting to note that there appears to be no correlation between the type of S_C phase and the nature of the phase occurring below S_C in temperature.

THE TILT ANGLE IN THE S_C PHASE OF HEXYL 4-(4′-DECYLOXYPHENYL)BENZOATE (HDPB), $C_{10}H_{21}OPhPhCOOC_6H_{13}$

Previous measurements on this compound[7] seemed to show that d is independent of T throughout the S_C and S_A ranges. A number of other similar cases has also been reported but, in all cases, the range of existence of the S_C phase is relatively small, typically less than 10 °C. The phase behaviour for HDPB is:

$$\text{Cr } 60\,^\circ\text{C } S_C \; 67\,^\circ\text{C } S_A \; 84\,^\circ\text{C I}$$

In view of the potential importance of these results for a proper understanding of the S_C phase, we have made more accurate measurements of the layer spacings in HDPB. The results, which have a relative accuracy of ±0.1 Å, are shown in Figure 1. Variation in d is less than 2% over the S_C range and d is always less than the most extended molecular length, in both S_A and S_C phases. Because the molecular conformation in the smectic phases is unknown and because thermal fluctuations of the molecules will in any case reduce the effective length of the molecules,[7,11,14] we define the effective molecular length (l_{eff}) as equal to the layer spacing in the S_A phase. The tilt angle, which is zero for the S_A phase, is then the angle between the centre of the orientational distribution function and the layer normal, and it is assumed that the width of the distribution function (and hence the value of l_{eff}) is insensitive to temperature. The tilt angle, defined by $\theta = \cos^{-1}(d/l_{eff})$ is also shown in Figure 1. It is clear that

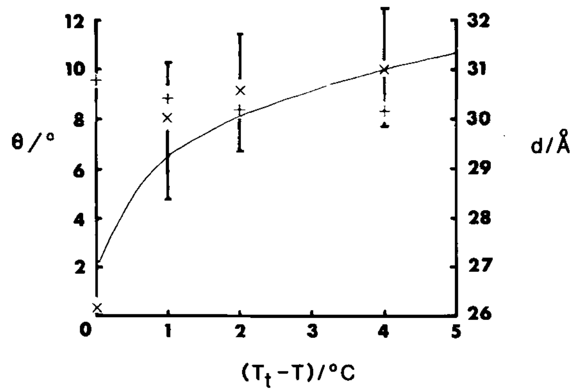

FIGURE 1 Layer spacings (d, +) and tilt angles (θ, X) for HDPB $\{\theta = \cos^{-1}(d_c/l_{eff})\}$. The solid line is from the esr data of Luckhurst and Timimi.[15]

the tilt angle is small ($d = l_{eff}$) which makes accurate values, and hence any temperature dependence, difficult to obtain by this method. However, the tilt angle through the S_C phase has been determined in this case from e.s.r. measurements[15] which show θ to increase smoothly with decreasing temperature from a zero value at the S_C–S_A transition. The X-ray data are entirely consistent with the e.s.r. results, although they are not adequate on their own to define accurately the temperature dependence of θ up to the transition. It is clear therefore that this is a normal S_A–S_C behaviour, and we believe that this is also true of the other published cases of "constant" d spacings throughout S_A and (short) S_C phases. There is thus no real evidence for a second type of S_C–S_A transition.

SMECTIC C–NEMATIC OR ISOTROPIC SYSTEMS

The most extensively studied of these systems is perhaps the series of 4-*n*-alkyloxybenzoic acids, where an S_C phase occurs when the chain contains seven or more carbon atoms. Earlier models for this system assumed an extended conformation for the hydrogen-bonded dimers, but clear evidence for a non-linear conformation was provided by Blumstein and Patel who measured d spacings for the even-membered homologs in the series having from 8–18 chain carbon atoms. These d-spacings increase regularly by an average of 4.5 Å for each additional two methylene residues in the chain, leading to a tilt angle for the chain axis of 28 ± 5°.[13] With the tilt angle of the chain known, an extrapolation to zero chain length leads to an estimate of that part of the d spacing attributable to the core, about 3.7Å. This requires the core axis to make a very small angle, *ca* 13°, with the layer surface and a correspondingly large angle, *ca* 77°, with the layer normal. One of us has shown[12] that this requirement can be met by assuming that the molecular conformation in the S_C phase is that found in the room-temperature crystal phase of the acids yielding S_C phases. This conformation is characterised by a *gauche* orientation of C(γ) and O about the C(α)—C(β) bond of the chain, the relevant torsion angle being 70 ± 2°.

The homologous series of 4-*n*-alkyloxycinnamic acids is very similar to that of the 4-*n*-alkyloxybenzoic acids and yields an S_C phase where there are nine or more carbons atoms in the chain. It seemed worthwhile to see what information could be obtained as to average molecular conformation in the S_C phase of these acids. Measurements of d spacing in the even homologs having 10–18 chain carbon atoms are given in Table I. Surprisingly, *d* spacings for this series are smaller, for a given number of chain atoms, than for the corresponding alkyloxybenzoic acids. However, with the exclusion of the anomalously small C_{16}–C_{18} increment, indicative of enhanced chain melting in the S_C phase of the latter homolog, the average increment in *d* spacing in ascending the series is 4.4 Å, very similar to that observed in the alkyloxybenzoic acid series. This increment leads to a tilt angle for the chain axis of 30°, within the limits of error identical to that found for the previous series. Applying the factoring technique of Blumstein and Patel to calculate the contribution of the core to *d* leads to a value of 1.0 ± 0.5 Å, once again pointing to a conformation in which the core axis is nearly parallel to the layer surface (see Figure 2).

The contribution of the core to *d* is relatively insensitive to the exact conformational model adopted, provided that the gross overall conformation is as described. For our calculations we have assumed that C(α) of the chain is coplanar with the core and that there is a *gauche* orientation of O and C(γ) about the C(α)—C(β) bond analogous to that found in the crystal structures of the alkyloxybenzoic acids. The sharper angle between core and chain axes which would be required in the present series is achieved by a small rotation about the O–C(α) axis.

No crystal structure data are thus far available for the smectogenic alkyloxycinnamic acids but, in analyses of the even-membered nematogenic homologs having from 2–8 chain carbon atoms, which have extended linear conformations, Bryan and Hartley[16] pointed out that chain packing became progressively less efficient as chain length increased, and they predicted that a transformation to an alkyloxy-

TABLE I

Layer spacings and tilt angles for the alkyloxycinnamic acids[a]

n	*d*/Å	*a*/Å	θ(calc)/deg	θ(obs)/deg
10	25.6	32.2	51	
12	29.2	34.7	50	50 ± 5
14	34.7	37.2	47	
16	38.7	39.8	46	
18	39.6	42.3	47	

[a] θ(calc) obtained from the model discussed in the text as $\tan^{-1}(a/d)$ where *d* is the observed layer spacing and *a* is the projection onto the layer of the distance between the terminal carbon atoms of the acid dimer (see Figure 2). $\Delta a/\text{Å} = 2 \times 2.54 \sin 30° = 2.54$. Van der Waals radii of 2.0 Å for the terminal —CH_3 groups are included in the calculations.

benzoic acid like conformation was probable for the higher homologs. While the data presently available do not confirm this directly, the occurrence of such a conformation in the S_C phase lends some support to this suggestion.

An interesting question arises as to the physical significance of the directly observed tilt angle in these systems where the molecular conformation is so markedly non-linear. As mentioned earlier, this angle will be sensitive to the particular experimental technique used to measure it. We offer here a few comments on this angle as observed by X-ray diffraction in the alkyloxybenzoic and alkyloxycinnamic acid S_C phases in the few cases where a sufficiently well aligned sample could be prepared which allowed a direct measurement.

In the X-ray case, the tilt angle is the angle between the clearly defined layer normal and the normal to a line joining the centres of the diffuse scattering peaks. The latter normal will usually be the direction of the aligning field. Although this direction is clearly related to some average electron density distribution along the molecule, it is far from obvious what particular 'long axis' of the molecule is thus defined when the molecule is far from linear, as in the present cases.

Data have been obtained for the C_{16} benzoic acid and for the C_{12} cinnamic acid (Tables I and II), and an earlier measurement has been made by Chistyakov[17] for the C_9 alkyloxybenzoic acid. In all cases, comparison of the calculated and directly observed tilt angles shows that, within the fairly large limits of experimental error, the effective long axis defined by the X-ray measurement is that joining the two ends of the molecule (see Figure 2). To define l_{eff} for a molecule requires a specification of average molecular conformation. In the X-ray case, positive evidence for the use of anything other than the most extended conformation can only be obtained by making measurements of d for a homologous series. Provided that the tilt angle is relatively large ($\gtrsim 30°$) its calculation from $\cos^{-1}(d/l)$ is in fact not very sensitive to the assumed molecular length. Thus, for the 4-non-

TABLE II

Layer spacings and tilt angles for 4-*n*-hexadecyloxybenzoic acid

$T/°\text{C}$	110	120	130
$d/\text{Å}$	40.8	40.2	39.6
$\theta(\text{obs})/\text{deg}$		all 45 ± 5	
$\theta(\text{calc})^a/\text{deg}$	40	40	42

[a] θ(calc) was obtained as for the cinnamic acid.

yloxy[17] and the 4-hexadecyloxybenzoic acids (Table II), the assumption of a fully extended conformation leads to tilt angles close to those calculated for the detailed model, although the measurements of *d* for the homologous series show clearly that the average molecular conformation is in reality quite different from this. This is *a fortiori* true for the alkyloxycinnamic acids, where use of the fully extended molecular conformation leads to calculated tilt angles which are too large; e.g. for the C_{12} acid 57° as against the 50° both directly observed and derived from our model.

The deduction of average molecular conformation in the S_C phases of these acids has interesting implications for the rapid molecular rotations which must be occurring in all S_C phases.[5,6,17] It seems clear that the molecules cannot rotate as rigid bodies about their minimum axes of inertia, otherwise a different mean tilt angle for the chains would result. Overall rotation of the molecule must be coupled to individual rotations of cores and chains in such a way as to retain the average zig-zag conformation observed. We also note that deuterium nmr studies[19,20] suggest considerable chain disorder in smectic C (and other) liquid crystal phases, but this can perhaps be reconciled with the extended chain conformation implied by the X-ray results by

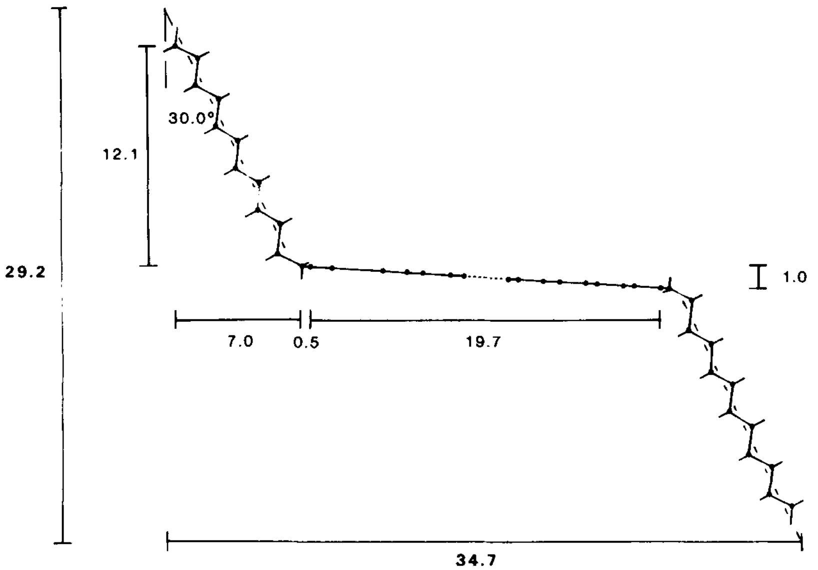

FIGURE 2 Molecular conformation adopted in the S_C phases of the 4-alkyloxycinnamic acids showing the calculated tilt angle in the case of the C_{12} acid: $\tan^{-1}(34.7/29.2) = 50°$

noting that the latter are giving only the average space required perpendicular to the layer. The results therefore suggest that a wriggling chain acts in this sense equivalently to a rigid chain in its fully extended conformation.

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References

1. T. R. Taylor, S. L. Arora and J. L. Fergason, *Phys. Rev. Lett.*, **25**, 722 (1970).
2. G. R. Luckhurst and F. Sundholm, *Mol. Phys.*, **21**, 349 (1971).
3. J. Doucet, A. M. Levelut and M. Lambert, *Mol. Cryst. Liq. Cryst.*, **29**, 317 (1973).
4. C. A. Wise, D. H. Smith, and J. W. Doane, *Phys. Rev.*, **7A**, 1366 (1973).
5. Z. Luz and Y. S. Meiboom, *J. Chem. Phys.*, **59**, 275 (1973).
6. J. Doucet and A. M. Levelut, *J. Phys.* (*Paris*), **38**, 1163 (1977).
7. A. J. Leadbetter in *The Molecular Physics of Liquid Crystals*, (Eds. G. R. Luckhurst and G. W. Gray) Academic Press, London and New York, 1979, Ch. 12, p. 285.
8. S. Diele, P. Brand and H. Sackmann, *Mol. Cryst. Liq. Cryst.*, **16**, 105 (1972).
9. A. de Vries, *Mol. Cryst. Liq. Cryst. Lett.*, **41**, 27 (1977).
10. W. H. de Jeu and A. de Poorter, *Phys. Lett.*, **61A**, 114 (1977).
11. A. J. Leadbetter and E. K. Norris, *Mol. Phys.*, **38**, 669 (1979).
12. R. F. Bryan, P. Hartley, R. W. Miller and M. S. Shen, *Mol. Cryst. Liq. Cryst.*, **62**, 281 (1980).
13. A. Blumstein and L. Patel, *Mol. Cryst. Liq. Cryst.*, **48**, 151 (1978).
14. A. de Vries, A. Ekachai and N. Speilberg, *Mol. Cryst. Liq. Cryst. Lett.*, **49**, 143 (1979).
15. G. R. Luckhurst and B. A. Timimi, *Phys. Lett.*, **75A**, 91 (1979).
16. R. F. Bryan and P. Hartley, *Mol. Cryst. Liq. Cryst.*, **69**, 47 (1981).
17. I. G. Chistyakov, A. D. Inozemtseva and R. I. Zharenov, *Sov. Phys. Crystallogr.*, **21**, 314 (1976).
18. A. J. Leadbetter and R. M. Richardson in *The Molecular Physics of Liquid Crystals*, (Eds. G. R. Luckhurst and G. W. Gray) Academic Press, London and New York, 1979, Ch. 20, p. 451.
19. J. Charvolin and B. Deloche in *The Molecular Physics of Liquid Crystals* (Eds. G. R. Luckhurst and G. W. Gray) Academic Press, London and New York, 1979, Ch. 15, p. 343.
20. N. Boden, L. D. Clark, R. J. Bushby, J. W. Emsley, G. R. Luckhurst and C. P. Stockley, *Mol. Phys.*, **42**, 565 (1981).