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CHAIN ORDERING IN SMECTIC C PHASES

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Abstract: A model of S_C phase has been proposed in which in addition to the ordering of the rigid portions of the molecules, orientational ordering of the end hydro-carbon (H-C) chains is also taken into account. The layer spacing calculated from this model takes into account the tilt directions of both, the rigid portions as also of the H-C chains. Our x-ray diffraction results agree well with the predictions of the model.

Several models of the smectic C(S_C) phase have been put forward[1]. These models take into account the orientational ordering of the rigid portions. However none of them takes a proper account of the chain ordering in this phase. In this paper we propose a model for the S_C phase in which the main emphasis will be on the importance of considering the ordering of the alkyl chains. Our x-ray diffraction results from aligned samples confirm the proposed model.

The fact that the chains play an important role in the S_C phase is suggested by several observations. Firstly, in general for lower chain length only nematic phase is stable whereas S_C phase stabilizes as the chain length increases. This can be seen from the phase diagram for p-n-Alkoxy Benzylidene-p-Amino Benzoic Acids (mBABA) (Fig.1). Thus,

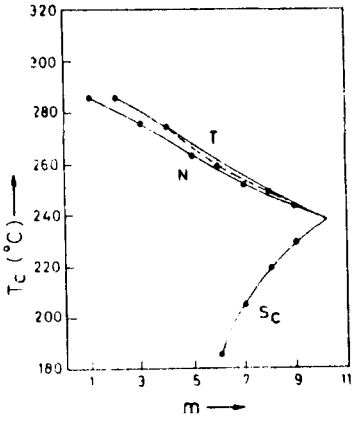


FIGURE 1 Phase diagram of mBABA.

chain-chain interactions are important in stabilizing the S_C phase. Second important indication follows as a consequence of the role of dipoles pointed out by McMillan[2] in stabilizing S_C phase. Fig.2a shows the structure of mBABA molecule along with the observed fact that these molecules form dimers[3]. It can be noted that with

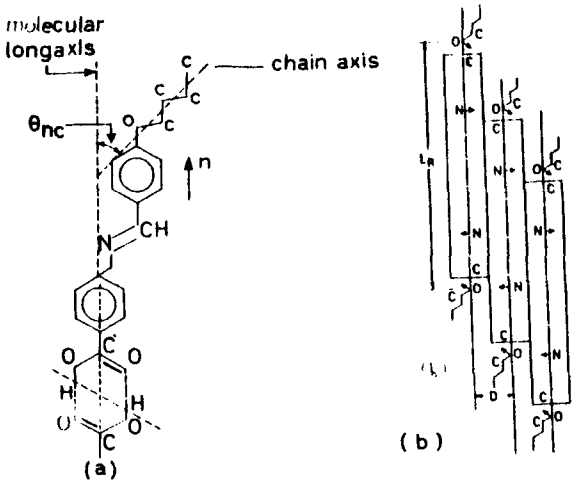


FIGURE 2 (a) mBABA molecule
(b) Schematic representation of mBABA indicating the positions of permanent dipoles.

each dimer unit there are four dipole moments one each at the two oxygen and two nitrogen sites. Fig.2b gives a schematic representation of three neighbouring dimers with their dipole moments shown explicitly. It is seen that C-O-C part of the chain should get ordered as soon as the dipole moments get ordered in S_C phase. From the work on the deuterated samples in the nematic phase it has been reported[4,5] that it is normally the last three carbon atoms in the alkyl chain which are considerably disordered. Otherwise the order parameters for the other segments are nearly the same as that for the first segment. Thus, pinning of C-O-C is transmitted through the alkyl chain and helps the chains to order. Thirdly, the fact that chains of alkoxy benzoic acids are ordered in the crystalline state is well established by the studies of

Bryan[6]. Hence it is only natural to expect that in the smectic phase there will be a remanance of this ordering.

It is important to realize that the bond angles C-O-C etc. tend to keep to their natural values. Thus, the chain direction makes an angle θ_c with respect to the long axis as in Fig.2a. If the chains are considered to be parallel to each other, then this angle would be locked in space, and the layer spacing as seen from Fig.3a, will

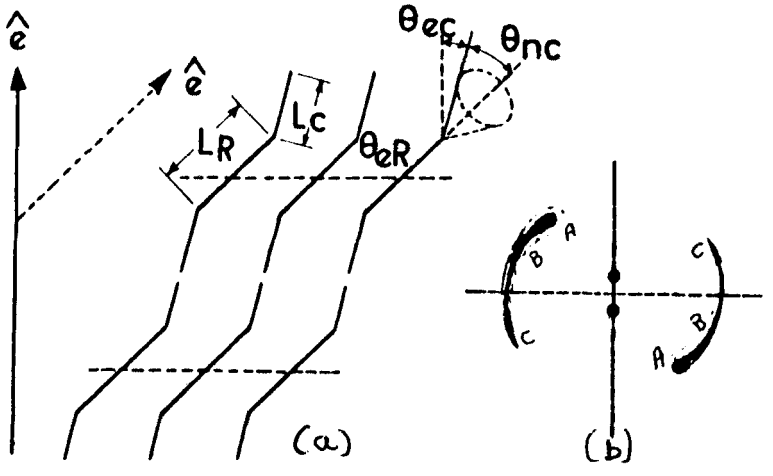


FIGURE 3 (a) Arrangement of molecules in the S_C phase with chains aligned (b) Corresponding expected x-ray diffraction pattern.

be given by

$$d_1 = L_R \cos\theta_{eR} + L_c \cos\theta_{ec}$$

where L_R - length of the rigid portion

L_c - Chain length

θ_{eR} - Angle between the layer normal, $\hat{e}$ and the long axis (the tilt angle)

θ_{ec} - Angle between the layer normal and the chain axis.

Conventionally, the layer spacing was determined by the relation,

$$d_2 = L \cos\theta_{eR}$$

where $L = L_R + L_c \cos\theta_c$

Inherent in this equation is the assumption that in space the chains can take up all possible directions lying on a cone of angle θ_c around the director, $\hat{n}$. When the chains are parallel to each other, equation (2) is no longer valid and one has to use equation (1) for calculating θ_{eR} from the observed layer spacing. It is evident from Fig.3a that the chains cannot be taken more or less parallel to the layer normal[6,7], since even if $\theta_{eR} = \theta_{nc}$, θ_{ec} need not be zero. The ordered chains of two consecutive layers can be non-interpenetrating or interpenetrating. Typical examples of these two cases where the chain axes are considered to be in the plane of $\hat{n}$ and $\hat{e}$, are shown in Fig.3a and 4a respectively. Also shown in Figs.3b and 4b are the x-ray diffraction patterns

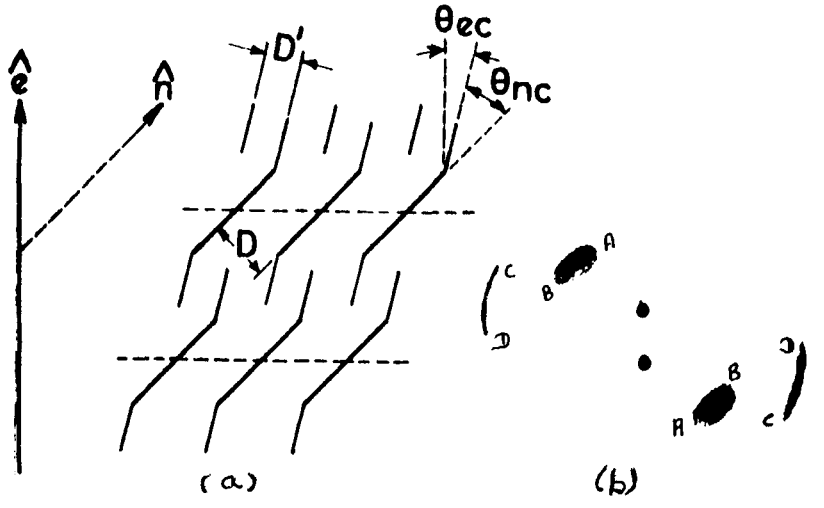
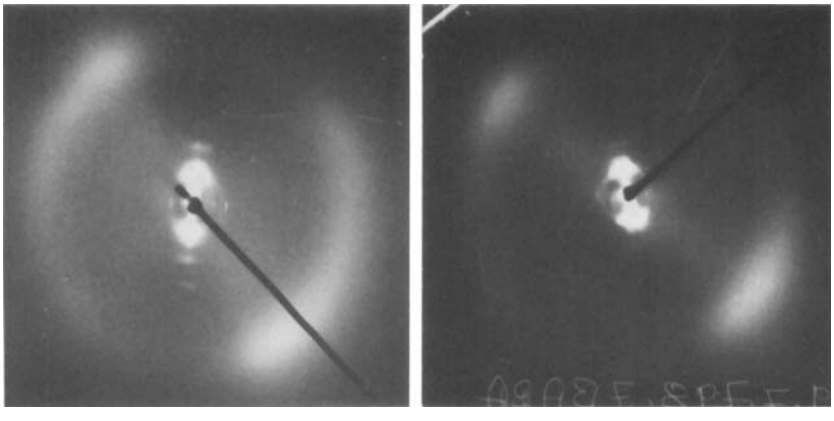


FIGURE 4 (a) Molecular arrangement in S_c phase with interpenetrating chains (b) Corresponding expected diffraction pattern.

expected correspondingly, from the arrangements as in Figs.3a and 4a respectively. It is easily seen for example from Figs.3a, b that the contribution to the diffracted intensity from the central rigid part will be along the arc AB while that from the chains form an assymmetric segment BC in continuation of this arc. Hence, our contention is that the study of the portion BC will give important information regarding the chain ordering. Such information can be supplemented further by NMR or neutron diffraction studies on deuterated samples

or by spin probe studies. In case the chains overlap, the diffraction from the chains would not form a natural continuation of AB as in the previous case but would fall on a circle of larger radius as shown by segment CD in Fig.4b. This is because when the chains overlap the average interchain distance D' will be smaller than D, the average distance between the rigid portions and hence diffraction maxima for the chain portions should occur at a larger diffraction angle. In order to observe the effect of chain ordering, it is necessary to have a monodomain sample where the rigid portions as well as the chains are aligned. If the chains are disordered, one would get symmetric maxima on either side of the segment AB.

Our x-ray diffraction patterns of the oriented samples of mBABA show conclusively that the chains order and give rise to diffraction maxima which are not centred around the equator. X-ray diffraction patterns with monodomain samples of 6 and 7BABA are shown in Figs.5a and 5b respectively. Here the samples were heated to nematic phase in a capillary of 0.5 mm diameter and they were aligned in a magnetic field of 1.6 KG. Then the samples were cooled to get a monodomain S_C phase. These photographs clearly show that they are of the type Fig.3b and imply that the chains are ordered and that the overlap between the chains from neighbouring planes, if any, is negligible. It is worth noticing from



(a) 6BABA (b) 7BABA

FIGURE 5 X-ray diffraction pattern of aligned S_C phase.

the photographs that in the S_C phase the director is not held along the magnetic field direction. The alignment is probably a total effect of an aligned nematic phase and the action of capillary on the chains which helps to get monodomain chain alignment at the S_C-N phase transition.

Conclusions

We conclude that in those S_C phases where the dipole-dipole interaction is important, the alkyl chains are ordered [this need not be true for S_C phases in general] . This chain ordering can be studied by x-ray diffraction and Figs.5a and 5b show a clear evidence of chain ordering of the type shown in Fig.3a. Such ordering affects the conventional way of calculating the tilt angle from the layer spacing from eqn.2, and eqn.1 gives a better relationship between the layer spacing and the tilt angle.

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