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ON THE DIFFERENCE BETWEEN SOLID CRYSTALS AND LIQUID CRYSTALS WITH THREE-DIMENSIONAL ORDER*

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ABSTRACT - The most important experimental differences between solid crystals and liquid crystals with three-dimensional order are suggested to be that liquid crystals with optically active molecules form twisted structures, whereas solid crystals do not, and that similar liquid crystal phases of different compounds mix in all proportions whereas solid crystal phases generally do not.

Some current models are discussed and found inadequate. A new model is proposed in which the main difference between solid crystals and liquid crystals with three-dimensional order is that in the solid crystals the alkyl chains at the ends of the molecule have very little disorder or no disorder at all, whereas in the liquid crystals the alkyl chains are slightly disordered.

<u>Introduction</u> - The discovery that there are liquid crystal phases with three-dimensional order[1,2] raised the question whether these phases should be classified as <u>liquid</u> crystals or as <u>solid</u> crystals.[2,3]

De Vries and Fishel[2] gave the following reasons for classifying the smectic <u>H</u> phase of BBEA (4-<u>n</u>-butyloxybenzal-4'-ethylaniline) as a <u>liquid</u> crystal phase:

1. There is no supercooling at the transition from the nematic phase to this phase.

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2. The observed changes in the microscopic texture during the formation of the phase from the nematic phase would not be expected for the crystallization of a solid phase.

3. The microscopic texture of the phase resembles that of a smectic B phase.

4. The phase can be made to flow.

Doucet, Lambert, and Levelut[3,4] proposed that the main difference between the solid phase and the tilted smectic B phase of TBBA (4-n-terephthal-bis-butylaniline) is a rotational motion of the molecules around their long axes in the B phase. Apart from whether or not this hypothesis is correct, it cannot be the fundamental difference between solid crystals and liquid crystals with three-dimensional order[5] because TBBA has other liquid crystal phases,[6] at temperatures below the range of the tilted B phase, which clearly do not have molecules rotating around their long axes.[7]

De Gennes and Sarma,[8] to explain the difference between a smectic B phase and a solid, proposed for the smectic B phase a model with strong forces within the smectic layers but weak forces between them. This model was developed further by De Gennes,[9] who distinguished two cases: (1) very weak interactions between the layers, and (2) somewhat stronger interactions between the layers. For very weak interactions one gets the Sarma model: the layers can slip freely on each other. It is evident that this would give a structure with no three-dimensional order, and thus this model is not relevant to our discussion. If the interactions between the layers are "somewhat stronger", i.e., strong enough to give three-dimensional order, De Gennes considers the resulting smectic B phase to be "really a crystal".[9] The difference between the regular solid phase and this "crystalline" smectic B phase, according to De Gennes,[9] is that in the solid phase the aliphatic chains at the ends of the molecules are strongly aligned whereas in the B phase they are in a disordered "molten" state.

In this note we will attempt to show (1) that liquid crystals with three-dimensional order are not ordinary solid crystals, and (2) that the aliphatic chains in these phases are not in a molten state. We will also propose a model of what then, in our opinion, is the difference between solid crystals and liquid crystals with three-dimensional order.

No Ordinary Crystals - Above we have listed four experimental differences between solid crystals and liquid crystals with three-dimensional order. A more fundamental difference, however, appears to be their different behaviour toward incorporating optically active molecules in their structure. A crystal structure of an optically active compound has a single three-dimensional lattice, just like any other crystal structure, but the lattice of a three-dimensional smectic phase becomes twisted if the molecules are optically active.[10]

Another fundamental difference appears to be what happens when two compounds with similar structures are mixed. In crystalline solids one very seldom observes the formation of mixed crystals over a full range of compositions. Liquid crystals with three-dimensional order, however, appear to follow the behaviour of the less ordered liquid crystals and to form mixed phases in all proportions.[11]

It might also be noted here that crystal structures generally differentiate between the "up" and "down" orientations of a molecule, but that smectic structures probably do not do this.

No Molten Chains - We have always maintained[12,13] that the alkyl end-chains in liquid crystal phases are predominantly in the extended zig-zag conformation because the layer thickness in the ordinary smectic A phase and the apparent molecular length in the isotropic liquid phase just above the clearing point are essentially equal to the length of the extended molecule.[13] Supporting evidence came from the observation[14] that the intermolecular distance in liquid crystals at low temperatures is very similar to that in lipid structures with rigid hydrocarbon chains.[15]

A recent detailed study[16] has now significantly strengthened this argument by showing (a) the condition under which the alkyl chains do in fact become disordered, and (b) the experimental evidence for this disorder. The alkyl chains in the compound TCOB (trans-1,4-cyclohexane-di-n-octyloxybenzoate) were disordered because of the large intermolecular distance caused by a bulky group in the central part of the molecule. The experimental evidence for the disorder of the alkyl chains in TCOB consisted of four independent observations: (1) The intermolecular distance was much larger than for other compounds (5.35 Å as compared to 5.0 Å). (2) The difference between the length of the extended molecule and the smectic layer thickness was about 2.5 Å greater than in other compounds. (3) The sharp outer diffraction ring was superimposed on a broad maximum. (4) The tilted B phase had no three-dimensional order. In liquid crystals with three-dimensional order all four of these indications are absent. This leads to the conclusion that extensive disorder in the alkyl chains is absent, too.

Necessary Ingredients for Three-Dimensional Order - It has long been evident that the following three elements are necessary for the establishment of three-dimensional order in liquid crystals: (1) The individual smectic layers have a two-dimensional lattice. (2) The orientation of this lattice in successive layers is correlated ("rotational coupling"). (3) The position of this lattice in successive layers is correlated ("translational coupling").[17]

Since all liquid crystals have alkyl chains at one or both ends of the molecule, it is clear that rotational coupling and translational coupling will both depend mainly on the interactions between the alkyl chains.[9]

Rotational Versus Translational Coupling - The study on TCOB[16] shows that even with molten alkyl chains there still can be two-dimensional order in the smectic layers. Also, the biaxiality of the C phase and of the tilted B phase of TCOB[18] indicates that there still is sufficient rotational coupling between the layers. The absence of three-dimensional order in the tilted B phase of TCOB,[16] then, points clearly to an absence of translational coupling in this tilted B phase. The same conclusion was reached earlier[17] for some normal B phases. These indications of translational coupling as the weakest link in the establishment of three-dimensional order in liquid crystals agree with a similar indication from the Sarma model.[8]

The existence of twisted ordered smectic phases[10] further emphasizes the dominance of rotational coupling over translational coupling in liquid crystals. In a twisted ordered smectic phase the lattices of adjacent layers are still strongly coupled as far as their orientation is concerned, but over any extended area the correlation between the positions of the molecules of adjacent layers is destroyed.

A comparison of the data on TCOB[16] and BBEA[2] shows the importance of the order in the alkyl chains for the correlation between the layers: with molten chains (TCOB) there is no translational coupling in the tilted B phase; with ordered chains (BBEA) there is strong translational coupling. In both cases there is rotational coupling.

A New Model - As argued above, the translational and rotational coupling between layers takes place via the alkyl chains. Introduction of disorder in these chains reduces the translational coupling and eventually destroys it, whereas the rotational coupling may remain intact. The difference between solid crystals and liquid crystals with three-dimensional order appears to be in the strength of the translational coupling relative to the rotational coupling. All of this leads us to propose the following model:

1. In the solid crystalline phase the alkyl chains have very little disorder or no disorder at all. Rotational and translational coupling are both strong, and both are maintained in structures with optically active molecules.

2. In liquid crystals with three-dimensional order the alkyl chains are slightly disordered (not more than a few kinks per alkyl chain[19]). Translational coupling is much weaker than rotational coupling. Where the two compete, as in structures with optically active molecules, the translational correlation is destroyed so as to achieve a more favourable rotational arrangement.

3. In the few cases in which the alkyl chains are extensively disordered ("molten" chains), as in TCOB, the translational order is gone and there is no three-dimensional order.

It follows that either one of the following two conditions would increase the disorder in the ends of the alkyl chains and thus decrease the tendency to form liquid crystals with three-dimensional order: (a) longer chains, and (b) larger distances between the molecules within the layer. The effect of lengthening the chains is illustrated very nicely by the results of Levelut, Doucet and Lambert[20] on four compounds with different chain lengths. The effect of increasing the intermolecular distance is demonstrated by the data on TCOB.[16]

Regarding the miscibility of two liquid crystal phases with three-dimensional order we note the following. If the two-dimensional order within the layers is very high, it might be difficult to mix the two components within a single layer. On the other hand, since the interaction between adjacent layers is mainly via the alkyl chains, it might be easy to mix layers of the two components,[21] in particular since the rotational coupling could be very well maintained and even the translational coupling might not be too seriously affected.

If liquid crystals with three-dimensional order have a non-zero shear modulus, it would be appropriate to call them liquid-crystalline solids.

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