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Effect of Molecular Structure on Mesomorphism.4. Factors Governing Polymorphism of Smectic Liquid Crystals

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EFFECT OF MOLECULAR STRUCTURE ON MESOMORPHISM.4.[1] FACTORS GOVERNING POLYMORPHISM OF SMECTIC LIQUID CRYSTALS

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A three-dimensional energy surface is proposed as a model to account for smectic polymorphism. This model allows interplay between the two factors relating to phase transformations: (1) thermodynamic stabilities of the phases and (2) accessibility of a phase from the preceding phase. Experimental observations are rationalized using this model and predictions are made based on it.

The relationship between free energy and molecular aggregation is best described by means of a multi-dimensional surface.[2] In this letter a three dimensional surface will be utilized for ease of conceptualization. Such an energy surface for liquid crystalline materials is one consisting of "valleys" and "peaks". The "valleys" correspond to stable (equilibrium) configurations of molecules; "peaks" represent unstable, high-energy configurations. It should be noted here that there is an energy associated at every temperature with every configuration that can be envisioned. For example at a temperature above a smectic-nematic transition there is still an energy associated with that particular smectic arrangement. The energy simply is higher than the energy of the nematic phase and a pathway was available for the smectic to nematic transformation. The phases are separated on this energy surface by an energy barrier.[3] Thus the nematic and not the smectic, phase is observed at that temperature. The same type of analysis can be applied to the polymorphism of smectic mesophases. At any one given temperature all smectic arrangements have an energy associated with each of them. These numerous "valleys" are separated from each other by "peaks" and "ridges". The thermodynamically most stable

smectic phase at a given temperature is the one which has the deepest valley (lowest free energy). Figure 1 below illustrates that point.

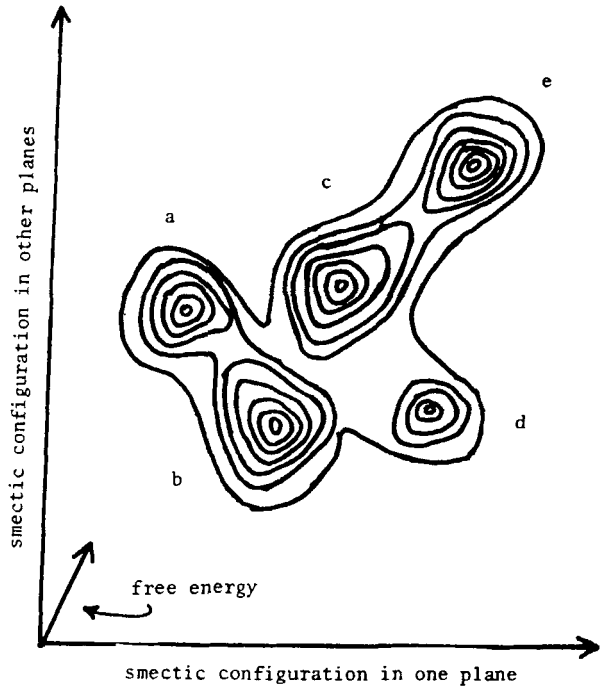

FIGURE 1. A schematic isobaric, isothermal three-dimensional energy surface (seen from above) representing isoenergetic regions for five different smectic arrangements of molecules. Whichever smectic has the deepest valley has the most stable structure.

In order to directly relate molecular structure to smectic type the most stable smectic arrangement must be populated.[4] This point will be dealt with later.

The preceding discussion has considered smectic configurations and their energies at one temperature only. To include the effect of temperature changes in the energy surface diagram the smectic configurations will be reduced to one coordinate. The relative stabilities of the various smectic phases may well change with changes in temperature and the barrier heights between the phases may well also

fluctuate. The transformations between specific smectic phases are often unique. This sequence of smectic types (polymorphic varients[5]) shown on a heating or cooling cycle is of great current interest. As Lydon[2] has pointed out there are two factors to be considered when discussing transitions among various phases: (1) thermodynamic stability of the phases and (2) the accessibility of one phase from its precursor phase. Most workers have considered the first factor only and have assumed that all transitions are to the most stable phase. It is possible that, due to the accessibility factor the most stable smectic phase (at a given temperature) may not be obtained simply because its lower "valley" is separated by a "ridge" or "peak" (barrier) of too great an energy to allow its being seen experimentally. Figure 2 describes a model for this.

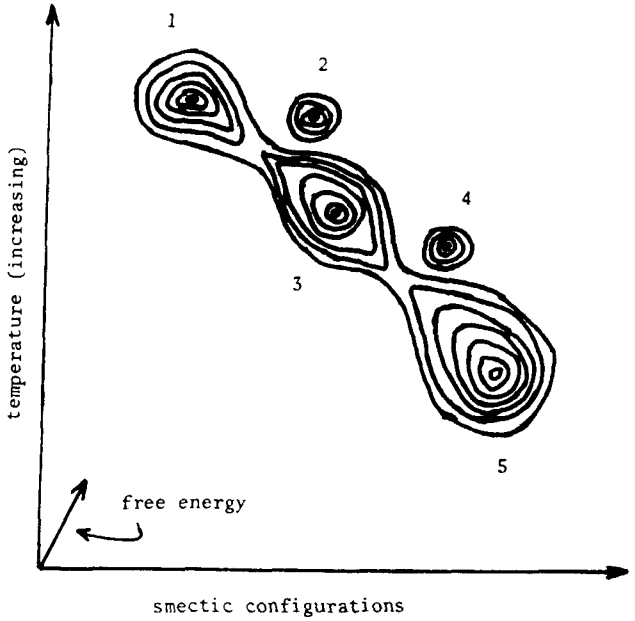

FIGURE 2. A schematic isobaric three-dimensional energy surface (seen from above) representing isoenergetic regions for five different smectic arrangements of molecules.

Note from this figure that the smectic phases seen on cooling are, in order, 1→3→5. Smectics 2 and 4 are not seen due, not to their thermodynamic instability but to their inaccessibility from precursor smectic phases.

This model accounts satisfactorily for the following:

(1) Energetics. Presents all configurations (phases) seen in a "normal" heating or cooling cycle and shows the energetic relationships between them.

(2) Supercooling. A three-dimensional diagram can better depict the energy barriers between phases which actually give rise to supercooling effects, but a two-dimensional diagram[6,7] is often quite useful in this regard.

(3) Polymorphic variants. Permits a physical description (combining the two factors described by Lydon[2]) of which phases are seen, in what order they are seen, and why (energetically) they are seen.

(4) Missing smectic phases. Accounts for "missing" smectics in a series as alluded to by Sackmann et al.[5] and used so well by Billard.[6]

(5) Correlation of structure with smectic type. Modifications in polymorphic varients are experimentally found with small change in molecular structure. As noted by McMillan[8] the "valleys" may be very shallow. Small changes in molecular structure may modify barrier heights, drastically altering accessibilities of one phase from another. Effect of structural modification of constituent molecules on barrier energetics should be a major focus of attention.

(6) "Kinetic smectic phases?"[4] Predicts possibility of "kinetic" smectic phases. These would be phases experimentally seen because of inaccessibility of a more stable "thermodynamic" smectic phase. It may well be possible to obtain these hidden, more stable smectics by use of such techniques as quench cooling. Lydon[2] may well have discovered such phases by rapid cooling methods. Such methods permit entrance onto the energy surface at points not normally available by routine heating and cooling cycles.

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