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ANOMALOUS SMECTIC MESOMORPHISM OF 4,4'-di-n-PENTYLOXYAZOXYBENZENE

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Calorimetric and optical texture studies reveal the existence of a previously unrecognized, stable, highly ordered and enantiotropic smectic phase of C_5(4,4'-di-n-pentyloxyazoxybenzene). This represents a distinctly anomalous behaviour as the next five homologs, C_6 - C_{10}, do not exhibit such a highly ordered smectic phase. It is shown that configurational melting of the alkyl end-chains can largely account for the observed thermodynamic parameters of the solid-smectic transition of C_5.

p-Azoxyanisole and its higher homologs constitute a classic series of liquid crystals which have received considerable experimental and theoretical attention in the past. Extensive thermodynamic data on this series (abbreviated hereafter as C_n, where n is the number of carbon atoms in their alkyl end-chain) were first reported by Arnold[1] for the first twelve homologs, C_1 - C_{12}. Based on his and a few other investigations[2-8] it was considered so far that the lowest member of this series which can exhibit an enantiotropic smectic-nematic transition(Sm-N) is C_7, the smectic phase in this case being of the C type. In this letter we report the observation of a hitherto unrecognized, stable and enantiotropic smectic phase of C_5. Our calorimetric and optical texture evidence indicates that this phase is very highly ordered and that it is unlike the smectic phases seen in any of the immediate higher homologs of this series. A qualitative analysis of the thermodynamic data suggests that the solid-smectic transition of C_5 may arise primarily from an order-disorder transition involving the alkyl end-chains.

C_5 purchased from Eastman Kodak Co. was purified by column chromatography and then dried in vacuum. The nematic-isotropic (N-I) transition temperature was found to be 396.2°K. Calorimetric data were obtained using a Perkin-Elmer differential scanning calorimeter (Model DSC-2) at a scan rate of 5°K/min. The transition temperatures were determined both from DSC and thermal microscopy and are accurate to within ±0.5°K.

Figure 1 shows the DSC results obtained during both heating and cooling cycles. The three <u>endothermic</u> transitions had been reported earlier by Arnold[1] and Smith[2]; our values of the enthalpy (ΔH) of all three transitions are in agreement with theirs to within ±5%. It is significant that we see three and not just two exothermic peaks during the cooling cycle as well. If the endothermic transition at 341.5°K is indeed a solid-solid transition as was presumed hitherto, then given its large ΔH (5.3 Kcal/mole), the solid form stable at the higher temperature can be normally expected to supercool rather easily and exist as a metastable phase at room temperature for several hours or even days, before completely coverting to the stable solid. Such a slow transition would then be unobservable using a relatively fast technique as the DSC, <u>both</u> while cooling and upon <u>immediate</u> reheating of the sample. For example, our calorimetric and infrared studies[9] of C_3 and C_4 show that they both exhibit solid-solid transitions at 378.5 and 324.0°K, respectively. Their respective ΔH

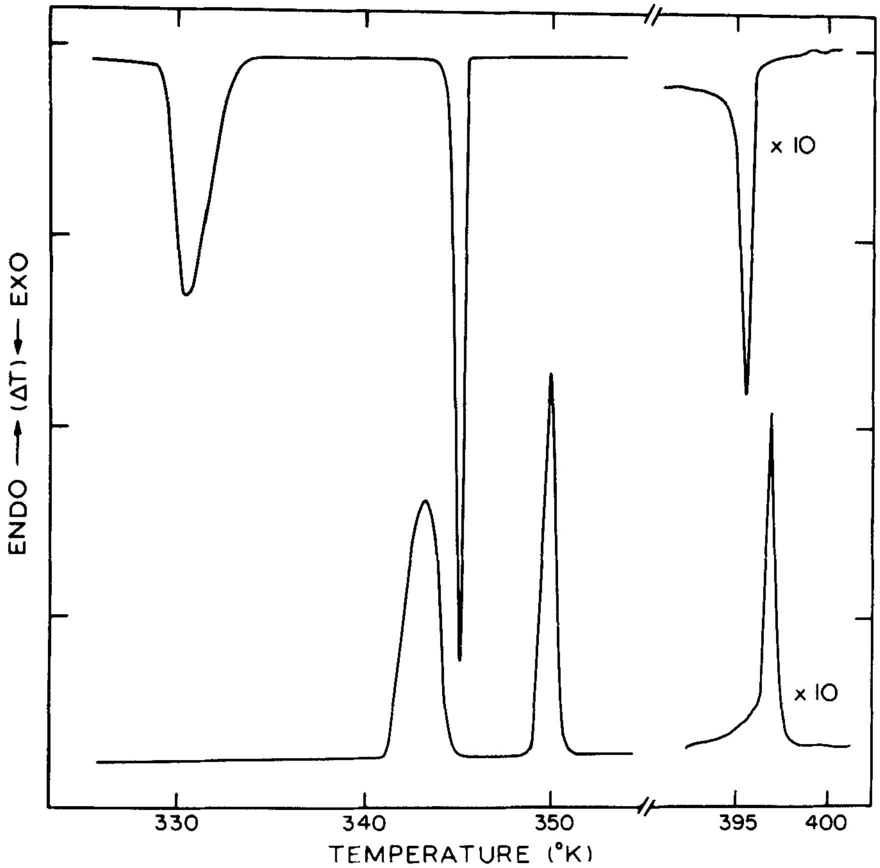

FIGURE 1: DSC curves of C_5. The lower and upper traces correspond, respectively, to the heating and cooling cycles. For the N-I transition, the vertical scale factor employed is ten times more sensitive.

values are also quite large, being ~ 5.2 and 3.0 Kcal/mole. In these cases as also in CBOOA,[10] it is found that solid-solid transitions with relatively large ΔH values do conform to the behavior explained above. In contrast, the lowest temperature transition of C_5 could be detected by DSC during every cooling and reheating cycle without fail. The transition temperature was also found to be the same on the first heating as well as the subsequent reheating cycles. This behavior is in accordance with the existence of a stable, enantiotropic phase in between the solid and nematic phases. As the DSC data by themselves can not reveal the exact nature of this intermediate phase, we have also studied its microscopic texture. These observations, discussed below, strongly indicate that the endothermic transition at 341.5°K is a solid-smectic and not a solid-solid transition.

Figure 2 shows the textures of the crystalline and smectic phases observed between crossed polarizers. The mosaic texture of the smectic phase testifies to its highly ordered nature. This is also in agreement with the relatively high ΔH (3.5 Kcal/mole) of the Sm-N transition at 349.5°K. We have now undertaken miscibility studies in order to determine whether this smectic phase belongs to any of the highly ordered smectic types[11] whose structure is already known. The results of these experiments will be published later.

The texture of the smectic phase was identical irrespective of whether it was obtained by heating the crystalline solid or by cooling the nematic phase. The latter observation rules out the possibility that the mosaic texture could be the result of strain cracks that may attend a solid-solid transition. A cover slip pressed over a thin sample of the smectic phase could be displaced although the viscosity in this phase was much greater than that in the nematic phase. Also, by pressing on the cover slip with a fine steel needle it was possible to observe a net reversible change in the mosaic texture. This is a further confirmation that the phase in question is not a polymorphic modification of of the solid phase, but is in fact a mesophase.

Preliminary X-ray powder diffraction photo-

FIGURE 2: Microscopic textures observed between crossed polarizers; x 250. (a) solid phase, 341°K; (b) smectic phase, 345°K.

graphs showed that the smectic phase exhibits several maxima in the low angle region. However, they were fewer and less intense than in the crystalline phase. This trend is in accord with previous X-ray studies of other highly ordered mesophases.[12,13]

Based on our DSC and thermal microscopy data, the different transition temperatures (°K) of C_5 can be represented as follows:

$$\text{Solid} \underset{333°}{\overset{341.5°}{\rightleftarrows}} \text{Smectic} \underset{345°}{\overset{349.5°}{\rightleftarrows}} \text{Nematic} \overset{396.2°}{\longleftrightarrow} \text{Isotropic}$$

Compared to C_5, the ΔH of the Sm-N transition in $C_6 - C_{10}$ are all an order of magnitude smaller.[1,14] The smectic phase of all these higher homologs is of the C type; also it is only a monotropic transition[15] in C_6. In this light, the occurrence of an enantiotropic, highly ordered smectic phase in C_5 points to the distinctly anomalous behaviour of this mesogen.

In the crystalline phase, the alkyl end-chains of the C_5 molecules are expected to be in the fully extended, trans conformation.[4] From proton NMR studies[16,17] it is seen that the spectral second moment, $\overline{(\Delta H)^2}$, in the smectic phase of C_5 is comparable to that in the nematic phase, but much smaller than that in the crystalline phase. This indicates that considerable intramolecular motions are permitted in the smectic phase, although these are quenched in the crystalline phase. On this basis, a closer scrutiny of the thermodynamic data suggests a plausible mechanism underlying the solid-smectic transition of C_5. The observed entropy of this transition is $(7.8 \pm 0.4)R$, where R is the gas constant. Based on the NMR results, if nearly all this entropy can be attributed to the liberation of intramolecular degrees of freedom and the sum of the newly accessible molecular configurations is denoted by Ω, the total entropy would be given by R ln Ω. Thus Ω would be of the order of 2400. The only parts of the molecule which can give rise to such a large number of configurations are the flexible alkyl end-chains, where each C-C bond can exist in either the trans or two gauche states about the preceding C-C bond. Including the relative orientations of one end-chain with respect to the other, this leads to Ω values[18] in the range of 3^6 - 3^7, the resultant entropy change being 6.6 - 7.7 R. Although this is a qualitative estimate, it does serve to demonstrate that acquisition of configurational entropy by the two end-chains of the molecules can be a major contributory factor to the observed entropy of this transition. On this basis, the enthalpy of the transition per methylene group turns out to be ~ 0.6 Kcal/mole. This value is also in agreement with that observed for other aliphatic 'chain melting' transitions.[19]

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