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THERMAL BEHAVIOR OF TWO POLAR A-SMECTICS

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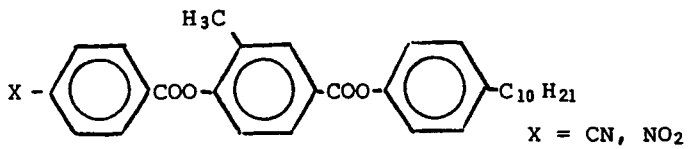
Abstract : The experimental X-ray diffraction data reported recently in the literature for a cyano and a nitro smectogen [1] are used to calculate some parameters of the smectic A phase, such as the molecular area of the paraffin tails and the degree of head to head association of the molecules. It is shown that the presence of a lateral methyl group on the aromatic cores enhances the head to head association of the molecules. It is, finally, suggested that the slight interruption observed in the temperature variation of the layer spacing could be related to a poor miscibility of the head to head and the side by side associated molecules.

Liquid crystalline compounds with polar cyano and nitro end groups were recently described in the literature [1] to produce bilayered smectic A phases. Their chemical structure is the following :



The thickness of the smectic layers was carefully measured with X-ray diffraction. Ranging from 46 to 61 Å, the thickness was found to depend strongly upon temperature. Its rate of increase diminishes as the temperature is lowered for the cyano derivative, whereas it grows appreciably for the nitro derivative. Furthermore, it was clearly shown that in the case of the cyano compound, the temperature variation of the spacing exhibits a short interruption of $\sim$ 0.4 Å at $\sim$ 123°C.

In a preceding paper [2], we proposed a model for the bilayer structure of the smectic A mesophases of polar mesogens, in which the smectic layers are formed by the intimate and random mixture of single molecules arranged side by side in an antiparallel way, on one hand, and of pairs of molecules associated head to head, on the other.

The variation of the smectic spacing was attributed to the variation of the degree of head to head association of the molecules.

In the present paper, the molecular area S of the paraffin tails and the degree τ of head to head association of the molecules will be calculated for the cyano and nitro mesogens mentioned above, using the experimental data of Madhusudana *et al.* [1].

The calculation of the parameter S is straightforward. Indeed, regardless of whether the polar single-tailed molecules are associated head to head or side by side, the molecular area of the paraffin chains is given by :

$$S = 2\ V / d\mathcal{N} \qquad (1)$$

where V is the molar volume, d the layer spacing and $\mathcal{N} = 6.02\ 10^{23}$ the Avogadro's number *.

Whereas values of d are experimentally available [1], values of V have unfortunately not been determined so far. However, it is possible to give a good estimate of them, knowing that the density of mesogens at room temperature generally lies very close to unity, and that the corresponding thermal expansion coefficient is about $8\times10^{-4}\,°K^{-1}$ [3]. The cyano and nitro compounds under consideration being almost identical from the geometrical standpoint, we considered that their molar volume is also identical ; we assumed that the temperature variation of the molar volume is given by :

$$V(cm^3\ mole^{-1}) = 500 + 0.4\ T\ (°C) \qquad (2)$$

The results obtained are illustrated in Fig. 1.

Let us consider now the calculation of the degree of association τ. Assuming as previously [2] that the molecular area σ of the aromatic stems is identical for single and associated molecules, and that there is no volume contraction in the association process, one can easily show that :

$$\tau = 2 - (2\ V / \sigma d) = 2 - S / \sigma \qquad (3)$$

Actually, the value of σ is not yet available experimentally moreover, it is not easy to determine because of the presence of the lateral methyl groups which form knobs on the aromatic parts of the molecules. But the value of V / σ can be estimated much more readily, for it represents the length of the molecules in the smectic A phase with the aromatic stems and the paraffin chains both standing perpendicular to the layers. Of course, this length is slightly shorter than that measured with molecular models (33 Å [1]), due either to the

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*) Spread in a smectic layer of thickness d, N molecules of smectogen occupy a volume $NV/\mathcal{N}$ and cover an area $NV/d\mathcal{N}$. The aromatic cores located inside, and the N paraffin tails covering both faces of the layer, each paraffin chain occupies an average area $S = 2\ V/\mathcal{N}d$.

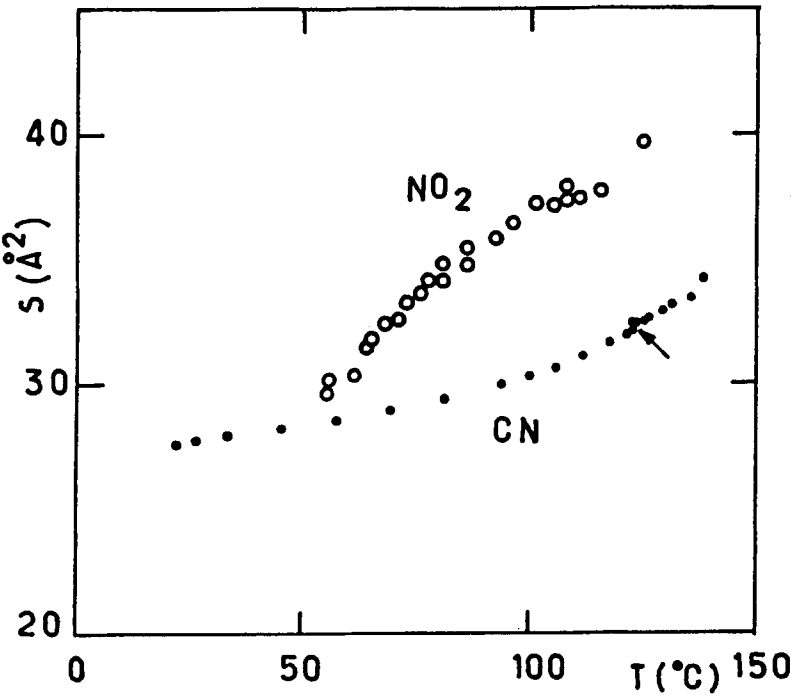

FIGURE 1 Molecular area of paraffin tails as a function of temperature.

thermal fluctuations of the director around the layer normal [4], or to the conformational disorder of the paraffin chains. Using the de Vries' value of the order parameter of A smectics, one finds for the length of the molecules a value of 31.5 Å. The results obtained are illustrated in Fig. 2.

Inspection of Figs 1 and 2 calls upon the following comments. First, the degree of association τ is found to be significantly larger than 1/2. According to the elementary two-state Boltzmann model presented earlier for polar A-smectics [5], this indicates that the cyano and the nitro molecules both prefer to associate with themselves head to head rather than side by side. The tendency towards the head to head association is, furthermore, stronger for the cyano than for the nitro derivative ; the end group of the former has indeed a higher dipole moment ($\sim$ 3.94 Debyes) than that of the latter ($\sim$ 3.57 Debyes) [6]. Second, the degree of association of the cyano derivative in the smectic phase is able to grow considerably upon cooling and even to almost reach unity at room temperature, indicating that almost all of the molecules are associated head to head, without steric hindrance from the aliphatic tails as suggested previously [2]. This is no doubt related to the high values of the molecular

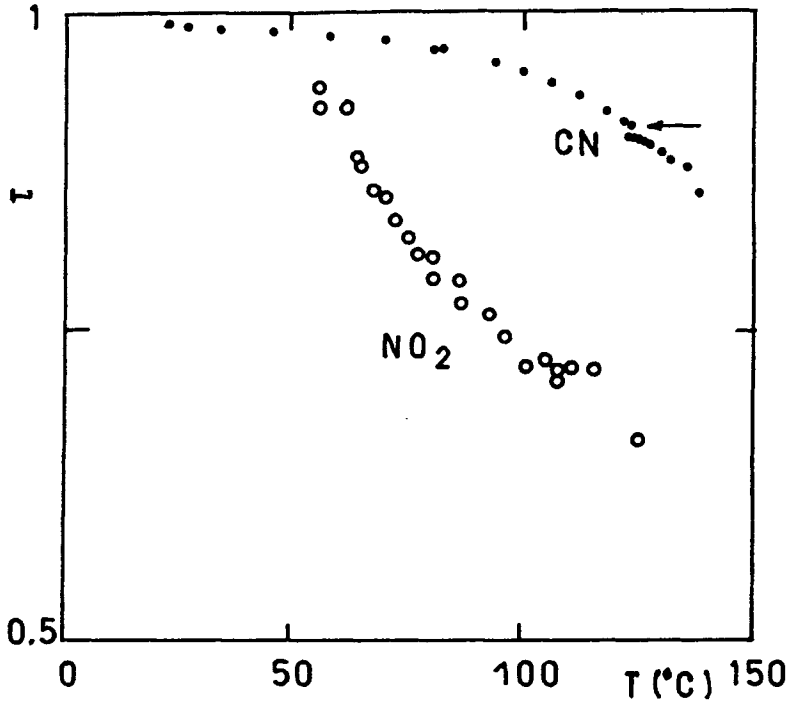

FIGURE 2 Degree of head to head association of molecules as a function of temperature

area S (Fig. 1), which are larger than 27 Å^2 and correspond, therefore, to enough room for the paraffin chains to adopt a disordered conformation without constraint. Using relation (3), it is obvious that the molecular area σ of the aromatic stems is equal to S when $\tau = 1$; *i.e.* $\sigma = 27$ Å^2 . This large value of σ compared to that usually found for other smectogens (22 Å^2) [3] is due to the presence of the lateral methyl knob on the aromatic stem of the molecules and is clearly responsible for the high bottom values of S.

Finally, the short interruption observed for the cyano derivatives in the variation of the layer thickness as a function of temperature [1] — which is also visible in Figs 1 and 2 (see arrows) — has apparently no obvious geometrical reason to exist : the two branches of $d(T)$ seem to be indeed the prolongation of one another on both sides of the jump, and the values of the geometrical parameters of the smectic phase, notably those of the molecular area S, do not present any specific feature in the neighborhood of the discontinuity. In our opinion, this might be an indication of phase transition between two smectics, as suggested in a previous paper [5] . Probably, the interactions between the head to head and the side by side associated molecules would not be as

favorable as those among like species, and a miscibility gap similar to that often observed with poorly miscible liquids would be induced. The narrowness of the phase separation observed here would then suggest that the system is not very far from being under conditions of homogeneity. It would be interesting to test the validity of such an explanation, by trying to enhance homogeneity through the addition to the system of a "solvent" or of a second component and, counter-wise, by favoring heterogeneity through an increase of pressure, which enlarges the intensity of interactions.

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