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EXPERIMENTAL EVIDENCE CONCERNING TWO DIFFERENT KINDS OF SMECTIC C TO SMECTIC A TRANSITIONS*

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ABSTRACT: Experimental evidence is presented indicating that there are two distinctly different kinds of smectic C to smectic A transitions. The first type is second order with zero tilt in both phases, the second type is first order with a non-zero tilt angle in both phases. The model for the second type of transition is an "uncoupling" of the tilt directions of adjacent layers in the smectic A phase.

INTRODUCTION

It has been recognized by some authors[1,2,3] that there are apparently two different types of smectic C phases: those with a large and essentially temperature independent tile angle (C_1 phases[3,4]) and those with a much smaller tilt angle that is strongly temperature dependent and goes to zero at the C to A transition (C_2 phases[3,4]). It has also been recognized that C_1 phases never yield A phases on heating, whereas C_2 phases apparently always do[1,3].

Enlarging upon this subdivision we have noted earlier[4] that there appears to exist a third type of C phases, C_3 phases, which also yield an A phase on heating but with a different behavior of the tilt angle at the phase transition. In this note we now present new evidence that two different kinds of C to A transitions do in fact exist, and that they have quite dissimilar characteristics.

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THE $\underline{C}_2$ TO $\underline{A}_2$ TRANSITION

This transition has most thoroughly been studied in TBBA. Taylor, Arora, and Fergason[1] were the first to report that for the $\underline{C}$ phase of this compound the tilt angle is strongly temperature dependent and goes to zero at the $\underline{C}_2$ to $\underline{A}_2$ transition. This has been subsequently confirmed by EPR[5], x-ray[6,7], and NMR[2,8] measurements. The heat of transition has been found to be zero or very close to zero[8], and McMillan's theory[9]--which was developed precisely for this kind of $\underline{C}$ to $\underline{A}$ transition--does indeed predict that this is a second order phase transition.

THE $\underline{C}_3$ TO $\underline{A}_3$ TRANSITION

No detailed information has been published so far on the $\underline{C}_3$ to $\underline{A}_3$ transition. The first indication of its existence was a report by Diele, Brand, and Sackmann[10], which noted that for a number of compounds the thickness of the smectic layer did not change significantly over the full temperature range of the $\underline{C}$ and $\underline{A}$ phases combined. Since for other $\underline{A}$ and $\underline{C}$ phases there exists a strong one-to-one relationship between tilt angle and layer thickness[11], we postulated on the basis of this report that in these $\underline{A}$ and $\underline{C}$ phases, which we called $\underline{A}_3$ and $\underline{C}_3$ phases, the tilt angle remained constant[4] also.

We have now obtained more extensive data on layer thickness as a function of temperature from our own investigation of one of the compounds reported on by Diele et al.[10], and the results are represented in Figure 1. Although there is a considerable spread in the data due to random errors, it is clear that there is a very strong indication that the

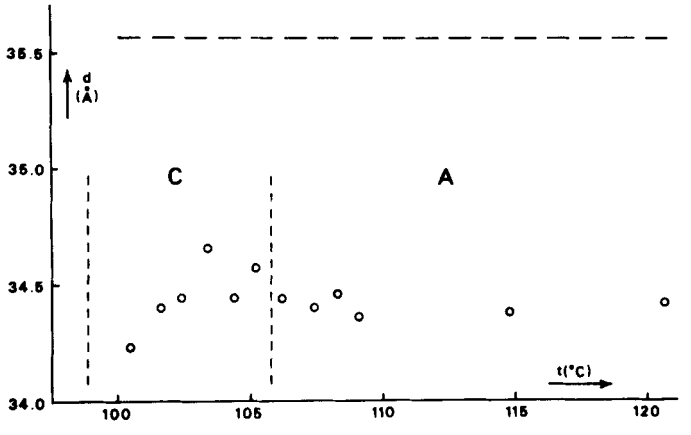

FIGURE 1. Layer thickness in the smectic C and A phases of n-pentyl-4(4'-n-decyloxybenzylideneamino)-cinnamate. The vertical broken lines are the transition temperatures (B-C and C-A), the horizontal broken line in the expected layer thickness for molecules perpendicular to the layers (1.7 Å less[12] than the length of the extended molecule, 37.27 Å).

layer thickness, and therefore the tilt angle, indeed does not change significantly at the C_3 to A_3 phase transition. Also, it is quite evident that the tilt angle in the A_3 phase is not zero as is generally assumed for A phases; in our case it is approximately 15°. To reconcile this tilted arrangement of the molecules in a smectic layer with the observed optical uniaxial character of the A_3 phase[10], we suggest that in this phase the tilted layers are stacked in a random fashion[4,13] (random with reference to the direction in which the molecules are tilted). In the C_3 phase, as in all C phases, the layers would be stacked in an ordered manner.

A literature search revealed interesting information on the enthalpy change for the $\underline{C}_3$ to $\underline{A}_3$ transition. For the C_{12} homologue of the compound investigated now by us--a compound also listed in the paper by Diele et al. as having the same layer thickness in the $\underline{C}$ and the $\underline{A}$ phase, and therefore virtually certain to have the same behavior of the tilt angle--it has been reported by Saupe[14] that the enthalpy change for the $\underline{C}$-$\underline{A}$ transition is 0.146 kcal/mol, about 6 times larger than for other $\underline{C}$-$\underline{A}$ transitions listed by him. This $\underline{C}$ to $\underline{A}$ transition, a $\underline{C}_3$ to $\underline{A}_3$ transition, is therefore clearly a first order transition.

SUMMARY

For the $\underline{C}_2$ to $\underline{A}_2$ transition both theory and experiment appear to agree in indicating that this transition is second order and that the tilt angle is zero at the transition point.

The $\underline{C}_3$ to $\underline{A}_3$ transition, on the other hand, is clearly first order. The tilt angle remains constant at a value of about 15° during the transition, and the transition can be interpreted in terms of an "uncoupling" of the directions of tilt in adjacent layers. A similar $\underline{C}$-$\underline{A}$ transition appears to have been found by De Jeu and De Poorter[15].

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