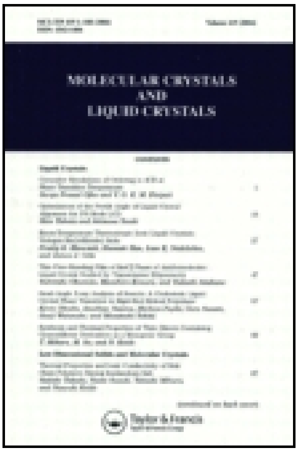

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X-Ray Diffraction Study of 90.8 and 100.6

P. R. Alapati [a] , N. V. S. Rao [a] & T. K. Ghosh [a]

[a] Faculty of Physical Sciences, North Eastern Regional Institute of Science and Technology, Itanagar, 791 109, INDIA

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X- RAY DIFFRACTION STUDY OF 9O.8 AND 10O.6

P. R. ALAPATI, N.V.S. RAO AND T. K. GHOSH
Faculty of Physical Sciences,
North Eastern Regional Institute of Science and Technology
Itanagar - 791 109, INDIA

Abstract As a part of our detailed comparative studies of groups of Liquid Crystalline compounds belonging to N(p-n-Alkyloxy Benzylidene) P'- Alkylanilines, (nO.m's), we present here the phase transition studies of the compounds 9O.8 and 10O.6 using X-Ray diffraction study. The compounds 10O.6 and 9O.8 exhibit ACFG phase variant. The temperature dependence of tilt angle in Sm C and Sm F phases in both of the compounds is presented. A comparative study of tilt angle measured by different experimental techniques is also presented.

INTRODUCTION

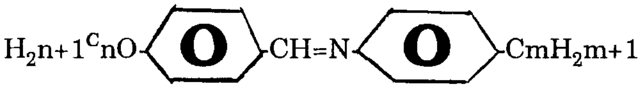
In recent years N(p-n-alkyloxy benzylidene) p-n- alkylanilines, commonly referred to as nO.m compounds, have become focus of interest because not only they exhibit subtle but rich polymesomorphism at ambient temperature but also they can be utilised as model systems for different physical studies. In particular, interest has been focused on smectic liquid crystalline phases, which have been abundantly exhibited by higher homologues of nO.m compounds, in which the degree of order within the layers changes quite often in a very subtle way from one phase to another. Apart from the commonly observed smectic A and smectic C phases the uncommon smectic F phase is also present in a number of higher homologues[1]. When smectic C thermal range is very short, being only of the order of 1K, its structural investigation presents a special experimental challenge. Here we present the structural investigations by X-ray diffraction in two higher homologues of nO.m compounds namely 10O.6 and 9O.8 both exhibiting ACFG phase variant.

EXPERIMENTAL

The compounds 10O.6 and 9O.8 were synthesized following the procedure described elsewhere[2]. The X-ray diffraction experiments were carried out using Ni filtered CuK_α radiation and a Laue camera. Samples were contained in glass capillaries of diameter 0.5 to 1.0 mm and held perpendicular to the incident X-ray beam. The samples were aligned perpendicular to the direction of the incident X-ray beam in a magnetic field of strength 0.4 T.The temperature stability in these experiments was $\pm$ 0.2^{0}C.

RESULTS AND DISCUSSION

The molecular formulae; the phase sequence and the transition temperatures (in degrees centigrade) of 10O.6 and 9O.8 are presented below.



10O.6 n = 10 and m = 6

9O.8 n = 9 and m = 8

$$10O.6\ S_G \xleftrightarrow{75} S_F \xleftrightarrow{79.2} S_C \xleftrightarrow{80.3} S_A \xleftrightarrow{89.5} \text{Isotropic}$$

$$9O.8\ S_G \xleftrightarrow{77} S_F \xleftrightarrow{79.1} S_C \xleftrightarrow{80.3} S_A \xleftrightarrow{87.1} \text{Isotropic}$$

The smectic phases in 10O.6 and 9O.8 have been characterised as A, C, F and G by thermal microscopy.

The X-ray diffraction photographs of 10O.6 in smectic A, smectic C and smectic F phases are displayed in plate 1. The direction of the layer normal is perpendicular to the line joining the maxima of the outer diffused reflections in smectic A phase. The growth of a distinct in-plane positional ordering characterising the smectic F phase from the liquid like molecular arrangement within the smectic layers of A and C phase is reflected in the X-ray photographs. The average intermolecular spacing (D) and the layer thickness (d) are calculated following the relations used by de Vries[3]

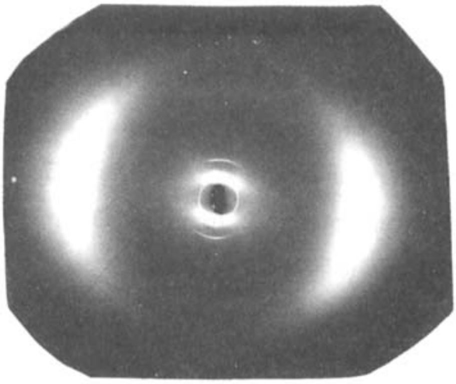
$$1.117\lambda = 2D \text{ Sin } \Theta$$

$$\lambda = 2d \text{ Sin } \Theta$$

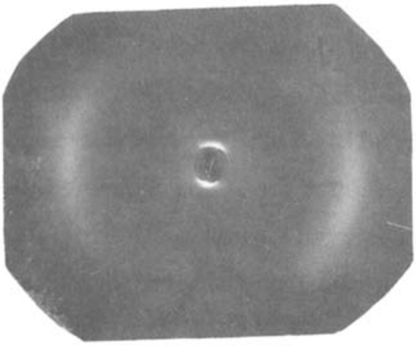
where λ (1.54 Å) is the wave length of the X-ray beam and Θ is the angle of diffraction. The average intermolecular spacing (D) obtained from outer maxima for 10O.6 and 9O.8 are found to be temperature independent and are 5.12 ± 0.05Å for 10O.6 and 4.98 ± 0.05 Å for 9O.8. These values are found to be in good agreement with the observed values in other nO.m compounds[4]

The variation of layer thickness (d) with temperature in different phases is illustrated in Figure 1 for 10O.6 and 9O.8. The experimental values of molecular length obtained in smectic A phase are 30.6 ± 0.1Å for 10O.6 and 32.6 ± 1.0Å for 9O.8. The layer thickness is almost constant in smectic A phase, while decreases with temperature in smectic C and smectic F phases. Moreover, the variation of layer thickness in smectic G phase of 10O.6 is in accordance with the literature data[5] in other compounds. While the temperature dependence of layer thickness in the reported[4] smectic G phase of 9O.8 indicates an orthogonal molecular arrangement rather than tilted molecular arrangement as reported by thermal microscopy.

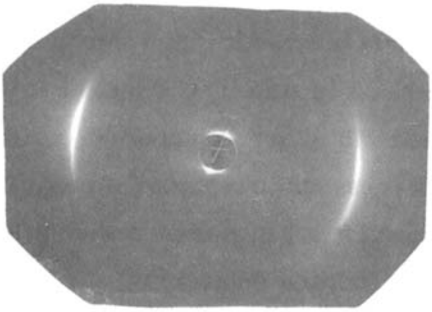
The smectic C phase thermal range is short in both of the compounds, 1.1K in 10O.6 and 1.2K in 9O.8, and its structural investigation of primary order parameter of smectic C phase viz., tilt angles presents an interesting feature. The smectic C phase possesses a finite tilt angle between the layer



Smectic A at 84·0 °C



Smectic C at 79·4 °C



Smectic F at 75·4 °C

PLATE 1 X-ray photographs of Smectic A, Smectic C and Smectic F phases of 10O.6.

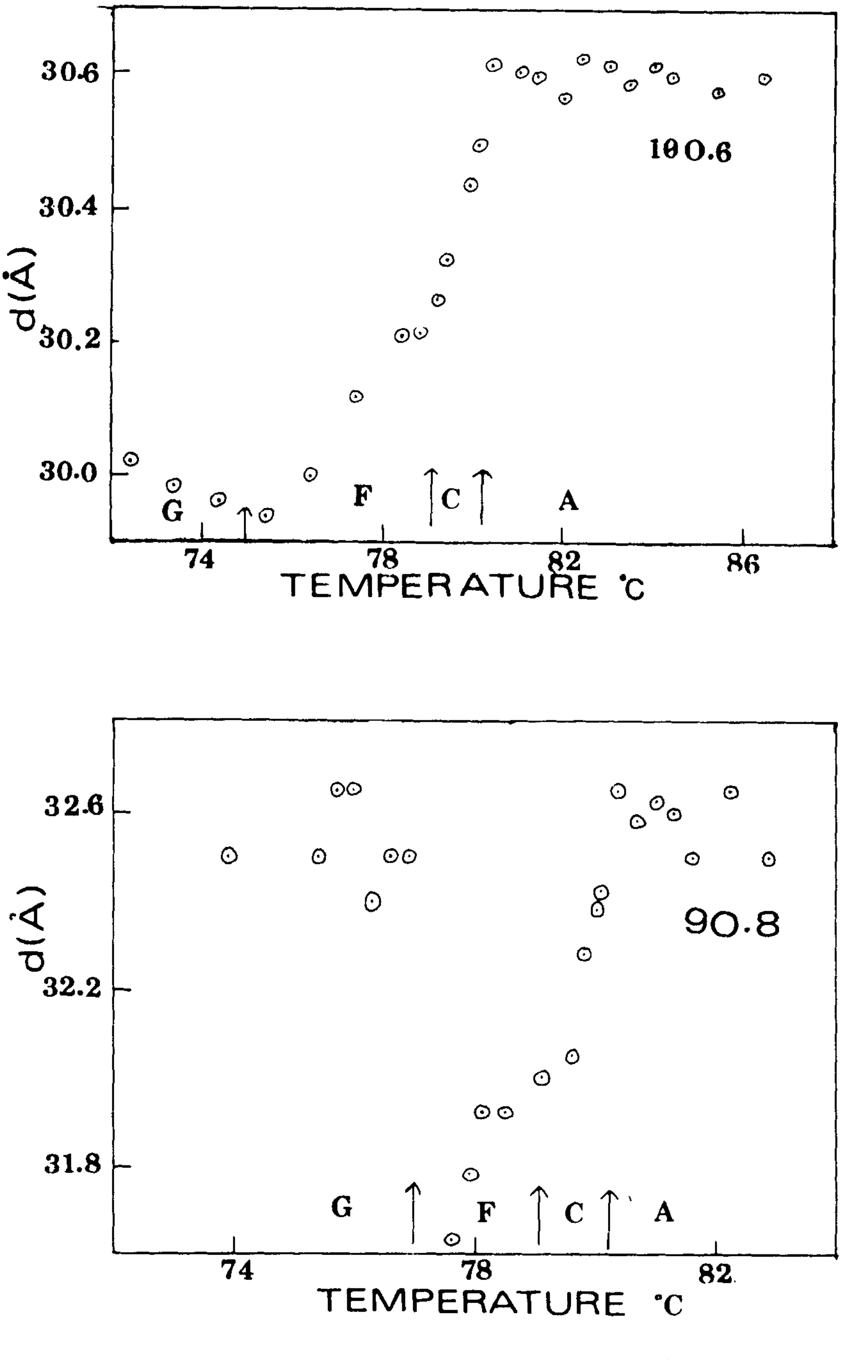


FIGURE 1 Variation of layer thickness, d(Å), with temperature in 100.6 and 90.8.

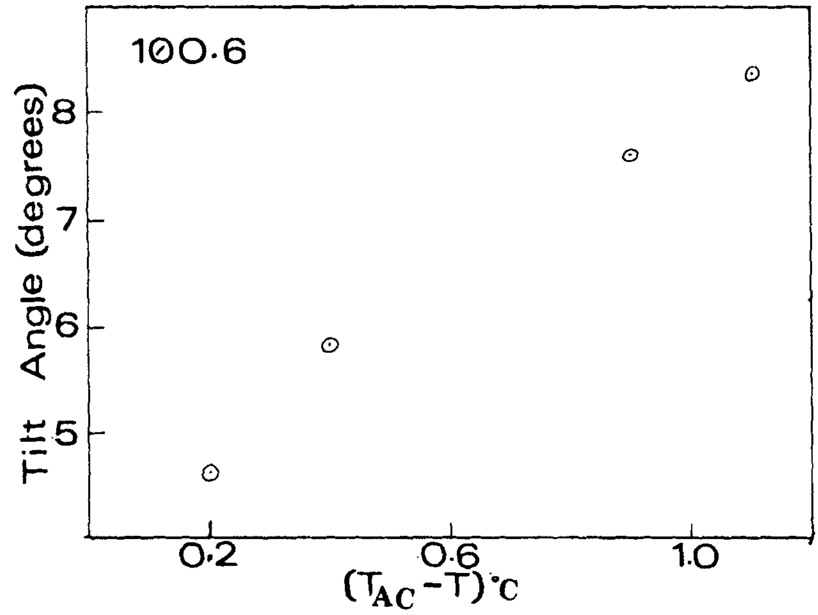
normal and the director. If the molecule is linear then there is single tilt angle, but for mesogens like 10O.6 and 9O.8 with their zig-zag molecular structure there are at least three tilt angles, one associated with the core region and the other two with the alkyl-chain regions of the smectic layer. The monodomain sample of the smectic C phase required for the determination of the tilt angle by X-ray diffraction is readily obtained by repeated recycling of smectic A phase in the presence of magnetic field. The temperature is further decreased until the transition to smectic C phase occurs, at which temperature the director tilts with respect to the layer normal, which remains parallel to the magnetic field. The tilt angle was obtained from

$$\Theta_t = \mathrm{Cos}^{-1}\,(d_C/d_A)$$

Where d_C and d_A are the layer thickness in the smectic C and smectic A phases respectively. Since the molecular conformation (in particular, the chain conformation) in the smectic phase is unknown and furthermore thermal fluctuations will reduce the effective molecular length, this is taken as the layer spacing d_A of the smectic A phase. The tilt angle which is assumed to be zero in the smectic A phase grows continuously with decreasing temperature in the smectic C phase. The tilt angles determined in this way for 10O.6 and 9O.8 are plotted as a function of temperature in figure 2, the experimental error is $\pm 1^\circ$. The tilt angle is observed to grow rapidly from its value of zero at T_{AC}, the smectic A - smectic C phase transition temperature, as expected for a continuous transition and reaches a maximum value of 8.4° in 10O.6 and 12.6° in 9O.8 prior to the formation of the smectic F phase at which the tilt angle increases to 11.1° in 10O.6 and 13° in 9O.8.

The temperature dependence of the tilt angle is fitted to the expression

$$\Theta_t = A\,(T_{AC} - T)^{\beta}$$



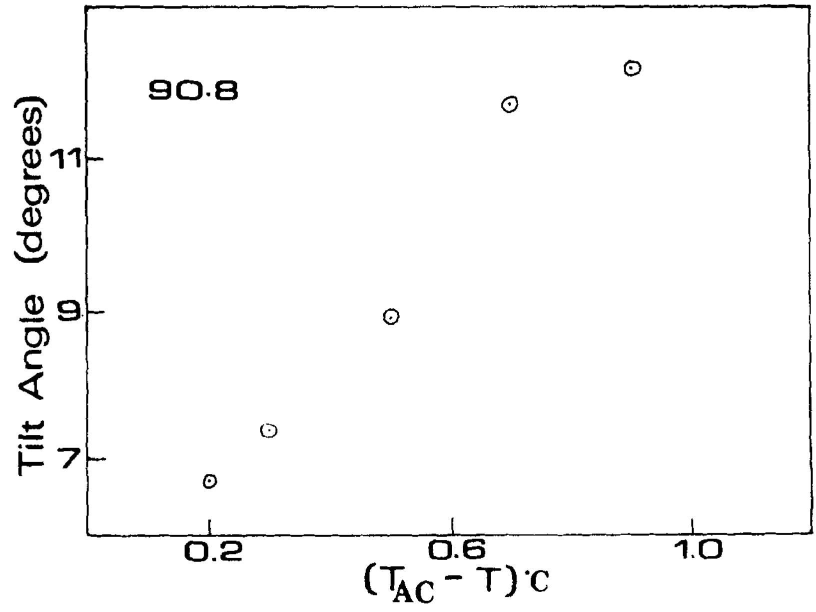


FIGURE 2 Variation of tilt angle, θ_t, with temperature in 100.6 and 90.8.

proposed by de Gennes[6] to quantify the difference in the measured tilt angles. The best fit which is in good agreement with experiment, was obtained with T_{AC} = 353.45 K for 10O.6 and T_{AC}=353.35 K for 9O.8. The exponent ß was determined to be 0.34$\pm$0.04 for 10O.6 and 0.39 $\pm$ 0.04 for 9O.8 is in good agreement with the values reported in literature (Table 1).

Table 1: The exponent ß and the coefficient A for different compounds.

Compound	ß	A	Technique	Reference
10O.6	0.34+0.04	8.0	X-ray	Present Work
10O.6	0.31	7.6	Dielectric	7
9O.8	0.39+0.04	9.2	X-ray	Present Work
5O.5	0.41+0.04	13.3	X-ray	8
7O.4	0.31+0.04	11.4	ESR	9
7O.4	0.38	11.1	Dielectric	7

The results support de Gennes' prediction for the exponent of ß = 0.35 exhibiting the non-classical approach. Unlike ß the coefficient A which may be identified as the tilt angle where T = (T_{AC} - T) is 1K are quite different for different mesogens. The molecular origins of this relatively large deference in the A coefficients for these mesogens are not apparent - indeed their interpretation presents another problem to elucidate the structural details. Further, tilt angle values reported in the literature for a given compound are dispersed depending upon the material and experimental methods used. However, for 10O.6 the tilt angle values obtained from X-ray diffraction method are higher than the values obtained from dielectric method by 1 to 3°.

ACKNOWLEDGEMENTS

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