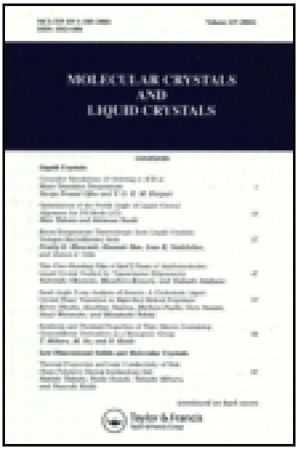

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Low-Frequency Dielectric Investigations of Smectic-C Tilt Angle

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Low-Frequency Dielectric Investigations of Smectic-C Tilt Angle

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Low-frequency dielectric studies are carried out to determine the molecular tilt in liquid crystalline smectic-C phase in some of the schiff base *n*(*p*-*n*-alkoxybenzylidene) *p*-*n*-alkyl anilines viz., nO.m compounds. The influence of smectic-C thermal range, thermal fluctuations and range of smectic-A phase and the odd-even effect in a homologous series are investigated for the equilibrium smectic-C tilt angle value. The growth of tilt angle as relevant order parameter is discussed in the context of de Gennes critical model and other mean field models. Order parameter exponent β supports the de Gennes model characterised by long range gauge invariance of tilt order fluctuations over smectic layers. The observed smectic-C thermal span and the value of maximum tilt angle are found to agree with McMillan molecular model.

Keywords: Schiff base compounds; smectic-A and C phases; dielectric absorption; tilt angle

INTRODUCTION

Recently, there is a considerable amount of growing interest in the experimental determination [1–3] of physical properties of thermotropic liquid crystals i.e., the relevant order parameter, molecular length, tilt angle, elastic coefficients etc., due to their crucial role in evaluating their viability in display devices. Further, the investigations of smectics, particularly the tilted phases [4, 5] attained considerable interest and importance due to their micro second response times in a preferred geometry compared to their conventional nematic counterparts operating at millisecond response. The N(*p*-*n*-alkoxybenzylidene) *p*-*n*-alkylanilines (nO.ms) are a family of mesogenic compounds which exhibit a rich variety of polymorphism [6–10] with commonly occurring nematic, smectic-A, smectic-C, smectic-B phases in addition to smectic-F and smectic-G phases at ambient temperatures with varying thermal ranges. The temperature dependent (or independent) tilt angle θ of the director (with layer normal) serves a prime and pivotal characteristic feature [11] of the smectic-C phase in harnessing its structural geometry in spatial light modulators. The tilt angle is observed [12] to be temperature dependent in the compounds possessing either a high temperature nematic and smectic-A phases or smectic-A phase only.

The nature of smectic-A to smectic-C (AC) transition and the temperature dependence of tilt angle were discussed by de Gennes [13] in an attempt to focus the experimental feasibility of Helium-4 super conducting lambda (λ) like situation underlined by the gauge invariance of long range tilt order parameter and the comparison of suppression of second sound with zero tilt angle at the AC transition. McMillan developed a molecular field theory [14] to explain the occurrence of smectic-C tilt angle, followed by the ferroelectric and antiferroelectric ordering based on the contributions of the out-board dipolemoments and in-plane or inter-plane coupling of dipolar interactions. Though Meyer's prediction [15] of ferroelectricity in smectic-C phase with a chiral centre heralds a new era in the applied aspects of smectic-C liquid crystals, it could not throw much light about the molecular origin and dependence of the fundamental tilt order.

The chiral smectic-C (or smectic-C*) optimal utilisation conditions (low viscosity and large spontaneous polarisation) are achieved [16, 17] by doping a smectic-C liquid crystal with a chiral component (i.e., a ferroelectric smectic-C* liquid crystal mixture). These features will provide an opportunity to design an attractive and practical ferroelectric liquid crystal cell with a comparative fast switching and perhaps as a better substitute to the conventional sluggish twisted nematic cell. It is also reported [18] that the tilt angle of the chiral smectic-C liquid crystal exhibiting ferroelectric properties can influence the operational characteristics of electro-optic devices. Hence, it is of fundamental interest to measure the temperature dependence of the tilt angle in chiral and nonchiral compounds. Moreover, the determination of temperature variation of tilt angle is an experimental challenge when the smectic-C thermal range is very small (a small fraction of a degree in some compounds), as such the experimental results can throw light on the realistic nature of smectic-C molecule as pictured by the theoretical models.

The measurement of tilt angle and its variation with temperature has been reported by Optical [19–22], X-ray [23–26], ESR [27–30] Mossbauer [31], NMR [32, 33] and dielectric absorption [34–37] techniques in various compounds. However, the smectic-C tilt angle has been characterised with reference to

1) the directions of principal optic axes in optical studies
2) the long axis of the molecules in X-ray studies and
3) the direction of major axis of the macroscopic magnetic susceptibility of a domain in magnetic resonance (NMR and ESR) experiments etc.

The low-frequency dielectric absorption studies describe the orientational relaxation mechanism associated with the molecular dipole moments and provide information about the anisotropic liquid crystalline phases and their macroscopic tilt angle. It has been demonstrated [36] that the dielectric investigations can be used as a successful tool to determine the tilt angle from the observed maximum values of imaginary part of the (parallel component) low frequency dielectric spectrum, $\varepsilon''_{\parallel}$(max), measured in a homeotropically aligned smectic-A phase sample, while cooling it into the smectic-C phase. It is also observed [36] from the experimental results that the homeotropic geometry gives more accurate results of tilt angle rather than the planar geometry, due to

(a) the well defined orientation of the smectic layers with respect to the applied field,
(b) the minimised director distortions due to the surface effects and
(c) the ease in obtaining a Debye type of domain to study relaxation behaviour.

We present here the temperature dependence of the tilt angle of the molecules in the smectic-C phase of different compounds of the N(*p*-*n*-alkoxybenzylidene)*p*′-*n*-alkylanilines, viz., nO.m homologues (with n and m = 5 to 10) measured by dielectic method. In addition to the temperature dependence of tilt angle with smectic-C melting and clearing temperatures, the effect of thermal range of high temperature smectic-A and smectic-C phases and the effect of flexible alkyl and alkoxy end chain lengths of nO.m compounds are also discussed.

EXPERIMENTAL

The general molecular formula of nO.m compounds is

The compounds studied were synthesised as reported [38] earlier. The relevant transition temperatures (in K) and their thermal span are given in Table I.

The dielectric cell consists of two conducting glass plates separated by a mylar spacer of 100 μm thickness. The resistance of ITO layer was found to be typically of the order of 0.003 kΩ/sq. cm. The cell was calibrated with known standard organic liquids. The empty cell capacitance variation with temperature was found (from 35°C to 100°C) be less than 0.01%. Required homeotropic alignment was obtained by first heating the sample to isotropic temperature and then cooling it slowly at a rate of 0.1 K/min across the IN or IA transition in the presence of a magnetic field of strength 5 kG. To achieve a good alignment the heating and cooling cycles at the specified rate were repeated. Further, the obtained homeotropic alignment was confirmed by the microscopic studies. The temperature of the sample was controlled with an Instec milli kelvin temperature controller monitored through P.C. to an accuracy of ±0.01 K. The dielectric absorption measurements were carried out using an **HP** 4192A LF Impedance analyzer (5 Hz–13 MHz). The electric field was applied parallel to the homeotropically aligned sample between the glass plates.

RESULTS AND DISCUSSION

Though the stability of orthogonal arrangement of molecules in the smectic-A layers is governed by their elastic properties, the thermal energy introduces

TABLE I Phase transition temperatures (in Kelvin) of nematic to smectic-A (NA), isotropic to smectic-A (IA), Smectic-A to smectic-C (AC), smectic-C to smectic-B (CB), smectic-C to smectic-F (CF) and smectic-C to smectic-G (CG) transitions, thermal span of smectic-A phase, $(\Delta T)A = (T_{NA/IA} - T_{AC})$ and thermal span of smectic-C, $(\Delta T)_c = (T_{AC} - T_{CB/CF/CG})$ as the case may be for different compounds of nO.m series

Compound	*NA/IA*	*AC*	*CB*	*CF*	*CG*	*$[\Delta T]_A$*	*$[\Delta T]_C$*
5O.5	327.55*	326.25		322.15		1.3	4.1
7O.4	347.75*	337.95			336.15	9.8	1.8
8O.6	359.15	348.75	343.95			10.4	0.8
8O.7	359.95	347.55	347.35			12.4	0.2
9O.6	360.15	353.65		350.65		6.5	3
10O.6	360.65	351.65		351.15		9	0.5
10O.8	365.85	360.75		358.95		5.1	1.8
10O.9	364.15	360.15	358.15			4	2
10O.10	362.15	359.25		358.15		2.9	1.1

* Denotes nematic-smectic-A (NA) transition

the director fluctuations to result in a spontaneous tilt angle in smectic-C phase. The fluctuation amplitude attains [39] maximum value at T_c and the elastic constant controlling the tilt fluctuations become soft. However, in the presence of a weak electric field (i.e., the field used for the measurement of dielectric constant, applied in a direction parallel to the director), the tilt fluctuation suffers a maximum perturbation near T_c. In the case of a non-chiral smectic-A phase, the amount of induced dipolemoment and there by the tilt fluctuations due to the applied electric field are too small to be detected by dielectric measurements. However, in smectic-C phase, the tilt is the characteristic property and contributes considerably to the dipolemoment. On the experimental side, the decrease in temperature partially contributes to the dielectric absorption to result in the increase of tilt angle. And as such, this absorption can be studied experimentally [39] through the complex dielectric constant studies. However, the contribution to imaginary part results from the different molecular processes of collective and non-collective excitations.

The frequency dependence (10 kHz–6 MHz) of $\varepsilon'_{\parallel}$ and $\varepsilon''_{\parallel}$ for various nO.m compounds (in smectic-A and -C phases) suggests an orientational relaxation behaviour as observed in our systematic studies of the relevant smectic phases. The variation of $\varepsilon''_{\parallel}$ (max) with temperature in smectic-A and smectic-C phases of the compund 10O.8 is shown in Figure-1. The $\varepsilon''_{\parallel}$ (max) is found to decrease linearly with decreasing temperature in smectic-A phase for all of the compounds. This is due to the fact [40] that the dipoles associate with the central part of the molecules in different smectic layers are at a greater distance than that of a pair of molecules in the same layer. This situation leads to the increased antiparallel correlation for the dipole moment components along the director. Consequently, the effective moment $\mu_{\parallel}$ in this direction is reduced, leading to a decrease of parallel component of dielectric constant $\varepsilon_{\parallel}$ which in turn decreases the $\varepsilon''_{\parallel}$ (max).

In smectic-C phase, the observed deviation from the linear behaviour of $\varepsilon''_{\parallel}$ (max) with temperature reflects the temperature (from the extrapolated linear behaviour in the smectic-A phase) dependent variation of tilt angle (with respect to layer normal) tuned by the director fluctuations in smectic-C phase. The tilt angle is calculated using [36] the formula

$$\theta = \mathrm{Cos}^{-1}\{[\varepsilon''_{\parallel}(\mathrm{max})_c]/[\varepsilon''_{\parallel}(\mathrm{max})_A]\}^{1/2} \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

where $\varepsilon''_{\parallel}$ $(\mathrm{max})_c$ is the measured value of $\varepsilon''_{\parallel}$ (max) in the smectic-C phase and $\varepsilon''_{\parallel}$ $(\mathrm{max})_A$ is the value of $\varepsilon''_{\parallel}$ (max) in the smectic-C phase obtained by the linear extrapolation from the smectic-A phase.

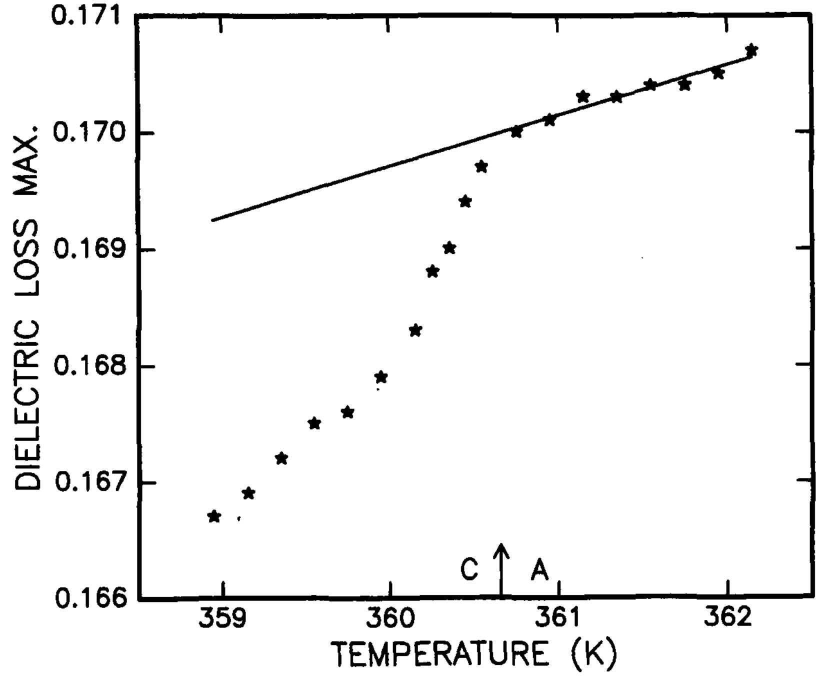

FIGURE 1 The temperature variation of dielectric loss maximum in the smectic-A and -C phases with the extrapolated solid curve in 10O.8.

The temperature dependence of tilt angle observed for various nO.m compounds is illustrated in Figure-2. It may be noticed that the temperature axis is taken as

$$T_C^U = [T_{AC} - T]/[T_{AC} - T_X] \qquad (2)$$

unlike the usual $T = [T_{AC} - T]$, while the new scale is introduced for a comparative study and analysis of growth of relevant order parameter in the domain of varying length of flexible end chain and other parameters. The T_X in the denominator is the lower critical point (i.e., smectic-C to smectic-F or -B or -G transition temperature, T_{CF}, T_{CB}, or T_{CG}) of smectic-C phase.

The tilt angle with a zero value in smectic-A phase is found to grow continuously with the decreasing temperature in the smectic-C phase of all the compounds. The maximum values obtained for the tilt angle of various compounds are presented in Table-II. It is apparent from the experimental results (Fig. -2) that the tilt angle increases nonlinearly with temperature

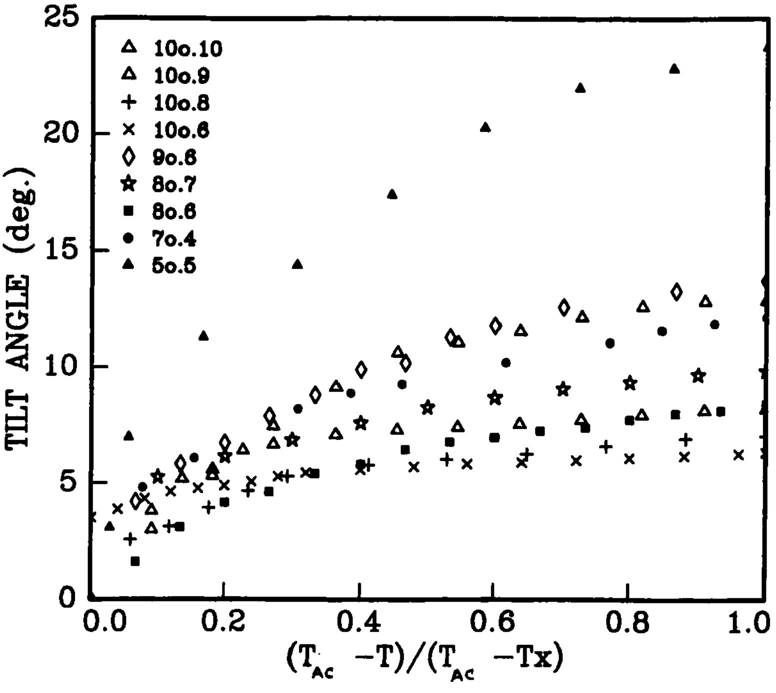

FIGURE 2 The temperature (T^U_C) variation of smectic-C tilt angle (in degrees) in various nO.m compounds.

TABLE II Observed maximum value of smectic-C tilt angle θ_{max} (in degrees) and the critical exponent β, the value of constant A along with the variance value obtai ned by fitting (to eqn.-3) the observed temperature dependence of tilt angle for different nO.m compounds

Compound	θ	β	*A*	*Variance*
5O.5	24	0.403	14.65	0.00016
7O.4	11	0.378	11.18	0.00007
8O.6	8.4	0.365	9.68	0.00004
8O.7	9.8	0.355	17.16	0.00012
9O.6	15	0.354	9.27	0.00431
10O.6	6.2	0.313	7.67	0.00036
10O.8	7	0.309	6.26	0.00553
10O.9	12.9	0.302	10.47	0.00176
10O.10	8.2	0.303	8.78	0.00173

from zero value at T_{AC} (the smectic-A to smectic-C transition temperature) to a maximum value. The maximum values of tilt angle obtained by this method (24° for 5O.5, 7° for 10O.8, and 11° for 7O.4) are in good agreement with the literature data by X-rays (23.6° for 5O.5 [23] and $10 \pm 1°$ for

10O.8 [41]) and ESR (11.5° for 7O.4 [27]) measurements. The observed temperature variation of tilt angle is found to be similar to the that reported [36] for other mesogens.

The present dielectric studies in the wake of the reported data on nO.m compounds (Tab.-III) reveal that the odd numbered alkyl (m) end chain compounds in 5O.m, 8O.m and 10O.m series and the odd numbered alkoxy (n) end chain compounds in nO.6 and nO.7 series possess larger equilibrium tilt angle values than their immediate even numbered members.

This alternative trend of smectic-C equilibrium tilt angle is also found in agreement with the Luckhurst's prediction [45] of smectic-C occurrence and the dominating interaction of McMillan's [14] in-plane out-board dipole moments. A similar trend of odd-even effect is observed at Isotropic-Nematic (IN) and Nematic-Smectic A (NA) interfaces due to the alternating contributions of the transverse dipolemoments (projected by the cis-trans like configurations of their respective odd-even end chains alkyl or alkoxy) as detailed by Marcelja's [46] model.

The temperature dependence of the tilt angle is found to obey the power law behaviour [47] given by

$$\theta = A(T_{AC} - T)^{\beta} \qquad \ldots\ldots(3)$$

TABLE III Smectic-C tilt angle maximum value θ_{max} (in degrees) for various nO.m compounds specified with the number of methyline units in the alkoxy(n) or alkyl(m) end chains along with the reference values

Compound	*n/m*	θ_{max}	*Ref.*
5O.m	5	24.0	pw
	6	14.0	42
	7	17.0	42
8O.m	6	8.4	pw
	7	9.8	pw
10O.m	6	6.2	pw
	8	7.0	pw
	9	12.9	pw
	10	8.2	pw
nO.6	5	14.0	42
	7	16.2	42
	8	8.4	pw
	9	15.0	pw
	10	6.2	pw
nO.7	4	8.0	43
	5	17.0	42
	7	11.5	44
	8	9.8	pw

pw-Present work.

where β is the critical exponent relevant to the smectic-C order parameter following the AC transition.

The values obtained for the exponent β and the coefficient 'A' in this method are presented in the Table-II. The β values are found to be in good agreement with those obtained [23, 36] by the other experimental techniques.

It is observed from the results (Tab.-II) that most of the nO.m systems adopt a β value more or less in the vicinity of de Gennes predicted [11] value 0.35 (rather than the mean field value of 0.5). This result underlines the successful realisation of an experimentally inaccessible λ-transition situation through the observed liquid crystalline AC transition as predicted by de Gennes. It also signifies the importance of the strong and characteristic long range tilt order parameter fluctuations. It is also noticed that either the thermal span of the relevant smectic-C phase (for the unique growth of tilt order) or the thermal span of high temperature smectic-A phase (to introduce underlying pre-transitional fluctuations) have insignificant effect for the supposed long range guage invariance of smectic-C order parameter.

However, the difference among the values of the coefficient, A is due to the possible molecular origin of the mesogenic effect.

A meticulous observation of the results reveals that the β value is found to decrease with the increase in the number of carbon atoms (or the length of the flexible part of the nO.m molecule). Similar trend of smectic-C β-behaviour is reported [48] in terephthalylidene-bis-(4*n*)-alkyl anilines (TB*n*A compounds). The increase of β value (from the vicinity of de Gennes value) to the mean field value (with increasing flexible length) is predicted as the liquid crystalline molecule's trend to set in the phenomenological mean field regime, due to the fact of decreasing essential rigidity nature of the molecule. The results of 10O.m series (m = 6, 8, 9 and 10) provide a case for the relatively free alkyl chain length variation, where as the overall trend of nO.m compounds presents the case of the more rigidly bridged alkoxy end chain. It is apparent that the effect of rather rigidly mediated alkoxy chain length on the value of β is more than that due to relatively flexible alkyl chain length in promoting the mean field behaviour.

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ANSWERS TO THE COMMENTS OF THE REFEREE FOR THE MANUSCRIPT LC-PP053

1. The headings and definitions of symbols given in Tables-I, II and III reprovided in the legends.
2. The units for ITO layer resistivity is changed and given in standard units of ohm/sq. cm in the experimental part.
3. The temperature range over which the change of empty cell capacitance is claimed to be less than 0.01% is in between 30–100 °C and is specified in the experimental part of the text of the paper.
4. The lower critical point is described as the temperature at which the smectic-C phase changes into the other lower temperature smectic phase in the decreasing order of temperature i.e., smectic-C to smectic-F transition temperature as T_{CF} etc., as given in the text.
5. The obtained maximum smectic-C tilt angle values by the present method are given in the discussion part for a ready reference in comparison with the X-ray and ESR values. However, the Table-I, II and III are also retained.
6. Infact 'A' happens to be the constant value relevant to the molecular system under investigation and it need not be same for the different compounds studied. The difference in the **A** value for differing nO.m compounds is discussed in text of the paper as due to molecular origin.
7. The uncertainity in β value is 0.25% (if its value is taken as rounded off to third decimal place). However, the variance value is also provided as the fouth column in the Table-II to demonstrate the goodness of the fit.
8. The notation given for the symbols in Figure-2 is provided clearly at the left top corner of the figure itself.
9. The equation for tilt is changed in the text of the paper as

$$\theta = \mathbf{Cos}^{-1}\{[\varepsilon''_{11}(\max)_C]/[\varepsilon''_{11}(\max)_A]\}^{1/2}$$