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Elucidation of the de Vries behaviour in terms of the orientational Order parameter, apparent tilt angle and the field-induced tilt angle for novel smectics investigated by Polarized Infrared spectroscopy

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We report experimental results of the orientational order parameter, the apparent tilt angle 9 and the field-induced tilt angle for three novel chiral smectic liquid crystalline materials 10 11 investigated using IR polarised spectroscopy. The common feature in these materials is use of the core 5-methyl-2- pyrimidine benzoate as the central part of the mesogen. This core is 12 13 terminated by siloxane/carbosilane chains on one of the ends and by the chiral alkoxy chains on the opposite. These compounds exhibit low concomitant layer shrinkage at the SmA* to 14 SmC* transition temperature, and within the SmC* phase itself. The maximum layer 15 shrinkage in SmC* is observed as $\sim 1.5\%$. We calculate the apparent orientational order 16 parameter, S_{app} in the laboratory reference frame from the observed IR absorbance for 17 homeotropic aligned samples and the true order parameter, S, is calculated using the 18 measured tilt angle and is also interpolated from Iso-SmA* transition temperature to closer to 19 SmC* phase. The apparent tilt angle in SmA* phase calculated from a comparison of order 20 parameters S and S_{app} is found to be significantly large. A low magnitude of S_{app} found for 21 homeotropic aligned samples in SmA* phase indicates that the order parameter plays a vital 22 role in determining the de Vries characteristics, especially of exhibiting larger apparent tilt 23 24 angles. Furthermore there is a significant increase in the true order parameter at temperatures close to SmA* to SmC* transition temperature in all of the three compounds. The planar-25 26 aligned samples are used to study the dependence of the induced tilt angle on the applied 27 electric field. The generalized Langevin–Debye model given by Shen et al. reasonably fits the experimental data on the field-induced tilt angle. The results show that the dipole moment 28 of the tilt correlated domain in SmA* diverges as temperature is lowered to the SmA* -29 30 SmC* transition temperature. The generalized Langevin-Debye model is found to be extremely effective in confirming some of the conclusions of the de Vries behaviour. 31 32

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35 I. INTRODUCTION

Liquid crystals constituted of calamitic rod-like mesogens and long chains attached to the two 36 37 ends of the mesogen normally form smeetic phases. Smeetic liquid crystalline phases are perceived as one-dimensional piling up of the two-dimensional fluid layers, the single 38 39 dimension is denoted by the density wave vector [1-2]. The layer normal is parallel to the density wave vector; the positional and the orientational order parameters govern the 40 characteristics of smectic liquid crystals. The long molecular axis is almost collinear with the 41 director in smectic A phase similar to that in a nematic phase, whereas in the smectic C 42 phase, the director is tilted with respect to the layer normal. If the molecules are optically 43 44 active, smectic C phase is chiral and the spontaneous polarization emerges normal to the tilt plane, the latter is constituted by the director and the layer normal [3]. The director forms a 45 46 helicoidal structure in which the helical axis lies parallel to the layer normal [4]. The pitch of the helix so formed lies generally in the μ m optical wavelength range. 47

48 Based on an extensive study of the SmA to SmC transition of most smectics [5-11] it has been inferred that a continuous transition from SmA to SmC phase can be described by a 49 complex number ψ (= $\Theta e^{i\phi}$), where Θ is the magnitude of the tilt angle of the director from 50 the layer normal and ϕ is the azimuthal angle of the direction of the tilt. However, it should 51 52 be emphasized that the disorder-order type transition had been considered as a useful basis-of especially in relation to the molecular biaxiality [12-13], and in explaining a small change in 53 the layer thickness at the SmA* to SmC* transition temperature. Such a transition may thus 54 be important to exploring the first order or weakly first-order transitions. de Jeu et al. [14] 55 56 and Adriaan de Vries [17] reported that SmA to SmC transition in some smectics such as 70.5 could be of the disorder-order type because X-ray diffraction studies revealed a 57 negligible change in the smectic layer spacing at the transition temperature. They found that 58 the long molecular axis is tilted by an angle of $\sim 16^{\circ}$ from the layer normal, at a temperature 59 close to the transition temperature. Furthermore the orientational order parameter in SmA is 60 61 significantly lower than unity. An importance of the orientational order parameter (S) on the layer spacing first realised by Leadbetter and Richardson provided the basis of de Vries 62 63 work. Different models, as slight variants of each other are: non-correlation, symmetric, asymmetric and diffuse cone. These were proposed to explain the various experimental 64 results obtained by de Vries [18-20]. Out of these models, the diffuse cone is the most widely 65 66 accepted one. In this model, de Vries considered a probability distribution function, $P(\theta) =$

 $b\sin\Theta exp[f(T)\cos^2\Theta]$. The suggestion of an importance of the orientational order 67 parameter based on the Maier-Saupe model for nematics made initially by Leadbetter and 68 Richardson inspired de Vries to insert $cos^2 \Theta$ term in the above distribution function [21]. 69 According to this model, the director is tilted with respect to the layer normal in the SmA 70 71 phase but it is distributed randomly to form a diffuse cone in order to ensure the uniaxiality 72 of SmA phase. The characteristics of de Vries smectics are thus quite distinct from those of a conventional smectic A phase. At the SmA to SmC transition, the rotational symmetry of 73 the azimuthal distribution is lost and consequently the net molecular tilt angle increases 74 sharply with a reduction in temperature. The compounds that use siloxane, carbosilane end 75 76 chains exhibit nano phase separation and the large field-induced tilt angles observed in SmA* 77 usually reflect exhibit de Vries characteristics [15,16, 22-24].

78 The main objective of this paper is to find roles of the orientational order parameter and of azimuthal distribution of the director, in determining the de Vries smectic characteristics of 79 80 large (i) apparent as well as (i) large field-induced tilt angle in SmA* phase found in three 81 novel compounds i.e., DR276, DR118 and DR133 and to determine their role on the smectic 82 layer spacing. We use the characterization technique of polarised infrared spectroscopy. We calculate the apparent order parameters S_{app} for homeotropically aligned samples in the 83 laboratory frame and then proceed to measure the real order parameter (S) by using the 84 experimentally obtained values of tilt angle near to the SmA* to SmC* transition and using 85 the interpolated procedure described here. Finally we determine the apparent tilt angle for the 86 87 entire range of temperatures in SmA* phase and SmC* phases. Results of the field-induced tilt angle on the applied voltage (electric field = voltage/cell spacing) are presented for 88 89 homogeneously aligned liquid crystalline samples. The obtained induced-tilt angle is fitted to 90 the theoretical model in order to elucidate the de Vries scenario.

91 **II. EXPERIMENT**

92 A. Materials









Cr 52°C SmC* 94°C SmA 114°C I (**DR118**)

FIG. 1. Molecular structures of the compounds DR276, DR133 and DR118 and the transition
 temperatures determined by differential scanning calorimetry (DSC) are givem. The phase
 transition temperatures are also obtained by polarized optical microscopy. The cooling rate
 used for both techniques used is 1 °C/min.

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108 The chemical formulae, phase sequences and the phase transition temperatures of three compounds, DR276, DR118 and DR133 are given in Fig. 1. The compounds DR276 and 109 110 DR133 use 5-phenyl 2- pyrimidine benzoic acid core. The core for both compounds is terminated by tri-carbosilane undecyloxy and trisiloxane- undecyloxy chains for DR276 and 111 112 DR133 respectively on one of their ends. On the opposite end, the core for all the three compounds is terminated by a chiral alkyloxy tail and CH₃ group is attached to the chiral 113 114 carbon atom. Carbosilane or trisiloxane groups together with the $(CH_2)_{11}$ spacer promote 115 nanophase separation and facilitate formation of the smectic C phase. In DR118, however the 116 ester group that links the two phenyl rings in the mesogen is absent. Similarities in the 117 molecular structures of these compounds thus include terminations by the chiral alkoxy chain 118 on one of the ends and the bulky siloxane or carbosilane tail on its opposite ends. The latter 119 as suggested earlier gives rise to nanophase sublayer like separation and lamellar ordering 120 with a well-defined layer structure. Bulky carbosilane/siloxane groups are also known to 121 promote SmC phase [25]. An esterified molecular core in DR133 enhances the mesogen's 122 polarity and creates flexibility in the molecular conformation [26], whereas the methyl 123 group to the chiral carbon atom leads to the emergence of the spontaneous polarization [27]

in the three cases. It has been found that silicon or fluorine termination also promote de Vries

- 125 like smectic behaviour [28-29].
- 126

Material	Layer Shrinkage*	Reduction Factor *	Layer Spacing (Å)*	Optical tilt (Θ_{ind})(degrees)*	IR tilt angle (degree)	po (Debye)
DR276	1.9%	0.3	44	26.6	25	790
DR133	1.7%	0.3	41.6	34.5	26	650
DR118	1.2%	0.2	42.4	35.5	30	1570

127 **Table 1:** de Vries characteristics of the three compounds

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*These	values	are	obtained	from	references	16 and 41.
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129 **B. IR Spectroscopic Measurements**

130 The polarized IR spectroscopic measurements are carried out using Bio-Rad FTS-6000 spectrometer. The investigated spectral range extends from 450 cm⁻¹ to 4000 cm⁻¹. The 131 spectrometer is equipped with liquid nitrogen cooled Mercury Cadmium Telluride (MCT) 132 detector of IR radiation and a computer-controlled wire grid rotation polarizer. A hot stage 133 134 with a temperature stability of better than $\pm 0.1^{\circ}$ C forms a part of the experimental measuring 135 set-up. An average of 64 scans of the spectra are recorded. This gives rise to a spectral resolution of 2 cm^{-1} and to the signal to noise ratio higher than 2000. The cell preparation 136 137 techniques include the adoption of the careful procedures for obtaining both homeotropic and 138 planar alignments of compounds on the windows of the cell. For both alignments, Zinc 139 Selenide (ZnSe) windows with a thin layer of indium tin oxide (ITO) sputtered on to them are 140 used in an IR liquid crystalline cell. A Mylar spacer of 5 µm thickness separates the two 141 overlapping windows. For achieving a 'planar alignment', both windows are coated with 142 polymer solution RN1175 (Nissan Chemicals), following which the windows are kept in a vacuum oven at 250 °C for one hour. The aligning solution on the windows is thus 143 polymerised and this forms a thin planar-alignment layer. The alignment layers of the cell 144 145 are rubbed antiparallel using a commercial rubbing machine. For obtaining the homeotropic 146 alignment layer, the windows are coated with the solution of chromolane in ethyl alcohol. The alignment layer is subsequently cured for 1 hr at a temperature of 120 °C which allows 147

the alcohol to evaporate. The IR spectra are recorded for different temperatures and 148 especially for smaller increments in temperature close to the SmA* to SmC* phase transition 149 temperature. DC bias voltages of both polarities are applied across the electrodes of the IR 150 cell. The polarizer is rotated from an angle of 0° to 180° in steps of 20° . For each step of the 151 polarizer direction, the IR spectra are recorded as a function of the applied voltage. This 152 procedure is repeated for different temperatures of the sample in the cell. A Voigt function 153 is used to fit the absorbance profile of the phenyl ring C-C stretching mode at 1605 cm⁻¹ for 154 each applied voltage and temperature. The Perkin Elmer Grams Research (PEGR) program is 155 156 used to find the intensity and the spectral width of the recorded spectral line while Origin-8 program is used to fit each absorbance profile to the Voigt function. The thickness of the 157 158 fabricated cells prior to their fillings is measured using a UV-VIS spectrometer (Avaspec-159 2048) based on using the technique of the interference of waves that produce fringes and using its commercial software. 160

161 III. RESULTS AND DISCUSSIONS

Three homeotropically aligned cells are prepared by filling each cell with a different compound that is to be investigated. Infrared spectroscopic measurements are made on aligned sample cells after each cell in turn is carefully mounted in to the hot-stage fixed to the rotation Table of the optical Polarizing microscope.

166 A. Results on homeotropically aligned IR cells

167 Prior to carrying out IR measurements, sample textures are recorded by a polarizing optical microscope. Single domain textures are observed in SmA* phase. The texture confirms 168 perfect homeotropic alignment in each case. Multi-domain textures attributed to the 169 170 azimuthal freedom of the tilting directions are observed at the SmA* - SmC* transition temperature. Infrared measurements exhibit absence of IR dichroism in SmA phase. This 171 172 indicates that the azimuthal angle made by the director on the substrate surface can take all 173 values ranging from 0 to 2π with equal probability. Absorbance profile is normally 174 independent of the projection of the director on to the plane of the windows when the spectral 175 profile is integrated over an area of the IR beam of diameter $< 10 \mu m$. Figs. 2(a), 2(b) and 2(c) illustrate the normalized absorbance of the C-C stretching phenyl vibration band, $\binom{A_{per}}{A_{iso}}$ 176

(the absorbance due to a projection of the square of transition moments along the windows of the cell normalized by the similar absorbance measured in the isotropic phase. The phenyl band is chosen due to its transition dipole moment being almost collinear with the long

molecular axis. As the sample cell is cooled from isotropic phase to SmA* phase, a sudden 180 181 drop in the absorbance is detected with temperature. This demonstrates a sudden decrease in 182 the projections of the square of the transition dipole moments normal to the direction of IR 183 beam, brought about by an almost perfect homeotropic alignment of the mesogens on to the substrates. In the vicinity of SmA*- SmC* phase transition temperature, the absorbance is 184 observed to decrease sharply with a decrease in temperature close to the I-SmA* phase in 185 186 DR133 and in other two cases the decrease occurs over 2 to 3 C temperature and after the 187 transition the absorbance rises gradually. This observation





FIG. 2. Absorbance of the phenyl band as a function of temperature/phase for (a) DR276, (b)DR133 and (c) DR118.

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198 implies a progressive increase in the apparent tilt angle of the mesogens in SmA* phase and it 199 increases further as the temperature is reduced to SmA* to SmC* transition temperature. A continuous small step increase in absorbance at the SmA* to SmC* transition is observed in 200 201 these cases as opposed to a sharp increase at the transition temperature in a conventional 202 smectic compound, C7 [30]. In SmC* phase, the absorbance displays increasing trend as 203 temperature is lowered since the mesogens increasingly tilt with a reduction in temperature 204 from the layer normal. The mesogen is perpendicular to the substrates in a homeotropic 205 alignment .

206 The apparent orientational order parameters S_{app} in SmA* and SmC* are calculated from the

207 experiments conducted on the homeotropically aligned samples and these are plotted in Figs.

208 3(a), 3(b) and 3(c)





FIG. 3. Variation of the apparent order parameter (S_{app}) with temperature for homeotropically
aligned cells of (a) DR276 (b) DR133 and (c) DR118.

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for the compounds DR276, DR133 and DR118.

In the experiment on a homeotropic aligned LC cell, the IR beam is incident parallel to the smectic layer normal. In the laboratory frame of reference, IR absorbance is given by [31-32]:

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$$A_{per}/A_{Iso} = 1 - S_{app} P_2(\cos\beta_l) + \frac{1}{2} D_{app} \sin^2\beta_l \cos 2\gamma_l$$
(1)

where the apparent orientational order parameter, for the long and the short molecular axes are S_{app} , and D_{app} (the latter is also the molecular biaxiality order parameter) respectively. $P_2(\cos \beta_l) = \frac{1}{2}(3\cos^2\beta_l - 1)$ is the second Legendre polynomial. The direction of the IR transition dipole moment relative to the long axis of mesogens in the molecular frame of reference is denoted by the polar angle β_l and azimuthal angle, γ_l . Since $\beta_l < 6^\circ$ for the phenyl C-C stretching vibration band, two $\sin^2\beta_l$ terms in Eq. (1) contribute only 1% of the total absorbance and hence these terms can be neglected. We thus approximate Eq. (1) as

$$S_{app} \approx 1 - \frac{A_{per}}{A_{Iso}} \tag{2}$$

The apparent orientational order parameter in the laboratory frame of reference, S_{app} , is thus calculated using Eqn (2) from the normalized absorbance.



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255 FIG. 4. Results of the order parameters for (a) DR 276 (b) DR133 and (C) DR118: The 256 apparent order parameter (S_{app}) [black squares] calculated with respect to the fixed laboratory frame of reference, the green triangles denote the true order parameter, S, calculated by using 257 258 Eq. (5) and the experimentally obtained tilt angles measured close to the SmA* to SmC* 259 transition temperature, red filled circles denote the interpolated values of S. These order parameters are used to calculate the apparent molecular tilt angle (blue squares) plotted for 260 the entire range of temperatures in a homeotropically aligned cell. 261

263 Locally, the symmetry of the distribution function changes from uniaxial to biaxial at the SmA* to SmC* transition temperature at the level of a single smectic layer. In this case, the 264 265 tilt plane formed by the director and the smectic layer normal is the only plane of symmetry of the system. For the tilted smectic phases however, the most convenient option is to choose a 266 reference frame fixed to the local director and to the tilt plane. A new reference frame called 267 the local frame is thus obtained from rotating the laboratory frame of reference by an angle θ 268 269 about the X-axis [refer Fig. 5]. In this local frame of reference, P = 0 and S is the true 270 molecular order parameter as for the nematics. The tilt affects the magnitude of the order 271 parameters. Finally, the absorbance in the local frame of reference is written as [32,33]:

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$$A = \frac{1}{2} [A_Z \sin^2 \theta + A_Y \cos^2 \theta + A_X]$$
(3)





FIG. 5. Representation of experiments performed on homeotropically aligned samples. X, Y, 274 Z denote the axes of the laboratory frame of reference; x, y, z are the axes of the molecular 275 reference frame. Θ is one of the Euler angles which describe the orientation of the molecular 276 277 reference frame versus the laboratory reference frame. The direction of the IR transition 278 dipole moment μ relative to the long axis of mesogens in the molecular frame of reference is 279 denoted by the polar angle β_l and azimuthal angle γ_l . The inset shows the definition of the local system described in the text: X', Y' Z' are axes of the local frame of reference, θ is the 280 281 in-layer tilt angle made by the director, $\theta = \langle \Theta \rangle$ (averaging is done for a single smectic layer). 282

where A_X , A_Y and A_Z are components of absorbance that are now described by S, D and P in the new frame of reference. Further, above equation is [32]:

285
$$A = 1 - SP_2(\cos\theta)P_2(\cos\beta_l) + \frac{1}{2} \left[DP_2(\cos\theta) - \frac{1}{2}C\sin^2\theta \right] \sin^2\beta_l \cos 2\gamma_l$$

where *C* is the mixed biaxiality used to denote coupling between *D* and *P*. *S*, *D*, and *C* denotethe true order parameters in the new chosen reference system.

On comparing Eqs. (1) and (4), we find that the apparent orientational order parameter is equal to the true orientational order parameter (*S*) of the molecules, multiplied by $P_2(\cos \theta)$ [32]:

$$S_{app} = S P_2(\cos \theta) \tag{5}$$

(4)

where $P_2(\cos \theta)$ is the second order Legendre polynomial of the tilt angle θ . S_{app} is measured in the laboratory frame. On using values of the experimentally calculated tilt angles near the SmA*-SmC* transition temperature and the measured values of S_{app} , S (solid green triangles in Fig. 4) are calculated from the tilt angle. Results for S for the three compounds at temperatures close to SmA* – SmC* transition temperature are plotted in Fig. 4. The interpolated values of S (red circles) for the remaining temperatures by assuming zero tilt angle at the I to SmA* phase transition temperature are obtained by using the following equation: [34]

$$S = S_{app} + A\tau^{\beta} \tag{6}$$

300 where, β , A are constants.

 $\tau = 1 - \frac{T}{T_{I-SmA^*}}$, where τ is the reduced temperature, and T_{I-SmA^*} is the Isotropic to 301 SmA* transition temperature. Experimentally, it is found that the apparent order parameter for 302 the short axis or the molecular biaxiality order parameter (D_{app}) is negligible at the I to 303 304 SmA* transition and an assumption of the zero tilt angle at I-SmA* transition temperature is therefore justified. The calculated value acts as the lower bound values of the tilt angle by 305 306 noting that this angle cannot be less than zero. Finally, the tilt angle for the entire range of 307 temperatures is calculated using Eq (5) and using interpolated Eq (6) and the actual values of 308 S. The tilt angle is calculated from Eq (5). From these results, we infer that the mesogen is tilted by a finite angle in the SmA* phase of DR276, DR133 and DR118. As the angle is large 309 310 enough, de Vries behavior is confirmed.

311 **B. Planar-aligned samples**



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FIG. 6. Optical textures of planar-aligned sample of DR276 for two temperatures (a) 84°C, 0
V and (b) 85°C at 40 V in SmA* phase.



FIG. 7. Polar plots of the absorbance profile in terms of the polariser angle for the compoundDR118, as an example.

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321 Here we present the results of the measurements on the absorbance profile for a planar-322 aligned cells as a function of the electric field across the cell. Fig. 6 gives the optical 323 textures for DR118 at different voltages, as an example, where the quality of the alignment is 324 high. The IR spectra are recorded for each temperature by varying the magnitude of the 325 negative and positive voltages. The corresponding absorbance profiles $A(\Omega_p)$ for the C-C 326 phenyl stretching vibrations as a function of the angle by which the polarizer is rotated under 327 the application of the positive and negative DC voltages are determined. Fig. 7 shows a polar 328 plot of A with respect to Ω_p plotted by using the experimental data for the opposite polarities 329 of the applied DC voltage, as an example. A unique absorbance profile is created for each 330 temperature and applied voltage and is fitted to the following equation [35, 24],

$$A(\Omega_p) = -\log_{10}[10^{-A_{\parallel}} + (10^{-A_{\perp}} - 10^{-A_{\parallel}})sin^2(\Omega_p - \Omega_{max})$$
(7)

The angle that the polarizer makes with a reference direction is denoted by Ω_p . The highest values of the absorbance of a band are given by A_{\parallel} for $\Omega_p = \Omega_{max}$. For the polarizer angle, $\Omega_p = 90^o + \Omega_{max}$ the absorbance for the phenyl C-C stretching band is a minimum and is denoted by A_{\perp} . Equation (7) is fitted to the polar plots obtained for different temperatures and different voltages of opposite polarities. The fit gives us values of Ω_{max} for which the 336 absorbance is a maximum for a fixed volage. The induced IR tilt angle (Ω_{ind}) as a function of 337 electric field is determined from the saturated values of Ω_{max} for positive and negative 338 applied voltages. The de Vries smectics with a chiral carbon are known to display unusual 339 electro-optical characteristics, in terms of the apparent tilt angle and the birefringence. These 340 are modelled using several approaches [36-37]. Clark et al. used the Langevin-Debye model 341 to qualitatively elucidate the electro-optical properties of the smectics. Initially, the same 342 Langevin-Debye model was proposed by Fukuda et al. [38] to explain the V-shaped switching 343 in an antiferroelectric liquid crystal. The Clark model is based on the assumption that the 344 mesogens are distributed over a cone of a fixed cone-angle in the absence of an applied 345 electric field [39] in SmA* phase. On application of an electric field (E_{ap}) , the free energy 346 includes the term involving the proportionality factor of the local dipole moment (p) and the 347 azimuthal angle i.e. *pEcosq*. However, this approach though successful in general did prove short of explaining the experimentally observed sigmoidal response of tilt angle as function of 348 the electric field obtained. Following which Shen et al. introduced a quadratic term in the 349 350 field in the free energy function for the orientational distribution of the mesogens having a 351 term dependent on E_{ap} of the second order with two degrees of freedom: azimuthal φ as well 352 as the tilt (Ω) angles. This model was called the generalized Langevin-Debye model [40]. 353 Shen et al. constrained the values of Ω (E_{ap}) to change within specified narrow range of 354 values. The experimental results determined the upper and the lower limiting values of Ω . The birefringence value in the absence of electric field sets the lower limit for Ω_{min} while the 355 maximum angle Ω_m for large applied fields determines the upper limit. The expression of the 356 357 free energy function in the generalised Langevin-Debye model is written in the form [40]:

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$$U = -\mathbf{p}\left(1 + \alpha \frac{\mathbf{p}}{|\mathbf{P}|} \cdot \mathbf{E}_{ap}\right) \cdot \mathbf{E}_{ap} = -p_0 \mathbf{E}_{ap} \sin \Omega \, \cos \varphi \, \left(1 + \alpha \mathbf{E}_{ap} \cos \varphi\right) \tag{8}$$

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where $\mathbf{p} = p_0 \sin\Omega$ denotes the mean value of the dipole moment of the domain having the azimuthal angle which is not degenerate. The first term on the R.H.S. of Eq. (8) accounts for the free energy related to the interactions of the dipoles with E_{ap} . The second term quadratic in E_{ap} is associated with the scaling phenomenological parameter (α). The tilt susceptibility for the sigmoidal response seen in the plot of the experimental data of the tilt angle as a function of E_{ap} is described by the quadratic term. The mean field molecular orientational distribution function can be defined as,

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$$f(\Omega,\varphi) = \exp[-U/k_B T] / \int_{\Omega_{min}}^{\Omega_{max}} \int_{0}^{2\pi} exp[-U/k_B T] \sin\Omega d\Omega d\varphi$$
(9)

The average value of a physical parameter $\langle X \rangle$ can be calculated from the given molecular distribution using the following equation,

370
$$\langle X \rangle = \int_{\Omega_{min}}^{\Omega_{max}} \int_{0}^{2\pi} X(\Omega, \varphi) f(\Omega, \varphi) sin\Omega d\Omega d\varphi$$
(10)

Further, the dielectric tensor is averaged and is diagonalized in the laboratory frame of reference to derive the electric field dependent optical tilt Ω_{ind} (E_{ap}) as follows:

374
$$\tan 2\Omega_{ind} = \frac{\langle \sin 2\Omega \cos \varphi \rangle}{\langle \cos^2 \Omega - \sin^2 \Omega \cos^2 \varphi \rangle}$$
(11)







(b)





FIG. 8. The voltage dependence of the molecular IR tilt angle (Ω_{ind}), determined from the absorbance profiles of the C-C phenyl ring stretching vibration at different temperatures in the SmA* phase close to the SmA* - SmC* transition for (a) DR276 (b) DR118 and (c) DR133 at 1605 cm⁻¹ respectively. The symbols correspond to the experimental data, while the solid lines are fits to the generalized Langevin-Debye model given in section 3.2. The thickness of the sample is 5 µm.

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FIG. 9. The local dipole moment p_o obtained from the fitting of the experimental data to the Shen *et al.* model plotted as a function of the temperature in SmA* phase for (a) DR276, (b) DR118 and (c) DR133.





FIG.10. Plots of the temperature dependence of the phenomenological scaling factor α for (a) DR276, (b) DR1118, and (c) DR133.

The dependence of the apparent tilt angle for IR (Ω_{ind}) with electric field at 431 temperatures close to the SmA* to SmC* transition for DR276, DR118 and DR133 are 432 plotted in Fig. 8. It is similar to the plots of the apparent optical tilt found as (Θ_{ind}) and 433 434 birefringence Δn [16, 43,41] by using the automated Time-resolved Polarimeter technique. 435 The layer shrinkage, the molecular tilt and the birefringence of these three compounds is 436 summarized in Table 1. A plausible connection between the apparent tilt angle and birefringence had first been suggested by Lagerwall et al. [44]. The plots show that Ω_{ind} is 437 low for higher temperatures in SmA* phase and the plot displays a linear trend on the applied 438 439 electric field. However, as the temperature reaches the SmA^* to SmC^* transition temperature, 440 there is dramatic enhancement in the electro-clinic response even at low applied electric fields 441 and the plot turns out to be nonlinear. This is a signature of a large cone angle and a large pre-442 transitional effects. In the vicinity of the transition temperature T_{AC} , Ω_{ind} increases rapidly to a value of $\sim 23^{\circ}$ and then continues to rise gradually with the applied field, finally attaining a 443 saturation at a value of 27° in the SmA* phase. Therefore, the response is sigmoidal in shape 444 445 rather than of the Langevin type, the latter is commonly observed in conventional smeetics.

The experimental values of the tilt angle obtained by IR spectroscopy, i.e. $\Omega_{\rm ind}$ have 446 been fitted to the generalized Langevin-Debye model using Eq. 11. The plots indicate that the 447 optical tilt saturates at 30°, *i.e.* $\Omega_{max} = 30^{\circ}$ for DR118 and at 25° and 26° for DR276 and 448 449 DR133, respectively. The dependence of the fitting parameters p_0 and α on temperature for the three compounds approaches a maximum value close to the SmA* to SmC* phase 450 transition. This increase can be attributed to an increase in the size of the tilt correlated 451 domain. DR118 has the highest value of p_o : 1050 Debye at 95.5 °C and increases to 1570 452 Debye at 94.5°C, while DR133 has the lowest value of 540 Debye at 94.5 °C and 650 Debye 453 at 93 °C as shown in Figs. 9(a), 9(b) and 9(c). Fig. 10 represents the plots of scaling 454 455 parameter α with respect to temperature. The phenomenological scaling parameter α exhibits 456 a linear increase as temperature is decreased from I to the SmA* to SmC* phase transition 457 temperature. Its value lies within a range of 0.4 to 1.2 for all the three compounds.

Our findings support the finding that the orientational distribution function is of the diffuse cone type rather than of the sugar loaf type as had been suggested by some authors [45] from the X-ray small angle scattering. It has been argued that the x-ray scattering arises from the entire molecule rather than from the central core part of the mesogen. However, it is clear from these results and the ensuing discussion that the orientational order parameter plays a key role in leading to the de Vries characteristics. The properties of de Vries smecticsare found to be different from conventional smectics.

465 IV. CONCULSIONS

466 The technique of polarized IR spectroscopy gives results for the orientational order 467 parameters, the interpretation of which advances the understanding of the de Vries smectics. 468 The three novel mesogens described here exhibit de Vries- like characteristics of having (i) a 469 significantly large electro-clinic response, (ii) a low orientational order parameter in SmA* 470 and (iii) large apparent tilt angles in SmA* phase. The orientational order parameter for these 471 compounds is found to be low in magnitude (less than 0.5) in the SmA* phase in comparison 472 to the conventional smectics (~ 0.8). This implies that a large apparent tilt angle emerges in the SmA* phase. The true order parameter increases significantly close to the SmA* - SmC* 473 474 transition temperature, whereas it jumps at the transition temperature and finally saturates at 475 low temperatures. These findings confirm the validity of the theory of Saunders *et al.* [46] on 476 de Vries materials proposed a decade ago. The dependence of the field-induced tilt angle on 477 the applied electric field is explained by the generalized Langevin-Debye model of Shen et 478 al. The results provide a clear evidence of the applicability of the diffuse-cone model of de 479 Vries elucidated by Shen et al. [40] in which the cone tilt angle is restricted to lie within a 480 range of values in between Ω_{\min} and Ω_{\max} . These are the two limiting values of the apparent tilt angle with temperature/field. The dependence of the apparent tilt angle on the applied 481 electric field strikingly resembles the large dependence of the observed tilt angle on the field 482 483 measured in electro-optical experiments [47].

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