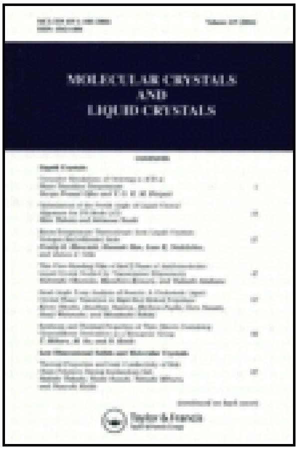

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Spontaneous Polarization in Tilted Smectics

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The rapid electro-optic response of ferroelectric liquid crystals (FLCs)–spontaneously polar phases–makes them candidates for the next generation of liquid crystal displays and a considerable effort has been underway to establish design rules for synthesizing more responsive materials. Herein we describe the key features of a simple theory [D. J. Photinos and E. T. Samulski, *Science*, **270**, 783 (1995)] which suggests that polarity is indigenous to tilted smectics and not a consequence of mesogen electrostatic attributes, e.g. dipole moment and/or molecular chirality. We suggest classes of prototypical FLCs and NMR experiments which could critically test the theory.

Keywords: FLC NMR smectics; spontaneous polarization

1. INTRODUCTION

To date, ferroelectricity in liquid crystals [1] has been observed only in chiral tilted smectic phases formed by molecules with incompletely averaged transverse dipole moments. Thus, *tilt, chirality* and *transverse dipoles* seem to be three indispensable requisites for the appearance of spontaneous polarization, *P*, in the sense that no example of a (real) ferroelectric liquid crystal (FLC) exists in which either of these three attributes is missing. It has been argued that [2–7] tilt and/or chirality are not necessary for ferroeletricity in liquids but such arguments stipulate unusual molecular constitutions and hitherto unrealized phase structures.

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The role of these three attributes, and particularly the way in which they cooperate in order to give rise to P is not fully understood. The arguments put forth by Meyer[8] have elucidated the symmetry aspect of this problem but of course much more needs to be learned in order to understand FLC materials to the point of being able to systematize their design. For example, P obviously cannot exist unless the molecules posses dipole moments, but to what extent are the *inter*molecular dipole-dipole interactions essential to the creation of P? The answers range from complete dominance[3–6] to near irrelevance[9,10]. Similarly, it is generally accepted that molecular chirality causes the twisting of the director in the S_C* phase and also provides the asymmetry that could prevent the vanishing of the transverse component of the molecular dipole moment, but does P stem from the chiral part of the intermolecular interaction? Again there are theories based entirely on chiral interactions[11,12] and others which treat them as insignificant perturbations[9, 10, 13, 14].

It is indeed surprising that despite the high and growing interest in FLC applications, there are no generally accepted answers to basic questions of this kind. Furthermore, if one wishes to attempt a deeper understanding of the known FLCs–as opposed to examining various theoretical possibilities of obtaining a ferroelectric state in fluids–one has to include a fourth attribute, namely the characteristic *bent core-chain molecular structure* which is invariantly encountered in all FLCs, and in fact in virtually all known low molar mass tilted smectic phases. The core is essentially rigid and provides for the orientability of the molecules whereas the chain (linked at an *angle* to the core axis) is flexible and provides the requisite fluidity which, together with the orientability, is believed to give rise not only to the mesogenicity (as observed say in nematics) but also to the smectic layering (which may be viewed as submolecular segregation into core-rich and chain-rich layers) *and* to the tilted ordering[15]. Thus, if a theory of ferroelectricity in tilted smectics is to be usable for materials design purposes it should fully explain why these four attributes, *tilt, chirality, transverse dipole* and *bent core-chain structure* need always be present and, it should explain their individual roles. In other words, a useful theory should explain what would happen if any one of these attributes were absent. In this spirit we have recently proposed a theory[10] which implies the following roles and interconnections:

i) The bent core-chain structure, when placed in a (not necessarily chiral) tilted smectic environment leads *inevitably* to polar ordering of the transverse axis of the chains along the tilt plane normal, even in the case of non-chiral flexible molecules possessing the full (statistical) symmetries of common smectogens.

ii) This indigenous polarity (IP) requires the presence of transverse molecular dipoles *only* if it is to be manifested as electric polarization.

iii) Introduction of such dipoles on aliphatic chains–stereoregular substitution of a specific hydrogen–necessarily introduces a chiral center and renders the molecule chiral.

According to this theory[10], which will be referred to as the Indigenous Polarity Theory (IPT) for brevity, the intermolecular interactions which give rise to ferroelectricity are the same interactions (primarily excluded volume) which produce the tilted phase itself (and the concurrent IP); dipolar and chiral interactions are not needed but dipoles are indispensable for reporting the IP in the form of P and chirality is the chemically unavoidable side effect of endowing the molecules with the appropriate dipole moments. Therefore, dipolar and chiral interactions (although not needed) are always present to some extent in FLCs but this does not necessarily mean that they promote ferroelectricity. (In fact it can be argued that in some cases the interactions among transverse dipoles could oppose ferroelectric ordering.) This is an essential feature that differentiates the IPT from theories in which dipolar or chiral interactions are assumed to underlie ferroelectricity[11,12]. However, the possibility of ferroelectricity being derived from non-polar/chiral interactions is not new: It was pointed out by R. G. Priest[9], on the basis of the general tensor character of the S_C mean field of rigid molecules, that an interaction which need not be intrinsically polar can give rise to ferroelectric order if the molecules are chiral. Later on, W. J. A. Goossens[13] gave an explicit example of spontaneous polarization obtained from chiral rigid smectogens interacting *via* electrostatic quadrupole moments. From the symmetry point of view the situation is illustrated by the well known examples of molecules having the symmetry of a fish[1, 16]. This picture is carried over to flexible molecules in the context of the so-called Boulder model[14, 17], where it is shown that spontaneous polarization can be obtained from chiral smectogens experiencing constraints in the form of confinement within a volume having the shape of a (non chiral) bent cylinder. What is new in the IPT is that polarity is obtained even for the most symmetric flexible molecules that can form a non-chiral S_c phase. More details on the IPT can be found in Ref.10. In part II.A of this contribution we shall give a simplified qualitative picture of the molecular ordering emanating from the IPT and use it to discuss the implications of the IPT in connection with some basic experimental facts from NMR spectroscopy and dielectric relaxation measurements on FLCs. In part II.B we indicate a class of smectogens which should be amenable to a quantitative test of the theory through the computation of P with an IPT potential derived by fitting local C—H bond order parameters determined in the S_C* phase by off-magic-angle spinning/separated local field NMR experiments (Part II.C).

2. RESULTS AND DISCUSSION

A. Indigenous Polarization Theory

Consider the primitive mesogen molecular model shown in Figure 1. It mimics minimally the bent core-chain structure and the flexibility of real smectogens in that it consists of three linear segments representing the mesogenic core (in the middle) and two "end-chains" linked at an angle to the core; the latter segments are allowed to perform simultaneous 180° flips about the core axis. For labeling purposes one side of this planar molecule is black and the other white. There are thus just two equiprobable conformations, say (a) and (b) in Figure 1. The dispositions shown in (c) and (d) can be obtained from (b) and (a) respectively, by rigid rotations of the entire molecule and therefore need not be counted as additional conformations. (They are shown simply to facilitate the subsequent description.)

In a smectic environment each such conformation (n) orients according a probability distribution $f_n(\omega, |R_z|)$ which depends on i) its orientation ω relative to the director (**D**) frame of the phase and ii) on the magnitude of the projection R_z of its end-to-end vector along the smectic plane normal

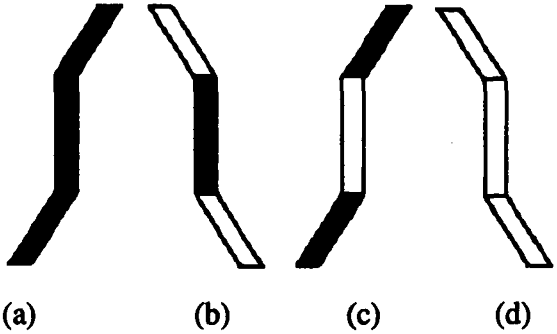


FIGURE 1 Four dispositions of a primitive mesogen having two equiprobable conformations.

(Z). The distribution favors the long range "nematic-like" orientational ordering of the mesogen cores along **D** and also the effective stacking of the molecules within the smectic layers as dictated by the core-chain segregation constraints (see Figure 2). To follow more clearly the implications of such a distribution on the polar order, consider the packing requirements in the limit of high ordering (i.e. when the core segments have to be parallel to **D** and the molecules have to reside exactly within the layers). As a result, in the S_A phase where **D** and Z coincide, all four arrangements shown in Figure 1 are equiprobable and thus both sides (black and white) of each segment will on the average be equally exposed in any given direction. This lack of polarity is indicated by the grey shading of the primitive mesogens' superposed conformations in Figure 2. Once the tilt sets in, however, the four arrangements become inequivalent. For example, looking at the tilt plane, i.e., along the C_2 axis of the S_C phase as in Figure 3, the arrangements shown for the pair of mesogens in (a) are more favored than the pair in (b) –where although the cores are still parallel to **D**, the chains are penetrating into the neighboring layers–or in (c) where the molecules are confined within the layers but now the cores are making a large angle with **D**. Accordingly, in the case depicted in Figure 3, the *cores* would expose both of their sides with equal probability (no polarity) whereas the chain segments would expose their black side (Fig. 3(a)) more than the white one along the given direction of the C_2 axis, i.e., they develop transverse polar order along the C_2 axis (indigenous polarity). Consequently, if a dipole moment were attached say perpendicular to the black side of the chain segments, a spontaneous polarization P would be obtained. (Such IP obviously would not occur for the core segment.)

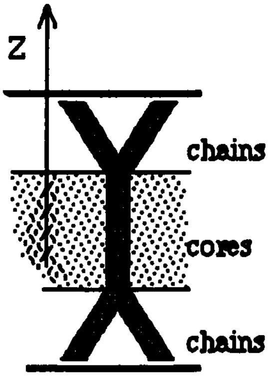


FIGURE 2 Schematic illustration of equiprobable conformations of the primitive mesogen in the S_C phase; the local director **D** and the layer normal Z are coincident in this uniaxial phase.

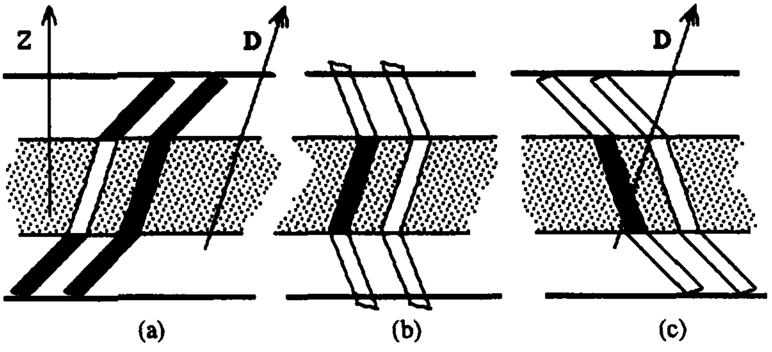


FIGURE 3 Possible arrangements of the primitive mesogen in the S_C phase wherein the chain segments are tilted more than the core segments; **D** is the local director.

Note, moreover, that on the average, the two basic conformations occur with the same probability in all of the three arragements (a), (b), (c) shown in Figure 3, i.e., the two conformations remain equiprobable. *The polarity does not result from the favoring of one conformation over the other but rather from the coupling of the conformations with orientations* (a given conformation has to adopt a particular orientation in order to be accommodated). Figure 3 applies to a situation where the tail segments are more titled than the cores. The same arguments are applicable to the alternative situation[18] shown in Figure 4 where the ordering (see arrangement 4(a)) is depicted to correspond to more tilted cores than chains. In that case we show arrangement 4(b) which is disfavored because the cores are packed inefficiently within the layers although the core segments are along the director, and arrangement 4(c) which corresponds to an unfavorable orientation of the cores relative to the director. Again the ordering of the core is non-polar and the ordering of the chains is polar, albeit of the opposite sign to that in Figure 3.

An immediate implication of these illustrations is that the reorientational motion of the core about its long axis need not show essential differences on going from the S_A to the S_C (S_C*) phase. This is in marked contrast with the implications of models based on chiral or polar interactions[11,12] and, more generally, of arguments which base ferroelectricity on "biased rotation"[17,19]. This implication of the IPT is clearly supported by a variety of dielectric relaxation measurements in the microwave regime[20–22] which show no discontinuities in the dielectric strength or the relaxation time at the S_A to S_C* transition nor any difference in the fast reorientational motion between the ferroelectric S_C* and its racemic mixture[21]. The latter further indicate that chiral interactions are rather insignificant in connection with

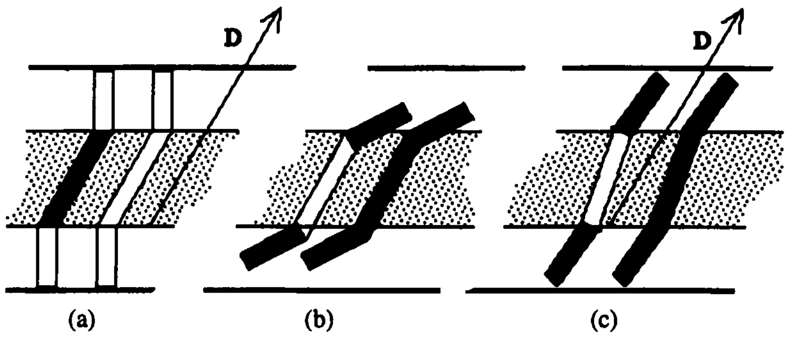


FIGURE 4 Alternative arrangements of the primitive mesogens in the S_C phase having the core segments more tilted than the chain segments.

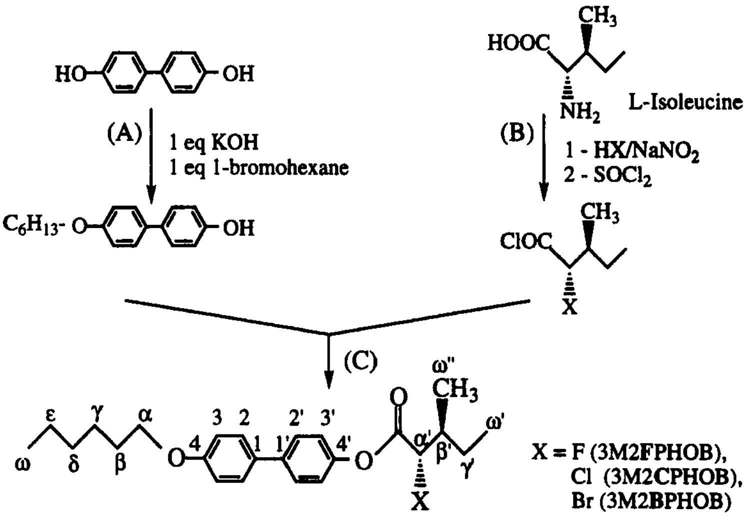
ferroelectricity. A similar strong indication is obtained from carbon-13 NMR measurements of C—H segmental ordering in ferroelectric S_C* and racemic mixtures[23] (see part II.C). The NMR measurements give practically identical C—H bond order parameter profiles implying the absence of substantial chiral interactions in the S_C* phase.

B. Prototypical FLC Materials

In order to critically test the ideas in the IPT description of spontaneous polarization, it is necessary to study a class of FLCs which exhibit varying polarizations *P* within a minimally varying mesogen structure. To this end we have focused attention on the series of 4′-((2*S*, 3*S*)-3-methyl-1-halopentanoyloxy)-4-hexyloxybiphenyls. The synthetic scheme for this series of FLCs is outlined in Scheme 1. The α-haloacylchlorides were prepared according to literature methods[24–26] and coupled with 4-hexyloxy-4′-hydroxybiphenyl to obtain the enantiomerically pure α-halo ester compounds[27]. While 3M2CPHOB and 3M2BPHOB have been reported before [28] the synthetic route used is susceptible to racemization. Here we report an alternate route (B in Scheme 1) that circumvents racemization and we use this to prepare 3M2FPHOB which is believed to be a new potential FLC compound.

The thermodynamic properties of the FLCs were analyzed by DSC. The second heating as well as cooling scans were recorded and are shown in Figure 5.

The mesophases were identified by optical microscopy and the phase assignments were made during cooling. For all three compounds a smectic A mesophase with a focal conic texture could be readily recognized. Upon further cooling only the chloro- and bromo derivatives exhibit a S_C*



SCHEME 1

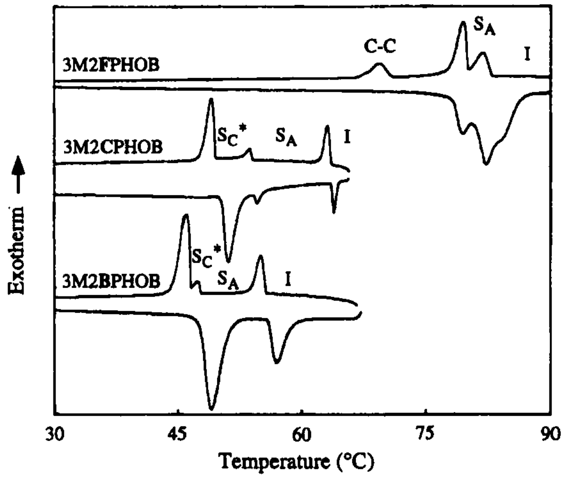


FIGURE 5 DSC Thermograms of 3M2FPHOB, 3M2CPHOB and 3M2BPHOB: second heating and cooling scans.

mesophase (which appears as a broken focal conic texture). M. Ozaki *et al.* [28] have reported the values of *P* for the Cl-dervative; we are attempting to determine *P* for the Br-and F-derivatives.

C. C—H Bond Order Parameters *via* NMR

In order to facilitate a test of the IPT description of spontaneous polarization we have improved a method for extracting local bond orientational order parameters from NMR studies of FLCs in the S_C* phase. The C—H bond orientational ordering in FLCs can be studied without labeling the mesogen from the carbon-proton dipolar couplings with a technique known as carbon-13 separated local field (SLF) spectroscopy[23]. The goal of our study is to obtain C—H order parameter in the chiral tail of FLC, the site that is identified with the magnitude of the spontaneous polarization. Since the proton-proton dipolar splittings are quite large, very high decoupling power is required to remove proton-proton dipolar couplings in order to obtain first order spectra. By using off-magic-angle spinning technique, all of the dipolar couplings are reduced by a factor of $(3\cos^2\theta-1)/2$, where θ is the angle between the spinning axis and the magnetic field. This reduction occurs because the mesophase director – the axis about which the dipolar interaction are partially averaged – is aligned along the spinning axis if the spinning rate is fact enough to overcome the torque for liquid crystals with positive magnetic susceptibility. Therefore, for θ-values close to but less than 54.7° only moderate decoupling power is required to remove the proton-proton dipolar couplings using a homonuclear dipolar decoupling sequence. This lower decoupler power also facilitates temperature stability.

The alignment of the S_A phase of 3M2CPHOB with the director along the spinning axis can be accomplished by slow cooling from isotropic phase at about a 200 Hz spinning rate. For the S_C* phase, experiments showed that the supramolecular helix of 3M2CPHOB does not form in the magnetic field using a 1 kHz spinning rate and cooling slowly from S_A phase. Therefore, high resolution carbon-13 spectra can be acquired for 3M2CPHOB in both the S_A and S_C* phases.

The SLF spectra consist of carbon-13 chemical shifts on the ω_2 dimension and carbon-proton dipolar splittings on the ω_1 dimension. From the values of the carbon-proton splittings ($\Delta\nu$), the dipolar coupling constants (D) can be calculated by the equation, $\Delta\nu = f[(3\cos^2\theta - 1)D + J]$, where f ($=0.42$ for the BLEW-48 homonuclear dipolar decoupling sequence) is a scaling factor characteristic of the dipolar decoupling sequnce and J is the C—H scalar coupling constant.

The biphenyl moiety of the FLC molecule has effective D_2 symmetry, and therefore, the dipolar coupling constant for each C—H pair is given by

$$D_{\mathrm{CH}} = -\frac{\gamma_C\gamma_H h}{8\pi^2 r_{\mathrm{CH}}^3}[(3\cos^2\theta_{\mathrm{CHZ}} - 1)S_{zz} + (\cos^2\theta_{\mathrm{CHX}} - \cos^2\theta_{\mathrm{CHY}})(S_{xx} - S_{yy})]$$

where r_{CH} is the internuclear distance and $\theta_{\mathrm{CH}\alpha}$ is the angle between r_{CH} and the molecular α-axis fixed to the mesogen core. γ_C and γ_H are magnetogyric ratios and h is Planck's constant. The order parameter of the biphenyl core of the molecule (S_{zz}, $S_{xx}-S_{yy}$) can be obtained by least-squares calculation optimization of experimental and calculated carbon-proton dipolar coupling constants on the rings by varying the biphenyl geometry.

The aliphatic chains are quite flexible and it is not easy to interpret measures of the D_{CH} values in terms of local orientational ordering preferences. However, one can readily obtain the C—H bond order parameters for each CH, CH_2, and axially symmetrical CH_3 groups using the SLF technique and

$$S_{CH} = -\frac{4\pi^2 r^3 D_{CH}}{\gamma_C \gamma_H h} = -4.407 \times 10^{-5} D_{CH}$$

where $r = 0.110\,\mathrm{nm}$.

The pulse sequence we employ is shown in Figure 6. Spectra showing clearly resolved C—H dipolar couplings in both alkyl chains of the FLC (Fig. 7). Subtle changes in the S_{CH} are apparent as one goes from the S_C^* to the S_A phase of 3M2CPHOB.

3. CONCLUSIONS

A direct experimental proof of the indigenous polarity in tilted non-chiral smectics would entail the measurement of a first rank quantity other than polarization. To our knowledge, no such experiments have been attempted in liquid crystals. Consequently, further testing of the theory, at least for the time being, will be based on its ability to correctly interpret and predict experimental results on FLC compounds. In this context it is worth noting that the IPT is capable in very direct and simple terms [10] of accounting for the rather striking sign reversal of polarization observed in certain

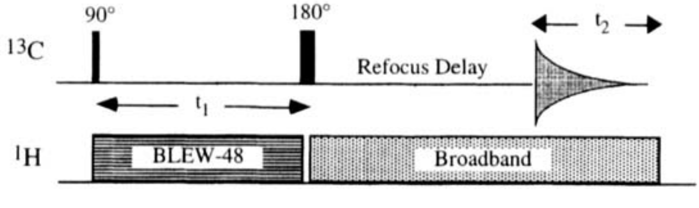


FIGURE 6 Pulse sequence of SLF. During the t_1 evolution period, asynchronous homonuclear dipolar decoupling sequence (BLEW-48) is used so that only carbon-proton coupling is allowed to evolve and carbon-proton dipolar couplings can be determined in ω_1 dimension. Broadband proton decoupling is applied during refocus delay and acquisition to provide sharp carbon-13 spectrum in ω_2 dimension.

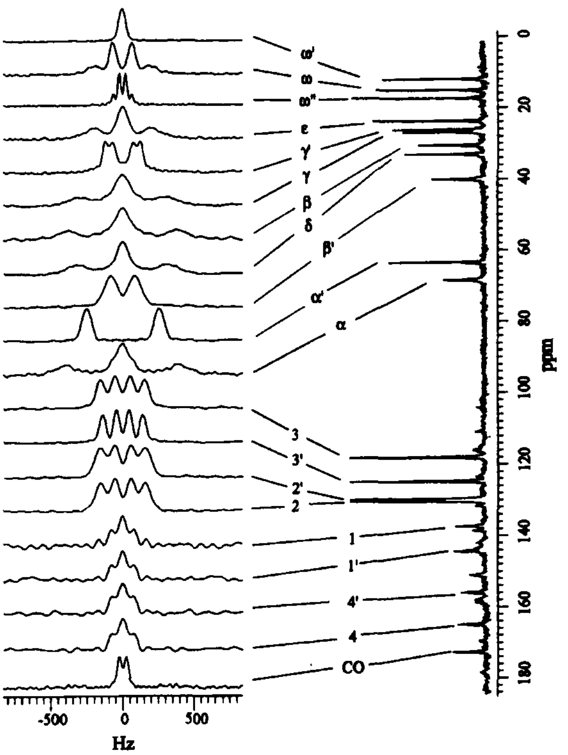


FIGURE 7 SLF spectra of 3M2CPHOB in S_C^* phase. All carbon-13 NMR spectra were obtained by using a Bruker MSL360 spectrometer and a Bruker CP/MAS probe with 7 mm rotor. The angle between the spinning axis and the magnetic field was set to 51.8°. The FLC samples were placed inside a 5 mm glass insert sealed with Kel-F end-caps. The 90° pulse width for proton decoupler was 13 μs, $\gamma B_1/2\pi = 19$ kHz. A less than 1% duty cycle (percent on time of the proton decoupler) was used to minimize the effect of radiofrequency heating. The spectra in S_C^* phase were taken at 2 K below the $S_A - S_C^*$ transition. The carbon-13 spectra with broadband proton decoupling are shown on the right and the carbon-proton dipolar splittings in the ω_1 dimension of SLF are on the right.

FLCs. Furthermore, quantitative tests of the IPT are being carried out by simultaneous calculations of the spontaneous polarization and of the segmental order parameters as measured by NMR on the class of typical FLCs illustrated in part II.B. Although such calculations involve the treatment of the many structural and conformational complexities encountered in real smectogens, preliminary results obtained for several compounds and over a broad temperature range are quite encouraging. Hence, the extensions of the IPT to more elaborate modeling (e.g., incorporating mesogen isomerizations, energetics, and atomistic details) in conjunction with NMR measurements of local order parameters should provide a general framework for systematically evaluating how molecular structural changes in mesogens will impact the magnitude of the observable ferroelectricity in this technologically important class of materials.

Acknowledgments

It was a privilege to witness Al Saupe's early illustrations of the utility of NMR for interrogating the microscopic features of liquid crystals and his sustained delineation of intrinsically important problems in liquid crystal physics. Al's characteristic low-key style of announcing his discoveries provided a much-needed perspective on these fascinating fluids in an era saturated with hype about their potential applications. This work was supported by NSF grant DMR-9412701.

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