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Molecular Topology of Three Ring Nematogens from ^{13}C-^{1}H Dipolar Couplings

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Molecules in their liquid crystalline phase undergo rotational motion about the long axis of the molecule and the shape adopted by the rotating molecule plays an important role in influencing the mesophase morphology. In this context, obtaining the topology and the relative orientation of the different sub-units are important steps. For studying the liquid crystalline phase, ^{13}C NMR spectroscopy is a convenient method and for certain specifically designed nematogens, the 2-dimensional separated local field (2D-SLF) NMR spectroscopy provides a particularly simple and straight forward means of arriving at the molecular topology. We demonstrate this approach on two three ring based nematogens designed with a phenyl or a thiophene ring at one of the termini. From the ^{13}C-^{1}H dipolar couplings of the terminal carbon obtained using the 2D-SLF NMR technique, the order parameter of the local symmetry axis of the terminal phenyl ring as well as of the long molecular axis could be easily estimated. For the thiophene nematogen, the lack of symmetry of the thiophene moiety necessitates some additional computational steps. The results indicate that the thiophene unit has its local ordering axis oriented away from the long molecular axis by a small angle, consistent with a bent structure expected in view of the thiophene geometry. The experiment also demonstrates the ability of the 2D-SLF NMR to provide high resolution spectra by separation of several overlapped resonances in terms of their ^{13}C-^{1}H dipolar couplings. The results are consistent with a rod-like topology of the core of the investigated mesogens. The investigation demonstrates the potential of the 2D-SLF NMR ^{13}C spectroscopy for obtaining atomistic level information and its utility for topological studies of different mesogens.

Introduction

Molecules exhibiting thermotropic liquid crystalline property are anisometric in nature.[1,2] Depending upon the molecular shape, they are generally classified into calamitics and discotics.[3,4] Calamitics are rod-like in shape while discotics possess disk shape. In recent past, however, many molecular shapes deviating from the above two and displaying a wide range of fascinating mesophases have emerged.[5-8] For instance bent, star, λ, H, and S shaped molecules have been synthesized and their mesophase morphologies are studied.[5-8] These developments emphasize that the molecular topology is a crucial parameter in designing novel mesogens with different properties.[9,10] The orientation or alignment of the topologically different mesogens is dictated by the molecular shape as it rotates about its long axis and the consequent packing requirements.[11] A quantitative measure of the alignment of the molecules in mesophases is the orientational order parameter $S = \frac{1}{2}<(3\cos^2\theta-1)>$, where θ is the angle between the director and the long axis of the molecule and the bracket denotes the thermal average.[12] For mesogens built with rigid rod-like core and flexible terminal chains, the molecular axis is essentially parallel to the core unit, which is also the director axis.[13,14] For instance, Wulf,[15] defined the molecular axis as an axis passing through the centers of phenyl rings for a three ring calamitic mesogen. Goodby[11,16] has suggested that in general, the molecular axis may be identified by considering the space filling models of the molecule and by determining the minimum mass inertia axis through the atomic centres. For non-linear mesogens such as bent core or star mesogens, the director axis and the molecular axis for the side-arms are non-collinear.[17,18] In this scenario, we observe that NMR can provide direct experimental evidence regarding the alignment of the liquid crystal molecules and the order parameter of the long axis of the molecule. Particularly, for mesogens with properly positioned structural moieties, it is possible to get the information from the dipolar couplings measured from the 2D-SLF NMR experiment in a straight forward manner. In recent years, studies on thermotropic liquid crystals employing the 2D-SLF NMR approach are increasingly gaining attention.[19-23] For instance the SLF technique has been applied to study calamitic mesogens,[19,24] columnar liquid crystals,[23,25] H-bonded mesogens,[26-28] ferroelectric liquid crystals[29] and banana mesogens[17] and valuable information derived. Thus in the case of a bent core mesogen the C-H dipolar couplings obtained from the separated local field experiment for the aromatic rings have been used to obtain the local order parameter tensors.[17] Similarly the obtained ^{1}H-^{13}C dipolar couplings in the solid and the columnar phases of the discotic compound 1,2,3,5,6,7-hexaoctyloxy-rufigallol have been interpreted to show that the three nonequivalent aliphatic chains in the compound exhibit vastly different structural and dynamical characteristics.[25] Sets of ^{1}H-^{13}C dipolar couplings have been obtained for the symmetric liquid crystal dimer CB7CB from the 2D NMR experiment which have been used to investigate the origin of the conformational changes that occur in this system when it changes from the achiral nematic to the chiral twist-bend nematic phase.[30] Hence the SLF-2D approach has become a very valuable tool for the study of a variety of liquid crystalline systems. Analogous to studies on membrane proteins,[31] these experiments can provide orientational information, just by an examination of the spectrum. The experiment provides a two-dimensional plot of the chemical shifts versus the ^{13}C-^{1}H dipolar couplings. Both these parameters are very sensitive to the details of alignment and also the molecular topology in terms of how the various individual molecular moieties are organized with respect to a common orienting axis. In several studies of calamitic mesogens where phenyl rings are constituent of the core, the resemblance of the spectral features reflect the similar alignment of the molecules, with the magnitudes of the dipolar couplings providing an estimate of the order parameters.[24,27,28,32] When other structural features are added to this, as for instance, a lateral crown-ether inserted in one of the phenyl rings, the characteristic patterns that establish the position and orientation of the crown-ether are clearly observed.[33] In other examples of different molecular shapes such as thiophene incorporated as a part of the core unit, it is possible to obtain a quick and reliable initial estimate of the alignment from the 2D spectra.[34,35] In this work, we explore using ^{13}C-^{1}H dipolar couplings in the nematic phase to provide ordering and orientational information in specifically designed nematogens. Accordingly, a three ring based mesogen with a phenyl ring at one end has been designed such that the dipolar coupling of the para-carbon of the terminal phenyl ring could be used to assess the orientation and order along the long axis of the molecule. A more exact estimate of the order parameters of the core group is subsequently obtained by taking all the relevant dipolar couplings into consideration. The strategy is also extended to another nematogen with a terminal thiophene ring. In this case, thiophene being a five membered ring, the orientation of thiophene with respect to the long axis needs to be taken into account and the experimentally observed ^{13}C-^{1}H dipolar couplings interpreted accordingly. The obtained order parameter information has been used to visualize the relative orientation of the different sub-units of the core and further discussed in terms of the mesophase properties.

Experimental details

The synthetic details and spectral data of Mesogens I and II are provided in ESI†. ^{1}H and ^{13}C NMR spectra of the mesogens in CDCl$_3$ were obtained on a Bruker AV-III 400 MHz instrument at room temperature using tetramethylsilane (TMS) as an internal standard. The resonance frequencies of ^{1}H and ^{13}C were 400.23 and 100.64 MHz respectively.

The solid-state NMR experiments were performed on a Bruker AV-III 500 MHz NMR spectrometer. The ^{1}H and ^{13}C resonance frequencies were 500.17 and 125.79 MHz, respectively. In all the experiments, the proton 90° pulse width was 4 μs. The spectra in the nematic phase of the samples were recorded using a double resonance static probe-head equipped with a 5 mm horizontal solenoid coil. The ^{13}C spectra were obtained by cross polarization (CP) with a contact time of 2 ms and 62.5 kHz r. f. field strength on both the ^{1}H and ^{13}C channels. SPINAL-64[36] decoupling scheme was applied during the acquisition of carbon signal with a strength of 30 kHz. A total of 148 scans were collected using a relaxation delay of 10 s to avoid sample heating. SAMPI-4[37], a 2D-SLF scheme was employed under static condition to obtain high resolution SLF spectra that resolve ^{13}C-^{1}H heteronuclear dipolar couplings on the basis of ^{13}C chemical shifts. SAMPI-4 pulse sequence is shown in Fig. S1 of ESI†. The application of SAMPI-4 pulse sequence to various liquid crystalline molecules has been demonstrated in earlier work.[24,27,28,32,38] The SAMPI-4 experimental conditions for Mesogen I /Mesogen II were as follows: Contact time τ = 3 ms/2.5 ms, number of data t_1 points 128/148, number of data t_2 points 1518/2048, number of scans 16/16, relaxation delay 15 s/12 s. A shifted sine bell window function was applied to the time domain data, and the spectrum was processed in the phase sensitive mode.

Results and Discussion

Fig. 1 shows the molecular structures of the two rod-like mesogens that are examined in the present work. The core of the mesogens consists of three rings connected by ester and azomethine units. The core ends with a phenyl or a thiophene ring at one of the terminus while the other terminus comprises of a decyloxy chain. The synthesis and the mesophase characteristics of Mesogen II are reported in literature[39] while Mesogen I is a new molecule. Both the mesogens exhibit enantiotropic nematic mesophase as supported by hot-stage optical polarizing microscope (HOPM) (see Figs. S2 and S3 in ESI†) and DSC studies with the transition temperatures between 103°C (TC-N) and 135°C (TN-I) for Mesogen I and 103°C (TC-N) and 122.4°C (TN-I) for Mesogen II. The associated enthalpies measured by DSC are consistent with those nematogens listed in literature.[40]

^{13}C NMR studies of DBPPD

Solution phase

The proton decoupled ^{13}C NMR of Mesogen I and Mesogen II in $CDCl_3$ recorded at room temperature are shown in Figs. 2a and 3a respectively. Corresponding to the three rings and two linking units in the core, 14 lines are expected for each of the mesogen. All these fourteen lines are well resolved in the experimental spectra and are observed with varying intensities in the region 110-166 ppm. For the terminal decyloxy chain, the spectrum showed lines in the range 14-69 ppm. To assign the spectrum, ACD Chemsketch (version 3.0) software is used to iterate the spectrum and the assigned chemical shift values of all the core unit carbons of both the mesogens are listed in Table 1. In the case of Mesogen I, six of the lines with high intensities in the interval of 113-166 ppm are attributed to mrthine carbons of the phenyl rings. For the Mesogen II, four such intense lines are noticed in the same region due to the presence of only two phenyl rings. The quaternary carbons of the core unit of both mesogens appear in the range 120-166 ppm. The characteristic imine carbon is noticed at 160.5 ppm and 153.0 ppm for Mesogens I and II respectively. In the case of the thiophene unit of Mesogen II, the methine carbons (C12-C14) are observed in the range 127-134 ppm and the quaternary (C11) is seen at 142.7 ppm. For the terminal decyloxy chain, the spectra for both the mesogens are very similar. Of the nine lines observed, the one centered at 29.4 ppm is contributed by two methylene carbons. The characteristic oxymethylene is noticed at 68.4 ppm while the terminal methyl is observed at 14.1 ppm. These spectral features are in conformity with the molecular structure depicted in Fig. 1.

Nematic phase

^{13}C NMR spectra in the nematic phase were recorded after heating the samples to the isotropic phase and then cooling to the nematic phase (Mesogen I at 130˚C, Mesogen II at 115˚C) in the magnetic field. The spectra of the Mesogens I and II aligned in the magnetic field are shown in Figs. 2b and 3b respectively. In contrast to solution spectra, the spectra in the nematic phase are spread out due to the alignment of the molecules and the anisotropy of the chemical shifts. Thus signals of the carbons in the core unit observed in the region 110-165 ppm in solution, are observed in the range 130-215 ppm for both mesogens. However, the number of resolved peaks in the nematic phase is lower in contrast to the solution spectrum due to the increased line-width and also due to overlap. The increase in chemical shift values for the carbons of the core unit and a decrease for the terminal decyloxy chain in the nematic phase for both the mesogens in contrast to solution values indicate parallel alignment of the molecules with the magnetic field in the mesophase.[41] The assignment of the spectrum in the nematic phase is carried out by comparing structurally similar molecules and also using the 2D-SLF spectra discussed subsequently. For Mesogen I (Fig. 2b), the spectrum in the range 134-157 ppm shows five peaks among which the peak at 151.3 ppm with a high intensity is attributed to two methine carbons of the phenyl ring. Similarly the peak that appears at 189.1 ppm is also intense and broad and could result from resonances of more than a single carbon. The quaternary carbons of the core unit showed low intensity peaks and are observed in the range 165-210 ppm. Ring-I of both the mesogens resemble the phenyl ring in 4-hexyloxy benzoic acid for which the chemical shift assignment in the nematic phase has been reported earlier.[28] Using this similarity, resonances of carbons C1 to C4 of both the mesogens have been identified. For the assignment of other carbons like the imine carbon and the terminal *C-H* carbon of ring-III, the 2D-SLF spectrum comes in handy. A large ^{13}C-^{1}H dipolar coupling observed for these carbons, help to distinguish them from quaternary carbons, which show a smaller dipolar splitting. For the terminal decyloxy chain, seven peaks can be distinguished in the region 12-64 ppm. For Mesogen II, methine carbons of the phenyl ring showed four peaks in the range 134-157 ppm. The quaternary carbon peaks appear in the range 170-214 ppm. The imine carbon signal can be identified at 184.5 ppm. For the assignment of the thiophene ring carbons, the 2D-SLF data have been utilized as discussed in the next section. Table 1 lists the assigned chemical shift values of all the core unit carbons along with their alignment induced shift (AIS).

Dipolar Couplings and Orientational Order Parameter

The 2D-SLF NMR experiments were carried out in the nematic phase for both the mesogens. Fig. 4a shows the spectrum obtained at 130˚C in nematic phase for Mesogen I in which well resolved contours for the different carbons are observed. In 1D spectrum in the nematic phase (Fig. 2b) corresponding to the 14 carbons of the core unit, 10 resolved peaks are observed whereas the 2D showed 12 well resolved contours. The remarkable feature of the spectrum is the clear separation of the three sets of contours at 189.1 ppm (marked in red color) that indicates that three carbons were overlapped in the 1D spectrum at this chemical shift. The corresponding 1D cross-section of the spectrum along the dipolar axis (Fig. 4b) highlights the three well resolved peaks. From the position of the lines and the magnitudes of the dipolar couplings, the assignment of the peaks has been done as follows. The imine carbon (C10) has a characteristic chemical shift range that overlaps with quaternary carbons in the core. It also has a dipolar coupling whose magnitude is typically in the range of 3 to 5 kHz depending upon the order parameter of the system.[24,27,32,42] Hence the contours that appear at a dipolar coupling value of 3.25 kHz are assigned to C10. Similarly the smaller dipolar coupling corresponds to a quaternary carbon which has only a long range coupling to protons and is assigned to the C11 carbon. The observation of contours with a very large dipolar coupling of 11.41 kHz is very unusual and to the best of our knowledge this is the first observation of such a large dipolar coupling in a calamitic mesogens constructed with phenyl rings. These peaks are assigned to C14 carbon at the para position of the third phenyl ring based on the following considerations. All carbons along the para axis of the phenyl rings have their shielding tensor with the highest shielding direction parallel to the para axis.[43] This result in large AIS for them due to the alignment with the magnetic field of the long axis of the molecule that is nearly parallel to the para axes. Thus the methine carbon (C14) at the para position of the terminal phenyl ring is expected to have large AIS. This also means that the *C-H* vector of the C14 carbon will be essentially parallel to the magnetic field and show a large dipolar coupling. Hence the third set of contours that appear at 189.1 ppm with a large dipolar coupling of 11.41 kHz is attributed to this carbon. Thus this carbon provides a remarkably large dipolar coupling very different from all the other phenyl ring carbons (which are typically of the order of 2 kHz), due to its unique location at the terminus of the core of the molecule. It has been observed in several studies of liquid crystals in their nematic and smectic-A phases that the para axis of the phenyl ring with the largest order parameter is very close to the long molecular axis along which the molecule orients in the magnetic field.[44] Based on this, in the present case, the large dipolar coupling of the para carbon of the terminal phenyl ring may be expected provide the order parameter S of the long axis of the molecule, which can be calculated from $D_{Exp}=D_{Rigid}*S$. Here D_{Exp} is the experimentally observed motionally averaged dipolar coupling between proton and carbon and D_{Rigid} is the rigid lattice value taken to be 22.68 kHz for an assumed distance of 1.1 Å between them. From this relation, a value of 0.5 is obtained for S. It will be interesting to examine how this value compares with a more detailed estimate of the order parameters obtained from utilizing the dipolar couplings of all the carbons in the core unit.

The local order parameters S'_{zz} and $(S'_{xx}–S'_{yy})$ of the phenyl rings of the core unit are determined from the experimental dipolar oscillation frequencies obtained from the SAMPI-4 experiment, by following the established methods reported earlier.[17,24,27,28,32,42,45] The dipolar oscillation frequencies can be related directly to the dipolar coupling only for an isolated *C-H* pair. However, in the case of the methine carbons of the phenyl ring, the experimental dipolar frequency has two components namely, the coupling to the attached proton at the *ipso* position $D_{C\text{-}Hi}$ and also a coupling to the nearby non-bonded proton at the *ortho* position $D_{C\text{-}Ho}$. The final measured dipolar frequency expressed as $f=\sqrt{[(D_{C\text{-}Hi})^2+(D_{C\text{-}Ho})^2]}$. Since the non-protonated quaternary carbons experience couplings to two equivalent protons at the *ortho* positions, the dipolar frequency will be $f=\sqrt{2}*(D_{C\text{-}Ho})$. Similarly for C14 methine carbon of Mesogen I, final measured dipolar frequency can be expressed as $f=\sqrt{[(D_{C14\text{-}H14})^2+2(D_{C14\text{-}H13})^2]}$ where $D_{C14\text{-}H14}$ is coupling between C14 methine carbon and its attached proton and $D_{C14\text{-}H13}$ is coupling of C14 carbon to its two equivalent non-bonded protons at the *ortho* positions. Since the phenyl rings undergo π flip about the para-axis, the D_2 symmetry is assumed for the phenyl ring. The local order parameters namely, S'_{zz} and $(S'_{xx}–S'_{yy})$ relevant to such a case can be calculated from dipolar coupling by using the following equation[46]

$$D_{C\text{-}H}=K\{½(3\cos^2\theta_z-1)S'_{zz}+½(\cos^2\theta_x-\cos^2\theta_y)(S'_{xx}–S'_{yy})\} \tag{1}$$

where $K=-h\gamma_H\gamma_C/4\pi^2r^3_{CH}$, with γ_H and γ_C are the gyromagnetic ratios of protons and carbons respectively, r_{CH} is the distance between the proton and carbon nuclei and θ_x , θ_y and θ_z are angles between r_{CH} dipolar vector and the coordinate axes. For the phenyl rings, the C_2 axis is taken as *z*-axis while *x*-axis is the in-plane axis perpendicular to *z*. In equation (1), standard bond distances, namely 1.1 Å for the *C–H* bond and 1.4 Å for the *C–C* bond, are taken for calculating *K*. Owing to the uncertainty involved in the position of the *H* atom as determined by X-rays, the two *C–C–H* bond angles are slightly varied around 120° (assumed for an ideal hexagonal geometry) during fitting.[47] The S'_{zz} and $(S'_{xx}–S'_{yy})$ for the phenyl rings of the core are listed in Table 2.

It is noticed from Table 2 that the order parameters S'_{zz} along the respective para-axes of the three rings are nearly the same and also that the biaxial contribution $(S'_{xx}–S'_{yy})$ is about an order of magnitude smaller. This could be taken to indicate an uniaxial ordering of the mesogens with the director essentially parallel to the para axes of the benzene rings. The maximum value of 0.5 observed for the ring-III could be approximated to be the overall uniaxial order parameter of the mesogen. It may be noted that an estimate of the order parameter of the long axis of the molecule was made earlier with just only the dipolar coupling of the C-14 carbon and a value of 0.5 was obtained for S. It is now noticed that the same value is obtained, albeit with some approximations, from a detailed consideration of individual dipolar couplings of all the carbons in the core unit. Thus the presence of the terminal methine carbon greatly facilitates a quick and staright forward estimation of the order parameter. This advantage is not available in the case of other known calamitic liquid crystals where both the ends of are generally decorated with either alkyl/alkoxy chains or polar substituents.[48-51] However, in these cases detailed calculations as indicated above can be used to obtain all the relevant order parameters.

For the case of Mesogen II, thiophene replaces benzene as the third ring. Thiophene has an irregular pentagonal geometry in contrast to the symmetrical hexagonal shape of the phenyl ring. Consequently, it orients differently compared to benzene, which is reflected clearly in the 2D-SLF spectrum shown in Fig. 5 where the thiophene contours are marked in red color. Thus, while the chemical shift range somewhat overlaps with the methine carbons of benzene, the dipolar couplings of all the *C-H* carbons of thiophene are distinct. Quite interestingly, the values differ from those carbons of not only of the phenyl rings, but also among themselves. The notable feature of the spectrum is the high dipolar couplings of thiophene carbons (4.8-6.3 kHz) in comparison to all the phenyl ring *C-H* carbons of the core unit (~ 2.0 kHz) with the exception of imine carbon (3.70 kHz). These dipolar couplings have valuable information about how the thiophene moiety is oriented with respect to the rest of the molecule. However, the absence of a local symmetry axis makes the estimation of the orientation of thiophene with respect to the long axis of the molecule somewhat complex. The geometry of thiophene has been obtained from DFT calculations of the mesogen which is shown in the Fig. S4 of

ESI†. For the two phenyl rings in the core of the Mesogen II, the local order parameters have been calculated using the procedure outlined earlier for Mesogen I. For arriving at the order parameters of thiophene, a similar approach is employed. However, since thiophene has a lower symmetry than the phenyl rings, three order parameters namely, S'_{zz}, $(S'_{xx}–S'_{yy})$ and S'_{xz} are required for an arbitrary choice of the axis system.[52] Here, we chose the direction parallel to the bond by which thiophene is connected to the rest of the mesogen as the z-axis, with the expectation that the order about this direction is likely to be the largest. Choosing this direction also has the advantage of comparing thiophene order parameters with those of the phenyl rings. On the assumption that the other order parameters are likely to be small, we initiated the fit to only two order parameters namely S'_{zz} and $(S'_{xx}–S'_{yy})$. The angle between the z-axis and the *C-C* bond β is also slightly varied to improve the quality of the fit. At this stage we also added the third order parameter and recalculated the results, but found that the inclusion of the S'_{xz} did not improve the result significantly. The final values of the obtained parameters are listed in Table 2. From the Table 2 it is observed that the major order parameters of the phenyl rings are the same, but that of the thiophene is slightly smaller. This can be interpreted to indicate that while the long molecular axis is essentially parallel to the para axes of the phenyl rings, the local ordering axis of thiophene is slightly tilted away from the long axis. With the assumption of a uniaxial ordering for the molecule and from the ratio of order parameters of the thiophene to the phenyl ring, this angle of tilt has been estimated to be 13˚. It is interesting to note that for a symmetric bent core mesogen with the thiophene as the central unit whose structural details have been reported recently[53], a bending angle of 150˚ between the side arms has been obtained. This corresponds to a tilt angle of 15˚ between the thiophene and any one of the side arms. This compares very well with the value estimated from the present study where the molecule can be considered as a part of the bent-core liquid crystal. In the same study mentioned above, the SLF-2D NMR approach has been applied to a banana mesogen with the phenyl ring as the central unit and a bend angle of 130˚ has been obtained. Thus the methodology compares well with others applied to bent-core and banana mesogens where ^{2}H quadrupole splitting, quantum chemical calculations and ^{13}C chemical shift measurements have been employed to investigate the systems. [17,54-56]

As in the case of Mesogen I with benzene as the terminal unit, we also examined the possibility of using the dipolar couplings of the thiophene methine carbons C12, C13 and C14 for estimating directly the order parameter of the long molecular axis. For this purpose, as before, we used the simple relation $D_{Exp}=D_{Rigid}*S*[(3\cos^{2}\theta–1)/2]$, and the thiophene geometry. We obtained a value 0.5 for the order parameter that is consistent with all the three measurements. To achieve this we needed to tilt the thiophene unit by about 10˚ which is consistent with the tilt angle of 13˚ mentioned above. For multi-functionalised thiophenes that are employed for functional organic materials, the free *C-H* vectors would not be available for accessing the information about orientation through the ^{13}C-^{1}H dipolar couplings. In this context, the Mesogen II can be considered as a model molecule for structurally complex thiophenes used for specific applications.

The atomistic information obtained from the 2D NMR about the orientation of mesogens as well as its sub units can be useful in assessing the molecular shape and its influence on the mesophase charatcteristics. From the molecular structure point of view, similarity exists among Mesogens I and II except at the third ring. Interestingly, both exhibit enantiotropic nematic phase with different tranisition temperatures. Though the T_{C-N} temperatures are same for both the mesogens, considerable variation in the T_{N-I} are noticed. As a result, the mesophase stabilities are different. For instance, the phase stability for Mesogen II is 19.4˚C whereas the same for Mesogen I is 32˚C. Thus the higher thermal as well as phase stabilities for Mesogen-I in contrast to Mesogen II can be rationalised by considering the shape. The Mesogen I is more rod-like than the Mesogen II in which the thiophene is tilted slightly away from the core. This brings a slight bend for the Mesogen II at the terminal position. It may be mentioned that if the molecular anisotropic polarisabilities are taken into account, Mesogen II should show better mesophase or thermal stability due to the presence of polarisable sulphur atom in thiophene. The experimentally observed phase transitions, on the other hand, suggest that the molecular shape is playing a more dominant role than the molecular anisotropic polarisability in influencing phase transitions in these mesogens. This is consistent with the well accepted hypothesis that the rod-like cores organise better than the non-linear cores in the condensed phase owing to better packing which profoundly influences the phase characteristics.

Conclusions

The utility of ^{13}C NMR spectroscopy to provide a means of estimating the orientation of a mesogen as well as its constituent fragments in a straightforward way was investigated. Two three-ring based nematogens designed with a phenyl or a thiophene ring at one of the termini were studied. From the ^{13}C-^{1}H dipolar coupling of the carbon at the para position of the terminal phenyl ring obtained using the 2D-SLF NMR technique, the order parameter of the local symmetry axis of the phenyl ring as well as of the long molecular axis was easily estimated. The results are consistent with a rod-like structure anticipated for the molecule. In the case of the thiophene nematogen, the results indicated that the thiophene unit has its local ordering axis oriented away from the long molecular axis by a small angle. This is consistent with a bent structure expected in view of the thiophene geometry. The investigation demonstrated the potential of ^{13}C NMR spectroscopy for obtaining atomistic level information and its utility for topological studies of mesogens. The experiment also demonstrated the ability of the SLF technique to provide high resolution spectra by separation of several overlapped resonances in terms of their dipolar couplings, greatly facilitating the assignment to get the structure in liquid crystalline phase. The results obtained on the topology of the two different mesogens could be rationalized in terms of their mesophase properties.

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† Electronic Supplementary Information (ESI) available: It contains Synthetic details, Figure of SAMPI-4 pulse sequence, OPM pictures, Thiophene model from DFT for calculating order parameter. See DOI: 10.1039/b000000x/

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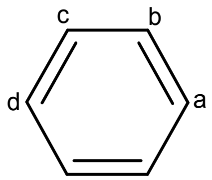
Table 1: ^{13}C NMR data of Mesogens I and II in solution and liquid crystalline phase.

C. No	Mesogen I				Mesogen II			
	Solution (ppm)	130˚C			Solution (ppm)	115˚C		
		Chemical Shift (ppm)	AIS (ppm)	Dipolar Oscillation Frequencies (kHz)		Chemical Shift (ppm)	AIS (ppm)	Dipolar Oscillation Frequencies (kHz)
1	163.6	209.7	46.1	1.16	163.5	212.4	48.8	1.15
2	114.4	134.1	19.7	1.96	114.3	133.8	19.4	2.03
3	132.3	155.4	23.1	1.91	132.2	156.2	23.9	2.08
4	121.5	169.6	48.1	1.15	121.5	173.3	51.7	1.19
5	165.1	196.9	31.8	0.67	165.0	197.7	32.7	0.78
6	149.3	202.4	53.1	1.19	149.2	204.9	56.0	1.07
7	121.9	139.7	17.8	2.06	121.9	139.8	17.9	2.16
8	122.5	144.0	21.5	1.90	122.4	144.0	21.6	1.97
9	149.6	202.4	52.8	1.19	148.9	212.4	63.1	1.15
10	160.5	189.1	28.6	3.25	153.0	184.5	31.5	3.70
11	136.2	189.1	52.9	1.49	142.7	173.3	30.5	1.34
12	128.9	151.3	22.4	2.00	130.4	156.2	25.8	4.85
13	128.9	151.3	22.4	2.00	127.7	170.2	42.5	5.46
14	131.5	189.1	57.6	11.41	132.3	175.0	42.7	6.24

Table 2: Order parameters of aromatic ring and the corresponding calculated ^{13}C-^{1}H dipolar oscillation frequencies for the Mesogens I and II.[a]



Mesogen	T (˚C)	Ring	Angle		S'_{zz}	$(S'_{xx}-S'_{yy})$	Calculated Dipolar Oscillation Frequencies (kHz)			
			θ_b	θ_c			b	c	a	d
I	130	I	120.7	120.9	0.48	0.059	1.96	1.92	1.14	1.15
		II	120.4	121.2	0.49	0.060	2.07	1.89	1.16	1.17
		III	119.9	120.7	0.50	0.035	2.06	2.02	1.57	11.4
II	115	I	120.5	120.3	0.50	0.053	2.03	2.08	1.17	1.16
		II	119.8	120.6	0.50	0.049	2.16	1.98	1.15	1.16
		Thiophene	β		S'_{zz}	$(S'_{xx}-S'_{yy})$	C11	C12	C13	C14
			9.6		0.46	0.001	-	4.86	5.47	6.25

[a] In the figure above the table, *b* and *c* are methine carbons, *a* and *d* are quaternary carbons respectively for ring-I and II whereas for ring-III of Mesogen I *b, c and d* are methine carbons and *a* is quaternary carbon.

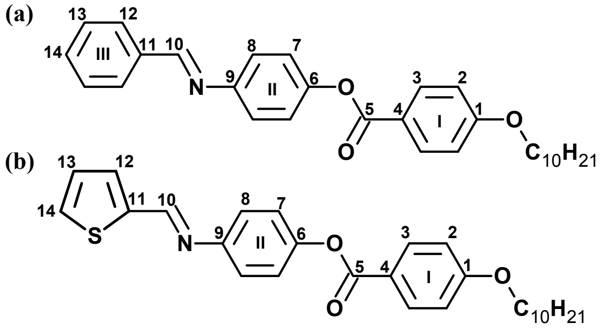


Figure 1: Molecular structure of (a) Mesogen I and (b) Mesogen II

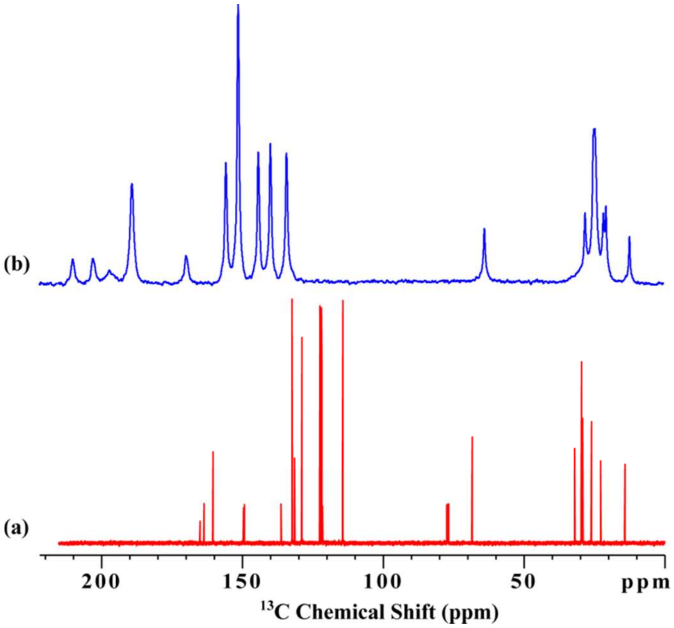


Figure 2: (a) Proton-decoupled ^{13}C NMR spectrum of the Mesogen I in solution. (b) ^{13}C spectrum of the static oriented sample of the Mesogen I at 130°C in the nematic phase.

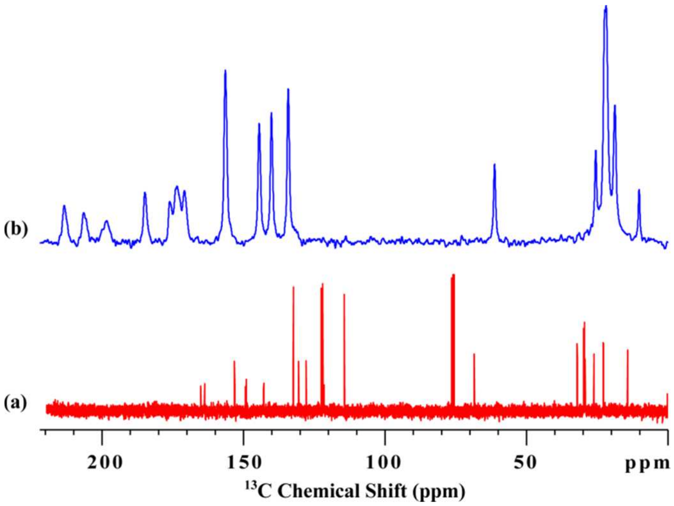


Figure 3: (a) Proton-decoupled ^{13}C NMR spectrum of the Mesogen II in solution. (b) ^{13}C spectrum of the static oriented sample of the Mesogen II at 115°C in the nematic phase.

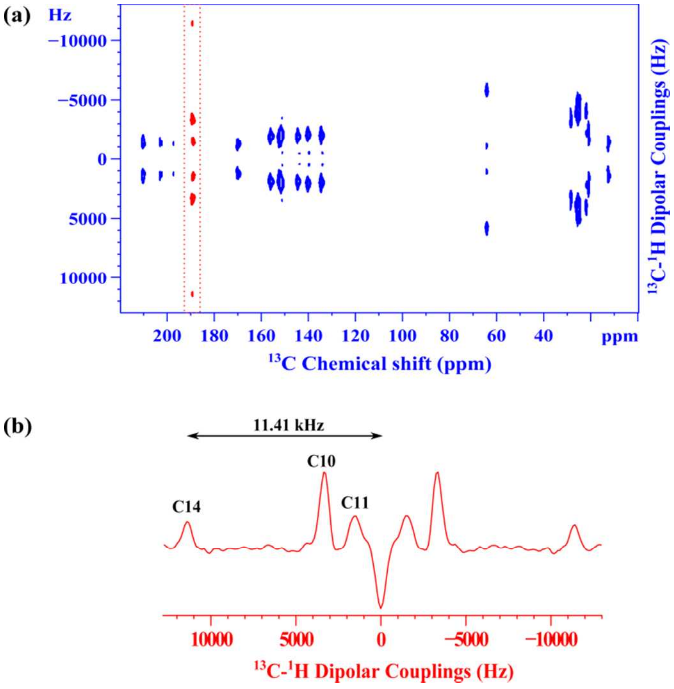


Figure 4: (a) 2D SAMPI-4 spectrum of the Mesogen I at 130°C. (b) ^{13}C-^{1}H dipolar coupling slice at 189.1 ppm (marked red color inside dotted rectangle box) shows dipolar coupling triplets for C11-H (inner; 1.49 kHz) of ring-III, C10-H (middle; 3.25 kHz) of azomethine and C14-H (outer; 11.41 kHz) of ring-III.

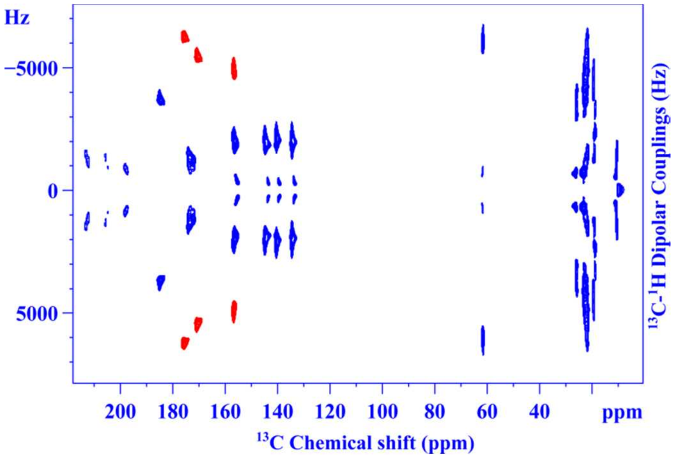
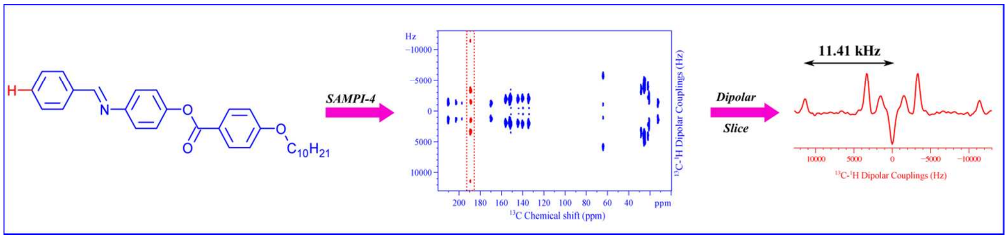


Figure 5: 2D SAMPI-4 spectrum of the Mesogen II at 115°C. Thiophene contours are marked in red color for clear distinction.



Facile way of finding order parameter as well as orienting axis by 13C-1H dipolar couplings for three ring based nematogen with a terminal C-H vector.
135x31mm (300 x 300 DPI)