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Assignment of the ^{13}C NMR Spectrum by Correlation to Dipolar Coupled Proton-Pairs and Estimation of Order Parameters of a Thiophene Based of a Liquid Crystal

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Abstract:

Materials with widely varying molecular topologies and exhibiting liquid crystalline properties have attracted considerable attention in recent years. ^{13}C NMR spectroscopy is a convenient method for studying such novel systems. In this approach the assignment of the spectrum is the first step which is a non-trivial problem. Towards this end, we propose here a method that enables the carbon skeleton of the different sub-units of the molecule to be traced unambiguously. The proposed method uses a heteronuclear correlation experiment to detect pairs of nearby carbons with attached protons in the liquid crystalline core through correlation of the carbon chemical shifts to the double-quantum coherences of protons generated through the dipolar coupling between them. Supplemented by experiments that identify non-protonated carbons, the method leads to a complete assignment of the spectrum. We initially apply this method for assigning the ^{13}C spectrum of the liquid crystal 4-n-pentyl-4'-cyanobiphenyl oriented in the magnetic field. We then utilize the method to assign the aromatic carbon signals of a thiophene based liquid crystal thereby enabling the local order-parameters of the molecule to be estimated and the mutual orientation of the different sub-units to be obtained.

Keywords: Proton DQ-Correlation, Liquid crystals, ^{13}C NMR spectroscopy, Spectral assignment, Chemical shifts, Order parameters

Introduction

The study of partially ordered systems such as liquid crystals has been of significant interest over past several decades, not only due to their technological importance, but also due to a desire to understand their behaviour at the fundamental level in terms of the molecular organisation and dynamics. A significant part of such studies were on thermotropic liquid crystals, which in the early stages of the development of the field, were classified essentially as rod-like or disc-like[1-4]. The design of these molecules was also well established. For example, the rod-like molecules typically consisted of a rigid-core and a flexible terminal chain in one or both the ends[5-8]. In recent years, however, this concept has changed and many systems having different shapes such as bent core, star, λ, H, and S have also been shown to exhibit the liquid crystalline properly[9-11]. In this approach, in addition to phenyl rings other structural motifs such as thiophene are also being exploited[12-19]. Thiophene is a five membered ring and is one of the important groups extensively used in functional organic materials. The importance of thiophene arises from its ability to undergo a wide range of chemical reactions. Both low molecular weight oligomers and high molecular weight polymers based on thiophene are used in many niche research areas like organic LED's, plastic electronics, solar cells and so on[20].

With the advent of many new systems, it is also necessary to characterise these molecules in terms of their structure, mobility and molecular organisation. Of the many techniques available for this, NMR has been shown to be capable of providing detailed information with atomistic resolution[21-23]. Deuterium NMR spectroscopy is a powerful technique for obtaining the molecular dynamics and order of mesogens[24-26]. However, it requires uniform/selective deuterium labeling of the sample. It has been shown in recent years that natural abundance ^{13}C NMR technique is a useful alternative capable of providing extensive information about the mesophase[19, 27-29]. With ^{13}C NMR spectroscopy, two NMR parameters are available for characterising the liquid crystals namely, the alignment induced ^{13}C chemical shift (AIS) and the ^{13}C-^{1}H dipolar couplings, the latter parameter obtained by employing the separated local field (SLF) 2D NMR technique[30-35]. In all the above cases, the first important step is the assignment of the ^{13}C spectrum which is crucial. For assignment of a spectrum in the solution state, a plethora of techniques are available[36, 37]. But in the case of solids and partially ordered systems, the problem of assignment of the ^{13}C spectrum is much more acute due to the dominance of the homo-and the hetero- nuclear dipolar couplings. In the case of solids, several spectral editing techniques[38-40] as well as 2D correlation experiments[41-44] for assigning the carbon spectrum have been developed over a period of time. In contrast, for magnetic field oriented liquid crystalline molecules, the assignment of the spectrum remains a major problem. This is because the magnetic field induced shift in the oriented phase is dependent on the components of both the anisotropic chemical shielding tensor σ and the order parameter tensor S. Thus, the chemical shift in the liquid crystalline phase is given by [45],

$$\delta_{LC} = \delta_{iso} + 2/3\, S_{aa} [\sigma_{aa} - ½ (\sigma_{bb} + \sigma_{cc})] + 1/3 (S_{bb} - S_{cc})(\sigma_{bb} - \sigma_{cc}) + 2/3(S_{ab}\sigma_{ab} + S_{bc}\sigma_{bc} + S_{ac}\sigma_{ac}) \qquad \text{...... (1)}$$

where δ_{LC} and δ_{iso} are the chemical shifts respectively in the liquid crystalline and isotropic phases and $\sigma_{\alpha\beta}$ and $S_{\alpha\beta}$ are components respectively of the chemical shift and the order parameter tensors in the molecular coordinate system (a,b,c). The order parameters in the liquid crystalline phase depend on the particulars of the construction of the mesogenic molecule and other external parameters such as the temperature. The order parameters are highly variable and so also are the positions of the resonance lines in the spectrum. Progress in the utilization of the ^{13}C spectra so far has been based essentially on assignments arising out of systematic comparison of data of different liquid crystals coupled with chemical reasoning and intuition. There have been earlier efforts to provide solution to the problem of assignment. These include recording the spectrum of the liquid crystal as a mixture with another liquid crystal of opposite diamagnetic susceptibility at the critical temperature[46] and the use of off-magic angle spinning[47]. These experiments however require additional efforts in terms of either sample preparation or extra accessories. In this article, we present a new approach which is a robust assignment strategy for the ^{13}C spectrum of the oriented liquid crystalline molecule. We propose a proton double-quantum coherence (DQC) – carbon single-quantum coherence (SQC) correlation experiment wherein the proximity of protons attached to neighbouring carbons is utilized as a means of identifying these carbons. The proton DQ coherence is generated through the dipolar coupling between the protons using two $\pi/2$ pulses with a delay between them[48,49]. The evolved coherence is monitored in a 2D experiment by monitoring the ^{13}C signal generated by a ^{1}H - ^{13}C cross-polarization sequence. Similar approaches adapted for solid samples under magic angle spinning conditions have been proposed recently for obtaining accurate proton chemical shifts and for structure elucidation[41,44]. In the 2D spectrum, for a pair of coupled protons, cross-peaks appear at the sum of their of resonance frequencies. Thus the presence of the double-quantum peaks indicates proximity between two protons. For protons that are located on next neighbor carbons, cross-peaks of identical DQ frequencies appear along the cross-sections of each one of the two carbon resonances. Herein lies the advantage of the approach for spectral assignment. By identifying pairs of contours that have the same frequencies in the proton dimension, one can walk through a network of such coupled protons, thereby identifying the corresponding carbon skeleton leading to the assignment of the spectrum. Since resonance frequencies of two protons get added, the use of DQ coherence in general leads to higher resolution than that available with the use of single quantum coherence (SQC) evolution. The disadvantage of the use of DQC however is that the efficiency of DQ excitation and reconversion is variable and depends on the coupling strength between protons versus the excitation/reconversion period. Additionally multiple quantum coherences have in general shorter transverse relaxation times and dephase faster compared to single quantum coherences.

The usefulness of the experiment proposed here is initially demonstrated for the liquid crystal 4-n-pentyl-4'-cyanobiphenyl (5CB). Subsequently it is applied to the problem of assignment of resonances of a novel thiophene based liquid crystal. The obtained chemical shifts are then used for estimating the order parameters of the different segments of the liquid crystalline molecule and to estimate the bent angle between the phenyl and the thiophene moieties.

Experimental:

The sample of 5CB was purchased from Sigma Aldrich and was used without further purification. A novel thiophene based liquid crystalline sample of *4-{[(4-Deccyloxyphenyl) Carbonyl] Oxy} Phenyl Thiphene-2-Carboxylate (*2-DCPTC*)* was kindly provided by Dr. T. Narasimhaswamy. The NMR experiments were performed in the nematic phases of these samples at a field of 500.18 MHz on a Bruker Avance – III 500 solids NMR spectrometer using a 4mm triple resonance STMAS probe under static conditions. For obtaining individual proton chemical shifts, single quantum ^{1}H-^{13}C HETCOR[50] experiment was carried out on the static sample. Two dimensional ^{1}H double quantum -^{13}C single quantum correlation spectra were obtained with the pulse sequence shown in figure 1. Following the first two 90^0 pulses with a delay τ between them, multiple quantum proton coherences are generated[49,50]. The selection of the double quantum coherence during the t_1 period was accomplished by using appropriate phase cycling[51]. In the oriented phase of the liquid crystal, strong proton homo-nuclear dipolar interactions are present. Therefore, to allow evolution only under chemical shifts of protons, the FSLG[52] homonuclear dipolar decoupling sequence was employed. A180^0 pulse applied at the middle of the t_1 period on the carbon nuclei refocuses the heteronuclear dipolar couplings. The third 90^0 proton pulse followed by the τ period converts the evolved DQ magnetization to in-phase SQ coherence. A short cross polarization (CP) period transfers the proton magnetization to carbons which are observed during the detection period t_2 under heteronuclear the dipolar decoupling sequence SPINAL-64[53]**.** A 2D matrix s (t_1, t_2) is generated that correlates proton double quantum frequencies in the t_1 dimension and anisotropic carbon chemical shifts in the t_2 dimension. The FSLG decoupling was carried out with a basic cycle of duration of 26.12μs and with an r.f field amplitude of 62.5 kHz. The flip pulse of angle 54.7^0 applied before and after the $t_1$period served to increase the sensitivity of the experiment. The t_1 increment was set to 104.48 μs corresponding to four basic FSLG cycles. For the SPINAL-64 heteronuclear decoupling during t_2 period an r.f field of 33.3 kHz was used. R.F. field strength of 62.5 kHz was applied for all other proton and carbons pulses. The duration τ for double quantum excitation was optimized by measuring the ^{13}C signal intensity of aromatic carbons in several experiments with different τ values and was set to 38 μsec. The ramped cross polarization contact time was kept short to ensure transfer of magnetization from protons to the directly attached carbons. Spectra were acquired in the States-TPPI method[54]. For the carbon dimension, the adamantane methylene peak at 29.5 ppm was used as the chemical shift reference while for the proton dimension the water proton peak at 4.7 ppm was used as the external chemical shift reference. Other experimental details are given in the respective figure captions. It is noticed that the DQ-SQ correlation experiment takes almost twice longer than the HETCOR experiment. This is the result of factors that affect DQ excitation efficiency such as the variation in the value of the dipolar coupling between protons at different segments of the molecule and the effect of strong couplings to other protons. Further, shorter transverse relaxation times of multiple quantum coherences also contribute to the loss of intensity and a reduction in signal to noise.

Results & Discussion:

The experiment was initially carried out on the liquid crystal 5CB. The structure of 5CB and its 1D ^{13}C spectrum recorded at the room temperature are shown in the figure 2A.The assignment of the spectrum[55] is also shown in the figure. In the spectrum, the aliphatic and the aromatic peaks are clearly separated out. In the aromatic part, carbons with attached proton are distinguished from the quarternary carbons due to their higher intensity, each peak being the result of signals from two equivalent carbons due to the symmetry of the phenyl rings about the para axis. However, between the methine carbon peaks as well as between the quarternary carbon peaks, the assignment is essentially based on the molecular structure. In the aliphatic part, the methyl peak stands out at around 11 ppm, but the assignment of the rest of the peaks is not straight forward. The problem of assignment is mitigated to some extent in the 2D ^{1}H-^{13}C HETCOR spectrum (Figure 2B). Here all the aromatic methine carbons are again identified based on the cross-peaks observed in the proton dimension. The diasteriotropic α protons are observed to have different chemical shifts and these peaks are identified in the proton dimension because of the larger chemical shift of these protons due to their proximity to the phenyl rings. The proton chemical shifts obtained from this spectrum along with the corresponding carbon chemical shifts are listed in Table 1. Additional crucial information regarding assignment, particularly for the aromatic part comes from the ^{1}H (DQ) – ^{13}C (SQ) correlation spectrum shown in Figure 2C obtained using the pulse sequence shown in figure 1. In the spectrum, the contours along the proton dimension appear at the sum of chemical shifts for two dipolar coupled protons. The following proton double quantum correlation peaks can be identified. Two contours are observed along the C_{ω} carbon at 1.80 ppm and 2.50 ppm. The peak at 1.80 ppm arises from correlation between the C_{ω} methyl proton with another proton of the same methyl group and is confirmed from the SQ proton chemical shift of 0.9 ppm listed in table 1.The peak at 2.50 ppm arises from correlation of C_{ω} and C_{δ} protons and occurs at the sum of the two individual chemical shifts (vide table 1). In the case of C_{δ} carbon, two peaks at 2.5 ppm and 3.2 ppm are expected. Of these, the peak at 3.2 ppm that is observed in the 2D spectrum, corresponds to a correlation between a C_{δ} proton with another proton of the same group, i.e., C_{δ} – C_{δ} correlation and is confirmed from the SQ proton chemical shifts of 1.6 ppm. The peak expected at 2.5 ppm corresponds to C_{δ} – C_{ω} proton correlation as discussed above for the case of C_{ω} carbon. It is not visible in the 2D spectrum, but can be observed as a weak peak on a slice extracted (not shown) along the C_{δ} carbon chemical shift. It has been observed that DQ coherences involving methylene protons provide weak peaks and are sometimes not observable due to short T_2' of these coherences in spite of employing homonuclear decoupling.[41] Further it is likely that the relative freedom for rotation about the C-C bond averages the inter-group dipolar couplings to a small value requiring a longer DQ excitation period τ. The chemical shifts of β, γ and δ protons are the same as seen in the HETCOR spectrum (Table 1). Correspondingly the intra-group DQ correlation peaks among protons at the β and at the γ carbon sites also occurs at 3.2 ppm as in the case of δ protons. For the same reason, the inter-group correlation (i.e. C_δ – C_γ, and the C_γ – C_β) peaks also will have the same frequency. For the C_α carbon a contour is observed at 6.0 ppm in the proton dimension which corresponds to the sum of chemical shifts of the diasteriotropic protons listed in table 1. However, the long range inter-group connectivity is not visible in the spectrum.

In the study of liquid crystalline materials, the aromatic core has a crucial role. On the one hand, this part is involved in intermolecular interactions and on the other hand it gives the molecule a shape that results in different classification of liquid crystals such as the calamitics, discotics, bent-core etc. Being relatively rigid, the core is also amenable to detailed quantitative study in terms of local as well global order parameters[2-6]. Hence accurate characterisation of the NMR spectrum is a crucial step in further investigation of the dynamics of the aromatic core. Figure 2C displays the proton double quantum peaks corresponding to aromatic carbons 2, 3 and 2’, 3’ and the corresponding double quantum shifts are listed in table 2. In the figure, for both the C_2 and the C_3 carbons, contours are observed at the same value of 11.7 ppm along the proton dimension, which is very close to the sum of the chemical shifts of the individual protons equal to 11.6 ppm. Similarly for the $C_{2'}$ and the $C_{3'}$ carbons also show contours with identical shifts of 12.7 ppm, equal to the sum of the individual proton chemical shifts. This clearly indicates that the C_2 and the C_3 carbons are in the same phenyl ring while the $C_{2'}$ and the $C_{3'}$ carbons are in the other phenyl ring. To the best of our knowledge, there is no other experiment other than the ^{13}C- ^{13}C INADEQUATE experiment[56, 57] that can give such unambiguous information in samples with ^{13}C in natural abundance.

Using the information obtained from the above experiment as the basis, one may proceed to further assign the spectrum such as the quarternary carbons or distinguish carbons in different molecular segments using other experiments. For example a long contact time HETCOR experiment[50] (Figure 2D) shows cross peaks for the quarternary carbons in a phenyl ring to methine protons on the same ring. Also cross-peaks observed for the C_2 and the C_3 carbons at the α proton chemical shift distinguish the benzene ring close to the aliphatic chain from the ring closer to the cyanide carbon. In the following section we describe the application of the method developed above to assign the carbon resonances in the aromatic part of a novel thiophene based liquid crystal.

The system under investigation is*4-{[(4-Deccyloxyphenyl) Carbonyl] Oxy} Phenyl Thiphene-2-Carboxylate (*2-DCPTC*)*[58]. As shown in figure 3A, this contains in the core unit two benzene rings and a thiophene unit. 2-DCPTC has a nematic range between 98.2 and 117.7 ^{0}C. The ^{13}C spectrum of the compound in its nematic phase recorded at 107^{0}C is displayed in figure 3B. In the aliphatic region most of the carbon peaks are overlapped and for the ten carbons, we can see only six peaks. Of these, the C_α carbon at around 62 ppm and the methyl carbon at around 11 ppm are easily assigned. Similarly, the corresponding proton resonances are also clearly identified in the 2D HETCOR spectrum shown in figure 3C. For reasons mentioned earlier, we restrict our focus in the rest of the discussion to the assignment of the aromatic part of the molecule with peaks appearing between 130 and 210 ppm. For the sake of convenience of the reader, the carbon assignments are already shown in the spectrum, though they were arrived at based on the experiments and results presented below.

In the aromatic region corresponding to 14 non-equivalent carbons, 12 peaks are observed. Of these the methine peaks of the two phenyl rings have contributions from two carbons each and are easily distinguished because of their higher intensities as those appearing at 131.3, 140.4, 140.9 and 152.8 ppm. The three remaining protonated carbon peaks belonging to thiophene are identified from the HETCOR spectrum shown in Figure 3C and they appear at 157.0, 161.5 and 171.8 ppm. The HETCOR spectrum also provides the proton chemical shifts corresponding to all the protonated carbons which are listed in Table 3. Having identified the proton attached carbons, the next crucial step in the assignment of the spectrum is the identification of the carbons belonging to the same structural unit and thereby the carbon skeleton. Towards this purpose, the proposed ^{1}H (DQ)-^{13}C correlation experiment comes handy. The 2D spectrum obtained from this experiment is shown in figure 3E. The inset in the figure shows the expanded aromatic part. The DQ proton shifts obtained from the spectrum are given in Table 4.The experiment is expected to provide the same proton DQ shifts for any two adjacent methine carbons. In the aromatic part of figure 3E, three pairs of high intensity contours having the same shifts along the proton dimension are easily identified. Of these, two pairs of contours identify signals from carbons belonging to the same phenyl ring. Thus contours along the DQ proton dimension at 11.1 ppm are due to carbons belonging to one ring. The corresponding carbon (proton) chemical shifts are 131.3 (5.5) and 152.8 (5.6) ppm. These signals are tentatively assigned to carbons (protons) at positions 2 and 3 in the phenyl ring I. Similarly the contours appearing at 11.6 ppm in the proton DQ dimension are assigned to the two closely spaced carbons (protons) appearing at 140.4 (5.8) and 140.9 (5.8) ppm. These signals are assigned to carbons at positions 7 and 8 in phenyl ring II. Chemically this ring has similar environment on both sides, resulting in nearly identical carbon chemical shifts.

For the thiophene, a pair of contours with high intensity and another pair with low intensity with proton DQ shifts of 13.5 and 13 ppm respectively are observed. Also one of the carbons (at 157.0 ppm) shows a correlation to the other two carbons. This carbon is easily identified as the methine carbon 13 which is at the centre of the CH network in the thiophene ring. The pair of contours of lower intensity could perhaps be attributed to carbons 13 and 14, thereby attributing the signal at 171.8 to carbon 14. The argument for this is that the corresponding ^{1}H - ^{1}H dipolar coupling could be significantly different from those corresponding to other pairs of carbons in the core, due to the different orientation of the H(13) – H(14) dipolar vector with respect to the long molecular axis and hence to the magnetic field. Additionally, carbon 14 is identified from its comparatively large chemical shift due to its proximity to sulphur. The remaining carbon is identified as carbon 12 with the chemical shift of 161.5 ppm.

For the final step of identifying the two phenyl rings in terms of their location in the molecule and for assigning the quarternary carbons, HETCOR experiment (figure 3D) with a long contact time is useful. It is observed from figure 3D that one of the phenyl ring carbons at 131.3 ppm shows a contour with a proton chemical shift corresponding to the α proton at 3.3 ppm, thus identifying the methine carbon 2 of ring I. Weak contours observed at 206.0 and 165.2 ppm have been assigned to quarternary carbons 1 and 4 of ring I from the shift along the proton dimension around 5.5 ppm. The broad peak around 195 ppm has been assigned to four carbons 5, 6, 9 and 10. Finally, the thiophene quarternary carbon at position 11 has been identified as the peak at 159.4 ppm. Some of these quarternary carbon assignments are not definitive, due to the small range of proton chemical shifts and the width of the contours in the proton dimension.

The assigned spectrum and the obtained chemical shifts in the liquid crystalline phase can be utilized to calculate the local order parameters of the different sub-units of the core unit using eq.1. This also provides an indication of the reasonableness of the assignments made. However, to accomplish this, the CSA parameters must be known. For ring I, due to its similarity to hexyloxybenzoic acid[59], the corresponding CSA parameters can be used. For the thiophene ring the CSA parameters have been estimated using a model compound[60]. For the phenyl ring of the mesogen two order parameters, viz. S'_{zz} and $(S'_{xx} - S'_{yy})$ are required to describe the local ordering corresponding to the C_2 symmetry of the ring. For the thiophene ring three order parameters, namely S'_{zz} and $(S'_{xx} - S'_{yy})$ and S'_{xz} are required[61]. From the chemical shifts of carbons 1-4 the values for the phenyl ring I have been obtained as $S'_{zz}= 0.51$and $(S'_{xx} - S'_{yy}) = 0.04$. For thiophene, the three protonated carbon chemical shifts have been used and the order parameters have been obtained as $S'_{zz}= 0.40$, $(S'_{xx} - S'_{yy}) = 0.22$ and $S'_{xz} = 0.004$. These values are in agreement with values obtained by using ^{1}H-^{13}C dipolar couplings for a thiophene liquid crystal with an azomethine connecting unit reported recently[62] and with values obtained generally for nematic liquid crystals[19, 27-33]. With the assumption that the para axes of the phenyl rings are oriented parallel to the director axis, the order parameters of the sub-units can be used to obtain the mutual orientation β of the phenyl and the thiophene sub-units from $S_{z'z'}(thio) \approx S(phe) * P_2(\cos\beta)$.[21] A value of 22^0 is obtained as the tilt angle between the local ordering axes of the thiophene and the phenyl rings. It may be possible to consider the liquid crystal with thiophene as a terminal unit, as one wing of a symmetric bent core mesogen with thiophene at the centre and with phenyl rings on either side. For one such mesogen the structural details have been reported recently[63]. A bent-angle of 150^0 between the side-wings has been observed which corresponds to a tilt angle of 15^0 between the thiophene and one of the side phenyl rings. The slightly smaller value compared to 22^0 observed in the present case may be attributed to a higher rigidity and to steric effects introduced due to the addition of the other bulky side-wing.

Conclusions:

A heteronuclear correlation pulse sequence for correlating double quantum proton frequencies to carbon chemical shifts in the static condition is considered for assigning the ^{13}C spectra of liquid crystalline molecules in their oriented phases. The experiment was utilized to detect selectively pairs of ^{1}H spins and correlate them to their attached carbons and to trace the carbon skeleton of the molecule from the appearance of identical double-quantum frequencies at different carbon sites. The method enabled spectral lines from different segments of the molecules to be assigned unambiguously. Combining with the HETCOR experiment, the utility of the method was demonstrated for assigning a majority of the spectral lines in the ^{13}C spectrum of liquid crystalline molecules oriented in the magnetic field. The method was applied to assign the spectrum of a thiophene based liquid crystal. The assignments were used to extract the alignment induced chemical shifts of different carbons. The order parameters of the different segments were obtained which lead to an understanding of how the thiophene is oriented with respect to the benzene rings. With the aromatic part being the focus of several investigations, the present technique is expected to be of significant use for a number of systems of different structure and topology.

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Table 1: ^{1}H and ^{13}C Chemical Shifts (in ppm) of 5CB

	4	1’	1	4’	3’	3	2’	2	γ	α	β	δ	ω
^{13}C	199.4	198.5	188.0	169.0	158.8	150.3	148.2	146.3	26.3	24.6	23.3	20.1	10.5
^{1}H	---	---	---	---	6.3	5.8	6.3	5.8	1.6	2.5 & 3.4	1.6	1.6	0.9

Table 2: Double Quantum Proton shifts (in ppm) of 5CB

	3’	3	2’	2	γ	α	β	δ	ω
ω	-----	-----	-----	-----	----	----	----	2.50	1.80
δ	----	----	----	-----	3.20	----	----	3.20	2.50
β	----	-----	-----	----	3.20	----	3.20	----	-----
α	----		---		----	6.0	----	----	-----
γ	----	----	----	----	3.20	----	3.20	3.20	-----
2		11.70		-----	-----	----	-----	----	-----
2’	12.70		-----	-----	-----	-----	-----	----	----
3	-----	-----	-----	11.70	-----	-----	-----	-----	----
3’	-----	------	12.70	-----	-----	----	-----	-----	----

Table 3: ^{1}H and ^{13}C Chemical Shifts (in ppm) of 2-DCPTC

Carbon No.	^{13}C (solution state)[@]	^{13}C (nematic phase)	^{1}H (nematic phase)
α	67.1	62.0	3.3
1	163.7	206.0	----
2	114.4	131.3	5.5
3	132.4	152.8	5.6
4	121.3	165.2	----
5	164.9	196.1	----
6	147.9	194.7	----
7	122.8	140.9	5.8
8	122.6	140.4	5.8
9	148.7	195.3	----
10	160.5	196.1	-----
11	132.8	159.4	-----
12	133.7	161.5	6.5
13	128.1	157.0	7.0
14	134.9	171.8	6.0

[@] From ref (58)

Table 4: Double Quantum Proton Shifts (in ppm) of 2-DCPTC

Carbon No.	14	12	13	3	7	8	2
2	---	---	---	11.1	---	---	---
8	---	---	---	---	11.6	---	---
7	---	---	---	---	---	11.6	---
3	---	---	---	---	---	---	11.1
13	13.0	13.5	---	---	---	---	---
12	---	---	13.5	---	---	---	---
14	----	---	13.0	---	---	---	---

Figure Captions:

Figure (1). Pulse scheme for the two-dimensional ^{1}H (DQ) - ^{13}C HETCOR experiment. The coherence transfer path way diagram is given below. The following phase cycle was used ϕ_1 = (8) 0, 0, 4, 4, 0, 0, 4, 4, 2, 2, 6, 6, 2, 2, 6, 6, 4, 4, 0, 0, 4, 4, 0, 0, 6, 6, 2, 2, 6, 6, 2, 2; ϕ_2 = (8) 4, 0, 0, 4, 4, 0, 0, 4, 6, 2, 2, 6, 6, 2, 2, 6, 0, 4, 4, 0, 0, 4, 4, 0, 2, 6, 6, 2, 2, 6, 6, 2; ϕ_3 = 0, 0, 2, 2; ϕ_4 = 0, 1, 2, 3, 1, 0, 3, 2, 2, 3, 0, 1, 3, 2, 1, 0; ϕ_5 = 0; ϕ_6 = 0; ϕ_7 = 1, 0, 1, 0, 0, 1, 0, 1; Receiver = 2, 0, 0, 2, 0, 2, 2, 0, 2, 0, 0, 2, 0, 2, 2, 0.

Figure (2). Spectra of 5CB recorded in its nematic phase at room temperature. (A) Proton decouple ^{13}C spectrum obtained using ^{1}H – ^{13}C cross-polarization. (B) Two- dimensional ^{1}H- ^{13}C HETCOR spectrum. 16 transients were collected for each of the 128 t_1 points with 104.48 μs increment per point and with a recycle delay of 12 s. The CP contact time was 200 μs. Total experimental time was 6.8 h. (C) Two dimensional ^{1}H (DQ)-^{13}C HETCOR spectrum. For each of 128 t_1 slices, 32 scans were coadded with a recycle delay of 12 s. The total experimental time was 13.7 h. (D) Two-dimensional ^{1}H-^{13}C HETCOR spectrum with long CP contact time (1.0 ms). The experimental parameters are same as **(**B**).**

Figure (3). The chemical structure (A) and spectra of 2-DCPTC recorded in its nematic phase at 107^{0}C. (B) Proton decouple ^{13}C spectrum obtained using ^{1}H – ^{13}C cross-polarization. (C) Two- dimensional ^{1}H- ^{13}C HETCOR spectrum. 64 transients were collected for each of the 74 t_1 points with 104.48 μs increment per point and with a recycle delay of 17 s. The CP contact time was 100 μs. Total experimental time was 22.4 h. (D) Aromatic part of the two-dimensional ^{1}H-^{13}C HETCOR spectrum with long CP contact time (1.0ms). 64 transients were collected for each of the 92 t_1 points with 104.48 μs increment per point and with a recycle delay of 20s. Total experimental time was 32.7 h. (E) Two dimensional ^{1}H (DQ)-^{13}C HETCOR spectrum. For each of 55 t_1 slices, 160 scans were coadded with a recycle delay of 20 s. The total experimental time was 48.8 h. Inset shows the expanded aromatic part.

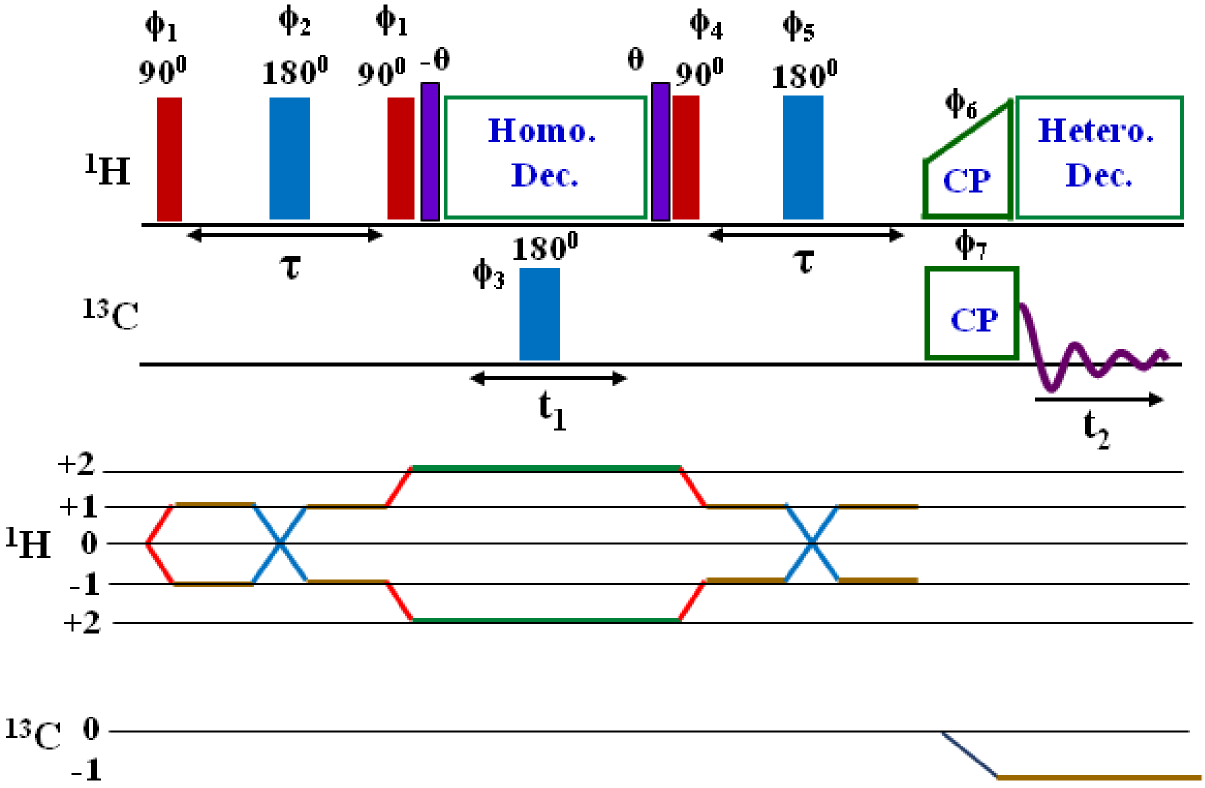
φ1
90⁰
φ2
180⁰
φ1
90⁰
-θ
θ
φ4
90⁰
φ5
180⁰
φ6
¹H
Homo. Dec.
CP
Hetero. Dec.
τ
φ3
180⁰
τ
φ7
¹³C
CP
t1
t2
+2
+1
¹H 0
-1
+2
¹³C 0
-1

Figure (1)

(B)

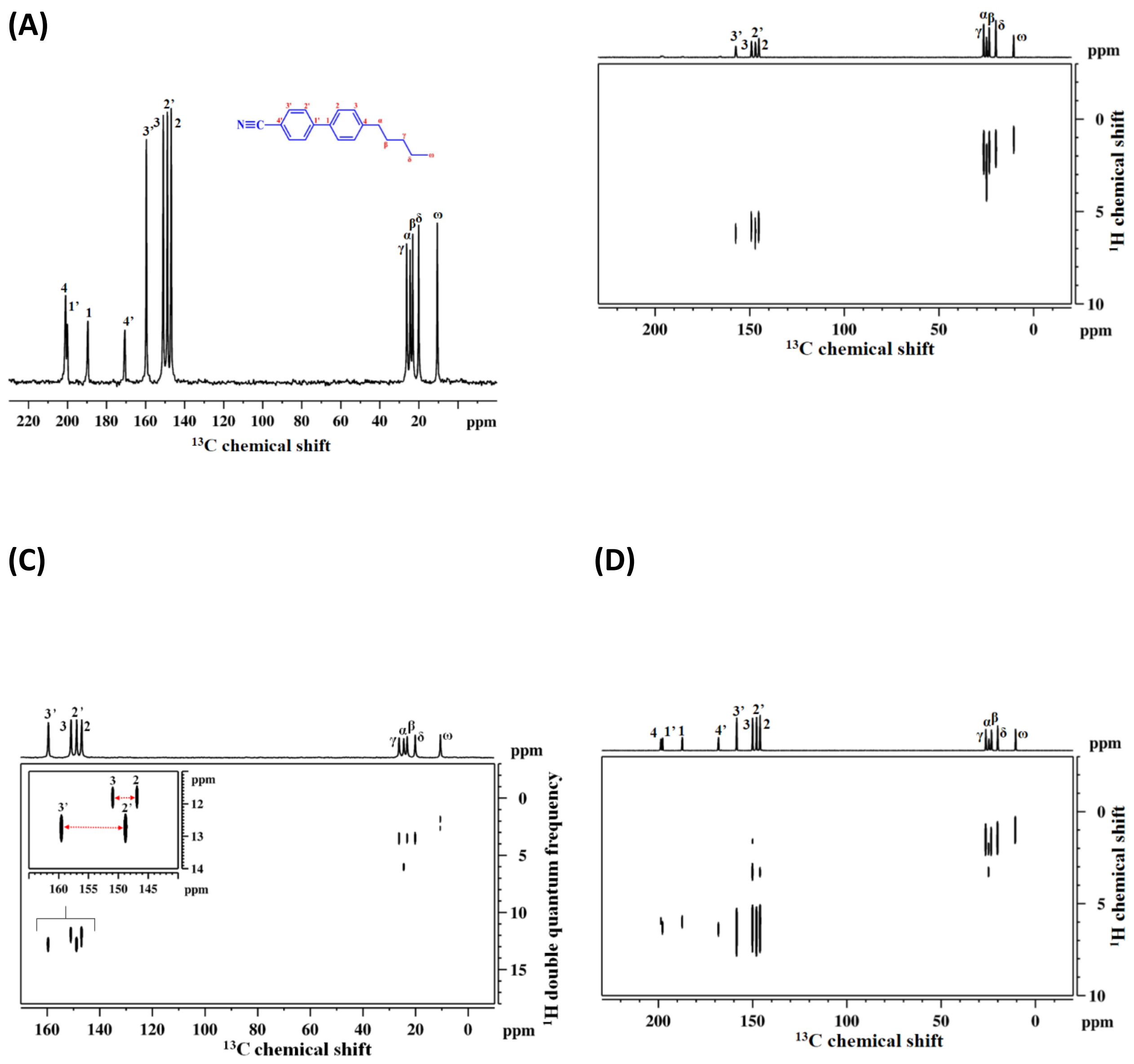
(A)
N≡C
4 1' 1 4' 3' 3 2' 2
γ α β δ ω
220 200 180 160 140 120 100 80 60 40 20 ppm
^{13}C chemical shift
(B)
3' 3 2' 2 γ α β δ ω
ppm
0 5 10
^{1}H chemical shift
200 150 100 50 0 ppm
^{13}C chemical shift
(C)
3' 3 2' 2 γ α β δ ω
ppm
12 13 14
160 155 150 145 ppm
0 5 10 15
^{1}H double quantum frequency
160 140 120 100 80 60 40 20 0 ppm
^{13}C chemical shift
(D)
4 1' 1 4' 3' 3 2' 2 γ α β δ ω
ppm
0 5 10
^{1}H chemical shift
200 150 100 50 0 ppm
^{13}C chemical shift

Figure 2

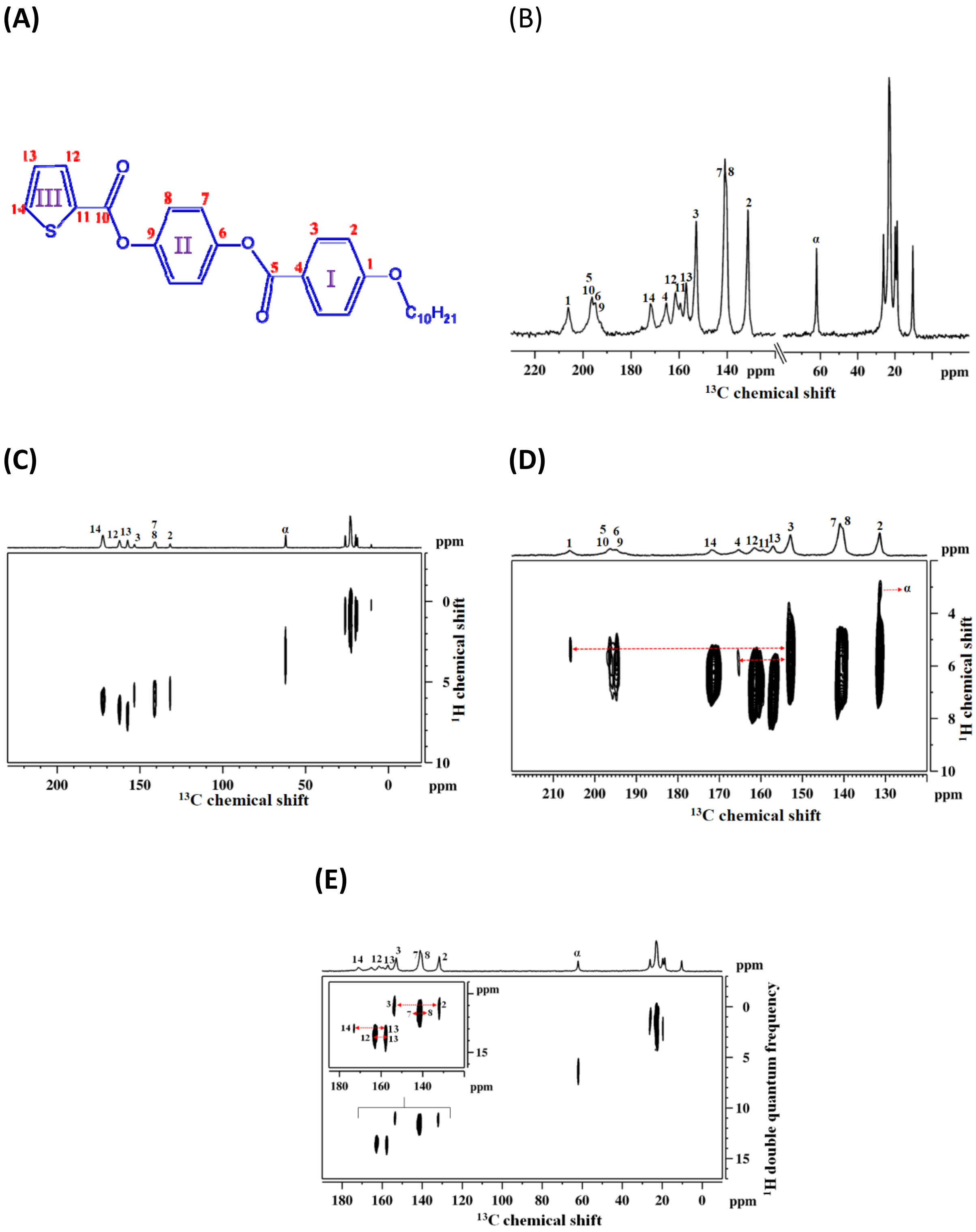
(A)
(B)
(C)
(D)
(E)
III
II
I
S
O
$C_{10}H_{21}$
1
2
3
4
5
6
7
8
9
10
11
12
13
14
α
ppm
^{13}C chemical shift
^{1}H chemical shift
^{1}H double quantum frequency
220
200
180
160
140
60
40
20
150
100
50
0
210
190
170
130
120
80

Figure 3

Table of Contents Graphics:

^{13}C Spectral Assignment by Correlation to Proton Double Quantum Coherence - Order Parameters of a Thiophene Based Liquid Crystal