

Solid-State NMR Characterization of a Novel Thiophene-Based Three Phenyl Ring Mesogen

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Thermotropic liquid crystals are increasingly gaining importance as functional materials.¹ Among the calamitic liquid crystals, thiophene-based mesogens have drawn the attention due to their attractive applications.^{2–7} Incorporation of thiophene in the mesogen core increases the optical anisotropy, decreases the melting point, promotes a negative dielectric anisotropy, and reduces viscosity.^{2,5} Thiophene materials are also well-known for their semiconducting properties^{8–10} and would be useful for polarized light emission as backlight panel for liquid crystal display devices. Much of the literature pertaining to thiophene liquid crystals deals with 2,5-substitution.^{2–6} However, the introduction of a mesogen at the third position of the thiophene ring favors further structural manipulation to get dimers, oligomers, and polymers that may find interesting applications.¹¹ In this study, we report a new thiophene-containing mesogen and demonstrate its liquid crystalline property and molecular order using natural abundance ¹³C solid-state NMR (1D and 2D) techniques. Solid-state NMR techniques have been used for probing the dynamics, molecular packing, and orientational order for various classes of thermotropic liquid crystals.^{12–22} However, most of the 2D separated local field

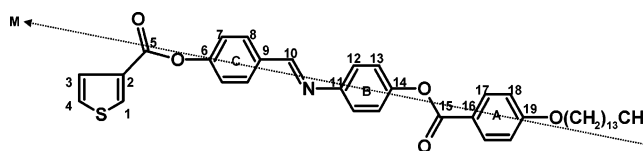


Figure 1. Chemical structure of TCPMAPTdB.

(SLF) techniques²³ that have been used to measure heteronuclear dipolar couplings require high radiofrequency (rf) power and therefore are not useful to study temperature-sensitive mesogens. In this paper, we utilized a very low rf power 2D PITANSEMA²⁴ (polarization inversion time-averaged nutation spin exchange at the magic angle) experiment not only to resolve aromatic resonances but also to determine the orientational order of the mesogenic core and the orientation of the thiophene ring with respect to the molecular axis.

The molecular structure of the mesogen is shown in Figure 1. The mesogen was synthesized using a multistep procedure as described for its lower (C12 alkoxy chain) homologue recently.²⁵ The nematogen 4-[(thien-3-ylcarboxy)phenyl]-methylenamino}phenyl-4-tetradecyloxybenzoate (TCPMAPTdB) consists of three 1,4-disubstituted phenyl rings linked through ester and azomethine units. The terminal group is comprised of a C14 alkoxy chain. The compound exhibits an enantiotropic nematic phase as confirmed by the optical polarizing microscope and differential scanning calorimetry. Figure 2 shows the characteristics threaded nematic texture at 251 °C while heating the sample. The mesogen undergoes crystal to nematic phase transition at 141.3 °C and clearing at 252.3 °C. The transitional enthalpies of these phase changes are 4.58 and 0.21 kcal/mol, respectively. Though the incorporation of thiophene is known to reduce the melting point of the mesogen, in the present case, the high melting and clearing temperatures are attributed to the presence of three phenyl rings, ester, and azomethine

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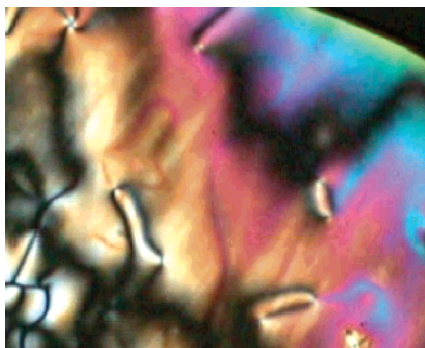


Figure 2. Photomicrograph of characteristic nematic phase of TCPMAPTdB at 251 °C while heating under optical polarizing microscope.

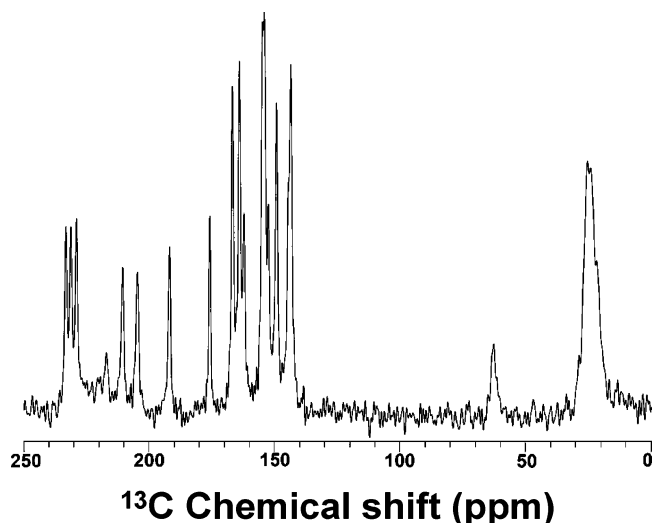


Figure 3. Static ^{13}C chemical shift spectra of TCPMAPTdB at 150 °C. The spectrum was acquired using a Chemagnetics/Varian Infinity 400 MHz solid-state NMR spectrometer and a 5 mm triple resonance MAS Chemagnetics probe. A 50 kHz rf field strength for CP, ~ 75 kHz decoupling of protons, 1 ms contact time for cross polarization, 512 scans, and a recycle delay of 3 s were used. The chemical shift assignment of ring A carbons was done by comparing with the nematic phase spectrum of 4-butoxy benzoic acid (spectra given in Supporting Information). Since the phenyl rings undergo rapid reorientation along the para axis, the ortho carbons are chemically equivalent and also the meta carbons.

linking groups. The phase stability (111 °C) indicates that the overall molecular polarizability is high when compared to that of 2,5-disubstituted thiophene mesogens.^{2,5}

A one-dimensional static ^{13}C chemical shift spectrum of TCPMAPTdB in nematic phase is shown in Figure 3. The alignment of the molecule in the external magnetic field is evident from the spectral resolution and chemical shift values as well. The assignment of peaks from aromatic methine carbons is difficult due to the overlap of phenyl and thiophene carbon resonances in the region 142–170 ppm (Figure 3). The chemical shift region 175–235 ppm represents the quaternary carbons of the thiophene, phenyl ring, and also the ester and azomethine linking units. Although the relative intensity of the peaks could provide information about the protonated and nonprotonated carbons, the precise assignment of all the signals is not straightforward. To overcome this difficulty, we used a recently developed 2D PITANSEMA technique that provides the correlation of the chemical shift and C–H dipolar coupling values. Figure 4 shows the 2D PITANSEMA spectrum of TCPMAPTdB at 150 °C. The dramatic improvement of the resolution in the

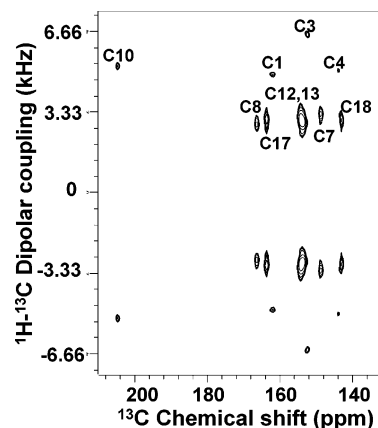


Figure 4. 2D PITANSEMA spectrum of TCPMAPTdB at 150 °C. $\tau_1 = 10 \mu\text{s}$, $\tau_2 = 15 \mu\text{s}$, 128 t_1 increments, 16 scans, and a 3 s recycle delay were used. An experimentally measured scaling factor of 0.6 was used.

region 142–170 ppm facilitates the identification of phenyl and thiophene ring methine carbons. The enhancement of resolution primarily arises due to the difference in the dipolar coupling values of thiophene and phenyl ring carbons. The PITANSEMA spectrum (Figure 4) shows nine dipolar coupled doublets for 10 methine carbons (C1, C3, C4 of thiophene; C7, C8, C12, C13, C17, C18 of phenyl rings; and C10 of the azomethine linking unit) present in the molecule. The assignment of the thiophene versus the phenyl methine carbons is simplified in the 2D spectrum as the former showed larger dipolar coupling values than the latter. The overlapping of contours for C12 and C13 carbons is due to similar dipolar coupling values. The individual assignment of all the carbons in the mesogen was accomplished using the 2D data, considering the substituent effect, comparing the solution NMR and structurally similar mesogens (mainly phenyl ring carbons) reported in the literature.^{16–18} The core fragment of the mesogen consists of 19 chemically different carbons, and their chemical shift values are listed in Table 1 (in Supporting Information). The peaks from the terminal alkoxy chain (C14) are seen in the region 22–63 ppm, and the peak at 25 ppm is very broad accounting for chemically equivalent CH_2 carbons. Since the ordering of the entire mesogen is primarily dictated by the core unit, emphasis of the present study is on the carbons of the core unit.

It is well-known that mesogens consisting of linking units result in the noncollinearity of the molecular axis and para axes of the phenyl rings. A tilt angle of 3–10° has been typically used in defining the molecular frame of the nematogen.²⁶ To determine the molecular axis of TCPMAPTdB, the 2D PITANSEMA data obtained from 4-butoxybenzoic acid, which shows nematic phase ($T_{\text{CN}} 147.5$ °C– $T_{\text{NI}} 161$ °C) at 150 °C, was used. Due to the presence of intermolecular hydrogen bonding, the alkoxy benzoic acids are known to exist in dimeric form even in the mesophase. In such systems, coincidence of the molecular axis and para axis is possible. By considering the dipolar coupling values of 4-butoxybenzoic acid (see Supporting Information) and TCPMAPTdB, it was assumed that the molecular axis (M)

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(Figure 1) of TCPMAPTdB makes a 6° tilt with respect to the para axes of the phenyl rings. The examination of C–H dipolar coupling values of TCPMAPTdB further provides information about the molecular geometry. In contrast to the phenyl ring C–H dipolar couplings, the thiophene ring methine carbons showed higher values (Figure 4; the values are given in Table 1 in the Supporting Information). These results suggest that the thiophene ring is not on the molecular axis, which can be attributed to the linkage to rest of the core unit at the third position.

In view of the uniaxial nature of the nematic phase and by assuming the cylindrical symmetry of TCPMAPTdB, the orientational ordering was calculated using the measured C–H dipolar coupling values of phenyl rings and azomethine carbons in the equation: $D = -S(h\gamma_C\gamma_H/4\pi^2r_{CH}^3)(3\cos^2\theta - 1)/2$; where D is the measured C–H dipolar coupling, r_{CH} is the internuclear distance (assumed to be 1.1 Å in this study), and θ is the angle between the C–H vector and the magnetic field minus the 6° tilt angle (i.e., 120 – 126° for the aromatic C–H and 114 – 116° for the azomethine C–H). The order parameters were determined to be 0.52 at 150°C and 0.47 at 180°C for the ring A, 0.50 at 150°C and 0.47 at 180°C for the ring B, and 0.52 at 150°C and 0.48 at 180°C for the ring C. The variation, slightly larger than the experimental errors (given in the Supporting Information), in the order parameters of three phenyl rings may be due to the difference in their substituents.²⁶ On the other hand, higher order parameters were found for the azomethine linking unit: 0.64 and 0.60 at 150 and 180°C , respectively. These values are consistent with the nematic phase exhibited by the calamitic compounds.²⁶ The decrease in the order parameter values with the increasing temperature is very low as the measurement temperatures were not closer to the clearing temperature (252.3°C). Using the order parameter of the ring C to which thiophene ring is linked, the orientation

of the C–H vectors of the thiophene ring with respect to the magnetic field were determined. The values are 38.7° , 38.7° , and 33.23° for the C_1 –H, C_3 –H, and C_4 –H bonds, respectively. These values denote that the thiophene ring is tilted away from the molecular axis while the para axes of the phenyl rings are closer to the molecular axis. A comparison of the experimental results obtained from 3-substituted thiophene-based mesogens containing two (data not shown) and three phenyl rings suggests that the thiophene ring orientation is similar in both types of molecules, which may be essential for its functional property. This atomistic level geometrical information is otherwise very difficult to obtain in the mesophase. Therefore, we believe that the experimental approach employed in this study will be highly valuable to study other thermotropic (including nonlinear) liquid crystals such as banana, metallo-mesogens, and columnar mesogens. It should be noted that the use of ^{13}C chemical shift anisotropic tensors^{19,27,28} and the influence of dynamics could be fruitful in determining the geometry of liquid crystals at nanoscopic level resolution.

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Supporting Information Available: Table 1 showing experimentally measured ^{13}C chemical shift and ^1H – ^{13}C dipolar coupling values of TCPMAPTdB; molecular structure, ^{13}C chemical shift spectrum, and 2D PITANSEMA spectrum of 4-butoxy benzoic acid. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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