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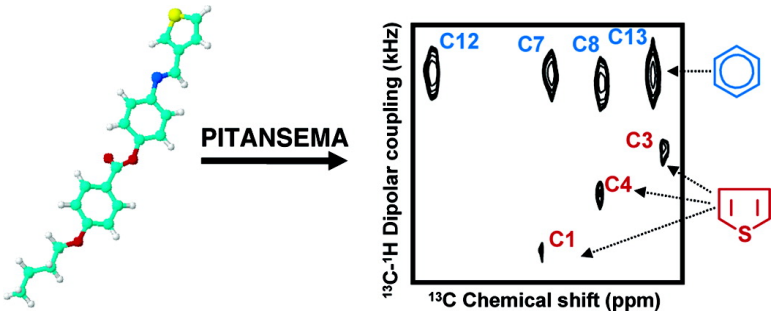

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A 2D Solid-State NMR Experiment To Resolve Overlapping Aromatic Resonances of Thiophene-Based Nematogens

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Thiophene-based molecules have been shown to be highly valuable in the design of organic electronics such as light emitting diodes, thin film transistors, photovoltaic cells, electrochromic cells, molecular electronic junctions, and biosensors.[1−4] Another important application of thiophene-based molecules is polarized emission for which liquid crystalline property is a prerequisite.[5] The key step in designing such molecules is to characterize not only the mesophase behavior but also the structural details at atomistic-level resolution. In this context, solid-state NMR spectroscopy is a powerful technique that can provide structural details pertaining to various phases of such materials.[6−9] Despite the recognized importance of these molecules, there are no detailed NMR studies on them. One of the reasons could be due to the overlap of aromatic resonances in the chemical shift spectrum of the mesophase as these materials essentially contain several phenyl and thiophene rings. As a consequence, it is difficult to determine the geometry and dynamics of the aromatic rings. Since the core fragment is the heart of the mesogen, it is important to develop new approaches to overcome these difficulties. In this study, for the first time, we demonstrate the feasibility of resolving aromatic resonances using a 2D solid-state NMR experiment on a thiophene mesogen and measuring heteronuclear dipolar couplings in the liquid crystalline phase without isotopic labeling.

The molecular structure of a thiophene mesogen 4-{[thien-3-ylmethylene]amino}phenyl-4-butoxybenzoate (TMAPB)[10] is shown in Figure 1. The ^{13}C chemical shift spectrum of TMAPB obtained at 130 °C (T_{CN} = 124 °C; T_{NI} = 153.8 °C) is also given in Figure 1. While the narrow spectral lines in Figure 1 indicate that the molecule is well-aligned in the external magnetic field, the only resonances that are not well-resolved are from the methine carbons of phenyl rings and the thiophene ring (138−162 ppm). In addition, the spectral resolution decreases when the temperature is increased as the span of chemical shift anisotropy as well as the degree of alignment decrease with the increasing temperature. Such a low-resolution spectrum often hampers further characterization of the molecule, particularly the core fragment of the nematogen that decides the liquid crystalline property.

To overcome this difficulty, a 2D separated local field (SLF) experiment that correlates the ^{13}C chemical shift and ^{1}H−^{13}C dipolar coupling was carried out. In recent years, 2D SLF experiments have been increasingly used to measure heteronuclear dipolar couplings from liquid crystalline samples to determine the orientational order.[11−13] However, these 2D techniques typically use high radio frequency (rf) power (about several hundred watts for ^{13}C and >1 kW for ^{15}N), which can increase the sample temperature due to rf heating.[14,15] Increase in the sample temperature alters the orientation of the molecule in the mesophase and could also cause a phase change. To overcome this problem, we have recently developed a low rf power 2D NMR technique: polarization inversion time-averaged nutation spin exchange at the magic angle (PITANSEMA).[16,17] It suppresses homonuclear dipolar coupling among protons and provides very high-resolution heteronuclear dipolar coupling spectra that can be used to measure the orientational order of an aligned molecule. In this study, we demonstrate the utility of this technique to resolve the overlapping aromatic resonances of TMAPB.

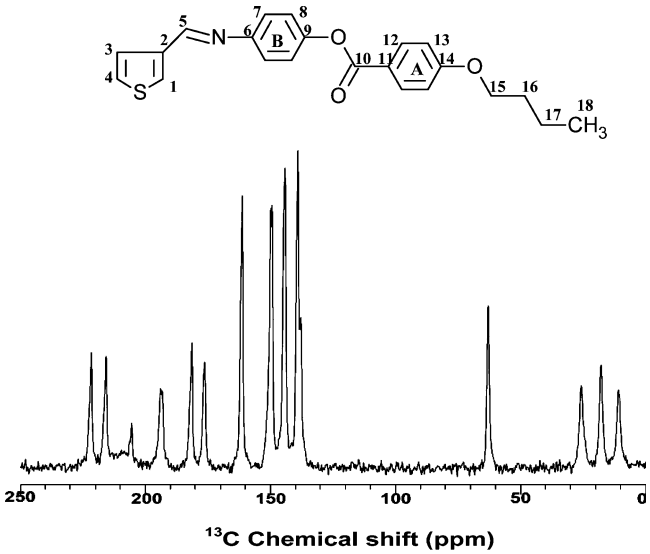

Figure 1. Molecular structure and the nematic phase ^{13}C chemical shift NMR spectrum of TMAPB at 130 °C. The spectrum was acquired using a Chemagnetics/Varian Infinity 400 MHz solid-state NMR spectrometer and a 5-mm triple resonance MAS Chemagnetics probe. A 50 kHz rf field strength for CP, ∼75 kHz TPPM decoupling of protons, 1-ms contact time for cross polarization, 612 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 the Supporting Information). Since the phenyl rings undergo rapid reorientation along the para-axis, the *ortho*- and *meta*-carbons are chemically equivalent.

A 2D PITANSEMA spectrum of TMAPB is given in Figure 2. The ^{13}C chemical shift region (138−162 ppm) that showed poor resolution in Figure 1 is now well-resolved in the 2D spectrum. Even the C_5−H signal from the azomethine linking unit that is overlapping with the quaternary carbon of the aromatic ring in the 1D spectrum at 193.4 ppm (Figure 1) is clearly resolved in the 2D spectrum. This higher resolution is provided by the narrow lines in the second frequency (i.e., the dipolar coupling) dimension of the 2D spectrum. In addition, the resolution is enhanced by suppressing signals from quaternary carbons as they do not have a nearby proton. In the 2D spectrum, there are seven peaks corresponding to seven different C−H carbons of phenyl and thiophene

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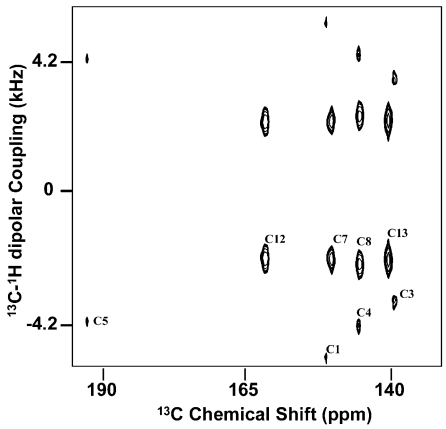

Figure 2. 2D PITANSEMA spectrum of TMAPB at 130 °C. An experimentally measured scaling factor of 0.6 was used. $\tau_1 = 10$ μs, $\tau_2 = 15$ μs, 128 t_1 increments, 16 scans, and a 3-s recycle delay were used.

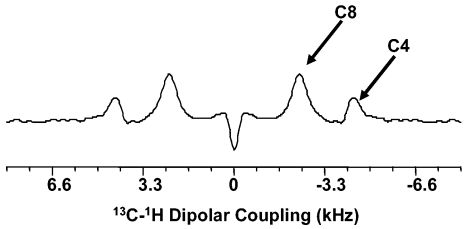

Figure 3. ^{13}C−^{1}H dipolar coupling slice obtained from Figure 2 at 144.4 ppm shows dipolar coupling doublets for ^{1}H−^{13}C8 (inner; 2.4 kHz) of ring B and ^{1}H−^{13}C4 (outer; 4.4 kHz) of thiophene ring.

rings. A C−H dipolar coupling slice taken from the 2D spectrum (Figure 2) contains two dipolar couplings corresponding to H−C_4 and H−C_8 and is shown in Figure 3. Since the molecular axis is nearly collinear with the para-axis of the phenyl rings, the smaller dipolar coupling value is assigned to the H−C_8 bond. Similarly, the four different pairs of peaks in the 2D spectrum with a dipolar coupling ±2.2−2.4 kHz belong to the phenyl ring methine carbons, while the three pairs of peaks in the region ±3.6−5.5 kHz originate from the thiophene C−H groups. Since 4-butoxy benzoic acid is the starting material for the synthesis and it represents ring A of TMAPB, we utilized the PITANSEMA spectrum of 4-butoxy benzoic acid (data given in the Supporting Information) as a reference to determine the molecular axis of TMAPB. The C−H dipolar couplings of the phenyl rings measured from TMAPB (Figure 2) and 4-butoxy benzoic acid are similar. Therefore, it is reasonable to assume that the molecular axis of TMAPB is nearly collinear with the para-axis of the phenyl rings as in 4-butoxy benzoic acid. Since the order parameters of phenyl and thiophene rings cannot differ significantly, the difference in the dipolar coupling values (Figure 2) clearly suggests that the orientation of the thiophene ring significantly differs from that of phenyl rings in TMAPB. This is because the substitution at the third position of thiophene (with azomethine) deviates the orientation of the ring from the molecular axis, while the 2,5-substitution of thiophene makes the ring part of the molecular axis.[18] The measured dipolar couplings are used to determine the order parameters (S) using $D = -S(h\gamma_C\gamma_H/4\pi^2 r_{CH}^3)(3\cos^2\theta - 1)/2$; where D is the measured C−H dipolar coupling and θ is the angle between the C−H vector and the external magnetic field axis. The order parameters are 0.51 (130 °C) and 0.44 (150 °C) for phenyl ring A, 0.53 (130 °C) and 0.46 (150 °C) for phenyl ring B, and 0.60 (130 °C) and 0.50 (150 °C) for the (azomethine) linking unit. These order parameters are consistent with the nematic phase of the sample. The measured dipolar couplings and the determined order parameters decreased with the increasing temperature and became zero at the clearing temperature (153.8 °C). Since the crystal structure of the molecule is unknown, by using the order parameter of ring B that is linked to thiophene, we determined the orientations of the thiophene C−H bonds from the molecular axis. The angles between the molecular axis and the methine bonds in the thiophene ring are 37 ± 2°, 40 ± 2°, and 43 ± 2° for H−C_1, H−C_3, and H−C_4, respectively.

The approach demonstrated in this study can be extended to the characterization of banana and other types of liquid crystals. In addition, 3D organization of the molecules can be determined as shown for biomacromolecules.[19] In view of the molecular kink between the central phenyl ring and the side phenyl rings in the banana mesogen, the C−H dipolar couplings that differ in magnitude can in principle be used to determine the geometry and bent angle.

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Supporting Information Available: Molecular structure, ^{13}C chemical shift spectrum, and a 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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