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Kenneth E. Maly^a; Gang Wu^a; Robert P. Lemieux^a

^a Department of Chemistry, Queen's University, Kingston, Ontario, Canada K7L 3N6,

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Solubility of thioindigo dopants in a smectic liquid crystal host evaluated by ^2H NMR spectroscopy

KENNETH E. MALY, GANG WU and ROBERT P. LEMIEUX*

Department of Chemistry, Queen's University, Kingston, Ontario,
Canada K7L 3N6

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The solubility of two partially deuterated thioindigo dopants in a smectic liquid crystal host was evaluated by variable temperature ^2H NMR spectroscopy and polarized microscopy. ^2H NMR spectra showed that the dopant (\pm)-6,6'-bis(2-octyloxy)-5,5'-dinitrothioindigo- d_6 forms a homogeneous solution with the smectic phases of the liquid crystal host (\pm)-4-(4-methylhexyloxy)phenyl 4-decyloxybenzoate (**PhB**) up to its saturation point of 3 mol%. These results are consistent with polarized microscopy observations of the dopant crystallizing out of solution upon reaching a concentration of 3 mol%. On the other hand, ^2H NMR spectra of (\pm)-5,5'-dichloro-6,6'-bis(2-octyloxy)thioindigo- d_6 dissolved in **PhB** showed evidence of a partitioning of the solution between smectic and isotropic microdomains, which increases with increasing dopant concentration—from 1.2 to 9.1 mol%. To a large extent, this smectic/isotropic microphase separation could not be detected by polarized microscopy. These results suggest that ^2H NMR spectroscopy can provide a more accurate determination of the occurrence and extent of microphase separation in doped liquid crystal samples.

1. Introduction

Chiral smectic liquid crystals exhibit unique chiral bulk properties which have been harnessed to produce thin film spatial light modulators with switching times ranging from microseconds (ferroelectric Goldstone-mode switching) to nanoseconds (electroclinic soft-mode switching) [1–4]. The induction of chiral bulk properties in smectic phases is most easily achieved by dissolving a chiral dopant in an achiral smectic liquid crystal host. For example, ferroelectric liquid crystal mixtures suitable for commercial display applications are normally obtained by dissolving a small amount of chiral dopant with very high polarization power into an achiral smectic C (SmC) liquid crystal mixture with low viscosity and broad temperature range. Such chiral dopants may not be mesogenic, but they must be completely soluble in the SmC liquid crystal phase so as not to alter other mesogenic bulk properties which are fine tuned through careful formulation of a large number of liquid crystalline components. Routinely, one can evaluate the solubility of a non-mesogenic dopant in a liquid crystal phase by measuring variations in phase transition temperature as a function of dopant concentration and by detecting the onset of phase separation using polarized microscopy.

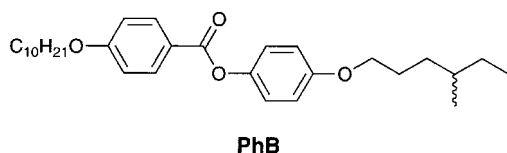
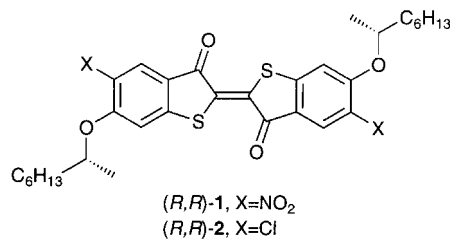
However, a series of papers published a decade ago by Leigh and co-workers signalled caution regarding the validity of these approaches through the use of ^2H NMR spectroscopy [5–9].

^2H NMR spectroscopy has been used extensively to measure orientational order parameters S in nematic liquid crystals [10]. The nucleus of deuterium is quadrupolar ($I = 1$) and the deuteron Zeeman levels are perturbed by the interaction of its quadrupolar moment with the electric field gradient (EFG) tensor. In an anisotropic liquid crystal phase, such interaction results in a quadrupolar doublet with a splitting $\Delta\nu_Q$ that is directly proportional to S . By virtue of this quadrupolar splitting, Leigh and co-workers showed that ^2H NMR can be useful to measure the solubility limit of deuterated solutes in liquid crystalline solvents with far greater accuracy than polarized microscopy [5–9]. For example, solutions of non-mesogenic deuterated ketones in nematic and smectic liquid crystal solvents were investigated by ^2H NMR, and a partitioning of the ketones between the mesophase and microscopic isotropic liquid domains was shown to exist at much lower concentrations than the solubility limits estimated by polarized microscopy [5, 6].

Chiral thioindigo derivatives have been used as chiral dopants to induce a ferroelectric SmC* liquid crystal phase that is sensitive to visible light [11–14]. We have recently shown that *trans-cis*-photoisomerization

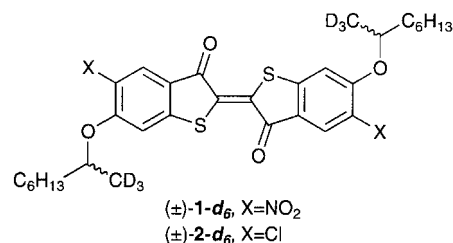
* Author for correspondence
e-mail: lemieux@chem.queensu.ca

of the thioindigo dopants (*R,R*)-**1** and (*R,R*)-**2** causes a modulation of the spontaneous polarization (P_s) without concomitant destabilization of the SmC* phase by virtue of the corresponding increase in transverse dipole of the thioindigo core [12, 13]. Thioindigo and simple derivatives of thioindigo are notorious for their lack of solubility in organic solvents, which proved to be a serious challenge to their use as dopants in liquid crystal phases [15]. We showed in an earlier study that unbranched alkoxy side-chains (C₆–C₁₂) improved the solubility of thioindigo in organic solvents, but only marginally in liquid crystal hosts [16]. The branched 2-octyloxy side-chains in **1** and **2** significantly improved the solubility of thioindigo in liquid crystal hosts. This made possible the induction of a chiral SmC* phase with a measurable spontaneous polarization by dissolving either (*R,R*)-**1** or (*R,R*)-**2** in the achiral liquid crystal host **PhB**, which forms a broad SmC phase between 32 and 68°C (see the table). The solubility of the thioindigo dopant depends strongly on the nature of the substituent *X*. Observations by polarized microscopy showed that dopant (*R,R*)-**1** is marginally soluble in **PhB**, with a solubility limit of *c.* 3 mol %. On the other hand, dopant (*R,R*)-**2** appeared to form a homogeneous solution with **PhB**, with no evidence of biphasic behaviour well into the SmC* phase at concentrations as high as 10 mol %.



Previous studies have shown that *trans-cis*-photoisomerization of dopant (*R,R*)-**1** in **PhB** causes a 2-fold increase in P_s that is invariant of dopant concentration

up to 3 mol %; this is consistent with (*R,R*)-**1** forming a homogeneous solution with **PhB** [12, 13]. However, the photomodulation of P_s achieved by photoisomerization of dopant (*R,R*)-**2** in **PhB** decreases (in relative terms) with increasing dopant concentration. Hence, P_s increases by a factor of 4.0 at 1.9 mol %, but only by a factor of 1.4 at 10 mol % [13]. These results indicated that (*R,R*)-**2** may not form homogeneous mixtures with **PhB**, which led to an assessment of dopant solubility in the smectic phases of **PhB** by ²H NMR spectroscopy. Herein, we report an analysis of the partially deuteriated racemic thioindigo dopants (±)-**1-d⁶** and (±)-**2-d⁶** in the liquid crystal host **PhB** by ²H NMR spectroscopy and polarized microscopy. The results show that **1** is completely dissolved in the SmC phase until it begins to crystallize out of solution upon reaching its solubility limit of 3 mol %, whereas **2** exists as a SmC/isotropic biphasic mixture at higher dopant concentrations.



2. Experimental

2.1. General

All ²H NMR spectra were recorded using a Bruker Avance 500 spectrometer operating at 76.77 MHz for ²H. Temperatures were adjusted to within ±0.2 K and are accurate within ±2 K. Samples were prepared in 5 mm NMR tubes by adding the appropriate amounts of dopant and liquid crystal host and heating the mixture to the isotropic phase to ensure complete mixing. The samples were allowed to equilibrate at each temperature for 5–15 min until reproducible spectra were obtained. ²H NMR spectra were recorded on stationary samples using a spin echo pulse sequence, collecting 4096 data points per scan over a 100 kHz spectral width. Depending

Table. Phase transition temperatures in °C for mixtures of (±)-**1-d⁶** and (±)-**2-d⁶** in the liquid crystal host **PhB** on cooling from isotropic liquid.

Dopant	χ_d^a	I	N	SmA	SmC	SmX	Cr
(±)- 1-d⁶	3.3	•	68	•	65	•	32
(±)- 2-d⁶	1.2	•	71	•	68.5	•	42
(±)- 2-d⁶	4.8	•	70	•	68	•	40
(±)- 2-d⁶	9.1	•	69	•	67	•	34
—	—	•	73	•	72.5	•	32

^a Dopant concentration in mol %.

on dopant concentration, 1000–50 000 scans were collected (with a 0.2 s delay between scans). The $\pi/2$ pulse width was determined using a D_2O sample to be 17 μs . Line broadening (50 Hz) and exponential multiplication were performed prior to Fourier transformation (FT). Microscopic texture analyses were carried out using a Nikon E-600 POL polarizing microscope fitted with an Instec HS1-i hot stage.

2.2. Materials

The liquid crystal host (\pm)-4-(4-methylhexyloxy)phenyl 4-decyloxybenzoate (**PhB**) was prepared according to a literature procedure [17]. The deuteriated thioindigo dopants (\pm)-**1-d⁶** and (\pm)-**2-d⁶** were prepared according to the procedure of Dinescu *et al.* using 2-octanol-1,1,1-*d*₃ and were recrystallized from hexanes prior to use [13, 18]. The deuterated alcohol was prepared in one step by reacting heptanol with CD_3MgI .

2.2.1. (\pm)-6,6'-Bis(2-octyloxy)-5,5'-dinitrothioindigo-*d*₆, (\pm)-**1-d⁶**

¹H NMR (400 MHz, $CDCl_3$) δ 0.90 (t, 6H), 1.31–1.86 (m, 20H), 4.68 (t, 2H), 7.12 (s, 2H), 8.34 (s, 2H). ¹³C NMR (100 MHz, $CDCl_3$) δ 14.3, 18.8, 22.8, 25.4, 29.4, 32.0, 36.2, 78.3, 109.4, 120.5, 124.6, 133.3, 139.8, 154.9, 157.9, 187.0. MS (EI) *m/z* 648 (M+ , 3), 420 (15), 419 (30), 418 (100), 237 (8), 115 (21). HRMS calcd. for $C_{32}H_{32}D_6N_2O_8S_2$: 648.2440; found: 648.2445.

2.2.2. (\pm)-5,5'-Dichloro-6,6-bis(2-octyloxy)thioindigo-*d*₆, (\pm)-**2-d⁶**

¹H NMR (400 MHz, $CDCl_3$) δ 0.90 (t, 6H), 1.32–1.87 (m, 20H), 4.56 (t, 2H), 6.96 (s, 2H), 7.91 (s, 2H). ¹³C NMR (100 MHz, $CDCl_3$) δ 14.4, 18.5, 22.9, 25.5, 29.4, 32.0, 36.3, 76.9, 108.1, 122.2, 123.4, 128.5, 134.5, 149.9, 160.5, 187.6. MS *m/z*; 630 (M+ 4, 4), 628 (M+ 2, 13), 626 (M+ , 16), 400 (24), 398 (82), 396 (100). HRMS calcd. for $C_{32}H_{32}D_6^{35}Cl_2O_4S_2$: 626.1959; found: 626.1966.

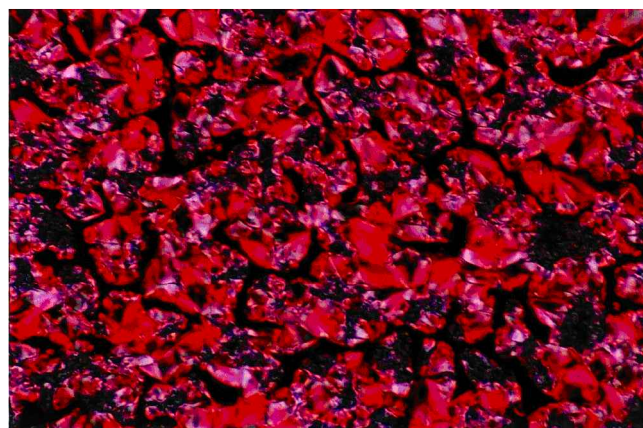
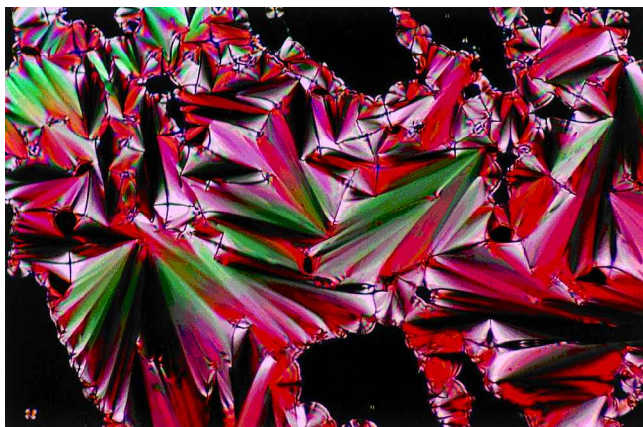


Figure 1. Textures of a 4.8 mol % mixture of (\pm)-**2-d⁶** in **PhB** observed by polarized microscopy (100 \times): homeotropic and fan textures of the SmA phase at 70°C (top); Schlieren and broken fan textures of the SmC phase at 68°C (bottom).

Figure 2. Textures of a 9.1 mol % mixture of (\pm)-**2-d⁶** in **PhB** observed by polarized microscopy (100 \times): broken fan/Schlieren texture of the SmC phase with coexisting isotropic domains at 67°C (top); uniform broken fan/Schlieren texture of the SmC phase at 61°C (bottom).

3. Results and discussion

Four different liquid crystal mixtures were prepared: a 3.3 mol % mixture of (\pm)-**1-d⁶** in **PhB** and 1.2, 4.8 and 9.1 mol % mixtures of (\pm)-**2-d⁶** in **PhB**. The transition temperatures of the four mixtures were measured by polarized microscopy on cooling and are listed in the table. Visual inspection of a thin film sample of the (\pm)-**1-d⁶/PhB** mixture by polarized microscopy revealed the growth of red needles (assumed to be (\pm)-**1-d⁶**) from the liquid crystal phase as the temperature was lowered below the clearing point (68°C). The extent of needle formation increased as the temperature was progressively lowered from the SmA to the SmC phase, although it was apparent that some dopant remained in solution, based on the red colour of the liquid crystal phase when viewed without crossed polarizers. No crystallization of (\pm)-**2-d⁶** could be detected by polarized microscopy in any of the three samples at temperatures as low as 55°C. Visual inspection of the 1.2 and 4.8 mol % (\pm)-**2-d⁶/PhB** mixtures as a function of temperature revealed no biphasic behaviour below the I–SmA phase transition (figure 1). In the 9.1 mol % mixture, small isotropic domains could be detected among the predominantly smectic domain at 67°C. These small isotropic domains could be observed at temperatures as low as 63°C, below

which a uniform broken fan/Schlieren texture became apparent (figure 2). A further change in texture consistent with a transition to a higher order smectic phase was observed around 57°C.

²H NMR spectra were recorded as a function of temperature and are shown in figures 3–6. Spectra of (\pm)-**1-d⁶** in **PhB** show a singlet in the isotropic phase (70°C) and a doublet in the SmA (67°C) and SmC (65 and 60°C) phases (figure 3). The magnitude of quadrupolar splitting $\Delta\nu_Q$ increases with decreasing temperature—from 21.5 to 23.9 kHz—as a result of increasing restrictions to molecular reorientation (increasing order parameter *S*). The general appearance of the spectra does not change appreciably going from the SmA to the SmC phase. The signal-to-noise ratio achieved in the SmA/C phases is rather poor because of the limited amount of dopant remaining in solution, although the spectra show no evidence of additional phase separation.

²H NMR spectra of (\pm)-**2-d⁶** in **PhB** show a sharp singlet in the isotropic phase, and a broad quadrupolar doublet in the SmA/C phases coexisting with an isotropic singlet in some cases. In the case of the 1.2 mol % sample, the spectrum shows an isotropic singlet at 70°C; upon cooling into the smectic phases, a broad doublet appears with a quadrupolar splitting $\Delta\nu_Q$ comparable to that

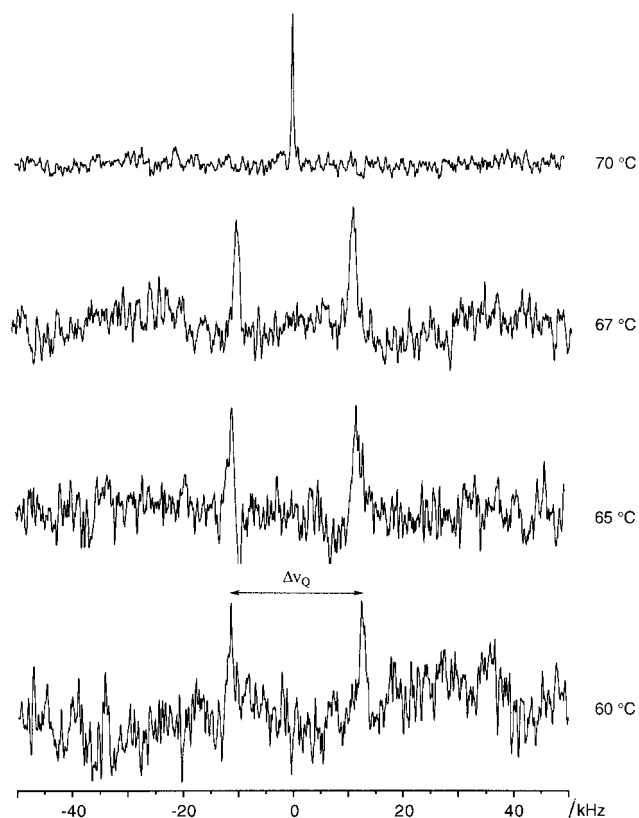


Figure 3. ²H NMR spectra of a 3.3 mol % mixture of (\pm)-**1-d⁶** in **PhB** as a function of temperature.

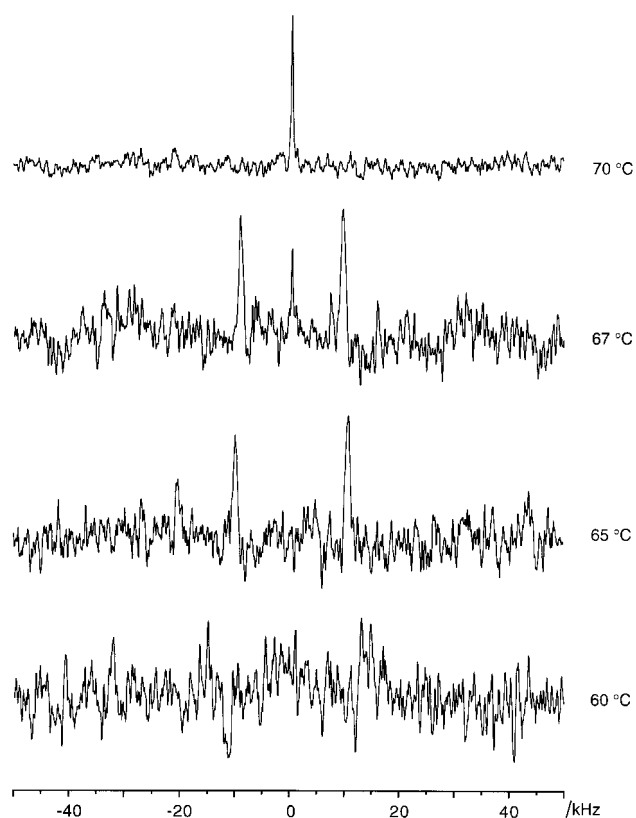


Figure 4. ²H NMR spectra of a 1.2 mol % mixture of (\pm)-**2-d⁶** in **PhB** as a function of temperature.

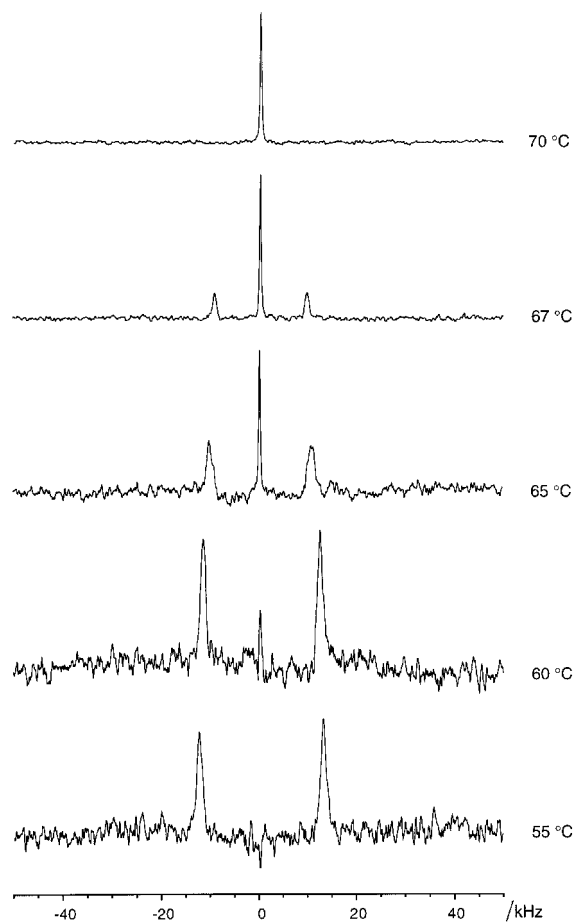


Figure 5. ^2H NMR spectra of a 4.8 mol % mixture of $(\pm)\text{-2-}d^6$ in **PhB** as a function of temperature.

observed in the previous case (figure 4). At 67°C, the quadrupolar doublet is accompanied by an isotropic singlet, which disappears upon further cooling to 65°C. At 60°C, the doublet is broadened to such an extent that it cannot be distinguished from the baseline noise as a result of a decrease in the rate of reorientation of smectic domains in the bulk sample. The 4.8 mol % sample shows a similar behaviour except that, upon cooling into the smectic phases, the isotropic singlet is more intense relative to the quadrupolar doublet and persists at lower temperatures, down to 60°C (figure 5). In the spectra of the 9.1 mol % sample, the isotropic singlet is detectable all the way down to 55°C, at which point the quadrupolar doublet cannot be distinguished from the noisy baseline, which is consistent with the observed phase transition to a higher order smectic phase (figure 6). In all three cases, the quadrupolar splitting $\Delta\nu_Q$ increases with decreasing temperature. In those cases showing an isotropic singlet and a quadrupolar doublet together, reproducible spectra were acquired over 4 h at constant temperature, thus ensuring full thermal equilibration of the samples. The detection of

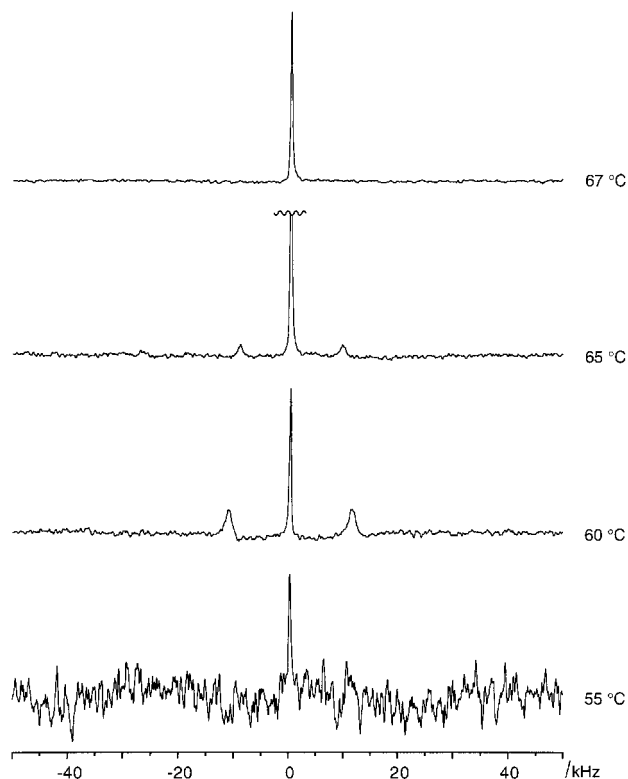


Figure 6. ^2H NMR spectra of a 9.1 mol % mixture of $(\pm)\text{-2-}d^6$ in **PhB** as a function of temperature.

an isotropic singlet together with a quadrupolar doublet is consistent with microphase separation of smectic and isotropic domains containing the deuterated dopant. Such microphase separation could not be detected by polarized microscopy in the 4.8 mol % sample, and only partially in the 9.1 mol % (see above).

4. Conclusions

As previously shown by Leigh and co-workers for a different combination of non-mesogenic dopant and liquid crystal host, this study demonstrates the usefulness of ^2H NMR in evaluating the homogeneity—or lack thereof—of mixtures composed of a non-mesogenic dopant and a liquid crystal host, and the superiority of the analysis over polarized microscopy. In the case of $(\pm)\text{-1-}d^6$ ^2H NMR spectra show that the dopant forms a homogeneous solution with the smectic liquid crystal phases of **PhB** all the way to its saturation point, which is consistent with P_s photomodulation results obtained with $(R,R)\text{-1}$. In the case of $(\pm)\text{-2-}d^6$, the ^2H NMR spectra indicate that the dopant is partitioned between smectic domains and isotropic microdomains over a range of temperature which increases with the dopant concentration, even though observations by polarized microscopy suggest otherwise. These results could explain why P_s photomodulation decreases with

increasing concentration of (*R,R*)-**2** if the isotropic/SmC partition coefficient of *cis*-(*R,R*)-**2** is different from that of *trans*-(*R,R*)-**2** due to differences in molecular shape. Studies aimed at expanding the use of ²H NMR to evaluate the solubility of a wide range of non-mesogenic dopants in smectic liquid crystal hosts are in progress.

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