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The Orientational Behavior of Small Molecules Dissolved in a Thermotropic Liquid Crystal Studied by NMR Spectroscopy†

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NMR spectra of acetonitrile, benzene, and 1a,2a,3e,4e,5e,6e-hexachlorocyclohexane(α -BHC) have been measured in liquid crystal of 1-(trans-4-*n*-butylcyclohexyl)-trans-4-cyanocyclohexane (ZLI1538 from Merck) at variable temperatures. The molecular structure of α -BHC did not show any discernible changes due to the temperature or to the nematic or smectic phases. The order parameters of these solutes decreased with a lowering of the temperature of measurement in the smectic phase, although they increased in the nematic phase. And hence, a trend already reported in the smectic phases of aromatic compounds has been confirmed for the smectic phase of aliphatic compound treated here. In case of α -BHC as a solute, formation of a plastic crystal was observed below 36°C. This fact means that the solute as well as the solvent molecules obtain degree of freedom of rotation although they lose that of translation, when temperature is lowered and the transformation occurs from a smectic to a plastic crystal. From this fact, acquisition of a degree of freedom of rotation is also suggested as a reason of the decrease in the order parameter in the smectic phase on decreasing the temperature. A new triplet signal appeared for acetonitrile when temperature was lowered in the smectic phase, and a formation of new phase was evidenced. The H–H and C–H direct couplings from the new triplet were about three times larger than those from the originally existing triplet, indicating a higher degree of orientation in the new phase.

Keywords: NMR, order parameter, temperature dependence, nematic phase, smectic phase

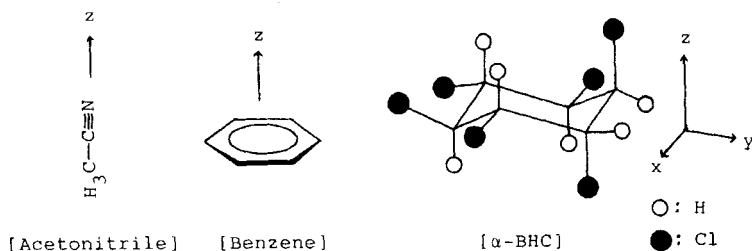
†NMR Study of Molecules in Anisotropic Systems. VIII.

INTRODUCTION

Nuclear magnetic resonance spectra of molecules dissolved in liquid crystal solvents provide important information regarding the molecular orientation not only of the solute in itself but also of the solvent for the mesophase. Among several phases of the liquid crystal, smectic phases have recently attracted the attention of various investigators.¹⁻⁵ The smectic phase differs from the nematic one in that molecular orientation is not so easily disturbed by thermal motion once it is accomplished by a slow cooling from a nematic phase in an external magnetic field. Usually, a solute dissolved in a smectic phase gives rise to NMR signals broader than those observed in a nematic phase, indicating higher restriction of the motion in this phase. In these senses, the smectic phase is said to resemble a solid phase more than the nematic phase does. In the above NMR studies of smectic phases, some characteristic features of molecular ordering are reported.¹⁻⁵ For example, the degree of order of solute molecules decreases on decreasing the temperature of measurement. This fact is usually interpreted by the notion that a solute molecule is expelled from an aromatic core region of the liquid crystal to a peripheral alkyl chain region on lowering the temperature because of a tendency of the aromatic core region to form a rigid layer of smectic phase.

Among various kinds of thermotropic liquid crystals, cyanobicyclohexane compounds are unique in that they orient perpendicular to an applied magnetic field because of their negative diamagnetic anisotropy.⁶ One of these compounds, 1-(trans-4-*n*-butylcyclohexyl)-trans-4-cyanocyclohexane (ZLI1538 from Merck), is known to form a S_B phase between 28 and 54°C and a nematic phase between 54 and 79°C.⁷ This compound was also reported to form a plastic crystal at 11°C when benzene is dissolved by 3.4 wt%.⁸

In the present paper, different kinds of solutes are examined by NMR spectroscopy to discuss the orientational profiles at variable temperatures in ZLI1538. The solutes used are acetonitrile, benzene, and 1a,2a,3e,4e,5e,6e-hexachlorocyclohexane(α -BHC), which are linear, disk-shaped, and nearly spherical, respectively.



EXPERIMENTAL

Acetonitrile and benzene were distilled and stored over molecular sieve 4A. ZLI1538 (Merck) and α -BHC were used without further purification. No impurity peaks were detected in the NMR spectra measured below. Acetonitrile, benzene, and α -BHC were dissolved in ZLI1538 by 1.0, 3.2, and 1.5 wt%, respectively, in the ^1H NMR measurement, and an 1.5 wt% solution of acetonitrile was used for the ^{13}C NMR measurement.

Samples were sealed in 5 mm o.d. (for the ^1H spectrum) or 8 mm o.d. (for the ^{13}C spectrum) NMR tubes under a nitrogen atmosphere. ^1H and ^{13}C NMR spectra were measured on a Varian XL-200 NMR spectrometer operating at 200 MHz for ^1H . ^{13}C NMR spectra were obtained under an internal lock mode by inserting the 8 mm tube inside a 10 mm o.d. NMR tube and by filling the peripheral part with D_2O , whereas ^1H NMR spectra were obtained under a no-lock mode. The sample was first heated to an isotropic phase and then cooled slowly to obtain spectra at variable temperatures. The temperature of measurement was read within an error of $\pm 0.1^\circ\text{C}$ by a thermometer attached to the spectrometer. The variation in the temperature was also within this range throughout the measurement.

The ^{13}C spectrum shown in Figure 7 was obtained at 50.309 MHz and at 25°C for the 1.5 wt% solution of acetonitrile. A number of 240k fid's were accumulated against a spectral width of 12.5 kHz with an acquisition time of 0.64 sec after a waiting time of 0.5 sec: a convolution difference was taken to reduce the very broad background of the solvent ($\text{CD} = 0.001$ and $\text{CD} = 1.0$). A mode of gated decoupling was adopted for the improvement of S/N ratio.

RESULTS AND DISCUSSION

1. The spectrum of α -BHC in ZLI1538

α -BHC possesses the C_2 symmetry and gives rise to an AA'BB'CC' spin system. The temperature dependence of its ^1H NMR spectrum dissolved in ZLI1538 (1.5 wt%) is shown in Figure 1. For this sample, sharp solvent peaks reappeared at 36°C when cooled through the nematic and smectic phases, and formation of a plastic crystal was supported. Quite a similar result was observed for 2.1 wt% 1a,2e,3e,4e,5e,6e-hexachlorocyclohexane(δ -BHC) at 41°C . Such a plastic crystal formation was communicated with the same liquid crystal containing 3.4% benzene.⁸ Analysis of the ordered spectra of α -

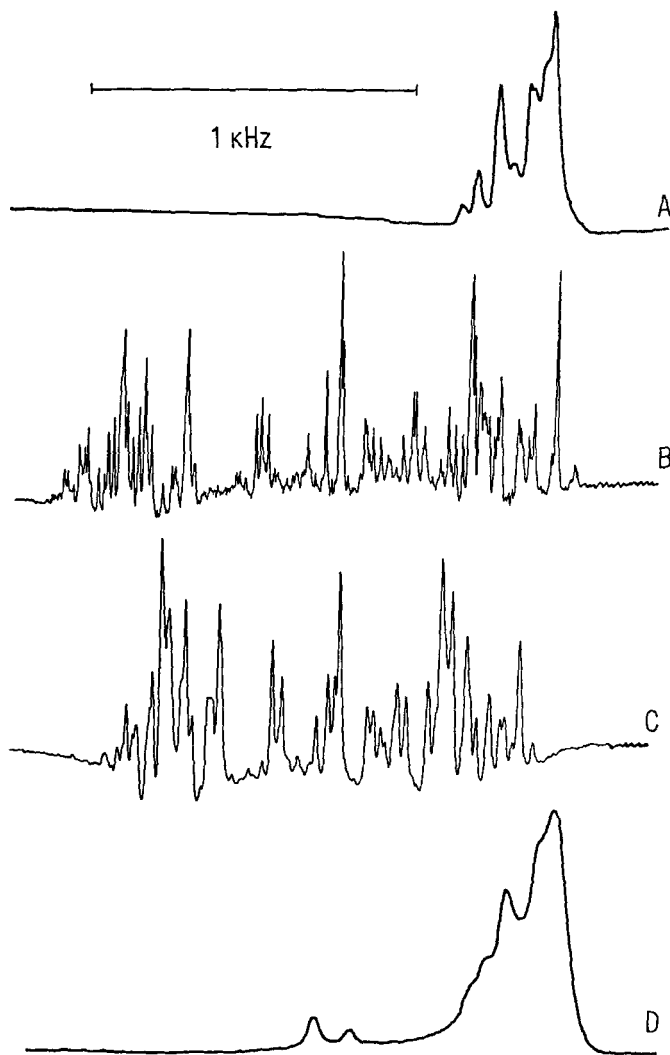


FIGURE 1. Temperature dependence of the ^1H NMR spectrum for the solution of α -BHC dissolved in ZLI1538. 79.8°C(A), 64.6°C(B), 54.6°C(C), and 36.8°C(D).

BHC affords the order parameters as well as the structural parameters⁹ at variable temperatures in the nematic and smectic phases. As is seen from the temperature dependence of the order parameter shown in Figure 2, the degree of order of the solute molecule decreases on lowering the temperature in the smectic phase, whereas it increases on lowering the temperature in the nematic phase. This fact may be

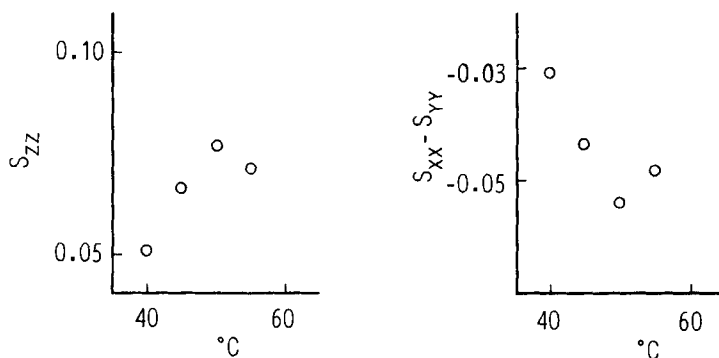


FIGURE 2. Temperature dependence of the order parameters for α -BHC in ZLI1538 at the nematic and the smectic phases. The transition temperature observed was around 70°C, 50°C, and 36°C for the isotropic to nematic, the nematic to smectic, and the smectic to plastic transitions, respectively.

explained by the idea that a solute molecule is expelled from the core region to the alkyl chain region on lowering the temperature, as already reported by several investigators.¹⁻⁵ However, the formation of a plastic crystal at temperatures just below the smectic phase suggests an alternative explanation: the solute and solvent molecules can acquire a partial disorder of rotation on lowering the temperature even in the smectic phase, leading to a reduction in the degree of order. In this sense, more detailed study of the plastic crystal would be valuable also for understanding the ordering profiles in the smectic phase.

The structural parameters of α -BHC derived at variable temperatures are listed in Table I. The solute molecule is not shown to undergo any deformations between the nematic and the smectic phases.

2. The spectrum of benzene in ZLI1538

^1H NMR spectra of benzene dissolved in ZLI1538 are shown in Figure 3 at variable temperatures. The NMR measurements were made from 74.8 to 23.3°C, and hence a plastic crystal formation reported⁸ at 11°C was not observed in the present study. The spectra in the nematic and smectic phases afford the order parameter of benzene (Figure 4). Here, the spectra are analyzed by citing indirect couplings¹⁰ and the direct couplings of D_{HH} (ortho), D_{HH} (meta), and D_{HH} (para) are obtained. These couplings are then simulated to derive the order parameter S_{zz} by a program SHAPE¹¹ after modifying to apply to the D_{6h} system. A distance of 2.481 Å¹⁰ is assumed between the ortho

TABLE I
Structural and order parameters of α -BHC in ZLI1538 at variable temperatures

	54.6°C	49.6°C	44.6°C	39.7°C
Distance ratios:				
r_{12}/r_{45}	0.798 ± 0.001	0.799 ± 0.002	0.798 ± 0.009	0.804 ± 0.010
r_{13}/r_{45}	1.205 ± 0.004	1.206 ± 0.001	1.203 ± 0.006	1.208 ± 0.008
r_{14}/r_{45}	1.328 ± 0.007	1.328 ± 0.004	1.327 ± 0.016	1.349 ± 0.010
r_{15}/r_{45}	1.200 ± 0.008	1.202 ± 0.005	1.204 ± 0.007	1.225 ± 0.033
r_{16}/r_{45}	0.783 ± 0.005	0.781 ± 0.003	0.777 ± 0.004	0.787 ± 0.012
r_{34}/r_{45}	0.984 ± 0.002	0.985 ± 0.002	0.985 ± 0.014	0.990 ± 0.012
r_{35}/r_{45}	0.843 ± 0.002	0.844 ± 0.002	0.843 ± 0.009	0.845 ± 0.004
r_{36}/r_{45}	1.291 ± 0.006	1.290 ± 0.006	1.286 ± 0.001	1.279 ± 0.001
Order parameters:				
S_{zz}	0.0659 ± 0.0006	0.0699 ± 0.0017	0.0612 ± 0.0045	0.0468 ± 0.0038
S_{xx}	-0.0544 ± 0.0006	-0.0585 ± 0.0015	-0.0499 ± 0.0036	-0.0371 ± 0.0027
S_{xz}	0.0025 ± 0.0005	0.0023 ± 0.0002	0.0027 ± 0.0012	0.0023 ± 0.0009

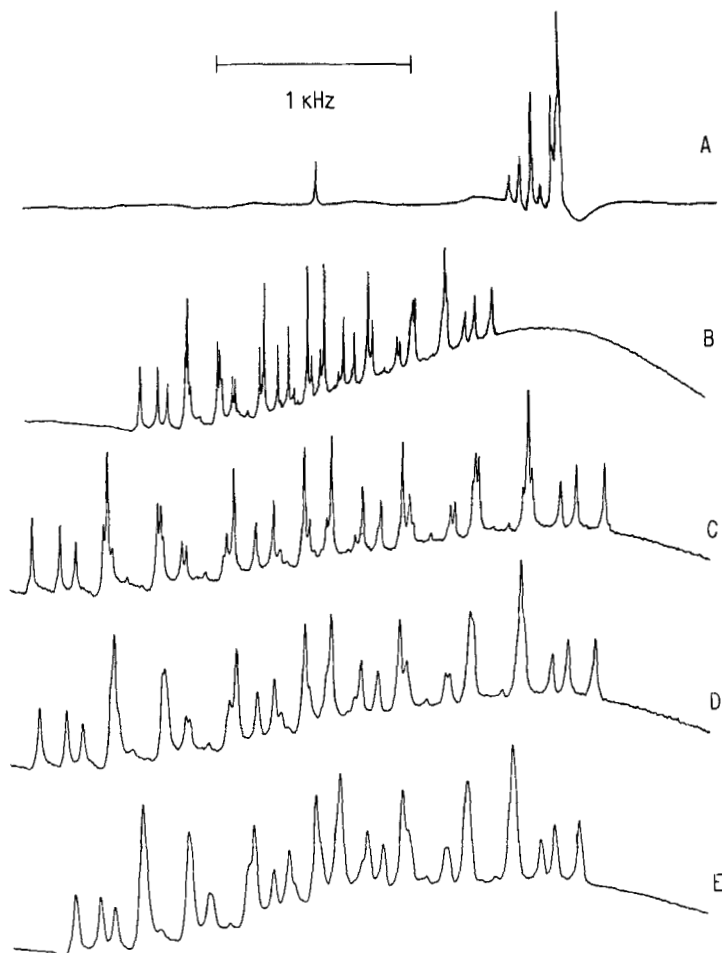


FIGURE 3. Temperature dependence of the ^1H NMR spectra for benzene dissolved in ZLI1538. 74.8°C(A), 62.8°C(B), 54.8°C(C), 33.8°C(D), and 23.8°C(E).

protons, and corrections of the harmonic vibrations are assumed to be +1.6, +0.9, and +0.7%¹⁰ for D_{HH} (ortho), D_{HH} (meta), and D_{HH} (para), respectively, considering the inversed sign of S_{zz} in the present study. The degree of order of benzene increases on lowering the temperature in the nematic phase, but it decreases on doing so in the smectic phase.

3. The spectrum of acetonitrile in ZLI1538.

Acetonitrile gives rise to a triplet with a spacing of $3D_{\text{HH}}$ when oriented in a liquid crystal. An order parameter S_{zz} can be derived from a spectrum according to the following equation.¹²

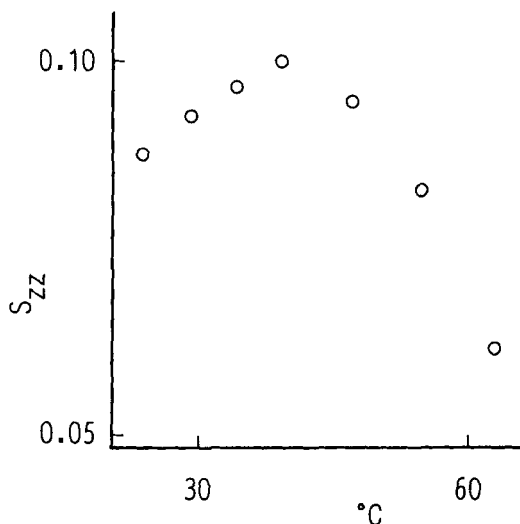


FIGURE 4. Temperature dependence of the order parameter S_{zz} for benzene in ZLI538 at the nematic and the smectic phases. The transition temperature observed was 65°C and 40°C for the isotropic to nematic and the nematic to smectic transitions, respectively.

$$D_{HH} = -(h/4\pi^2)\gamma_H^2(1/r_{HH}^3)(-1/2)S_{zz}$$

The distance of r_{HH} is assumed¹³ to be 1.814 Å in the present study. The temperature dependence of the spectrum is shown in Figure 5, and that of S_{zz} is plotted in Figure 6. Here, acetonitrile is also assumed to orient with its long axis (z axis) parallel to the long axis of the liquid crystal solvent which itself orients perpendicular to the external magnetic field, leading to a negative value of D_{HH} . The transition temperature for the nematic to the smectic phases is changed from 54°C to 48°C by the addition of acetonitrile as shown in Figure 6. The ordering is seen to be decreased on decreasing the temperature of measurement in the smectic phase. This trend has already been observed in a smectic phase of liquid crystals containing aromatic group(s) in a molecule.¹⁻⁵ It is confirmed also for the liquid crystal without an aromatic ring in the present study.

As a remarkable fact, a new triplet appears for acetonitrile below the temperature of nematic to smectic transition (Figure 5). The direct coupling D_{HH} is about three times larger for this new triplet than that for the original one, and it does not show such a large temperature dependence as observed for that of the original triplet. The spacings

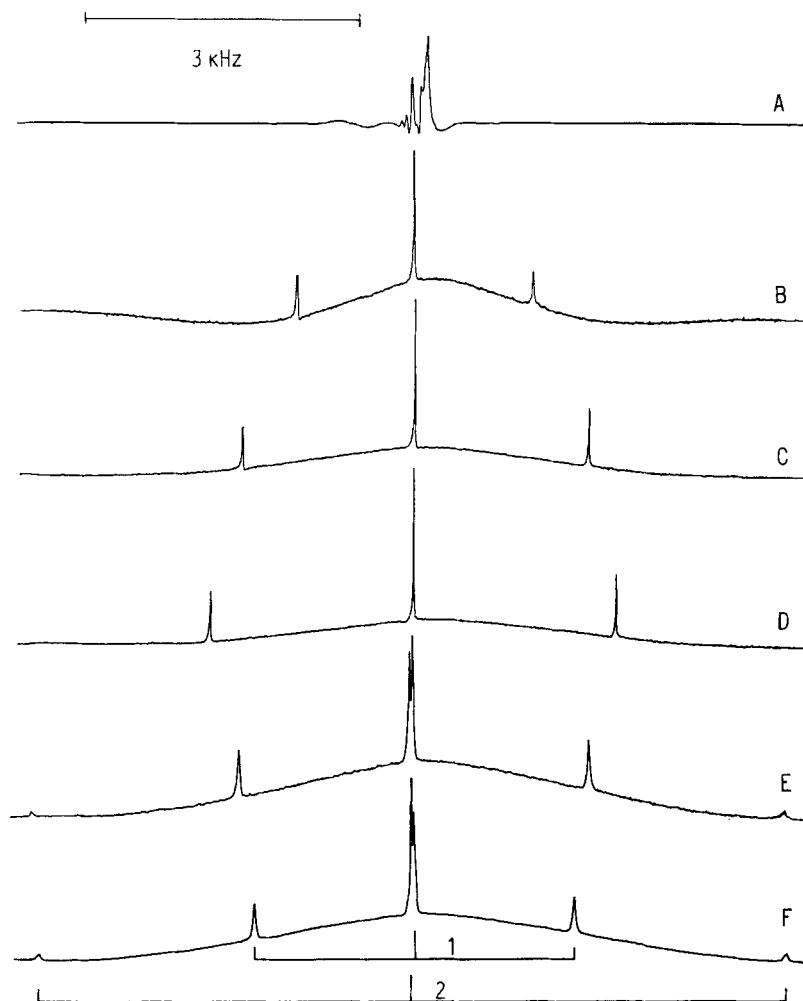


FIGURE 5. Temperature dependence of the ^1H NMR spectrum for acetonitrile dissolved in ZLI1538. 74.8°C(A), 69.7°C(B), 57.8°C(C), 47.8°C(D), 32.8°C(E), and 26.8°C(F).

of the triplets, *i.e.*, $3D_{\text{IIIH}}$, are 1741.5 Hz and 4082.1 Hz for the components 1 and 2, respectively, at 26.8°C. Some data points are lacking in Figure 6 for a new triplet just below the nematic to smectic transition because of a low signal to noise ratio in the outermost weak peaks. The signals of the two sets of triplets did not change even when the sample position was changed in the NMR probe. And hence, a macroscopic separation of the sample into two different phases was

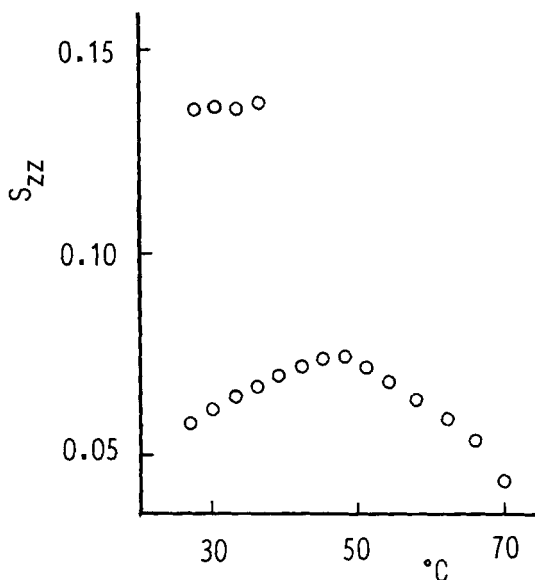


FIGURE 6. Temperature dependence of the order parameter S_{zz} for acetonitrile in ZLI1538 at the nematic and the smectic phases. The transition temperature observed was 72°C and 42°C for the isotropic to nematic and the nematic to smectic transitions, respectively. Below 42°C, a new triplet appeared (see Figure 5), the order parameter of which is also plotted.

excluded from a reason for the appearance of the two sets of triplets.

A ^{13}C NMR spectrum is shown in Figure 7, which also supports an existence of two states for acetonitrile in the liquid crystal as clearly evidenced in the relatively strong signals of the methyl group. A new quartet appears which exhibits a direct coupling D_{CH} about three times larger than that for the originally existing quartet. That is, the

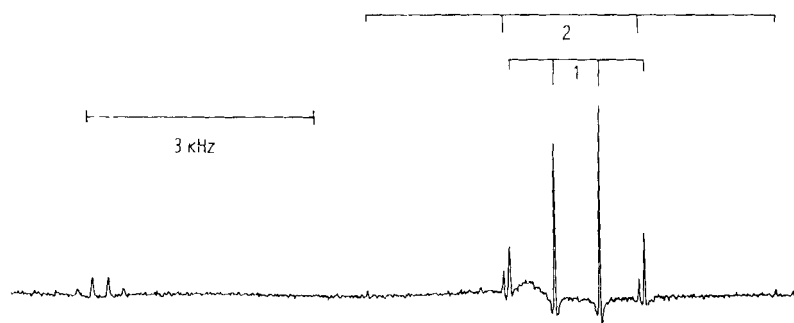


FIGURE 7. The ^{13}C NMR spectrum of acetonitrile dissolved in ZLI1538 at 25°C.

spacings in the methyl quartets which are equal to $J_{CH} + 2D_{CH}$, are 593.5 and 1785.1 Hz for the components 1 and 2, respectively. The new triplet has an intensity of about 1/5 of the original quartet in conformity with the result from the 1H NMR spectrum for the same sample at the same temperature. These results suggest that a new phase is formed in the smectic range of ZLI1538 containing acetoni-trile. Similar results have been reported for 4-*n*-butyloxybenzylidene-4-*n*-octylaniline and its mixture with 4-4'-heptyloxyazoxybenzene, for which a two-phase region of S_A and S_B is observed in the 2H NMR study.⁴

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