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The Smectic Phase of p. p'-di-n-Heptylazoybenzene: A ^{1}H NMR study of Its Anisotropy of Diamagnetic Susceptibility and of Its Use for Measuring Proton Chemical Shift Anisotropies

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The Smectic Phase of *p,p'*-di-*n*-Heptylazoxybenzene: A ^{1}H NMR Study of Its Anisotropy of Diamagnetic Susceptibility and of Its Use for Measuring Proton Chemical Shift Anisotropies

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The anisotropy of the diamagnetic susceptibility of the smectic liquid crystal *p,p'*-di-*n*-heptylazoxybenzene (HAB) has been measured by use of ^{1}H NMR. The value of $(\chi_\parallel - \chi_\perp)$ is found as e.g. $1.418 \cdot 10^{-6}$ at 318 K. Furthermore, we have observed local solvent effects of HAB on dissolved globular molecules, which are of the order of 0.10 to 0.19 ppm for methane, 0.37 to 0.44 ppm for tetramethylsilane, 0.35 to 0.40 ppm for tetramethylstannane, and 0.39 to 0.41 ppm for neopentane. These values are dependent on temperature and may lead to large uncertainties in the determination of proton chemical shift anisotropies. A theoretical treatment of the magnetic fields in the annulus of a double-wall tube and inside the inner tube filled with a smectic liquid crystal and variable angle between the applied field and the optic axis is also given.

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1. INTRODUCTION

The smectic phase of the liquid crystal *p,p'*-di-*n*-heptylazoxybenzene (HAB) has been fairly widely used as an orienting solvent in determinations of the ^{1}H chemical shift anisotropies of molecules.[1] For getting a better understanding of this liquid crystal (LC) we have measured the anisotropy of its diamagnetic susceptibility as a function of temperature, covering the isotropic, nematic and smectic phases. Furthermore, we have studied the variation of the ^{1}H chemical shifts of the solutes ^{13}C-methane, tetramethylsilane, tetramethylstannane and neopentane as a function of the angle between the applied magnetic field and the HAB LC optic axis in order to detect local solvent effects. Their knowledge is important since methane and TMS have been used as internal references in the determination of ^{1}H chemical shift anisotropies of molecules by using HAB and other smectic LC's as solvents.

2. EXPERIMENTAL

The spectra were recorded on a Bruker WH-9ODS FT spectrometer using quadrature detection and a variable temperature control unit. The samples were prepared in 5-mm double-wall tubes (Wilmad 517). D_2O was used as a locking and reference substance in the inter-wall space. The samples were turned in steps of 10° between 0° and 90°, which correspond to the situations where the liquid crystal optic axis is parallel and perpendicular to the external magnetic field.

3. THEORETICAL

In the present study we have measured the ^{1}H chemical shifts of the globular solute molecules (methane, tetramethylsilane, tetramethylstannane and neopentane), and the NMR splitting of the external reference signal (water in the present case) between the parallel and perpendicular orientations of the liquid crystal optic axis in steps of 10 degrees. Since an external referencing method was used, the expected chemical shift change arising from the 90° rotation of the sample tube because of the diamagnetic anisotropy of the LC must be known. The theory of this shift change is given in the present chapter. Furthermore, in order to understand the experimental behavior of the splitting of the reference signal, the theoretical treatment of Zimmerman and Foster[2] had to be generalized to a case where the LC optic axis makes an arbitrary angle α with the magnetic field direction.

The coordinate systems and numbering of the various regions in a cylindrical coaxial double tube are shown in Figure 1. First we consider the region 1, i.e. we give the magnetic field which the molecules experience inside the inner tube. In order to get the real effective field, one has to take into account two effects: First the so-called macroscopic field which depends on the shape of the sample cell and the bulk susceptibility of the sample cell and the sample, and second, the field arising from the continuum outside the Lorentz sphere. The resulting field can be written in the form

$$B_{1\mathrm{eff}} = B_0[1 + \tfrac{1}{2}\chi_5 - \tfrac{1}{6}(\chi_{1\parallel}\cos^2\alpha + \chi_{1\perp}\sin^2\alpha)] \qquad (1)$$

where

$$\chi_{1\parallel} = \chi_1 + \tfrac{2}{3} S_{\mathrm{LC}}\Delta\chi_1 \qquad (2)$$

$$\chi_{1\perp} = \chi_1 - \tfrac{1}{3} S_{\mathrm{LC}}\Delta\chi_1 \qquad (3)$$

χ_1 and χ_5 are the diamagnetic susceptibilities of the liquid crystal and air, respectively, $\Delta\chi_1$ is the molecular diamagnetic anisotropy, and S_{LC} the degree of order of the liquid crystal when the optic axis is parallel with the applied magnetic field ($\alpha = 0°$). From Eq. (1), one derives for

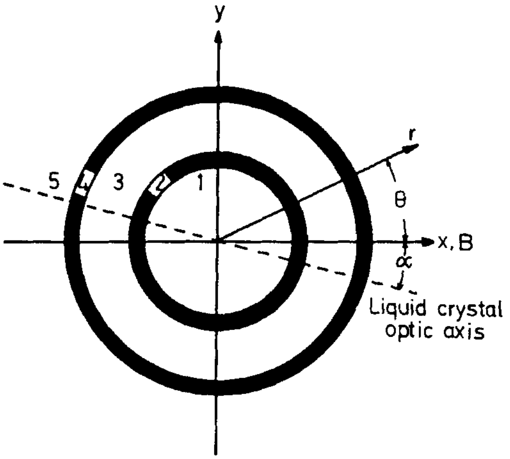

FIGURE 1 Numbering of the regions in a double tube system and definition of the coordinates used. Note that α is measured downwards from the x-axis. θ and r are polar coordinates.

the chemical shift change that the solute molecules should experience with the 90° sample rotation

$$\frac{\Delta B_{1\mathrm{eff}}}{B_0} = -\frac{1}{6}(\chi_{1\parallel} - \chi_{1\perp}). \tag{4}$$

Consequently, the experimentally observed deviations from the shift predicted by Eq. (4) yield local contributions, $\delta_{\parallel}^{\mathrm{loc}} - \delta_{\perp}^{\mathrm{loc}}$, in chemical shift differences, $\delta_{\parallel} - \delta_{\perp}$.

The field in the inter-wall region 3, B_3, of the double tube system is, to first order in susceptibility, equal to the x-component, B_{3x}, of the field. We can therefore write

$$B_3 \approx B_{3x} = A + B\cos 2\theta + C\sin 2\theta \tag{5}$$

where r and θ are polar coordinates (see Figure 1), and

$$A = B_0\left(1 + \frac{1}{2}\chi_5 - \frac{1}{6}\chi_3\right) \tag{6}$$

$$B = \frac{B_0}{2}\left[\left(\frac{a_1}{r}\right)^2(\chi_{1\parallel}\cos^2\alpha + \chi_{1\perp}\sin^2\alpha - \chi_2) - \left(\frac{a_2}{r}\right)^2(\chi_3 - \chi_2)\right] \tag{7}$$

$$C = -\frac{B_0}{2}\left(\frac{a_1}{r}\right)^2(\chi_{1\parallel} - \chi_{1\perp})\sin\alpha\cos\alpha. \tag{8}$$

χ_2 and χ_3 are the diamagnetic susceptibilities of the tube glass and reference substance, respectively, and a_1 the inner radius of the inner tube. The above equations include the two field contributions discussed in the case of B_1. In the present connection, the most interesting quantity is the splitting, $\Delta(\alpha)$, of the external reference signal observed in an NMR spectrum. Using Eq. (5) we can derive for $\Delta(\alpha)$ the relation

$$\Delta(\alpha) = \sqrt{\Delta_{\parallel}^2\cos^2\alpha + \Delta_{\perp}^2\sin^2\alpha} \tag{9}$$

where

$$\Delta_{\parallel} = \left(\frac{a_1}{a_3}\right)^2(\chi_{1\parallel} - \chi_2) - \left(\frac{a_2}{a_3}\right)^2(\chi_3 - \chi_2) \tag{10a}$$

and

$$\Delta_{\perp} = \left(\frac{a_1}{a_3}\right)^2(\chi_{1\perp} - \chi_2) - \left(\frac{a_2}{a_3}\right)^2(\chi_3 - \chi_2). \tag{10b}$$

a_2 is the outer radius of the inner tube, and a_3 the inner radius of the outer tube. $\Delta_{\parallel}$ and $\Delta_{\perp}$ give the splittings with $\alpha = 0°$ and $\alpha = 90°$, re-

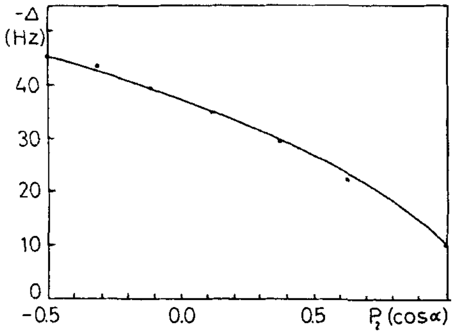

FIGURE 2 The water line splitting, $-\Delta$, as a function of $P_2(\cos\alpha)$. The solid curve was calculated from Eq. (9). (●) are experimental points with errors ±1 Hz.

spectively. The experimental and calculated $\Delta(\alpha)$ values for one set of measurements are shown in Figure 2. As one can see, the agreement is very good.

The direction angles where the B_3 field is maximum and minimum are obtained from the equation

$$\theta_0 = \frac{1}{2} \arccos \left[\pm \frac{\Delta_\parallel \cos^2\alpha + \Delta_\perp \sin^2\alpha}{\sqrt{\Delta_\parallel^2 \cos^2\alpha + \Delta_\perp^2 \sin^2\alpha}} \right] \tag{11}$$

From Eqs. (10a) and (10b), we get

$$\Delta_\parallel - \Delta_\perp = \left(\frac{a_1}{a_3}\right)^2 (\chi_{1\parallel} - \chi_{1\perp}) \tag{12}$$

and consequently, Eq. (4) leads to

$$\frac{\Delta B_{1\,\mathrm{eff}}}{B_0} = -\frac{1}{6}\left(\frac{a_3}{a_1}\right)^2 (\Delta_\parallel - \Delta_\perp). \tag{13}$$

$\Delta_\parallel$ and $\Delta_\perp$ are measurable quantities, a_3 and a_1 are known radii of the tubes. Consequently, one can determine experimentally the chemical shift which the globular molecules in a cylindrical sample cell should experience as a consequence of the 90° sample rotation. For a comparison of chemical shifts in an anisotropic phase with shifts in an isotropic phase Eq. (13) is transformed to

$$\frac{\Delta B_{1\,\mathrm{eff}}}{B_0} = -\frac{1}{4}\left(\frac{a_3}{a_1}\right)^2 (\Delta_{\mathrm{aniso}} - \Delta_{\mathrm{iso}}) \tag{14}$$

and instead of Eq. (12) we have

$$\Delta_{\text{aniso}} - \Delta_{\text{iso}} = \frac{2}{3}\left(\frac{a_1}{a_3}\right)^2 (\chi_{1\parallel} - \chi_{1\perp}). \qquad (15)$$

Δ_{aniso} and Δ_{iso} are the reference signal splittings when the sample is anisotropic and isotropic (heated to isotropic phase), respectively. From the dimensions of the tube system (Wilmad 517), one derives for $(a_3/a_1)^2$ the value of 0.310 ± 0.011.

4. RESULTS AND DISCUSSION

The anisotropy of the diamagnetic susceptibility of HAB

The measurement technique of diamagnetic anisotropy is based on the use of ^{1}H NMR as suggested by Bernheim and Krugh,[4] and later on applied by Rose[5] to MBBA. In this method, the anisotropy, $\chi_{1\parallel} - \chi_{1\perp}$, is obtained from Eq. (15) given in the previous chapter.

For the ^{1}H NMR measurements we used water (D_2O) as a reference and lock substance in the annulus of the coaxial double tube system. The splitting, Δ, of the water line was measured as a function of temperature from 344 K to 314 K. The results are shown in Figure 3.

The use of Eqs. (15) and (12) leads to diamagnetic anisotropies which are given in Table I and shown graphically in Figure 4. The Δ_{iso} value was found to be practically independent of temperature: at 340 K $\Delta_{\text{iso}} = -36.6$ Hz, while at lower temperatures $\Delta_{\text{iso}} = \frac{1}{3}(\Delta_{\parallel} + 2\Delta_{\perp})$ assumes the values of -36.4 Hz (314 K), -37.1 Hz (318 K) and -37.7 Hz (320 K) with experimental uncertainty of ± 1 Hz in each case.

The diamagnetic anisotropy obtained from the measurements, $\chi_{1\parallel} - \chi_{1\perp}$ is, as shown by Eqs. (2) and (3), equal to the product of the degree

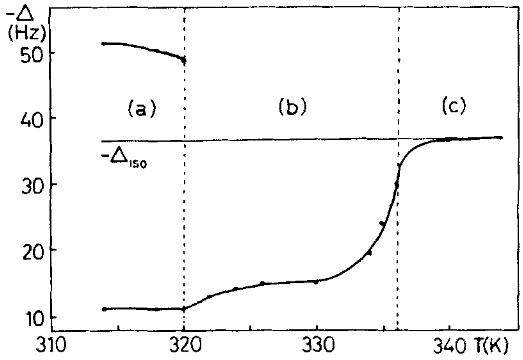

FIGURE 3 The water line splitting, $-\Delta$, as a function of temperature. (a) Smectic, (b) nematic, and (c) isotropic phase.

TABLE I

The differences of water line splittings ($\Delta_\parallel - \Delta_\perp$) or ($\Delta_{aniso} - \Delta_{iso}$) and diamagnetic anisotropy of HAB as a function of temperature.

T(K)	($\Delta_\parallel - \Delta_\perp$) or ($\Delta_{aniso} - \Delta_{iso}$) (ppm)[a]	$\chi_{1\parallel} - \chi_{1\perp}$ (ppm)[a]
314	0.447	1.440
318	0.440	1.418
320	0.429	1.382
322	0.260	1.257
324	0.249	1.203
326	0.239	1.555
330	0.239	1.555
334	0.198	0.918
335	0.136	0.657
336	0.070	0.339
340	0.	0.
344	0.	0.

[a] Estimated average errors ±0.11 ppm for $\Delta_\parallel - \Delta_\perp$ and ±0.088 ppm for $\chi_{1\parallel} - \chi_{1\perp}$.

of order of the liquid crystal, S_{LC}, and to the actual molecular susceptibility anisotropy, $\Delta\chi_1$. Thus the curve shown in Figure 4 gives the relative dependence of S_{LC} upon temperature. If one chooses the $\chi_{1\parallel} - \chi_{1\perp}$ values of 0.339 ppm (336 K) and 0.657 ppm (335 K) (near to the isotropic-nematic phase change point) as basis, then the value of 1.440 ppm (314 K) would mean a 4.2- to 2.2-fold increase in S_{LC} provided that $\Delta\chi_1$ remains constant. This leads to a conclusion that near to the isotropic-nematic phase change the degree of order of the liquid crystal falls within the range of 0.24 to 0.46. This is somewhat lower than predicted by the Maier-Saupe theory,[6] but agrees with a generally observed trend.[5,7]

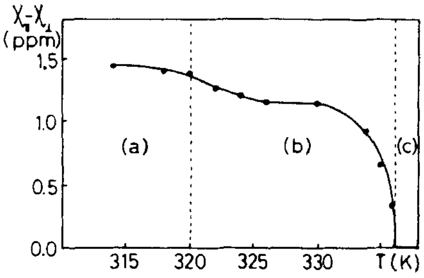

FIGURE 4 Anisotropy of diamagnetic susceptibility, $\chi_{1\parallel} - \chi_{1\perp}$, of HAB at various temperatures. (a) Smectic, (b) nematic, and (c) isotropic phase.

^{1}H chemical shifts of globular molecules

The experimental ^{1}H chemical shifts of ^{13}C-methane at various temperatures are given in Table II. Since the shifts were measured with respect to an external water reference, they include a contribution arising from the diamagnetic anisotropy of the liquid crystal. These contributions can be calculated from Eqs. (13) and (14). Table II lists also the corrected chemical shifts. The comparison of the shift differences, $\delta_\parallel - \delta_\perp$, at 320 K and lower temperatures yields differences of 8.9 to 15.2 Hz (0.10 to 0.17 ppm) in local shielding effects on methane as a consequence of the sample rotation by 90°.

Also the ^{1}H chemical shifts, $\delta_\parallel$ and $\delta_\perp$, of methane, tetramethylsilane, tetramethylstannane and neopentane were measured in the smectic phase of HAB at 292 K and 304 K or at 304 K and 312 K. The results are given in Table III. They show that the differences of the local contributions at $\parallel$ and $\perp$ orientations, $\Delta\delta_{\mathrm{local}}$, are the same (appr. 0.40 ppm at 304 K) within the experimental uncertainty for all the $(CH_3)_4X$ (X = Si, Sn, C) compounds and more than twice as large as the one observed for methane.

The experimental ^{1}H chemical shift anisotropies of various types of molecules range from −7 to +22 ppm[1], which for an assumed average degree of order of $S = 0.07$ correspond to observed chemical shift

TABLE II

The ^{1}H chemical shifts of ^{13}C-methane in HAB with respect to an external HDO reference as a function of temperature. Shifts are given in Hz (at 90 MHz) and are accurate to ±0.5 Hz.

	Experimental		Corrected for diamagnetic anisotropy	
T(K)	$\delta_\parallel$	$\delta_\perp$	$\delta_\parallel^{a}$	$\delta_\perp^{b}$
344	394.4		394.9	
340	395.4		394.9	
336	393.2		389.8	
335	387.9		385.0	
334	386.7		381.1	
330	387.0		377.5	
326	388.0		377.5	
324	389.2		376.4	
322	389.4		375.5	
320	390.6	402.4	373.5	394.2
318	392.8	400.2	373.5	394.8
314	396.4	400.8	373.5	395.3

[a] From Eq. (14).
[b] From Eq. (13).

TABLE III

The ^1H chemical shifts of globular solute molecules in HAB as a consequence of a 90° rotation between the *LC* optic axis and the applied magnetic field. All values in ppm.

Params.	Measured shift $\delta_\parallel - \delta_\perp$			Variation of water reference splitting $\Delta_\parallel - \Delta_\perp$			Calculated shift[a]			Difference in local effects $\Delta\delta_{local}$[b]		
Molecule T(K)	292	304	312	292	304	312	292	304	312	292	304	312
$^{13}CH_4$	0	−0.03		0.36	0.33		−0.19	−0.18		0.19	0.15	
$(CH_3)_4Si$	0.25	0.19		0.36	0.33		−0.19	−0.18		0.44	0.37	
$(CH_3)_4Sn$		0.18	0.14		0.41	0.40		−0.22	−0.21		0.40	0.35
$(CH_3)_4C$		0.20	0.18		0.39	0.40		−0.21	−0.21		0.41	0.39

[a] From Eq. (13).

[b] Estimated error ±0.02 ppm in each case.

changes by 90° sample rotation of approximately -0.5 to $+1.5$ ppm. Consequently, the shift of a reference signal due to local effects plays an important role in determinations of proton chemical shift anisotropies and the observed variations may introduce errors as large as 30% of the anisotropy. Futhermore the observed shift of any dissolved molecule very probably contains an unknown contribution of local effects which, as our measurements indicate, increases with molecular volume.

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