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Determination of order parameters of liquid crystals: use of dipolar oscillations enhanced by Lee–Goldburg decoupling

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Lee–Goldburg decoupling has been applied to enhance dipolar oscillations during the t_1 period of the two-dimensional experiment used for obtaining order parameters of the liquid crystal *N*-(4-ethoxybenzylidene)-4-*n*-butylaniline (EBBA) at different temperatures. The order parameters of the aromatic core obtained by this method are in agreement with values obtained from the ^{2}H NMR spectra of a selectively labelled compound and are observed to follow the empirical Haller equation.

1. Introduction

Natural abundance ^{13}C NMR provides a convenient method for the study of order in liquid crystals. Two-dimensional variable angle spinning has been used extensively for this purpose [1]. In addition, chemical shift measurements [2] and dipolar splittings due to coupling to heteronuclei such as ^{2}H, ^{15}N [3] and ^{19}F [4, 5] have also been shown to be useful for such studies. We have earlier proposed the use of carbon–proton dipolar couplings, determined from the transient oscillations observed during Hartmann–Hahn (HH) cross polarization, for the determination of the order parameter of nematic liquid crystals [6]. In the separated local field two-dimensional version of this experiment, several proton–carbon dipolar couplings and the corresponding order parameters could be determined. These oscillations are highly damped due to the dipolar coupling among the protons. Consequently the two-dimensional cross peaks are broad and hard to observe. In the case of solids, Wu *et al.* [7] have shown that the use of Lee–Goldburg (LG) decoupling [8] during cross polarization results in the removal of homonuclear dipolar coupling, leading to a reduction of the linewidth along the dipolar axis. We have applied this method to the case of the liquid crystal *N*-(4-ethoxybenzylidene)-4-*n*-butylaniline (EBBA). The order parameters of the liquid crystal have been determined at different temperatures and the values obtained compared with those obtained from ^{2}H NMR. The core order parameter is observed to follow the established temperature dependence.

2. Experimental

The experiments were carried out on a sample of liquid crystal EBBA (figure 1) in its nematic phase at 309, 318, 332 and 344 K. One- and two-dimensional

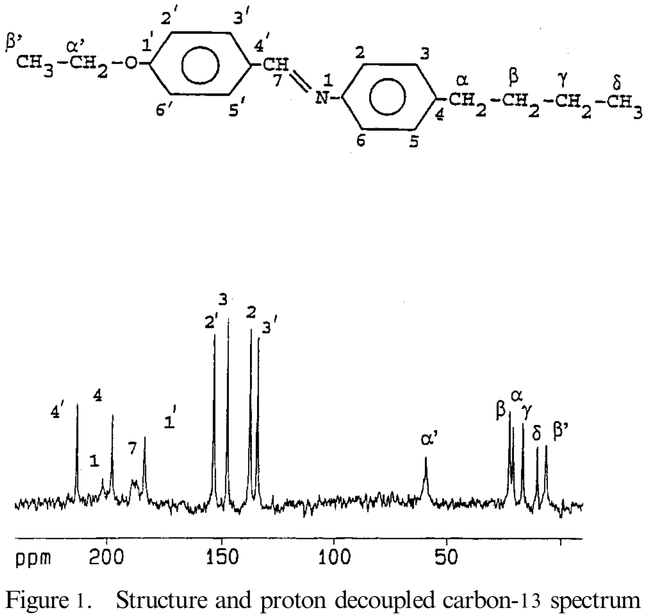

Figure 1. Structure and proton decoupled carbon-13 spectrum of EBBA recorded at 75.47 MHz at 318 K.

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^{13}C NMR spectra were recorded at 75.47 MHz with a Bruker DSX-300 FTNMR spectrometer. The pulse sequence shown in figure 2 was used for recording the two-dimensional spectra. Proton magnetization is transferred to the carbons during the initial HH contact period t_a. During t_b the remaining proton magnetization is destroyed with the proton rf being switched off while the ^{13}C magnetization remains spin-locked. The latter undergoes oscillatory transfer between protons and carbons during the t_1 period. During this period the proton offset and carbon power level are changed to satisfy both LG and HH conditions so that magnetization exchange between proton and carbon takes place under homonuclear proton spin decoupling. During the t_2 period carbon magnetization is acquired with proton decoupling. It has been shown by Bielecki *et al.* [9] that the frequency-switched LG sequence is more effective in removing homonuclear dipolar couplings than the original scheme proposed by Lee and Goldburg [8]. However the requirement of a 3 μs delay for phase and frequency switching on our instrument led to large phase distortions and adversely affected implementation of this scheme.

The effect of LG decoupling is illustrated in figure 3, where the lengthening of the dipolar oscillations for the case of the C_7 carbons is shown. The two-dimensional spectra were collected as phase sensitive spectra and the States algorithm [10] was used for the two-dimensional Fourier transformation. Spectra were symmetrized about the ω_1 axis. Typically 30 complex t_1 domain data sets were acquired with 16 scans for each data point. The t_1 increment was 50 μs. The delay between scans was kept long (45 s) to avoid rf heating which is more in this experiment due to the high value of ^{13}C rf power used to satisfy HH match during LG decoupling. The homonuclear decoupling during t_1 leads to a scaling of the heteronuclear dipolar couplings; the theoretical scaling factor of 0.82 has been assumed here. Using widths of the peaks along the ω_1 direction the maximum error in the measured dipolar couplings and order parameters has been estimated as ±5%.

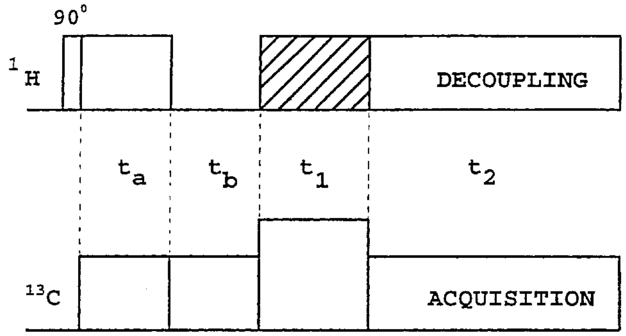

Figure 2. Pulse sequence for the two-dimensional experiment for the observation of dipolar oscillations under LG decoupling of protons during t_1. The spectra were recorded using a rf field of 60 kHz for the protons. For carbon-13, the rf fields were 60 kHz during the preparation period ($t_a + t_b$) and 125 kHz during the evolution period (t_1).

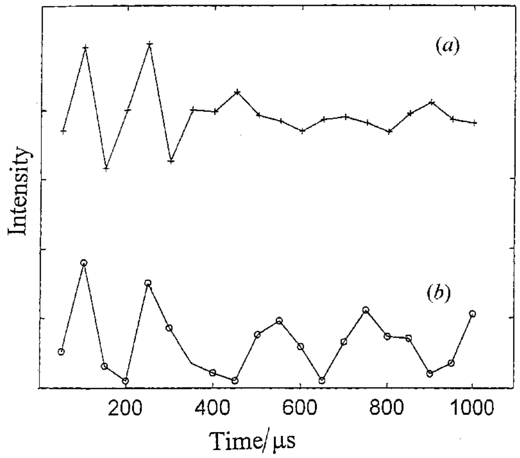

Figure 3. The intensities of the C_7 carbon of EBBA as a function of t_1 obtained after Fourier transformation along t_2 of the two-dimensional data-set obtained using the pulse scheme shown in figure 2; (*a*) with on resonance proton rf during t_1 and (*b*) with LG decoupling during t_1.

^{2}H NMR spectra of EBBA labelled at the 2- and 6-positions were also recorded at the temperatures indicated above on the DSX-300 FTNMR spectrometer at a resonance frequency of 46.07 MHz.

3. Results and discussion

Figure 1 shows the proton decoupled ^{13}C spectrum of EBBA at 318 K. The spectral lines were initially assigned in the isotropic phase using the two-dimensional DQFCOSY sequence [11]. In the nematic phase the assignment of the methylene α′ peak of the ethoxy moiety and the α, β, γ peaks of the aliphatic chain were based on the assignments in the isotropic phase. However of the two methyl peaks, the high field peak appearing at 6.5 ppm (figure 1) was assigned to the methyl carbon belonging to the O–CH_2–CH_3 group, unlike in the solution phase, where this peak appears at a lower field compared with that of the other methyl carbon. This change was made based on the experimentally determined order parameters, which is discussed below. The assignment of the benzylidene carbon based on earlier reports [3, 6] could also be confirmed due to the presence of the cross peaks in the two-dimensional spectrum which distinguish it from other aromatic quaternary carbons. The assignments of the aromatic part are based on earlier reports on the homologous compound *N*-(4-methoxybenzylidene)-4-*n*-butylaniline (MBBA) [3, 12]. The two-dimensional spectrum recorded at 318 K is shown in figures 4 (*a*) and 4 (*b*) for the aliphatic and aromatic regions, respectively. The cross peaks have

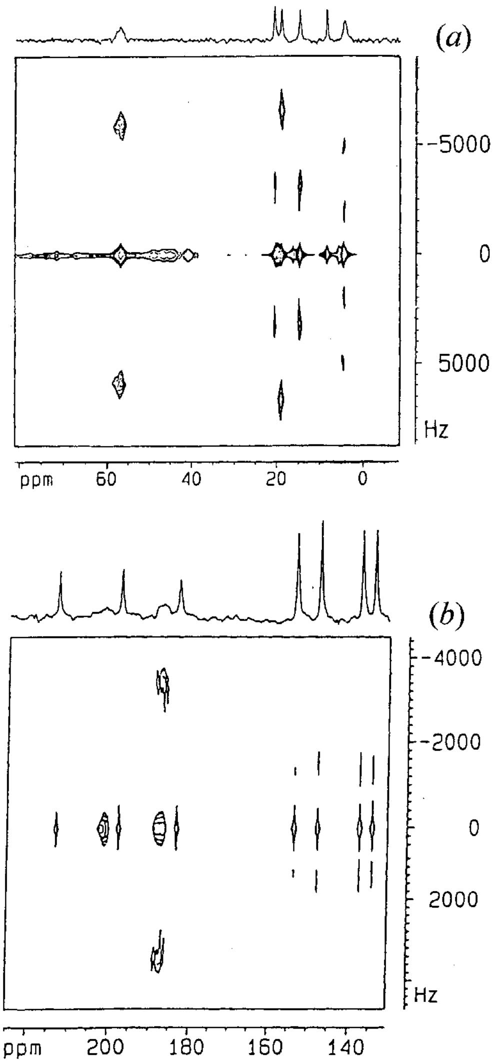

Figure 4. Two-dimensional spectrum of (*a*) the aliphatic carbons, (*b*) aromatic carbons of EBBA recorded at 75.47 MHz and at 318 K. The data-set was collected on a Bruker DSX-300 NMR spectrometer with 16 scans acquired for each of the set of 30 complex t_1 data points. The time domain was zero filled to 256×4096 points and Fourier transformed using the States algorithm. The projection along ω_2 axis of the two dimensional spectrum is also shown.

much higher intensities with the LG decoupling during t_1 than without it, due to the reduced linewidth. The cross peak, after appropriate scaling, gives the transient oscillation frequency f which is related to the dipolar and the indirect spin–spin coupling constants as follows [6, 13]:

For the C$\underline{\text{H}}$ group, $f = (D + J/2)$; and for the CH$_2$ group $f = \sqrt{2}(D + J/2)$.

For the methyl group, three cross peaks may be expected at frequencies

$$f = (D + J/2),\ \sqrt{3}(D + J/2) \text{ and } 2(D + J/2). \qquad (1)$$

Here,

$$D = \left(\frac{\gamma_I \gamma_S}{4\pi r_{IS}^3}\right) S_{CH} \qquad (2)$$

where γ_I, γ_S are the gyromagnetic ratios of protons and carbons respectively, r_{IS} is the internuclear vector, and S_{CH} is the order parameter along the dipolar vector. In figure 4 (*a*), cross peaks have been observed for all the carbons of the aliphatic chain except for one of the methyl carbons. Each of these carbons and its directly bonded protons have been considered as an isolated group. From the frequency of the cross peaks, the CH dipolar couplings and the corresponding order parameters averaged over several conformations have been calculated by neglecting J and assuming $((\gamma_I\gamma_S)/(4\pi r_{IS}^3))$ to be equal to 22.68 kHz, corresponding to a proton–carbon distance of 1.1 Å. Protons attached to the neighbouring carbons will alter the oscillation frequency as discussed in detail for the aromatic carbons. But for the aliphatic carbons this influence is taken to be negligible.

For the methyl carbon which is appearing at 6.5 ppm, two of the three cross peaks mentioned earlier, equation (1), are observed and these have been assigned to peaks expected at D and $2D$. This leads to an averaged dipolar coupling and order parameter for this methyl group which are comparable to those of the C_γ carbon but less than that of C_α' carbon. This methyl peak has been assigned as due to the C_β' carbon for the following reason. In general, the mobility towards the end of the aliphatic chain increases and the order parameter decreases significantly. For liquid crystals such as 5CB, 6CB and 7CB the ratio of order parameter of the terminal methyl group to that of its neighbouring methylene group ranges from 0.70 to 0.025 [14]. In the present case, if the methyl peak at 6.5 ppm is assigned to the C_β' carbon, this ratio is around 0.50 at all four temperatures of the experiment. On the other hand, if this peak is assigned to the C_δ carbon the corresponding numbers range between 0.77 and 1.00. This indicates that it is appropriate to assign this peak to C_β' rather than to C_δ. The low field methyl peak at 10.5 ppm is then assigned to the C_δ carbon. The absence of a cross peak in the dipolar dimension for this carbon indicates that the dipolar coupling in this case is very nearly zero. The order parameters S_{CH} for the aliphatic carbons at four different temperatures are shown in table 1.

In the aromatic part, apart from the protonated carbons of the phenyl group, the benzylidene carbon (C_7) shows intense cross peaks. The latter are particularly difficult to observe without the LG decoupling as, in the one-dimensional spectrum, the benzylidene carbon is broadened due to coupling to the neighbouring nitrogen.

Table 1. Order parameters S_{CH} for the aliphatic carbons and S for the aromatic core of EBBA, at four different temperatures.

	Temperature/K			
Carbon	309	318	332	344
α	0.27	0.26	0.23	0.21
β	0.17	0.14	0.11	0.10
γ	0.18	0.14	0.10	0.09
α’	0.26	0.23	0.20	0.16
β’	0.14	0.13	0.10	0.08
Core	0.67	0.57	0.47	0.36

From the corresponding dipolar coupling the order parameters of the liquid crystalline core S has been calculated with the assumption that the molecular order can be described by a single order parameter and that the preferred axis of orientation of the molecule lies in the plane of the rigid azomethine group [3] and by using [15]:

$$D = S(\gamma_I \gamma_S / 4\pi r_{IS}^3)(3\cos^2\theta - 1)/2 \qquad (3)$$

where θ is the angle between the director and C_7H bond. As in the case of MBBA [3, 6] values of 114° for the angle $C_4'C_7H$ and 3.5° for the angle between the director and the $C_4'C_7$ bond have been assumed and the calculated values of S are shown in table 1. Following Magnuson *et al.* [16], the values of S thus obtained are fitted to the empirical Haller equation [17]

$$S = S_0(1 - T/T^*)^f \qquad (4)$$

where T^* is the nematic–isotropic transition temperature. The fit (figure 5) yielded a value of $S_0 = 0.96$, $f = 0.20$ and $T^* = 346.3$ K.

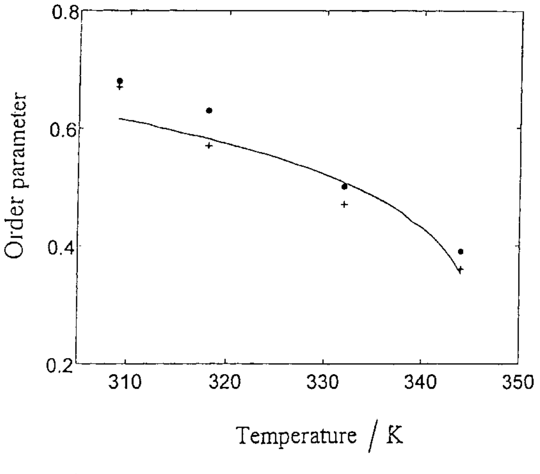

Figure 5. Order parameter of the aromatic core of EBBA at different temperatures; + corresponds to values obtained from the C_7H dipolar couplings, ● corresponds to those obtained from the deuterium NMR. The solid line has been obtained by fitting the former to the empirical Haller equation.

From the S values of the core at different temperatures, the proton–carbon dipolar couplings of the aromatic carbons can be calculated, assuming a perfect hexagonal geometry of the phenyl ring and fast flip motion about the *para*-axis. The couplings D_o, D_m of each of the carbons in the *ortho*-position to its own proton and the proton attached to the neighbouring meta carbon, respectively, were taken into account. In cases where the carbon is coupled to more than one proton, with different coupling strengths, the evolution of magnetization during cross polarization is predicted to take place in a ‘locked mode’ [18], and the dipolar oscillation frequencies were calculated as $(D_o^2 + D_m^2)^{1/2}$. These were compared with the experimental values after scaling. There is a good correlation between calculated and experimental values, as shown in table 2.

The deuterium NMR spectrum (figure 6) of selectively deuteriated EBBA is a doublet of doublets; the larger doublet separation is due to quadrupole splitting of the deuterons and the smaller doublet separation arises due to dipolar couplings to neighbouring protons. From the quadrupole splitting, the molecular order parameters of EBBA have been calculated at different temperatures using a quadrupole coupling constant of 187 kHz for the aromatic C–D bond [19] and are shown in figure 5. These values agree well with those calculated from ^{13}C experiments.

Table 2. Experimental and calculated dipolar oscillation frequencies of the aromatic C_3 carbon of EBBA at different temperatures.

	Dipolar oscillation frequency/kHz	
Temperature/K	Experimental	Calculated
309	2.15	2.44
318	1.92	2.10
332	1.50	1.32
344	1.24	1.09

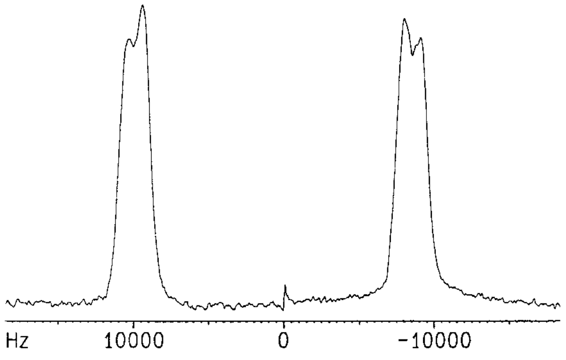

Figure 6. ^2H NMR spectrum of EBBA labelled at 2- and 6-positions, recorded on a DSX-300 NMR spectrometer at 318K and 46.07 MHz.

4. Conclusion

The use of Lee-Goldburg decoupling during the t_1 period in a two-dimensional separated local field experiment, in which dipolar oscillations are used to estimate the proton–carbon dipolar couplings in a liquid crystal sample, yields enhanced resolution for the cross peaks. This leads to the estimation of the averaged order parameters along the aliphatic chain. The order parameter of the long axis of the molecule has been estimated from the C_7 H dipolar coupling at different temperatures. These values are in reasonable agreement with those estimated by the standard procedure in which ^{2}H NMR spectra of selectively labelled compounds are used.

The dipolar oscillation frequencies for the protonated aromatic carbons are influenced by more than one coupling. The agreement between experimental and calculated values in these cases indicates that these frequencies can be used to estimate the order parameters in systems such as cyanobiphenyls; work on these systems is in progress.

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