Assignment of the quadrupolar splittings in fully deuteriated alkyl chains of liquid crystalline compounds The case of 4-*n*-hexyloxy-4'-cyanobiphenyl

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Assignment of the quadrupolar splittings in fully deuteriated alkyl chains of liquid crystalline compounds

The case of 4-*n*-hexyloxy-4'-cyanobiphenyl

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There have been disagreements about the assignment of the quadrupolar splittings in the deuteriated *n*-hexyl chain in 4-*n*-hexyloxy-4'-cyanobiphenyl (6OCB); these are resolved by comparing the splittings of the deuteron resonances in the fully deuteriated chain compound with those in the material with a selectively deuteriated chain. The methods available for assigning the quadrupolar splittings in fully deuteriated chains are then applied to 6OCB and it is concluded that measurement of spin-lattice relaxation times, T_1, is the best method.

1. Introduction

Deuterium NMR has proved to be the most important method for investigating the orientational order of molecules in liquid crystalline phases. The reasons are twofold: the simple nature of the spectra, and the equally simple relationship between the quadrupolar splittings, Δv_i, and site-specific, local order parameters, S^i_{CD}. There is, however, one major draw-back in that the spectra do not contain enough information to allow an unambiguous assignment of the Δv_i to positions of the deuterons in alkyl chains. This problem is highlighted by the case of 6OCB, which was studied first by Counsell *et al.* [1], as part of a test of a molecular mean field theory developed for flexible molecules. The theory is based on that introduced originally by Marcelja [2], and modified subsequently by Emsley, Luckhurst and Stockley [3]. The essential step in such theories is the construction of $U_{\text{ext}}(n, \beta, \gamma)$, a conformationally-dependent potential of mean torque for a molecule which can exist in n conformations in a uniaxial liquid crystalline phase. The angles β and γ are those made by the director in a reference frame fixed in a rigid fragment of the molecule. The potential is assumed to be second-rank, thus

$$U_{\text{ext}}(n, \beta, \gamma) = - \sum_{2,k} \varepsilon_{2,k}(n) C_{2,k}(\beta, \gamma), \qquad (1)$$

where the $C_{2,k}(\beta, \gamma)$ are modified spherical harmonics, and the interaction parameters,

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$\varepsilon_{2,k}(n)$ are the sum of contributions, $\varepsilon_{kp}(j)$, from each rigid sub-unit in the molecule, so that

$$\varepsilon_{2,k}(n) = \sum_p \varepsilon_{kp}(j)D_{pk}^2(\Omega_j(n)), \tag{2}$$

with $D_{pk}^2(\Omega_j(n))$ the second-rank Wigner function which describes the orientation, $\Omega_j(n)$, of fragment j in the reference axes in conformation n.

The potential of mean torque is used to calculate order parameters, $S_{CD}^i(n)$ for C–D bonds in the nth conformation, and then the conformationally-averaged values are obtained from

$$S_{CD}^i = \sum_n p_{LC}(n)S_{CD}(n). \tag{3}$$

The probabilities, $p_{LC}(n)$, of the conformations in the liquid crystalline phase are given by

$$p_{LC}(n) = Z^{-1}\exp\{-U(n,\beta,\gamma)/kT\}, \tag{4}$$

with

$$Z = \sum_n \int \exp\{-U(n,\beta,\gamma)/kT\}\sin\beta\,d\beta\,d\gamma. \tag{5}$$

Here $U(n,\beta,\gamma)$ is the total mean potential, and is

$$U(n,\beta,\gamma) = U_{ext}(n,\beta,\gamma) + U_{int}(n), \tag{6}$$

where $U_{int}(n)$ is that part of the mean potential which depends on n and which does not vanish in the isotropic phase. For n-alkyl chains it has been usual to assume a model for $U_{int}(n)$ such that only the *trans*, t, and *gauche* $\pm$, $g\pm$, forms generated by rotation about the C–C bonds are populated, and in this case

$$U_{int}(n) = N_g E_{tg}, \tag{7}$$

where N_g is the number of *gauche* forms in a conformer, and E_{tg} is the energy difference between t and $g+$ or $g-$.

When applying this model to the experimental data, the calculated S_{CD}^i are brought into best agreement with the observed values derived from the quadrupolar splittings by adjusting the $\varepsilon_{2p}(j)$ and E_{tg}. This procedure has been applied to several kinds of mesogen with good agreement being obtained between observed and calculated S_{CD}^i. However, in most cases the Δv_i have not been assigned unambiguously and the correct assignment has been taken to be that which produces the best agreement with theory.

For 6OCB the theories give the best agreement with experiment when the Δv_i are assumed to decrease sequentially along the chain towards the methyl group [1,4]. However, a study by Poon *et al.* [5] suggests that the S_{CH}^i, determined from ^{13}C–H dipolar couplings do not show this steady decrease, but have a reversal at positions 3 and 4. This experiment relies on an assignment via ^{13}C chemical shifts, and the assumption that the variation of these with position is the same in the liquid crystalline and isotropic phases. In a liquid crystalline phase the position of a resonance line depends on σ_{izz}, the component along the field direction of the shielding tensor, σ_i. For
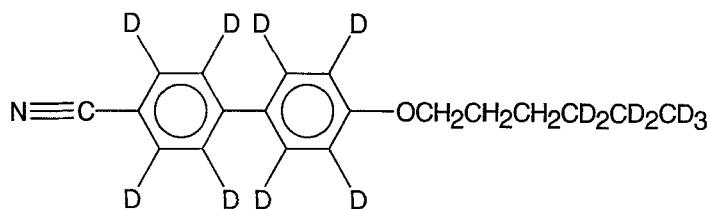
Figure 1.   Structure of 6OCB-d_{15}.

molecules with a positive anisotropy in their magnetic susceptibility, which is the case for 6OCB, σ_{izz} is given by

$$\sigma_{izz} = \sigma_i^0 + \tfrac{2}{3}S_{aa}^i\{\sigma_{iaa} - \tfrac{1}{2}(\sigma_{ibb} + \sigma_{icc})\} + \tfrac{1}{3}(S_{bb}^i - S_{cc}^i)(\sigma_{ibb} - \sigma_{icc}). \qquad (8)$$

S_{aa}^i etc. are local order parameters for the principal axes of the shielding tensor of the *i*th nucleus. Equation (8) can be expressed as

$$\sigma_{izz} = \sigma_i^0 + \sigma_{izz}^{\text{aniso}}. \qquad (9)$$

The term σ_i^0 is the shielding of the *i*th nucleus in an isotropic phase, so that the change in shielding on entering a liquid crystalline phase is

$$\sigma_{izz} - \sigma_i^0 = \sigma_{izz}^{\text{aniso}}. \qquad (10)$$

The anisotropic contribution, $\sigma_{izz}^{\text{aniso}}$, may vary with position in the chain so as to change the relative chemical shifts, and so the assignment of Poon *et al.*, is not unambiguous. Indeed the concensus has favoured the assignment based on agreement with the predictions of the theoretical models.

We report here experiments on a specifically deuteriated 6OCB-d_{15}, whose structure and pattern of deuteriation are shown in figure 1, which give a virtually unambiguous assignment of the Δv_i, and which show that Poon *et al.*, were correct, and that the theoretical models produce the wrong assignment. Having obtained an assignment, it is possible to assess the success of methods of relating the Δv_i in 6OCB to positions of the deuterons, and which could be easily applied to similar compounds.

2.   Experimental

2.1.   *Synthesis of 6OCB-d_{15}*

An important intermediate for the specific deuteriation of 6OCB is 4-hydroxy-4′-bromobiphenyl-d_8 which was prepared from 4-hydroxybiphenyl-d_9 followed by esterification to obtain biphenyl-d_9-4-phenylsulphonate and bromination to yield 4-bromobiphenyl-d_8-4-phenylsulphonate. Saponification to give 4-hydroxy-4′-bromobiphenyl-d_8 and subsequent cyanation gave 4-cyano-4′-hydroxybiphenyl-d_8 (**I**). The individual steps are described in detail by Zimmerman [6]. The other intermediate required is the specifically deuteriated *n*-hexyl bromide-d_7(**II**). This was obtained by homologation [6, 7] of the Grignard compound of *n*-propyl bromide-d_7 with α, ω-dibromopropane. The alkylation of (**I**) with (**II**) was done using cylohexanone/K_2CO_3 in the usual way. The final product, 6OCB-d_{15}, was verified by NMR, TLC and mass spectrometry ($M_Z = 294$). The specific deuteriation was better than 98 per cent.
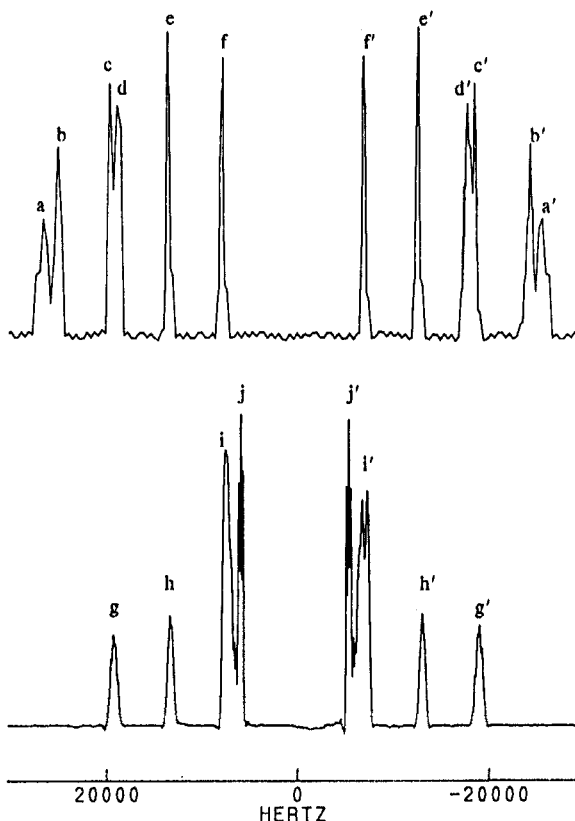
Figure 2.   30·7 MHz spectra of the deuterons in 6OCB-d_{13} (top), and 6OCB-d_{15} (bottom) at approximately 330 K.

3.   Results and discussion

3.1.   *Assignment by comparing the ^2H spectra from fully and partially deuteriated alkyl chains*

Figure 2 shows the spectrum from the six groups of deuterons in a sample of 6OCB, which has a fully deuteriated alkyl chain and a fully protonated biphenyl group, 6OCB-d_{13}, recorded at approximately 330 K. Peaks f and f' are from the CD_3 deuterons. The assignment in doubt concerns peaks c,c' and d,d', and this is achieved by recording the ^2H spectrum from 6OCB-d_{15}, whose spectrum is also shown in figure 2, again at approximately 330 K. The quadrupolar splittings are strongly temperature dependent, and, although the temperature of the sample is maintained to a precision of 0·1°C, the temperatures of different samples cannot be set equal to one another with a sufficient precision to identify whether peaks g and g' in the spectrum of 6OCB-d_{15} correspond to c and c' or d and d' in the spectrum of 6OCB-d_{13}. The problem is overcome by comparing ratios of splittings in the two samples over a range of temperatures. Thus, peaks h and h' in the spectrum of 6OCB-d_{13} are readily assigned to peaks e and e' in the spectrum of 6OCB-d_{15}, and all previous studies agree that these stem from the deuterons at position 5 in the carbon chain. Peaks g and g' in figure 2 are then assigned by comparing the ratios of the splittings $(h - h')/(g - g') = R_1$ in the spectra of 6OCB-d_{15} with the ratios $(e - e')/(d - d') = R_2$ and $(e - e')/(c - c') = R_3$ in the spectra of 6OCB-d_{13}. R_1 varies from $0·677 \pm 0·005$ close to T_{NI} to $0·697 \pm 0·005$ at an

approximate $T_{\text{NI}}-T$ of 20°C. The two ratios obtained from data on 6OCB-d_{13} over the same temperature range have values in the ranges of $R_2 = 0.707 \pm 0.005$ to 0.725 ± 0.005, and $R_3 = 0.673 \pm 0.005$ to 0.699 ± 0.005. Clearly this identifies R_1 for 6OCB-d_{15} with R_3 for 6OCB-d_{13}, and so peaks g and g' correspond to c and c', and these belong to deuterons at position 4 in the carbon chain.

These experiments confirm the assignment made by Poon *et al.* [5], that $\Delta v_3 < \Delta v_4$, and the complete assignment of the quadrupolar splittings is $\Delta v_1 > \Delta v_2 > \Delta v_4 > \Delta v_3 > \Delta v_5 > \Delta v_6$.

3.2. *Assignment from chemical shifts*

If chemical shifts can be resolved and assigned in the isotropic phase, and can be obtained for the liquid crystalline phase, then an assignment is possible if the anisotropic contribution, $\sigma_{izz}^{\text{aniso}}$, does not change the relative shifts. As noted earlier, this does work for the ^{13}C shifts in 6OCB, but the uncertainty of what determines the magnitudes of $\sigma_{izz}^{\text{aniso}}$ makes this an unreliable method for other compounds.

Proton and deuterium shifts can be obtained for isotropic samples, but only deuterium shifts are easily obtained, albeit with low precision, for liquid crystalline samples. For 6OCB the resonances from protons at positions 1 and 2 are the only ones of the methylene groups which are clearly resolved and assignable on isotropic samples at 500 MHz. For liquid crystalline samples, the shifts of the deuterons at the same positions can also be obtained as the centres of the quadrupolar doublets in the ^{2}H spectrum at 30.7 MHz and they have the same relative values as those in the isotropic phase.

3.3. *Relaxation rates*

The spin-lattice relaxation rates of deuterons in liquid crystalline materials, T_{1i}, are determined by overall motion of the molecules (MR), rotations about bonds (IR) [8, 9], and director fluctuations (DF) [10]. The simplest models of the DF mechanism predict a dependence on Δv_i^2, but this mechanism is believed to be unimportant for ^{2}H relaxation at 30.7 MHz [11]. Models for relaxation based on MR and IR [8, 9, 12] all predict that T_{1i} values should decrease monotonically along a chain attached to a large, rod-like group such as the cyanobiphenyl group in 6OCB. Thus, if these mechanisms dominate the T_{1i} values, then the resonances in 6OCB-d_{13}, shown in figure 2, should have relaxation rates in the order $T_{1a} < T_{1b} < T_{1d} < T_{1c} < T_{1e} < T_{1f}$. The values of T_{1i} were measured for a sample of 6OCB-d_{13} at approximately 330 K by the inversion recovery method using the pulse sequence $180° - \tau - 90°$. The values of T_{1i} obtained are

Peaks	a, a'	b, b'	c, c'	d, d'	e, e'	f, f'
T_{1i}/ms	11	22	51	40	88	311

The values of T_{1i} are obtained by measuring the intensities of the peaks, and this is difficult when peaks partially overlap, as occurs for peaks c and d, which are those whose assignment was previously in doubt. The peak overlap will introduce errors into the absolute values of the T_{1i}, but a confirmation that the relative values are correct can be easily obtained by recording spectra with τ set so that the peaks are at their null points, which occurs for $\tau = 0.693\, T_{1i}$. Figure 3 shows peaks c and d for such settings of τ over a range where the two peaks change from being inverted, pass through zero, and become positive, and this clearly shows that d relaxes faster than c.

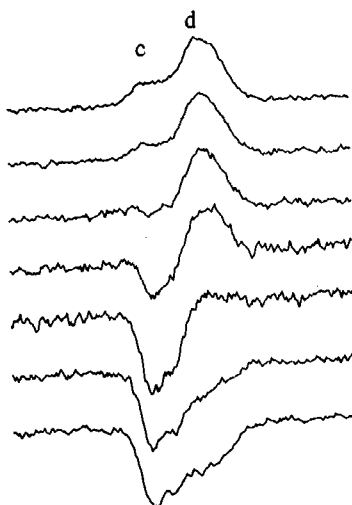Thus, the T_{1i} in 6OCB do in fact decrease sequentially down the alkyl chain, and

Figure 3.   Part of the spectra obtained from the inversion recovery sequence for values of $\tau = 16$ (bottom) to 28 ms, showing peaks c relaxing at a slower rate than d.

this would appear to be a good way of assigning the quadrupolar doublets in compounds of similar shape. Note that the sequential reduction in T_{1i} along a chain in compounds $C_nD_{2n+1}X$ may not occur when X is small, or when it is large and disc shaped.

3.4. *Assignment from COSY deuterium spectra*

The 2D COSY experiment can be used to assign first-order proton spectra, and the same experiment has been shown to be useful for assigning quadrupolar doublets in liquid crystals [13]. This experiment is particularly useful when there are two deuteriated alkyl chains in the mesogen, when the COSY spectrum clearly shows connections within but not between chains. A COSY spectrum was recorded of the deuterons in 6OCB-d_{13}, but with the disappointing result that connections are seen between all deuterons, so that it is not possible to decide which deuterons are neighbours in the chain.

4.   Conclusions

Of the methods available for assigning the quadrupolar doublets of deuterons in the fully deuteriated chains of liquid crystal, the only certain method is the synthesis of partially deuteriated derivatives. This is, however, a difficult and lengthy task. The results obtained for 6OCB suggest that comparing values of T_{1i} provides a simple, fast method, and this is recommended over the use of chemical shifts. The latter, however, for ^{13}C also gives the correct assignment for 6OCB, but will not necessarily be successful for other mesogens.

The failure of the theoretical models to predict the correct assignment for 6OCB could be indicating a major inadequacy in these models, or may be more trivially a result of choosing inappropriate geometrical parameters. Clearly, however, this discrepancy between theory and experiment warrants further investigation.

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