

## STUDY OF LIQUID CRYSTAL CONFORMATION BY MULTIPLE QUANTUM NMR: *n*-PENTYL CYANOBIPHENYL

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The multiple quantum NMR spectrum of 4-cyano-4'-*n*-pentyl- $d_{11}$ -biphenyl in the nematic phase is presented. The subspectra of the higher quantum transitions are easier to interpret than the single quantum spectrum. A preliminary analysis of the biphenyl conformation indicates that the dihedral angle is  $32 \pm 1^\circ$ .

### 1. Introduction

In this letter we show the application of multiple quantum NMR to the analysis of molecular conformation. The proton spectrum of 4-cyano-4'-*n*-pentyl- $d_{11}$ -biphenyl (5CB- $d_{11}$ , fig. 1) is used in a preliminary analysis of the biphenyl moiety. The NMR spectrum of 5CB- $d_{11}$  and an analogous molecule have previously been used to study the order parameters of the nematic mesophase [1,2]. However, the single quantum spectrum of 5CB- $d_{11}$  is complex and difficult to analyze for structural parameters without further deuterium substitution. Here we show that the higher quantum transitions are well resolved and allow simple and direct assignment of spectral lines to a theoretical model. The predictions of group theory are easily checked against the spectral features of the six- and seven-quantum regions.

In section 2 we briefly describe the technique of multiple quantum NMR in liquid crystals. Section 3 describes some experimental details and section 4

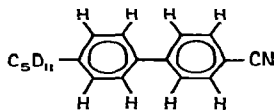


Fig. 1. The molecule 4-cyano-4'-*n*-pentyl- $d_{11}$ -biphenyl (5CB- $d_{11}$ ). The multiple quantum NMR spectrum of the biphenyl group protons is used to determine the nematic phase order parameters and the angle of twist between the rings.

presents a simple analysis of the biphenyl conformation in 5CB- $d_{11}$  based on the multiple quantum spectrum. In section 5 we discuss the requirements for a more complete analysis.

### 2. Multiple quantum NMR in liquid crystals

In conventional single quantum NMR, the selection rule determining the number of possible transitions is  $\Delta M = \pm 1$  for a change in the total magnetic quantum number. In multiple quantum NMR transitions corresponding to  $\Delta M = M_i - M_j$  for all allowed  $M_i$  and  $M_j$  may be observed [3-5]. The number of eigenstates with quantum number  $M_i$  decreases as  $|M_i|$  increases and so the highest order (largest  $\Delta M$ ) transitions are fewest in number.

In the proton NMR of liquid crystal molecules the major spectral features are due to intramolecular dipolar couplings. Intermolecular couplings are usually negligible due to rapid diffusion. As the number of protons increases, an analysis of the spectrum may become intractable due to the many overlapping lines. Multiple quantum NMR simplifies the spectrum by reducing the number of lines in a given spectral width. For  $N$  protons the  $N - 1$  and  $N - 2$  quantum transitions are usually sufficient to determine all dipolar couplings. Resolved transitions in lower orders may also be used to improve the analysis.

### 3. Experimental

The liquid crystal 4-cyano-4'-*n*-pentyl- $d_{11}$ -biphenyl ( $T_{C-N} = 23^{\circ}\text{C}$ ,  $T_{N-I} = 31^{\circ}\text{C}$ ) was synthesized by the procedure of Gray and Mosley [6] with a slight modification. An olefin which was produced as a side product from the reduction of 4-bromo-4'-pentanoyl- $d_9$ -biphenyl was further reduced to 5CB- $d_{11}$  by platinum oxide and deuterium gas in ethyl acetate at atmospheric pressure. The isotopic purity was found to be approximately 98%. A sample of about 400 mg was sealed under vacuum in a 6 mm o.d. glass tube. All spectra were taken at a regulated temperature of  $26.0^{\circ}\text{C}$ .

The spectrometer is a homebuilt Fourier transform instrument equipped with a persistent superconducting magnet operating at a proton Larmor frequency of 182 MHz. A four-pulse sequence ( $90_{\phi}$ ,  $\tau$ ,  $90_{\phi}$ ,  $t_1/2$ ,  $180_{\phi}$ ,  $t_1/2$ ,  $90_{\phi}$ ,  $\tau$ ) described elsewhere [3] was used to acquire a multiple quantum free in-

duction decay. A spin echo was produced by the 180 pulse and served to remove broadening due to magnet inhomogeneity. The multiple quantum orders were separated by time proportional incrementation of the rf phase [3,4]. Fourier transformation of the signal yielded a spectrum similar to that shown in fig. 2, but with line intensities dependent on the value of the parameter  $\tau$  in the pulse sequence. Averaging magnitude spectra obtained from different  $\tau$  values ensures that the resulting intensity distribution will more closely resemble that expected from a completely non-selective excitation process.

Six 16k multiple quantum free induction decays were obtained for values of  $\tau$  ranging from 0.4 to 1.4 ms. An increment of  $1.0 \mu\text{s}$  in  $t_1$  defined the effective acquisition dwell time. The magnitude spectra of 32k Fourier transforms were averaged to obtain the spectrum of fig. 2. With this choice of parameters, the frequency resolution of the spectrum is 30.5 Hz. The average linewidth is approximately 120 Hz.

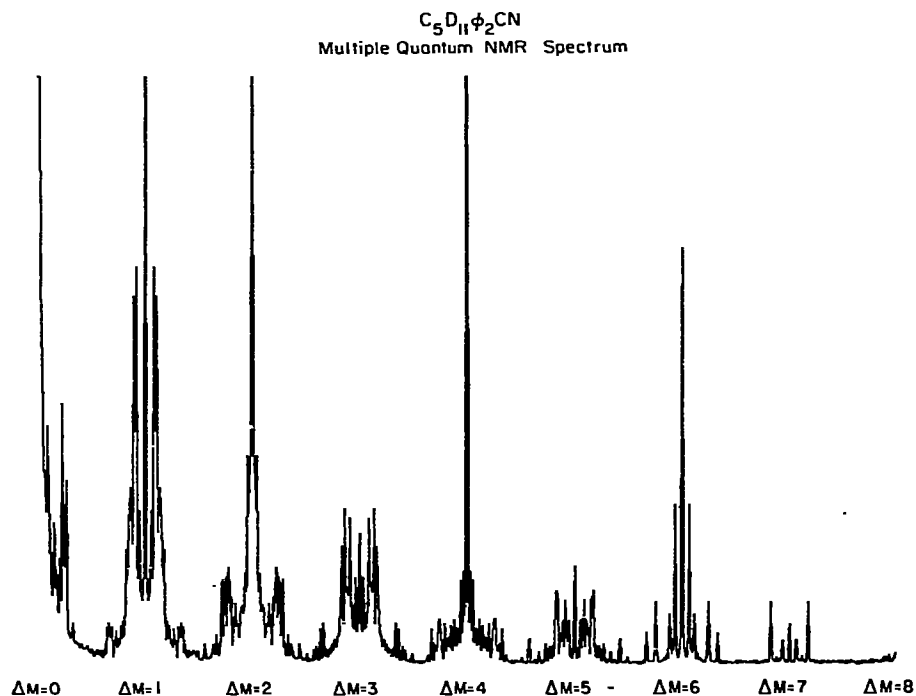


Fig. 2. Proton multiple quantum NMR spectrum of 5CB- $d_{11}$ . The multiple quantum subspectra are separated according to the order of the transitions. The change in magnetic quantum number,  $\Delta M$ , for each group of lines is indicated beneath the subspectra. Only one half of the symmetric zero- and eight-quantum regions is shown. The full width shown is 500 kHz.

#### 4. Results and analysis

The multiple quantum spectrum of  $5CB-d_{11}$  is shown in fig. 2. The one-quantum region is indeed very complex and impossible to analyze at this level of resolution. Expanded traces of the six- and seven-quantum regions are shown in fig. 3. The stick spectra in fig. 3 will be discussed below. To find the dipolar coupling constants, consider as a simple case the

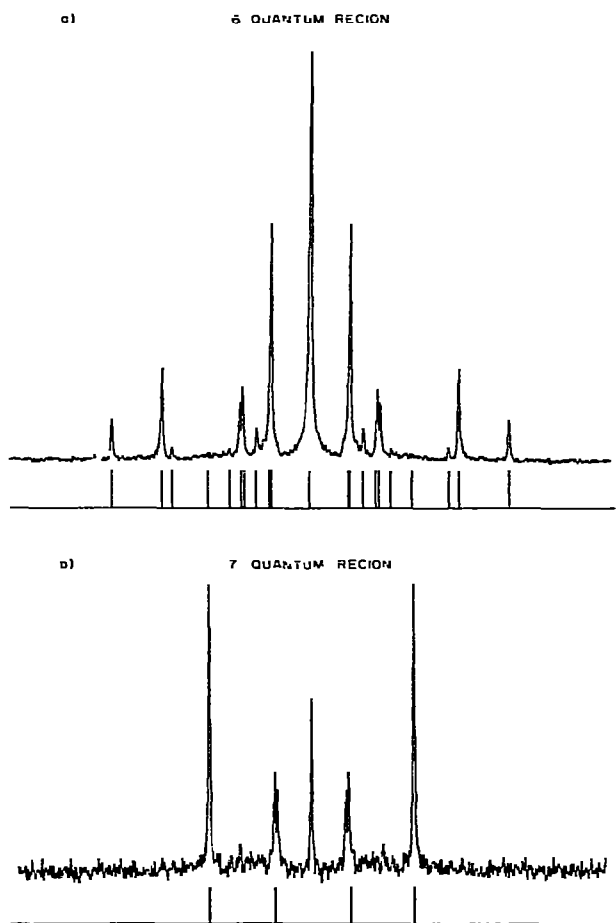


Fig. 3. Experimental and theoretical six- and seven-quantum spectra of  $5CB-d_{11}$ . The spectral width of the traces is 62.5 kHz. Beneath the experimental spectra are shown the theoretical transition frequencies based on a least-squares iterative fit of the couplings in table 1. All the lines in the theoretical spectra are of unit height. (a) Six-quantum region. (b) Seven-quantum region. The central line here is an artifact arising from the method of acquisition.

molecular fixed axis system of fig. 4. We first assume the couplings are an average of the four equivalent conformations related by the dihedral angle  $\phi$  (the angle of twist between the rings) [7-9]. Since the two rings are asymmetrically substituted, they may be distorted from a phenyl ring geometry differently. This implies a permutation symmetry isomorphous with the  $D_2$  point group for the proton spins. There are then a total of twelve unique dipolar couplings. Three order parameters may be obtained from the spectra. From group theory it may be shown that the number of lines expected in the  $N - 1$  spectrum of  $N$  protons is related to the number of distinct types of spins. By distinct it is meant that couplings to these spins form a distinct set. For the above choice of symmetry there are four distinct protons in the biphenyl group. This should give rise to four doublets in the seven-quantum spectrum. In a similar manner it is predicted that the six-quantum spectrum should consist of forty-one lines (fourteen doublets, six triplets). If  $R = R'$  in fig. 4, then further symmetry of the biphenyl group leads to a prediction of a different number of lines. For this case a permutation group isomorphous with the  $D_4$  point group is appropriate. There are then seven unique dipolar couplings and only two independent order parameters,  $S_{zz}$  and  $S_{xx} - S_{yy}$ , can be obtained from the spectra. We then predict four seven-quantum lines (two doublets) and twenty-one six-quantum lines (seven doublets,

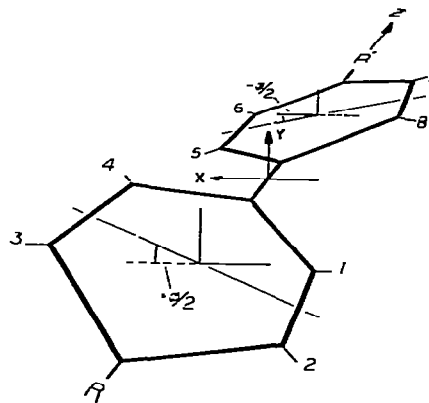


Fig. 4. Schematic diagram of the biphenyl moiety. The molecular fixed axis system is shown with the origin centered on the C-C inter-ring bond. The  $x$  axis bisects the dihedral angle  $\phi$  and the  $z$  axis lies along the para-substituted carbons. For  $5CB-d_{11}$   $R = CN$  and  $R' = C_5D_{11}$ .

three triplets). Comparing these results with fig. 3 indicates that any asymmetry of ring distortion is small. We therefore use as a simple first approximation the  $D_4$  point group in our model for the biphenyl group symmetry.

The experimental spectrum was fit to theoretical transition frequencies using the seven dipolar couplings as parameters in a least-squares iterative computer program. The iterative portion of this program is similar to the LAOCN3 computer program [10]. In addition, the program calculates allowed multiple quantum transitions based on the symmetry relations among the eigenstates. If it is not necessary to calculate all orders for a fit, then the computer memory requirement of this program is much less severe than that of a conventional single quantum simulation and iteration. This is because only those submatrices of the hamiltonian actually involved in the transitions need to be diagonalized. A total of twenty-four lines from the five-, six- and seven-quantum orders were used in the iteration to produce a fit with an rms error of 26 Hz. The theoretical six- and seven-quantum line positions are shown as stick spectra in fig. 3. The resulting coupling constants are given in table 1.

We may now interpret these couplings in terms of a model for molecular geometry and internal motion. For the possible motion about  $\phi$ , two models may be considered. In the first, only the lowest energy state in the potential well is appreciably populated and no averaging over other states is performed. This is the model usually chosen for substituted biphenyls [7-9]. As the potential barrier to rotation is expected to be

only a few kcal/mole [11], a model which averages over the rotation should be more appropriate. Previous work on 4,4'-dichlorobiphenyl has shown that the difference in fits obtained from these two models is small [7]. In our case, the couplings are not as precisely determined as those for 4,4'-dichlorobiphenyl and the first model proves adequate.

The two order parameters and some of the parameters defining the geometry may be found from the coupling constants. In a simplified model, we assume a phenyl ring geometry equal to that of benzene ( $r_{12} = 2.48 \text{ \AA}$ ,  $r_{14} = 4.30 \text{ \AA}$ ,  $r_{C-H} = 1.08 \text{ \AA}$ ) and find  $S_{zz}$  to be  $0.568 \pm 0.001$ . Taking a value of the inter-ring C-C bond length equal to that of biphenyl (1.50  $\text{\AA}$ ) [12], we then vary  $S_{xx} - S_{yy}$  and  $\phi$  over a number of values. As in the work on 3,3',5,5'-tetrachlorobiphenyl [8], it is found that the rms deviation of calculated to observed couplings exhibits a sharp minimum with respect to  $\phi$ . For 5CB- $d_{11}$  this minimum is at  $\phi = 32 \pm 1^\circ$ . The minimum with respect to variations of  $S_{xx} - S_{yy}$  is much less pronounced and occurs at  $0.057 \pm 0.002$ . The final rms deviation at the minimum is 15.8 Hz.

## 5. Discussion

The value of the dihedral angle  $\phi$  in 5CB- $d_{11}$  has not been previously reported. However, NMR of 5CB- $d_{11}$  and an analysis of the single quantum spectrum have indicated that  $32^\circ$  is a reasonable value [13]. The rms deviation of the fit of calculated to observed couplings is larger than expected from experimental errors in the  $D_{ij}$ . The use of a benzene geometry for the phenyl rings contributes to the deviation. The couplings  $D_{14}$  and  $D_{23}$  are not equal within the experimental uncertainty and so ring distortion should be included in the model. In addition, slight splittings of lines in the seven-quantum spectrum of fig. 3 are evidence for deviations from the  $D_4$  symmetry assumed in this analysis. The inclusion of vibrational averaging of the nuclear coordinates is expected to further reduce the deviation between the model and experimental coupling constants [2].

Before proceeding with a more detailed modeling of the biphenyl structure, two aspects of the experiment require investigation. The first is the addition of deuterium decoupling to the multiple quantum

Table 1  
Experimental coupling constants for 4-cyano-4'-*n*-pentyl- $d_{11}$ -biphenyl

Dipolar couplings (Hz)		Scalar couplings a) (Hz)	
$D_{12}$	$-4477 \pm 1$	$J_{12}$	8.0
$D_{13}$	$48 \pm 2$	$J_{13}$	0.0
$D_{14}$	$389 \pm 2$	$J_{14}$	2.0
$D_{15}$	$-1742 \pm 2$	$J_{15}$	0.0
$D_{16}$	$-364 \pm 2$	$J_{16}$	0.0
$D_{23}$	$381 \pm 3$	$J_{23}$	2.0
$D_{26}$	$-148 \pm 3$	$J_{26}$	0.0

a) Assumed values.

pulse sequence. The use of the 180 pulse in the presence of proton–deuteron couplings will complicate the spectrum in its full analysis. There are several ways to approach this problem. Currently we are investigating the use of double quantum deuterium decoupling [14]. As the largest proton–deuteron coupling has been estimated to be  $\approx 100$  Hz [3], and the deuterium spectrum is approximately 50 kHz, the double quantum decoupling requirements are moderate.

The second point involves the resolution of the multiple quantum spectrum. Obtaining all orders simultaneously increases the computer storage required to maintain the frequency precision. One solution would involve the use of selective preparation of multiple quantum transitions [15] which would require the acquisition of only one or several orders.

## 6. Conclusions

We have presented the simplification of a complicated NMR spectrum by the use of multiple quantum transitions. This technique has allowed line assignments to a theoretical spectrum to be made from a reduced set of well-resolved lines in the high-order spectra without the need for selective isotope labeling. Symmetry characteristics of *n*-pentyl cyanobiphenyl are clearly displayed in these spectra. Computer requirements for spectral fitting are much less severe than in the normal single quantum case. With increased resolution and deuterium decoupling the experimental coupling constants should be determined with greater precision, allowing an improvement in analysis over our extremely simple  $D_4$  symmetry model for the biphenyl group.

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