Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

# Nematic and Smectic Ordering of 4-n-Octyl-4′-cyanobiphenyl Studied by Carbon- 13 NMR

B. M. Fung [a] , Chi-Duen Poon [a] , Mahinda Gangoda [a] , Eric L. Enwall [a] , Tuan A. D. Diep [a] & Chuong V. Bui [a]

[a] Department of Chemistry, University of Oklahoma, Norman, Oklahoma, 73019, U.S.A.

Version of record first published: 20 Apr 2011.

To cite this article: B. M. Fung , Chi-Duen Poon , Mahinda Gangoda , Eric L. Enwall , Tuan A. D. Diep & Chuong V. Bui (1986): Nematic and Smectic Ordering of 4-n-Octyl-4′-cyanobiphenyl Studied by Carbon- 13 NMR, Molecular Crystals and Liquid Crystals, 141:3-4, 267-277

To link to this article: http://dx.doi.org/10.1080/00268948608079614

*Mol. Cryst. Liq. Cryst.*, 1986, Vol. 141, pp. 267–277
0026-8941/86/1414-0267/$20.00/0

Printed in the United States of America



# Nematic and Smectic Ordering of 4-*n*-Octyl-4′-cyanobiphenyl Studied by Carbon-13 NMR

B. M. FUNG, CHI-DUEN POON, MAHINDA GANGODA, ERIC L. ENWALL, TUAN A. D. DIEP, and CHUONG V. BUI

*Department of Chemistry, University of Oklahoma, Norman, Oklahoma 73019, U.S.A.*

(*Received July 28, 1986*)

A new NMR method called RHODIUM (*R*emoval of *HO*monuclear *DI*polar-couplings and the *U*se of off-*M*agic-angle-spinning) has been applied to study the molecular ordering of 4-*n*-octyl-4′-cyanobiphenyl (8CB) as a function of temperature. C—H dipolar coupling constants of various carbon atoms in 8CB were obtained from natural abundance carbon-13 NMR. Order parameters of the benzene rings and those of the C—H bonds in the octyl chain were calculated from the dipolar coupling constants. The order parameter of the —CN axis can also be calculated from the chemical shift of the —CN group. The results are consistent with the second order nature of the smectic A-nematic phase transition in 8CB.

*Keywords:* 4-*n*-octyl-4′-cyanobiphenyl, 8CB, order parameters, carbon-13 NMR

## I. INTRODUCTION

Many physical and spectroscopic methods have been used to study the ordering of liquid crystals. Nuclear magnetic resonance (NMR) probes the ordering and motion of individual parts of the liquid crystal molecules, offering the advantage of obtaining information on the molecular level.[1] Molecular ordering of liquid crystals has been studied extensively by deuterium NMR, using specially deuterated compounds.[1] Investigations of detailed molecular ordering by proton and carbon-13 NMR have often been limited to small solute molecules, because extensive dipolar couplings usually make it impossible to

obtain dipolar coupling constants for individual pairs of nuclei in a liquid crystal.

Recently we have developed a method called RHODIUM (Removal of HOmonuclear DIpolar-couplings and the Use of off-Magic-angle-spinning) to study molecular ordering of liquid crystals by carbon-13 NMR in natural abundance.[2,3] Using this method, C—H dipolar coupling constants for individual carbon atoms in a liquid crystal molecule can be measured, and order parameters can be obtained without special isotopic labelling. The principles of this method are: (1) the liquid crystal sample is spun rapidly (~1 kHz) at an angle slightly different from the magic angle (54.7°), so that the nematic or smectic director aligns along the spinning axis, and dipolar couplings are reduced by a factor of $(3\cos^2\theta - 1)/2$,[4–6] where $\theta$ is the angle between the spinning axis and the magnetic field ($B_o$); (2) an efficient homonuclear dipolar decoupling sequence (BLEW-48)[7,8] is applied to remove proton-proton dipolar couplings, so that proton-carbon couplings cause first-order splittings in the carbon-13 spectrum;[9] (3) a two-dimensional technique called separated local field spectroscopy (SELOFIS)[10–13] is used to resolve the coupling patterns of individual carbon atoms. Details of this method and its application to the study of EBBA,[2] 5CB, 6CB, and 7CB[3] have been described elsewhere.

In this paper, we report the application of the RHODIUM method to study the nematic and smectic ordering of 4-*n*-octyl-4′-cyanobiphenyl (8CB).

## II. EXPERIMENTAL

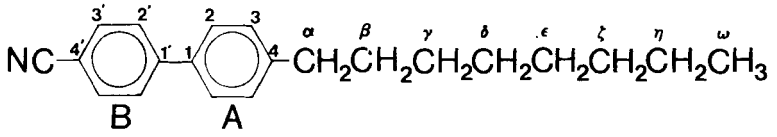
8CB was obtained from EM Chemicals, Hawthorne, New York. According to the manufacturer, its transition temperatures are, in °C: K(21.5)$S_A$(33.5)N(40.5)I. The smectic A phase can be aligned with its director along the rotor axis when the sample is gradually cooled from its nematic phase while it is rapidly spun.

All NMR spectra were measured with a Varian XL-300 NMR spectrometer, using a variable-angle spinning probe manufactured by Dotty Scientific, Columbia, South Carolina.

For least squares fitting of the spectra, data from the XL-300 spectrometer were transmitted as plot data commands at 9600 baud and captured with an Apple IIe computer where they were converted into a table of x, y coordinate values and stored directly as a text file on a floppy disk. Other experimental details were given in a previous paper.[3]

## III. RESULTS

The proton-decoupled carbon-13 spectrum of 8CB




at 36.0°C is shown in Figure 1. The chemical shifts of 8CB in an isotropic phase (in $CDCl_3$) were assigned previously.[14] Due to the closeness of the aliphatic carbon signals and the larger linewidths in the liquid crystalline phases, the β and ζ peaks in the spectrum (Figure 1) overlap, as do the δ and ϵ peaks. This is in contrast to 5CB, 6CB, and 7CB, for which all the carbon signals are resolved in the nematic phase with off-magic-angle spinning.[3]

In the two dimensional SELOFIS method, spectra in the $\omega_2$ dimension show chemical shifts of different carbons, similar to those in Figure 1. Spectra in the $\omega_1$ dimension show proton-carbon splittings of individual peaks. Those for the protonated aromatic carbons at two temperatures are shown in Figure 2.

When an appropriate dipolar decoupling sequence is used, the spectra in the $\omega_1$ dimension are first order[2,3,8,9] and the splitting between adjacent peaks in a multiplet is given by

$$\Delta\nu = f\cdot[(3\cos^2\theta - 1)D + J], \tag{1}$$

where $f$ is a scaling factor characteristic of the dipolar decoupling sequence, $D$ is the C-H dipolar coupling constant, and $J$ is the C—H scalar coupling constant. We found that the BLEW-48 sequence[7] is most efficient for dipolar decoupling with moderate radiofrequency power ($\gamma\beta_2/2\pi \approx 20$ kHz).[8,9] Its scaling factor is $f = 0.420$.

Each spectrum in parts (a) and (c) in Figure 2 is a superposition of four peaks which result from couplings of the carbon with the directly bonded proton and the ortho proton, respectively. The splittings ($\Delta\nu$) can be obtained by deconvolution of the spectrum into four Lorentzians using least squares analysis. Parts (b) and (d) in Figure 2 show the computed spectra and their components. Couplings with other protons are not resolved. However, it is of interest to note that the linewidths of the four carbons show the relation $3>2\approx 2'>3'$ due to different contributions of unresolved long range dipolar couplings with protons in other parts of the molecule. This is reasonable

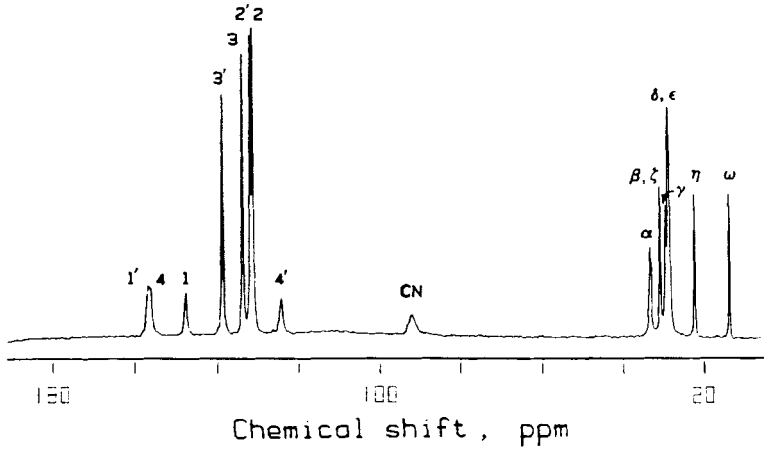



FIGURE 1 Proton-decoupled C-13 spectrum of 8CB at 75.4 MHz and 36.0°C. The sample was spun at the rate of 1 kHz with $\theta = 45.4°$.

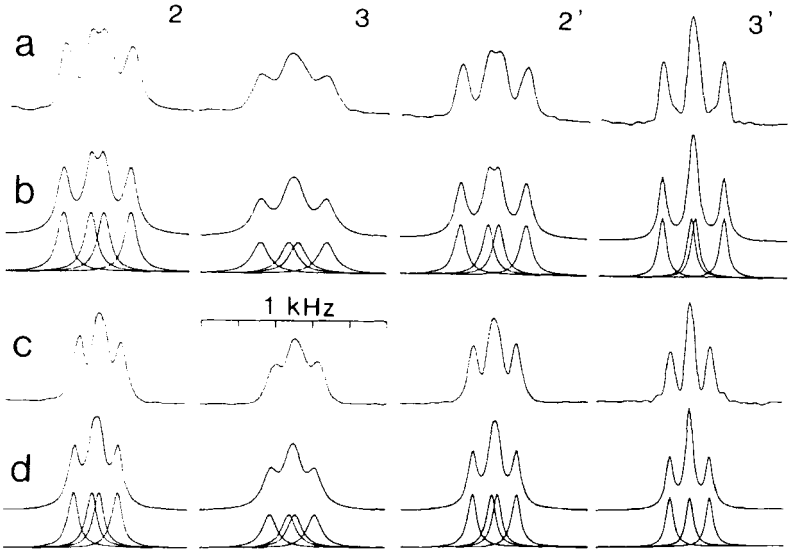



FIGURE 2 C-13 spectra of the protonated aromatic carbons of 8CB obtained by the RHODIUM method at 75.4 MHz with $\theta = 45.7°$. These are spectra in the $\omega_1$ dimension and show splittings due to directly bonded and ortho protons. (a) Experimental spectra at 21.3°C. (b) Corresponding computed spectra and their components. (c) Experimental spectra at 37.9°C. (d) Corresponding computed spectra and their components.

when one inspects the structure of 8CB as depicted in the beginning of this section, noting that the two benzene rings exhibit a dihedral angle of about 30° and undergo rapid jumps between four equilibrium conformations in the liquid crystalline phase.[15,16]

The carbon peaks for all the $CH_2$ groups in 8CB showed triplets in the $\omega_1$ dimension of the SELOFIS spectra due to coupling with the two directly bonded protons. Long range couplings were not resolved. The spectrum of the $CH_3$ group showed a broad peak at $\theta < 48°$ because of unresolved long-range couplings, but the quartet splitting could be resolved when $\theta$ is closer to the magic angle. This is similar to the situation of 6CB, which is discussed in more detail elsewhere.[3]

Since the scalar coupling constant $J$ has negligible anisotropy for C—H pairs,[17] its isotropic value can be used in Equation (1). The $J_{CH}$ values for directly bonded pairs have been determined,[14] and those for the ortho C—H pairs of the aromatic rings are taken as +1 Hz.[18] The sign of $\Delta\nu$ cannot be determined from a single experiment, but can be chosen by comparing the results obtained from several values of $\theta$. Therefore, the $D_{CH}$ values can be calculated from equation (1) without ambiguity. The results are listed in Table I.

At every temperature, each benzene ring in 8CB has four $D_{CH}$ values. From these values, the order parameters of each ring can be calculated.[17] In the calculation, the distances of C2—C3 = 0.1379

TABLE I

$D_{CH}$ (kHz) of 8CB at different temperatures (°C)

| Carbon number | 21.3 | 25.4 | 28.6 | 31.6 | 34.7 | 36.3 | 37.9 |
|---|---|---|---|---|---|---|---|
| 2 | 1.91<br>−1.51 | 1.78<br>−1.42 | 1.60<br>−1.38 | 1.56<br>−1.34 | 1.40<br>−1.18 | 1.28<br>−1.12 | 1.06<br>−1.07 |
| 3 | 1.74<br>−1.58 | 1.70<br>−1.46 | 1.56<br>−1.43 | 1.51<br>−1.38 | 1.33<br>−1.23 | 1.21<br>−1.14 | 1.02<br>−1.06 |
| 2′ | 1.74<br>−1.51 | 1.65<br>−1.43 | 1.58<br>−1.40 | 1.57<br>−1.38 | 1.33<br>−1.21 | 1.19<br>−1.11 | 1.01<br>−1.04 |
| 3′ | 1.43<br>−1.57 | 1.34<br>−1.51 | 1.29<br>−1.43 | 1.20<br>−1.36 | 1.04<br>−1.24 | 0.87<br>−1.21 | 0.74<br>−1.07 |
| α | 5.60 | 5.65 | 5.46 | 5.26 | 4.85 | 4.42 | 3.86 |
| β,ζ | 3.42 | 3.19 | 3.11 | 2.95 | 2.56 | 2.40 | 2.11 |
| γ | 4.34 | 4.31 | 4.08 | 3.88 | 3.52 | 3.16 | 2.99 |
| δ,ε | 4.33 | 4.30 | 4.07 | 3.87 | 3.36 | 3.10 | 2.75 |
| ω | – | −0.01 | −0.02 | −0.05 | +0.08 | +0.11 | +0.11 |

nm and C2′—C3′ = 0.1373 nm from X-ray data[19] were used, and the C—H distances were assumed to be 0.108 nm. The H—C—C angles were varied alternately in least squares calculations until consistent results were obtained. The calculated order parameters are listed in Table II and plotted in Figure 3. The bond angles obtained were: H2—C2—C3, 120.0 ± 0.1°; H3—C3—C2, 120.1 ± 0.1°; H2′—C2′—C3′, 120.0 ± 0.1°; H3′—C3′—C2′, 120.9 ± 0.1°C. These are in good agreement with the results obtained for 5CB, 6CB, and 7CB.[3] The slightly larger H3′—C3′—C2′ angle causes $D_{CH}$ of the directly bonded C—H pair at the 3′ position to be about 25% smaller than those at other positions (Table I). Similar decreases in $D_{CH}$ for 5CB, 6CB and 7CB[3] and in the deuterium quadrupolar splitting of 5CB[15] were also observed.

The major axis of the cyano group essentially coincides with the $C_2$ axis of the benzene ring to which it is attached. Therefore, $S_{zz}$ for this part of the molecule can be determined from the chemical shift of the cyano carbon ($\delta_{aniso}$):

$$\delta_{aniso} = \delta_{iso} + (2/3)S_{zz}[\delta_{zz} - \tfrac{1}{2}(\delta_{xx} + \delta_{yy})] + (1/3)(S_{xx} - S_{yy})(\delta_{xx} - \delta_{yy}), \quad (1)$$

where $\delta_{xx}$, $\delta_{yy}$ and $\delta_{zz}$ are principal components of the chemical shift tensor of the —CN group in the molecular axis system, and $\delta_{iso} = (\delta_{xx} + \delta_{yy} + \delta_{zz})/3$. Since $(S_{xx} - S_{yy}) << S_{zz}$ for 8CB (Table II) and $\delta_{xx} \approx \delta_{yy}$ for the cyano group,[20] $S_{zz}$ can be calculated from the measured chemical shift ($\delta_{aniso}$) provided that the chemical shift anisotropy $\Delta\delta = \delta_{zz} - (\delta_{xx} + \delta_{yy})/2$ is known. From the measurement of $\delta_{aniso}$ as a function of $\theta$, we have found that $\Delta\delta = -330$ ppm for the cyano group in 8CB.[21] Thus, $S_{zz}$ can be readily calculated from Equation (2) by neglecting the last term. The results are plotted in Figure 3.

We must emphasize that this method *cannot* be used to obtain $S_{zz}$ from chemical shifts of other carbons, for which $\delta_{xx}$ is usually quite different from $\delta_{yy}$. To calculate $S_{zz}$ this way for MBBA and EBBA[22]

TABLE II

Order parameters of the benzene rings in 8CB at different temperatures (°C)

| | 21.3 | 25.4 | 28.6 | 31.6 | 34.7 | 36.3 | 37.9 |
|---|---|---|---|---|---|---|---|
| Ring A | | | | | | | |
| $S_{zz}$ | 0.699 | 0.648 | 0.630 | 0.611 | 0.540 | 0.509 | 0.478 |
| $S_{xx} - S_{yy}$ | 0.021 | 0.018 | 0.032 | 0.030 | 0.025 | 0.027 | 0.041 |
| Ring B | | | | | | | |
| $S_{zz}$ | 0.690 | 0.659 | 0.634 | 0.616 | 0.546 | 0.518 | 0.471 |
| $S_{xx} - S_{yy}$ | 0.036 | 0.035 | 0.035 | 0.031 | 0.034 | 0.041 | 0.044 |

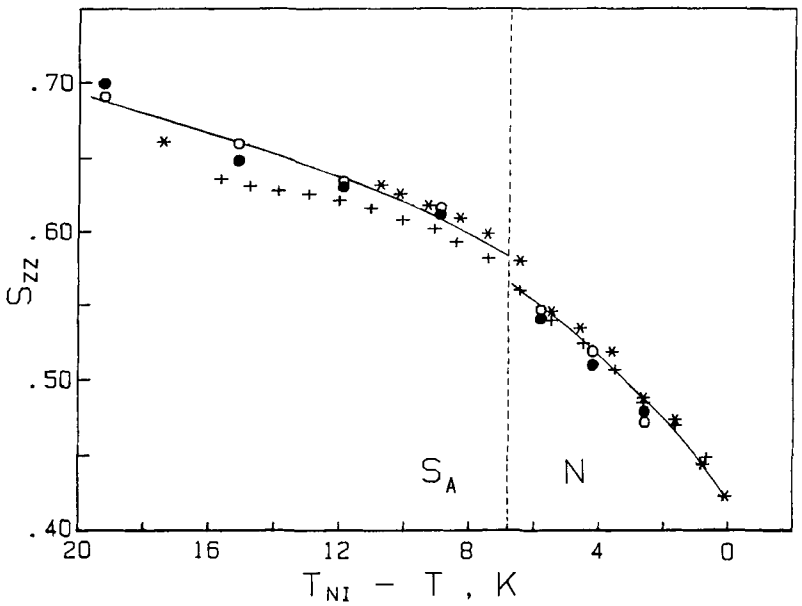



FIGURE 3 $S_{zz}$ of the benzene rings in 8CB as a function of temperature. •: Values for the A ring obtained by the RHODIUM method; ○: values for the B ring obtained by the RHODIUM method; + and ∗: values for the B ring obtained from -CN chemical shifts in two different experiments.

is a more serious mistake, because these molecules have less than $D_2$ symmetry and it requires five order parameters to define their ordering. Therefore, Equation (2) is not at all applicable.

For the aliphatic carbons, the order parameter of each C—H bond can be directly calculated from the equation

$$S_{CH} = -\frac{\gamma_C \gamma_H}{4\pi^2 r^3 D_{CH}}, \tag{3}$$

where the $\gamma$'s are magnetogyric ratios and $r$ is the C—H distance. Using the value of $r = 0.110$ nm for $sp^3$ carbons, results obtained from the data in Table I are plotted in Figure 4. Each $S_{CH}$ is the weighted average of the order parameter of a C—H bond over a large number of conformations of the aliphatic chain. Since the peaks of the $\beta$ and $\zeta$ carbons and those of the $\delta$ and $\epsilon$ carbons overlap (Figure 1), the $D_{CH}$ values are averaged values. Therefore, $S_{CH}$'s of these segments cannot be determined individually and are not included in Figure 4.

$D_{CH}$ values can be directly obtained from one-dimensional experiments with BLEW-48 decoupling provided that the peaks in the

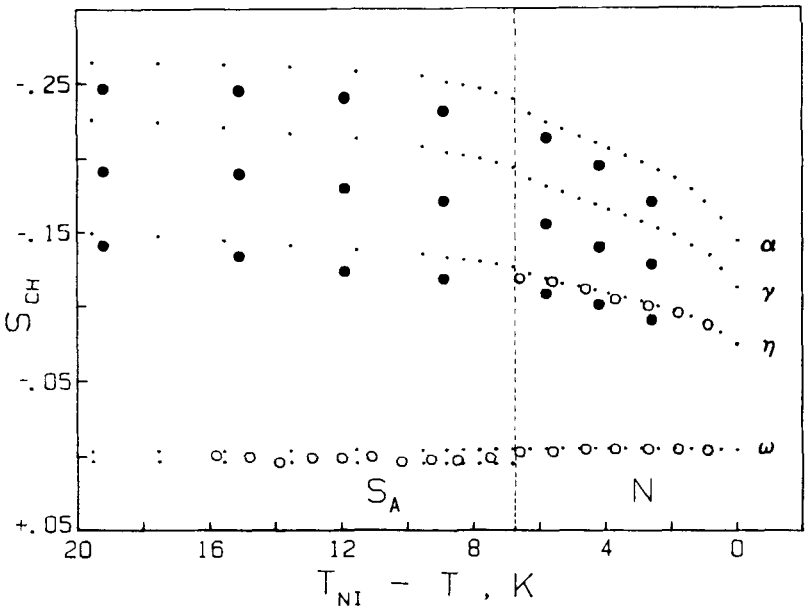



FIGURE 4 $S_{CH}$ of some aliphatic segments in 8CB as a function of temperature. •: Results from 2D experiments at $\theta = 45.7°$; ○: results from 1D experiments at $\theta = 52.9°$; dotted lines: data from ref. 26. Two sets of points for the methyl group in the smectic A are plotted for the latter; see text for explanation.

spectrum do not overlap. This is the case for signals of the η and ω carbons in 8CB with $\theta \sim 52 - 53°$. It takes much less time to measure the one-dimensional spectra, and they have better digital resolution. $S_{CH}$ values for the η and ω carbons obtained from one-dimensional spectra are plotted in Figure 4 together with other data.

## IV. DISCUSSION

The chain ordering of 8CB-$d_{17}$ (perdeuterated *n*-octyl) was studied in detail by N. Boden *et al.* using deuterium NMR,[23] and theoretical analysis of the results has been given.[24] A comparison between their data and ours is important in evaluating the results of both methods.

The deuterium quadrupolar splitting $\Delta\nu_D$ is determined by the deuterium quadrupole coupling constant ($e^2qQ/h$), the asymmetry parameter of the electric field gradient (η), and the order parameters of the principle axes of field gradient tensor ($S_{aa}$, $S_{bb}$ and $S_{cc}$):

$$\Delta\nu_D = \frac{3}{2}\frac{e^2qQ}{h}[S_{aa} + \frac{\eta}{3}(S_{bb} - S_{cc})]. \quad (4)$$

In the analysis of deuterium NMR data, it is usually assumed that the electric field gradient tensor of the C-D fragment is nearly axially symmetrical (i.e. $S_{aa} >> \eta\,(S_{bb} - S_{cc})/3$), and its major axis coincides with the C-D bond (i.e. $S_{aa} = S_{CH}$).[1] The value of $e^2qQ/h$ for aliphatic C-D segments without other substituents on the carbon is about 168 kHz.[25] Then, $S_{aa}$ can be readily calculated from Equation (4). Although the signs of $\Delta\nu_D$ cannot be determined from the deuterium NMR spectra, an inspection of Table I shows that $D_{CH}$ for the methyl group is small but changes sign during the smectic A-to-nematic phase transition. However, because of the small splittings observed for the methyl group in the carbon-13 spectra, the accuracy of its $D_{CH}$ value is not very high. Therefore, values of $S_{CH}$ calculated from the deuterium data[26] in the smectic A phase are plotted in Figure 4 with both signs for the methyl group, while negative values of $S_{CH}$ are plotted for other cases. The data in Figure 4 show that the absolute values of $S_{CH}$ obtained from deuterium NMR are generally somewhat larger than those obtained from carbon-13 NMR. The reasons for the discrepancy may be: (1) a systematic difference in the temperature calibrations in the two laboratories; (2) inaccuracies in the experimental data (about 5% in the present work); (3) partial overlapping of the signal of the $\gamma$ carbon with those of the $\delta$ and $\epsilon$ carbons (especially in the smectic A phase), which makes their $D_{CH}$ values less accurate; (4) inherent errors in the assumptions about the electric field gradient as stated above; and (5) errors in the estimated values of C—H distance and $e^2qQ/h$ for deuterium. Considering these factors, the agreement between the carbon-13 data and the deuterium data can be regarded as being quite reasonable. We note that better agreement was observed for 5CB at $T_{NI} - T = 4$ K.[3]

The work of Boden *et al.*[23] did not include order parameters of the benzene rings, because ring-deuterated 8CB was not studied. On the other hand, the RHODIUM method yields $D_{CH}$ values for all C—H pairs for which the carbon-13 signals are resolved. For the aromatic rings, two $D_{CH}$ values can be measured for each carbon (Table I), and the order parameters and bond angles can be determined (Table II). The results in Table II show that $S_{zz}$'s for the two rings in 8CB are essentially the same. $S_{xx} - S_{yy}$ is small and not very sensitive to temperature, a result similar to that of 5CB.[15] The ratio between $S_{zz}$ of the ring with the octyl chain and $S_{CH}$ of the $\alpha$-$CH_2$ group is fairly constant, with an average of $-2.68 \pm 0.10$. If it is assumed that the $\alpha$-$CH_2$ group undergoes rapid rotation with respect to the benzene ring and its $S_{xx} - S_{yy}$ and $S_{xz}$ values are very small, this ratio should be equal to $2/(3\cos^2\phi - 1)$, where $\phi$ is the $C_4$—$C_\alpha$—$H_\alpha$ angle. A

straightforward substitution yields $\phi = 107 \pm 1°$, which is very reasonable and in agreement with the result for 5CB, 6CB, and 7CB.[3]

The data in Figures 3 and 4 show that $S_{zz}$ for both rings and $S_{CH}$'s for the octyl chain exhibit only small changes at the transition temperature from the smectic A to the nematic phase. In the meantime, the temperature dependence of the order parameters in the smectic A phase is less than that in the nematic phase. This implies larger changes in the slopes of $S_{zz}$ and $S_{CH}$ with respect to temperature, which is consistent with the second order nature of the smectic A-nematic phase transition. In contrast, the chain order parameters of 4,4′-di-n-heptyloxyazoxybenzene rather than their slopes show large discontinuities at the smectic C-nematic phase transition,[23] which is first order.

In summary, we have studied the core and chain ordering of 8CB in its smectic A and nematic phases with the RHODIUM method. Results of the carbon-13 NMR study yield information on molecular ordering comparable to that obtained from deuterium NMR, with the advantage of not requiring isotope substitution.

## Acknowledgment

This material is based upon work supported by the National Science Foundation under Grant CHE-8318840.

## References

1. J. W. Emsley, *Nuclear Magnetic Resonance of Liquid Crystals* (D. Reidel, Dordrecht, 1985).
2. B. M. Fung and J. Afzal, *J. Am. Chem. Soc.*, **108**, 1107 (1986).
3. B. M. Fung, J. Afzal, T. L. Foss and M.-H. Chau, *J. Chem. Phys.*, **85**, in press (1986).
4. J. Courtieu, D. W. Alderman and D. M. Grant, *J. Am. Chem. Soc.*, **103**, 6784 (1981).
5. J. Courtieu, D. W. Alderman, D. M. Grant and J. P. Bayles, *J. Chem. Phys.*, **77**, 723 (1982).
6. B. M. Fung and M. Gangoda, *J. Chem. Phys.*, **83**, 3285 (1985).
7. D. P. Burum, N. Linder and R. R. Ernst, *J. Magn. Reson.*, **44**, 173 (1981).
8. B. M. Fung, to be published.
9. B. M. Fung *J. Magn. Reson.*, **66**, 525 (1986).
10. J. S. Waugh, *Proc. Nat. Acad. Sci. U.S.A.*, **73**, 1394 (1976).
11. R. K. Hester, J. L. Ackerman, B. L. Neff and J. S. Waugh, *Phys. Rev. Lett.*, **36**, 1081 (1976).
12. J. S. Waugh and S. Opella, *J. Chem. Phys.*, **66**, 4919 (1977).
13. E. F. Rybaczewski, B. L. Neff, J. S. Waugh and J. S. Sherfinski, *J. Chem. Phys.*, **67**, 1231 (1977).
14. C.-D. Poon, J. Afzal, M. Gangoda and B. M. Fung, *Magn. Reson. Chem.*, **24**, in press (1986).

15. J. W. Emsley, G. R. Luckhurst and C. P. Stockley, *Mol. Phys.*, **44**, 565 (1981).
16. S. W. Sinton, D. B. Zax, J. B. Murdoch and A. Pines, *Mol. Phys.*, **53**, 333 (1984).
17. J. W. Emsley and L. C. Lindon, *NMR Spectroscopy Using Liquid Crystal Solvents* (Pergamon Press, Oxford, 1975).
18. H. O. Kalinowski, S. Berger and S. Braun, *$^{13}$C-NMR Spektroskopie* (Georg Thieme Verlag, Stuttgart, 1984).
19. W. Haase, H. Paulus and R. Pendzialek, *Mol. Cryst. Liq. Cryst.*, **100**, 211 (1983).
20. B. M. Fung, *J. Am. Chem. Soc.*, **105**, 5713 (1983).
21. C.-D. Poon, B. M. Fung and M. Gangoda, to be published.
22. R. Teeäär, M. Alla and E. Lippmaa, *Org. Magn. Reson.*, **19**, 134 (1982).
23. N. Boden, L. D. Clark, R. J. Bushby, J. W. Emsley, G. R. Luckhurst and C. P. Stockley, *Mol. Phys.*, **42**, 565 (1981).
24. C. J. R. Counsell, J. W. Emsley, N. J. Heaton and G. R. Luckhurst, *Mol. Phys.*, **54**, 847 (1985).
25. B. M. Fung, in "*Critical Evaluation of Chemical and Physical Structural Information*," D. R. Lide, Jr. and M. A. Paul, (ed.) (National Academy of Sciences, Washington, D.C., 1974), pp. 436–448.
26. C. P. Stockeley, Ph.D. Thesis, University of Southampton (1982).