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Orientational ordering in the nematic phase of 4-alkyl-4′-cyanobicyclohexanes

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The orientational ordering of three liquid crystals (*trans,trans*-4-*n*-alkyl-4′-cyanobicyclohexanes) has been investigated using ^{13}C NMR. 2D proton-encoded local field spectroscopy was used to determine the ^{13}C-^{1}H dipolar coupling constants, from which the order parameters were calculated. Semi-empirical linear relations between the obtained order parameters and anisotropic ^{13}C chemical shifts were established. It was found that the order parameters of the major axis of the cyclohexane rings are smaller than those of liquid crystals with phenyl rings, and the order parameters of the C–H bonds in the aliphatic chains also behave differently.

1. Introduction

Many physical properties of liquid crystals are related to the presence of orientational ordering, which can be studied by a variety of methods, such as IR and Raman spectroscopy, X-ray diffractometry, dielectric relaxation, and NMR spectroscopy. NMR provides the most detailed information at the molecular level because different segments of the molecules can be studied. ^{1}H NMR is effective for the study of small molecules dissolved in liquid crystalline solvents [1]. ^{2}H NMR can give much information on bulk liquid crystals [2], but the preparation of deuteriated liquid crystals requires elaborate synthetic work. The use of natural abundance ^{13}C NMR spectroscopy to study the orientational ordering of liquid crystals has been carried out in this laboratory for some time [3–5]. The method used combines separated local field (SLF) spectroscopy and off magic angle spinning (OMAS), and has been proven to be very efficient [5]. Several years ago, an improvement on the 2D SLF technique was made by Pines and co-workers [6–9]. The new method is called either proton-detected local field [6–9] or proton-encoded local field (PELF) spectroscopy [10]. The OMAS technique [11–14] is usually adopted to reduce dipolar interactions so that a lower decoupling power can be used to avoid rf overheating [5]. For systems with smaller dipolar interactions, the NMR experiment can be performed in a 'normal' probe without OMAS, while rf overheating is avoided by careful control of experimental conditions.

The 2D SLF and PELF methods can be used to obtain order parameters of molecular segments, but require long spectrometer time and extensive data processing. On the other hand, the order parameters can be readily related to the anisotropic chemical shifts. After the order parameters have been determined from 2D studies at several different temperatures, it is possible to study the ordering behaviour of liquid crystals in small steps of temperature variation by combining the 1D and 2D data [5, 15, 16]. Although this approach has been used to study a large number of compounds, almost all of them have positive anisotropy of the magnetic susceptibility ($\Delta\chi$). Perhaps the only exception is a previous study in this laboratory on several 4-alkenyl-4′-cyanobicyclohexanes [17]. For further investigation on the orientational ordering of liquid crystals having negative $\Delta\chi$, we have used the PELF method to carry out a detailed study on three 4-alkyl-4′-cyanobicyclohexanes. A comparison of the results is made with those for the alkenyl compounds and those of similar liquid crystals having one or two phenyl rings.

2. Experimental

Three *trans,trans*-4-*n*-alkyl-4′-cyanobicyclohexanes, with *n*-propyl, *n*-pentyl, and *n*-heptyl chains, were obtained from EM Chemicals, Hawthorne, New York, and used without further purification. Hereafter, these liquid crystals are abbreviated as CCH3, CCH5, and CCH7, respectively. Their nematic ranges, as given by the manufacturer, are 58–80, 62–82, and 71–83°C, respectively.

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The NMR experiments were carried out on a Varian UNITY/INOVA 400 spectrometer, using an indirect detection probe manufactured by Nalorac Corporation, Martinez, California. The reason for using an indirect detection probe was its higher efficiency for proton decoupling. Because the CCH*m* liquid crystals have $\Delta\chi < 0$, the major axis of the molecules orient perpendicular to the magnetic field and the dipolar couplings are about half of that for compounds with $\Delta\chi > 0$ and similar order parameters. Therefore, with the application of an efficient dipolar decoupling sequence (BLEW-48 [18]) in the evolution period and an efficient broadband decoupling sequence (SPINAL-64 [19]) in the acquisition period, it was sufficient to use moderate decoupler power (22 kHz) without OMAS.

The assignment of the ^{13}C peaks in the isotropic phase was made based on 2D ^{13}C-^{13}C connectivity (INADEQUATE [20]), and the assignment of the ^{13}C peaks in the nematic phase was deduced correspondingly.

3. Results and discussion

Using the 2D proton-encoded local field (PELF) technique, the normal proton-decoupled ^{13}C NMR spectrum is obtained in the ω_2 dimension, and ^{1}H-^{13}C splittings are observed in the ω_1 dimension. The 2D PELF spectra of CCH5 at $T/T_{\mathrm{NI}} = 0.97$ are shown in figure 1. Each kind of proton splits the carbon peak into a doublet. Thus, every carbon in the terminal chain (α, β, γ, δ, and ω) is split by the directly bonded protons into a doublet, while the α and δ carbons show another partially resolved small doublet due to coupling with the neighbouring protons. The large central peak is due to all other protons whose splittings are unresolved. For each carbon in the rings, there is a pair of peaks with a large splitting due to the axial protons, and a partially resolved small doublet due to long range coupling, the assignment of which cannot be made unambiguously. For the CH$_2$ carbons in the ring (2, 2′, 3, 3′), each shows another pair of peaks with intermediate splitting due to the equatorial protons.

In the 2D slices, each pair of splitting is a combination of dipolar coupling and scalar coupling expressed by the following equation

$$\Delta v = f[2D + J] \qquad (1)$$

where f is a scaling factor for the dipolar decoupling sequence, D is the C–H dipolar coupling constant, and J is the C–H scalar coupling constant. The theoretical value of the scaling factor f is 0.424 for the BLEW-48 sequence [18], but an experimental value of 0.414 was found to agree better with the experimental data [10]. The scalar coupling constants were obtained from heteronuclear 2D J-resolved experiments in the isotropic phase of the liquid crystals. Since the anisotropy of the scalar coupling constants is negligible compared with the magnitude of dipolar coupling constants, the isotropic J values were used in equation (1) directly for the calculations.

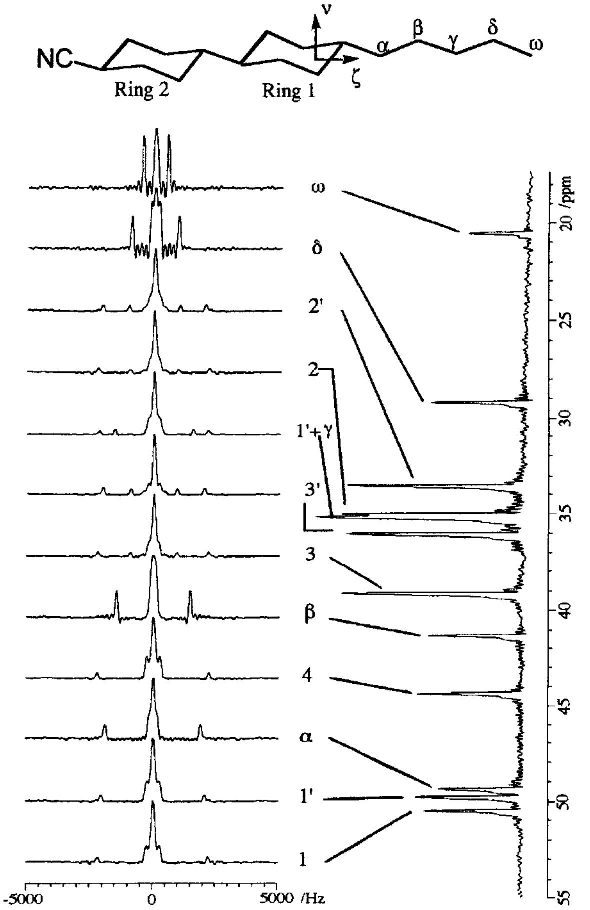

Figure 1. ^{13}C NMR spectra of CCH5 at $T/T_{\mathrm{NI}} = 0.97$ with slow sample spinning (16 Hz) parallel to the field. The spectrum on the right is a normal 1D spectrum; spectra on the left are traces in the ω_1 dimension in a 2D PELF experiment. The coordinate system used for the cyclohexane ring is also shown; the primed numbers refer to ring 2.

The orientational ordering of the two cyclohexane rings can be described using an ordering matrix defined by Saupe [21]. Assuming a perfect chair conformation for each ring and considering that the two substituents in positions 1 and 4 (1′ and 4′) are different, the symmetry of each ring is C_s. Therefore, the ordering matrix is defined by three independent order parameters $S_{\zeta\zeta}$, $S_{\xi\xi} - S_{vv}$, and $S_{\xi v}$. A molecular Cartesian coordinate system is chosen so that the v axis is parallel to the axial C–H bonds, the ζ axis is on the σ_h plane, and the ξ axis is perpendicular to the σ_h plane (figure 1). Since there are insufficient data to determine all three order parameters and $S_{\xi v}$ is expected to be quite small, it can be assumed to be zero without causing an appreciable error

[17, 22–24]. Then, the order parameters can be calculated by using the equations [23, 24]

$$S_{\zeta\zeta} = (4\pi^2 r^3/\gamma_C \gamma_H h)[D_{CH}(a) + D_{CH}(e)/\cos^2(\Phi - 90^\circ)] \quad (2)$$

$$S_{\xi\xi} - S_{vv} = -(4\pi^2 r^3/\gamma_C \gamma_H h)[D_{CH}(a) - D_{CH}(e)/\cos^2(\Phi - 90^\circ)] \quad (3)$$

where r is the C–H distance, γ is the gyromagnetic ratio, a means 'axial,' e means 'equatorial,' and Φ is the H–C–H bond angle. Φ was taken as 107.5° and r was taken as 0.110 nm. Since the rings are not necessarily in perfect chair conformation and the axial C–H bonds are not all completely parallel to each other, the dipolar coupling constants for the C–H bonds in the same ring are not identical. Therefore, their average was used in the calculations, as were the dipolar coupling constants for the equatorial C–H bonds.

Because of the flexibility of the aliphatic chain, it is difficult to describe its detailed orientational ordering from the available data. Therefore, it is assumed that each C–H bond is axially symmetric and its order parameter in each segment of the chain can be calculated by using the equation [4, 5]

$$S_{CH} = -(4\pi^2 r^3/\gamma_C \gamma_H h)D_{CH}. \quad (4)$$

It has been shown that the order parameters can be related to anisotropic ^{13}C chemical shifts ($\Delta\delta = \delta_{LC} - \delta_{iso}$) by a semi-empirical linear equation [15, 16] in all cases studied:

$$\Delta\delta \approx aS + b. \quad (5)$$

For an axially symmetric C–H bond, S is the same as S_{CH} in equation (4). For a 1,4-di-substituted phenyl ring where the two-fold axis is taken as the z axis, S_{zz} obeys equation (5), while $S_{xx} - S_{yy}$ is usually very small and shows no systematic temperature dependence [15, 16]. In the present case, we found that both $S_{\zeta\zeta}$ and $S_{\xi\xi} - S_{vv}$ for the cyclohexane rings exhibit systematic temperature dependence. Therefore, equation (5) is treated as purely empirical to examine whether it is applicable to both parameters. The results of the calculations are summaried in tables 1 and 2 for the rings and table 3 for the chains. For carbon atoms 2 and δ, the changes in the anisotropic chemical shifts are too small to give meaningful correlations; therefore they are not listed in

Table 1. Parameters and correlation coefficients (R^2) for the linear relation between the order parameter $S_{\zeta\zeta}$ and the ^{13}C chemical shift, equation (5), for various carbon atoms in the cyclohexane rings. Data obtained at four temperatures were used for the correlation. The primed numbers refer to ring 2 in figure 1.

Compound		1	2	3	4	1′	2′	3′	4′
CCH3	a	18.32	—	0.926	3.175	6.477	−0.466	1.104	4.883
	b	−3.36	—	0.214	−0.030	1.142	0.067	0.318	0.113
	R^2	1.000	—	0.976	1.000	0.999	0.916	0.936	0.893
CCH5	a	6.294	−0.785	1.127	3.663	6.80	−0.492	1.136	6.741
	b	0.077	1.668	0.183	−0.074	0.288	0.065	0.294	−0.594
	R^2	0.995	0.982	0.998	0.992	0.998	0.955	0.973	0.999
CCH7	a	6.180	—	1.274	3.626	5.864	−0.486	0.940	16.52
	b	0.126	—	0.139	−0.028	0.601	0.156	0.366	−3.417
	R^2	1.000	—	1.000	1.000	0.996	0.964	0.953	0.986

Table 2. Parameters and correlation coefficients (R^2) for the linear relation between the order parameter $S_{\xi\xi} - S_{vv}$ and the ^{13}C chemical shift, equation (5), for various carbon atoms in the cyclohexane rings. Data obtained at four temperatures were used for the correlation. The primed numbers refer to ring 2 in figure 1.

Compound		1	2	3	4	1′	2′	3′	4′
CCH3	a	58.14	—	2.939	10.08	19.66	−1.421	3.347	14.92
	b	−2.98	—	0.233	0.0358	1.238	0.0608	0.335	0.174
	R^2	0.999	—	0.976	0.999	1.000	0.922	0.935	0.905
CCH5	a	20.63	−1.467	3.680	12.02	22.21	−1.642	3.573	24.34
	b	0.154	1.530	0.199	−0.031	0.226	0.074	0.279	−0.927
	R^2	0.999	0.814	0.994	0.998	0.982	0.982	0.980	0.968
CCH7	a	19.11	—	3.938	11.20	18.46	−1.534	2.970	52.07
	b	0.335	—	0.183	0.0963	0.622	0.155	0.368	−3.367
	R^2	0.998	—	0.997	0.994	0.999	0.972	0.962	0.991

Table 3. Parameters and correlation coefficients (R^2) for the linear relation between the order parameter S_{CH} and the ^{13}C chemical shift, equation (5), for various carbon atoms in the chains. Data obtained at three temperatures were used for the correlation.

Compound		α	β	γ	δ	ε	ζ	ω
CCH3	*a*	−10.66	−8.65	−30.39				
	b	2.409	0.113	0.106				
	R^2	0.998	0.998	0.998				
CCH5	*a*	−21.49	−25.51	−17.59	−13.92			−30.07
	b	1.81	−0.483	0.278	0.164			0.037
	R^2	0.933	1.000	0.990	0.999			0.997
CCH7	*a*	−22.69	−26.45	−24.47	—	−25.51	−13.94	−28.43
	b	1.613	0.198	0.766	—	−0.247	0.076	0.192
	R^2	0.980	1.000	0.999	—	0.999	0.999	0.993

these tables. Judging from the high correlation coefficients, it can be concluded that very good linearity was found for all the carbon atoms. Thus, the order parameters of different molecular segments at other temperatures can be calculated from the ^{13}C chemical shifts using the parameters *a* and *b* listed in the tables. The results are plotted in figures 2–4 for the three liquid crystals studied.

The Haller equation [25], which describes the temperature dependence of the order parameter, has been found to be applicable to many systems [15, 16, 26–28]:

$$S(T) = S_0(1 - T/T^*)^F. \tag{6}$$

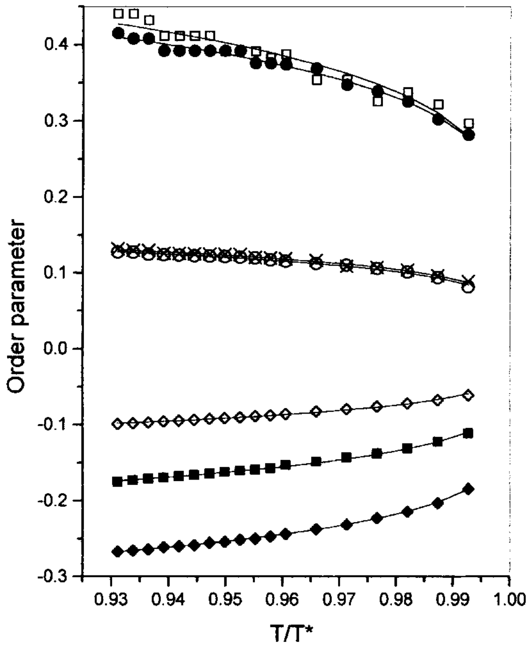

Figure 2. Plot of order parameters of carbon atoms of CCH3 against the reduced temperature T/T^*. □: $S_{\zeta\zeta}$, ring 1; ●: $S_{\zeta\zeta}$, ring 2; ×: $S_{\xi\xi} - S_{\nu\nu}$, ring 1; ○: $S_{\xi\xi} - S_{\nu\nu}$, ring 2; ◆: $S_{\text{C-H}}$, α; ■: $S_{\text{C-H}}$, β; ◇: $S_{\text{C-H}}$, γ (For CCH3, γ is the same as ω, which is used to designate the CH_3 group). the solid curves were obtained by fitting the experimental data to the Haller equation (6).

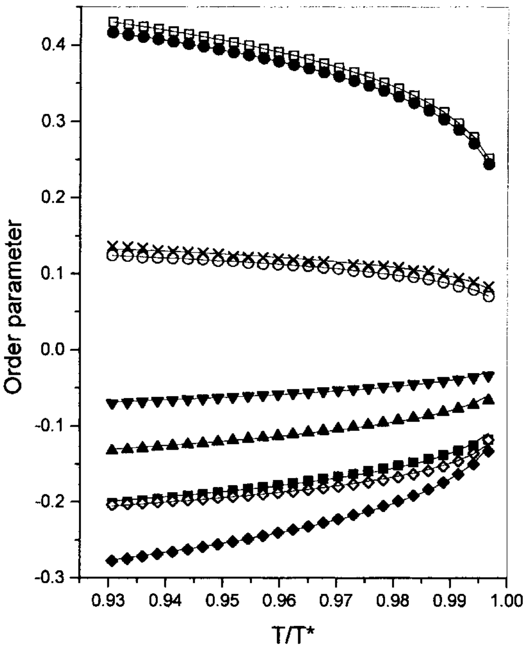

Figure 3. Plot of order parameters of carbon atoms of CCH5 against the reduced temperature T/T^*. The symbols are the same as those in figure 2, plus ▲: $S_{\text{C-H}}$, δ; ▼: $S_{\text{C-H}}$, ω. The solid curves were obtained by fitting the experimental data to the Haller equation (6).

The parameter S_0 is the order parameter of the molecular segment when the temperature is extrapolated to zero, the parameter *F* indicates how fast this limit is approached, and T^* is a parameter very close to the transition temperature. The solid curves in figures 2–4 were obtained by fitting the experimental data to the Haller equation, and the results are quite satisfactory. The parameters obtained from the fitting are summarized in table 4, where Ring 1 refers to the ring with the alkyl chain and Ring 2 refers to the ring with cyano group. In the fitting procedure, T^* was first used as a variable parameter to fit to equation (6) for the two rings separately; then the average value for the two rings was utilized for all the C–H fragments in the chain and in a

Table 4. Values of S_0 and F obtained by fitting the order parameters to the Haller equation.

Compound		$S_{\zeta\zeta}$		$S_{\xi\xi}-S_{\nu\nu}$								
		Ring 1	Ring 2	Ring 1	Ring 2	α	β	γ	δ	ε	ζ	ω
CCH3	S_0	0.688	0.658	0.212	0.212	−0.526	−0.383	−0.220				
	F	0.176	0.172	0.190	0.181	0.258	0.305	0.311				
CCH5	S_0	0.688	0.664	0.202	0.205	−0.540	−0.335	−0.319	−0.256			−0.145
	F	0.176	0.175	0.184	0.163	0.252	0.196	0.165	0.253			0.280
CCH7	S_0	0.671	0.684	0.212	0.237	−0.527	−0.338	−0.312	—	−0.290	−0.233	−0.131
	F	0.169	0.182	0.191	0.217	0.239	0.224	0.224	—	0.222	0.255	0.326

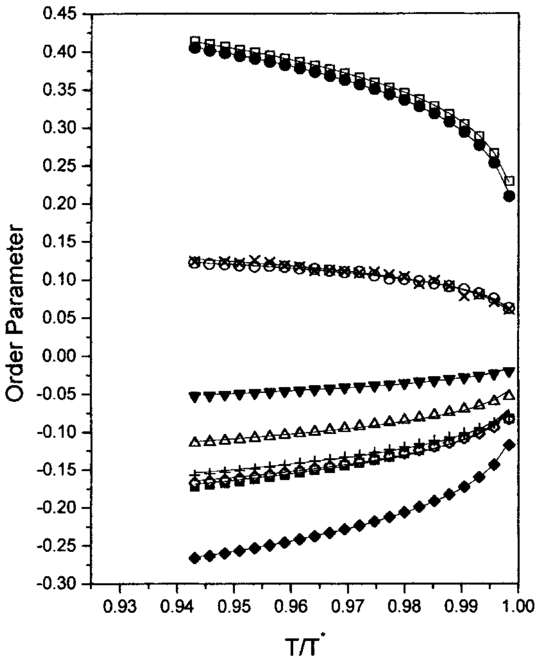

Figure 4. Plot of order parameters of carbon atoms of CCH7 against the reduced temperature T/T^*. The symbols are the same as those in figures 2 and 3, plus Δ: $S_{\text{C-H}}$, ζ; + : $S_{\text{C-H}}$, ε. The solid curves were obtained by fitting the experimental data to the Haller equation (6).

second fitting for the rings. The T^* values for liquid crystals CCH3, CCH5 and CCH7 are 350.0, 354.2 and 354.2 K, respectively, which are slightly lower than the clearing points of these liquid crystals.

From the results shown in figures 2–4 and table 3, the following conclusions can be made. (1) Although the order parameter $S_{\zeta\zeta}$ for the ring with the alkyl chain is slightly higher than that for the ring with the cyano group, the difference is within experimental error. Therefore, we can consider that the major axes of the two rings are essentially parallel or even coincide with each other. Because of the rigidity of the bicyclohexane unit, the values of $S_{\xi\xi}-S_{\nu\nu}$ for the two rings are essentially the same for each compound. (2) The $S_{\zeta\zeta}$ and their limiting values are lower than the S_{zz} and their limiting values of the corresponding cyanobiphenyls [15, 16], indicating that the mesogenic property of the bicyclohexane unit is not as good as that of the biphenyl unit. On the other hand, the order parameter of the phenyl ring in 4-cyanophenylcyclohexanes is larger than that of cyanobiphenyls [23, 24], but the reason for this lack of systematic change is not clear. (3) The limiting $S_{\zeta\zeta}$ values of the three compounds are the same within experimental error. This means that, when extrapolated to the perfect orientation, the length of the terminal aliphatic chain does not affect the orientation of the core appreciably. In contrast, the $S_{\zeta\zeta}$ values of 4-alkenyl-4′-cyanobicyclohexanes are affected by the length of the chain and the location of the double bond [18]. (4) In the CCH*m* liquid crystals, for a perfect all *trans*-conformation, the C–H bond order parameter for the chain carbon atoms should be close to −0.5, i.e. $(3\cos^2 90° - 1)/2$, since the dihedral angle of the C–H bond and the molecular axis is 90°. However, only the limiting S_{CH} values of the α carbons approaches this value. This indicates that, even at very low temperature, appreciable segmental motions of the chains would still exist in these compounds. (5) There is a general trend of decreasing order parameters along the chain. This is unlike the cyanobiphenyls, for which an odd–even alternation of the C–H bond order parameter along the chain [29, 30] is seen. A detailed analysis of this awaits sophisticated molecular dynamics simulations. (6) The parameter F indicates how fast the carbon reaches its perfect orientation. In general, the F values for the chains are considerably larger than those for the cores. This means that, although the aliphatic chain has a much higher flexibility than the core, it reaches the limiting conformation at a faster rate.

4. Conclusion

In conclusion, we have studied the orientational ordering of three *trans,trans*-4-*n*-alkyl-4′-cyanobicyclohexanes in their nematic phase by 2D and 1D ^{13}C NMR spectroscopy. As with liquid crystals containing phenyl rings, linear relations between anisotropic ^{13}C chemical shifts and order parameters can be established. The order parameter values of the major molecular axis in these compounds are smaller than in the corresponding cyanobiphenyls.

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References

[1] EMSLEY, J. W., and LINDON, J. C., 1975, *NMR Spectroscopy using Liquid Crystal Solvents* (Pergamon Press).
[2] EMSLEY, J. W. (editor), 1985, *NMR of Liquid Crystals* (Reid).
[3] FUNG, B. M., and AFZAL, J., 1986, *J. Am. chem. Soc.*, **108,** 1107.
[4] FUNG, B. M., AFZAL, J., FOSS, T., and CHAU, M.-H., 1986, *J. chem. Phys.*, **85,** 4808.
[5] FUNG, B. M., 1996, in *Encylopedia of Nuclear Magnetic Resonance*, edited by D. M. Grant and R. K. Harris (Chichester: Wiley), p. 2744.
[6] SCHMIDT-ROHR, K., NANZ, D., EMSLEY, L., and PINES, A., 1994, *J. phys. Chem.*, **98,** 6668.
[7] HONG, M., SCHMIDT-ROHR, K., and PINES, A., 1995, *J. Am. chem. Soc.*, **117,** 3310.
[8] HONG, M., PINES, A., and CALDERELLI, S., 1996, *J. phys. Chem.*, **100,** 14 815.
[9] CALDERELLI, S., HONG, M., EMSLEY, L., and PINES, A., 1996, *J. phys. Chem.*, **100,** 18 696.
[10] FUNG, B. M., ERMOLAEV, and YU, Y., 1999, *J. magn. Reson.*, **138,** 28.
[11] COUTIEU, J., ALDERMAN, D., and GRANT, D. M., 1981, *J. Am. chem. Soc.*, **103,** 6784.
[12] COUTIEU, J., ALDERMAN, D., GRANT, D. M., and BAYLE, J. P., 1982, *J. chem. Phys.*, **77,** 723.
[13] TEÄÄR, R., ALLA, M., and LIPPMAA, E., 1982, *Org. magn. Reson.*, **19,** 134.
[14] COURTIEU, J.-P., BAYLE, J., and FUNG, B. M., 1997, *Progr. NMR Spectrosc.*, **26,** 141.
[15] GUO, W., and FUNG, B. M., 1991, *J. chem. Phys.*, **95,** 3917.
[16] TONG, T.-H., BAYLE, J. P., and FUNG, B. M., 1997, *Liq. Cryst.*, **22,** 165.
[17] RICHTER, W., SCHADT, M., and FUNG, B. M., 1990, *Liq. Cryst.*, **8,** 63.
[18] BURUM, D. P., LINDER, N., and EARNST, R. R., 1981, *J. magn. Reson.*, **44,** 173.
[19] FUNG, B. M., KHITRIN, A. K., and ERMOLAEV, K., 2000, *J. magn. Reson.*, **142,** 97.
[20] BAX, A., FREEMAN, R., and KEMPSELL, S. P., 1980, *J. Am. chem. Soc.*, **102,** 4849.
[21] SAUPE, A., 1964, *Naturforsch. (a)*, **19,** 161.
[22] BASTIANSEN, O., FERNHOLT, L., SEIP, H. M., KARBARA, H., and KUCHITSU, K., 1973, *J. mol. Struct.*, **18,** 163.
[23] FRECH, C. B., SCHADT, M., and FUNG, B. M., 1988, *Liq. Cryst.*, **3,** 713.
[24] FRECH, C. B., FUNG, B. M., and SCHADT, M., 1989, *Proc. SPIE*, **1080,** 215.
[25] HALLER, I., 1975, *Proc. solid state Chem.*, **10,** 103.
[26] GASPAROUS, H., LALANNE, J. R., and MARTIN, B., 1979, *Mol. Cryst. liq. Cryst.*, **51,** 221.
[27] VELLO, A. M., and DIOGO, A. C., 1989, *Liq. Cryst.*, **5,** 349.
[28] MAGNUSON, M. L., FUNG, B. M., and BAYLE, J. P., 1995, *Liq. Cryst.*, **19,** 823.
[29] EMSLEY, J. W., FUNG, B. M., HEATON, N. J., and LUCKHURST, G. R., 1987, *J. chem. Phys.*, **87,** 3099.
[30] FORSTER, P., and FUNG, B. M., 1988, *J. chem. Soc. Faraday Trans. 2*, **84,** 1083.