Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Orientational ordering in the nematic phase of 4-alkenyl-substituted bicyclohexylnitriles

Wolfgang Richter[ab]; B. M. Fung[a]; Martin Schadt[c]
[a] Department of Chemistry and Biochemistry, University of Oklahoma, Norman, Oklahoma, U.S.A. [b] Technische Universität, Berlin [c] Central Research Units, F. Hoffmann-La Roche and Co. Ltd, Basel, Switzerland

To cite this Article Richter, Wolfgang , Fung, B. M. and Schadt, Martin(1990) 'Orientational ordering in the nematic phase of 4-alkenyl-substituted bicyclohexylnitriles', Liquid Crystals, 8: 1, 63 — 73
To link to this Article: DOI: 10.1080/02678299008047330
URL: http://dx.doi.org/10.1080/02678299008047330

LIQUID CRYSTALS, 1990, VOL. 8, NO. 1, 63-73

Orientational ordering in the nematic phase of 4-alkenyl-substituted bicyclohexylnitriles

by WOLFGANG RICHTER† and B. M. FUNG
University of Oklahoma, Department of Chemistry and Biochemistry, Norman, Oklahoma 73019, U.S.A.

and MARTIN SCHADT
Central Research Units, F. Hoffmann-La Roche and Co. Ltd, CH-4002 Basel, Switzerland

(Received 16 September 1989; accepted 10 January 1990)

The orientational ordering of a series of 4-alkenyl-substituted bicyclohexyl liquid crystals was studied by natural abundance ^{13}C NMR spectroscopy. A combination of the methods of variable angle spinning (VAS) and separated local field spectroscopy (SLF) was used. Rapid sample spinning about an axis forming an angle of about 65° with respect to the magnetic field forces the nematic director to align parallel to the spinnin axis, leading to narrow peaks in the ^{13}C NMR spectrum. The two-dimensional NMR spectroscopic method SLF allows the observation of decoupled ^{13}C signals in the ω_2 dimension and first-order C–H splitting patterns in the ω_1 dimension, from which the C–H dipolar coupling constants for individual pairs of nuclei can be obtained. Then, the order parameters for different molecular segments can be calculated. The method was applied to five different 4-alkenyl-substituted cyanobicyclohexanes. For the compounds studied, the dependence of the ring order parameters on the alkenyl chains shows the same trend as the melting and clearing temperatures and the elastic constants.

1. Introduction

For the intelligent design of new liquid-crystalline substances, it is important to understand the behaviour of liquid crystals on the molecular level. In particular, we are interested in correlating orientational ordering and molecular structure.

Orientational ordering in liquid crystalline phases has been measured by a variety of methods, such as IR and Raman spectroscopy, X-ray diffractometry, dielectric relaxation, and NMR spectroscopy. The latter gives the most detailed information about molecular ordering because different parts of a molecule can be explored separately. In the past, many liquid-crystalline systems have been investigated by ^{1}H and ^{2}H NMR spectroscopy [1]. Proton NMR gives highly resolved peaks only for small molecules in liquid crystal solutions, but not for bulk liquid crystals [2]. Deuterium NMR has been successfully applied to the measurement of orientational ordering of many liquid crystals [1], but the synthesis of deuterated materials is usually rather elaborate.

We have developed and continue to improve upon a technique that allows the measurement of orientational ordering in liquid-crystalline phases using natural abundance ^{13}C NMR spectroscopy [3-11]. This method combines separated local field

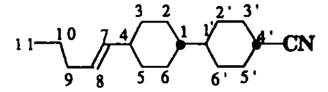
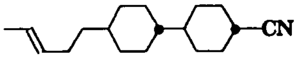
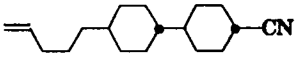
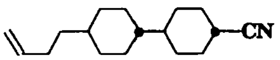
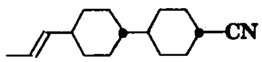
---

† Exchange student from Technische Universität Berlin.

spectroscopy (SLF) [12–15] and variable angle spinning (VAS) [16–21] and has been used to perform systematic investigations of the orientational ordering of several classes of liquid crystals. Systems studied include 4-*n*-alkyl-4′-cyanobiphenyls (*k*CBs) [4, 5, 7], their alkoxy analogues (*k*OCBs) [6], a series of 1-(4′-cyano-phenyl)-*trans*-4-alkenyl-cyclohexanes and 1-(4′-cyanophenyl)-*trans*-4-alkyl-cyclohexanes [8, 9], and two series of ferroelectric liquid crystals [10, 11]. Both the presence and the position of the double bond have been shown to affect the physical properties of these materials [8, 9].

Recently, several new classes of bicyclohexane liquid crystals with alkenyl side chains have been reported [22, 23]. Upon shifting the alkenyl double bond from even to odd side-chain positions, strong odd–even effects were found for the elastic ratio k_{33}/k_{11}, for the elastic expression $\kappa = k_{11} + (k_{33} - 2k_{22})/4$, as well as for the visco-elastic ratio γ_1/κ (in these expressions, k_{11}, k_{22} and k_{33} are the splay, twist and bend elastic constant, respectively, and γ_1 is the rotational viscosity). The wide range of material properties makes these alkenyls suitable materials for virtually all LCD applications, including TN–LCD, OMI–LCD, and STN–LCD. To correlate their molecular structure and bulk properties with their orientational ordering, we have carried out SLF/VAS investigations of five of these compounds, the structural formulae and nematic ranges of which are given in table 1. For these 1-(4′-cyano-cyclohexyl)-*trans*-4-alkenyl-cyclohexanes [22, 23], an abbreviated nomenclature is commonly used. The general name is 'nd_mCC', *n* being the number of carbon atoms beyond the double bond, *m* being the number of bonds between the double bond and the rigid core, and CC refers to the two cyclohexane rings.

Table 1. Structures and transition temperatures of alkenyl cyanobicyclohexanes studied in this work.

Nomenclature	Structure	T_m/°C	T_{NI}/°C
3*d*$_1$CC		59·3	91·7
1*d*$_3$CC		79·4	99·7
0*d*$_4$CC		20·1	54·7
0*d*$_3$CC		50·7	79·8
1*d*$_1$CC		64·9	99·7

2. Experimental and data treatment

The liquid crystal materials were synthesized at Hoffmann La Roche, Basel, Switzerland, as described previously [22, 23]. The nematic ranges of these compounds are listed in table 1. The compound **0*d*$_4$CC** has a smectic phase below 37°C, which will not be considered here.

The ^{13}C NMR spectra were obtained using a Varian XL-300 spectrometer with a VXR data system and a variable angle probe manufactured by Doty Scientific. We used the basic SLF pulse sequence in a version with a ^{13}C spin echo and the BLEW-48 decoupling sequence [24]. We must emphasize that the proper setting of experimental parameters for BLEW-48 decoupling is crucial to the success of the SLF/VAS technique.

Details of experimental conditions and data processing have been described previously [4–7], except for the calibration of the angle β between the spinning axis and the magnetic induction, B_0. We measured the ^{19}F splitting of a sample of 10 per cent $CF_2Cl-CCl_3$ in the liquid-crystalline solvent ZLI 1167. The ratio between the splittings of a spinning sample and a nonspinning sample is $(3\cos^2\beta - 1)/2$ if the director is aligned parallel to the spinning axis, and $-(3\cos^2\beta - 1)/4$ if the director is distributed in a plane perpendicular to the spinning axis. The latter is the case here since the liquid crystal solvent has a positive anisotropy of the magnetic susceptibility, and β is larger than the magic angle.

3. Spectral analysis

3.1. *General*

The SLF/VAS method allows the measurement of individual C–H dipolar coupling constants in nematic, smectic A and smectic C liquid-crystalline phases [3–11].

The essence of the VAS technique is to spin a nematic, smectic A or smectic C liquid crystal sample rapidly about an axis forming an angle β with the magnetic field B_0, so that the director would align along the splinning axis under specific conditions [16–21]. For nematic liquid crystals with a negative anisotropy of the magnetic susceptibility ($\Delta\chi < 0$), as is the case of the bicyclohexylnitriles, the nematic director is aligned along the spinning axis when β is larger than 54·74° (the magic angle) and the spinning rate is large enough to overcome the magnetic torque [18, 19]. In a field of 7 T, a spinning rate of 1 kHz is sufficient. Then, the dipolar couplings are reduced by a factor of $(3\cos^2\beta - 1)/2$, and sharp ^{13}C signals can be observed. The SLF is a 2D NMR method in which ^1H–^1H dipolar decoupling is applied during the evolution period, and broadband decoupling is applied during the acquisition period. The result of the two-dimensional SLF/VAS NMR method is spectra with broadband decoupled sharp ^{13}C signals in the ω_2 dimension, and ^{13}C–^1H coupled spectra in the ω_1 dimension. As an example, the SLF/VAS spectra of **1*d*$_3$CC** are shown in figure 1; spectra of other compounds studied in this work are shown elsewhere [25]. The peaks were assigned according to the results of a 2D-INADEQUATE [26] experiment.

The splitting of a multiplet in the ω_2 dimension is given by [3–9]

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

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 [24], and the experimental value depends on the proton resonance offset [27]. In general, appreciable bandwidths of the proton resonance would lead to imperfection in proton–proton dipolar decoupling. This is the major source of experimental uncertainty in the VAS/SLF method, which we estimate to be 5–10 per cent. We have used an averaged value of $f = 0{\cdot}42$ in our work [3–11], which yielded order parameters in good agreement with those obtained from deuterium NMR experiments for cyanobiphenyls.

Scalar coupling constants were obtained from measurements in isotropic solution and from the literature [28]. Considering that their values are small compared to the

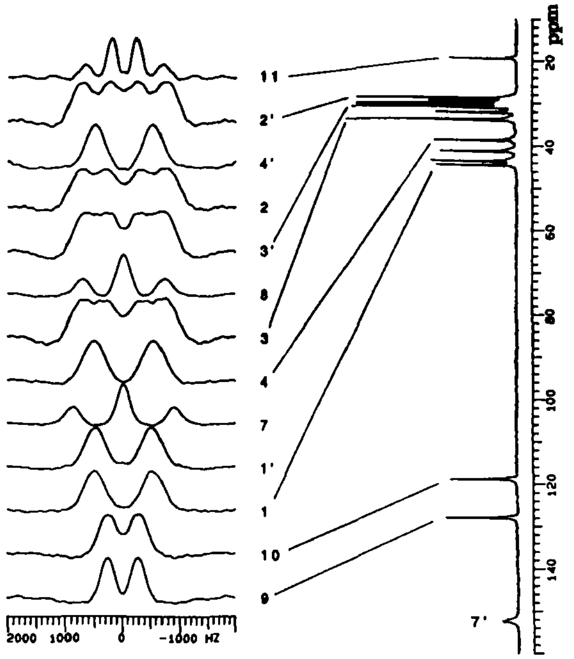


Figure 1. Carbon-13 NMR spectra of **1d**$_3$**CC** at 75·4 MHz and 83°C. The spectra were obtained using the VAS/SLF method described in the text. The angle β was 66·1°, and the spinning rate was 1·0 kHz. The first spectrum in the ω_2 dimension is shown on the right-hand side. Spectra in the ω_1 dimension are shown on the left-hand side; the cyano peak (7′) is not shown because it does not have any splitting.

dipolar couplings, it can be safely assumed that the differences in scalar couplings between liquid-crystalline phase and isotropic solution is negligible without appreciable error.

3.2. *Carbon atoms belonging to a ring*

In the ω_1 dimension, each peak of the tertiary carbon atoms in the cyclohexane rings appears as a doublet due to splitting by the directly bonded proton (carbons 1, 4, 1′ and 4′ in figure 1). Long range couplings are not resolved. The splittings of these doublets can be directly measured from the spectra. Each peak for the other ring carbon atoms (carbons 2, 3, 2′, and 3′ in figure 1) appears as a doublet of doublets due to splittings by the two attached nonequivalent protons (*axial* and *equatiorial*). Because of unresolved long-range couplings, the peaks are rather broad, and the multiplets had to be deconvoluted by a lineshape analysis. Therefore, we fitted the experimental signals to the sum of four gaussian peaks, using a nonlinear least squares method called SPIRAL [29]. This is a very powerful algorithm, and the standard errors of the splittings are usually 0·5 per cent or less. Therefore, the line shape analysis is not a limiting factor in the accuracy of the order parameters. The large C–H splitting is assigned to that by the *axial* proton, and the small splitting is assigned to that by the *equatorial* proton.

The dipolar coupling constants for all the C–H pairs at two different temperatures are given in table 2.

Table 2. C–H dipolar coupling constants of alkenyl cyanobicyclohexanes in kHz. The numbering of the carbon atoms are shown in table 1. The experimental errors are estimated to be about 5 per cent.

Compound	**$3d_1$CC**		**$1d_3$CC**		**$0d_4$CC**		**$0d_3$CC**		**$1d_1$CC**	
Temperature/°C	74	82	83	92	36	43	64	71	82	90
1	4·1	4·1	4·9	4·2	4·1	3·8	4·6	4·4	5·0	4·8
2/6(*a*)	4·1	4·0	5·2	4·3	3·7	3·6	4·4	4·3	4·9	4·7
2/6(*e*)	2·1	2·0	2·7	2·2	1·5	1·4	2·1	2·0	2·5	2·3
3/5(*a*)	4·1	4·0	5·3	4·3	3·6	–	5·1	4·5	4·4	4·2
3/5(*e*)	2·0	1·9	2·5	2·2	1·5	–	2·1	1·9	2·2	2·2
4	4·3	4·1	4·9	4·3	3·7	3·7	4·9	4·3	5·3	4·3
1′	4·2	4·0	4·8	4·0	3·6	3·6	4·8	4·2	4·8	4·3
2′/6′(*a*)	4·0	3·7	5·0	4·1	3·6	3·6	4·3	4·1	4·7	4·4
2′/6′(*e*)	2·1	1·9	2·4	2·2	1·8	1·7	2·2	2·1	2·5	2·4
3′/5′(*a*)	4·0	3·8	4·8	4·2	3·6	3·5	4·4	4·0	4·3	4·3
3′/5′(*e*)	1·9	1·8	2·3	2·0	1·8	–	2·1	1·9	2·2	1·6
4′	4·2	3·9	5·2	4·5	3·9	3·7	4·5	4·4	4·8	4·5
7	3·3	3·1	4·3	3·5	3·5	3·3	3·9	3·6	3·2	3·2
8	3·2	3·1	3·7	3·2	2·6	2·6	3·0	2·7	3·3	3·3
9	3·3	3·1	2·9	2·7	2·4	2·4	2·3	2·0	2·7	2·7
10*a*	1·4	1·3	2·8	2·7	1·5	1·4	5·8	5·2		
10*b*							2·4	2·2		
11*a*	1·0	1·0	2·7	2·0	1·6	1·5				
11*b*					1·2	1·2				

3.3. *Carbon atoms belonging to a chain*

The carbon atoms of the chains appear in the ω_1 dimension as doublets (carbons 9 and 10 in figure 1), triplets (carbons 7 and 8) or quartets (carbon 11), depending on the number of attached hydrogen atoms. Their splittings can be determined from the spectra either directly or by spectral deconvolution. The peak for the last methylene carbon atom in the compounds with a terminal double bond (**$0d_3$CC** and **$0d_4$CC**) appears as a doublet of doublets since the attached hydrogens are not equivalent. These signals were subjected to the lineshape analysis, as described above. The calculated dipolar coupling constants are also listed in table 2.

4. Determination of the order parameters

4.1. *Ordering of the rigid core*

To describe the orientational ordering of the cyclohexane rings, we use an ordering matrix defined by Saupe [30]. Assuming a perfect chair conformation for each ring [8, 31] 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 quantities, conveniently chosen as $S_{\zeta\zeta}$, $S_{\xi\xi} - S_{\nu\nu}$, and $S_{\xi\nu}$. A molecular cartesian coordinate system is chosen as follows: The ν-axis is parallel to the axial C–H bonds, and the ζ axis is parallel to a straight line between the atoms 1 and 4′, as shown in figure 2.

Since there are insufficient data to determine all three order parameters, $S_{\xi\nu}$ is assumed to be zero, which would not cause an appreciable error [8]. The other

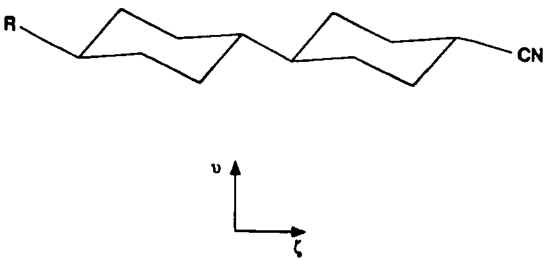


Figure 2. Molecular coordinate system used in this work.

ordering parameters can be calculated by [8]

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

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

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. The radius r was taken as 0·110 nm, and Φ was taken as 107·5° [31]. Since the two sets of D_{CH} values (for either e or a) for each ring are not identical but are close within experimental error, their averages were used in the calculations. The calculated order parameters for all compounds at the same reduced temperature (T/T_{NI}) of 0·95 are given in table 3.

Table 3. Order parameters for individual segments of alkenyl cyanobicyclohexanes at T/T_{NI} = 0·95. The experimental errors are estimated to be 5–10 per cent.

Compound		**3d_1CC**	**1d_3CC**	**0d_4CC**	**0d_3CC**	**1d_1CC**
First ring	$S_{\zeta\zeta}$	0·28	0·35	0·26	0·31	0·33
	$S_{\xi\xi} - S_{\nu\nu}$	0·08	0·10	0·09	0·11	0·10
Second ring	$S_{\zeta'\zeta'}$	0·28	0·33	0·25	0·30	0·32
	$S_{\xi'\xi'} - S_{\nu'\nu'}$	0·08	0·10	0·07	0·09	0·09
7	$S_{C\text{-}H}$	−0·15	−0·19	−0·15	−0·17	−0·14
8	$S_{C\text{-}H}$	−0·14	−0·16	−0·12	−0·13	−0·15
9	$S_{C\text{-}H}$	−0·15	−0·13	−0·10	−0·10	−0·12
10*a*	$S_{C\text{-}H}$	−0·05	−0·12	−0·07	−0·26	
10*b*	$S_{C\text{-}H}$				−0·11	
11*a*	$S_{C\text{-}H}$	−0·04	−0·11	−0·06		
11*b*	$S_{C\text{-}H}$			−0·05		

4.2. *Ordering of the flexible chain*

Because of the flexibility of the aliphatic chain, it is difficult to describe its detailed orientational ordering. Therefore, we assume that each C–H bond is axially symmetric and calculate its order parameter in each segment of the chain by the equation

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

The calculated order parameters of the chain segments are also given in table 3.

4.3. *Calculation of order parameters via chemical shift anisotropy*

The ^{13}C chemical shifts of all peaks are a function of temperature because the order parameters are temperature dependent. The observed chemical shift is related to the

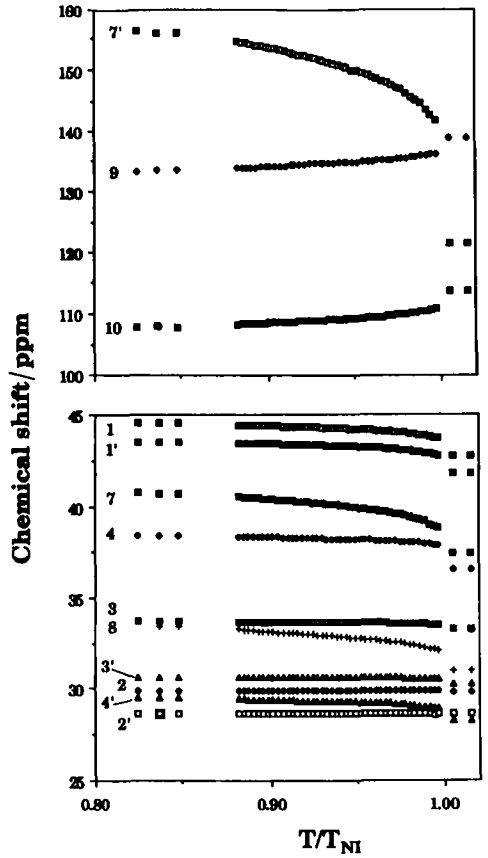


Figure 3. Temperature dependence of ^{13}C chemical shifts of **0*d*$_3$CC** with VAS at $\beta = 66{\cdot}1°$. Only two data points for each carbon are shown for $T/T_{NI} > 1$ because the chemical shifts did not change with temperature in the isotropic phase.

order parameters by [2]

$$\delta_{obs} = \delta_{iso} + (2/3)S_{\zeta\zeta}[\delta_{\zeta\zeta} - (\delta_{\xi\xi} + \delta_{\nu\nu})/2] + (1/3)(S_{\xi\xi} - S_{\nu\nu})(\delta_{\xi\xi} - \delta_{\nu\nu}) + (2/3)(S_{\xi\nu}\delta_{\xi\nu} + S_{\xi\zeta}\delta_{\xi\zeta} + S_{\nu\zeta}\delta_{\nu\zeta}), \qquad (5)$$

where δ_{iso} is the isotropic chemical shift. For our system, the off-diagonal elements of the ordering matrix are zero, and $(S_{\xi\xi} - S_{\nu\nu}) \ll S_{\zeta\zeta}$. Therefore, equation (5) can be simplified to

$$\delta_{obs} \approx \delta_{iso} + (2/3)S_{\zeta\zeta}\Delta\delta, \qquad (6)$$

where $\Delta\delta = \delta_{\zeta\zeta} - (\delta_{\xi\xi} + \delta_{\nu\nu})/2$. Thus, $\Delta\delta$ can be calculated by fitting one or two values of the order parameter $S_{\zeta\zeta}$ obtained from the SLF/VAS experiments into equation (6). In turn, the values of $\Delta\delta$ thus obtained can be used to calculate $S_{\zeta\zeta}$ as a function of temperature from the values of the chemical shift. Because of the dropping of the $(S_{\xi\xi} - S_{\nu\nu})$ term, the values of $\Delta\delta$ may not be very accurate; however, this would not increase the error in the values of $S_{\zeta\zeta}$ appreciably because $\Delta\delta$ functions only as a proportionation constant by using equation (6) to obtain the temperature dependence of $S_{\zeta\zeta}$. As an example, the ^{13}C chemical shifts of **0*d*$_3$CC** are plotted against the temperature in figure 3. The order parameters as functions of temperature for the

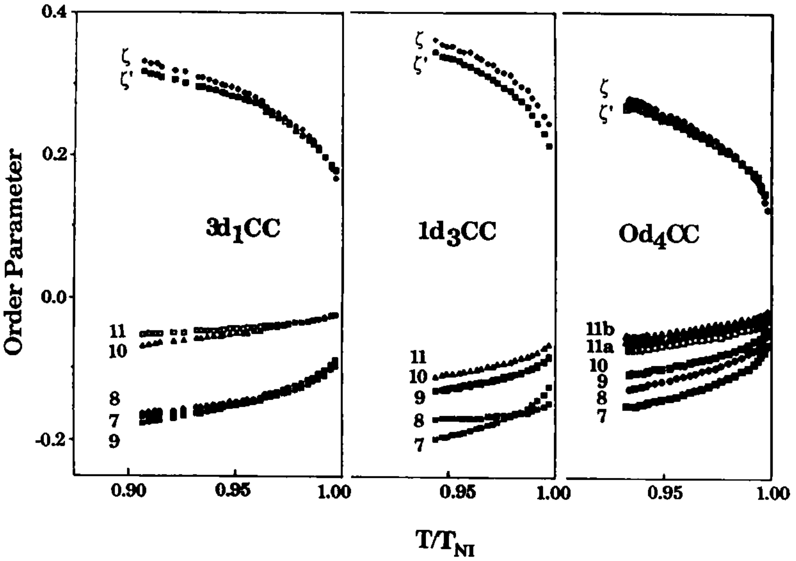


Figure 4. Temperature dependence of the order parameters of $3d_1$CC, $1d_3$CC and $0d_4$CC.

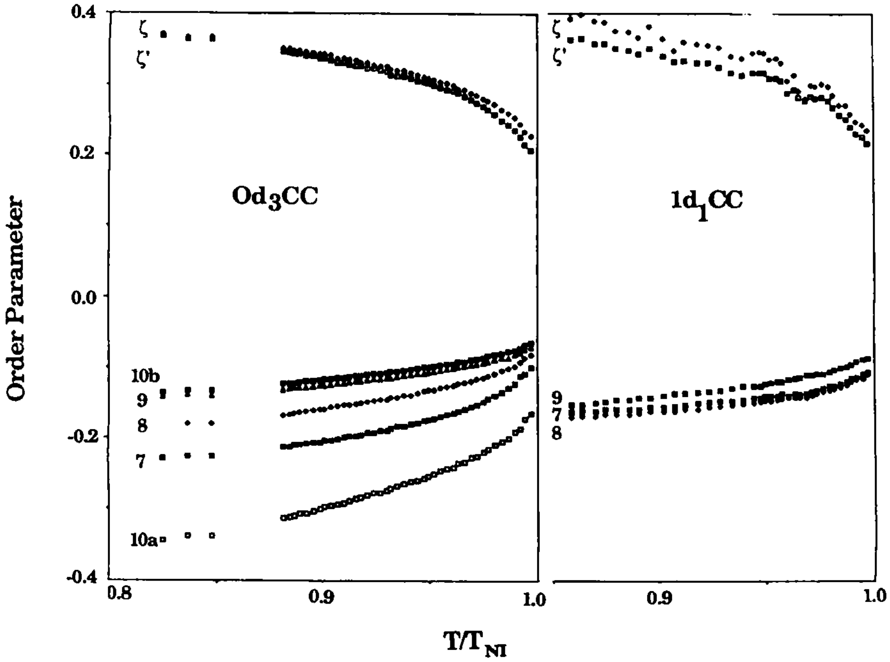


Figure 5. Temperature dependence of the order parameters of $0d_3$CC and $1d_1$CC.

five compounds studied are given in figures 4 and 5, respectively. In the case of the chain ordering, S_{CH} is used instead of $S_{\zeta\zeta}$. To check the validity of this method, we have studied the temperature dependence of the order parameters of several systems by carrying out the SLF/VAS experiment at five different temperatures, and compared the results with those obtained from chemical shifts. The data agree with each other within experimental error. Details of the results will be presented separately.

By using the chemical shifts to determine the temperature dependence of the order parameters, a great deal of spectrometer time can be saved. However, we must emphasize that at least one VAS/SLF experiment must be performed as a starting point to obtain the order parameters through C–H dipolar coupling constants at a given temperature unless accurate values of $\Delta\delta$ are available. The use of estimated values of chemical shift anisotropy to calculate order parameters [18, 32, 33] is not advisable.

5. Discussion

Several interesting conclusions can be drawn from the results presented in table 3 and figures 4 and 5. First, the order parameters of the two rings are such that $S_{\zeta\zeta}$ is in general slightly larger than $S_{\zeta\zeta'}$. Nevertheless, the differences are comparable to experimental errors, and we cannot be sure that they are really significant. Therefore, it is possible that the ζ and the ζ' axes are essentially collinear. $S_{\zeta\zeta}$ is generally about 25 per cent smaller than the corresponding value in the analogous phenylcyclohexanes [8, 9]. However, we must note that the nematic director may form different angles with the ζ axis (figure 2) in the two types of compounds, and a comparison of core ordering cannot be made simply based on the values of $S_{\zeta\zeta}$. In fact, it is most likely that the director does not coincide with the ζ axis of the bicyclohexyl compounds for the following reason. Considering the molecular geometry, the sign of $S_{\zeta\zeta}$ has been taken as positive and those of S_{CH} have been assigned as negative. Therefore, the optimum value of S_{CH} would be equal to $-0{\cdot}5$ times the order parameter of the director. Since many of the values of S_{CH} are more negative than half of the corresponding values of $S_{\zeta\zeta}$ and $S_{\zeta\zeta'}$ for the compounds studied (table 3), the ζ or ζ' axis could not be the nematic director of the bicyclohexyl liquid crystals. For this reason, we cannot address the problem of biaxiality in these compounds quantitatively even though the values of $S_{\xi\xi} - S_{\nu\nu}$ and $S_{\xi\xi'} - S_{\nu\nu'}$ are quite appreciable (about 1/3 of $S_{\zeta\zeta}$ and $S_{\zeta\zeta'}$, respectively). On the other hand, $S_{\zeta\zeta}$ and $S_{\zeta\zeta'}$ would be proportional to the order parameter of the director because the cyclohexane rings are rigid in these compounds. Therefore, it is appropriate to correlate their structures and properties with the values of $S_{\zeta\zeta}$.

From the data in table 3 and figure 4, it is clear that the position of the double bond has a considerable influence on the ordering of the rings. Comparing the molecules with equal chain length, the values of $S_{\zeta\zeta}$ have the order **1*d*$_3$CC** > **3*d*$_1$CC** > **0*d*$_4$CC**. Although this order does not follow any trend with regard to the position of the double bond, it coincides nicely with the trends of melting and clearing temperatures of these compounds (table 1). The difference implies that the position of the double bond in the chain may affect the main field of the nematic phase. However, details of this aspect remain to be studied.

The length of the chain also affects the order parameter of the core. Comparing the values of $S_{\zeta\zeta}$ for **0*d*$_3$CC** and **1*d*$_3$CC**, we found that the addition of a methyl group to the terminal double bond increases the ordering of the core (table 3). On the other hand, when the double bond is located next to the core, as in the cases of **1*d*$_1$CC** and **3*d*$_1$CC**, increasing the chain length causes the core parameter to decrease (table 3). This observation substantiates the above suggestion that the alkenyl chain may affect the nematic main field of these systems. In both sets of compounds, the differences in $S_{\zeta\zeta}$ again correspond to the differences in the melting and clearing temperatures (table 1).

When $S_{\zeta\zeta}$ of all five compounds are compared, they follow the order **1*d*$_3$CC** > **1*d*$_1$CC** > **0*d*$_3$CC** > **3*d*$_1$CC** > **0*d*$_4$CC**. As stated above, this order is the same as those for the melting and clearing temperatures of these compounds. More importantly, it corresponds to those of the elastic constants, especially the bend elastic constant k_{33} [23]. Since the elastic constants and their ratios strongly affect the performance of liquid crystal displays, the present results would be valuable in further investigations of the relations between molecular ordering and other bulk physical properties.

The C–H bond order parameters generally decreases with the increase in the distance of the carbon atom from the core, with the exception of the terminal alkenyl C–H bond in **0*d*₃CC** (table 3). Since the C–H bond order parameter is a weighted average for all possible conformers, the statistical probabilities of which depend on the rotational barriers and other interaction parameters [7], an exact analysis of the S_{CH} values of for the compounds studied here is difficult. Nevertheless, we note that their trends are almost the same as those of the corresponding alkenyl phenylcyclohexyl liquid crystals [7–9]. This seems to indicate that the coupling of the chain motions to the external field is similar for the two types of compounds having the same alkenyl chain.

In conclusion, we have studied the orientational ordering of five alkenyl cyanobicyclohexanes in their nematic phase by 2D ^{13}C NMR spectroscopy. The order parameters of the cyclohexane rings show the same trend as the melting and clearing temperatures and elastic constants of the compounds studied. Trends for the order parameters of the chains are similar to those of the corresponding alkenyl cyanophenylcyclohexanes.

This material is based on work supported by the National Science Foundation under grant DMR-8704223.

References

[1] EMSLEY, J. W. (editor), 1985, *NMR of Liquid Crystals* (Reidel).
[2] EMSLEY, J. W., and LINDON, J. C., 1975, *NMR Spectroscopy using Liquid Crystal Solvents* (Pergamon Press).
[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., POON, C.-D., GANGODA, M., ENWALL, E. L., DIEP, T. A., and BUI, C. D., 1986, *Molec. Crystals liq. Crystals*, **141**, 267.
[6] POON, C. D., WOOLDRIDGE, C. M., and FUNG, B. M., 1988, *Molec. Crystals liq. Crystals*, **157**, 303.
[7] FORSTER, P., and FUNG, B. M., 1988, *J. chem. Soc., Faraday Trans. II*, **84**, 1083.
[8] FRECH, C. B., FUNG, B. M., and SCHADT, M., 1988, *Liq. Crystals*, **3**, 713.
[9] FRECH, C. B., FUNG, B. M., and SCHADT, M., 1989, *SPIE Proc.*, **1080**, 215.
[10] POON, C.-D., and FUNG, B. M., 1989, *Liq. Crystals.*, **5**, 1159.
[11] POON, C. D., and FUNG, B. M., 1989, *J. chem. Phys.*, **91**, 7392.
[12] WAUGH, J. S., 1976, *Proc. natn. Acad. Sci. U.S.A.*, **73**, 1394.
[13] HESTER, R. K., ACKERMAN, J. L., NEFF, B. L., and WAUGH, J. S., 1976, *Phys. Rev. Lett.*, **36**, 1081.
[14] WAUGH, J. S., and OPELLA, S., 1977, *J. chem. Phys.*, **66**, 4919.
[15] RYBACZEWSKI, E. F., NEFF, B. L., WAUGH, J. S., and SHERFINSKI, J. S., 1977, *J. chem. Phys.*, **67**, 1231.
[16] COURTIEU, J., ALDERMAN, D. W., and GRANT, D. M., 1981, *J. Am. chem. Soc.*, **103**, 6784.
[17] COURTIEU, J., ALDERMAN, D. W., GRANT, D. M., and BAYLES, J. P., 1982, *J. chem. Phys.*, **77**, 723.
[18] TEEÄÄR, R., ALLA, M., and LIPPMAA, E., 1982, *Org. magn. Reson.*, **19**, 134.
[19] HEESCHEN, W. A., ALDERMAN, D. W., and GRANT, D. M., 1984, *J. magn. Reson.*, **59**, 318.

[20] Bayle, J. P., Khandar-Shahabad, A., and Courtieu, J., 1986, *Liq. Crystals*, **1**, 189.
[21] Fung, B. M., and Gangoda, M., 1985, *J. chem. Phys.*, **83**, 3285.
[22] Schadt, M., Buchecker, R., Leenhouts, F., Boller, A., and Petrzilka, 1985, *Molec. Crystals liq. Crystals*, **139**, 1.
[23] Schadt, M., Buchecker, R., and Müller, K., 1989, *Liq. Crystals*, **5**, 293.
[24] Burum, D. P., Linder, N., and Ernst, R. R., 1981, *J. magn. Reson.*, **44**, 173.
[25] Richter, W., 1989, M.S. Thesis, University of Oklahoma.
[26] Mareci, T. H., and Freeman, R., 1982, *J. magn. Reson.*, **48**, 158.
[27] Fung, B. M., 1986, *J. magn. Reson.*, **66**, 525.
[28] Kalinowski, H.-O., Berger, S., and Braun, S., 1984, *^{13}C-NMR-Spektroskopie* (Georg Thieme Verlag).
[29] Jones, A., 1970, *J. Comput.*, **13**, 201.
[30] Saupe, A., 1964, *Z. Naturf.* (*a*), **19** 161.
[31] Bastiansen, O., Fernholt, L., Seip, H. M., Kambara, H., and Kuchitsu, K., 1973, *J. Molec. Struct.*, **18**, 163.
[32] Luzar, M., Rutar, V., Seliger, J., and Blinc, R., 1984, *Ferroelectrics.*, **58**, 115.
[33] Blinc, R., Dolinsek, J., Luzar, M., and Seliger, J., 1988, *Liq. Crystals*, **6**, 663.