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

# Orientational ordering of 4-substituted phenylcyclohexanes studied by carbon-13 two-dimensional N.M.R.

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**To cite this Article** Frech, Cheryl Baldwin , Fung, B. M. and Schadt, Martin(1988) 'Orientational ordering of 4-substituted phenylcyclohexanes studied by carbon-13 two-dimensional N.M.R.', Liquid Crystals, 3: 6, 713 — 722
**To link to this Article: DOI:** 10.1080/02678298808086526
**URL:** http://dx.doi.org/10.1080/02678298808086526

LIQUID CRYSTALS, 1988, VOL. 3, NOS. 6 AND 7, 713–722

# Orientational ordering of 4-substituted phenylcyclohexanes studied by carbon-13 two-dimensional N.M.R.

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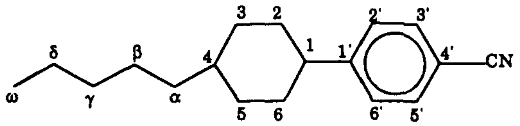
An N.M.R. method combining the techniques of separated local field spectroscopy (SLF) and variable angle spinning (VAS) is valuable in the investigtion of nematic liquid crystals. Rapid sample spinning causes the nematic director to align along the spinning axis, resulting in narrow peaks in the C-13 N.M.R. spectrum. SLF is a two-dimensional N.M.R. method which produces a first order splitting pattern for each carbon signal from which C–H dipolar coupling constants can be determined. The order parameters for all segments of the liquid crystal molecule can then be calculated. Results for three 4′-cyanophenylcyclohexanes are considered here. These compounds are trans-substituted at the 4 position of cyclohexane ring with *n*-pentane (PCH5), 1-pentene ($3d_1$CP) and 3-pentene ($1d_3$CP), respectively.

## 1. Introduction

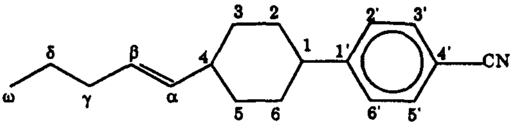
Fascinating and unique to chemists and physicists, materials scientists and electrical engineers alike, liquid crystals exhibit orientational ordering, often without long-range spatial ordering. A fundamental understanding of the behaviour of liquid crystals at the molecular level is vital in the intelligent design of novel liquid crystals and liquid crystal mixtures for future applications. Thus, various physical and spectroscopic methods have been employed to probe orientational ordering of liquid crystal systems including dielectric relaxation, infrared spectroscopy, X-ray diffraction and nuclear magnetic resonance, N.M.R. Among these methods, N.M.R. probably offers the most detailed information at the molecular level since chemically distinct nuclei often exhibit distinguishable signals. The focus of N.M.R. investigations of liquid crystals has traditionally been proton and deuterium N.M.R. applications [1]. Proton N.M.R. is suitable for the study of small solute molecules in liquid crystal solutions [2], but is not widely applicable to pure liquid crystal phases because the peaks are often poorly resolved. Deuterium N.M.R. has been successfully applied to the study of orientational ordering and motions of liquid crystals through measurements of quadrupole splittings and relaxation, respectively [1]. Difficulty in the syntheses of deuterated materials is a major obstacle of this approach.

We have developed and continue to improve upon a powerful technique which uses natural abundance carbon-13 N.M.R. spectroscopy to probe orientational ordering of nematic and smectic A liquid crystals [3–6]. The combination of separated local field spectroscopy (SLF) [7–10] and variable angle spinning (VAS) [11–16] has been used to perform systematic investigations into the orientational ordering of a series of 4-*n*-alkyl-4′-cyanobiphenyls (*k*CBs) [4, 5] and their alkyloxyl analogues (*k*OCBs)

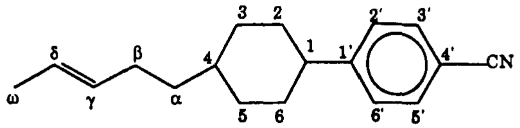
[6]. Recently, polar alkenyl liquid crystals composed of a rigid phenylcyclohexyl core with a side chain containing a double bond have been introduced [17–19]. Both the presence and position of the double bond have been shown to affect markedly the physical properties of these materials [19]. In this work, we report the results of SLF/VAS investigations of two 1-(4′-cyanophenyl)-trans-4-alkenylcyclohexanes, $3d_1$CP and $1d_3$CP, and the analogous alkyl compound, PCH5, the formulae of which are



**PCH5**



**3d1CP**



**1d3CP**

The alkenyl phenylcyclohexyl liquid crystals are abbreviated $xd_{4-x}$CP to identify the double bond position [18]. The $x$ refers to the number of carbons in the alkenyl chain beyond the double bond, and the subscript indicates the number of bonds placed between the rigid core and the double bond. The alkyl phenylcyclohexyl liquid crystals are traditionally abbreviated PCH$n$, with $n$ referring to the alkyl chain length and PCH denoting the rigid phenylcyclohexyl core [20].

## 2. Experimental and data treatment

PCH5 was obtained from EM Chemicals, Hawthorne, New York, and the alkenyl liquid crystals were synthesized at Hoffmann-LaRoche, Basel, Switzerland, as described previously [17]. All were used without further purification. Nematic ranges for these materials are: PCH5, 30–55°C; $3d_1$CP, 16–58·5°C; $1d_3$CP, 60–73·7°C.

All C-13 N.M.R. spectra were obtained using a Varian XL-300 spectrometer with a VXR-4000 data system and a variable angle probe manufactured by Doty Scientific. Basic experimental details including calibrations of temperature and the angle of the spinning axis have been described previously [4]. Some important improvements have been made recently, and they are described in the following.

The basic SLF pulse sequence has been changed from a ‘double window’ version [4, 21] to a single proton window with a carbon-13 spin echo and the BLEW-48 dipolar decoupling sequence [22] as shown in figure 1. A 2 per cent duty cycle (per cent on-time for the proton decoupler) was used to avoid excessive r.f. heating. The r.f. power was 20 W, and $\gamma B_2/2\pi$ varied from 21 to 25 kHz, depending on the angle and temperature.

The accuracy of the results obtained from SLF/VAS relies on the correct setting of the 90° pulse width of the proton decoupler. The value should be accurate to within

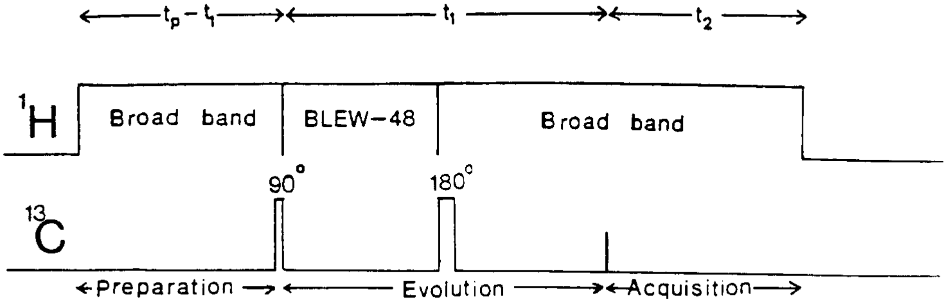


Figure 1. Single window SLF sequence incorporating BLEW-48 homonuclear dipolar decoupling.

about 5 per cent. Since the decoupler efficiency depends on the probe tuning and the dielectric constant of the sample for the same input power, we devise an *in situ* method for calibrating the proton decoupler 90° pulse width. With the sample in the probe at a desired temperature, a decoupler pulse was applied to the proton channel and the resultant *proton* FID was detected through the carbon channel. Even though the receiver circuit was tuned to match the C-13 resonance frequency, the proton signal was strong enough to be easily detected. Thus, by observing the proton signal intensity as a function of decoupler pulse width, the *in situ* proton 90° pulse width can be quickly determined.

The rotors were fitted with a double O-ring cap with a 1 mm threaded hole in the centre to avoid trapping an air pocket in the rotor. After the sample was loaded into the rotor and the cap properly positioned, a Kel-F screw was inserted into the threaded hole, the excess sample was carefully cleaned from the rotor top, and a layer of rapid-drying Epoxy was applied to seal the cap. This procedure avoids the problem of sample leakage which had plagued us for some time.

A Varian VXR-4000 data station was used for data processing. Since the single-window version of the 2D SLF method does not use phase information, the interferograms can be constructed from only the real part of the Fourier transformed data of the free induction decays. Especially for the non-protonated aromatic carbons, this method of data processing offers a marked improvement over the conventional method of using both the real and imaginary parts of the spectra to construct the interferograms.

Some of the multiplets in the $\omega_1$ dimension overlap slightly, and accurate splittings must be determined by line-shape analysis. In our previous work, we fitted the data to the sum of lorentzian functions [3–5]. Since then, we have found that the use of a gaussian line broadening function for exponential multiplication of the interferogram preceding the second Fourier transform produces peaks which can be fitted to the sum of gaussian functions with much better overall agreement. The non-linear least squares algorithm Spiral [23] was used to fit the data.

## 3. Spectral analysis

### 3.1. *Overview*

The SLF/VAS method allows the measurement of C–H dipolar couplings by combining the individual benefits of separated local field spectroscopy and variable angle spinning. For nematic liquid crystals with positive anisotropy of the magnetic susceptibility ($\Delta\chi > 0$), rapid sample spinning at speeds high enough to overcome the magnetic torque (> 1 kHz at 7 T) causes the nematic director to align along the spinning axis when the angle ($\theta$) between that axis and $B_0$ is equal to or less than the magic angle [12, 13]. This reduces dipolar couplings by a factor of $(3\cos^2\Theta - 1)/2$ and sharp peaks can be observed in the carbon-13 spectra using only moderate proton decoupler power provided that $\theta$ is between *ca.* 40° and 54° [13, 16]. The 2D SLF method uses a decoupling sequence in which proton–proton dipolar decoupling is applied during the evolution period and broadband proton decoupling is applied during the acquisition period (figure 1). The net result of the SLF/VAS method produces spectra in two dimensions: the $\omega_2$ dimension shows proton-decoupled carbon-13 spectra and the $\omega_1$ dimension shows proton–carbon splittings for individual carbon atoms. The SLF/VAS results in both dimensions for the alkenyl liquid crystal 1$d_3$CP are shown in figure 2.

The splitting between adjacent peaks in a multiplet in the $\omega_1$ dimension is given by [3–5]

$$\Delta\nu = f[(3\cos^2\Theta - 1)D + J], \qquad (1)$$

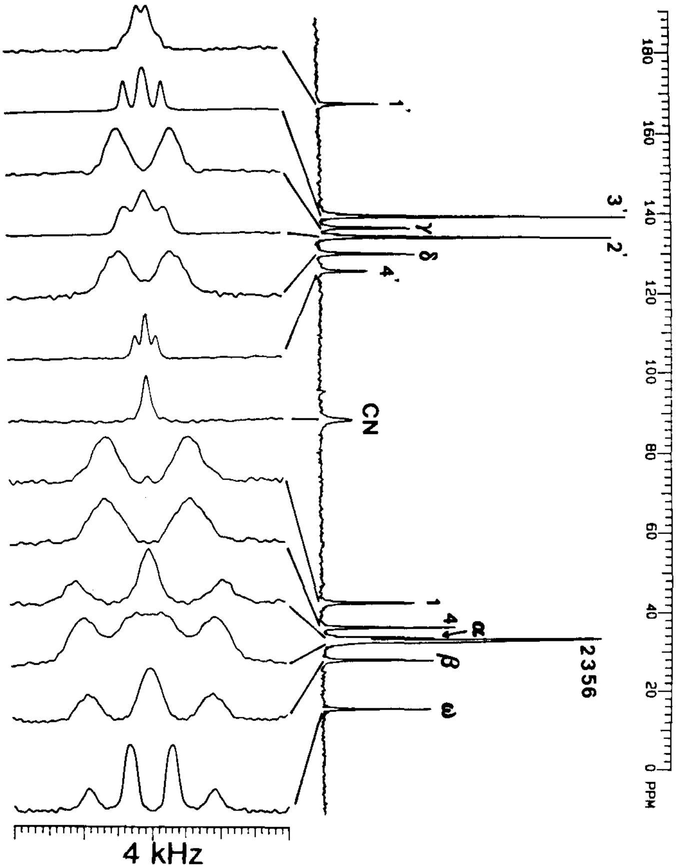


Figure 2. Carbon-13 SLF/VAS spectra of 1$d_3$CP at 75 MHz: temperature = 63·7°C; $\Theta$ = 44·8°; spinning rate = 1·1 kHz. Spectra in the $\omega_1$ dimension are shown on the left and the first spectrum in the $\omega_2$ dimension is shown on the right.

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. We have shown that the BLEW-48 sequence [22] is the most efficient dipolar decoupling sequence for liquid crystals, and has a scaling factor of 0·420 [24]. Scalar coupling constant values for directly bonded C–H pairs were obtained from proton-coupled carbon-13 spectra in isotropic solution ($CDCl_3$) and are listed elsewhere [25]. $J_{C\text{-}H}$ values for two bond couplings are assumed to be $-6$ Hz for the C1′–H1 pair and $+1$ Hz for other aromatic C–H pairs [26].

### 3.2. *Aromatic carbons*

The phenyl ring in phenylcyclohexyl liquid crystals has four types of carbon atoms: two pairs of protonated carbons, 2′(6′) and 3′(5′), and two different quaternary carbons, 1′ and 4′. The spectrum of each protonated carbon consists of a doublet of doublets due to splittings by the directly bonded and ortho protons, respectively. Values of $\Delta\nu$ were obtained from line-shape analysis by fitting each spectrum to the sum of four gaussian functions with a least-squares procedure. The experimental

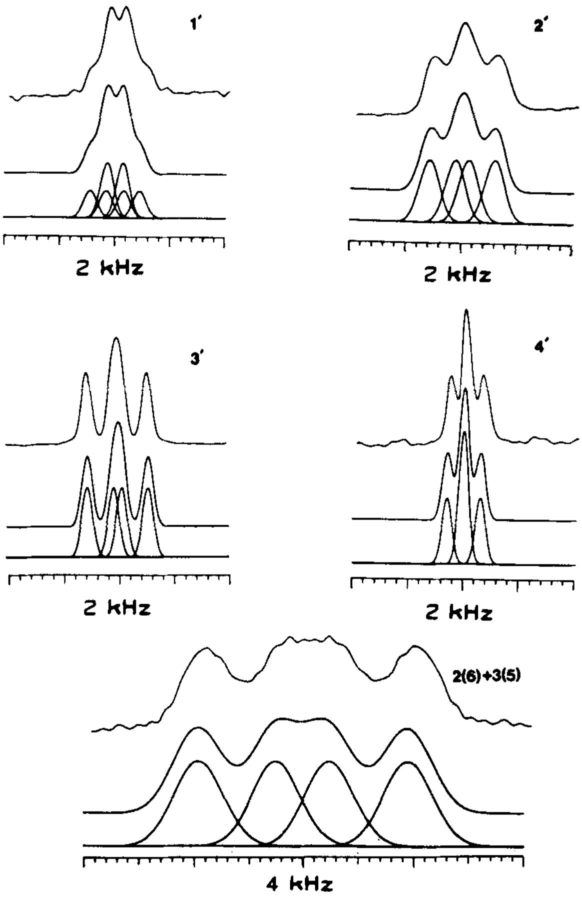


Figure 3. Carbon-13 spectra of the aromatic carbons and the cyclohexyl carbons 2, 3, 5, and 6 of 1$d_3$CP in the $\omega_1$ dimension. In each group, the experimental spectrum is on top, the calculated spectrum is in the middle and the components of the calculated spectrum are on the bottom.

and calculated spectra of the protonated aromatic carbons in 1$d_3$CP are shown in figure 3 as an illustration of the results obtained. Of the protonated carbons, 2′ shows a larger linewidth than 3′ owing to unresolved long-range coupling with nearby cyclohexyl protons.

The quaternary carbon 4′ couples with two identical protons in the ortho position to give rise to a genuine 1:2:1 triplet. The exact splittings were obtained from line-shape analysis due to slight overlapping of the peaks (figure 3).

In addition to its two identical ortho protons, the quaternary carbon 1′ couples with proton 1 of the attached cyclohexyl group. Thus, the $\omega_1$ carbon-13 spectrum of carbon 1′ consists of a doublet of triplets which can be resolved by spectral deconvolution (figure 3). The signs of $\Delta\nu$ cannot be determined from these experiments. They were assigned by assuming that $S_{zz'}$ is positive (*vide infra*) and by considering the geometry of the phenyl ring. Since it is known that the phenylcyclohexanes orient with the nematic director parallel to $B_0$, the assumption of $S_{zz'} > 0$ should be valid. Thus, the dipolar coupling constants ($D_{\text{C-H}}$) for the aromatic carbons of PCH5, 3$d_1$CP and 1$d_3$CP at $T_{\text{NI}} - T = 10$ K calculated according to equation 1 are listed in table 1.

Table 1. $D_{\text{C-H}}$ values (kHz) for the phenyl ring at $T_{\text{NI}} - T = 10$ K. The errors are about 5 per cent.

| | PCH5 | 3$d_1$CP | 1$d_3$CP |
|---|---|---|---|
| C1′-H2′ | 0·69 | 0·69 | 0·81 |
| C2′-H2′ | 1·29 | 1·40 | 1·54 |
| C2′-H3′ | −1·15 | −1·13 | −1·26 |
| C3′-H3′ | 1·02 | 1·19 | 1·29 |
| C3′-H2′ | −1·21 | −1·17 | −1·27 |
| C4′-H3′ | 0·69 | 0·73 | 0·81 |
| C1′-H1 | −0·62 | −0·67 | −0·75 |

### 3.3. *Cyclohexyl carbons*

The substituted cyclohexyl carbons 1 and 4 show dipolar C–H coupling with their attached axial protons and no resolvable long-range couplings. Thus, values of $\Delta\nu$ for the calculation of $D_{\text{C-H}}$ were directly obtained from the $\omega_1$ spectra.

Carbons 2, 3, 5 and 6 show a broad, unresolved peak in the $\omega_2$ spectrum which can be seen in figure 2 for 1$d_3$CP. The 2(6) and 3(5) carbon-13 peaks are resolved in isotropic solution and are separated by only ~0·6 p.p.m. [25]; the inability to resolve these peaks in the SLF/VAS experiment is due to the increased linewidths for the liquid crystals. In the $\omega_1$ dimension, a very broad multiplet is observed for all four carbons. The multiplet consists of a doublet of doublets resulting from the coupling of both axial and equatorial protons to each carbon, and long-range couplings are not resolved. The doublet of doublets was deconvoluted by fitting the spectrum to the sum of four gaussian functions. The results for the cyclohexyl carbons of 1$d_3$CP are shown

Table 2. $D_{\text{C-H}}$ values (kHz) for the cyclohexyl ring C–H pairs at $T_{\text{NI}} - T = 10$ K. The errors are about 5 per cent.

| | PCH5 | 3$d_1$CP | 1$d_3$CP |
|---|---|---|---|
| 1 | 5·74 | 5·48 | 6·26 |
| 4 | 5·86 | 5·48 | 6·47 |
| 2, 3, 5, 6 axial | 5·62 | 5·47 | 6·14 |
| 2, 3, 5, 6 equatorial | 3·03 | 3·26 | 3·51 |

in figure 3. The axial splitting was identified by comparing the magnitudes of $\Delta\nu$ values obtained from the deconvoluted spectrum to $\Delta\nu$ for carbons 1 and 4 which are coupled only to axial protons since the trans substituents are in the equatorial positions. $D_{\text{C-H}}$ values for the cyclohexyl ring were calculated from $\Delta\nu$ according to equation 1 and are listed in table 2.

### 3.4. *Aliphatic carbons*

Values of $\Delta\nu$ for the aliphatic carbons can generally be measured directly from their $\omega_1$ spectra (figure 2). The $CH_2$ carbons in PCH5 and 1$d_3$CP appear as triplets while the $CH_3$ ($\omega$) carbon is split into a quartet by the directly bonded protons. Long-range couplings are not resolved. Each of the double bond carbons in 1$d_3$CP ($\gamma$ and $\delta$) is split into a doublet by the directly bonded vinyl proton. The $\delta$ carbon shows some long-range splitting by the $\gamma$ proton which is estimated to be ~ 100 Hz. Two sets of accidentally degenerate peaks occur in 3$d_1$CP: the 2′ and the $\beta$ carbons, as well as the 2, 3, 5, 6 and the $\gamma$ carbons. Deconvolution with line-shape analysis was required to resolve successfully the peaks in the $\omega_1$ spectra into their components for the calculation of $\Delta\nu$. $D_{\text{C-H}}$ values calculated from $\Delta\nu$ data for the aliphatic C–H pairs are compiled in table 3.

Table 3. $D_{\text{C-H}}$ values (kHz) for the aliphatic C-H pairs at $T_{\text{NI}} - T = 10$ K. The errors are about 5 per cent.

| | PCH5 | 3$d_1$CP | 1$d_3$CP |
|---|---|---|---|
| $\alpha$ | 5·22 | 4·59 | 4·93 |
| $\beta$ | 4·31 | 4·65 | 4·50 |
| $\gamma$ | 4·33 | 4·56 | 3·80 |
| $\delta$ | 2·76 | 1·82 | 4·05 |
| $\omega$ | 1·55 | 1·41 | 3·00 |

## 4. Discussion

Since the mesogenic core in the phenylcyclohexanes has a low symmetry, five order parameters are required to describe its orientational ordering. However, if there are internal motions to increase the effective symmetry, the number of order parameters needed to relate the dipolar coupling between nuclei may be reduced. In the nematic phase, both phenyl rings in cyanobiphenyls undergo rapid jumps between four equilibrium positions and have effective $D_2$ symmetry [27, 28]. The situation of the phenyl ring in phenylcyclohexyls is similar because the ring also undergoes rapid rotations and/or jumps, as evidenced by the equivalence of the carbons and protons in the 3′ and 5′ as well as in the 2′ and 6′ positions, respectively. Thus, the dipolar coupling constant for each C–H pair is given by [2]

$$D_{ij} = -\frac{\gamma_i\gamma_j h}{8\pi^2 r_{ij}^3}[(3\cos^2\Theta_{ijz'} - 1)S_{z'z'} + (\cos^2\Theta_{ijx'} - \cos^2\Theta_{ijy'})(S_{x'x'} - S_{y'y'})], \qquad (2)$$

where $r_{ij}$ is the internuclear distance and $\Theta_{ij\alpha}$ is the angle between $r_{ij}$ and a molecular axis ($\alpha$). In this system, $z'$ is the twofold axis of the phenyl ring, and $x'$ is the in-plane axis perpendicular to $z'$. Our choice for the axis systems of the phenyl and cyclohexyl rings, respectively, is shown in figure 4. From the spectra of the four types of aromatic carbons, six $D_{\text{C-H}}$ values involving the four hydrogen atoms in the phenyl ring were

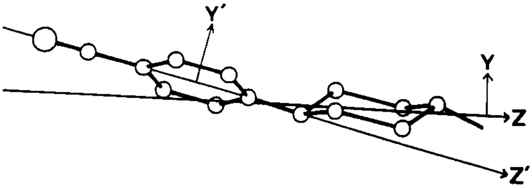


Figure 4. Choice of molecular axes for the phenyl ring ($z'$) and the cyclohexyl ring ($z$) used in this work.

determined (table 1). These data were used to calculate $S_{zz'}$ and $S_{xx'} - S_{yy'}$ of the benzene ring as well as the H2′-C2′-C3′ and C2′-C3′-H3′ bond angles according to equation (2). The results are listed in table 4. In these calculations, it was assumed that the benzene rings have hexagonal symmetry, $r_{\text{C-C}}$ is 0·140 nm [29, 30], and $r_{\text{C-H}}$ is 0·108 nm [30, 31]. Vibrational corrections were not used. The coupling constant between $C_{1'}$ and $H_1$ was not used in the least squares calculations since it is a coupling across two rings.

The situation of the cyclohexyl ring is more complicated. Cyclohexane itself has $D_{3d}$ symmetry, while trans-1,4-distributed cyclohexanes have $C_{2h}$ or $C_s$ symmetry, depending on whether or not the two substituents are identical. In either case, three order parameters ($S_{zz}$, $S_{xx} - S_{yy}$ and $S_{xy}$) are needed to describe the orientational ordering of the cyclohexyl ring. If there is a distortion of the perfect chair conformation, the symmetry may be reduced to $C_i$. This is probably the case for the phenylcyclohexyls, because $D_{\text{C-H}}$ for the axial C–H pairs of the six carbons are somewhat different, except for $3d_1$CP (see table 2), implying that the six axial C–H bonds are not strictly parallel to each other. However, the differences are quite small and can be neglected. Since there are insufficient data to determine all three order parameters for the $C_s$ symmetry, it is assumed that $S_{xy} = 0$. Using the axis system shown in figure 4, it can be readily shown that

$$S_{zz} = -\frac{4\pi^2 r^3}{\gamma_C \gamma_H h}[D_{\text{C-H}}(a) + \sec^2(\Phi - 90°)D_{\text{C-H}}(e)], \tag{3}$$

and

$$S_{xx} - S_{yy} = -\frac{4\pi^2 r^3}{\gamma_C \gamma_H h}[D_{\text{C-H}}(a) - \sec^2(\Phi - 90°)D_{\text{C-H}}(e)], \tag{4}$$

where $r$ is the C–H distance, $\gamma$s are the magnetogryric ratios, $a$ = axial, $e$ = equatorial, and $\Phi$ is the H–C–H bond angle. Taking $r = 0{\cdot}110$ nm and $\Phi = 107{\cdot}5°$ [32], the value $S_{zz}$ and $S_{xx} - S_{yy}$ can be calculated from the $D_{\text{C-H}}$ values in table 2 and the results are included in table 4. It must be pointed out that the accuracies of the calculated order parameters are uncertain due to the assumption of $S_{xy} = 0$.

The aliphatic chain is quite flexible, and it is not easy to describe its exact orientational ordering. A convenient way to handle this problem is to consider the C–H bond order of each $CH_2$ group and the $CH_3$ group by using the equation

$$S_{\text{C-H}} = -\frac{4\pi^2 r^3 D_{\text{C-H}}}{\gamma_C \gamma_H h} = -4{\cdot}407 \times 10^{-5} D_{\text{C-H}}, \tag{5}$$

in which $r = 0{\cdot}110$ nm was used. The results of the three phenylcyclohexyls are listed in table 4.

Table 4. Order parameters and bond angles for $T_{NI} - T = 10$ K. Errors in the order parameters are about 5 per cent or less, and those in the angles are about 0·050.

| | PC5 | $3d_1$CP | $1d_3$CP |
|---|---|---|---|
| | For the phenyl ring | | |
| $S_{z'z'}$ | 0·535 | 0·525 | 0·577 |
| $S_{x'x'} - S_{y'y'}$ | 0·067 | 0·037 | 0·037 |
| < H2′-C2′-C3′ | 118·96 | 119·43 | 119·57 |
| < C2′-C3′-H3′ | 119·93 | 120·18 | 120·43 |
| | For the cyclohexyl ring | | |
| $S_{zz}$ | 0·394 | 0·399 | 0·441 |
| $S_{xx} - S_{yy}$ | 0·101 | 0·084 | 0·101 |
| | For the aliphatic chain | | |
| $S_{C\text{-}H}$ | | | |
| $\alpha$ | −0·230 | −0·203 | −0·217 |
| $\beta$ | −0·190 | −0·205 | −0·198 |
| $\gamma$ | −0·191 | −0·201 | −0·168 |
| $\delta$ | −0·121 | −0·080 | −0·178 |
| $\omega$ | −0·068 | −0·062 | −0·132 |

Some comments about the data in table 4 are now appropriate. First, the calculated bond angles for the phenyl ring show that the H2′-C2′-C3′ angle in all of the phenylcyclohexyl liquid crystals investigated are somewhat less than 120° because of the steric effect of the cyclohexyl rings. On the other hand, the C2′-C3′-H3′ angle is equal to or slightly larger than 120° because the neighbouring -CN group is less bulky. These situations are similar to those in the cyanobiphenyls [4-6]. Secondly, $S_{z'z'}$ for the phenyl ring is about 24 per cent larger than $S_{zz}$ for the cyclohexyl ring in each compound, and $(S_{xx} - S_{yy})/S_{zz}$ for the cyclohexyl ring is larger than 0·2, while $(S_{x'x'} - S_{y'y'})/S_{z'z'}$ for the phenyl ring is about 0·1. However, since the assumption of $S_{xy} = 0$ was made in calculating the order parameters of the cyclohexane ring, a meaningful interpretation of these results awaits the adoption of theoretical model. Thirdly, at $T_{NI} - T = 10$ K, $S_{z'z'}$ as well as $S_{zz}$ are the same for PCH5 and $3d_1$CP within experimental error, while those for $1d_3$CP are larger by about 10 per cent. However, $S_{C\text{-}H}$ for the $\alpha$-$CH_2$ group in $1d_3$CP is less negative than that in PCH5 by about 7 per cent (the $\alpha$-carbon in $3d_1$CP is a vinyl carbon and has a different C-C-H angle; therefore it should not be compared with the other two compounds). This difference may be a result of the influence of the alkenyl 'tail' on the ordering of the rigid core, which would be an interesting phenomenon for further exploration. Finally, a general decrease in the C-H order parameters along the length of the aliphatic chain is observed for all three compounds. This trend was also observed for the *k*OCB liquid crystals [6], and is in contrast to the trend observed for the *k*CBs [4, 27, 33, 34] for which an alternation in C-H order parameters was observed along the chain. A theoretical consideration of the chain ordering in the phenylcyclohexyls will be published separately [35].

This material is based on work supported by the National Science Foundation under grant CHE-8318840. We thank a referee for helpful comments concerning the order parameters of the cyclohexane ring.

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