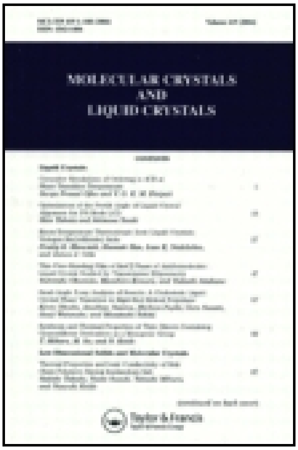

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

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Version of record first published: 19 Dec 2006.

To cite this article: Chi-Duen Poon , Catherine M. Wooldridge & B. M. Fung (1988): Orientational Ordering of 4-n-Alkyl-oxy-4′-Cyanobiphenyls Studied by 2D Carbon-13 NMR, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 157:1, 303-318

To link to this article: http://dx.doi.org/10.1080/00268948808080239

Mol. Cryst. Liq. Cryst. Inc. Nonlin. Opt., 1988, Vol. 157, pp. 303–318
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Printed in the United States of America

ORIENTATIONAL ORDERING OF 4-*n*-ALKYLOXY- 4'-CYANOBIPHENYLS STUDIED BY 2D CARBON-13 NMR

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Abstract The orientational ordering of four 4-*n*-alkyloxy-4'-cyanobiphenyls (5OCB, 6OCB, 7OCB and 8OCB) in their nematic phase at $T_{NI} - T = 10K$ was studied by carbon-13 NMR. The technique used is a combination of separated local field spectroscopy (SLF) and variable angle spinning (VAS). Rapid sample spinning of these compounds causes the nematic director to align along the spinning axis, resulting in narrow peaks in the C-13 NMR spectra. The 2D method of SLF produces a first order splitting pattern for each carbon signal, from which C-H dipolar coupling constants can be determined. The order parameters for each phenyl ring and each aliphatic C-H segment can then be calculated. Results for the *k*OCB series are presented.

INTRODUCTION

Orientational ordering is the most prominent characteristic of liquid crystals. It can be studied quantitatively by many different physical techniques, such as dielectric relaxation,

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infrared spectroscopy, X-ray diffraction, and nuclear magnetic resonance (NMR). Among these methods, NMR probably gives the most detailed information at the molecular level since it probes each nucleus via its distinct signal. For this reason, NMR has been used extensively to investigate the orientational ordering of liquid crystals[1]. Proton NMR is suitable for the study of small solute molecules in liquid crystal solutions[2], but does not offer detailed information for pure liquid crystalline phases because the peaks are usually poorly resolved. On the other hand, deuterium NMR has been applied very successfully to study the orientational ordering and motions of liquid crystals through measurements of quadrupolar splittings and relaxation, respectively[1].

We have recently developed a powerful technique to apply carbon-13 NMR to study the orientational ordering of nematic and smectic A liquid crystals[3-5]. The technique involves a combination of separated local field spectroscopy[6-9] (SLF) and variable angle spinning[10-15] (VAS), and has been used in a systematic investigation of the orientational ordering of 4-*n*-alkyl-4'-cyanobiphenyls (*k*CB's)[4,5]. A similar study on the alkyloxyl analogs of the cyanobiphenyls (*k*OCB's) has now been completed and the results are reported here.

EXPERIMENTAL

All C-13 NMR spectra were obtained by using a Varian XL-300 spectrometer with a VXR data system. Basic experimental details were described previously[3-5]. Some important improvements have been made since then, and they are discussed elsewhere[13].

The compounds used in this work were purchased from EM Chemicals, Hawthorne, New York. Their nematic ranges as specified by the manufacturer are 48-68°C for 5OCB, 57-75.5°C for 6OCB, 54-74°C for 7OCB, and 67-80°C for 8OCB. The latter also has a smectic A phase from 54.5-67°C; the study of this phase is in progress.

OVERVIEW

The application of magic angle spinning (MAS) and variable angle spinning (VAS) to the NMR study of liquid crystals was introduced independently by two research groups in 1981-1982[10-12]. Since then, this technique has been applied to a number of different systems[3-5,14-22].

It has been shown that, when a nematic liquid crystal with positive anisotropy of the magnetic susceptibility ($\Delta\chi>0$) is spun rapidly about an axis forming an angle θ with respect to the magnetic field, the nematic director will align along the spinning axis for $\theta \leq \cos^{-1}(1/\sqrt{3}) = 54.7°$ when the spinning rate is high enough to overcome the magnetic torque[11,12]. Because of the macroscopic alignment of the molecules, the proton-decoupled C-13 spectrum shows narrow peaks with linewidths on the order of 10-20 Hz. Thus, signals for all chemically non-equivalent carbon atoms are usually completely resolved, except for compounds with aliphatic chains longer than 7 carbons or those with one or more cyclohexane rings.

For $\theta < 54.7°$, C-H dipolar couplings are not averaged to zero with rapid sample spinning, and splitting of the carbon-13 peaks is observed when proton decoupling is not used.

However, the completely coupled spectrum is complicated and difficult to analyze due to the presence of extensive proton-proton dipolar couplings. The solution to this problem is to use a decoupling sequence which removes H-H dipolar couplings but preserves C-H dipolar couplings[23]. The splittings in the C-13 spectrum then become first order, and the separation between two adjacent peaks in a multiplet is

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

where f is a scaling factor of the decoupling sequence, D is the C-H dipolar coupling constant, and J is the C-H scalar coupling constant. We have shown that the "windowless" BLEW-48 sequence[24] is the most efficient dipolar decoupling sequence for liquid crystals[25], since moderate rather than high decoupling power should be used to avoid excessive rf heating.

The C-H coupled C-13 spectrum of a nematic or oriented smectic A liquid crystal usually consists of many overlapping peaks. Fortunately, the splitting pattern of each type of carbon atom can be resolved by using the 2D technique of SLF, in which dipolar decoupling is applied during the evolution period, and broadband decoupling is applied during the acquisition period. As an example of the results, the C-13 NMR spectra of 6OCB in both dimensions are shown in Fig. 1; the spectra of other compounds are similar.

According to Eq. (1), the splitting due to C-H dipolar interaction is largest for $\theta = 0°$ and vanishes for $\theta = 54.7°$. It should be noted that H-H dipolar couplings also vary with the same angular dependence. Because of experimental limitations, the efficiency of the dipolar decoupling sequence decreases with the increase of H-H interaction, affecting the accuracy of the results. As a compromise between efficient dipolar decoupling and sizable splitting ($\Delta\nu \approx 1$ kHz), we usually use $\theta \approx 45°$. It has been shown that a variation of θ within several degrees gives the same values of D within experimental error[4].

ORIENTATIONAL ORDERING OF THE PHENYL RINGS

Each phenyl ring in *k*OCB has four types of carbon atoms : two pairs of protonated carbons and two different quarternary carbons. The spectrum of each protonated carbon consists of a doublet of doublets due to splittings by the directly bonded and the *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 least-squares calculations. The experimental and calculated spectra of the protonated aromatic carbons in 6OCB are shown in Fig. 2 as an illustration of the results obtained. The linewidth for the 3' carbon is the smallest because it is farthest away from other protons.

For the quaternary carbons, the coupling with two identical protons in the *ortho* positions gives rise to a genuine 1 : 2 : 1 triplet (Fig. 1). This is in contrast to our previous results of the *k*CB series, for which splittings of the quaternary carbons were not resolved[5]. The better spectral resolution was obtained from improved experimental techniques and data processing[13]. With these improvements,

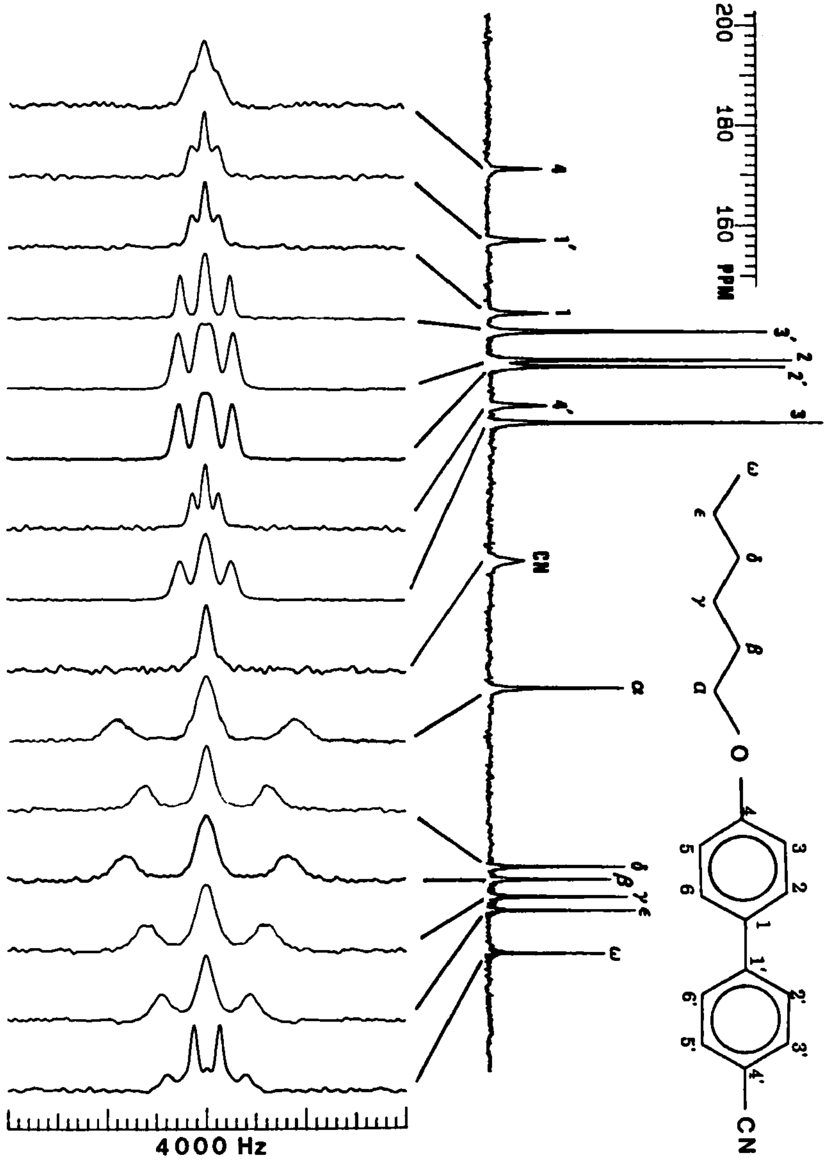

FIGURE 1 C-13 NMR spectra of 6OCB at 75 MHz and 65.5°C;θ = 45.3° and the spinning rate was 1.2 kHz. Spectra in the ω_1 dimension are shown on the left hand side and the first spectrum in the ω_2 dimension is shown on the right hand side.

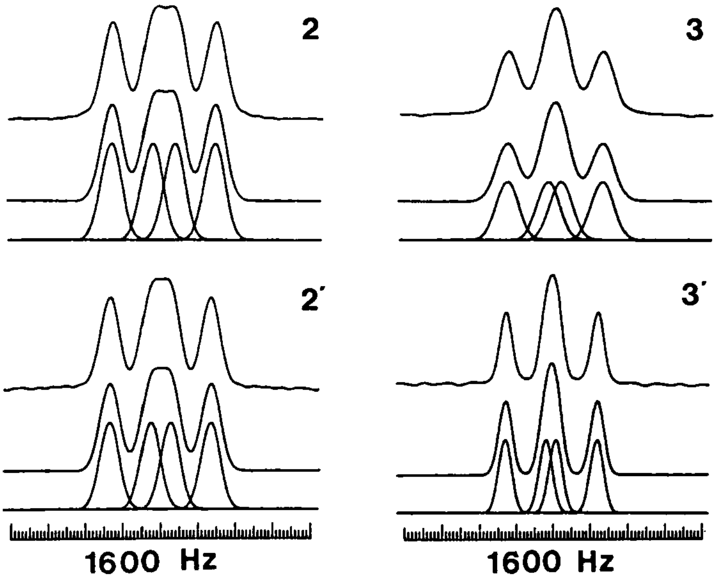

Figure 2 C-13 spectra of the protonated aromatic carbons of 6OCB in the ω_1 dimension. In each group, the experimental spectrum is in the top, the calculated spectrum is in the middle, and the components of the calculated spectrum are on the bottom.

we can now observe the triplet splitting of the quaternary carbons in *k*CB's as well[13]. Since unresolved long-range couplings cause broadening of the triplets, the exact splittings were obtained from line-shape analysis. Using values of J_{CH} determined in isotropic solutions[26], D_{CH} for 5OCB, 6OCB, 7OCB and 8OCB at $T_{NI} - T = 10K$ were calculated from $\Delta\nu$ and θ according to Eq. (1), and are listed in Table I.

Table I. C-H dipolar coupling constants (kHz) of the phenyl rings in *k*OCB at $T_{NI} - T = 10K$. The experimental errors are about 5%.

C–H pairs	5OCB	6OCB	7OCB	8OCB
	Ring with alkyloxyl group			
1–(2,6)	0.64	0.66	0.75	0.70
2–2	1.30	1.33	1.60	1.49
2–3	–1.06	–1.07	–1.29	–1.14
3–2	–1.09	–1.10	–1.34	–1.19
3–3	1.10	1.11	1.31	1.23
4–(3,5)	0.65	0.70	0.76	0.72
	Ring with cyano group			
1'–(2',6')	0.66	0.65	0.80	0.70
2'–2'	1.25	1.25	1.53	1.38
2'–3'	–1.06	–1.07	–1.31	–1.15
3'–2'	–1.09	–1.10	–1.35	–1.19
3'–3'	1.01	1.02	1.23	1.06
4'–(3',5')	0.66	0.65	0.81	0.70

From these values, the order parameters and the C-C-H angles can be readily evaluated[4]. In the calculation, it was assumed that the benzene rings have hexagonal symmetry and C-C bond lengths of 0.140 nm[27,28]; the C-H bond length was taken as 0.108 nm[28,29]. Then, the six D(C-H) values for each phenyl ring were used to calculate the four unknown parameters by a least-squares procedure. The results are given in Table II.

TABLE II. Order parameters and bond angles of the phenyl rings in *k*OCB at $T_{NI} - T = 10K$. The calculated errors in the order parameters were about 0.001, and those in the angles were 0.05°.

	5OCB	6OCB	7OCB	8OCB
	Ring with alkyloxy group			
S_{zz}	0.490	0.494	0.593	0.529
$S_{xx}-S_{yy}$	0.049	0.037	0.076	0.047
$\angle H_2C_2C_3$	118.9°	119.3°	118.8°	119.1°
$\angle C_2C_3H_3$	119.7°	120.1°	119.5°	119.8°
	Ring with cyano group			
S_{zz}'	0.490	0.492	0.604	0.531
$S_{xx}'-S_{yy}'$	0.047	0.051	0.061	0.058
$\angle H_2'C_2'C_3'$	119.2°	119.1°	119.2°	119.0°
$\angle C_2'C_3'H_3'$	120.1°	120.0°	120.1°	120.0°

Several interesting features are noted from the data in Table II. First, the order parameters of the two phenyl rings in each compound are equal within experimental error. Although the two rings are not coplanar[27] and undergo rapid rotation with respect to each other in the nematic phase[30,31], their equal order parameters imply that they can be treated together as a rigid core. Second, at the same reduced temperature ($T_{NI}-T = 10K$), the core order parameters do not increase steadily with the increase of the length of the aliphatic chain: those for 7OCB are the largest among the four compounds studied. Third, the H_2-C_2-C_3 angle (average value = 119.0 ± 0.2°) and the H_2'-C_2'-C_3' angle (119.1 ± 0.1°) are slightly smaller than the normal bond angle of 120°. This is a result of the steric effect of the two phenyl rings on each other. On the other hand, the –OR substituent at the 4 position and the –CN substituent at the 4' position are not as large as the phenyl ring. Therefore, the C_2-C_3-H_3 angle (119.8 ± 0.2°) and the C_2'-C_3-H_3' angle (120.0 ± 0.1°) are much closers to 120°. This situation is slightly different from that of the *k*CB series[4], for which the first segment (CH_2) in the alkyl group is bulkier than the first segment (O) in the alkyloxyl group of the *k*OCB's.

ORIENTATIONAL ORDERING OF THE ALIPHATIC CHAIN

Values of $\Delta\nu$ for the aliphatic carbons can be directly measured from their spectra (Fig. 1). Each CH_2 carbon in 6OCB appeared as a triplet. The CH_3 (ω) carbon was split into a quartet by the directly bonded protons; each component of the quartet was further split into a triplet by the two protons in the adjacent CH_2 group. On the other hand, the splittings for the CH_3 carbon in 5OCB and 7OCB were very small and their spectra did not show resolvable splittings for $\theta \approx 45°$. Therefore, their $\Delta\nu$ values were obtained from spectra taken at $\theta \approx 53°$. Since the methyl signal is *ca.* 8.6 ppm up-field from the closest methylene signal, its proton-coupled peaks at this angle do not overlap with other peaks. Therefore, it was not necessary to use the SLF method; simple 1D measurements with BLEW-48 decoupling were made for expediency.

The order parameter of each C-H bond can be calculated by assuming an axial symmetry and a bond length r = 0.110 nm:

$$S_{CH} = \frac{-4\pi^2 r^3 D_{CH}}{\gamma_C \gamma_H h} = -4.407 \times 10^{-5} D_{CH}, \qquad (2)$$

where γ_C and γ_H are magnetogyric ratios, and h is Planck's constant. The results of the *k*OCB series are given in Table III.

TABLE III. Order parameters for the C-H bonds in the aliphatic chains of *k*OCB. The experimental errors in D(C-H), from which these values were calculated according to Eq. (2), were about 5%. Values in parentheses were obtained from deuterium quadrupole splittings reported in ref. 28.

	5OCB	6OCB	7OCB	8OCB
α	−0.181	−0.180(−0.186)	−0.221	−0.197(−0.203)
β	−0.163	−0.167(−0.176)	−0.206	−0.176(−0.196)
γ	−0.110	−0.115(−0.129)	−0.159	−0.141(−0.159)
δ	−0.113	−0.119(−0.133)	−0.172	−0.150(−0.149)
ε	−	−0.086(−0.091)	−0.131	−0.125(−0.128)
ξ	−	−	−0.122	−0.119(−0.128)
η	−	−	−	−0.084(−0.085)
ω	+0.004	−0.046(−0.050)	−0.006	−0.039(−0.042)

The chain orientational order of deuterated 6OCB and 8OCB was studied by deuterium NMR over a wide range of temperature[32]. The order parameters of the C-D bonds are related to the quadrudupolar splittings by

$$\Delta\nu = \frac{-3}{2}\frac{e^2qQ}{h}\left[S_{zz} + \frac{\eta}{3}(S_{xx} - S_{yy})\right] \quad . \qquad (3)$$

If it is assumed that the deuterium quadrupole coupling constant $e^2qQ/h = 168$ kHz [33] and the assymmetry parameter $\eta = 0$ in Eq. 3, the values of S_{zz} can be readily calculated. They are listed in Table III to compare with the present data. The results of the two types of experiments agree with each other to within 5-10%. The discrepancies could be due to experimental errors (a temperature gradient of 1K in our work and imperfection in BLEW-48 decoupling in our work) plus the assumptions involved (axial symmetry for the C-H or C-D bond, r_{CH} = 0.110 nm, and e^2qQ/h = 168 kHz). Considering these factors, the overall agreement is quite satisfactory. In the study of 6OCB-d_{13}, it was mentioned that the assignments of the γ and δ deuterons were not unambiguous[32]. By comparing the carbon and deuterium results (Table III), we suggest that the assignment of the deuterium data for the γ and δ CD_2 in 6OCB group should be reversed.

It is to be noted that the C-H bond order parameters show a gradual decrease along the aliphatic chain in each compound except a reversal for the γ and δ CH_2 groups (Table III). This is in contrast to the *k*CB series, for which an alternation of the C-H bond order parameter along the whole aliphatic chain was observed[4,32,34,35]. This is most likely due to the difference between the C-O-C angle and the C-C-C angle in the first segment of the aliphatic chains.

When the bond order parameters of the first three CH_2 groups are compared among different members of the *k*OCB series at the same reduced temperature ($T_{NI} - T = 10K$), it can be seen that the values for 7OCB are the largest (Table III), similar to the change in the ordering of the aromatic core as discussed in the previous section. For the methyl (ω) group, there is a significant alternation in S_{CH} with the odd/even number of the aliphatic chain. When the oxygen atom is taken into account in counting the total chain length, this odd/even alternation is similar to that in the *k*CB series[4,35].

SUMMARY

Orientational ordering of 5OCB, 6OCB, 7OCB, and 8OCB at $T_{NI} - T = 10$ K was investigated by carbon-13 NMR in natural abundance with a combination of VAS and SLF. First-order splittings were observed for each type of carbon atom. C-H dipolar coupling constants were obtained from the spectra, and order parameters of both phenyl rings and each C-H segment

investigation of core and chain order parameters of homologous compounds may prove to be very useful in understanding the basic properties of liquid crystals at the molecular level.

ACKNOWLEDGEMENT

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

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