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A database for the determination of orientational ordering of nine classes of liquid crystals using carbon-13 chemical shifts

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The orientational ordering of nine classes of liquid crystals, namely 4-*n*-alkyl-4'-cyanobiphenyls (*n*CB), 4-*n*-alkoxy-4'-cyanobiphenyls (*n*OCB), 4-*n*-alkoxybenzilidene-4'-*n*-alkylanilines (*n*Om), 4'-cyanophenyl 4-alkylbenzoates (*n*CPB), 4'-*n*-alkylphenyl 4-*n*-alkoxycinnamates (Cin-*n*-*m*), esters of α -chloro carboxylic acids and 4-*n*-alkyl-4'-hydroxybiphenyls (An, Bn and Cn), 4,4'-di-*n*-alkyldiphenyldiacetylenes (PTTP), 4-*n*-alkylphenyl 4'-*n*-alkoxybenzoates (\bar{n} Om), and 4-*n*-alkoxyphenyl 4'-*n*-alkoxybenzoates (\bar{n} O \bar{m}), have been investigated by the use of ¹³C NMR. The order parameters of the phenyl rings were determined by using a 2D ¹³C NMR technique known as separated local field (SLF) spectroscopy in combination with variable angle spinning (VAS). The order parameters obtained were then correlated with their corresponding anisotropic 1D ¹³C chemical shifts in their nematic and smectic phases to give a linear relationship in each case. The parameters obtained in the linear correlations provide a convenient way to obtain the order parameters from direct measurement of the ¹³C chemical shifts for other homologous members of these classes of liquid crystal.

1. Introduction

The presence of long range orientational ordering is a fundamental characteristic of liquid crystals, and nuclear magnetic resonance (NMR) is perhaps the most powerful method to study this property at the molecular level. The order parameters of various molecular segments in a liquid crystal can be obtained from deuterium quadrupole splitting, C–H dipolar coupling, and ¹³C chemical shift. The study of deuterium quadrupole coupling is a very general method in liquid crystal research [1, 2], but it requires the use of specially deuteriated compounds. The measurement of C–H dipolar coupling constants is most conveniently accomplished by using a 2D ¹³C NMR technique called separated local field spectroscopy (SLF) in combination with variable angle spinning (VAS) [3, 4]. The SLF/VAS method is very effective and has been applied to study the orientational ordering of a large number of liquid crystals [3, 4], but its widespread application is limited by the requirement of special software and hardware and prolonged spectrometer time. The

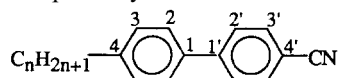
measurement of ¹³C chemical shifts is very straightforward, but the calculation of order parameters from the results requires the knowledge of the components of chemical shift tensors [5], which is not available for most liquid crystals.

In our previous work, it was shown that the order parameters of the phenyl rings and the aliphatic C–H bonds in liquid crystals, which are determined by using the SLF/VAS technique, are linearly related to their ¹³C chemical shifts [6]. The linear correlation is applicable to different compounds in a homologous series which differ only in the length of the terminal alkyl chain. Thus, the establishment of these linear relations provides a convenient way for the determination of the order parameters of liquid crystals from their ¹³C chemical shift data, without the need of knowing the chemical shift tensors. In this paper, we present the linear correlation parameters for nine homologous liquid crystalline series. These parameters furnish a useful database for utilizing ¹³C chemical shifts to study the orientational ordering of different members of liquid crystals in these homologous series for a variety of purposes, including phase transition, the effect of solutes, and the properties of liquid crystal mixtures.

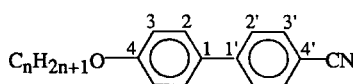
*Author for Correspondence.

2. Experimental

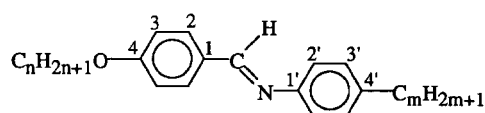
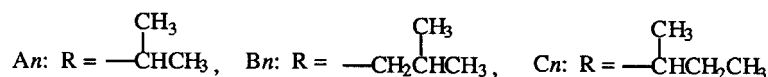
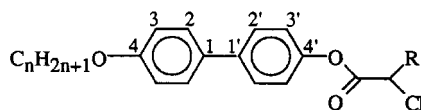
The nine homologous liquid crystal series are:



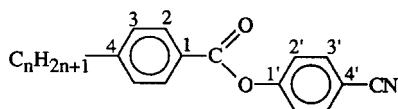
4-*n*-alkyl-4'-cyanobiphenyls (*n*CB)



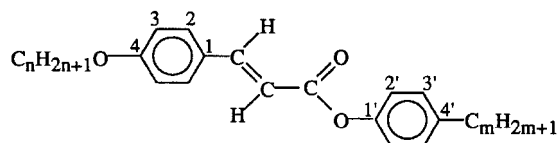
4-*n*-alkoxy-4'-cyanobiphenyls (*n*OCB)



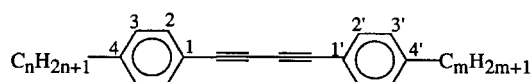
4-*n*-alkoxybenzilidene-4'-*n*-alkylanilines (*n*Om)



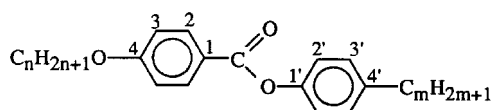
4'-cyanophenyl 4-*n*-alkylbenzoates (*n*CPB)



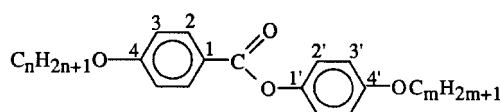
4-*n*-alkylphenyl 4-*n*-alkoxycinnamates (Cin-*n*-*m*)



4,4'-di-*n*-alkyldiphenyldiacetylenes (PTIP)



4'-*n*-alkylphenyl 4-*n*-alkoxybenzoates (\bar{n} Om)



4'-*n*-alkoxyphenyl 4-*n*-alkoxybenzoates (\bar{n} O \bar{m})

All 2D SLF/VAS experiments were performed on a Varian XL-300 NMR spectrometer at 75.4 MHz with the BLEW-48 decoupling sequence [7]. A variable-

angle spinning probe manufactured by Doty Scientific, Columbia, South Carolina, was used in these experiments. The ^{13}C chemical shift measurements were all made on a Varian VXR-500S spectrometer at 125.7 MHz. An indirect detection probe manufactured by Narolac Cryogenics Corporation, Martinez, California, was used to maximize the efficiency of proton decoupling. The data analysis for the SLF/VAS experiments were performed on either a VXR-4000 data station or a Sun 3/60 workstation. Details of the experimental setup and data processing have been reported previously [8, 9].

3. Results and discussion

In an NMR experiment, all nematic and many smectic liquid crystals have macroscopic alignment in the external magnetic field. With broadband proton decoupling, the ^{13}C NMR spectra show resolvable peaks which can be assigned to individual carbon atoms. The chemical shifts of the observed signals (δ_{obs}) in the liquid crystalline phases are often considerably different from those in the isotropic state (δ_{iso}), and are determined by the order parameter tensor and the anisotropic chemical shift tensor:

$$\begin{aligned}
 \delta_{\text{obs}} &= \delta_{\text{iso}} + \delta_{\text{aniso}} \\
 &= \delta_{\text{iso}} + \frac{1}{3} S_{zz} \left[\sigma_{zz} - \frac{1}{2} (\sigma_{zz} + \sigma_{yy}) \right] \\
 &\quad + \frac{1}{3} (S_{xx} - S_{yy}) (\sigma_{xx} + \sigma_{yy}) \\
 &\quad + \frac{2}{3} S_{xy} \sigma_{xy} + \frac{2}{3} S_{xz} \sigma_{xz} + \frac{2}{3} S_{yz} \sigma_{yz} \quad (1)
 \end{aligned}$$

where the S_{ij} s are components of the order parameter matrix, and the σ_{ij} s are components of the chemical shift tensor in the axis system of the order parameter matrix.

For systems with C_{2v} or higher symmetry, $S_{xy} = S_{xz} = S_{yz} = 0$. In addition, the term $S_{xx} - S_{yy}$ is usually very

small and independent of temperature. Therefore, equation (1) can be simplified to the approximate form [6]:

$$\Delta\delta = \delta_{\text{obs}} - \delta_{\text{iso}} \approx \frac{2}{3} S_{zz} \cdot \Delta\sigma + b = a \cdot S_{zz} + b \quad (2)$$

where $\Delta\sigma$ is the chemical-shift anisotropy and is defined as $\Delta\sigma = [\sigma_{zz} - (\sigma_{xx} + \sigma_{yy})/2]$, and b is an empirical constant. For 1,4-disubstituted phenyl rings in liquid crystals, the C_2 axis is taken as the z axis; for the C–H segments in the aliphatic chains, the C–H axis is considered to be approximately the z axis. Then, the subscript zz is dropped, and equation (1) can be rewritten to give

$$S = \alpha \cdot \Delta\delta + \beta \quad (3)$$

where $\alpha = 1/a$, and $\beta = -b/a$. Because of the pre-translational effect [10], the values of δ_{iso} should be obtained at a temperature several degrees above the clearing point.

It has been shown that the experimental results for several types of liquid crystals obey the semi-empirical equations (2) and (3) very well. The system studied includes $n\text{CB}$ and $n\text{OCB}$ [6], the Schiff's base $n\text{O.m}$ series [11], $n\text{CPB}$ [12], $\text{Cin-}n\text{-}m$ [13], the ferroelectric liquid crystals A_n , B_n , and C_n [14–16], PTTP [17], thioesters [18], and laterally substituted compounds [19–21]. Furthermore, for members in a homologous series which differ only in the number of carbon atoms in the terminal alkyl chain, the corresponding phenyl rings share a common linear correlation, and have the same α and β values. In practice, the best approach to reduce errors due to experimental uncertainties is the following. The order parameter of each phenyl ring is determined by using the 2D SLF/VAS method at a given temperature, and the ^{13}C chemical shift values at the same temperature are obtained without VAS. At least three compounds in a homologous series are studied at several temperatures each, and the data are pooled for the least squares fitting. Because different probes and spectrometers were used for these two types of experiments in our work, the temperature was calibrated with respect to the clearing point of the compound for the sake of consistency.

In our previous work, linear correlations were observed for the homologous series mentioned above. However, some of the data tabulated contained small errors [6], in other cases the correlation parameters were not presented explicitly [11], and the standard deviations in the fitting parameters were not given in the published data. Therefore, we have completely re-fitted the previous data to equation (3). The values of α and β and their standard deviations as well as the correlation coefficients of the linear least squares fittings are presented in a systematic way in tables 1 to 7. In

Table 1 Calculated values of α (in a unit of ppm^{-1}) and β (unitless) and their standard deviations for each ^{13}C nucleus in the phenyl rings and the CN group in $n\text{CB}$.

Carbon nucleus	α	$\Delta\alpha$	β	$\Delta\beta$	Correlation coefficient
1	0.0124	0.0006	-0.08	0.03	0.98
2	0.0339	0.0026	-0.10	0.05	0.96
3	0.0315	0.0021	-0.12	0.04	0.97
4	0.0117	0.0006	-0.09	0.03	0.98
1'	0.0122	0.0006	-0.09	0.03	0.98
2'	0.0326	0.0022	-0.16	0.05	0.97
3'	0.0238	0.0012	-0.10	0.03	0.98
4'	0.0108	0.0004	-0.07	0.03	0.98
CN	-0.0053	0.0004	-0.03	0.04	0.97

Table 2 Calculated values of α (in a unit of ppm^{-1}) and β (unitless) and their standard deviations for each ^{13}C nucleus in the phenyl rings and the CN group in $n\text{OCB}$.

Carbon nucleus	α	$\Delta\alpha$	β	$\Delta\beta$	Correlation coefficient
1	0.0113	0.0004	0.00	0.02	0.99
2	0.0288	0.0011	-0.03	0.02	0.99
3	0.0298	0.0011	-0.06	0.02	0.99
4	0.0117	0.0004	0.01	0.02	0.99
1'	0.0115	0.0005	-0.05	0.02	0.98
2'	0.0304	0.0010	-0.09	0.02	0.99
3'	0.0207	0.0008	0.00	0.02	0.99
4'	0.0086	0.0004	0.06	0.02	0.98
CN	-0.0047	0.0002	0.03	0.02	0.98

Table 3. Calculated values of α (in a unit of ppm^{-1}) and β (unitless) and their standard deviations for each ^{13}C nucleus in the phenyl rings of $n\text{O.m}$.

Carbon nucleus	α	$\Delta\alpha$	β	$\Delta\beta$	Correlation coefficient
1	0.0082	0.0009	0.14	0.05	0.94
2	0.0189	0.0020	0.11	0.05	0.95
3	0.0224	0.0022	0.10	0.05	0.95
4	0.0085	0.0009	0.15	0.05	0.94
1'	0.0132	0.0016	0.08	0.06	0.95
2'	0.0222	0.0018	0.17	0.04	0.97
3'	0.0205	0.0017	0.16	0.04	0.97
4'	0.0070	0.0006	0.19	0.03	0.97

addition, new results have been obtained for two other series of commonly studied liquid crystals, $\bar{n}\text{Om}$ and $\bar{n}\text{Om}$, and they are shown in tables 8 and 9, respectively. The correlation coefficients are quite high for all the series, confirming good linear relations between S and $\Delta\delta$ for all the series. Therefore, the tabulated values of α and β can be used to calculate the order parameter for each phenyl ring from the observed ^{13}C chemical shifts in any member of each homologous series at any temperature, in mixtures with other liquid crystals, and

Table 4. Calculated values of α (in a unit of ppm⁻¹) and β (unitless) and their standard deviations for each ¹³C nucleus in the phenyl rings in *n*CPB.

Carbon nucleus	α	$\Delta\alpha$	β	$\Delta\beta$	Correlation coefficient
1	0.0100	0.0006	0.02	0.03	0.99
2	0.0235	0.0014	-0.06	0.03	0.99
3	0.0250	0.0016	-0.01	0.03	0.99
4	0.0140	0.0011	-0.15	0.05	0.98
1'	0.0103	0.0008	0.04	0.03	0.98
2'	0.0256	0.0012	-0.07	0.04	0.98
3'	0.0237	0.0020	-0.08	0.05	0.97
4'	0.0110	0.0007	-0.08	0.04	0.99

Table 5. Calculated values of α (in a unit of ppm⁻¹) and β (unitless) and their standard deviations for each ¹³C nucleus in the phenyl rings in *Cin-n,m*.

Carbon nucleus	α	$\Delta\alpha$	β	$\Delta\beta$	Correlation coefficient
1	0.0079	0.0008	0.21	0.08	0.99
2	0.0198	0.0020	0.15	0.09	0.99
3	0.0213	0.0020	0.16	0.06	0.99
4	0.0117	0.0009	0.16	0.06	0.99
1'	0.0055	0.0006	0.31	0.05	0.98
2'	0.0134	0.0005	0.31	0.04	0.99
3'	0.0152	0.0015	0.26	0.04	0.99
4'	0.0089	0.0004	0.28	0.04	0.98

Table 6. Calculated values of α (in a unit of ppm⁻¹) and β (unitless) and their standard deviations for each ¹³C nucleus in the phenyl rings of PTPP.

Carbon nucleus	α	$\Delta\alpha$	β	$\Delta\beta$	Correlation coefficient
1	0.0080	0.0006	0.09	0.04	0.97
2	0.0201	0.0016	0.21	0.03	0.97
3	0.0188	0.0017	0.01	0.05	0.96
4	0.0077	0.0006	0.11	0.03	0.98

Table 7. Calculated values of α (in a unit of ppm⁻¹) and β (unitless) and their standard deviations for each ¹³C nucleus in the phenyl rings of A7, B7 and C7.

Carbon nucleus	α	$\Delta\alpha$	β	$\Delta\beta$	Correlation coefficient
1	0.010	0.002	0.0	0.1	0.79
2	0.034	0.006	-0.1	0.1	0.84
3	0.034	0.006	-0.2	0.1	0.85
4	0.012	0.002	-0.1	0.1	0.83
1'	0.012	0.002	-0.1	0.1	0.87
2'	0.031	0.006	-0.1	0.1	0.82
3'	0.028	0.004	-0.1	0.1	0.88
4'	0.010	0.002	0.0	0.1	0.83

Table 8. Calculated values of α (in a unit of ppm⁻¹) and β (unitless) and their standard deviations for each ¹³C nucleus in the phenyl rings of \bar{n} Om.

Carbon nucleus	α	$\Delta\alpha$	β	$\Delta\beta$	Correlation coefficient
1	0.0088	0.0011	0.09	0.06	0.97
2	0.0181	0.0020	0.07	0.05	0.96
3	0.0222	0.0024	0.06	0.05	0.96
4	0.0090	0.0011	0.09	0.05	0.98
1'	0.0088	0.0008	0.06	0.04	0.94
2'	0.0219	0.0021	0.06	0.05	0.95
3'	0.0242	0.0023	0.04	0.05	0.95
4'	0.0095	0.0007	0.02	0.04	0.94

Table 9. Calculated values of α (in a unit of ppm⁻¹) and β (unitless) and their standard deviations for each ¹³C nucleus in the phenyl rings of \bar{n} O \bar{m} .

Carbon nucleus	α	$\Delta\alpha$	β	$\Delta\beta$	Correlation coefficient
1	0.0113	0.0005	0.00	0.03	0.99
2	0.0220	0.0009	0.00	0.02	0.99
3	0.0266	0.0011	0.00	0.02	0.99
4	0.0115	0.0005	0.01	0.03	0.99
1'	0.0095	0.0005	0.07	0.03	0.99
2'	0.0207	0.0011	0.09	0.03	0.99
3'	0.0237	0.0012	0.06	0.03	0.99
4'	0.0107	0.0005	0.07	0.03	0.99

in the presence of non-mesogenic solutes. Similar linear correlations have been observed for several other series [18–21], but their structures are rather uncommon, and the results are not included here.

In tables 1–9, the correlation coefficients and percentage standard deviations are different for different series. In general, the results are more reliable when the study is made over wider temperature ranges and contained more homologous compounds in a series. Because the α term has a dominating contribution to the value of S , the overall standard deviations of the ring order parameters amount to 5–10 per cent for most cases, in spite of the relatively large percentage standard deviations for the β term. The results for the chloroesters (see table 7) contain the largest uncertainties because the data are more scattered than those of the other series [22]. The reason for this is that the structure of the R chain may affect the chemical shift tensors of the rings slightly. For the same reason, compounds with very short chains (methyl or ethyl) might have correlation coefficients slightly different from the homologous members with longer chains. The slopes of order parameters versus $\Delta\delta$ for the C–H bonds in the chains are rather dependent on the chain length [6]; therefore, general database sets cannot be compiled for the chains.

When the values of α and β in tables 1–9 are substituted into equation (3) to calculate the values of S , the standard deviations involved would give rise to systematic errors in the order parameters, but not their *changes* with respect to temperature or composition. Therefore, the use of ^{13}C chemical shift data to obtain the order parameters of phenyl rings can yield rather reliable results in experiments which aim at investigating the temperature or composition dependence of the physical properties of liquid crystals.

4. Conclusions

The results of an extensive study of the relation between ^{13}C chemical shifts and order parameters of the aromatic rings for twenty eight liquid crystals in ten homologous series, namely 4-*n*-alkyl-4'-cyanobiphenyls (*n*CB), 4-*n*-alkoxy-4'-cyanobiphenyls (*n*OCB), 4-*n*-alkoxy-benzilidene-4'-*n*-alkylanilines (*nO***m*), 4'-cyanophenyl 4-alkylbenzoates (*n*CPB), 4'-*n*-alkylphenyl 4-*n*-alkoxycinnamates (*Cin-n-m*), esters of α -chloro carboxylic acids and 4-*n*-alkyl-4'-hydroxybiphenyls (*An*, *Bn* and *Cn*), 4,4'-di-*n*-alkyldiphenyldiacetylenes (PTTP), 4'-*n*-alkylphenyl 4-*n*-alkoxybenzoates ($\bar{n}Om$), and 4'-*n*-alkoxyphenyl 4-*n*-alkoxybenzoates ($\bar{n}O\bar{m}$), have been summarized. Linear correlations between the order parameters of the phenyl rings and the ^{13}C chemical shifts in the rings have been established. The tabulated correlation parameters can provide a useful and convenient database for the determination of order parameters of other members in these homologous series from simple measurement of their corresponding ^{13}C chemical shifts.

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