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A STUDY OF THE ORDER PARAMETERS OF TWO LIQUID CRYSTALS BY ONE AND TWO DIMENSIONAL C-13 NMR

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The orientational ordering of six liquid crystalline compounds in two homologous series, namely 4-*n*-alkoxybenzilidene-4'-*n*-alkylanilines (*n*O.*m*) and 4,4'-di-*n*-alkyldiphenyldiacetylenes (PTTP), has been studied at different temperatures by 2D C-13 NMR with variable angle sample spinning. The carbon-proton dipolar coupling constants were obtained and the order parameters of the aromatic cores were calculated. The C-13 chemical shifts for each carbon nucleus in the aromatic cores were also measured as a function of temperature by 1D C-13 NMR. A linear correlation between the chemical shifts and the order parameters was observed for each homologous series. The results furnish a useful and convenient database for the evaluation of order parameters for these two series of liquid crystals from simple measurements of C-13 chemical shifts.

INTRODUCTION

The most fundamental characteristic of liquid crystals is the presence of long range orientational ordering, which can be characterized quantitatively by the order parameters. Among the methods available for the determination of order parameters of liquid crystalline phase, such as infrared and Raman spectroscopy[1-3] and X-ray diffractometry,[4] NMR gives the most detailed information about the molecular ordering in liquid crystals because the order parameters of individual molecular segments can be determined.[5] A two-dimensional (2D) C-13 NMR method was developed in this laboratory to study the orientational ordering of liquid crystals.[6,7] This method is a combination of separated local-field spectroscopy (SLF) and variable-angle spinning (VAS).[8,9] The SLF/VAS technique has been successfully applied to obtain molecular ordering information for many classes of liquid crystals.[8,9] The results obtained by this technique are in good agreement with other techniques such as deuterium NMR on deuterated samples, with the advantage that the natural abundance of carbon-13 nuclei in the samples are employed and no special synthesis is required.[7] The basic principle of the SLF/VAS method is to obtain the order parameters via the C-H dipolar couplings, D, which can be determined from the C-H dipolar splitting $\Delta\upsilon$ according to the equation:

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

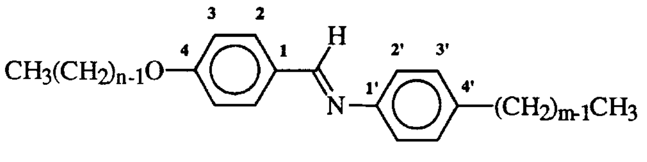
where f is a scaling factor characteristic of the dipolar decoupling sequence and in our case is equal to 0.420 for the BLEW-48 dipolar decoupling sequence,[10,11] J is the C-H scalar coupling, and θ is the angle between the spinning axis of the sample and the magnetic field.

For a phenyl ring with effective D_2 symmetry and the twofold axis taken as the z axis in the molecular frame, the dipolar coupling constant D_{ij} between two interacting nuclei i and j is related to the order parameters $S_{\alpha\beta}$ by the equation:[5]

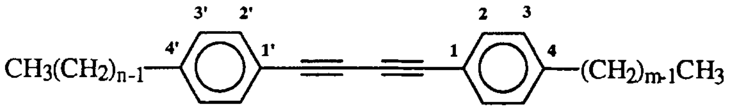
$$D_{ij} = -\frac{\gamma_i\gamma_j(h/2\pi)^2\mu_0}{2\pi\langle r_{ij}^3\rangle}\left[\left(3\cos^2\theta_{ijz} - 1\right)S_{zz} + \left(\cos^2\theta_{ijx} - \cos^2\theta i_{jy}\right)\left(S_{xx} - S_{yy}\right)\right] \tag{2}$$

where $\theta_{ij\alpha}$ is the angle between the internuclear vector r_{ij} and the molecular axis α, and $S_{\alpha\beta}$ are elements of the diagonalized and traceless order parameter matrix in the molecular frame with α, $\beta = x, y, z$. Because the dipolar coupling can be obtained from the splitting in the ω_1-dimension in the SLF/VAS spectra, the order parameters can be calculated by a least-square fit of a set of the dipolar coupling constants into Eq. (2). Since the 2D experiments are more time-demanding, a method using the C-13 chemical shifts obtained from conventional 1D C-13 spectra has also been developed in conjunction with the SLF/VAS method to investigate the orientational ordering of liquid crystals, the principle of which has been described previously.[12]

In this work, we have studied the orientational ordering of six liquid crystalline compounds in two homologous series of liquid crystals, namely 4-*n*-alkoxybenzilidene-4'-*n*-alkylanilines (*n*O.*m*) and 4,4'-di-*n*-alkyldiphenyldiacetylenes (PTTP). The *n*O.*m* compounds are perhaps the most extensively studied liquid crystals. In a previous report, we investigated the orientational ordering of several compounds in this series in relation to their phase transitions,[13] but did not present the correlation between the C-13 chemical shifts and the order parameters. The PTTP compounds have low viscosity and are useful as hosts for certain types of liquid crystal switches.[14] An early study of one of the PTTP compounds showed that the C-13 chemical shifts in the isotropic and the liquid crystalline phases are very different,[15] but the information was not utilized to study the orientational ordering quantitatively. In the present work, a linear relationship between the order parameter of each phenyl ring and the chemical shift of the corresponding carbon nuclei has been verified for both homologous series. The experimental parameters obtained in the linear relations can be used to calculate the order parameters for other members of these homologous series of liquid crystals from their C-13 chemical shifts. The results reported here complement those presented in earlier works, and furnish a convenient and useful database for the evaluation of order parameters of these classes of liquid crystals from simple measurements of C-13 chemical shifts.



*n*O.*m*



PTTP

EXPERIMENTAL

The SLF/VAS NMR experiments on the liquid crystals were carried out on a Varian XL-300 spectrometer at 75.5 MHz, using a variable-angle spinning probe manufactured by Doty Scientific, Columbia, SC. The angle between the spinning axis and the magnetic field was set at about 47° and calibrated by measuring the F-19 splitting of a sample of 2,2-difluoro-1,1,1,2-tetrachloroethane dissolved in the liquid crystalline solvent ZLI-1291 with and without sample spinning.[16] The spinning rate of the rotor was maintained at about 1 kHz. The data from the XL-300 NMR spectrometer was processed on a Sun 3/60 workstation. The splittings of the overlapping multiplets in the ω_1 dimension were deconvoluted by lineshape analysis, in which the experimental signal was fitted as a sum of several gaussian peaks, using a nonlinear least square method called SPIRAL implemented on an IBM RS/6000 workstation.

The C-13 chemical shifts were measured on a Varian VXR-500S spectrometer at 127.5 Hz using an NCC ID-500-5 5mm indirect detection probe manufactured by Narolac Corporation, Martinez, CA, to provide high proton decoupling efficiency. The samples were spun along the magnetic field, so that the director aligned along the field vector. The spinning rate was maintained at about 8 Hz to avoid the formation of spinning vortex. The decoupler duty cycle was set to about 0.5% with a 6-seconds overall cycling time to avoid radiofrequency overheating.

The compounds studied were synthesized according to original procedures reported in the literature.[17,18] The starting materials were purchased from Aldrich Chemical Company, Inc. and Frinton Laboratory, and were used without further purification. Column chromatography was performed on silica gel (Aldrich Chemical Company, Inc., 70-230 mesh, 60Å). The identities of the products were confirmed by ^{1}H-NMR at 300 MHz with a Varian XL-300 spectrometer. The purity and the transition temperatures of the final products were checked by the use of an Olympus BH-2 polarizing microscope equipped with a Linkham PR 600 heating stage. Some of the values are slightly different from those listed in previous studies.[17,18]

RESULTS AND DISCUSSIONS

The C-13 NMR spectra of six liquid crystals belonging to four homologous series were studied at three to four different temperatures each. The temperatures were calibrated relative to the isotropic-nematic transition temperature T_{NI} to exclude systematic errors. The carbon peaks were assigned by using the increment system described by Kalinowski, Berger and Braun,[19] and by considering the splitting patterns in the ω_1 dimension.

The 1D and 2D spectra of 5O.5 are shown in Figures 1 as an illustration. Due to the rapid rotation of the phenyl rings around the C_2 axis, the signals for the quaternary carbons are split into triplets by the two equivalent *ortho* protons. The signal for each proton-bearing carbon is split by the protons in *ipso* and *ortho* position, resulting in a doublet of doublets. Compared to the isotropic spectra, the aromatic peaks in the liquid crystalline phase always shift downfield. For samples spinning at an angle with respect to the magnetic field, the observed chemical shift δ_{obs} is related to the conventional chemical shift δ_{LC}, which is determined when the director is aligned along the magnetic field, by the relation:

$$\delta_{LC} - \delta_{iso} = 2(\delta_{obs} - \delta_{iso})/(3\cos^2\theta - 1) \tag{3}$$

Therefore, for samples spinning at an angle θ with respect to the magnetic field, the changes in the chemical shifts, δ_{LC} - δ_{iso}, are less than the corresponding for samples spinning along the magnetic field by a scaling factor of $(3\cos^2\theta-1)/2$.

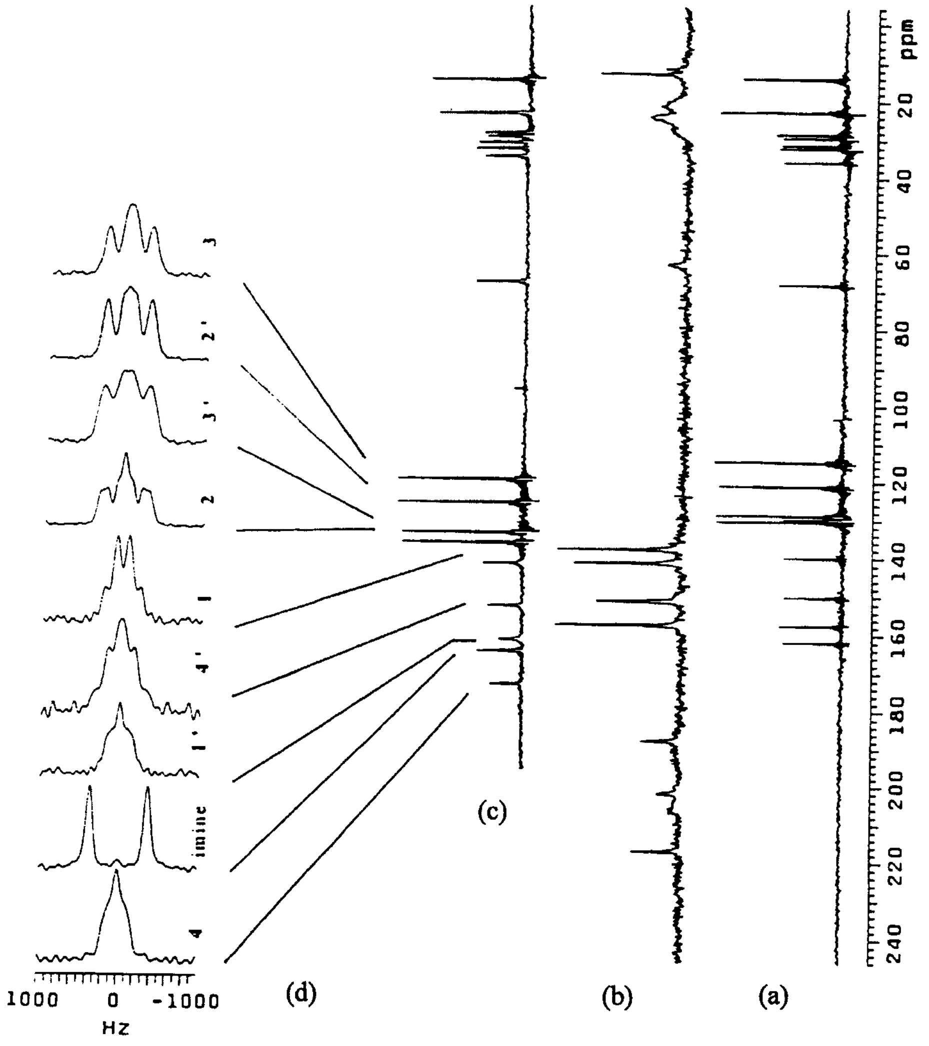


Figure 1. C-13 NMR spectra of 5O.5; (a) in an isotropic phase at 95°C; (b) in a nematic phase at T_{NI}-T ≈ 13°C, with the sample's spinning axis parallel to magnetic field; (c) in the nematic phase at T_{NI}-T ≈ 13°C, with the sample's spinning axis forming an angle of 47.1° with respect to the magnetic field; (d) traces in ω_1 dimension of the 2D SLF/VAS method for the spectrum in (c).

After calculating the dipolar coupling constants $D_{C\text{-}H}$ from the splittings in the ω_1 dimension in the 2D SLF/VAS spectra, the core order parameters were obtained by fitting the $D_{C\text{-}H}$ values into Eq. (2). This procedure gave a set of order parameters and C-C-H bond angles for each temperature. Each bond angle for different compounds in the same homologous series was then averaged at all temperatures measured. These averaged bond angles were then treated as constants to refine the order parameter calculations.

It has been shown that for a phenyl ring which possess effective D_2 symmetry, the relation between the order parameter and the chemical shift can be approximated by the semi-empirical equation:[12]

$$\delta_{LC} \approx \delta_{iso} + \frac{2}{3} S_{zz}\Delta\sigma + b \tag{4}$$

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. Eq. (4) can be rewritten to give

$$S = \alpha \cdot \Delta\delta + \beta \tag{5}$$

where $\Delta\delta = \delta_{LC} - \delta_{iso}$, $\alpha \approx 3/(2\Delta\sigma)$, $\beta = -3b/(2\Delta\sigma)$, and the subscript zz in S_{zz} is dropped. To obtain the general correlation for a homologous series, the changes in chemical shifts, $\Delta\delta$, for compounds of the same series were pooled together and correlated with their corresponding order parameters. The plots for the *n*O.*m* series are shown in Figure 2 as an illustration. The results for the linear least squares fitting are listed in Tables I and II for the two homologous series.

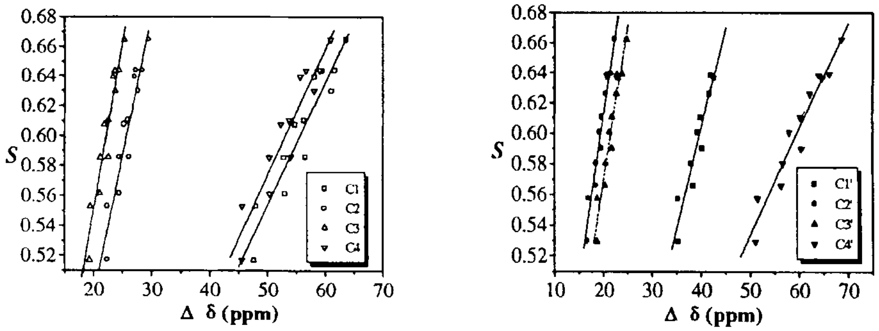


Figure 2. The order parameters plotted against the values of $\Delta\delta$ for the phenyl rings in *n*O.*m*.

TABLE I Calculated values of α and β and their standard errors $\Delta\alpha$ and $\Delta\beta$ for each C-13 nucleus in the phenyl rings of *n*O.*m*.

Carbon Nucleus	1	2	3	4	1'	2'	3'	4'
α	0.0082	0.019	0.022	0.0084	0.013	0.022	0.020	0.0069
$\Delta\alpha$	0.0009	0.002	0.002	0.0009	0.002	0.002	0.002	0.0006
β	0.15	0.12	0.11	0.15	0.08	0.17	0.16	0.19
$\Delta\beta$	0.05	0.05	0.05	0.05	0.06	0.04	0.04	0.03

TABLE II Calculated values of α and β and their standard errors $\Delta\alpha$ and $\Delta\beta$ for each C-13 nucleus in the phenyl rings of PTTP.

Carbon Nucleus	1	2	3	4
α	0.0080	0.020	0.019	0.0077
$\Delta\alpha$	0.0006	0.002	0.002	0.0006
β	0.09	0.21	0.01	0.11
$\Delta\beta$	0.04	0.03	0.05	0.03

In general, the changes in chemical shifts, $\Delta\delta$, are much larger for the 1, 4, 1' and 4' carbons than the 2, 3, 2' and 3' carbons for the following reason. For substituted benzenes, the major axis of the C-13 chemical shift tensor is usually quite close to the C-H or C-X bond axis. Since the C-X axis for the 1, 4, 1' and 4' carbons atoms coincides with the z axis, their chemical-shift anisotropy, $\Delta\sigma$, would be approximately equal to $3/(2\alpha)$. The C-H bonds for 2, 3, 2' and 3' carbons form an angle of *ca.* 60° with the z axis, resulting in smaller $\Delta\sigma$ and $\Delta\delta$ values, therefore larger α.

For an asymmetric compound, the two phenyl rings do not have a common C_2 axis, and their order parameters are slightly different. However, in the case of the PTTP series, the rings have a common C_2 axis, and the only difference between the two phenyl rings is the length of the alkyl chain they bear. As a result, the differences between the chemical shifts of the corresponding carbons in the two rings are negligible. Therefore, only one set of chemical shift data and order parameter is obtained for each compound in this series.

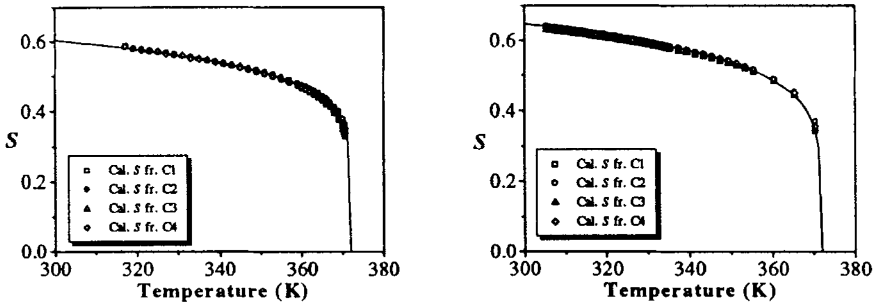


Figure 3. Temperature dependence of the core parameter *S*. Left, calculated *S* for PTTP24 from Eq. (5) using the chemical shift data; right, calculated *S* for PTTP36 from Eq. (5) using the chemical shift data.

After obtaining the values of the empirical constants α and β, the core order parameter *S* for each of the compounds at different temperatures was determined more systematically using chemical shift data measured by 1D C-13 NMR at closer temperature intervals. As examples, the temperature dependence of the core order parameters for PTTP24 and PTTP36 in the nematic phase are depicted in Figures 3. The temperature dependence of the order parameter can be fitted as a function of reduced temperature (T/T^*) by the following equation.[20]

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

where S_0 and F are empirical constants, T^* is a temperature slightly above T_{NI} and may be related to pre-transitional behavior. S_0 may represent the limit of the order parameter with decreasing temperature, and F may be considered as an indication of the rate of equilibration of a molecular fragment as temperature decreases. This empirical correlation may be regarded as a special case of the Landau-de Gennes theory to describe the molecular ordering for isotropic-nematic transitions.[21] The values of S_0, F and T^*-T_{NI} obtained from fitting the data to Eq. (6) are 0.758, 0.138, and 1.0 K, respectively, for PTTP24, and 0.840, 0.157, and 0.9 K, respectively, for PTTP36. In a study of the temperature dependence of the birefringence of the PTTTP series, Wu *et al.* obtained a value of *ca.* 0.241 for F by setting S_0 = 1.0, and $T^* = T_{NI}$.[22] However, we could not get a reasonable fit for our data by using S_0 = 1.0, and believe that the three-parameter fit is more appropriate.

CONCLUSIONS

A study of the relation between C-13 chemical shifts and order parameters for six liquid crystalline compounds in the *n*O.*m* and PTTP series has been performed. For each type of aromatic carbon nucleus in the same homologous series, a linear relation between $\Delta\delta$ and the order parameter S of the corresponding molecular segment is observed. The parameters of the linear correlations are tabulated, and they can be used for the evaluation of order parameters for the two series of liquid crystals from simple measurements of C-13 chemical shifts.

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