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Study of phase transitions in 4-*n*-alkoxybenzilidene-4′-*n*-alkylanilines by one and two dimensional ^{13}C NMR

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The phase transition of a series of homologous liquid-crystalline compounds, *n*O.*m* (4-*n*-alkoxybenzilidene-4′-*n*-alkylanilines), from the nematic phase to the smectic A phase has been studied by ^{13}C NMR. The order parameters, determined by a two dimensional technique called separated local field spectroscopy combined with off-magic angle spinning, of different molecular segments of these compounds are related linearly to the ^{13}C chemical shifts. Changes in the order parameters of the phenyl rings as well as those of the chains during the S_A–N transition depend on the nature of the phase transition. These changes are quantitatively related to the McMillan ratio, which is defined as the ratio between the S_A–N transition temperature (T_{S_AN}) and the nematic to isotropic transition temperature (T_{NI}), i.e. $M = T_{S_AN}/T_{NI}$. The S_A–N transition is first order for $M > M_{TCP}$, and second order for $M < M_{TCP}$, where TCP is the tricritical point. The value of M_{TCP} was found to be $0{\cdot}958 \pm 0{\cdot}004$, in excellent agreement with that obtained from spin probe studies ($0{\cdot}959 \pm 0{\cdot}005$) reported by Freed and co-workers [1].

1. Introduction

The nature of phase transitions between different liquid-crystalline phases has been a subject of considerable interest. Perhaps the most widely studied phase transition is between the smectic A phase and the nematic phase because of the common presence of these phases in those liquid-crystalline compounds which have broad applications in electro-optic devices. Quantitatively, the order of the S_AN phase transition can be described by the McMillan parameter, *M* [2], which is defined as the ratio between the S_A–N and N–I transition temperatures, i.e. $M = T_{S_AN}/T_{NI}$. For liquid crystals with the same core structure but different chain lengths, the S_A–N transition is first order if *M* is larger than M_{TCP}, where TCP is the tricritical point, and the transition is second order if *M* is smaller than M_{TCP} [1–3], In other words, compounds with a narrow nematic range undergo a first order S_A–N transition, and those with a wide nematic range undergo a second order S_A–N transition.

According to the theory of de Gennes [4], a first order S_A–N transition occurs when there are large fluctuations in the smectic and nematic order parameters (*S*). When the nematic range is extended, the coupling term between the order parameters of the two phases would be reduced. Consequently, we may expect a discontinuity in *S* during the first order S_A–N transition for compounds with a narrow nematic range, and a continuous change in *S* during the second order S_A–N transition for compounds with a wide nematic range. This was verified experimentally by Freed and co-workers [1, 3],

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who studied the order parameters and ESR linewidths of two spin probes dissolved in a series of homologous compounds, 4-*n*-alkoxybenzilidene-4′-*n*-alkylanilines, which are abbreviated as *n*O.*m*. These types of compounds are among the most extensively studied liquid crystals because they have rich polymorphism and are easy to prepare. Freed and co-workers found that the change in the order of the S_A–N transition (tricritical point) corresponds to a McMillan ratio of $M = 0{\cdot}959 \pm 0{\cdot}005$ for this series [1–3]. More recently, they have reported a model for the ordering of spin probes [5] and a further experimental study of their relaxation behaviour during the phase transition [6].

One of the problems of using spin probes is that their locations with respect to the liquid crystal host can vary with changes in the liquid-crystalline phase, and the results may also depend on the probe used [1]. On the other hand, order parameters of pure liquid crystals can be obtained from NMR spectroscopy. We have demonstrated that the order parameters of different molecular segments of a liquid crystal molecule can be determined by the use of ^{13}C NMR [7–20]. The method is a combination of the two dimensional separated local field (SLF) spectroscopy and variable angle spinning (VAS). Once the order parameters are determined for several compounds in a homologous series at several temperatures, they can be correlated with the ^{13}C chemical shifts obtained from the one dimensional spectra [16–20]. Then, the order parameters of other compounds in the same series can be obtained from the chemical shift data at a large number of temperatures by using these linear correlations. The values of the order parameters of different molecular segments of the liquid crystal molecules give more direct and detailed information on the orientational ordering than the data obtained from spin probe investigations, and the results of the order parameter measurements for the *n*O.*m* series will be compared with those obtained by Freed and co-workers [7, 8].

2. Experimental

The compounds 4O.6, 4O.7, 4O.8, 5O.6, 5O.7 and 6O.4 were purchased from Frinton laboratories and were recrystallized from hexane. The compounds 6O.3, 6O.5, 7O.4, and 7O.5 were synthesized in this laboratory by directly mixing the corresponding aldehydes and amines; they were also recrystallized from hexane.

The transition temperatures were determined by the use of an Olympus BH-2 polarizing microscope equipped with a Linkham PR 600 heating stage. In this work, we are only interested in the S_A–N and N–I transitions, the temperatures of which are given in table 1. Some of the values are slightly different from those listed in previous studies [1, 21]. The phase transitions observed by microscopy and NMR spectroscopy were sharp, indicating a high purity for each compound studies.

All the ^{13}C NMR experiments were carried out at 125·7 MHz on a Varian VXR-500 spectrometer. The off-magic angle spinning experiments were performed using a variable-angle probe manufactured by Doty Scientific.

3. Results and discussion

3.1. *Determination of order parameters by the SLF/VAS method*

In the past few years we have used two dimensional ^{13}C NMR to study the orientational ordering of a large number of liquid crystals [7–20]. The technique used has been described previously [7–20], and the details will not be repeated here. For the sake of clarity, the principles of the method are briefly reviewed below.

Table 1. The transition temperatures (°C) for *n*O.*m* homologues from polarizing microscopic studies. The first set of values was determined by sample heating, and the second set in parenthesis was measured during cooling.

Compound	S_A ↔ N	N ↔ I
4O.6	59·1	77·5
	(59·2)	(77·5)
4O.7	56·1	83·0
	(56·1)	(82·9)
4O.8	63·8	79·0
	(63·5)	(78·8)
5O.6	61·4	73·2
	(61·1)	(73·0)
5O.7	63·7	77·4
	(63·5)	(77·4)
6O.3	66·1	82·2
	(65·8)	(82·2)
6O.4	69·2	76·9
	(68·9)	(76·9)
6O.5	74·0	84·2
	(73·9)	(84·3)
7O.4	79·1	82·4
	(78·9)	(82·7)
7O.5	73·8	75·9
	(73·5)	(75·8)

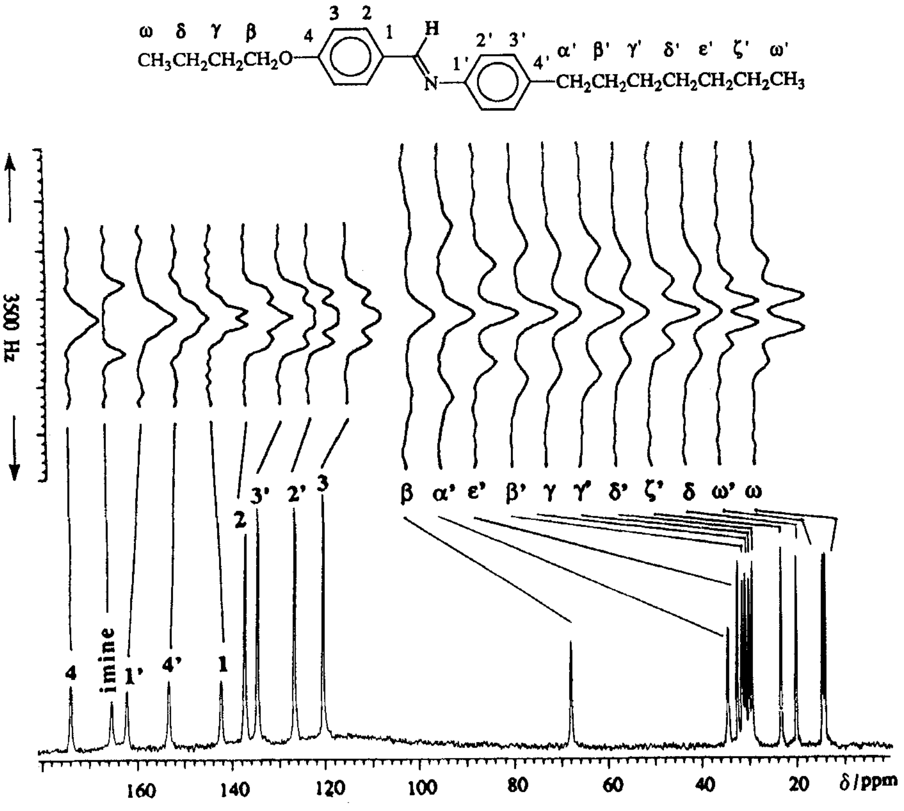

Figure 1. ^{13}C VAS/SLF spectra of 4O.7 at 127·7 MHz and 50·0°C. Spectra in the ω_1 dimension are shown on top, and the spectrum in the ω_2 dimension is shown at the bottom. The assignments are indicated in the molecular structure.

A nematic or smectic liquid crystal is spun rapidly (at a rate of 1–2 kHz) at an angle, β, with respect to the magnetic field, B_0, to reduce the dipolar couplings and obtain sharp ^{13}C peaks. The angle, β, in this work was chosen to be 47·9–48·0°. In the 2D SLF method, an efficient proton–proton dipolar decoupling sequence BLEW-48 [22] is applied during the evolution period, so that first order C–H couplings can be observed in the ω_1 dimension of the experiment. As an example, spectra of 4O.7 at $T = T_{NI} - 15°C$ are shown in figure 1. The normal 1D spectrum, containing chemical shift information, is obtained in the ω_2 dimension, and is shown at the bottom. It is gratifying to note that with VAS at high magnetic field, the ^{13}C peaks for all 11 carbons in the aliphatic chains are resolved. The assignment of the aromatic peaks was made in accordance with that for EBBA (4-*n*-ethoxybenzilidene-4′-*n*-butylaniline, or 2O.4) [7], and the assignment for the alkyl peaks follows that for cyanobiphenyls [23]. The spectra in the ω_1 dimension are shown on top, and they all exhibit first order C–H splittings: the methylene carbons are split into triplets, the methyl carbons are split into quartets, the imine carbon is split into a doublet, and the protonated aromatic carbons are split into multiplets due to couplings with *ipso* and *ortho* protons (C3 and C4 are coupled with the imine proton also). The splittings ($\Delta\nu$) for the overlapping multiplets can be easily obtained by fitting the spectra with a sum of the suitable number of gaussian peaks. Then, the dipolar coupling constants, D, can be calculated:

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

where f is a scaling factor for the dipolar decoupling sequence ($f = 0{\cdot}42$ for BLEW-48 [24]), and J is the scalar coupling constant.

Because of molecular symmetry and internal rotation, the order parameters S_{zz}, $S_{xx} - S_{yy}$, and the H–C–C bond angles for each phenyl ring can be calculated from the six C–H dipolar coupling constants by the use of least squares analysis [8]. The calculation of the order parameters of each ring is aided by allowing each ring to possess its own set of axes; the convention of the axis systems is such that the C_2 axis of each ring is defined as the z axis in the calculation, and the normal to the ring is defined as the y axis. The assignment of a separate axis system to each ring prevents the mathematical complications of transforming the molecular coordinates to a single axis system encompassing both rings. The average bond angles obtained from the results at several temperatures are: $\angle$C3–C2–H2 = 120·1 ± 0·4°, $\angle$C2–C3–H3 = 120·0 ± 0·5°, $\angle$C3′–C2′–H2′ = 120·0 ± 0·3°, and $\angle$C2′–C3′–H3′ = 119·4 ± 0·2°. The slight compression of the C2′–C3′–H3′ bond angle is likely due to the steric factor of the α-CH_2 group in the alkyl chain, and is consistent with the results of our previous studies [8–10]. For the alkyl chains, the order parameter of each C–H bond is a weighted average for all conformations, and is directly proportional to the corresponding C–H dipolar coupling constant [10]. The order parameters for 4O.6, 4O.7, and 4O.8 at $T - T_{NI} = 15°C$ are listed in tables 2 and 3.

The results in table 2 show that S_{zz} for the first ring is always slightly smaller than that for the second ring, but the differences are within experimental error. However, it is not unreasonable to expect the two phenyl rings to have different order parameters because their C_2 axes are not parallel [25]. The values of $S_{xx} - S_{yy}$ are quite small for both rings, indicating that, with rapid internal rotation (or jumps between four possible equilibrium positions), the biaxiality of each ring is small. It is interesting to note that the values of S_{zz} for 4O.7 at $T_{NI} - T = 15°C$ are smaller than those for 4O.6 and 4O.8 (see table 2), but at the S_A–N transition, S_{zz} for 4O.8 is the smallest (see later). This may be related to the different nematic ranges for the three compounds (18·3°C, 26·8°C, and

Table 2. Core order parameters at $T-T_{NI}=15°C$.

	S_{zz}	$S_{xx}-S_{yy}$	S'_{zz}	$S'_{xx}-S_{yy}$
4O.6	0·647±0·008	0·020±0·003	0·633±0·004	0·014±0·002
4O.7	0·612±0·006	0·023±0·002	0·598±0·017	0·014±0·007
4O.8	0·624±0·006	0·023±0·003	0·618±0·004	0·014±0·002

Table 3. C–H order parameters at $T-T_{NI}=15°C$. Experimental uncertainty in the order parameters is ~5 per cent.

Carbon	4O.6	4O.7	4O.8
Imine	−0·214	−0·188	−0·190
α	−0·248	−0·215	−0·221
β	−0·153	−0·151	−0·157
γ	−0·120	−0·110	−0·113
ω	−0·090	−0·086	−0·079
α'	−0·248	−0·241	−0·245
β'	−0·207	−0·189	−0·191
γ'	−0·167	−0·165	−0·132
δ'	−0·114	−0·126	−0·139
ε'	−0·118	−0·132	−0·148
ζ'	—	−0·085	−0·100
η'	—	—	−0·099
ω'	~0	−0·051	~0

15·3°C, respectively, for 4O.6, 4O.7, and 4O.8). The C–H order parameters for the α and γ carbons in the alkoxy chain follow the same trend as the core order parameters (see table 3). On the other hand, the values of S_{CH} for the alkyl chains are comparable to each other, except that the odd–even effect [26] makes $|S_{CH}|$ for the CH_3 group in 4O.7 considerably higher than the corresponding values of 4O.6 and 4O.8, which are essentially zero. For a clear comparison of this effect, the data in table 3 are plotted in figure 2. It is of interest to note that the values of $|S_{CH}|$ for the alkyl chains show less alternation along the chain than those values for alkylcyanobiphenyls (*n*CB) [26]. In comparison, the $|S_{CH}|$ values for the shorter alkoxy chain decrease monotonically towards the end of the chain and show no alternation. This result for the short alkoxy chain is not readily comparable with the appropriate alkoxycyanobiphenyl (*n*OCB) because 4OCB is monotropic.

3.2. *Determination of order parameters from ^{13}C chemical shifts*

To study the temperature dependence of a large number of homologous compounds over wide temperature ranges, it would take an enormous amount of spectrometer time if the 2D SLF/VAS method were used. Furthermore, experimental imperfections and small uncertainties in data analysis would make it difficult to determine very small changes in the order parameters during phase transitions. On the other hand, we can combine the SLF/VAS results with ^{13}C chemical shift data [16–20],

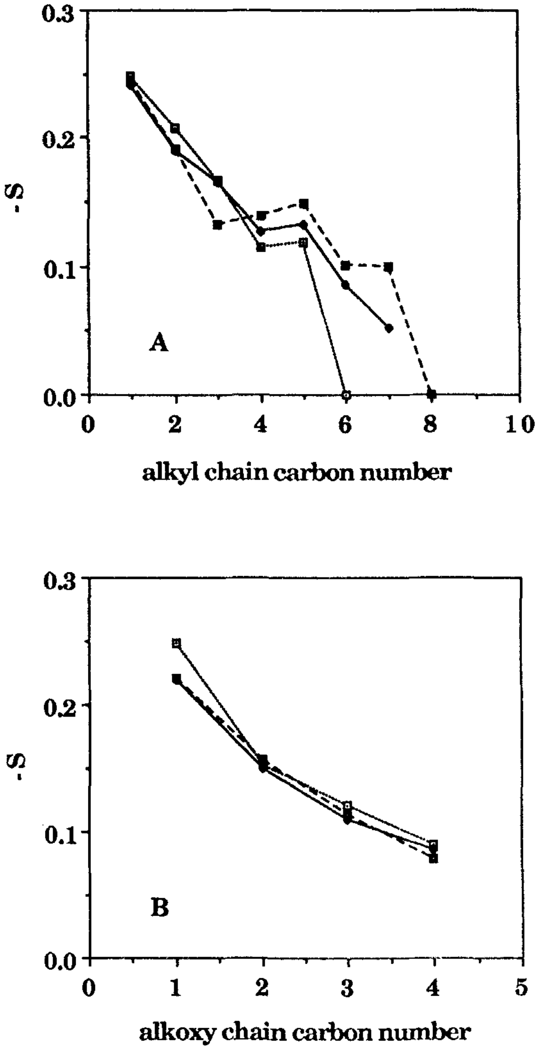

Figure 2. The C–H bond order parameters of the individual chains 4O.6 (□), 4O.7 (◆) and 4O.8 (■) at $T-T_{NI}=15°C$. The carbon numbers correspond to the carbons listed in table 3; the carbon number 1 is an α carbon, and the last carbon in the chain is an ω carbon. A, The alkyl chain; B, the alkoxy chain.

which are readily obtained from one dimensional NMR experiments and can be measured accurately as a function of temperature.

We have shown that a semi-empirical relation between 13C chemical shift and order parameter can be established for both the phenyl rings and the C–H bonds in the aliphatic chains [20]

$$\Delta\delta = aS + b, \tag{2}$$

where $\Delta\delta=\delta_{LC}-\delta_{iso}$, a and b are empirical constants, and the subscript in S_{zz} for the phenyl rings or S_{CH} for the chains is dropped (there is a misprint for the sign of b in [20]). With VAS, the anisotropic chemical shift is scaled by a factor of $(3\cos^2\beta-1)/2$; therefore, the observed value of $\Delta\delta$ in equation (2) should be divided by this factor.

Equation (2) is not strictly applicable for temperatures very close to the clearing point, at which both $\Delta\delta$ and S approach zero.

3.3. *Comparison of the order parameters of different homologous compounds*

To evaluate the constants a and b in equation (2) for the *n*O.*m* series, the order parameters for the phenyl rings and the alkyl chains in 4O.6, 4O.7, and 4O.8 were determined at three to five temperatures for each compound by the SLF/VAS method. Their values are correlated with the corresponding ^{13}C chemical shifts, assuming that each carbon atom in the phenyl rings and in the OCH_2 group of different homologous compounds has the same set of a and b values [20]. The corresponding values of a and b for the methyl group were determined previously from more extensive experimental data [20]. Then, these constants were used to calculate the order parameters of other compounds in the *n*O.*m* series from data of the ^{13}C chemical shifts as functions of temperature. In this part of the determination, the chemical shift data were obtained with normal slow sample spinning (16 Hz) at $\beta = 0°$ rather than using VAS, because $\Delta\delta$ has the optimal values for the normal slow spinning configuration. Since the samples must be macroscopically aligned in the magnetic field, the experiments were performed by lowering the temperature from isotropic to nematic to smectic A to higher smectic phases.

To illustrate the relation between ^{13}C chemical shifts and the orientational ordering of liquid crystals, several spectra of 6O.5 in the aromatic region are shown in figure 3. During the S_A–N transition, the two phases coexist because of a small temperature gradient in the sample tube. Consequently, two sets of ^{13}C peaks appear in the ^{13}C spectra. The differences in the chemical shifts between the liquid-crystalline phases and

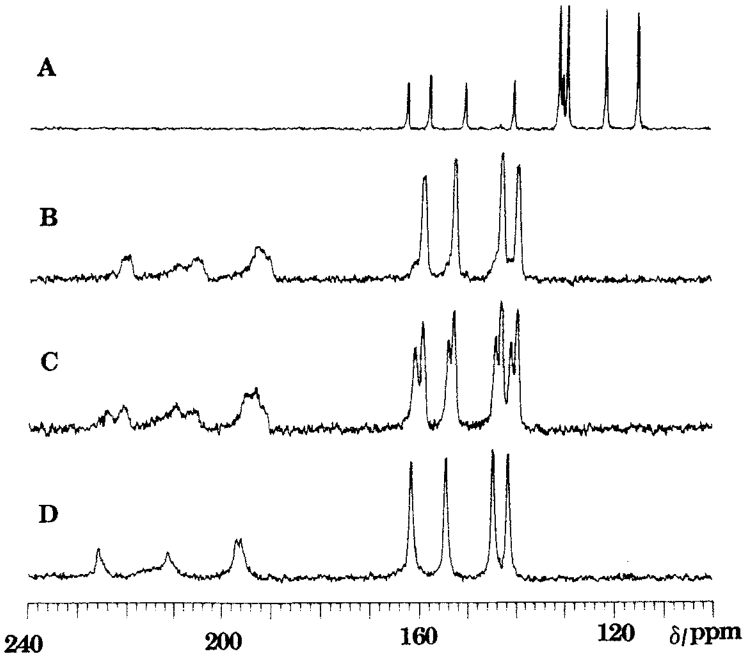

Figure 3. ^{13}C NMR spectra of 6O.5 at 125·7 MHz, aromatic region only. A, isotropic phase (85°C); B, nematic phase (74·5°C); C, nematic + smectic A phase (73·8°C); D, smectic A phase (72·8°C).

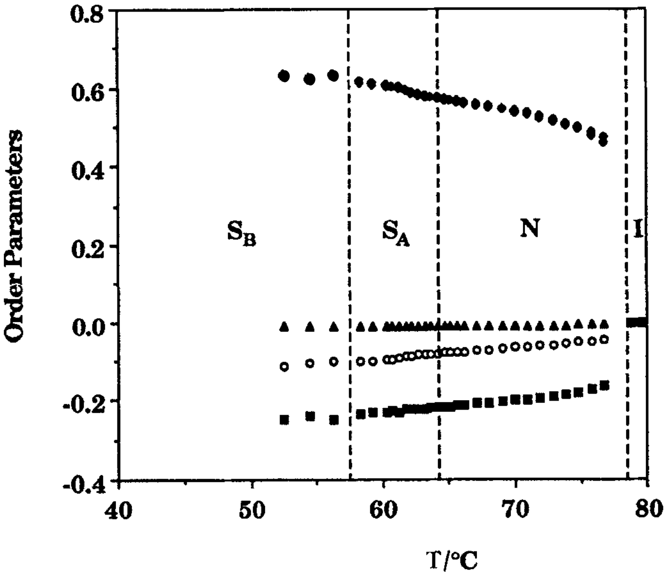

Figure 4. The order parameters of 4O.8 at different temperatures. The core order parameters are designated: ◆, S_{zz}; ◇, S'_{zz}. The C–H bond order parameters, S_{CH}, are designated: ○, ω-CH_3 (alkoxy); ▲, ω'-CH_3 (alkyl); ■, CH_2.

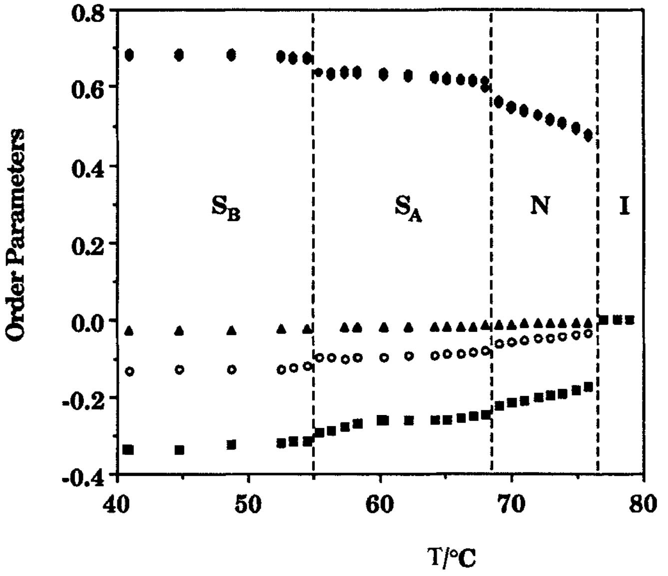

Figure 5. The order parameters of 6O.4 at different temperatures. ◆, S_{zz}; ◇, S'_{zz}; ○, ω-CH_3 (alkoxy); ▲, ω'-CH_3 (alkyl); ■, CH_2.

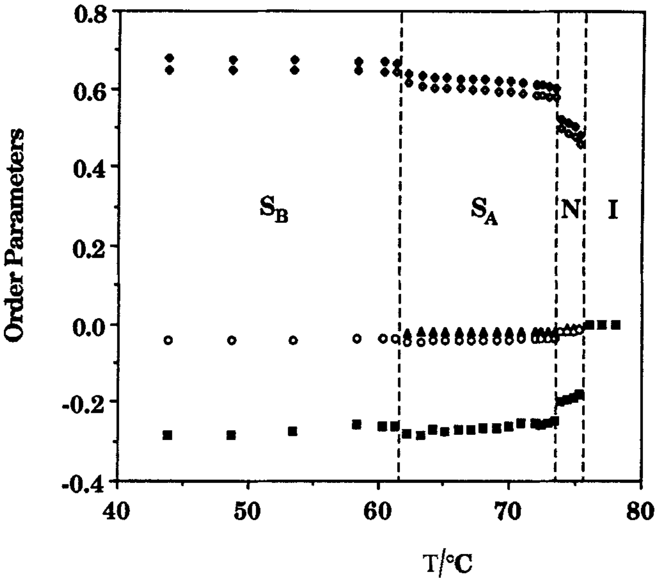

Figure 6. The order parameters of 7O.5 at different temperatures. ◆, S_{zz}; ◇, S'_{zz}; ○, ω-CH_3 (alkoxy); ▲, ω'-CH_3 (alkyl); ■, CH_2.

the isotropic phase are linearly related to S, as given by equation (2). The carbons in the aliphatic chains have smaller chemical shift anisotropy, and the splittings are obscured by line broadening. Two sets of ^{13}C peaks for the protonated phenyl carbons were also observed for 5O.6, 5O.7, 6O.4, 7O.4, and 7O.5 at the S_A–N transition temperature, but not for 4O.6, 4O.7, and 4O.8.

The order parameters (S) for 4O.8, 6O.4 and 7O.5 determined from the chemical shifts are plotted in figures 4, 5, and 6, respectively. Plots for other compounds are similar. The assignment of the methyl peaks is such that a CH_3 group in a chain with an odd number of atoms has a more negative order parameter [26]. Figure 4 shows that the order parameters of 4O.8 exhibit an inflection at the S_A–N phase transition, but do not show appreciable discontinuity. On the other hand, figures 5 and 6 show that the order parameters for both rings, the α-CH_2 group, and the CH_3 groups in 6O.4 and 7O.5 all exhibit discontinuities (ΔS) during the phase transition. The ratio $\Delta S/S$ for various groups are similar, indicating that during the phase transition the relative orientational ordering of the flexible chains changes as much as the ordering of the rigid core changes. Because of the odd-even effect, the C–H bond order parameter for the ω'-CH_3 group in 6O.4 is too small to show any appreciable discontinuity, but the corresponding data for 7O.5 do show a discontinuity during the S_A–N phase transition. For slow sample spinning at $\beta = 0°$, the ^{13}C peaks of other CH_2 groups are not so well resolved as those in the ω_2 spectrum shown in figure 1, and their order parameters could not be determined accurately.

Using this method, the order parameters of other homologous compounds in the *n*O.*m* series have been determined. Results of the order parameters for the phenyl rings of nine compounds at their S_A–N transition temperatures are plotted against the McMillan ratio in figure 7. Because S_{zz} for the two phenyl rings is slightly different (see figures 4–6), the average values are used in the plot to avoid overcrowding. Corresponding changes for the aliphatic chains are somewhat smaller and therefore

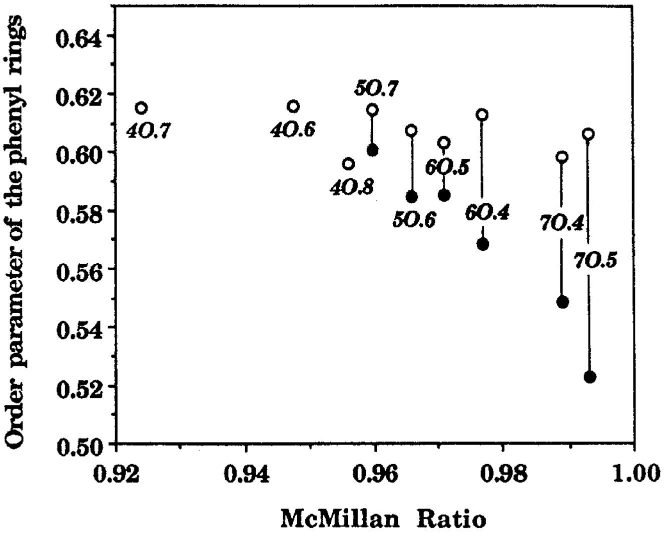

Figure 7. The average core order parameters, S_{zz}, plotted versus the McMillan ratio for the indicated *n*O.*m* compounds at the S_A–N transition temperature, ○, smectic A phase; ●, nematic phase.

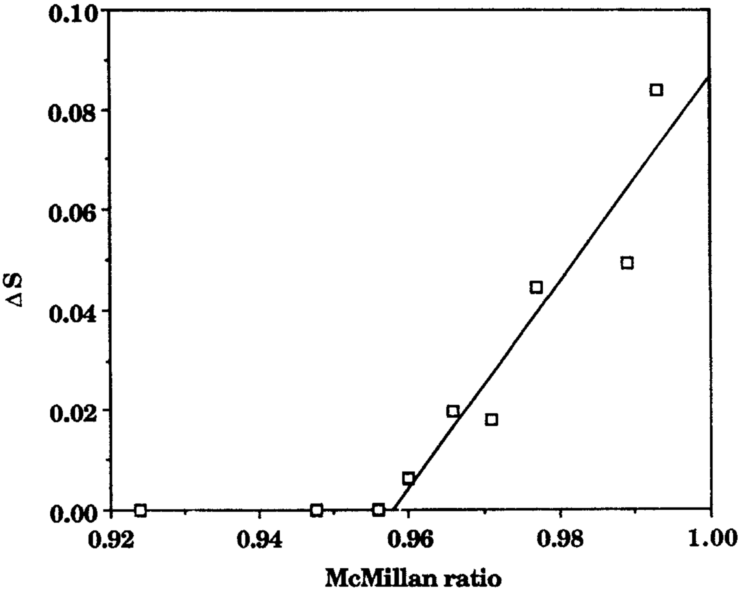

Figure 8. ΔS plotted versus the McMillan ratio for the *n*O.*m* compounds shown in figure 6. The solid line is the result of fitting the data to equation (3). Also shown are points for the 4O.*m* series, for which ΔS was essentially zero.

not considered. The data in figure 7 show that ΔS decreases with the decrease of the McMillan ratio, M, which corresponds to an increase in the nematic range. These results are similar to those obtained from spin-probe studies [1, 3]. However, it should be noted that the values of S_{zz} in figure 5 are somewhat smaller than the corresponding values obtained from ESR experiments [1]. A possible reason for this is that the C_2 axis of each phenyl ring forms a small angle with respect to the nematic director, making their S_{zz} values slightly less than the order parameter of the director. It is of interest to note that for the three compounds (4O.6, 4O.7, and 4O.8) which do not exhibit a jump in the order parameter during the S_A–N transition, the one that has the smallest nematic range (4O.8) more or less follows the trend for the nematic phase rather than the trend for the smectic phase (see figure 7).

To obtain a quantitative correlation, the values of ΔS for the compounds in the *n*O.*m* series are plotted as a function of the McMillan ratio M in figure 8. Freed and co-workers proposed that these two quantities are related by the equation [1]

$$\Delta S \propto (M - M_{TCP})^{\beta_2}, \tag{3}$$

where M_{TCP} is the tricritical point and β_2 is a constant close to unity. They found that $M_{TCP} = 0{\cdot}959 \pm 0{\cdot}005$ and $\beta_2 = 0{\cdot}94 \pm 0{\cdot}12$ for the *n*O.*m* series. Because of the scattering of the ΔS values obtained from our data (see figure 8), we have set $\beta_2 = 1{\cdot}0$ for the determination of the value of M_{TCP}. Data for compounds with $\Delta S = 0$ were, of course, not used in the least squares calculation. The result is $M_{TCP} = 0{\cdot}958 \pm 0{\cdot}004$, which is in excellent agreement with that obtained from spin probe studies [1].

4. Conclusions

The orientational ordering of 4O.6, 4O.7, and 4O.8 was studied by 2D ^{13}C NMR with off-magic angle spinning. The order parameters of the phenyl rings and the alkyl chains were determined and compared. Using these results, the order parameters of nine homologues in the *n*O.*m* series were determined from their ^{13}C chemical shifts. For compounds with a small nematic range, the order parameters S exhibit a discontinuity (ΔS) at the S_A–N transition. The ratios $\Delta S/S$ for the phenyl rings, the OCH_2 group, and the methyl groups are similar. The value of ΔS becomes smaller as the nematic range becomes larger. The tricritical point was found to be $M_{TCP} = 0{\cdot}958 \pm 0{\cdot}004$, below which the order parameters undergo a smooth change at the S_A–N transition. This value agrees very well with that obtained from ESR measurements ($M_{TCP} = 0{\cdot}959 \pm 0{\cdot}005$). The results show that direct measurements of the order parameters of the liquid crystal molecules confirm the experimental results of Freed and co-workers [1, 3] using spin probes and the theoretical work of de Gennes [4], both of which correlate the order of the S_A–N phase transition with the smectic and nematic order parameters.

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