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Condis Crystals of Small Molecule VI. The Differences Between Smectic and Condis Phases, Evaluated by a Solid State ^{13}C NMR Study of N,N′-bis(4-n-octyloxybenzal)-1,4-phenylenediamine (OOBPD)

Jinlong Cheng [b], Wei Chen [b], Yimin Jin [b] & Bernhard Wunderlich [a]

[a] Department of Chemistry, University of Tennessee, Knoxville, TN, 37996-1600

[b] Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, TN, 37831-6197

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Condis Crystals of Small Molecule VI. The Differences between Smectic and Condis Phases, Evaluated by a Solid State ^{13}C NMR Study of N,N'-*bis*(4-*n*-octyloxybenzal)-1,4-phenylenediamine (OOBPD)

JINLONG CHENG, WEI CHEN, YIMIN JIN, and BERNHARD WUNDERLICH*

**Department of Chemistry, University of Tennessee, Knoxville, TN 37996-1600 and Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6197*

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Carbon-13 NMR spectra have been obtained for N,N'-*bis*(4-*n*-octyloxybenzal)-1,4-phenylenediamine (OOBPD) in the condis and smectic phases. Sharp, well-resolved spectra were obtained without magic angle sample spinning in the smectic phases under the conditions of cross-polarization or single carbon pulse followed by high-power proton decoupling. The smectic I-to-smectic C transition involves a discontinuous change in ^{13}C chemical shifts due to a large degree to orientational disordering. Similar behavior was found between the spectra of smectic C and the isotopic state. Order parameters for various smectic phases are calculated based on the observed differences in ^{13}C chemical shift between the isotropic state and the smectic phase. The spectra were measured at different sample orientation with respect to the external magnetic field, and show that reorienting the smectic molecules in a magnetic field is facile. Larger difference can be found between the spectra obtained by cross polarization and those by single carbon pulse for a smectic liquid crystal that is closer in temperature to the condis phase. The condis-smectic transition is accompanied by the disappearance of the asymmetric chemical shift anisotropy (CSA) and the appearance of an axially symmetric CSA pattern due to the uniaxial molecular orientational motion and ordering.

Keywords: N,N'-bis(4-n-octyloxybenzal)-1,4-phenylenediamine (OOBPD), condis state, liquid crystal, smectic phase, conformational motion, orientational motion, solid state NMR, chemical shift anisotropy pattern, order parameter

*Author for correspondence.

INTRODUCTION

Previous calorimetry and structure analyses[1, 2] of the transitions of N,N'-*bis*(4-*n*-octyloxybenzal)-1,4-phenylenediamine (OOBPD), whose molecular structure is shown in Figure 1, have led to the assignment of the mesophase structures as detailed in Table I.[1] The condis phases K1 to K3 have been the subject of the last paper[1] in this series of publications[1–5] that deal with an effort to further the understanding of conformationally disordered crystals (condis crystals)[6, 7] and their differences from liquid and plastic crystals. It was shown by variable-temperature solid-state ^{13}C CP-MAS NMR and heat capacity analysis[1, 2] that: 1. K1 to K3 are still condis crystals; 2. stepwise freezing of the motion and disorder goes through several condis states (K1, K2, and K3); and 3. in addition to the stepwise changes, a large amount of conformational entropy remains in K3 and some of it is lost gradually at temperatures below the transition region. The disorder left freezes to a glassy condition. In the condis state, the crystals have lost the uniaxial orientational, and the translational disorder and mobility of the liquid crystals, but maintain still various degrees of conformational disorder and mobility.

In this sixth report, liquid crystal behavior of OOBPD will be examined by applying similar ^{13}C NMR techniques, *i.e.,* cross-polarization as well as single ^{13}C pulse followed by high-power proton-decoupling as was used before,[1] but without magic-angle sample spinning. When the sample is kept static, molecular orientational order and motion about the molecular director in the smectic phases produce an unique axially symmetric chemical-shift-anisotropy (CSA) pattern. The resonance positions in the ^{13}C CSA spectra of a liquid crystal depend strongly on the orientational order, governed mainly by the mesogen and can be used to calculate the order parameter *S*. It will be shown that the CSA patterns undergo more pronounced stepwise changes at those transitions between different smectic phases that have larger entropy changes. The CSA patterns for condis crystals, in contrast to liquid crystals, are rather broad and asymmetric due to the lack of translational

TABLE I

Phase assignment for OOBPD[a]

Phases		Temperature Range (K)
K3	condis	130[b]–385.5
K1	condis	385.5–415.4
H'	smectic	415.4–421.8
G'	smectic	421.8–427.2
I	smectic	427.2–436.7
C	smectic	436.7–476.5
N	nematic	476.5–504.8
M	isotropic melt	504.8–higher

[a] Data are measured on a melt-crystallized sample, after Reference 1.

[b] The condis phase changing to a glass at about 250 K was followed in our research only down to 130 K. No changes are expected at lower temperature.

and orientational motion of the molecule as a whole. Molecules in smectic phases are able to reorient to align themselves along the direction of the magnetic field of the NMR spectrometer, while molecules in condis phases cannot align because the remaining molecular motion is only conformational and thus not sufficient to change the orientation of the whole molecule. By comparing the NMR spectra of condis and smectic phases, the dramatic differences between the smectic and condis phases are highlighted. These differences can serve as a signature test to distinguish between the otherwise easily confused mesophases. The same test might also be helpful to distinguish between liquid crystals and condis crystals in polymeric systems.

EXPERIMENTAL

The OOBPD sample was the same as used in Reference 1. It was synthesized in our laboratory and recrystallized from chloroform. The purity was checked by ^{1}H and ^{13}C solution NMR spectra and no impurity was found within the limits of detection.

The nonspinning sample was measured on a Nicolet NT-200 NMR spectrometer operating at 50.3 MHz for ^{13}C. Two pulse sequences, namely, the cross-polarization (CP) with high-power proton decoupling depending and single ^{13}C pulse with high-power proton decoupling (Bloch-decay), were used to measure the CSA pattern of the static sample. The spin lock time in CP was 1 to 3 ms, recycle time was 3 s. In the Bloch-decay experiment, the excitation pulse width was 4 μs, corresponding to an 80° flip angle, the recycle time was 1.5 s. The proton decoupling field was about 52 kHz. Further experimental details can be found in the previous publication.[1]

To study the reorienting ability of the smectic molecules, two consecutive spectra are obtained, one before and one after changing the angle θ between the rotor axis and the direction of magnetic field. The angle θ could be varied from about 52° to 70°. Comparison between the two spectra shows the magnetic field influence on the orientational order of the liquid crystal.

RESULTS

The ^{13}C cross-polarization NMR spectra measured at 298, 393, 417, 423, 433, 451 K are shown in Figure 1. They correspond, from bottom to top, to phases K3 (condis), K1 (condis), H'(smectic), G'(smectic), I(smectic), and C(smectic). The single ^{13}C pulse with high-power proton-decoupling method, known as Bloch-decay, was used in addition to record spectra at the same temperatures. These Bloch-decay spectra for the condis phase K1 and smectic phases C, I, G', and H' are shown in Figure 2. A spectrum of a solution of OOBPD in chloroform is presented at the top of both Figures 1 and 2 to serve as a reference for the isotropic state. All spectra shown in Figures 1 and 2 were measured without sample spinning. The molecular structure is shown at the top of Figures 1 and 2, with the carbon atoms numbered from 1 to 7 for the mesogen and from 8 to 15 for the octyl chain. Notice that the molecule is symmetric about the central benzene ring.

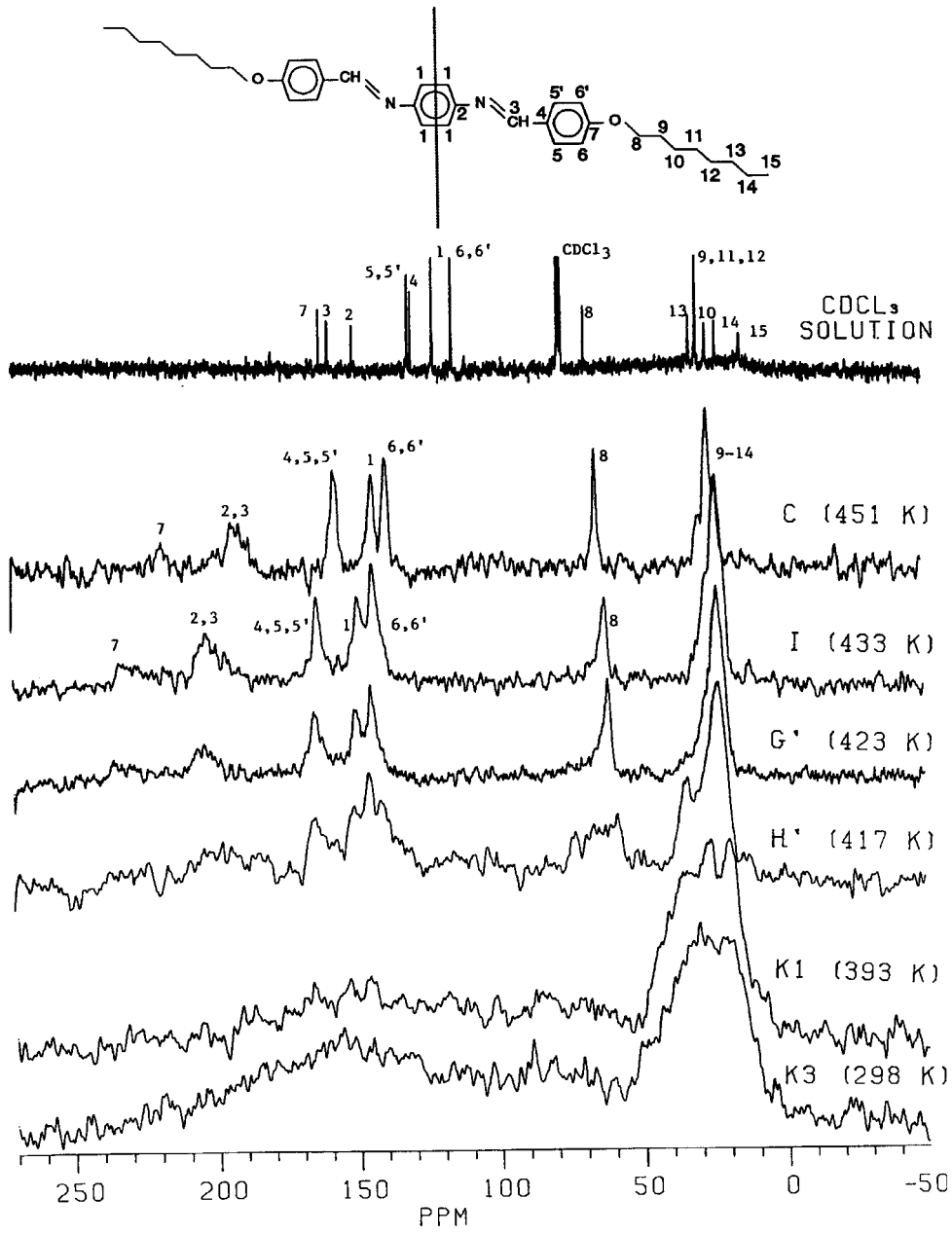


FIGURE 1 Proton dipolar decoupled ^{13}C NMR spectra (50.3 MHz) of a static sample of OOBPD recorded with cross-polarization at temperatures listed in the figure. The top spectrum is obtained on a $CDCl_3$ solution with the pulse sequence of single ^{13}C pulse with proton decoupling (Bloch-decay).

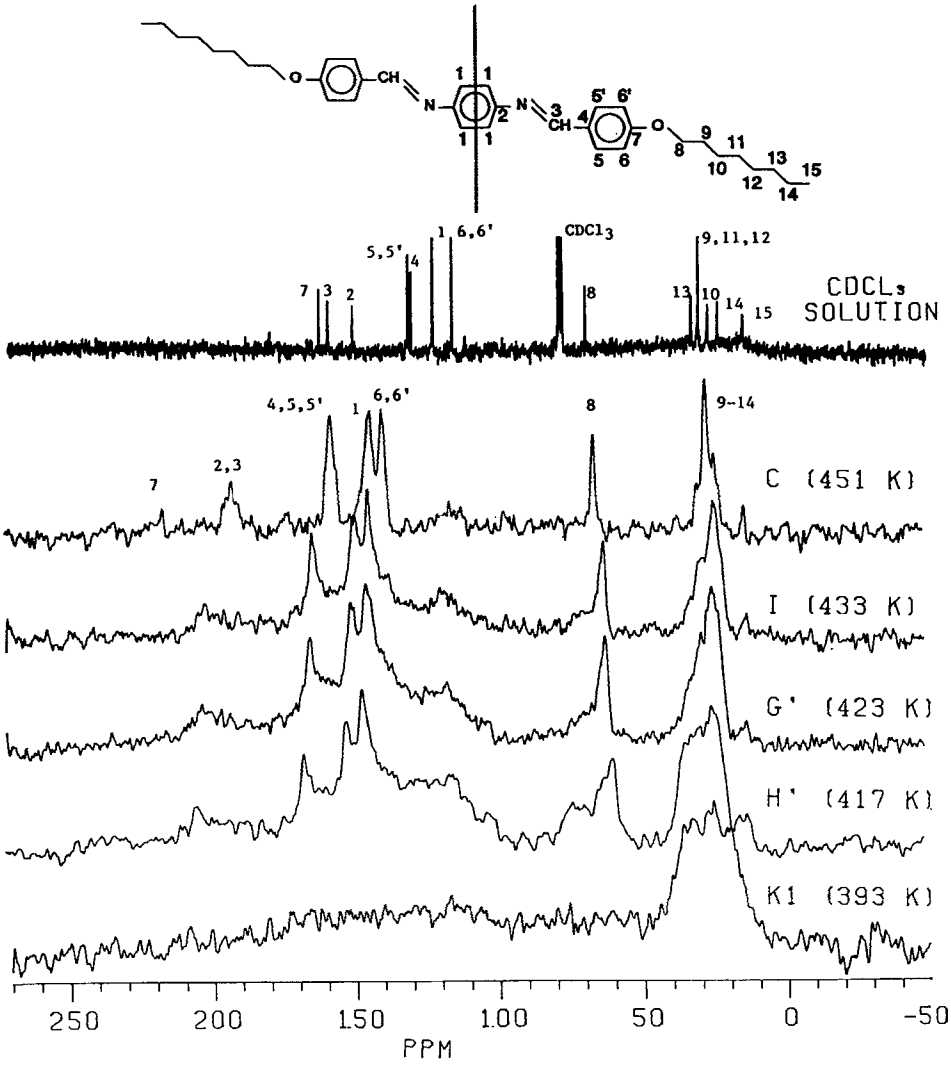


FIGURE 2 Proton dipolar decoupled ^{13}C NMR spectra (50.3 MHz) of a static sample of OOBPD recorded with single ^{13}C pulse at temperatures listed in the figure.

The peak assignments on the solution spectrum have been made in Reference 1. For the mesogen, the assignment is based on the empirically established substituent additivity effect in benzene derivatives. Substituent additivity effects in linear alkanes have similarly been used to assign the aliphatic spectral lines. The ^{13}C chemical shift assignments on the smectic phases, C, I, G', and H' were made by taking into account the line intensities and by assuming a quasi-continuous chemical shift variation from the isotropic phase spectrum. The line assignment is summarized in the spectra of Figure 1.

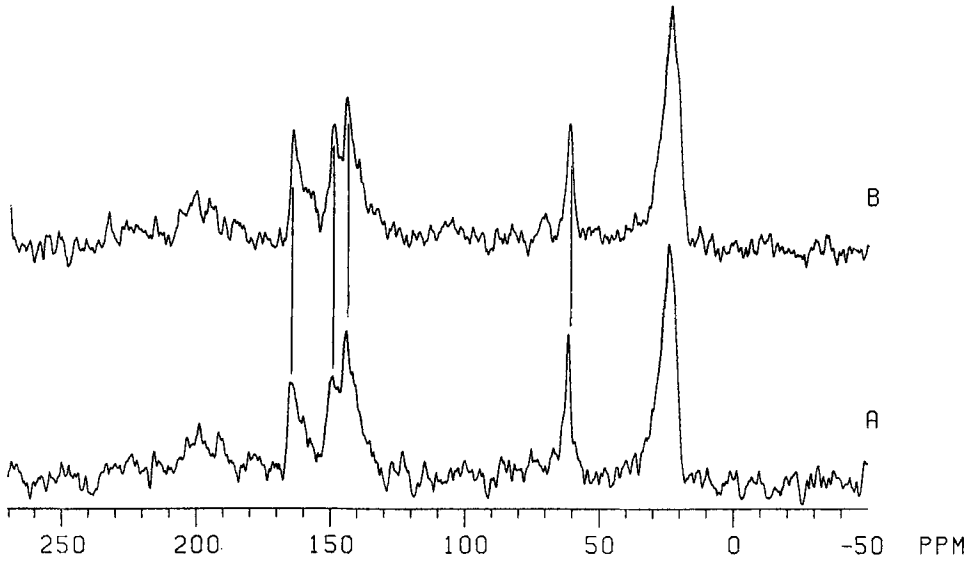


FIGURE 3 Proton dipolar decoupled ^{13}C NMR spectra (50.3 MHz) of a static sample of OOBPD recorded with CP in the smectic I phase (433 K). Spectrum A was obtained first, at an angle of 52° between the magnetic field direction and rotor long axis. Spectrum B was obtained immediately thereafter, changing the angle to about 70°. Time required for data collection for each spectrum is about 12 minutes.

To study the influence of the magnetic field on the orientational order of the liquid crystals, spectra were recorded at different angles of the sample rotor with respect to the magnetic field. Figure 3 shows an example, for the smectic phase I (433 K), obtained at two such angles separated by about 20°. The two spectra do not show any significant difference, indicative of easy reorientation of the mesogen.

DISCUSSION

Chemical-shift-anisotropy Patterns

Since all the experiments were performed without magic angle spinning (MAS), the proton-decoupled ^{13}C NMR spectra reflect the chemical-shift-anisotropy interactions. Reviews on the general aspects of CSA pattern can be found in the literature.[8, 9] The CSA interaction describes magnitude and direction of the three-dimensional electronic shielding of the nucleus under observation. The three most common cases of the line-shapes are depicted in Figure 4.

In the general case (top trace of Figure 4), three singularities are observed in the spectrum, corresponding to the three principal (orthogonal) elements of the shielding tensor. The line-shape shows no symmetry, therefore, it is called asymmetric. In

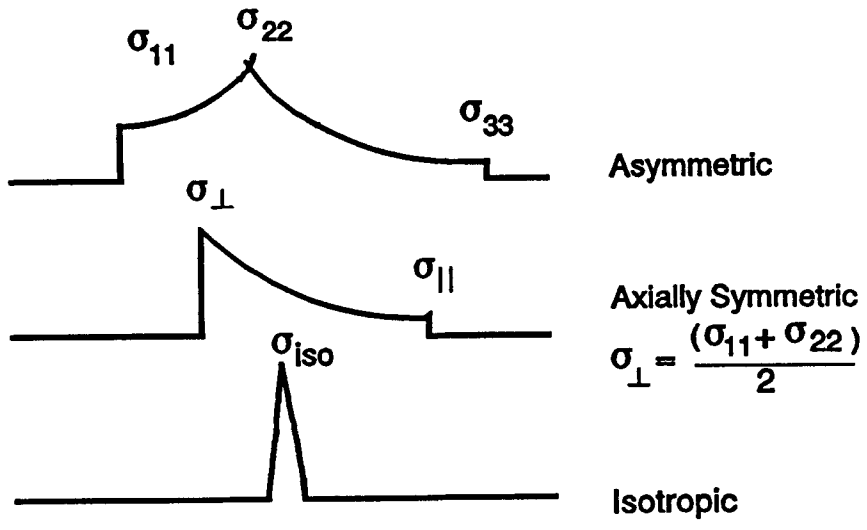


FIGURE 4 Typical chemical-shift-anisotropy (CSA) patterns.

the middle trace, the shielding is the same in two directions giving an "axially symmetric" tensor where the elements are described as $\sigma_{\|}$ for the unique direction and $\sigma_{\perp}$ for the two identical elements perpendicular to it. For comparison, the isotropic case is also depicted in Figure 4. The sharp, symmetric line indicates the resonance of the isotropic average of the three-dimensional (asymmetric) or two-dimensional (axially-symmetric) shielding tensor.

Since the chemical shielding is a three-dimensional quantity, it is expected to be sensitive to the presence of molecular motion. A well-studied example is the behavior of hexamethylbenzene[10] and other hexa-substituted benzene derivatives.[11] Below their disordering transition temperature these molecules are rigid in the crystal, and the nonprotonated aromatic carbons show, as a result, a CSA powder pattern resembling the asymmetric case. As the temperature is increased, the pattern becomes axially symmetric due to in-plane reorientation. Further increase of temperature may cause out-of-plane motion or flipping of the ring which further changes the CSA powder pattern from axially symmetric to isotropic.

Spectra of Smectic Phases

The spectra of the four smectic liquid crystal phases in OOBPD are compared in Figure 1 to the chloroform solution spectrum. In the liquid crystal phases molecular motion exists about the axis of the mesogen, and the fact that molecules are aligned preferentially with the molecular director **D** along the external magnetic field **H** should change the line shape from isotropic, as seen in solution, to largely axially symmetric. One expects thus shifts in the line positions. For the aromatic ^{13}C, the largest shielding occurs perpendicular to the aromatic plane, *i.e.* **D**, whereas for the attached aliphatic groups the smallest shielding occurs in direction **D**.[12–16]

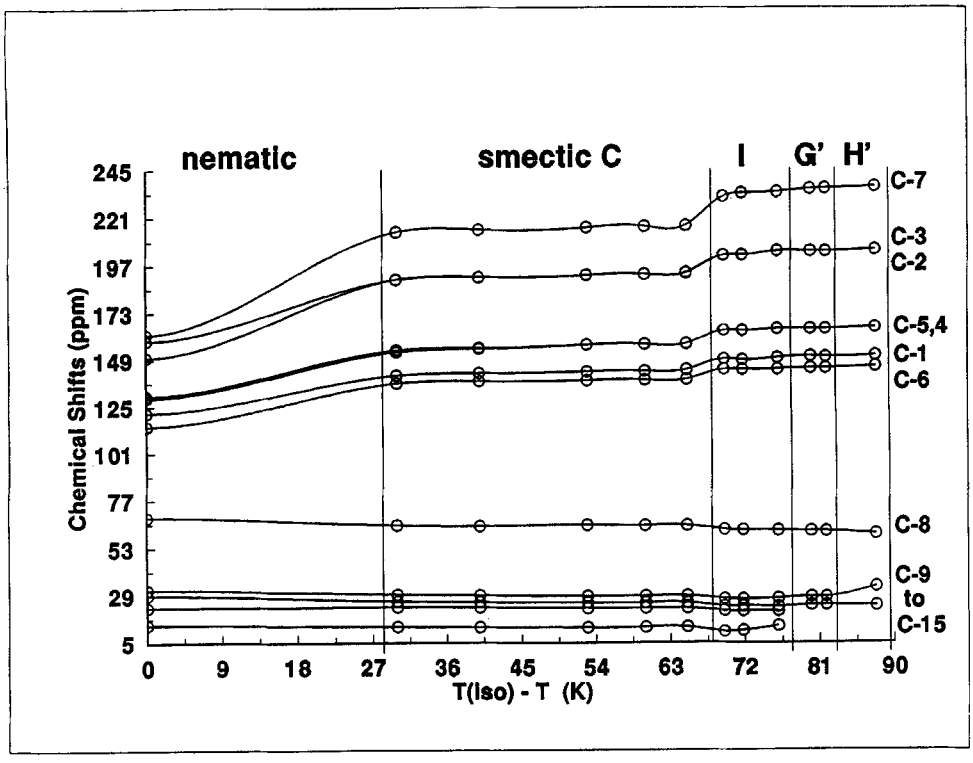


FIGURE 5 Chemical shift dependence of the carbons of a static sample of OOBPD with decreasing temperature. Phase assignments are indicated. Lines are drawn only as an indication to follow the chemical shift variation represented by the circles. The spectrum at T(iso) is that of the solution.

Thus, a downfield shift of the aromatic lines and an upfield shift of the aliphatic lines are expected in going from the isotropic state to a liquid crystal phase. This is, indeed, observed in Figure 1. The ^{13}C chemical shift changes are plotted in Figure 5 as a function of temperature for all the smectic phases. The nematic phase was not analyzed because its existence range is beyond the temperature capability of our NMR probe.

As the temperature is lowered from smectic C to smectic I, the resonances of the aromatic and aliphatic ^{13}C undergo further downfield and upfield shifting, respectively, indicating an increasing orientational order. The most pronounced change can be found for the aromatic ^{13}C nucleus on the *para* axis, for example, a change of 14 ppm was found for C-7 which is the most deshielded (most downfield) peak. In going from smectic phase I to phase G', a relatively small shift was found for all carbon atoms. For example, C-7 changes by only 4 ppm. This indicates that the transition from I to G' involves only minor orientational ordering in comparison to that from C to I. A large change in line-shape is, however, obvious between the

phases G' and H' (see Figure 1). The small chemical-shift differences between the phases G' and H' contain, thus, a larger error since it is difficult to measure the chemical shifts for phase H' due to their larger line-widths. The previous DSC study[1] showed that the entropy changes for the transitions C–I, I–G', and G'–H' were 9.0, 1.3, and 6.0 J K^{-1} mol^{-1}, respectively. Thus the largest line-shift and line-shape changes correspond to the larger entropy changes. But note, that the largest rearrangement in morphology observed by optical microscopy[2] is found in going from I to G'.

The ^{13}C NMR spectra of the smectic phases of OOBPD show several additional interesting results:

(1) Only one line is observed from each pair of *ortho*-positions (from the four C-1, C-5/C-5', and C-6/C-6'). This demonstrates unequivocally that the benzene rings reorient rapidly about their *para*-axes. In fact, this fast phenylene ring motion was already proven by the CP-MAS study in Reference 1. The motion begins already as 180°-flips in the condis phase K3.

(2) The single line from O–CH_2 (C-8) changes very little in its resonance position in going from smectic C to the isotropic state (from 64.4 ppm to 68.4 ppm). The same carbon atom in the nematic phase (between 476.5 and 504.8 K), is expected to have a chemical shift close to that of the isotropic melt. The reason for this small change is that the average angle between the O–CH_2 bond and the molecular director is not far from 54.7°, the "magic angle." A bond angle of Ar–O–CH_2 of 110° would yield an angle between the molecular director and the Ar–O bond of about 15°, a reasonable value. Such observation is typical for many low molecular mass liquid crystal molecules, and was found for the nematic phases of *p*-azoxy dianisole (PPA),[15] *p*-methoxy benzylidene *p'-n*-butylaniline (MBBA),[14] and series of *p*-alkoxyazoxybenzenes,[16] for example.

(3) In all smectic phases of OOBPD cross-polarization between the ^{1}H and ^{13}C spins is efficient and proceeds probably by intramolecular transfer since translational and orientational motion is rapid.

(4) The method of single ^{13}C pulse with high-power proton-decoupling (Bloch-decay) also leads to strong signals, as is shown in Figure 2. At high temperatures, for example, in the smectic C at 451 K, the CP and Bloch-decay spectra are essentially the same. At lower temperatures, the spectra obtained with the latter method exhibit, however, additional resonances between 110 and 140 ppm (absent in CP spectra). These features correspond to the isotropic solution spectral lines of C-1, C-5 and C-6, and are very broad with their intensities, increasing in the Bloch-decay spectrum as the temperature is decreased. They indicate formation of some three-dimensional structure more similar to condis crystals. More molecules adopt orientations different from those of the rotating molecules in the liquid crystal phase. Thus, a larger difference between the CP spectrum and the Bloch-decay spectrum can be detected for a smectic phase that is closer to the condis states. In the Bloch-decay spectra shown in Figure 2 the signals from the non-protonated carbon atoms, C-2, C-4, and C-7, as well as the fast rotating methyl carbon atom C-15, are absent or almost absent. This is due to the fact that these carbon atoms have a spin-lattice relaxation time that is about two orders of magnitudes greater than for the remaining carbons.[1]

Influence of the Magnetic Field on the Molecular Orientation

Oriented molecules contribute differently to ^{13}C NMR spectra, depending on the position of the molecular director with respect to the magnetic field. This is demonstrated in Figure 6 by the series of spectra for the aromatic carbons in hexamethylbenzene in its mesophase with the molecules carrying out in-plane motion (room temperature). The sample was spun, in this case, to achieve an averaged molecular orientation along the sample rotor axis. When the angle between the rotor axis and the magnetic field is adjusted from 52° to 70°, the spectral appearance and the peak position change drastically.

The ability of the molecules in the smectic phase of OOBPD to reorient in a strong magnetic field was investigated by the two spectra shown in Figure 3. Both

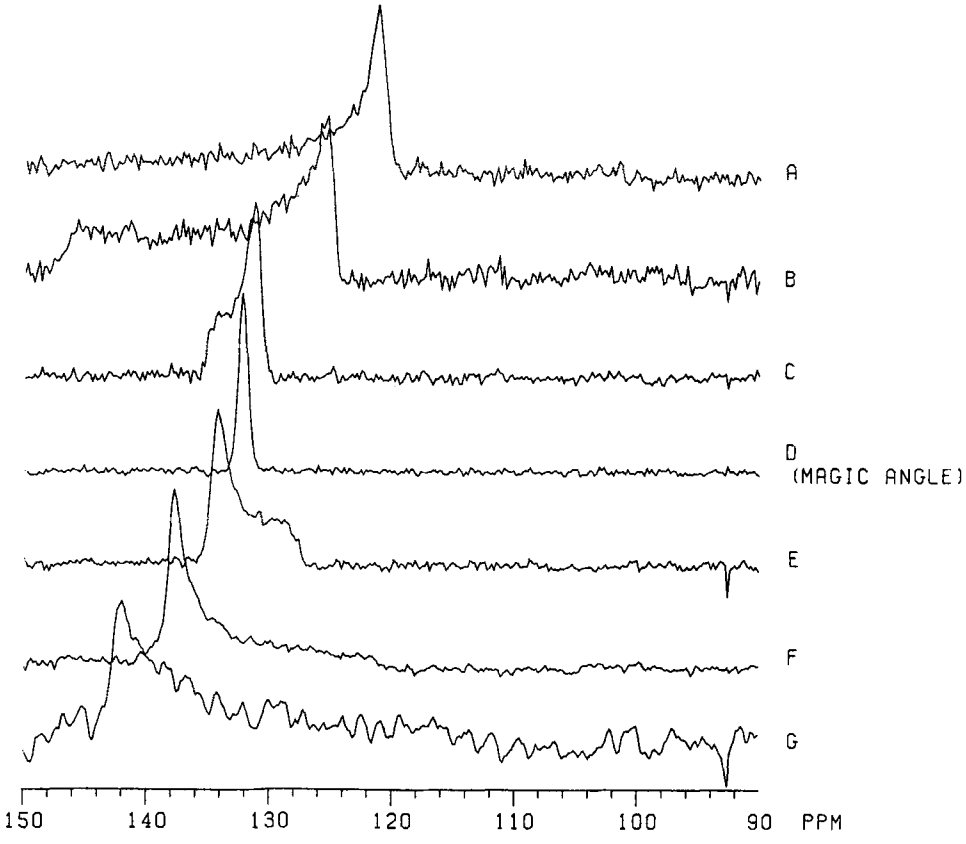


FIGURE 6 The ^{13}C NMR spectra of aromatic carbons in hexamethylbenzene. The sample was spun in this case to achieve an averaged molecular orientation which is along the sample rotor axis. Spectra A to G were measured when the angle between the rotor axis and the magnetic field is adjusted from 52° to 70°.

spectra were obtained at the same temperature, 433 K (phase I). Spectrum A was obtained first, at an angle of 52° between the vertical magnetic field direction and long axis of the rotor, and Spectrum B was obtained immediately after changing the angle to about 70°. There is no difference between the two spectra in terms of chemical shifts, line-shape, or signal intensities. These spectra indicate that the smectic I molecules of OOBPD are able to reorient themselves along the magnetic field after mis-alignment within a time much shorter than that required to collect the free-induction-decay (about 12 min). Similar spectra were taken for the other smectic phases with the same result, proving that all four smectic phases can reorient in the magnetic field.

Condis Phases

The non-spinning ^{13}C NMR spectra of the condis phases K1 and K3 are seriously broadened due to the not averaged ^{13}C chemical shielding anisotropy (Figures 1 and 2). The resonance for each magnetically distinguishable carbon atom resembles the asymmetric pattern of Figure 4. The broad CSA pattern for each carbon atom overlaps with those of other similar carbon atoms in the molecule making the spectrum impossible to interpret. In general, the dimensionality of the CSA of the condis state indicates that the orientational rotation and translation of the molecules as a whole has stopped. This clear differences between the smectic and the condis phases in a non-spinning ^{13}C NMR experiment provide, thus, a clear criterion to distinguish between smectic and condis phases.

It is easy to realize that the ^{13}C NMR spectrum obtained without spinning for a condis crystal should, however, be very similar to that of a well-ordered crystal, because in both cases the orientational and translational motion of the molecule as a whole are quenched and orientational and positional order is established.

To further distinguish between a condis crystal and a perfect crystal, one needs to examine the conformational features of the molecule, exhibited by the flexible aliphatic chains. For this purpose, the conformational-dependent ^{13}C chemical shifts and relaxation times measured under the conditions of magic-angle-spinning (MAS) and high power decoupling of protons must be analyzed for the chain methylene ^{13}C, as had been demonstrated before for the same OOBPD molecules,[1] a series of tetra-*n*-alkylammonium salts,[17,18] and several polymeric main-chain condis crystals.[19,20] In fact, several of the previously studied condis crystals do not undergo a condis-to-crystal transition, they become a condis glass on cooling. This unique behavior of the condis phase is due to, among other reasons, the molecular structural hindrance to crystallization or incompatibility between the hard core and flexible parts of the molecule.

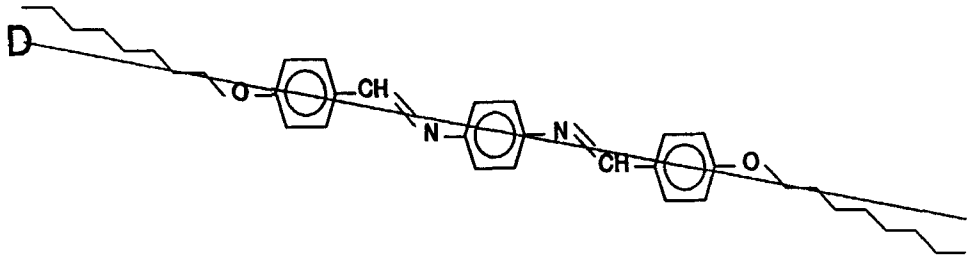
Between the condis phases K3 and K1, the spectra shown in Figure 1 show only slight differences for the alkyl chains in the region between 10 and 40 ppm. The octyl chain in the phase K1, being more conformationally mobile and disordered, seems to have better resolved spectral lines than K3. The details on the conformational disordering of alkyl chains have been shown in Reference 1.

Order Parameter for the Smectic Phases

The order parameter, S, defines the average orientation of the mesogen relative to the magnetic field,

$$S = {}^1/_2 <3\cos^2\theta - 1> \tag{1}$$

where θ is the angle between molecular director **D** and the magnetic field direction **H**. The vector **D** passes through the centers of the phenylene rings making an angle α with their *para*-axes:



For the aromatic ^{13}C nuclei on the *para* axis the chemical shift tensor σ produces a motionally averaged tensor $<\sigma>$ with components of $\sigma_\parallel$ along **D** and $\sigma_\perp$ perpendicular to **D**:[14]

$$\begin{aligned} \sigma_\parallel &= \sigma_{11}\cos^2\alpha + \sigma_{22}\sin^2\alpha \\ \sigma_\perp &= {}^1/_2\,(\sigma_{11}\sin^2\alpha + \sigma_{22}\cos^2\alpha + \sigma_{33}) \end{aligned} \tag{2}$$

where σ_{11}, σ_{22}, and σ_{33} are the principal elements of the tensor σ, and α is defined in Eq. (1). The observed chemical shifts $\Delta\sigma$ from the isotropic to liquid crystal phase are given by:

$$\Delta\sigma = (2/3)\, S\, (\sigma_\parallel - \sigma_\perp) \tag{3}$$

where S is the order parameter to be calculated.

From the average data for σ from studies of model compounds in the solid state,[12–16] values for the principal elements can be assumed to be $\sigma_{11} = -98$, $\sigma_{22} = -13$ and $\sigma_{33} = +108$ ppm relative to liquid-state benzene ($\sigma = 0$ ppm, or the chemical shift $\delta = 128.5$ ppm). The chemical shifts, δ, measured in this work can be converted to the shielding constant, σ, by the simple relation:

$$\sigma = 128.5 - \delta \tag{4}$$

With Eqs. (2), (3), and (4), the order parameter S can be calculated if the angle α is known. Several values for α have been proposed in literature[14, 15, 21] for mesogens containing the (–CH=N–)-group as a linkage between the phenylene rings, it ranges from 3.5 to 15°. Using these information and the measured chemical shifts for C-7 listed in Table II, S was calculated and is listed in Table II.

TABLE II

Measured chemical shifts for C-7 and calculated order parameter S at different temperatures

Phase/Temperature	G'/423 K	I/433 K	C/451 K	Isotropic
δ-values (ppm)[a]	235	231	217	161.9
σ-values (ppm)[b]	-106.5	-102.5	-88.5	-33.4
Δσ (ppm)[c]	-73.1	-69.1	-55.1	0
S (α=3.5°)[d]	0.76	0.72	0.57	—
S (α=6.5°)	0.76	0.72	0.58	—
S (α=10°)	0.77	0.73	0.58	—
S (α=15°)	0.80	0.76	0.60	—

[a] Measured from Figure 1.
[b] Converted from δ according to Eq. (4).
[c] Δσ is the difference in σ between the liquid crystal phase and isotropic state.
[d] For calculation of the order parameter S, Eqs. (2), (3) and $\sigma_{11} = -98$, $\sigma_{22} = -13$, and $\sigma_{33} = 108$ ppm are assumed.[12-16]

The calculated order parameter decreases with increasing of temperature, and decreases most in going from phase I to phase C which involves a large entropy change. The order parameters seem not to be very sensitive to the chosen angle α, but are rather sensitive to the observed differences in chemical shift from the isotropic state. It can also be seen that the order parameter S for the low-temperature smectic phases of OOBPD (H', G', and I) is larger than that in the nematic phase of MBBA (≤ 0.65),[14] while the smectic C in OOBPD has a similar S (0.58) to that of nematic MBBA at about 30 K below its clearing point.[14]

Attempts have also been made to utilize the chemical shift changes for the *ortho* carbon atoms in the aromatic rings to calculate the order parameters with formulas proposed by Pines and Chang.[14,15] The results are also in good agreement to those shown in Table II.

For carbon atoms along the octyl chains, there is an overlap of the numerous lines and because of this, detailed information on conformational disorder can not be obtained based on the non-spinning spectra. Our earlier study of ^{13}C CP-MAS has shown that alkoxy chain have developed considerable conformational mobility due to the disordered bonds undergoing fast exchange between *trans* and *gauche* conformations.[1] Several ^{2}H NMR studies on a number of liquid crystals of low molecular masses,[22] and side-chain liquid crystal polymers[23] have shown similar results for the mobility of the flexible alkyl chains.

CONCLUSIONS

This ^{13}C NMR study of OOBPD has led, in conjunction with the previous high resolution CP-MAS ^{13}C NMR study,[1] to a detailed description of molecular order and motion in its various smectic phases. Especially the differences between the smectic and condis crystal are elucidated in this paper.

It has been shown that: (1) When the sample is kept static, the smectic liquid crystals have sharp resonance lines in the ^{13}C NMR spectra. Condis crystals of the same molecules, in contrast, show only featureless broad lines. (2) In the smectic

phases, the ^{13}C NMR spectra obtained by cross polarization (CP) can be different from those measured by single ^{13}C pulse with high-power proton decoupling (Bloch-decay), even at the same temperature. The difference is hardly noticeable for smectic C, which exists at temperatures just below the nematic phase, but becomes increasingly significant for those smectics that exist at temperatures that approach the transition to the condis phase. (3) Under the influence of the magnetic field of the NMR spectrometer, reorienting the smectic phase molecules is facile. (4) As the temperature is lowered on going from phases C to H', the ^{13}C resonances of the aromatic and aliphatic carbon atoms undergo downfield and upfield shifting, respectively, indicating an increasing in orientational order. Based upon the observed changes of chemical shifts, order parameters can be calculated for the various smectic phases. They increase from 0.58 to 0.80 as the temperature is decreased from 451 K (smectic C) to 423 K (smectic G').

Acknowledgments

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