

Determination of Bond Distances and Bond Angles in a Liquid Crystal with Hydrogen Bonding

Chibing Tan[†] and B. M. Fung*

Department of Chemistry and Biochemistry, University of Oklahoma, Norman, Oklahoma, 73019-3051

Received: December 16, 2002; In Final Form: March 3, 2003

The structure of a liquid crystal with intramolecular hydrogen bonding, 5-butoxy-2[(4-butylphenyl)azo]phenol, was determined by using X-ray diffraction of a single-crystal and NMR studies in the nematic phase. Because the uncertainties in the positions of the hydrogen atoms are quite large in the X-ray structure, some of the bond distances and bond angles of the mesogenic core were determined by the use of ^{13}C NMR. For the liquid crystals in natural abundance, ^1H – ^{13}C dipolar coupling constants were obtained from the 2D technique of proton-encoded local field spectroscopy. For an analogue with deuterium substitution in the hydrogen-bonded position, ^2H – ^{13}C dipolar coupling constants were obtained from 1D ^{13}C – $\{^1\text{H}\}$ spectra. The dipolar coupling constants were used to calculate the order parameters of the phenyl rings, as well as the bond distances and bond angles in the hydrogen-bonded moiety.

Introduction

X-ray diffraction is the most powerful technique for the study of molecular structures in single crystals, but it cannot determine the positions of hydrogen atoms accurately. Neutron diffraction of deuterated compounds does yield such information, but the technique is difficult to apply to complex molecules in the fluid state. On the other hand, nuclear magnetic resonance (NMR) study of liquid crystals has been used extensively to determine molecular geometry, including the positions of hydrogen nuclei, through the measurement of dipolar coupling constants.^{1,2}

Most ^1H NMR studies of molecular geometry in liquid crystals have been carried out using small molecules dissolved in liquid crystalline solvents.¹ Application of ^1H multiple-quantum transitions, especially the use of partially deuterated molecules,³ makes it possible to extend the studies to molecules containing 8–10 nonequivalent protons,^{4,5} but the size of accessible molecules is still quite limited. For bulk liquid crystals, ^1H – ^1H dipolar coupling constants can be determined by using compounds with extensive partial deuteration.^{6,7} For compounds in natural abundance, the measurement of ^1H – ^{13}C dipolar coupling constants by the use of 2D local-field ^{13}C NMR provides a convenient method for the study of molecular geometry and orientational ordering of bulk liquid crystals.⁸ An improvement of the separated local field (SLF) spectroscopy called proton-detected local field (PDLF,⁹ or alternatively designated as proton-encoded local field, PELF¹⁰) spectroscopy increases the resolution of the 2D method and can provide more two-bond ^1H – ^{13}C dipolar coupling constants. A different method, which yields long-range dipolar coupling constants, is through the observation of ^2H – ^{13}C splittings in the ^{13}C NMR spectra of monodeuterated liquid crystals.¹¹ An analysis of the results of these two kinds of studies can yield the position of some of the hydrogen atoms without presumption of the relevant bond distances. Such an approach is particularly fruitful for the

study of hydrogen bonding, for which the use of assumed bond distance might not be quite prudent. Experimentally, deuteration of the hydrogen-bonded site can be easily achieved by deuterium exchange with a solvent.

Systematic studies on the effect of hydrogen bonding on the phase transition of liquid crystals were first made by Gray and co-workers.¹² The role of hydrogen bonding on the liquid crystalline phase has attracted increased attention in the past few years, and several reviews have been published.^{13–16} For liquid crystals with intermolecular hydrogen bonding, it has been shown that proton exchange is fast at the NMR time scale.¹⁷ Therefore, corresponding dipolar coupling constants cannot be obtained. However, proton exchange can be quite slow for systems with intramolecular hydrogen bonds. In fact, the complete geometry of salicylaldehyde dissolved in a liquid crystalline solvent was determined in an early ^1H NMR study.¹⁸ Bulk liquid crystals have much more complicated structures and require more elaborate experiments to determine the geometry of the hydrogen-bonded segment. Here, we report the use of ^{13}C NMR to determine the O–H and H \cdots N bond distances and the C–O–H and O–H \cdots N bond angles of a bulk liquid crystal containing intramolecular hydrogen bond.

Experimental Section

The diazo liquid crystal 5-butoxy-2[(4-butylphenyl)azo]-phenol (BBPAP) was synthesized according to procedures described in the literature.¹⁹ Its nematic range is 40.0–82.5 °C. Compared with the compound without the –OH group, there is an increase in the nematic–isotropic transition temperature; this is good evidence for the presence of intramolecular hydrogen bonding.¹⁹ The structure of this compound is shown in Figure 1.

The O-deuterated compound (denoted as BBPAP-*d*) was prepared by direct exchange of the O–H hydrogen with CH_3OD in an NMR tube followed by evacuation of the solvent, repeated three times.

The ^{13}C NMR experiments were performed using a Varian INOVA-400 NMR spectrometer. The sample was placed in a

* To whom correspondence should be addressed. E-mail: bmfung@ou.edu.

[†] Current address: Department of Biochemistry and Molecular Biology, University of Oklahoma Health Sciences Center, Oklahoma City, OK 73190-0001.

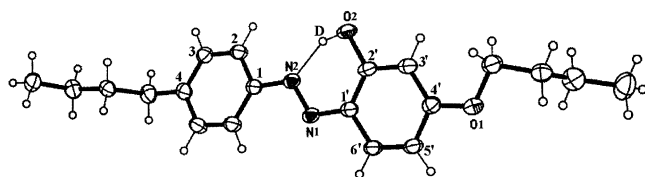


Figure 1. The structure of O-deuterated 5-butoxy-2-[(4-butylphenyl)azo]phenol (BBPAP-*d*) obtained from X-ray diffraction. The numbering of the atoms does not follow the IUPAC convention.

standard 5 mm tube and spun slowly (16 Hz) along the magnetic field; under this condition, the director aligns parallel to the field.⁸ The temperature calibration was made by observing the nematic to isotropic transition. To avoid excessive radio frequency (rf) heating, the ¹H decoupler (with a power $\gamma B_2/(2\pi) = 28$ kHz) was applied for only 50 ms for data acquisition, and the cycle time was set to be 30 s. For the PELF experiments, the homonuclear dipolar decoupling sequence BLEW-48²⁰ was used in the evolution period (with $\gamma B_2/(2\pi) = 43$ kHz), and the efficient broadband decoupling sequence SPINAL-64²⁰ was used in the acquisition period. For 1D ¹³C-¹H experiments, only the SPINAL-64 decoupling sequence was applied.

Single crystals of BBPAP-*d* were grown from methanol at about 4 °C. X-ray diffraction experiments were performed at 173 K on a Siemens P4 diffractometer using Mo K α radiation at $\lambda = 0.071\,073$ nm. The crystal data, the data collection conditions, and the refinement characteristics are given as Supporting Information.

Results and Discussion

X-ray Diffraction. The fractional coordinates of non-hydrogen atoms in BBPAP-*d* are given as Supporting Information. The labeling of non-hydrogen atoms of independent molecules is presented with the thermal ellipsoids in Figure 1. The BBPAP-*d* molecule does not show the well-known trans-cis isomerization of azobenzenes relative to the diazo N-N bond because the trans isomer is strongly stabilized by intramolecular hydrogen bonding. The phenyl rings in the molecules are essentially planar.

2D ¹³C NMR Study of Liquid Crystals. To obtain one-bond and some two-bond C-H dipolar coupling constants, the 2D PELF method^{9,10} was used to study the nondeuterated liquid crystal BBPAP. Because we are concerned with the intramolecular hydrogen bonding in these molecules, only the aromatic part of the spectra was studied. The spectra of BBPAP at 40.6 °C are displayed in Figure 2. In the PELF method, the normal 1D ¹³C NMR spectrum is shown in the ω_2 dimension, and ¹H-¹³C splittings are observed as doublets in the ω_1 dimension regardless of the number of protons attached to the carbon atom. The dipolar coupling constants (*D*) and scalar coupling constants (*J*) are related to the observed splittings ($\Delta\nu$) by

$$\Delta\nu = f(2D + J) \quad (1)$$

where *f* is a scaling factor determined by the ¹H-¹H dipolar decoupling sequence in the evolution period (for the BLEW-48 sequence, the theoretical value of *f* is 0.424²⁰ and its experimental value is 0.414¹⁰). The anisotropy of the *J* coupling is small¹ and was not taken into account in the calculations. The values of the isotropic scalar coupling constants were measured from the spectrum in the isotropic phase. The signs of $\Delta\nu$ cannot be determined from the spectra shown here and are assigned on the basis of geometric considerations. For peaks

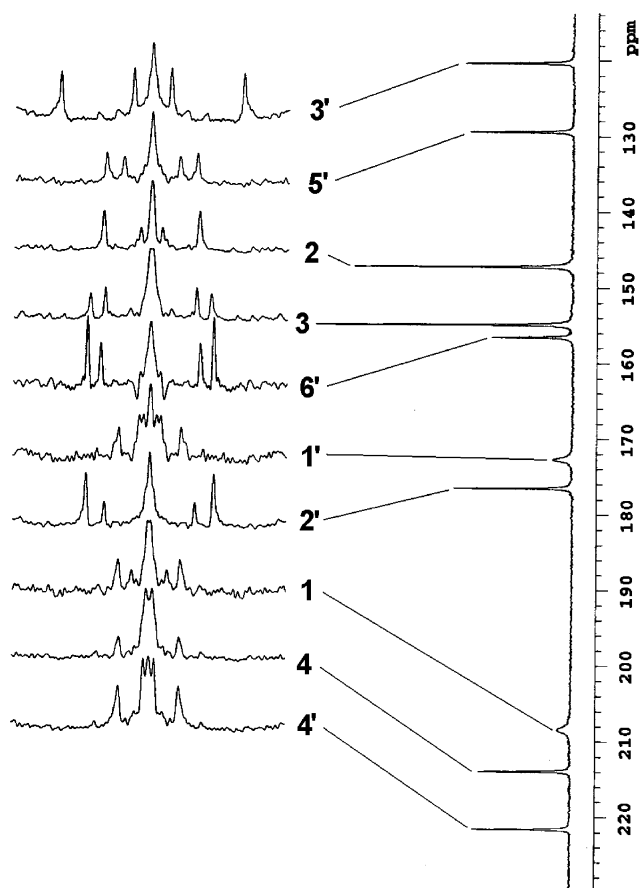


Figure 2. The aromatic region of ¹³C NMR spectra of 5-butoxy-2-[(4-butylphenyl)azo]phenol obtained from a 2D PELF experiment at 40.6 °C and 100 MHz. The spectrum on the right shows proton-decoupled ¹³C peaks in the ω_2 dimension; the spectra on the left show traces in the ω_1 dimension with ¹H-¹³C coupling.

that overlap, the values of $\Delta\nu$ were determined by using spectral deconvolution. The ¹H-¹³C dipolar coupling constants thus obtained for BBPAP are listed in Table 1.

1D ¹³C NMR Study of the Liquid Crystal Deuterated in the Hydrogen Bond Position. We have shown that long-range ²H-¹³C coupling constants can be readily obtained from the broadband-decoupled ¹³C-¹H spectra of monodeuterated liquid crystals.¹¹ This strategy has been used in the present study of the diazo liquid crystal with intramolecular hydrogen bonding. The ¹³C spectrum of BBPAP-*d* (Figure 3) shows that 7 of the 10 aromatic carbons are split into triplets because of coupling with the ²H nucleus. Because the deuteration is incomplete, the central peak of each doublet has a larger amplitude. For the 2' carbon, which is closest to the deuterium, there is a small isotope shift, so the center of the triplet does not coincide with the peak of the nondeuterated compound. As in the case of the nondeuterated compound (Figure 2), the C1 and C1' peaks are broadened by quadrupole relaxation of the neighboring ¹⁴N nuclei.

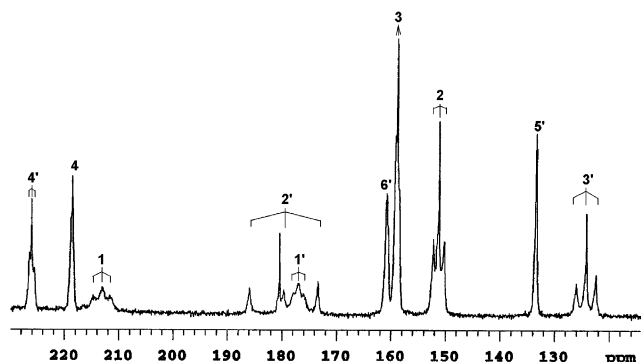
From the ²H-¹³C splittings, the corresponding dipolar coupling constants can be calculated by using eq 1, where *f* is now unity. The values of $\Delta\nu$ were obtained by spectral deconvolution for peaks that overlap. For comparison with the data obtained from the 2D PELF experiments, the ²H-¹³C dipolar coupling constants were converted to ¹H-¹³C dipolar coupling constants using the equation

$$D_{CH} = (\gamma_H/\gamma_D)D_{CD} = 6.5142D_{CD} \quad (2)$$

TABLE 1: ^1H – ^{13}C Dipolar Coupling Constants (Hz) for 5-Butoxy-2[(4-butylphenyl)azo]phenol (BBPAP)

| | exptl values ^a | calcd values |
|-----------|---------------------------|--------------|
| C1–H2 | 1032 | 1025 |
| C1–H3 | –199 | –224 |
| C2–H2 | 1490 | 1489 |
| C2–H3 | –1571 | –1538 |
| C3–H3 | 1905 | 1906 |
| C3–H2 | –1499 | –1532 |
| C4–H3 | 997 | 1004 |
| C4–H2 | –213 | –225 |
| C1'–H6' | 1037 | 1050 |
| C1'–H3' | –209 | –187 |
| C2'–H3' | –1602 | –1526 |
| C2'–H6' | 207 | 219 |
| C3'–H3' | 2932 | 2834 |
| C3'–H5' | 244 | 220 |
| C4'–H3' | 1004 | 1018 |
| C4'–H6' | –180 | –192 |
| C5'–H5' | 1404 | 1403 |
| C5'–H6' | –1420 | –1519 |
| C5'–H3' | 245 | 216 |
| C6'–H6' | 1992 | 2083 |
| C6'–H5' | –1638 | –1645 |
| C1'–(O2)H | 312 (352) | 382 |
| C2'–(O2)H | –1518 (–1487) | –1494 |
| C3'–(O2)H | –575 (–606) | –526 |
| C4'–(O2)H | (–150) | –152 |
| C1–(O2)H | –530 (–579) | |
| C2–(O2)H | –393 (–361) | |
| C3–(O2)H | –222 (–211) | |

^a The values in parentheses are data converted from ^2H – ^{13}C dipolar coupling constants.

**Figure 3.** The aromatic region of the ^{13}C NMR spectrum of O-deuterated 5-butoxy-2[(4-butylphenyl)azo]phenol at 40.6 °C and 100 MHz.

where γ_{H} and γ_{D} are the magnetogyric ratios of proton and deuterium, respectively. The data are also listed in Table 1, and their values are in reasonable agreement with the corresponding ones obtained from the PELF experiment.

Calculation of Molecular Geometry from Dipolar Coupling Constants. In the nematic phase, a phenyl ring with 1,4-disubstitution has an effective D_2 symmetry because it undergoes rapid jumps about its para axes, making the two ortho, as well

as the two meta, positions equivalent. An asymmetrically trisubstituted phenyl ring has a C_s symmetry because the phenyl ring is essentially planar. The dipolar coupling for a group with C_s symmetry is related to the order parameters, $S_{\alpha\beta}$, by^{1,2}

$$D_{ij} = -\frac{\gamma_i\gamma_j h}{8\pi^2 \langle r_{ij}^3 \rangle} [S_{zz} \langle 3 \cos^2 \theta_{ijz} - 1 \rangle + (S_{xx} - S_{yy}) \langle \cos^2 \theta_{ijx} - \cos^2 \theta_{ijy} \rangle + 4S_{xz} \langle \cos \theta_{ijx} \cos \theta_{ijz} \rangle] \quad (3)$$

where r_{ij} is the internuclear distance, and $\theta_{ij\alpha}$ is the angle that r_{ij} forms with the α axis of the coordinate system. The order parameters S_{zz} , $S_{xx} - S_{yy}$, and S_{xz} characterize the orientation of a rigid molecular segment only and not the entire liquid crystal molecule. For a 1,4-disubstituted phenyl ring that has D_2 symmetry, $S_{xz} = 0$. From symmetry consideration, the z axis is taken to be the para-disubstituted axis of each phenyl ring, the y axis normal to the ring, and the x axis in the plane of the ring. To calculate the coordinates of each nucleus, x_i , y_i , and z_i , it is more convenient to convert eq 3 to

$$D_{ij} = -\frac{\gamma_i\gamma_j h}{8\pi^2 \langle r_{ij}^3 \rangle} \{S_{zz} [2(\Delta z_{ij})^2 - (\Delta x_{ij})^2] + (S_{xx} - S_{yy})(\Delta x_{ij})^2 + 4S_{xz}(\Delta x_{ij})(\Delta z_{ij})\} \quad (4)$$

where $\Delta x_{ij} = x_j - x_i$ and $\Delta z_{ij} = z_j - z_i$.

To reduce the number of undetermined parameters in the calculations for 5-butoxy-2[(4-butylphenyl)azo]phenol, we used the coordinates of the C, N, and O nuclei determined in the X-ray diffraction experiments and assumed the C–H distance to be 0.109 nm for the phenyl rings. The experimental dipolar coupling constants listed in the second column of Table 1 were fitted to eq 4 for each ring, and the calculated values are listed in the last column of the table.

In general, the distances calculated from dipolar coupling constants are the effective values $\langle 1/r^3 \rangle^{-1/3}$. To obtain the equilibrium distance $\langle r \rangle$, corrections for molecular vibrations should be made by using normal-coordinate analysis. The correction terms can be quite substantial for some flexible molecules but are usually rather small for rigid molecules,¹ especially those involving indirectly bonded nuclei. For example, in the calculation of equilibrium distances in benzene, vibrational correction is about 4% for the directly bonded C–H pair but 1 order of magnitude smaller for H–H pairs and indirectly bonded C–H pairs.²² Because the mesogenic core in our case is rigid, the bridged hydrogen has no dipolar coupling with the directly bonded oxygen nucleus, and the dipolar coupling with the ^{14}N nucleus was not observed; the effect of vibrational corrections is considered to be within experimental error and was not taken into account in the calculations.

To account for the possibility that the moiety containing hydrogen bonding may not be exactly planar, further calculations were made by setting the order parameters S_{xy} and S_{yz} to nonzero

TABLE 2: Order Parameters and Bond Angles for the Asymmetrical Phenyl Ring and the Diazo Bridge of 5-Butoxy-2[(4-butylphenyl)azo]phenol at 40.6 °C

| Average Calculated Angles | | | | |
|---|---|---|-----------------------------------|-----------------------------|
| $\angle \text{H3}'\text{--C3}'\text{--C2}'$ | $\angle \text{H5}'\text{--C5}'\text{--C6}'$ | $\angle \text{H6}'\text{--C5}'\text{--C5}'$ | $\angle \text{C2}'\text{--O2--D}$ | $\angle \text{O2--D--N2}$ |
| $118.3^\circ \pm 1.1^\circ$ | $119.8^\circ \pm 1.5^\circ$ | $120.8^\circ \pm 1.1^\circ$ | $108.1^\circ \pm 1.5^\circ$ | $133.3^\circ \pm 1.8^\circ$ |
| Order Parameters | | | | |
| S_{zz} | $S_{xx} - S_{yy}$ | S_{xz} | | |
| 0.734 ± 0.020 | 0.036 ± 0.007 | -0.024 ± 0.002 | | |

TABLE 3: Order Parameters and Bond Angles for the Symmetrical Phenyl Ring of 5-Butoxy-2[(4-butylphenyl)azo]phenol at 40.6 °C

| average calculated angles | | order parameters | |
|---------------------------------------|---------------------------------------|-------------------|-------------------|
| $\angle\text{H2}-\text{C2}-\text{C3}$ | $\angle\text{H3}-\text{C3}-\text{C2}$ | S_{zz} | $S_{xx} - S_{yy}$ |
| $120.4^\circ \pm 0.6^\circ$ | $119.6^\circ \pm 0.7^\circ$ | 0.706 ± 0.020 | 0.032 ± 0.003 |

values, but the results do not differ from those obtained by using eq 4 within experimental error. Therefore, we can reasonably assume that the hydrogen-bonded moiety is essentially planar.

The coordinates obtained from the least-squares fitting were used to calculate the bond angles and distances, and the results are listed in Table 2. The distances between the nuclei involved in the hydrogen-bonded moiety are 0.1052 ± 0.0011 nm for O(2)–D and 0.1103 ± 0.0013 nm for N(2)···D (see Figure 1 for the numbering system). The distance between O(2) and N(2), as determined from X-ray diffraction data, is 0.1978 ± 0.0015 nm. The bond angles and order parameters of the phenyl ring not involved in hydrogen bonding were also calculated, and the results are listed in Table 3.

Conclusion. Using a combination of X-ray diffraction and NMR spectroscopy, we have determined the internuclear distances and bond angles in the hydrogen-bonded moiety of a compound, 5-butoxy-2[(4-butylphenyl)azo]phenol, in its nematic phase. The standard deviations of the calculated values are about 1%. This approach may be useful for the study of other hydrogen-bonded liquid crystals as well.

Acknowledgment. This work was supported by the U.S. National Science Foundation under Grant Number DMR-0090218. The X-ray experiments were carried out by Dr. Masood A. Khan.

Supporting Information Available: Crystal data, the data collection conditions, and the refinement characteristics and fractional coordinates of non-hydrogen atoms of O-deuterated BBPAP. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References and Notes

(1) Emsley, J. W.; Lincon, J. C. *NMR Spectroscopy Using Liquid Crystal Solvents*; Pergamon: New York, 1975.

(2) Emsley, J. W., Ed. *Nuclear Magnetic Resonance of Liquid Crystals*; D. Reidel: Dordrecht, Netherlands, 1985.

(3) Drobny, G.; Weitekamp, D. P.; Pines, A. *Chem. Phys.* **1986**, *108*, 179. Gochin, M.; Hugi-Cleary, D.; Zimmermann, H.; Pines, A. *Mol. Phys.* **1987**, *60*, 205.

(4) Rendell, J. C. T.; Burnell, E. E. *Mol. Phys.* **1997**, *90*, 541. Syvitski, R. T.; Burnell, E. E. *J. Magn. Reson.* **2000**, *144*, 58. Syvitski, R. T.; Burlinson, N.; Burnell, E. E.; Jeener, J. *J. Magn. Reson.* **2002**, *155*, 251.

(5) Field, L. D.; Ramadan, S. A.; Pierens, G. K. *J. Magn. Reson.* **2002**, *156*, 64.

(6) Sinton, S. W.; Zax, D. B.; Murdoch, J. B.; Pines, A. *Mol. Phys.* **1984**, *53*, 333.

(7) Emsley, J. W.; Luckhurst, G. R.; Gray, G. W.; Mosley, A. *Mol. Phys.* **1978**, *35*, 1499. Ciampi, E.; De Luca, G.; Emsley, J. W. *J. Magn. Reson.* **1997**, *129*, 207.

(8) Courtieu, J.; Bayle, J.-P.; Fung, B. M. *Prog. Nucl. Magn. Reson. Spectrosc.* **1994**, *26*, 141. Fung, B. M. In *Encyclopedia of Nuclear Magnetic Resonance*; Grant, D. M., Harris, R. K., Eds.; Wiley: Chichester, U.K., 1996; pp 2744–2751. Fung, B. M. *Prog. Nucl. Magn. Reson. Spectrosc.* **2002**, *41*, 171.

(9) Schmidt-Rohr, K.; Nanz, D.; Emsley, L.; Pines, A. *J. Phys. Chem.* **1994**, *98*, 6668. Hong, M.; Schmidt-Rohr, K.; Pines, A. *J. Am. Chem. Soc.* **1995**, *117*, 3310. Hong, M.; Pines, A.; Caldarelli, S. *J. Phys. Chem.* **1996**, *100*, 14815. Caldarelli, S.; Hong, M.; Emsley, L.; Pines, A. *J. Phys. Chem.* **1996**, *100*, 18696.

(10) Fung, B. M.; Ermolaev, K.; Yu Y. *J. Magn. Reson.* **1999**, *138*, 28.

(11) Canlet, C.; Fung, B. M. *J. Phys. Chem. B* **2000**, *104*, 6181. Canlet, C.; Fung, B. M. *Liq. Cryst.* **2001**, *28*, 1863. Tan, C.; Canlet, C.; Fung, B. M. *Liq. Cryst.*, in press.

(12) Gray, G. W.; Jones, B. *J. Chem. Soc.* **1953**, 1467. Gray, G. W.; Jones, B.; *J. Chem. Soc.* **1953**, 4179. Gray, G. W.; Jones, B.; Marson, F. *J. Chem. Soc.* **1957**, 393.

(13) Paleos, C. M.; Tsiourvas, D. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1696. Paleos, C. M.; Tsiourvas, D. *Liq. Cryst.* **2001**, *28*, 1127.

(14) Kato, T. In *Handbook of Liquid Crystals*; Dietrich, D., Goodby, J., Gray, G. W., Spiess, H.-W., Vill, V., Eds.; Wiley-VCH: Weinheim, Germany, 1998; pp 969–979.

(15) Krische, M. J.; Lehn, J.-M. *Struct. Bonding* **2000**, *96*, 3.

(16) Takashi, K. *Struct. Bonding* **2000**, *96*, 95.

(17) Kang, S. K.; Samulski, E. T. *Liq. Cryst.* **2000**, *27*, 371. Kang, S. K.; Samulski, E. T. *Liq. Cryst.* **2000**, *27*, 377.

(18) Diehl, P.; Henrichs, P. M. *J. Magn. Reson.* **1971**, *5*, 134.

(19) Der Veen, J. V.; Hegge, T. C. J. M. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 344. Pajak, I.; Galewski, Z.; Rospenk, M.; Sobczyk, L. *Liq. Cryst.* **2001**, *28*, 1003.

(20) Burum, D. P.; Linder, N.; Ernst, R. R. *J. Magn. Reson.* **1981**, *44*, 173.

(21) Fung, B. M.; Khitrin, A. K.; Ermolaev, K. *J. Magn. Reson.* **2000**, *142*, 97.

(22) Diehl, P.; Niederberger, W. *J. Magn. Reson.* **1973**, *9*, 495.