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A Structural Investigation of Octa-*n*-undecoxyphthalocyanine in the Solid and Liquid-Crystalline State and of Poly(octa-*n*-undecoxyphthalocyaninato)siloxane by High-Resolution Solid-State NMR Spectroscopy

A. P. M. Kentgens,*[†] B. A. Markies,[‡] J. F. van der Pol,[‡] and R. J. M. Nolte[ℱ]

Contribution from the SON/NWO HF-NMR Facility, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands, Department of Organic Chemistry, University of Utrecht, Padualaan 8, 3584 CH Utrecht, The Netherlands, and Department of Organic Chemistry, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands. Received February 22, 1990

Abstract: ^{13}C high-resolution NMR spectra of octa-*n*-undecoxyphthalocyanine (Pc) were measured in the solid and in the liquid-crystalline state. In the solid state, crystallographic splittings are observed which can be attributed to distortions of the molecular symmetry of the Pc core. These distortions are probably connected with the tilting angle between the planes of the Pc molecules and the axis of the columns formed by these molecules. Temperature-dependent measurements show that the N–H tautomerism in the Pc core displays no obvious asymmetries. Above 380 K the solid phase of the Pc molecules is transformed into a hexagonal-ordered columnar mesophase. In this mesophase the molecular Pc plane is perpendicular to the stacking axis, with the molecules rotating about the stacking axis. There is no clear deviation from the molecular D_{4h} symmetry in the mesophase. The side chains display a liquid-like conformation in the mesophase. Poly(octa-*n*-undecoxyphthalocyaninato)siloxane was studied as a model of the mesophase in which the columns are chemically fixed. Solid-state NMR reveals for this polymer a rigid hexagonally ordered structure even at ambient temperature. The side chains in the polymer show the same liquid-like conformation as in the mesophase. The differences between the chemical shifts observed in solution and in the mesophase and between the solution and the siloxane polymer are attributed to intermolecular ring current shieldings and can be calculated satisfactorily by using a classical Johnson–Bovey current loop approach.

Introduction

Phthalocyanines (Pc's) are well-known and extensively studied compounds because they exhibit a number of remarkable properties which allow their application in various areas.[1] A prominent feature of phthalocyanines is their semiconducting behavior which, taking their high chemical stability into account, makes them key compounds for application as one-dimensional (semi-) conductors in electronic or opto-electronic appliances.[2] These semiconducting properties are related to the large delocalized π-systems of the molecules. A prerequisite for obtaining conducting properties is to arrange the phthalocyanine units in highly ordered stacks with the goal to increase π–π overlap between different units, thus enabling charge carriers to travel freely in the stack from one unit to another. Furthermore, the molecules formally must have fractionally occupied valence shells.[3] In practice this is achieved by doping the material with electron acceptors, e.g., halogens or nitrosonium salts. It has been established that phthalocyanines octasubstituted with long (*n*-alkoxymethyl) aliphatic chains show an increased tendency to aggregate compared with unsubstituted phthalocyanines.[4] It was shown that these systems exhibit liquid crystalline behavior.[5] Above the solid-mesophase transition temperature the rigid planar phthalocyanines stack into hexagonally arranged columns.[6] For phthalocyanines substituted with *n*-alkoxymethyl derivatives, these columns appear, however, to be disordered.[7] In order to obtain optimal electrical conductivity, disordered columns are, of course, unfavorable. Recently it was shown that peripherally octasubstituted *n*-alkoxyphthalocyanines form hexagonally columnar mesophases with ordered columns, i.e., with a regular stacking distance of 3.4 Å which is exactly equal to the van der Waals thickness of aromatic compounds.[8,9] So far, it has not been possible to grow single crystals of these octa-*n*-alkoxy-substituted phthalocyanines. Although solid-state NMR is a powerful tool in order to gain more insight in the local ordering, dynamics, and electronic structure of the molecules in such systems, only a limited number of solid-state NMR studies of Pc's have appeared in the literature.[10–15] Here we like to present

the results of a high-resolution ^{13}C solid-state NMR study of octa-*n*-undecoxyphthalocyanine, in the solid state and in the liquid-crystalline state. Furthermore, the corresponding siloxane polymer was studied.

Experimental Section

Materials. Catechol was recrystallized three times from toluene and stored at 4 °C under nitrogen. 1-Bromoundecane, bromine, K[13]CN, and CuCN were commercial products and were used as received. DMSO and DMF were dried by storage over activated 4Å molecular sieves. Methylene chloride and chloroform were dried over CaCl$_2$ and distilled prior to use. Diethyl ether was dried over sodium and distilled prior to use.

Synthesis. The phthalocyanines $H_2Pc(OC_{11}H_{23})_8$ and $[OSiPc(OC_{11}H_{23})_8]n$ were prepared analogous to procedures reported previously.[8,16] [13]C enriched (approximately 5 times the natural abundance)

[†]SON/NWO HF-NMR Facility, University of Nijmegen.
[‡]Department of Organic Chemistry, University of Utrecht.
[ℱ]Department of Organic Chemistry, University of Nijmegen.

(1) Simon, J.; André, J.-J. *Molecular Semiconductors;* Lehn, J. M., Rees, Ch. W., Eds.; Springer Verlag: Berlin, 1985.

(2) (a) Simon, J.; Tournilhac, F.; André, J.-J. *Nouv. J. Chim.* **1986,** *10,* 295. (b) Simon, J.; Tournilhac, F.; André, J.-J.; *New. J. Chem.* **1987,** *11,* 383. (c) Simon, J.; Bassoul, P.; Norvez, S. *New J. Chem.* **1989,** *13,* 13.

(3) Marks, T. J. *Science* **1985,** *227,* 881.

(4) Knoesel, R.; Piechoki, C.; Simon, J. *J. Photochem.* **1985,** *29,* 445–452.

(5) Piechoki, C.; Simon, J.; Skoulios, A.; Guillon, D.; Weber, P. *J. Am. Chem. Soc.* **1982,** *104,* 5245.

(6) Guillon, D.; Weber, P.; Skoulios, A.; Piechocki, C.; Simon, J. *Mol Cryst. Liq. Cryst.* **1985,** *130,* 223.

(7) Guillon, D.; Skoulios, A.; Piechocki, C.; Simon, J.; Weber, P. *Mol. Cryst. Liq. Cryst.* **1983,** *100,* 275.

(8) van der Pol, J. F.; Neeleman, E.; Zwikker, J. W.; Nolte, R. J. M.; Drenth, W. *Recl. Trav. Chim. Pays-Bas* **1988,** *107,* 615.

(9) Otha, K.; Jacquemin, L.; Sirlin, C.; Bosio, L.; Simon, J. *New. J. Chem.* **1988,** *12,* 751.

(10) Diel, B. N.; Inabe, T.; Lyding, J. W.; Schoch, K. F., Jr.; Kannewurf, C. R.; Marks, T. J. *J. Am. Chem. Soc.* **1983,** *105,* 1551.

(11) Toscano, P. J.; Marks, T. J. *J. Am. Chem. Soc.* **1986,** *108,* 437.

(12) Meier, B. H.; Storm, C. B.; Earl, W. L. *J. Am. Chem. Soc.* **1986,** *108,* 6072.

(13) Kendrick, R. D.; Friedrich, S.; Wehrle, B.; Limbach, H. H.; Yannoni, C. S. *J. Magn. Reson.* **1985,** *65,* 159.

(14) Wehrle, B.; Limbach, H.-H. *Chem. Phys.* **1989,** *136,* 223.

(15) Wehrle, B.; Limbach, H.-H.; Zipplies, T.; Hanack, M. *Ang. Chem. Adv. Mat.* **1989,** *101,* 1783.

Octa-n-undecoxyphthalocyanine

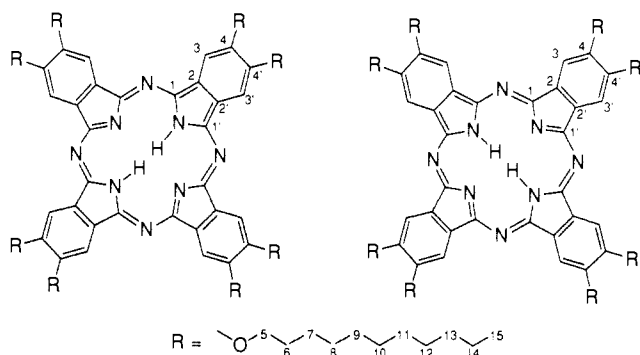*J. Am. Chem. Soc., Vol. 112, No. 24, 1990* 8801

Figure 1. The structure of octa-*n*-undecoxyphthalocyanine with the labels used for spectral assignment. Note that the primes are not used to distinguish between the two tautomers but to differentiate between carbons due to a lowered molecular symmetry in the crystal.

Table I. Structure and Cell Parameters of $H_2Pc(OC_{11}H_{23})_8$[a]

	solid phase at 25 °C	mesophase at 200 °C
	orthorhombic ($Z = 4$)	hexagonal
	$a = 53.6$ Å	$D = 33.9$ Å
	$b = 45.0$ Å	$h = 3.4$ Å
	$c = 4.3$ Å	$l = 4.6$ Å

[a] D, distance between the axes of neighboring columns; h, stacking period; l, average interatomic distance between the side chains.

Cu*CN was prepared according to a literature procedure.[11] Phthalocyanines, ^{13}C-labeled at the C1 and C1′ position (Figure 1), were synthesized by making use of 1,2-dicyano-4,5-bis(undecoxy)benzene, which was enriched 5 times at each CN group by reaction of 1,2-dibromo-4,5-bis(undecoxy)benzene with Cu*CN.

Solid-State NMR Spectroscopy. High-resolution solid-state NMR spectra were obtained on a Bruker AM 500 spectrometer (carbon frequency 125.7 MHz) equipped with a Bruker solid-state accessory. Spectra were recorded by using a broadband probehead with a 7 mm double air bearing magic angle spinning (MAS) assembly. Spinning speeds varying from 3500 to 6500 Hz were employed, at ≈4400 Hz overlap of side- and centerbands was avoided. Except for the spectrum of the mesophase, all spectra were obtained by using cross-polarization (CP) with 3 ms contact time and a repetition rate of 5 s. The proton and carbon 90° pulse width was 6 μs. Generally 2000 FID's were accumulated per spectrum. Spectra are referenced with respect to TMS by using adamantane as a secondary reference.

Results and Discussion

Electron Microscopy and X-ray Data. Electron microscopy of octa-*n*-undecoxyphthalocyanine reveals a microcrystalline texture with needle-shaped crystallites. From electron diffraction patterns it can be concluded that the Pc molecules stack in the needle direction.[17] Powder X-ray diffraction patterns of the solid phase can be indexed assuming an orthorhombic symmetry of the unit cell. From the 001 reflection, which corresponds to the translation of two Pc molecules within the stack, it may be concluded that this translation is approximately 4.3 Å. In differential scanning calorimetry (DSC) measurements a phase transition is observed at 356 K. Above the phase transition temperature a different diffraction pattern is observed, corresponding to a hexagonal lattice with ordered stacks of phthalocyanine molecules with an interplanar spacing of 3.4 Å, with the molecular plane perpendicular to the stacking axis.[7,8] The crystallographic data for H_2Pc-$(OC_{11}H_{23})_8$ (Figure 1) are summarized in Table I.

Spectral Assignment. The ^{13}C CP-MAS spectrum of the Pc core of $H_2Pc(OC_{11}H_{22})_8$ at room temperature is shown in Figure 2. The first striking feature of this spectrum is its high resolution compared to ^{13}C CP-MAS spectra of unsubstituted phthalocyanines that have been published so far.[11-14] This indicates that the samples consist of highly crystalline material, i.e., the molecules
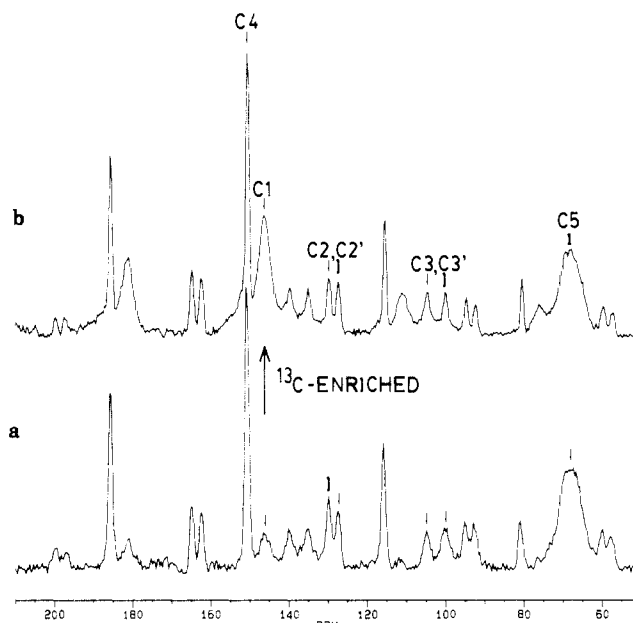

Figure 2. CP-MAS spectra of octa-*n*-undecoxyphthalocyanine with (b) and without (a) ^{13}C enrichment on the C1 position. Lines without labels are spinning sidebands.

have a well-defined environment. That the increased resolution is not simply due to the higher field (11.7 T, ^{13}C-frequency 125.7 MHz) used to record our spectra, e.g., by removal of residual [13]C–[14]N couplings, was verified by taking a spectrum of unsubstituted H_2Pc at 125.7 MHz. The resolution of this spectrum is comparable to that of Meier et al.[12] and Wehrle et al.,[14] with a line width of approximately 5 ppm. This means that the lines in H_2Pc are inhomogeneously broadened. As Meier et al.[12] studied crystalline α-H_2Pc and Wehrle et al.[14] α- and β-H_2Pc, the large line width in these systems cannot be attributed to the presence of amorphous material. There are three mechanisms that may be held responsible for these large line widths. First, in a polycrystalline sample, anisotropic bulk magnetic susceptibility effects lead to line broadening.[18] Second, in these large aromatic systems, ring currents play an important role. It has been shown by Okazaki and McDowell[19] that, although ring current effects in solution only lead to isotropic shifts, line broadening is produced when MAS is employed because the radial component of the field produced by the ring current is not averaged by MAS. Finally, it has to be taken into account that in the α- and β-phase of phthalocyanine, the molecules are tilted with respect to the stacking axis. This tilt lowers the site symmetry of the molecules and can thus lead to splittings of the resonances in the spectrum. These splittings may, due to the above mentioned broadening effects, no longer be resolved and thus lead to a further increase of the observed line widths.

From the high resolution of the spectra of the substituted phthalocyanines it seems that the paraffinic side chains do not hinder the molecules to crystallize in a neat crystalline phase. That line broadening effects operating on the unsubstituted phthalocyanine are less important here might be a result of the larger distance between the molecular stacks leading to a reduction of intercolumn ring current effects. Furthermore, inspection of the spectra in Figure 2 reveals that the crystallographic site symmetry of the molecules must indeed be lower than D_{4h}, i.e., more than four lines are observed for the phthalocyanine core. Except for the splittings, the lines may easily be assigned on the basis of their chemical shift by using simple addition rules (Table II). The only ambiguity is the assignment of the carbons C1 and C4. For this reason a sample was isotopically enriched with ^{13}C on the C1 position. From the increase in intensity of the line at 146 ppm

(16) van der Pol, J. F.; de Haas, M. P.; Warman, J. M.; Drenth, W. *Mol. Cryst. Liq. Cryst.* In press.

(17) van der Pol, J. F.; Neeleman, E.; Zwikker, J. W.; Nolte, R. J. M.; Drenth, W.; Aerts, J.; Visser, R.; Picken, S. J. *Liq. Cryst.* **1989**, *6*, 577.

(18) VanderHart, D. L.; Earl, W. L.; Garroway, A. N. *J. Magn. Reson.* **1981**, *44*, 361.

Table II. Observed Chemical Shifts for
Octa-*n*-undecoxyphthalocyanine[b]

assignment	solution	203 K	372 K	391 K	polymer
C1	148.3	153.5, 136.1	147.0	142.8	140.8
C1'			145.9		
C2	129.8	131.9, 126.7	129.9	127.4	126.5
C2'		129.5, 123.3	127.8		
C3	105.0	*a*	105.1	103.0	101.6
C3'		*a*	100.3		
C4	151.6	149.8	150.9	149.3	149.0

side chain	solution	203 K	372 K	391 K	polymer
C5	69.5	*a*	69.4	68.4	67.2
C13	32.0			32.5	33.0
C6 +	29.9				
C8 to	29.7	32.6	31.8	30.4	31.1
C12	29.5				
C7	26.5			27.0	27.6
C14	22.8	23.9	23.5	23.1	23.7
C15	14.2	14.6	14.5	14.3	14.7

a Position could not be determined due to overlap with spinning
sidebands. *b* In solution (CDCl₃) at room temperature, in the solid
state at 203 K and 372 K, in the mesophase at 391 K, and for the
siloxane polymer at room temperature.

it is clear that this line belongs to C1 (Figure 2b).

**N–H Tautomerism and Crystallographic Splittings in the Solid
State.** The width of the C1 resonance at 146 ppm is rather large
compared to the other resonances in the spectrum. This is a result
of the N–H tautomerism; the two protons in the inner core of the
phthalocyanine exchange between two tautomeric positions (Figure
1). At room temperature the exchange rate is only slightly faster
than the difference in resonance frequency of the C1 resonances
of the tautomers, i.e., the fast exchange limit has not yet been
reached. The effects of the N–H tautomerism are demonstrated
in Figure 3. At 203 K the exchange is slow on the NMR time
scale, and thus separate resonances at 155 and 137 ppm are
observed for the C1 carbons. The C2 doublet is also affected by
the tautomerism, and we now observe a doublet of doublets. The
C4 resonance is not affected by the exchange. Unfortunately,
the C3 resonances cannot be observed due to overlap with the
strong sidebands of the (enriched) C1 resonance. At temperatures
above 330 K up to the transition temperature, exchange is very
fast so that the C1 resonance is narrowed and even shows a small
splitting, due to the lowered site symmetry we hold responsible
for the splittings of the C2 and C3 resonances. That the splittings
are due to an asymmetry of the double minimum potential for
the tautomers, i.e., that one tautomer is energetically favorable
over the other because of crystal packing effects, as was observed
for β-Pc,[14] is very unlikely because none of the observed splittings
change when the temperature is increased from 298 to 370 K.

An evaluation of the observed line widths as a function of
temperature, by using a two-site exchange model, shows that the
activation energy for the tautomerism is of the same magnitude
as that found for α- and β-Pc,[12,14] as can be expected for an
intramolecular process. A very accurate evaluation of the process
detecting subtle asymmetries as was done in the ^{15}N study by
Wehrle and Limbach[14] is hindered due to overlapping lines in the
[13]C spectrum. As was discussed by Wehrle and Limbach[14] the
symmetry and kinetics of the tautomerism are determined by the
geometry of the phthalocyanine core, which, in turn, is influenced
by crystal packing effects. The crystal structure of β-Pc has been
determined accurately by X-ray crystallography.[20] Roughly
speaking we can say that the molecules are tilted over an angle
of 44.2° with respect to the stacking axis and that the molecules
are elongated along the axis in the molecule perpendicular to the
stacking axis. No exact structural data are available for α-Pc.
It has been reported, however, that the tilt with respect to the
stacking axis is smaller[21] (≈26°) and the molecular symmetry is
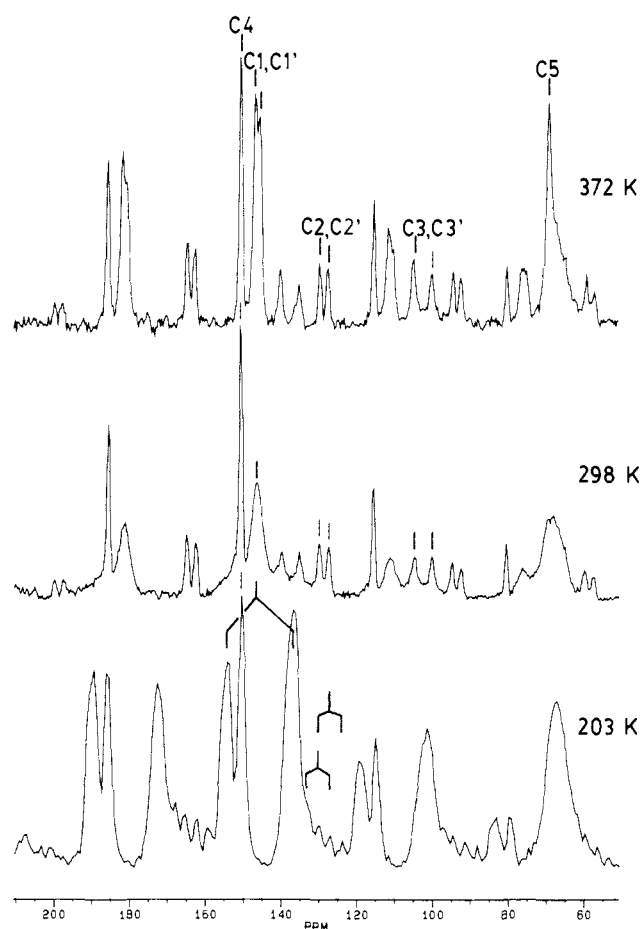higher than that of the β modification.[22] Wehrle and Limbach[14]

Figure 3. Temperature-dependent CP-MAS spectra showing the effect
of the tautomerism in the slow exchange (203 K), intermediate (298 K),
and fast exchange (372 K) limit.

hold the deviations of the molecular symmetry in β-Pc responsible
for the observed asymmetry in the tautomerism of the β-phase.
Except for the influence on the tautomerism, these crystallographic
differences express themselves in splittings in the ^{15}N and [13]C
spectra. For the C1 resonance of β-Pc two superimposed line pairs
were observed, i.e., not only does the asymmetry of the tautom-
erism lead to a splitting of the lines but also there appears to be
an extra crystallographic splitting of 3.5 ppm for the C1 resonance
of β-Pc, whereas no splitting is observed for the α-phase.[14] As
was already discussed, overlap in the rest of the spectra of un-
substituted Pc's is too severe to determine other splittings. In the
octasubstituted Pc studied here, a splitting of ≈1 ppm is observed
for the C1 resonance (along with a splitting of 2 and 5 ppm for
C2 and C3, respectively). It was established by X-ray analysis
that the intermolecular translation distance between molecules
along the stacking axis in the solid state is 4.3 Å. Assuming that
the interplanar distance of the Pc cores again is the van der Waals
thickness of 3.4 Å as in α- and β-Pc (and even in crown-ether-
substituted Pc[23]), we can calculate that the tilt of the molecules
with respect to the stacking axis must be approximately 38°. The
question that now arises is what determines the splittings observed
in the ^{13}C spectra. For porphyrins it has been shown that in case
of a low symmetry of the crystal structure, splittings may occur
due to intermolecular ring-current shielding, i.e., the averaged part
of the field due to ring currents in neighboring molecules may
be different for different carbons depending on the crystal
structure.[19,24] In the Pc's a similar situation occurs; due to the

(19) Okazaki, M.; McDowell, C. A. *J. Am. Chem. Soc.* **1984**, *106*, 3185.
(20) Robertson, J. M. *J. Chem. Soc.* **1936**, 1195.
(21) Suito, E.; Uyeda, N. *Kolloid Z. Z. Polym.* **1963**, *193*, 97.

(22) Assour, J. M. *J. Phys. Chem.* **1965**, *69*, 2295.
(23) Sirlin, C.; Bosio, L.; Simon, J.; Ahsen, V.; Yilmazer, E.; Bekaroglu, O. *Chem. Phys. Lett.* **1987**, *139*, 362.
(24) (a) Frydman, L.; Olivieri, A. C.; Diaz, L. E.; Frydman, B.; Morin, F. G.; Mayne, C. L.; Grant, D. M.; Alder, A. D. *J. Am. Chem. Soc.* **1988**, *110*, 336. (b) Frydman, L.; Olivieri, A. C.; Diaz, L. E.; Valasinas, A.; Frydman, B. *J. Am. Chem. Soc.* **1988**, *110*, 5651.

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tilt of the molecules within the stacks, different carbon atoms in a molecule are differently shielded due to ring current effects of neighboring molecules. For a molecule in a stack, its neighbors appear to be translated along the projection of the stacking axis in the plane of the molecule (Figure 4a).

As was discussed by Okazaki and McDowell[19] ring shifts in a MAS experiment can, except for line broadening effects, be calculated in the same way as in solution. Many approaches for the calculation of ring current effects exist;[25] a very widespread method is the classical current loop approach by Waugh and Fessenden and Johnson and Bovey.[26] In this approach the induced field, due to n electrons revolving in a pair of classical current loops of radius a at a distance p above and under the molecular plane, is calculated. This approach proved to be successful for some porphyrins.[19] The number of electrons n, the radius a, and the spacing of the current loops $2p$ have to be obtained by comparison of calculated and experimental values. For benzene, Johnson and Bovey considered the π electrons (so $n = 3$) in two loops with radius $a = 1.39$ Å and adjusted the loop spacing $2p = 1.28$ Å to match calculated and observed shifts. For phthalocyanines classical current loop calculations have been carried out by Janson et al.[27] for some single-ring and multiring silicon and germanium Pc's in solution. So called five loop pair calculations, where the ring current effects were calculated as the sum of four loop pairs for the benzene moieties and one loop pair for the central core of the Pc, appeared to be most successful. For the benzene moieties the original parameters of Johnson and Bovey were kept. For the central ring they obtained $n = 4.215$ and $a = 3.90$ Å, while p was kept at 0.64 Å. It was argued that these values are resonable if it is assumed that the π electrons of the nitrogen atoms are essentially localized. A more recent parametrization, also taking into account anisotropy shieldings due to proximate carbon atoms, was given by Marks and Stojakovic.[28] We have used the (larger) parameters of Janson et al.[27] to calculate splittings in the ^{13}C spectra from intermolecular ring current shielding due to a tilt of the molecules with respect to the stacking axis, taking direct neighbors and next nearest neighbors into account. Considering the large distance between the columns, intercolumn effects are negligible. We found that the calculated splittings are far too small to account for the observed splittings in the spectra. This is also the case when the parameters of the central current loop pair are altered, e.g., by including more electrons to take the nitrogen atoms into account. As we have calculated only *inter*molecular effects, a possible distortion of the molecule from perfect D_{4h} symmetry in the solid state is, of course, not taken into account. Calculation of *intra*molecular ring current effects, by using the parameters of Janson et al.[27] (Figure 4b), clearly demonstrates that small displacements of the carbon atoms can result in large shifts of their resonance frequencies and that when D_{4h} symmetry is lost sizable splittings can occur. Of course, these calculations cannot be used to calculate the distortion of the molecule because it is unknown as to how these molecular distortions affect the ring currents themselves. Moreover, a simple classical Johnson–Bovey approach is not suited for such a calculation. The only purpose of Figure 4b is to show the order of magnitude of the intramolecular effects. From our calculations we conclude that the observed splittings in our ^{13}C spectra are not directly due to a tilt of the molecules with respect to the stacking axis, which lowers the site symmetry, but rather to a distortion of the intramolecular symmetry which, as is suggested by the observations for α-, β-, and the octa-substituted Pc, is correlated with the tilt. To what extent these distortions influence the tautomerism in the octa-substituted Pc's should be studied by ^{15}N NMR, where the effects of the tautomerism are most pronounced and only a few lines are present. However, such a

Table III. Principal Values of the Chemical Shift Tensor of the C4 Carbon in the Solid State, the Mesophase, and in the Polymer

	σ_{11}	σ_{22}	σ_{33}
solid state	218	165	69
mesophase	208	178	72
polymer	212	165	70

Table IV[a]

carbon	M	CM	POL	E	S
C1	5.5	5.3	7.5	5.4	5.4
C2	2.4	3.1	3.3	3.7	2.5
C3	2.0	1.8	3.4	2.4	1.2
C4	2.3	1.0	2.6	1.9	0.3

[a] Difference in chemical shift between mesophase and solution spectrum (M) and calculated intermolecular ring current shieldings in ordered columns, taking neighbors and next nearest neighbors into account, with an averaging for rotating molecules (CM). Difference between observed shifts in the spectrum of the siloxane polymer and the solution spectrum (POL); calculated ring currents for fully eclipsed (E) and fully staggered (S) polymer conformations.

study requires ^{15}N enriched samples, which were not available.

Columnar Mesophase. As was established by X-Ray diffraction, octasubstituted n-alkoxyphthalocyanines form hexagonally columnar mesophases with ordered columns. Increasing the temperature in the CP-MAS experiments (Figure 5) on H_2Pc-$(OC_{11}H_{23})_8$ resulted in a strong decrease of signal intensity at temperatures above 380 K. This is shown in Figure 5c taken at 384 K where only some signal for C3 of the Pc core is left. The transition temperature found here is considerably higher than that determined by DSC. It should be noted, however, that DSC measurements gave some variations of the transition temperature for different samples. The high pressure submitted to the sample as a result of the sample spinning might also influence the transition temperature.

Direct pulse excitation combined with high power proton decoupling gives spectra with a good signal to noise (Figure 5b). The sudden decrease of cross-polarized signal for carbons C1, C2, and C4 implies that there are motions in the mesophase which reduce the heteronuclear dipolar interaction of these carbons with neighboring protons. Among the conceivable motions in the columnar structure, a rotation of the molecules about their 4-fold axes would be most effective in this respect. If the rotation is fast with respect to the heteronuclear dipolar interaction, the intramolecular contribution to the second moment will be reduced by a factor of 4.[29] Intermolecular contributions will also be greatly reduced. For C1, C2, and C4, with no directly bonded protons, the nearest protons are more than 2 Å away leading to a dipolar broadening of less than 2 kHz. Consequently, a rotation of several kHz would already greatly reduce the dipolar interaction for those carbons without directly bonded protons. An upper limit for the rotation frequency can be obtained from the principal values of the chemical shielding tensor as obtained from a spinning sideband analysis by using the method of Herzfeld and Berger.[30] The results of such an analysis for the C4 carbon in the solid state, in the liquid crystalline state, and in the corresponding siloxane polymer are given in Table III. In aromatic systems the most shielded direction, σ_{33}, is perpendicular to the plane of the ring.[31] So, if the rotational motion about the 4-fold axis in the mesophase is fast with respect to σ_{11}–σ_{22} as determined in the solid state, an axially symmetric tensor should be found. Table III shows that there is no averaging of the shielding tensor to axial symmetry in the mesophase. This means that the rotational motion cannot exceed $\sigma_{11} - \sigma_{22} = 6.3$ kHz by an order of a magnitude.

In the direct pulse excitation spectrum of the mesophase (Figure 5b) no splittings of the resonances of carbons C1, C2, and C3 are observed. This is in accordance with our conclusion that the

(25) Haigh, C. W.; Mallion, R. B. *Prog. Nucl. Magn. Reson. Spectrosc.* **1980**, *13*, 303.

(26) (a) Waugh, J. S.; Fessenden, R. W. *J. Am. Chem. Soc.* **1957**, *79*, 846. (b) Johnson, C. E., Jr.; Bovey, F. A. *J. Chem. Phys.* **1958**, *29*, 1012.

(27) Janson, T. R.; Kane, A. R.; Sullivan, J. F.; Knox, K.; Kenney, M. E. *J. Am. Chem. Soc.* **1969**, *91*, 5210.

(28) Marks, T. J.; Stojakovic, D. R. *J. Am. Chem. Soc.* **1978**, *100*, 1695.

(29) Abragam, A. *Principles of Nuclear Magnetism*; Oxford University Press: Oxford, 1983; pp 453–455.

(30) Herzfeld, J.; Berger, A. E. *J. Chem. Phys.* **1980**, *73*, 6021.

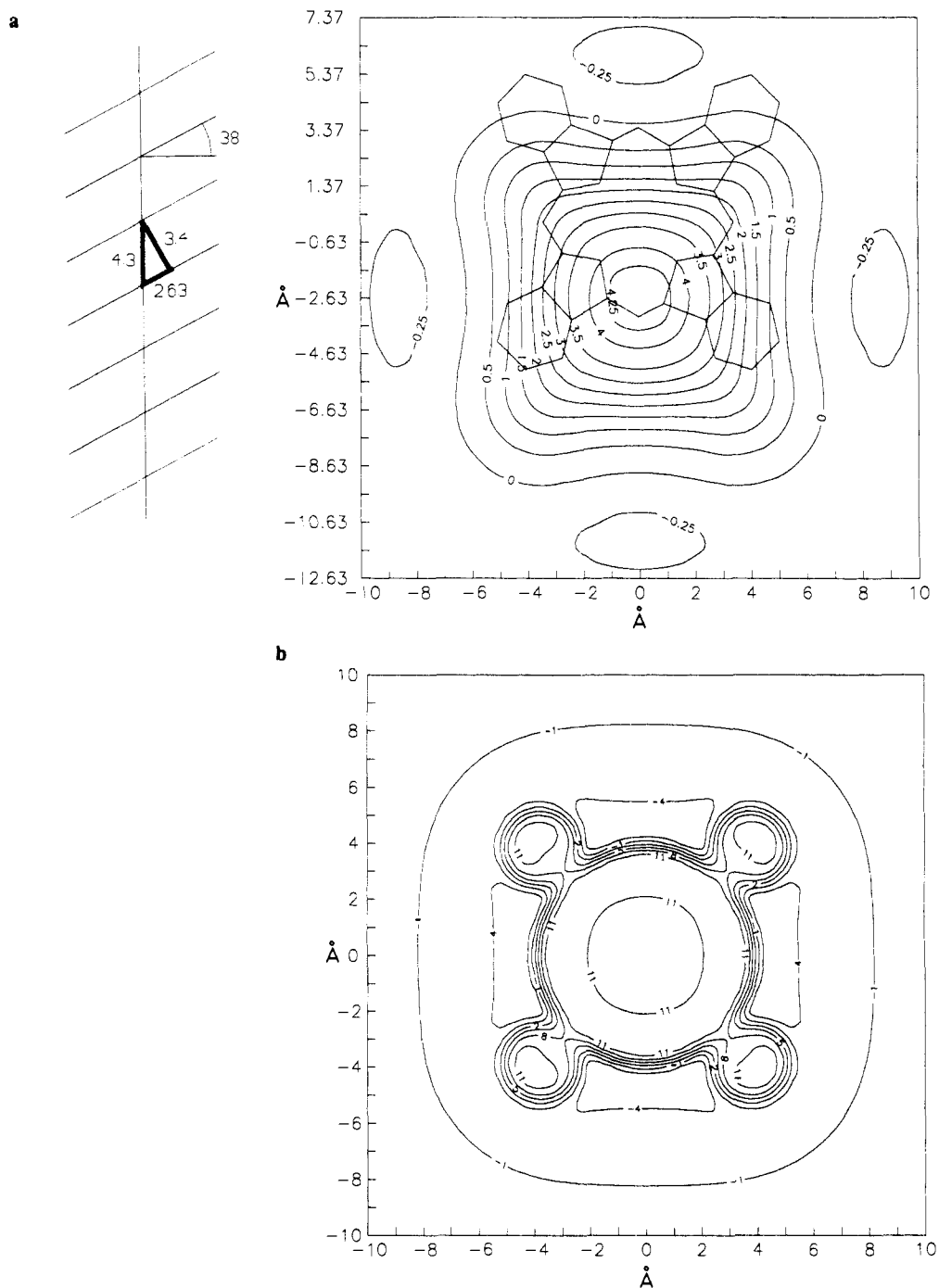(31) Veeman, W. S. *Prog. Nucl. Magn. Reson. Spectrosc.* **1984**, *16*, 193.

Figure 4. (a) Intermolecular ring current shieldings (in ppm) from a neighboring Pc molecule, in a stack with a tilt angle of ≈38°, as a function of the position with respect to the center of the Pc core in Å. (b) Intramolecular ring current shieldings in Pc.

molecular distortion of the phthalocyanine core is correlated with the tilt of the molecules with respect to the stacking axis. In the mesophase, where the stacking axis is perpendicular to the molecular planes, there is no obvious reason for a molecular distortion, i.e., the molecules retain D_{4h} symmetry, and thus no crystallographic splittings are observed. In this case it becomes interesting to compare the chemical shifts found in the mesophase with those found in solution (CDCl₃), as the differences should now be entirely determined by intermolecular ring current effects between neighboring Pc cores in the mesophase. Again, Johnson–Bovey current loop calculations were performed to calculate the observed shifts (Table IV). Calculations based on the five loop pair model employing the parameters of Janson et al.[27] result in far too large values for the incremental shift. As was mentioned before, they assume that the π electrons of the nitrogen atoms are localized. However, a diameter of 3.90 Å for the central current loop is used, which would locate the current loop even outside the position of

the outer nitrogens. Doing justice to the classical character of the Johnson–Bovey approach we performed calculations by using parameters for the central loop pair based on simple considerations. For instance, if the π electrons of the nitrogen atoms are localized, the central current loop pair should be located on the Cl carbons with four electrons in each loop. Considering four electrons in each current loop at a distance of 0.64 Å to the molecular plane, with a diameter of 2.94 Å, a satisfactory agreement with the observed values could be obtained (Table IV). This implies that the nitrogen π electrons are indeed localized. Note that the shifts were averaged to take the rotation of the molecules about their 4-fold axis into account. Keeping in mind that the accuracy of determining shifts in the solid-state spectra is 1 ppm, only the value calculated for carbon C4 seems a little small. This might be explained by assuming that the oxygens of the side chains attached to the C4 carbons participate in the π conjugation and thus somewhat affect the ring currents of the benzene moieties. Here
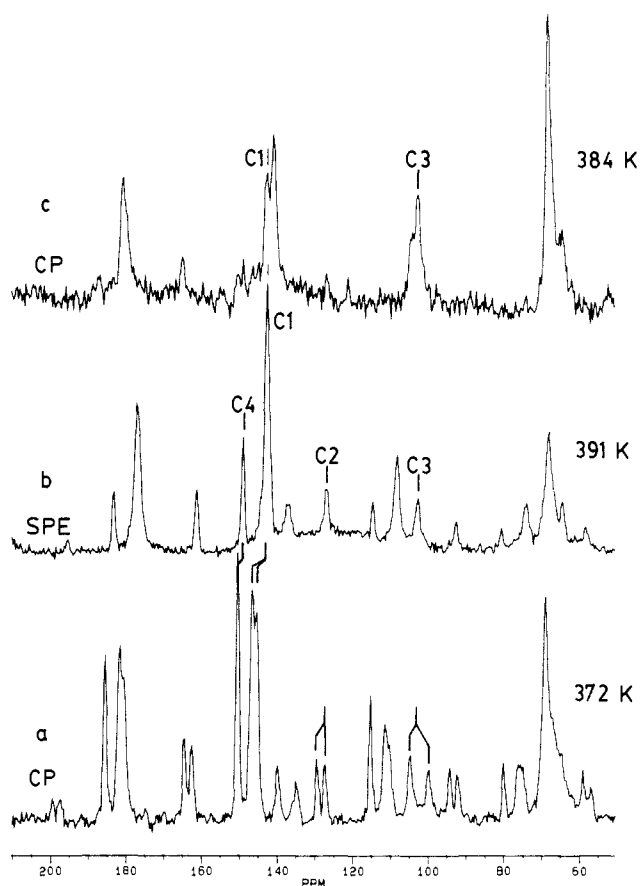
Figure 5. (a) CP-MAS spectrum of $H_2Pc(OC_{11}H_{23})_8$ just below the phase transition temperature. (b) Direct pulse excitation spectrum above the phase transition temperature and (c) CP-MAS spectrum above the phase transition temperature, demonstrating the increased mobility of the molecules.

Figure 6. CP-MAS spectrum of poly(octa-n-undecoxyphthalo-cyaninato)siloxane at ambient temperature.

we would like to point out that we did not try an exact parametrization of the Johnson–Bovey model for these compounds based on the observed C-13 shifts. Some variation of the parameters is of course possible as the accuracy of the shifts determined from solid-state spectra is only 1 ppm. It is clear, however, that these ring current effects play an important role in the observed shifts. From this viewpoint, it is reassuring that a good correspondence between observed and calculated shifts is obtained, by using the straightforward parameters of four electrons in a 2.94-Å loop.

Siloxane Polymer. We have included poly(octa-n-undecoxy-phthalocyaninato)siloxane in our study because this polymer can be considered as a model of the mesophase in which the ordered columns are chemically fixed, even at ambient temperatures. This approach is valuable in view of the electrical properties of these materials, since an increase in intracolumnar conductivity is observed at the transition from the solid phase to the mesophase.[16] This is thought to be related to the particular structure of the mesophase. The synthesis and electrical properties of the polymer of $Si(OH)_2Pc(OC_{11}H_{23})_8$ are described elsewhere.[32] Similar compounds and their properties have been described before.[33-36]

As can be seen in Figure 6, the spectrum of the siloxane polymer is similar to that of the columnar mesophase, i.e., no crystallographic splittings are observed, suggesting that no significant distortion of the molecular D_{4h} symmetry is present. Note that the spectrum was obtained by cross-polarization indicating that molecular reorientations, if present, are much slower than in the mesophase. Inspection of the chemical shifts (Table II) shows that the carbon resonances of the Pc core in the polymer have all shifted to high field compared to the mesophase. The upfield shift of carbon C1 is of course not surprising, as the two hydrogens in the center of the Pc core are replaced by the less electronegative Si. It is unlikely, however, that the upfield shifts of the other carbons are also due to this effect. As we have discussed for the mesophase, intermolecular ring current effects affect the resonance positions. In the calculation of the ring current shifts in the mesophase, the shifts were averaged to take a free rotation of the molecules about the stacking axis into account. In the polymer this rotation is absent on the NMR time scale, and thus ring current effects depend on the relative orientation of the molecules with respect to each other. Calculations show that the observed shifts correspond best with an (close to) eclipsed conformation of the molecules (Table IV). This conformation must be imposed by the long alkoxy side chains of the phthalocyanine, since for the unsubstituted polymer, $[Si(Pc)O]_n$, a large staggering angle (36°) was found.[34] With a small staggering angle, the side chains are allowed to be aligned more or less parallel to each other.

Because the carbon shifts are influenced by intermolecular ring current effects, the solid-state NMR spectra enable us to get information about the degree of polymerization of the sample. It is clear that incremental shifts due to intermolecular ring currents are different for chain ends, as they only have one direct neighbor. Also unreacted monomer units should give extra lines (or shoulders) in the spectra. Indeed, some clear shoulders, which were most pronounced on the C1 resonance were observed for one of the studied samples. In Figure 6 no obvious extra lines or shoulders are observed, indicating that the chains of the polymer sample studied consist of at least 25 monomer units, in accordance with FT–IR end group analysis.[32] More accurate SAXS experiments reveal a chain length of ≈100 monomer units.[32]

Side Chains. So far we have concentrated on the spectral parameters of the phthalocyanine core of the molecules. The resonances of the side chains, however, also display some remarkable features. Figure 7 displays the aliphatic region of the spectra, showing the resonances of the side chains as a function of temperature. At 203 K three rather broad lines are observed, illustrating the rigidity of the side chains at this temperature. At room temperature these resonances split up (Figure 7b), presumably because of a higher mobility of the side chains. Considering the splittings of resonances of individual carbons, the

(32) van der Pol, J. F.; Zwikker, J. W.; Warman, J. M.; de Haas, M. P. Recl. Trav. Chim. Pays-Bas. In Press.

(33) Warman, J. M.; de Haas, M. P.; van der Pol, J. F.; Drenth, W. Chem. Phys. Lett. 1989, 164, 581.

(34) (a) Dirk, C. W.; Inabe, T.; Schoch, K. F. Jr.; Marks, T. J.; J. Am. Chem. Soc. 1983, 105, 1539. (b) Diel, D. N.; Inabe, T.; Lyding, J. W.; Schoch, K. F., Jr.; Kannewurf, C. r.; Marks, T. J. J. Am. Chem. Soc. 1983, 105, 1551.

(35) (a) Sirlin, C.; Bosio, L.; Simon, J. J. Chem. Soc., Chem. Commun. 1987, 379. (b) Sirlin, C.; Bosio, L.; Simon, J. J. Chem. Soc., Chem. Commun. 1988, 236.

(36) (a) Sauer, T.; Wegner, G. Mol. Cryst. Liq. Cryst. 1988, 162B, 97. (b) Caresi, W.; Sauer, T.; Wegner, G. Makromol. Chem., Rapid Commun. 1988, 9, 651. (c) Sauer, T.; Wegner, G.; Makromol. Chem., Macromol. Symp. 1989, 24, 303.
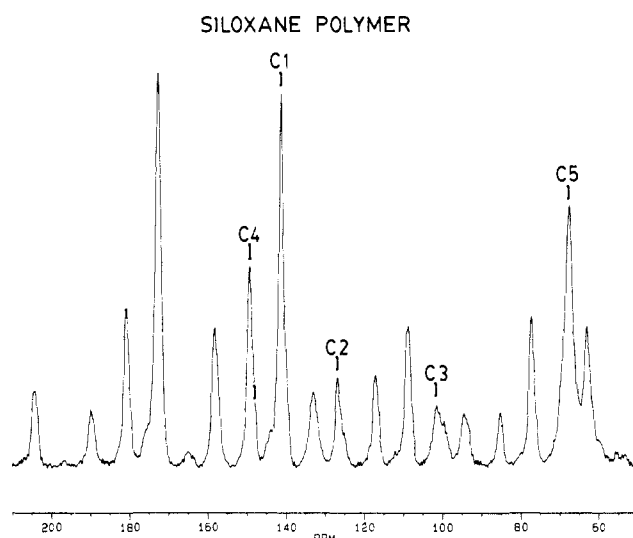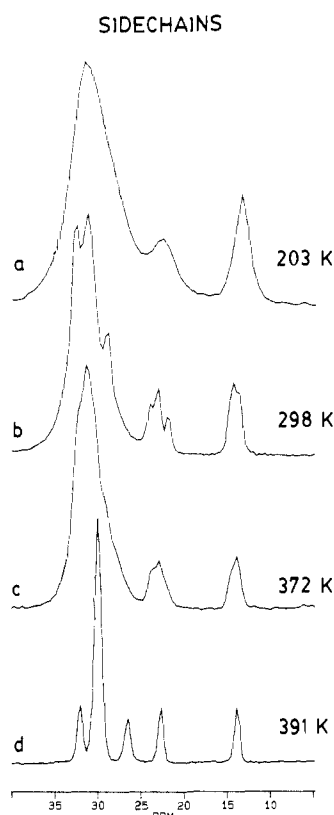
SIDECHAINS

Figure 7. Spectra of $H_2Pc(OC_{11}H_{23})_8$ showing the spectral region for the aliphatic side chains as a function of temperature.

motions of the side chains apparently involve highly restricted jumps between a small number of well-defined conformations. Remarkably, when going to higher temperature, the resolution of the spectrum decreases again (Figure 7c). A plausible explanation for this decline in resolution is that the motions of the side chains become of the same order of magnitude as the spinner frequency ($\approx$4 kHz) or the proton-decoupling frequency ($\approx$40 kHz). In either case the molecular motion will interfere with the coherent averaging, resulting in an increased line width. A drastic change in the side chain spectrum is observed when the tem-

perature is raised above the phase transition temperature (Figure 7d). The spectrum now consists of five well-resolved lines and is, except for the line width, identical with the side chain spectrum in solution. This means that the side chains are indeed very mobile in the mesophase, displaying a liquid-like order, as was also concluded from X-ray data.[8,17] It should be noted, however, that the side chain carbons give strong signals in the CP-MAS experiment even in the mesophase, indicating that the involved motions are spatially restricted as no full averaging of dipolar interaction occurs. The observed resonances of the side-chain carbons in the mesophase can be assigned by using simple addition rules,[37] without taking any specific steric effects into account but rather by using an approximation for nonrigid molecules. In the crystal phase the chains are obviously forced in a few specific conformations, different from the solution/mesophase conformation. In the spectra this is most clearly expressed by the resonance of side-chain carbon C7, which shifts substantially when going from the mesophase to the crystal phase. For the siloxane polymer, with its "fixed" mesophase structure, the side chains give, except for an increased line width due to lower mobility, indeed the same spectrum as the mesophase, so no constraints are imposed on the side chains upon polymerization.

Conclusions

It appears that high-resolution solid-state NMR is a valuable tool for studying local structure and dynamics of octasubstituted phthalocyanines in the solid as well as the liquid crystalline state. Well-resolved spectra are obtained which make it possible to observe crystallographic splittings due to molecular distortions. Moreover, it is possible to observe the process of N–H tautomerism in the phthalocyanine core. Furthermore, information on the dynamics of the molecules in the mesophase and in the corresponding siloxane polymer can be obtained.

(37) Shoulders, B.; Welch, S. C. *J. Chem. Educ.* **1987**, *64*, 915.