Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Preliminary communication ^{13}C CPMAS NMR of 5,10,15,20-tetrakis(4-*n*-dodecylphenyl)-porphyrin: dynamics of aliphatic chains in discotic lamellar mesophases

T. Akai; Y. Shimizu

To cite this Article Akai, T. and Shimizu, Y.(2000) 'Preliminary communication ^{13}C CPMAS NMR of 5,10,15,20-tetrakis(4-*n*-dodecylphenyl)-porphyrin: dynamics of aliphatic chains in discotic lamellar mesophases', Liquid Crystals, 27: 3, 437 — 441

To link to this Article: DOI: 10.1080/026782900202903

URL: http://dx.doi.org/10.1080/026782900202903

LIQUID CRYSTALS, 2000, VOL. 27, NO. 3, 437–441

Preliminary communication

^{13}C CPMAS NMR of 5,10,15,20-tetrakis(4-*n*-dodecylphenyl)-porphyrin: dynamics of aliphatic chains in discotic lamellar mesophases

T. AKAI* and Y. SHIMIZU
Osaka National Research Institute, AIST, 1-8-31 Midorigaoka, Ikeda,
Osaka 5638577, Japan

(*Received 28 August 1999; accepted 28 October 1999*)

Solid state ^{13}C CPMAS NMR spectra of 5,10,15,20-tetrakis(4-*n*-dodecylphenyl)porphyrin (C_{12}TPP) have been studied to elucidate the microscopic structures and dynamics in the mesophases. The temperature dependence of ^{13}C CPMAS NMR in the aliphatic regions is discussed mainly in relation to the phase transitions. The spectra for the aliphatic chains showed remarkable changes with the phase transition from crystal to lower mesophase (M'_L) and from lower to higher mesophase (M_L). It was found that the aliphatic chains partially melt in the M'_L phase, while they melt totally in the M_L phase. The spectra in the aromatic region did not vary greatly with the transitions from crystal to M'_L and from M'_L to M_L, which probably means that the molecular D_{4h} symmetries are distorted in these mesophases, as in the crystal, on the time scale observed by NMR (~ kHz).

Since the discovery of fast photoconduction in discotic mesogens, their electronic properties have been gained more interest with a view to applications in opto-electronics devices [1–4]. In this respect, porphyrin- and phthalocyanine-based mesogens are fascinating families of materials, because both show characteristic optical properties in the visible region due to their extended π-electron systems [5, 6]. Many compounds exhibiting hexagonal or rectangular columnar mesophases have been found and their electronic properties reported [7, 8]. However, discotic lamellar mesogens have been little studied.

The existence of the lamellar phase for discotic mesogens was first evidenced in 1983 by Davidson *et al.* in a CT complex of a long chain heterocyclic donor and TCNQ [9]. Several years later, we found that homologous series of long chain tetraphenylporphyrins (C_nTPP) exhibit the lamellar mesophase [10, 11]. Interestingly, they show two types of lamellar mesophase above alkyl chains with 11 carbons: lower and higher mesophases (M'_L and M_L) [10, 11]. From our preliminary results on fluorescence spectra and X-ray diffraction, it was proposed that M'_L is columnar, whereas the columnar structure is broken in M_L (see figure 1) [12, 13]. Their electronic properties were also studied, and it was shown that the photocurrent increases with the transition from the crystal to the lower mesophase [14]. Therefore, the mesomorphic C_nTPP series is a fascinating family of materials to study.

In understanding a mechanism for photoconduction in these mesophases, knowledge on the microstructures and dynamics of the molecules is of fundamental importance. As for the structure of the lamellar mesophase, there is no well-accepted universal concept except for the existence of a certain layered structure. Our knowledge and experience concerning lamellar mesogens suggest however that there exist some ordered structures in addition to the layered structure (empirically, the lamellar mesophase is very viscous compared with other liquid crystalline phases). For example, C_{12}TPP shows diffuse X-ray diffraction peaks at higher angles (corresponding to 4–10 Å periodicity) in addition to the sharp peaks from the lamellar structure [11]. Also, the mesomorphic behaviour of C_{12}TPP under high pressure strongly suggests that M'_L is a soft crystal or a conformationally disordered crystal [15, 16]. Various types of additional orderings may be possible, but such detailed structures in the lamellar phase have been scantily studied so far. To our best knowledge, the only structural study of the lamellar mesophase is that of Sakashita *et al.* for a β-diketonate copper complex [17]. With regard to the dynamic aspects of the molecules, no study has ever been performed.

---

*Author for correspondence; e-mail: akai@onri.go.jp

Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online © 2000 Taylor & Francis Ltd
http://www.tandf.co.uk/journals/tf/02678292.html

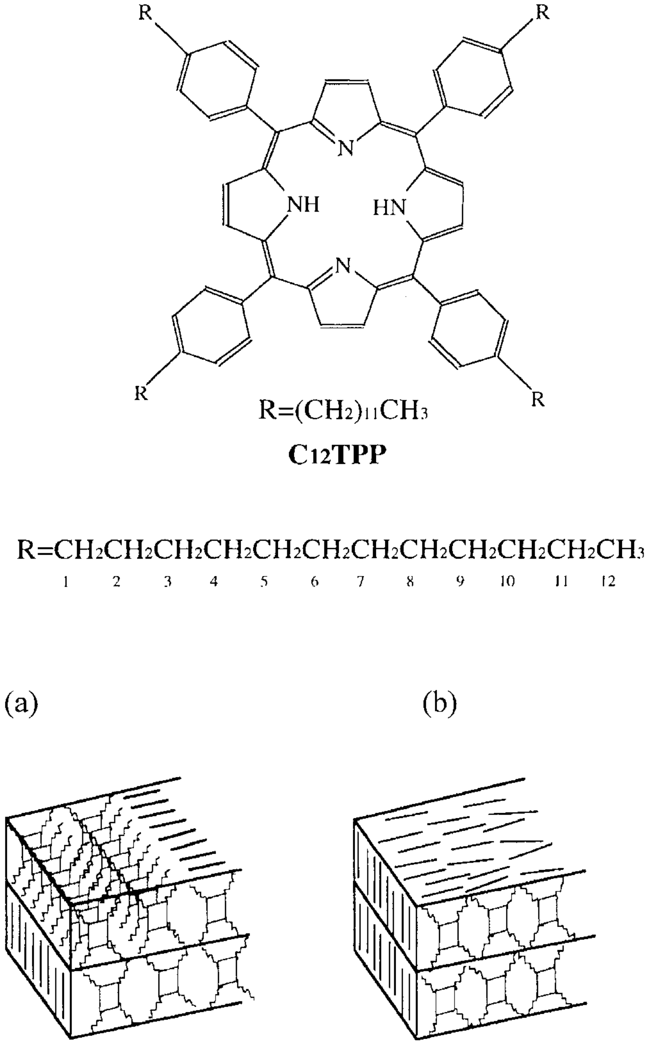

Figure 1. Molecular structure of 5,10,15,20-tetrakis(4-*n*-dodecylphenyl)prophyrin and proposed models for (*a*) the lower mesophase and (*b*) the higher mesophase.

To elucidate the detailed structure and the dynamic aspects of molecules in the lamellar mesophases of the C_nTPP family, we are currently studying the ^{13}C NMR or C_nTPP. In this preliminary communication, we report results on ^{13}C CPMAS NMR spectra for C_{12}TPP and discuss the dynamics and the structures in the two mesophases.

C_{12}TPP was prepared as described previously [11]. Table 1 lists the phase transition temperatures and the enthalpy and entropy changes for the phase transitions of C_{12}TPP. In the previous study, a structural analysis by X-ray diffraction was carried out and the interlayer spacing was found to be 31.1 Å and 29.9 Å at 40°C (M_L') and 135°C (M_L), respectively [10].

Solid state ^{13}C CPMAS NMR spectra were obtained using a Chemagnetics CMX200 spectrometer at 50.36 MHz. All the ^{13}C CPMAS NMR spectra were measured by a conventional method with contact time 2 ms. The 90° pulses for ^{1}H and ^{13}C were set to 4.5 µs. Typically, 1000 FIDs were accumulated with repetition time 3 s. The sample was spun at 4 kHz. A higher field signal for hexamethylbenzene was used as an external reference. Temperature was varied by flowing heated air into the probe head. A spectrum was recorded every 10°C from room temperature up to 170°C. The temperature was determined by measuring that of the air, so that a slight deviation from that in the sample was possible. To check the difference, several organic compounds with different melting points were examined, because the temperature in the sample tube could be determined from the abrupt change of the signal at the melting point. It was confirmed that the difference was less than 10°C even above 160°C where the deviation was thought to be a maximum. ^{13}C NMR spectra in solution were obtained using a JEOL GSX-270 spectrometer at 67.80 MHz. The solvent used was $CDCl_3$.

The ^{13}C CPMAS NMR spectra in the aliphatic region exhibited remarkable changes in the temperature ranges 30–40°C and 50–60°C, while little change was observed in other temperature ranges. These changes in the spectra certainly correspond to the phase transition from crystal (Cr) to M_L' and from M_L' to M_L, respectively. Figure 2 displays the variations in the ^{13}C CPMAS spectra in the aliphatic regions of C_{12}TPP with change in temperature. In the crystal, figure 2(*a*), there are five noticeable peaks centred around 15, 24, 28, 32 (broad and consisting of numerous resonance lines) and 38 ppm. With the phase transition from the crystal to M_L', all these peaks shift to higher field. The most intense peak marked by * is considerably narrowed. With the phase transition from M_L' to M_L, all the lines are narrowed to give six resonance lines—A (36.5 ppm), B (32.4 ppm), C (30.3 ppm), D (28.1 ppm), E (23.3 ppm) and F (14.5 ppm)—as shown in figures 2(*c*) and 2(*d*). From the intensities and the relative positions, it is possible to follow some major peaks as shown by

Table 1. Transition temperatures, enthalpies and entropies for the phase transitions of C_{12}TPP.

	Crystal		M_L'		M_L		Isotropic
T/°C		31		52		155	
ΔH/kJ mol^{-1}		46		14		23	
ΔS/JK^{-1} mol^{-1}		152		43		54	

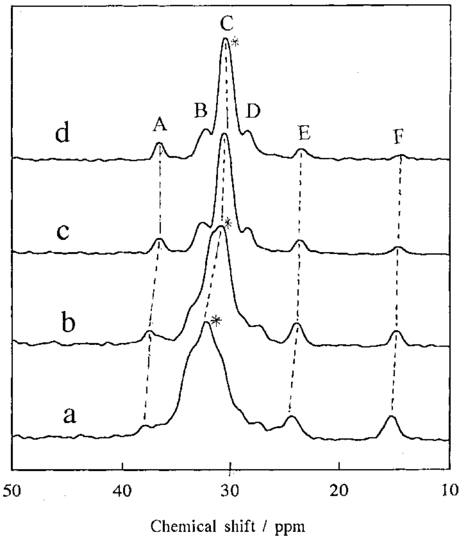

Figure 2. Solid state ^{13}C CPMAS NMR spectra in the aliphatic region of C$_{12}$TPP at (*a*) 23°C (Cr), (*b*) 50°C (M'_L), (*c*) 70°C (M_L) and (*d*) 120°C (M_L), respectively.

the broken lines in figure 2. To examine the temperature dependence of the position of each resonance (A, C, E and F) in more detail, the chemical shift is plotted as a function of temperature in figure 3. It is interesting to note that the chemical shift of peak A changes drastically with the transition from M'_L to M_L, while that of C changes with the transition from the crystal to M'_L.

In general, the ^{13}C isotropic chemical shift is mainly determined by the species of chemical bonding of the carbons, and it is modified by some magnetic inequivalences in the solid, resulting in the shift in peak position (≈ppm). To assign the contributions from the species of chemical bonding, we compare the chemical shift of the six resonances in the well-resolved spectra for M_L, figures 2(*c*) and 2(*d*), with those obtained for the solution. Table 2 lists the ^{13}C chemical shifts for C$_{12}$TPP in solution (CDCl$_3$). From the comparison, A is clearly assigned to C1, E to C11 and F to C12. B is assigned to an overlapped resonance of C2 and C3. The rest of the peaks, C (30.3 ppm) and D (28.1 ppm), should be assigned to the carbons in C4–C10 resonating from 29.785 to 29.436 ppm in solution. The resonance position of D deviates by 1 ppm in an up-field direction from the region. The reason for this is not clear, but it is natural to assign the resonance C to most of the carbons in C4 to C10 and the resonance D to one or a few outer carbons in C4 to C10.

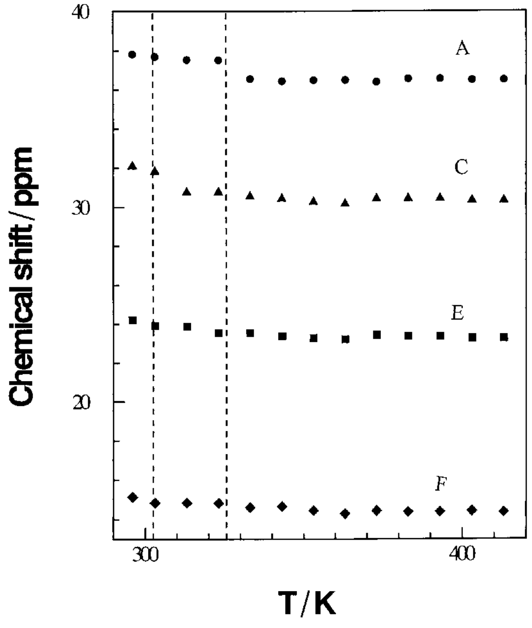

Figure 3. Temperature dependence of ^{13}C isotropic chemical shifts.

The additional splittings and the resonance shifts at lower temperature must be associated with the magnetic inequivalences in the solid state, figures 2(*a*) and 2(*b*). A most plausible explanation for the inequivalences is conformational changes in the aliphatic chains. Local magnetic fields arising from nearby molecules may also be a possible reason for the equivalences, but this effect should not be so large as to give rise to a shift as large as 1 ppm, because the side chains in C$_{12}$TPP are not packed densely [18]. Hence, we attribute the splittings and the shifts to conformational changes of the aliphatic chains.

Isotropic ^{13}C chemical shifts in relation to conformational change have been well studied for *n*-alkanes [18, 19]. It is known that resonances in interior methylene carbons appear at around 32–34 ppm when they are in the all-*trans*-conformation. When a γ-carbon is in a *gauche* conformation, the resonance position of ^{13}C shifts to higher field by 4–6 ppm (~28 ppm). When the chains melt and these two conformations (*trans-gauche*-conformation) are averaged in the NMR time scale [18, 19], the chemical shift of *trans-gauche* is the weighted average of the two and the resonance appears at around 30 ppm. It is also reported that the chemical shifts of ^{13}C for two terminal carbons ($-\underline{C}H_2-CH_3$ or $CH_2-\underline{C}H_3$) shift upfield with the melting of the alkane.

Table 2. ^{13}C chemical shifts for the aliphatic carbons in C$_{12}$TPP in CDCl$_3$.

C atom	^{13}C Chemical shift/ppm
C1	35.994
C2	31.987
C3	31.628
C4–C10	29.795, 29.741, 29.687, 29.597, 29.436
C11	22.751
C12	14.162

Based on this knowledge, we interpret the present results as follows. In the crystal, the most intense peak C of the aliphatic chains is located at around 32 ppm with minor noticeable peaks at around 34 and 31–30 ppm. It is implied that most parts of the chains are in the *trans*-conformation, while a minor fraction of the chains adopt the *trans-gauche* transformation. Therefore, it can be said that most of the aliphatic chains are fairly rigid in the crystalline phase. With the transition from the crystal to the lower mesophase, slight high-field shifts are observed for E and F (terminal carbons), as observed for the melting of alkanes. The peak C drastically shifts to higher field (31–30 ppm). In contrast, there is not so much change in the chemical shift for the resonance A (assigned to the most internal carbon, C1). The facts indicate that in the lower mesophase, the aliphatic chains partially melt, leaving the internal parts relatively rigid. This explains the fact that the lower mesophase in C_nTPP appears above $n = 11$ [11] because such partial melting is possible only when the aliphatic chains are of sufficient length. With the transition from M_L' to M_L, the resonance C shifts to 30 ppm to give a single resonance line, implying that almost all the aliphatic chains are in the *trans-gauche* conformation. As already mentioned, the resonance A, namely the resonance from C1, shows a considerable up-field shift with the phase transition and approaches the value obtained in solution. These results clearly show that the whole of the aliphatic chains melt in the M_L phase.

Lastly, we briefly mention how the ^{13}C CPMAS NMR spectra in the aromatic region change with temperature. Figure 4 displays the temperature dependence of the spectra in the aromatic region. Unlike the spectra in the aliphatic region, no drastic change was observed with the phase transitions except for slight decreases in line widths, probably due to the increased mobilities of the molecules. It is seen that the spectra exhibit complex resonance lines, the number of which is definitely larger than that of carbons with different chemical bonding. This kind of splitting is observed in crystals of phthalocyanine, porphyrins and their derivatives since the D_{4h} symmetry of the molecules is distorted by crystallographic asymmetries (tilt or spacing of the columns) in the crystal [20–23]. It is conceivable that these asymmetries are lost in the mesophases where the molecules rotationally fluctuate. Indeed, Kentgens *et al.* observed a dramatic change and a decrease of the resonance lines in the ^{13}C CPMAS NMR spectra of poly(octa-*n*-undecoxyphthalocyaninato)siloxane with the transition from crystal to the hexagonal columnar phase. As seen in figure 4, the number of resonance lines and the splitting pattern remain almost unchanged from the crystal to the upper mesophase, although there is a small shift of the peaks and a change in the relative intensities of the resonances. This probably means that there still exist some crystallographic asymmetries in both of the mesophases in the time scale observed by NMR spectra (≈ kHz). This is in accordance with other results suggesting the existence of a higher order structure in C_{12}TPP, as mentioned earlier. What is interesting is that even in the upper mesophase, the splittings from the crystallographic inequivalences are not averaged out, which means that the molecules do not rotate freely in this time scale (≈ kHz). However, more studies are necessary to reach a conclusion about the detailed structure in the mesophases. Assignments and detailed analysis of the ^{13}C NMR spectra are in progress and will be reported in a coming paper.

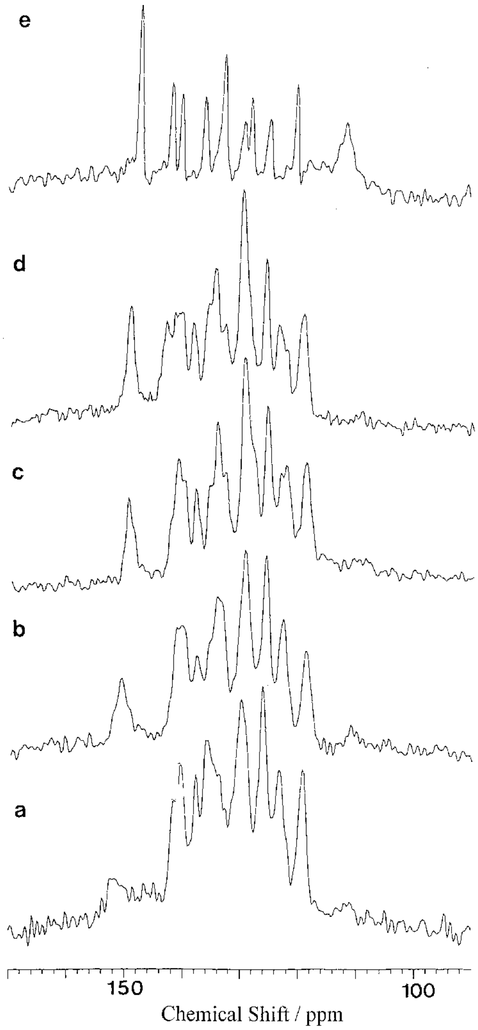

Figure 4. Temperature dependence of ^{13}C CPMAS NMR spectra in the aromatic region of C_{12}TPP at (*a*) 23°C (Cr), (*b*) 50°C (M_L'), (*c*) 80°C (M_L), (*d*) 130°C (M_L) and (*e*) 170°C (I), respectively.

In conclusion, the temperature dependence of the ^{13}C CPMAS NMR revealed that the aliphatic chains are mostly in the all-*trans* conformation and rigid in the crystal. With the transition to the lower mesophase, the aliphatic chains melt, leaving the internal part of the chain rigid. In the upper mesophase, all the chains melt and become liquid-like. From the ^{13}C CPMAS NMR for aromatic carbons, it is suggested that the molecular D_{4h} symmetry is distorted probably by some crystallographic inequivalences in both mesophases.

The authors thank Dr. H. Yamamoto for the measurement of the solution NMR.

References

[1] Boden, N., and Movaghar, B., 1998, in *Handbook of Liquid Crystals*, Vol. 2B, edited by D. Demu, J. W. Goodby, G. W. Gray, H. W. Spiess, and V. Vill (Weinheim: Wiley-VCH), Chap. IX.

[2] Simon, J., and Bassoul, P., 1993, in *Phthalocyanins*, Vol. 2, edited by C. C. Lenznoff, and A. B. P. Lever (Weinheim: Wiley-VCH), Chap. VI.

[3] Adams, D., Schuhmacher, P., Simmerer, J., Haussling, L., Siemensmeyer, K., Etzbach, K. H., Ringsdorf, H., and Haarer, D., 1994, *Nature*, **371,** 141.

[4] Simmerer, J., Glüsen, B., Paulus, W., Kettner, A., Schuhmacher, P., Adam, D., Etzbach, K. H., Siemensmeyer, J. H., Ringsdorf, H., and Haarer, D., 1996, *Adv. Mater.*, **8,** 815.

[5] Smith, K. N. (editor), 1975, *Porphyrins and metalloporphyrins* (Amsterdam: Elsevier).

[6] Dorphin, D. (editor), 1978, *The Porphyrins* (New York: Academic Press).

[7] Schouten, P. G., Warman, J. M., de Hass, M. P., Fox, M. A., and Pan, H.-L., 1991, *Nature*, **353,** 736.

[8] Schouten, P. G., Warman, J. M., de Haas, M. P., van Nostrum, C. F., Gelinck, G. H., Nolte, R. J. M., Copyn, M. J., Zwikker, J. W., Engel, M. K., Hanack, M., Chang, Y. H., and Ford, W. T., 1994, *J. Am. chem. Soc.*, **116,** 6880.

[9] Davison, P., Levelut, A. M., Strzelecka, H., and Gionis, V., 1993, *J. Phys. Lett.*, **44,** L823.

[10] Shimizu, Y., Miya, M., Nagata, N., Ohta, K., Matsumura, A., and Yamamoto, I., 1991, *Chem. Lett.*, 25.

[11] Shimizu, Y., Miya, M., Nagata, A., Ohta, K., Yamamoto, I., and Kusabayashi, S., *Liq. Cryst.*, **14,** 795.

[12] Shimizu, Y., and Higashiyama, T., 1998, *Proc. SPIE*, **177,** 3319.

[13] To be submitted.

[14] Shimizu, Y., Ishikawa, A., and Kusabayashi, S., 1986, *Chem. Lett.*, 1041.

[15] Maeda, Y., and Shimizu, Y., 1998, *Liq. Cryst.*, **25,** 537.

[16] Maeda, Y., and Shimizu, Y., 1999, *Liq. Cryst.*, **26,** 1067.

[17] Sakashita, H., Nishitani, A., Sumiya, Y., Terauchi, H., Ohta, K., and Yamamoto, I., 1988, *Mol. Cryst. liq. Cryst.*, **163,** 211.

[18] Van der Hart, D. L., 1981, *J. magn. Reson.*, **44,** 117.

[19] Sorita, T., Yamanobe, T., Komoto, T., Ando, I., Sato, H., Deguchi, K., and Imanari, M., 1984, *Makromol. Chem. rapid Commun.*, **5,** 657.

[20] Frydman, L., Olivieri, A. C., Diaz, L. E., Valasinas, A., and Frydman, B., 1988, *J. Am. chem. Soc.*, **110,** 5651.

[21] Rocha, J., Kolodziejski, W., Cavaleiro, J. A. S., and Klinowski, J., 1992, *J. coord. Chem.*, **25,** 205.

[22] Kentgens, A. P. M., Markies, B. A., van der Pol, J. F., and Nolte, R. J. M., 1990, *J. Am. chem. Soc.*, **112,** 8800.

[23] Lifshitz, E., Goldfarb, D., Vega, S., Luz, Z., and Ziemmermann, H., 1987, *J. Am. chem. Soc.*, **109,** 7280.