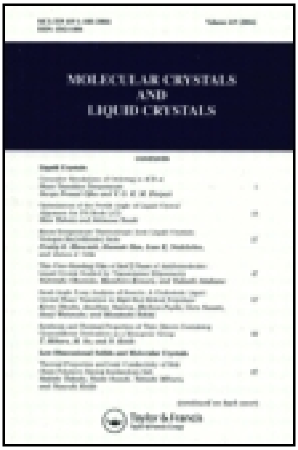


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Syntheses and Physical Properties of Ferrocene Derivatives (XIII)

Naotake Nakamura [a], Shigetaka Setodoi [a] & Tomonori Hanasaki [b]

[a] Department of Chemistry, Faculty of Science and Engineering, Ritsumeikan University, 1-1-1, Nojihigashi, Kusatsu, Shiga, 525-8577, Japan

[b] Department of Materials Science, Faculty of Science and Technology, Shizuoka Institute of Science and Technology, 2200-2, Toyosawa, Fukuroi, Shizuoka, 437-8555, Japan

To cite this article: Naotake Nakamura, Shigetaka Setodoi & Tomonori Hanasaki (2000): Syntheses and Physical Properties of Ferrocene Derivatives (XIII), Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 350:1, 93-101

To link to this article: http://dx.doi.org/10.1080/10587250008025236

Mol. Cryst. Liq. Cryst., Vol. 350, pp. 93-101
Reprints available directly from the publisher
Photocopying permitted by license only

Syntheses and Physical Properties of Ferrocene Derivatives (XIII)

Liquid crystallinity of ω-[4-(4-methoxyphenoxycarbonyl)phenoxycarbonyl] alkyl 4-ferrocenylbenzoate with octyl and nonyl groups as an alkyl one

NAOTAKE NAKAMURA[a*], SHIGETAKA SETODOI[a] and
TOMONORI HANASAKI[b]

[a]*Department of Chemistry, Faculty of Science and Engineering, Ritsumeikan University, 1–1–1, Nojihigashi, Kusatsu, Shiga 525–8577, Japan and* [b]*Department of Materials Science, Faculty of Science and Technology, Shizuoka Institute of Science and Technology, 2200–2, Toyosawa, Fukuroi, Shizuoka 437–8555, Japan*

(Received October 05, 1999; In final form December 10, 1999)

Two monosubstituted ferrocene derivatives, 8-[4-(4-methoxyphenoxycarbonyl)phenoxycarbonyl]octyl 4-ferrocenylbenzoate (MPAF-8) and 9-[4-(4-methoxyphenoxycarbonyl)phenoxycarbonyl] nonyl 4-ferrocenylbenzoate (MPAF-9), were synthesized and their phase transition behavior was studied using a differential scanning calorimeter, a polarizing microscope and an X-ray diffractometer. MPAF-8 exhibited two liquid crystalline phases in both heating and cooling processes at approximately room temperature. In the heating process, a crystal-crystal phase transition behavior was ascertained. The phase transition behavior of MPAF-9 was very similar to that of MPAF-8 except for the behavior of the crystal-crystal phase transition in the heating process. In MPAF-8, one crystalline phase was transformed into another crystalline phase completely. On the other hand, this transformation was observed in part in MPAF-9, and as a result, the melting behavior was observed two times in the heating process.

Keywords: Liquid Crystal; Ferrocene Derivative; Metallomesogen; Phase Transition

---

* Corresponding author/Tel: +81775612779, FAX: +81775612659, E-mail: nakamura@se.ritsumei.ac.jp

INTRODUCTION

Metallomesogens have recently attracted special attention as a new liquid crystalline material, because it is expected to show unique properties, such as electric, magnetic, chromatic properties and so on. Ferrocene derivatives are one of the typical metallomesogens. Recently, liquid crystallinity of the ferrocene derivatives has been investigated from several standpoints[1–3].

Monosubstituted ferrocene derivatives, ω-[4-(4-methoxyphenoxycarbonyl)phenoxycarbonyl] alkyl 4-ferrocenylbenzoate (abbreviated hereafter as MPAF-*n*, where *n* is the number of carbon atoms in a flexible spacer), have a characteristic chemical structure in which the flexible spacer is located between a phenyl ferrocenyl and a mesogenic group (see Fig. 1). A series of MPAF-*n* with *n* = 1, 2, 3, 4, 5, 6, 7, 10 and 11 was synthesized in our laboratory, and the physical properties including liquid crystallinity were studied by use of several methods, for example, thermal measurements[4], single-crystal structure analyses[5–10], Mössbauer spectroscopy[11] and so on. It was found that MPAF-*n* containing 4, 6, 10 and 11 carbon atoms in the flexible spacer show the liquid crystalline phases[4].

The series is lacking two members, which are MPAF-8 and 9. These are very interesting and important points in the study of the ferrocene derivatives whether those compounds exhibit liquid crystallinity or not. All of MPAF-*n* with even *n* synthesized in our previous work showed liquid crystallinity except for MPAF-2. Therefore, it is expected that MPAF-8 shows liquid crystallinity. In contrast to the even members, MPAF-1, 3, 5 and 7 did not show liquid crystallinity, while MPAF-11 showed liquid crystallinity. The investigation on liquid crystallinity of MPAF-9 is worthwhile, because MPAF-9 exists between non-liquid crystalline MPAF-7 and liquid crystalline MPAF-11.

In this work, the liquid crystallinity of MPAF-8 and 9 is investigated using a differential scanning calorimeter, a polarizing microscope and an X-ray diffractometer.

EXPERIMENTAL

The compounds, MPAF-8 and 9 were synthesized in accordance with the scheme of the synthetic process shown in Figure 1. This synthetic method was almost the same as that reported already[4, 12].

8-Bromooctanoic acid was prepared by an oxidation of 9-bromo-1-nonanol in *dil.* HNO_3 and was converted into 8-bromooctanoyl chloride using thionyl chloride. On the other hand, 4-methoxyphenyl 4-hydroxybenzoate was prepared from

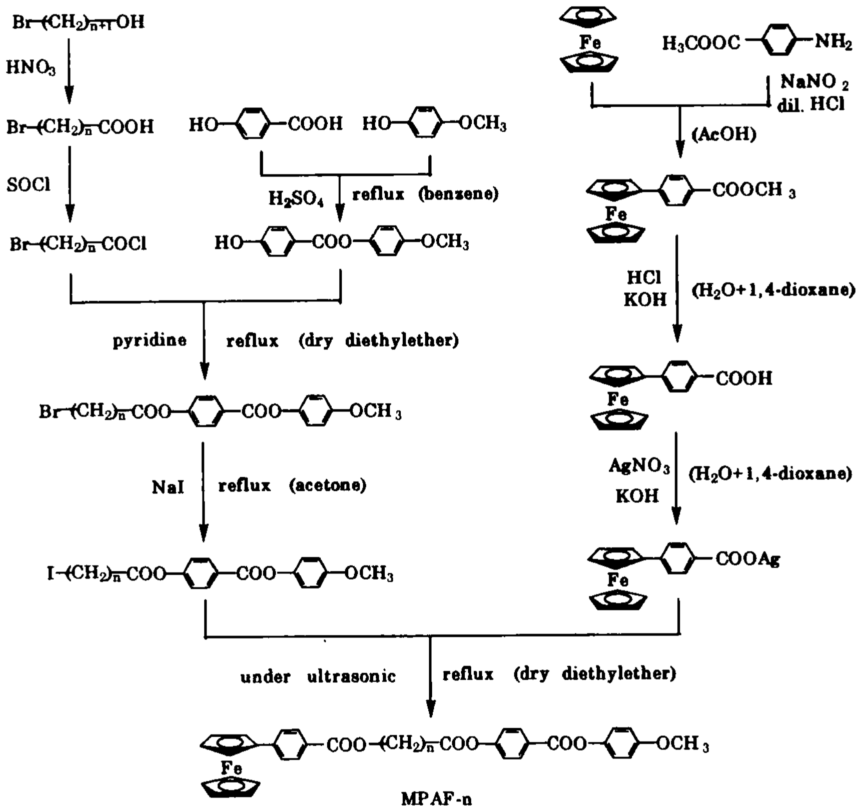


FIGURE 1 The synthetic scheme of MPAF-*n*

an esterification of 4-hydroxybenzoic acid and 4-methoxyphenol in benzene with H_2SO_4 as a catalyst. 8-Bromooctanoyl chloride and 4-methoxyphenyl 4-hydroxybenzoate were refluxed in dry diethylether under the presence of pyridine. Continuously, the conversion of the terminal bromine atom into an iodine one was carried out by dealing with NaI in acetone. On the other hand, 4-ferrocenylbenzoic acid was synthesized from methyl 4-aminobenzoate by diazotization, coupling and hydrolysis reactions. The acid was converted into its silver salt. MPAF-8 was obtained by the esterification between the products prepared by previous procedures. This reaction was carried out in a flask placed in an ultrasonic bath in order to accelerate the reaction. MPAF-8 was purified by precipitation by a gradual dilution of its benzene solution with methanol in addition to column chromatography (silica gel, dichrolomethane). After that, the compounds were dried thoroughly. The objective compound, MPAF-8, was obtained as orange powder crystals.

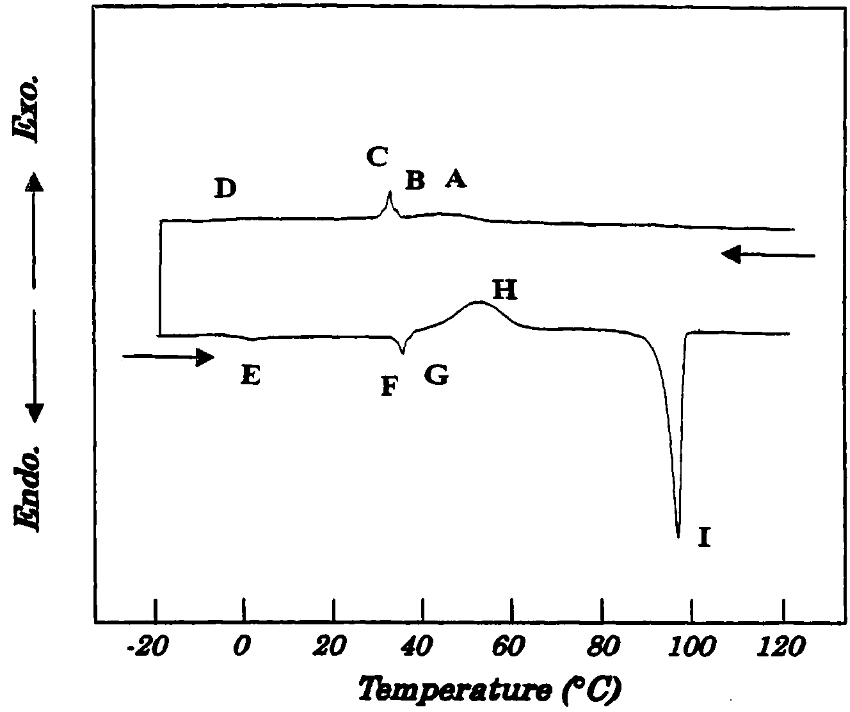


FIGURE 2 DSC curves of MPAF-8 (5.0°C/min). Each arrow indicates the direction of the temperature scanning

In the case of MPAF-9, all synthetic processes and the method of purification are the same as those of MPAF-8.

^{1}H-NMR (JEOL, JNMGX-400) spectra were used for an identification of the synthesized compounds. The purity of MPAF-8 and 9 was confirmed by a presence of only one spot through the TLC analyses in addition to the results of the ^{1}H-NMR spectra in which no other peaks were observed except for the identified peaks as the objective compounds.

The measurements and observations of the phase transition behavior were performed by the differential scanning calorimeter (Perkin-Elmer DSC-7, abbreviated hereafter as DSC), and the polarizing microscope (Nikon XTP-11) equipped with a heating and cooling stage (Mettler FP-800). The scanning rate of these measurements was 5°C /min, which is the same condition as the case of the other MPAF-*n* in our previous work. The measurements of small- and wide-angle X-ray diffractions were carried out using a Rotaflex (Rigaku-RU200B) equipped with a small-angle diffractometer (Rigaku CN203E) and wide-angle one (Rigaku

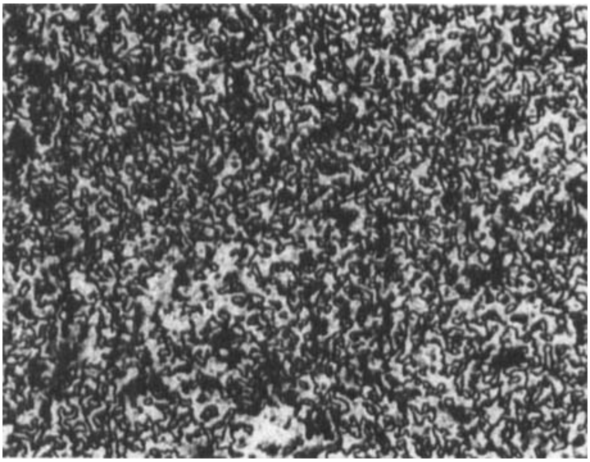


FIGURE 3 The texture of MPAF-8 in L.C.2 phase taken at 25°C (See Color Plate VII at the back of this issue)

2155R6). Temperature control for the specimens was made by a gas flow system[13] for the small-angle X-ray experiments and a heating system (Rigaku 2352A1 and 5188C3) for the wide-angle ones.

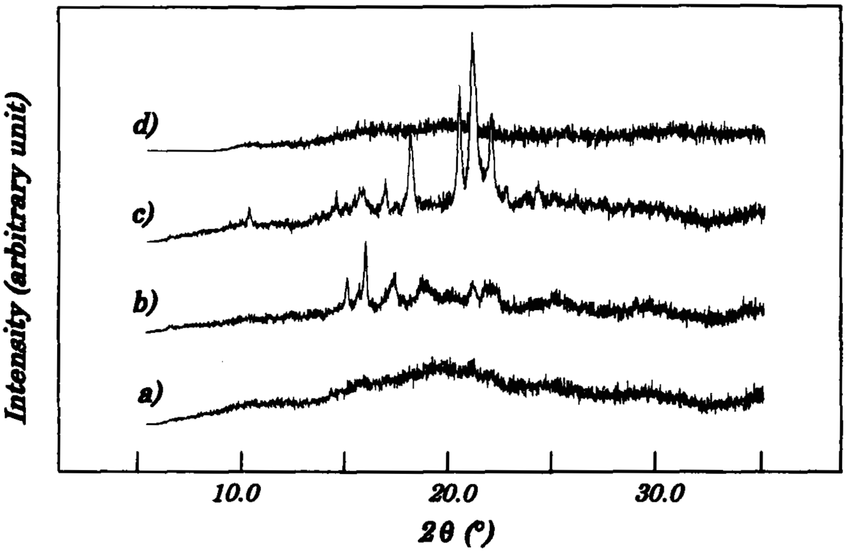


FIGURE 4 Wide-angle diffraction diagrams of MPAF-8 in heating process (2.0°C /min). (a) 15°C (b) 55°C (c) 70°C (d) 120°C

RESULTS AND DISCUSSION

In the case of MPAF-8, the sample melted at about 100°C and did not show liquid crystallinity by the heating from an as grown sample. Figure 2 shows the result of the DSC measurement started from a molten state. In the cooling process, a broad exothermic peak (A) between 60 and 40°C, a small exothermic peak (C) of about 35°C accompanied with a shoulder (B), and a little baseline shift (D) at 2°C were observed. According to the texture observations, no distinct optical texture changes were detected around the peak (A) temperature except for a slightly growing light. It may be considered that a little ordering of the molecules gradually takes place with decreasing temperature. The shoulder (B) was identified as a clearing point, because a typical schlieren texture and a high fluidity were observed below the corresponding temperature of the shoulder (B). This phase was defined as L.C.1 in accordance with our previous paper[4] and was identified to be the nematic phase by the result of the texture observation mentioned above. No texture change except a little change of the fluidity was observed from the temperature of shoulder (B) to –20°C, though the peak (C) was observed clearly by DSC. It was understood that the peak (C) is the phase transition point from L.C.1 to a new other liquid crystalline phase as was observed in MPAF-4, 6, 10 and 11[4]. This liquid crystalline phase was defined as L.C.2. Figure 3 shows the liquid crystalline texture of L.C.2 taken at 25°C. The schlieren texture is closely associated with the smectic liquid crystalline phase. A baseline shift (D) was considered to be a glass transition point because of the typical shape of the DSC curve. In the heating process, a baseline shift (E) at 4°C was identified to be the glass transition point. An endothermic peak (F) and a very small peak (G) around 37°C, a broad exothermic peak (H) between 42 and 70°C, and a sharp endothermic peak (I) at 93°C were observed subsequently. It is considered that peak (F) is a phase transition point from L.C.2 to L.C.1. According to the texture observations, the liquid crystalline texture vanished at about 40°C and a nuclei of a new crystal appeared in a dark field of view at about 45°C. The peak (G) was identified as a clearing point, and the broad peak (H) corresponded to the appearance and growth of the new crystal. This crystal grew gradually with increasing temperature from 42 to 60°C, and seemed to transform into another crystal continuously at about 60°C. This phenomenon was not clearly observed as the optical texture change under the polarizing microscope and distinct thermal changes in DSC measurements. Wide-angle X-ray diffraction patterns, however, change at around that temperature, as is shown later. Therefore, it is considered that this crystal-crystal phase transition behavior corresponded with the transformation from the unstable crystal (denoted by K1) into the stable one (denoted by K2). This stable crystal melted at around 93°C, which corresponded to that of peak (I).

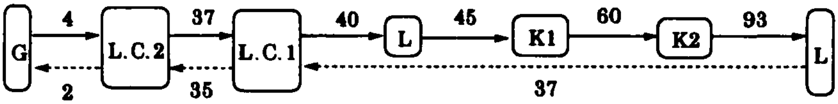
These phase changes could be confirmed by the X-ray diffraction method. The wide-angle diffraction diagrams of L.C.2, K1, K2 and L (liquid phase) of MPAF-8 are shown in Figure 4(a), (b), (c) and (d), respectively. The diagram (a) indicates a very broad peak at around 20° as 2 θ diffraction angle. In addition to this fact, a long spacing is also observed in L.C.2, as is listed in Table I. Therefore, L.C.2 is reconfirmed as the smectic liquid crystalline phase. As some strong reflections are observed in the diagrams of Figure 4 (b) and (c) at about 15–22° as 2 θ, these phases are considered to be crystalline ones. The diffraction angles and intensities observed in the K1 crystal were different from those of the K2 one. It seems that crystallinity of the K2 crystal is tighter compared with that of the K1 crystal. No reflection peaks were observed as a matter of course in the diagram of Figure 4 (d) which is taken at 120°C, under the liquid phase.

TABLE I Long spacings and model molecular lengths of MPAF-*n*[9]

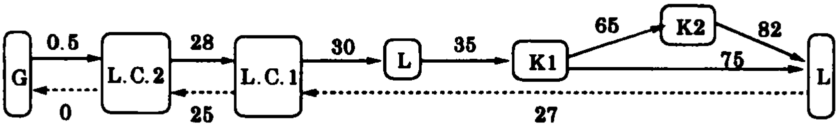
	Molecular length (L) / Å	*Long-spacing (d) / Å*	*d / L*
MPAF-4	27.6	30.5	1.10
MPAF-6	29.3	31.3	1.11
MPAF-8	31.6	33.3	1.05
MPAF-9	32.8	42.1	1.28
MPAF-10	33.7	36.1	1.07
MPAF-11	36.5	46.3	1.27

In the case of MPAF-9, the results of the DSC measurements, the texture observations and the X-ray diffraction experiments were very similar to those of MPAF-8, except for the crystal-crystal phase transition behavior. In the heating process from −20°C, the glass transition (0.5°C), L.C.2-L.C.1 phase change (28°C), and the clearing (30°C) were observed just as the case of MPAF-8. The L.C.1 and L.C.2 textures of MPAF-9 are highly similar to those of MPAF-8. Therefore, it may be considered that MPAF-9 shows the nematic and smectic phases like MAPF-8. After the clearing of L.C.1 phase, the nuclei of the crystal (defined as K1) appeared at about 35°C, and the K1 crystal grew gradually with increasing temperature. This K1 crystal, however, partially changed into another crystal (denoted by K2) at around 65°C. Because the rate of this crystal-crystal phase transition was very slow, the remaining K1 crystal melted at 75°C. The K2 crystal, which grew gradually after the melting of K1 crystal, melted at 82°C. That is, the melting behavior was observed two times in the heating process.

As a result, MPAF-8 and 9 showed two liquid crystalline phases which were identified to be the nematic (L.C.1) and the smectic (L.C.2) phases. The L.C.1 phase appeared from a super cooled liquid, and the glass transition from L.C.2



MPAF-8



MPAF-9

FIGURE 5 The phase transition behavior of MPAF-8 and MPAF-9 obtained from DSC measurements (5.0°C/min). G: glass state, L.C.1 and L.C.2: liquid crystalline phase, K1: metastable crystalline phase, K2: stable crystalline phase, L: liquid state. Arrows show the direction of temperature change. Numbers correspond to the phase transition temperature (°C)

phase happened without the crystallization under the condition of the measurements, that is, the scanning rate was 5°C/min. Consequently, the liquid crystalline phases were seemingly observed in both the cooling and the heating processes. Therefore, these liquid crystalline phases are metastable one and it is considered that these phases may vanish under the very slow scanning rate.

In order to measure the long spacings of liquid crystalline MPAF-*n*, the small-angle X-ray diffraction experiments were carried out at about 0°C. Although the samples were in a glass state at that temperature, the long spacings of the samples can be regarded as those of liquid crystals, and are summarized in Table I[9]. The table includes model molecular lengths calculated by a personal computer system. The ratio of the long spacing values and model molecular lengths give us some information on the molecular arrangement in the liquid crystalline phase. The ratio of MPAF-8 is about 1.1, and this value is nearly equal to those of other liquid crystalline MPAF-*n* with even *n*. This fact suggests that the molecular arrangements in L.C.2 of MPAF-*n* with even *n* are quite similar to each other. The ratio of MPAF-9 is estimated to be about 1.3 and the value is comparable to that of liquid crystalline MPAF-11. Therefore, nearly the same molecular arrangement probably exists in L.C.2 of MPAF-9 and 11.

The shlieren texture observed in L.C.2 of MPAF-8 and 9 suggests that possible types of the smectic liquid crystalline phase are three. These are smectic C, F and I. But, the result of the small-angle X-ray diffraction shows the existence of the long spacings, and that of the wide-angle X-ray diffraction indicates no distinct reflections. If the type of the liquid crystalline phase is smectic F or I, the reflection peaks should be observed in the wide-angle range of 2 θ in addition to the long spacings. Therefore, it is considered that the L.C.2 phase of MPAF-8 and 9 is the smectic C.

In conclusion, the phase transition behavior of MPAF-8 and MPAF-9 is shown in Figure 5 in detail. As is mentioned above, these compounds showed two liquid crystalline phases, which were considered to be the nematic phase and the smectic C one. The melting behavior of MPAF-9 was observed two times in one heating process. Such phase transition behavior was observed already in the other liquid crystalline MPAF-*n*[4].

Acknowledgements

KAWASAKI STEEL 21st Century Foundation is gratefully acknowledged for its partial support of the present work.

References

1) R. Deschenaux, F. Turpin and D. Guillon, *Macromolecules*, **30**, 3759 (1997).
2) C. Loubser and C. Imrie, *J. Chem. Soc., Perkin Trans.*, **2**, 399, (1997).
3) R. Deschenaux, I. Jauslin, U. Scholten, F. Turpin, D. Guillon and B. Heinrich, *Macromolecules*, **31**, 5647 (1998).
4) T. Hanasaki, M. Ueda and N. Nakamura, *Mol. Cryst. Liq. Cryst.*, **237**, 329 (1993).
5) N. Nakamura and S. Setodoi, *Mol. Cryst. Liq. Cryst.*, **319**, 173 (1998).
6) N. Nakamura and S. Setodoi, *Mol. Cryst. Liq. Cryst.*, **312**, 253 (1998).
7) N. Nakamura and S. Setodoi, *Mol. Cryst. Liq. Cryst.*, **326**, 177 (1999).
8) N. Nakamura and S. Setodoi, *Mol. Cryst. Liq. Cryst.*, **333**, 151 (1999).
9) N. Nakamura and S. Setodoi, *Mol. Cryst. Liq. Cryst.*, in preparation.
10) N. Nakamura, S. Setodoi and T. Takayama, *Mol. Cryst. Liq. Cryst.*, in press.
11) H. Sato, I. Kusudo, M. Sugiyama, T. Hanasaki and N. Nakamura, *Hyperfine Int.*, **93**, 1585 (1994).
12) N. Nakamura, T. Hanasaki and H. Onoi, *Mol. Cryst. Liq. Cryst.*, **225**, 269 (1993).
13) H. Kobayashi and N. Nakamura, *Cryst. Res. Technol.*, **28**, 717 (1993).