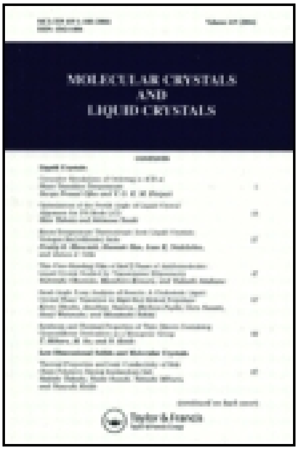

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Syntheses and Physical Properties of Ferrocene Derivatives (VII) PhaseTransition Behavior and Liquid Crystal Structure of 1,1′-Disubstituted Ferrocene Derivatives

Naotake Nakamura [a] , Rin Mizoguchi [a] , Mitsunori Ueda [a] & Tomonori Hanasaki [a] [b]

[a] Department of Chemistry, Faculty of Science and Engineering, Ritsumeikan University, 1-1-1, Nojihigashi, Kusatsu, Shiga, 525-77, Japan

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

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Syntheses and Physical Properties of Ferrocene Derivatives (VII) PhaseTransition Behavior and Liquid Crystal Structure of 1,1′-Disubstituted Ferrocene Derivatives

NAOTAKE NAKAMURA**, RIN MIZOGUCHI, MITSUNORI UEDA
and TOMONORI HANASAKI *

Department of Chemistry, Faculty of Science and Engineering, Ritsumeikan University, 1-1-1, Nojihigashi, Kusatsu, Shiga 525-77, Japan

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Liquid crystalline 1,1′-disubstituted ferrocene derivatives, 1,1′-bis[ω-[4-(4′-methoxyphenoxycarbonyl)phenoxy]alkoxycarbonyl] ferrocene (abbreviated hereafter to bMAF-*n*, $n = 2{\sim}12$, where n is a carbon number of the methylene chain units), were synthesized, and their phase transition behavior was studied using a differential scanning calorimeter and a polarizing microscope. The liquid crystal structures of the compounds were investigated by the X-ray diffraction method. Nine of eleven compounds of the samples showed liquid crystallinity. The liquid crystalline phases were identified as a nematic ($n = 3$ and $5{\sim}12$), a smectic C ($n = 5{\sim}12$) and a smectic F or I ($n = 11$ and 12). As a model structure of the smectic phase, a tilted structure with an expanded substituent is presented.

Keywords: Ferrocene; liquid crystal; metallomesogen; disubstituted derivatives; phase transition

INTRODUCTION

Many liquid crystalline compounds containing ferrocenyl moiety have been synthesized in recent years [1]. Such compounds have the possibility of

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*Present address: Department of Materials Science, Faculty of Science and Technology, Shizuoka Institute of Science and Technology, 2200-2, Toyosawa, Fukuroi, Shizuoka 437, Japan.

**Corresponding author.

applications in organic syntheses as an anisotropic solvent having a catalytic effect, in Mössbauer spectroscopy as a liquid crystalline Mössbauer marker, and so on. Monosubstituted [2], 1,1′- [3] and 1,3-disubstituted [4] ferrocene derivatives are known hitherto as the ferrocene-containing liquid crystals which have low molar mass. However, it seems that the temperature range and the stability of the liquid crystalline phases are more influenced by a manner of a linkage between the mesogenic and the ferrocenyl groups than the position and the number of substituents. That is, whether a methylene chain unit as a flexible spacer exists between the mesogenic and the ferrocenyl groups (type b)) or not (type a)) is considerably important [5].

In a previous paper [5], we reported the phase transition behavior of 1,1′-disubstituted ferrocene derivatives, 1,1′-bis[ω-[4-(4′-methoxyphenoxycarbonyl)phenoxy]alkoxycarbonyl]ferrocene (abbreviated hereafter to bMAF-*n*, where *n* is the number of carbon atoms in the methylene chain units). Figure 1 shows the general structure of bMAF-*n*. As can be seen from Figure 1, bMAF-*n* is a typical type b) compound. Five members of bMAF-*n*, that is bMAF-2, 3, 5, 10 and 11, had been synthesized in our laboratory, and four of them (bMAF-3, 5, 10 and 11) showed liquid crystallinity.

In the present study, six kinds of bMAF-*n* ($n = 4$, 6, 7, 8, 9 and 12) were newly synthesized, and thermal analyses and texture observations were made in order to discuss the even–odd effect about the phase transition behavior of bMAF-*n*. Furthermore, the liquid crystal structures of bMAF-*n* were investigated by X-ray diffraction methods. These experimental results will be described, and the phase transition behavior and the liquid crystal structures will be discussed in this paper.

EXPERIMENTAL

The synthetic procedures of bMAF-*n* were similar to those described in our previous paper [5]. The products were precipitated from a solution of methylene chloride by dilution with hexane. The purity of the products was checked by TLC analyses and their structures were confirmed by ^{1}H-NMR (JEOL, JNM, A-400) spectra.

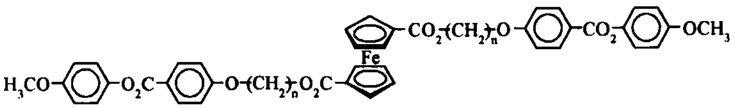


FIGURE 1 General structure of bMAF-*n*.

The thermal analyses were made by a differential scanning calorimeter (Perkin Elmer, DSC-7, abbreviated hereafter to DSC). The texture observations were carried out using a polarizing microscope (Nikon, XTP-11) equipped with a heating stage (Mettler, FP-800). In both measurements, the scanning rate was 5.0°C/min. An upper limit temperature in the heating process and a lower one in the cooling were approximately 20°C above its melting point and −20°C, respectively. Although the results for bMAF-2, 3, 5, 10 and 11 were already reported in our previous paper [5], these measurements were also made again in order to discuss the phase transition phenomena under the same conditions.

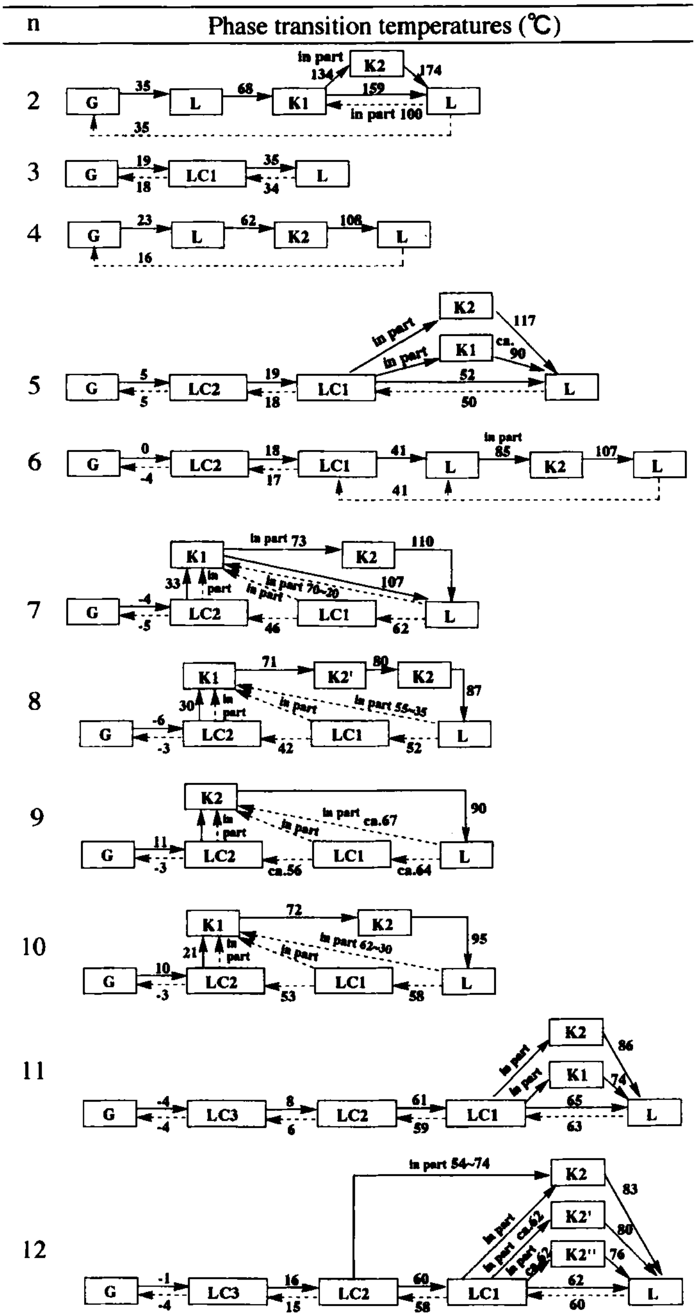
The X-ray measurements were performed using a small-angle X-ray diffractometer (Rigaku, CN203E5). Monochromatized CoKα radiation generated by Rigaku Ru-200 was used in order to avoid the influence of the 2nd X-ray of iron atoms existing in the samples. The samples for the X-ray measurements were prepared in the following manner. The compound loaded into a very thin-wall glass capillary was heated up to the liquid state by the same temperature rate in the DSC measurements, and then was cooled to the liquid crystalline state. The regulation of the sample temperature was made by a gas blow system designed in our laboratory [6].

RESULTS AND DISCUSSION

1. Phase Transition Behavior of bMAF-*n*

From the results of the DSC measurements and the polarizing microscopy observations, the phase transition behavior of bMAF-*n* after the first cooling is summarized in Table I. The phase transition temperatures were determined by the DSC except for several cases. The temperatures indicated by *ca.* in Table I were decided by the microscopy observations, since no clear phase transition peaks were observed by the DSC measurements. In the case of bMAF-5 and 11, the temperatures corresponding to the crystallization in the heating process were not noted in Table I, because these temperatures could not be identified both by the DSC measurements and the polarizing microscopy observations. The symbols K1, K2, K2′ and K2″, which indicate the crystal phases, were defined independently for each sample. Therefore, even if the crystal phases of several compounds were represented by the same symbol, these crystals are not necessarily the same structure from a crystallographic point of view.

TABLE I Phase transition temperatures of bMAF-*n*



——► heating process	G: glass state	K1: metastable crystal
- - - -► cooling process	L: liquid	K2': metastable crystal
	LC1: liquid crystal	K2": metastable crystal
	LC2: liquid crystal	K2: stable crystal
	LC3: liquid crystal	

As can be seen from Table I, nine kinds of bMAF-*n* except for bMAF-2 and 4 showed liquid crystallinity. Only one liquid crystalline phase (LC1) was observed for bMAF-3. Six members of bMAF-*n* ($n = 5 \sim 10$) showed two liquid crystalline phases (LC1 and LC2). Furthermore, bMAF-11 and 12 gave rise to three phases (LC1, LC2 and LC3). The texture under the polarizing microscope of the LC1 phase observed for bMAF-3 and 5~12 was a schlieren texture, and these compounds in this state distinctly exhibited fluidity. The microscopic texture of bMAF-5 and 6 in the LC2 phase was the schlieren texture and that of bMAF-7~12 was a broken fan-shaped texture. In the case of bMAF-11 and 12 which exhibited the LC3 phase, the texture of LC3 was also a broken fan-shaped texture, though a slight change of the texture was observed under the polarizing microscope at around the phase transition temperature corresponding to LC2-LC3. The explicit fluidity was not observed in the LC2 and LC3 phases. According to the results mentioned here, the LC1 phase is identified as a nematic one. It is considered that the LC2 phase is smectic C, because both of the schlieren and the broken fan-shaped textures were observed in this phase. The LC3 phase may be a smectic one, but the type of the smectic phase could not be identified by only microscopy observations. Therefore, this problem will be discussed later with the results of X-ray measurements.

As is well known from Table I, bMAF-*n* exhibits a complicated phase transition behavior. Five members of bMAF-*n* ($n = 2$, 5, 7, 11 and 12) exhibited a multiple melting behavior [7]. That is, two or three times the melting behavior was observed in one heating process. Over a wide temperature range including the ambient temperature, bMAF-*n* showed liquid crystallinity. However, as bMAF-5 and 7~12 partially crystallize from the liquid crystalline phase in the heating and/or the cooling processes, the liquid crystalline phases of bMAF-*n* are unstable. It seems that this complicated phase transition behavior and instability of liquid crystalline phases are characteristic of type b) compounds as pointed out in our previous paper [5]. Namely, it is considered that the orientations of the mesogenic groups of type b) compounds are apt to be more influenced by a thermal motion and a little conformation change of the methylene chain than that of type a) compounds.

The phase transition temperatures in the cooling process except for that of the crystallization are plotted in Figure 2. The glass transition temperatures of bMAF-*n* decrease with increasing number of carbon atoms in the methylene chain units ($n \leqq 6$) and converge to about −5°C ($n \geqq 9$). The methylene chain units may play a role of an internal plasticizer similar to a flexible spacer of a liquid crystalline main chain polymer. The transition

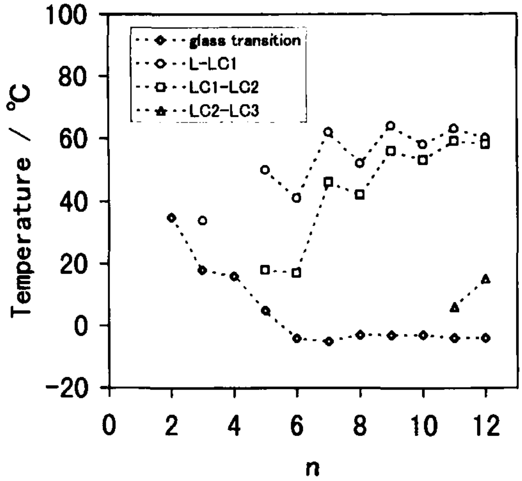


FIGURE 2 Plots of transition temperatures against the carbon number in the methylene chain.

temperatures corresponding to liquid-LC1 and LC1-LC2 increase with the increasing number of carbon atoms ($n \leqq 9$) accompanied by an even–odd effect. These temperatures converge to about 60°C ($n \geqq 9$). It is considered that the increasing of the temperatures is dependent on the increase of a geometric anisotropy owing to an elongation of the methylene chain units. This effect may not be appreciably influenced in the case of $n \geqq 9$ because of the relatively large influence of a flexibility in the methylene chain. The thermal stability of the smectic phases (LC2 and LC3) increases with the increasing number of the carbon atoms in analogy with other smectic liquid crystals which do not have ferrocenyl moiety. In addition, members with odd carbon number atoms are liable to exhibit liquid crystallinity in comparison with those of even carbon number atoms, as predicted in our previous paper [5].

2. Liquid Crystal Structures of bMAF-*n*

The results of X-ray measurements for the LC1 phase of bMAF-3 and 5~10 suggested that this phase was a nematic one consistent with the results obtained from the polarizing microscopy observations. That is, a very broad and weak reflection was observed at about $2\theta = 5\sim10°$. The precise measurements could not be performed for the LC1 phase of bMAF-11 and 12, because the temperature ranges of the LC1 phase of these compounds were very narrow (only a few degrees).

In the case of the LC2 phase, except for that of bMAF-5, sharp peaks corresponding to long spacings were observed in the small-angle region (about $2\theta = 3\sim4°$), which was accompanied by a second-order reflection. No significant peaks were detected in the wide-angle region ($2\theta = 10\sim20°$). Therefore, the LC2 phase has a layer structure, but has no order to the lateral direction in the layer. This result supports the results obtained from the texture observations using polarizing microscopy, which suggested the LC2 phase is smectic C. No peaks corresponding to the long spacing were observed in the LC2 phase of bMAF-5. As this compound has the shortest methylene chain units in the bMAF-*n* exhibited LC2 phase, it may be considered that the orientation of bMAF-5 molecules in this phase is less than that of other bMAF-*n* which have relatively longer methylene chains than those of bMAF-5.

The layer structure was observed in the LC3 phase of bMAF-11 and 12 as well as in LC2. Furthermore, several very weak peaks were detected in the wide-angle region. These peaks suggest an existence of the order for lateral direction in the smectic layer, that is, the LC3 phase is a higher ordered smectic one. A few kinds of higher ordered smectic phase are known, for example smectic F and I. The type of the LC3 phase, however, could not be identified, because the peaks observed here were not adequately strong enough to identify.

The long spacings for the LC2 and LC3 phases obtained by X-ray measurements are listed in Table II with a calculated model of molecular lengths of bMAF-*n*, which are estimated from molecular models of bMAF-*n* designed by a personal computer with the aid of a molecular modeling software program using normal bond distances and angles. It is an interesting problem whether the 1,1′-disubstituted ferrocene derivatives adopt a *trans* conformation ("S" shape) or a *cis* conformation ("U" shape) in the liquid crystalline state. The crystal and molecular structure of 1,1′-disubstituted ferrocene derivative determined by the X-ray diffraction was reported by M. A. Khan *et al.*, in 1989. The result indicated that the 1,1′-disubstituted derivative adopted the *trans* conformation [8]. The structure and arrangement of molecules in the liquid crystalline phase generally reflect those in the crystal phase. In fact, the results of the X-ray study in the liquid crystalline phase of the 1,1′-disubstituted derivative reported by M. A. Khan *et al.*, suggested that the conformation of the derivative in the smectic C phase was the *trans* conformation. In addition to this fact, if the molecule adopts the *cis* conformation, the molecule is very voluminous owing to the double capacity of the substituents. The steric bulkiness of the molecule will prevent a closed peaking such as the molecular arrangements in the higher

TABLE II List of long spacings and model molecular lengths

n	*Long spacing (Å)*		*Model molecular length (Å)*
	LC2	*LC3*	
5	–		48.3
6	27.9		50.2
7	28.9		53.4
8	27.4		55.1
9	30.1		58.1
10	29.1		59.6
11	33.9	34.5	62.7
12	31.2	35.7	64.5

ordered smectic phase observed in the LC3 phase of bMAF-11 and 12 studied here. Taking all things mentioned here into consideration, it may be considered that the molecules of bMAF-*n* adopt the *trans* conformation. Therefore, the model molecular lengths in Table II are estimated on this assumption.

The long spacing observed for the LC2 phase is nearly equal to half of the model molecular length. Taking into account this fact and the results of polarizing microscopy observations which suggested the LC2 phase is smectic C, we make a proposal. One of the appropriate structural models of the LC2 phase is shown in Figure 3. In this structural model, the angle between the long axis of the molecules and the layer plane is 60°, and the substituted groups overlap with those of the adjacent molecules in the neighboring layers. It is considered that the tilt angle, 60°, may be reasonable, because this tilt angle is observed by X-ray measurements on many normal long-chain compounds in which smectic-like arrangements are often associated [9]. When *trans* conformation was adopted, the overlapping of substituents causes the densely packed structure. Moreover, the interval between the terminal methoxy group and the ferrocenyl unit of the neighboring molecule is estimated to be about 4 Å long as is usually observed in ordinary organic crystals. Taking all things mentioned above into consideration, it may be considered that this structural model, which is the tilted structure accompanied by the overlapping of substituents, is a reasonable model.

The long spacing obtained in the LC3 phase is slightly longer than that of LC2. The differences between the two, however, suggest no drastic change of the layer structure. Therefore, it may be reasonable that almost the same structural model as the LC2 phase, which is a tilted structure with the overlapping of substituted groups, can be adopted to this LC3 phase. Several peaks were observed in the wide-angle region as mentioned above. Although these peaks cannot be indexed because of the weakness, the LC3

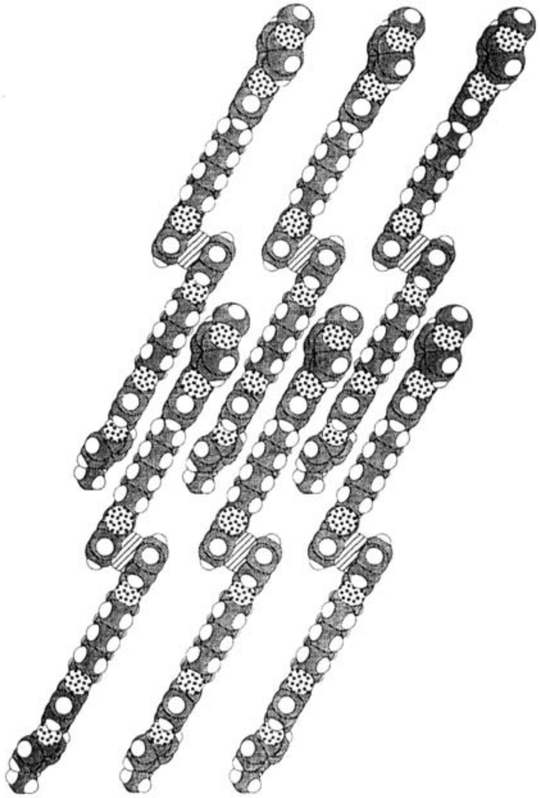


FIGURE 3 Model structure of the LC2 phase of bMAF-7.

phase is a higher ordered smectic one. The microscopic texture of the LC3 phase is the broken fan-shaped texture as already mentioned. According to these results, the LC3 phase can be regarded as the smectic F or I phases, of which the long axis is tilted about 60° and the layer structure is similar to the LC2 phase.

Acknowledgment

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