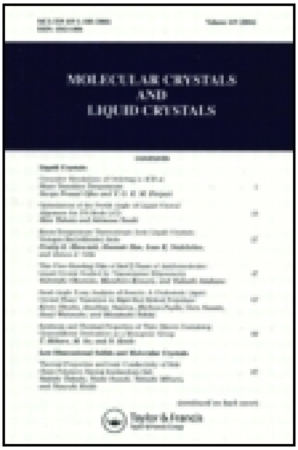

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Liquid Crystallinity of Unsymmetrical Ferrocene Derivatives (I) Synthesis of Unsymmetrically 1,1′-Disubstituted Ferrocene Derivatives and their Phase Transition Behavior

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Liquid Crystallinity of Unsymmetrical Ferrocene Derivatives (I) Synthesis of Unsymmetrically 1,1'-Disubstituted Ferrocene Derivatives and their Phase Transition Behavior

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A new series of unsymmetrically 1,1′-disubstituted ferrocene derivatives, 1-[4'-(4-substitutedbenzoyloxy)biphenyl-4-oxycarbonyl]-1′-alkoxycarbonylferrocene, was prepared and their phase transition behavior was studied by a differential scanning calorimeter and a polarizing microscope. Some structural parameters, such as the length of the alkyl chain and the nature of the terminal substituent, have been modified. In the case of no substituent at a terminal position of the mesogenic group, the derivative showed no liquid crystallinity. Monotropic liquid crystalline phases were observed for the derivatives having a polar terminal group. The compounds with a flexible alkoxy chain as the terminal group gave rise to an enantiotropic nematic phase.

Keywords: unsymmetrical ferrocene derivative; liquid crystal; phase transition; metallomesogen

INTRODUCTION

Metal-containing liquid crystals, called metallomesogens, have come to be attracting special attention owing to their expected unique properties, such as electric, magnetic, and chromatic properties[1]. A liquid crystalline ferrocene derivative is one of the typical metallomesogens. Most of the liquid crystalline ferrocene derivatives synthesized hitherto are symmetrically 1,1'-disubstituted ones[2]. These derivatives have the two same substituents containing mesogenic group at 1 and 1' positions in the ferrocene. As shown in Figure 1, the symmetrical derivatives can be classified into two types from the viewpoint of the molecular structure[3]. It seems that there is a difference in the liquid crystalline property between the type (a) and (b) compounds[3,4]. The type (a) compounds give rise to a stable enantiotropic liquid crystalline phase, but its melting point is relatively high, more than 400K. On the other hand, the type (b) compounds show the liquid crystallinity near ambient temperature. However its liquid crystalline phase is an unstable monotropic one. It may be favorable for applied studies that the stable liquid crystalline phase exists near ambient temperature.

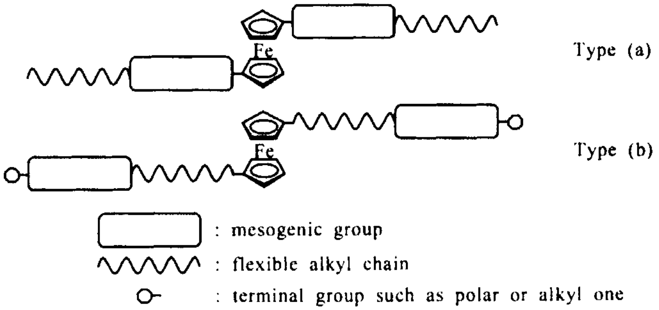
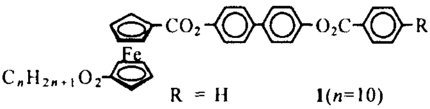


FIGURE 1 Schematic illustrations of symmetrically 1,1'-disubstituted ferrocene derivatives.

In the present study, a new series of ferrocene derivatives has been prepared, and their phase transition behavior was studied using a differential scanning calorimeter and a polarizing microscope. The compounds designed here were 1-[4'-(4-substitutedbenzoyloxy) biphenyl-4-oxycarbonyl]-1'-alkoxycarbonylferrocene. The general structure of the compounds is shown below.



R	
R = H	1(n=10)
CN	2(n=10)
CF_3	3(n=10)
OC_mH_{2m+1}	4(n=10, m=1,4,6,) and (n=8,9,10,12,13, m=7)

These compounds are unsymmetrically 1,1'-disubstituted derivatives. This structure can be regarded as a modification of the type (a) structure. That is, one mesogenic group is removed from one substituent of the type (a) structure. It can be expected that the relatively high melting temperature of the type (a) compound will be lowered by a reduction of mesogenic group constructed with two or three ring systems.

EXPERIMENTAL

The objective compounds were synthesized according to the scheme illustrated in Figure 2. The purification of product was made by a column chromatography and a recrystallization. The product obtained as an orange powder gave only one spot on the TLC analysis, and it was confirmed to be the objective compound using ^{1}H-NMR (JEOL, JNM-

EX400) spectra.

The thermal measurements were made by a differential scanning calorimeter (Perkin Elmer Pyris 1, abbreviated hereafter to DSC). The texture observations were carried out using a polarizing microscope (Nikon X2TP-11) equipped with a heating stage (LINKAM-600PM). The scanning rate was 5.0K/min in both measurements.

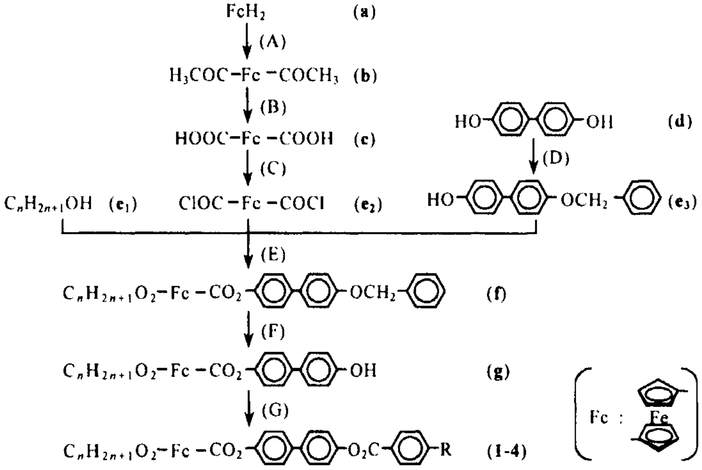


FIGURE 2 Scheme of synthetic process. (A) **a**/$AlCl_3$/CH_3COCl (initial molar ratio 1.0/2.5/2.8), CH_2Cl_2, yield 71%. (B) NaClO (excess), 87%. (C) **c**/$(COCl)_2$ (1.0/1.3), pyridine (cat.), CH_2Cl_2, 65%. (D) **d**/NaOH/benzylchloride (1.0/1.1/1.2) methanol, 68%. (E) $\mathbf{e}_1$/$\mathbf{e}_2$/$\mathbf{e}_3$/pyridine (2.2/1.0/0.9/2.2), CH_2Cl_2, 21%. (F) H_2/Pd(5%)-carbon(cat.), THF, 82%. (G) **g**/4-substitutedbenzoylchloride/pyridine (1.0/5.0/12.0), CH_2Cl_2, 79%.

RESULTS AND DISCUSSION

From the results of the thermal measurements and the texture observations, the phase transition behavior of the derivatives **1**-**4** after the 1st cooling is summarized in Table 1. Although a crystal-crystal phase transition behavior was observed in most of the derivatives, the characterization of each crystal phase was not carried out by appropriate method such as an X-ray diffraction one. Therefore, the behavior was not noted in Table 1 and no discussion was held in this paper.

The derivative **1**(n=10), which has three ring systems as the mesogenic group and no substituent at the terminal position of the mesogenic group, did not show the liquid crystallinity.

Monotropic liquid crystalline phases were observed for the derivatives **2**(n=10), **3**(n=10), and **4**(n=10, m=1). These compounds have a polar group at the terminal position of the mesogenic substituent. That is, the derivatives **2**(n=10), **3**(n=10), and **4**(n=10, m=1) have a cyano, a trifluoromethyl, and a methoxy groups, respectively. The derivative **2** (n=10) showed two liquid crystalline phases. In the cooling process, a typical schlieren texture was appeared at 402K under the polarizing microscope, and a high fluidity was observed in this phase. Such texture suggests that the phase is a nematic one. This schlieren texture immediately changed into a pseudo-isotropic one based on a homeotropic alignment. At the phase transition point (390K) detected by the DSC measurement, no texture change was observed under the polarizing microscope. Therefore, the phase below this transition temperature is regarded as the liquid crystalline one. However the phase type can not be determined, because the characterization by the X-ray

TABLE 1 Phase transition behavior of derivatives **1-4**.

Sample	Phase transition temperature / K
1(n=10)	Cryst. $\overset{404}{\underset{355}{\rightleftarrows}}$ I.L.
2(n=10)	Cryst. $\xrightarrow{416}$ I.L. Cryst. $\xleftarrow[387]{}$ meso1 $\xleftarrow[390]{}$ N $\xleftarrow[402]{}$ I.L.
3(n=10)	Cryst. $\xrightarrow{404}$ I.L. Cryst. $\xleftarrow[363^*]{}$ S_A $\xleftarrow[368^*]{}$ I.L.
4(n=10,m=1)	Cryst. $\xrightarrow{393}$ I.L. Cryst. $\xleftarrow[349]{}$ meso2 $\xleftarrow[352]{}$ meso1 $\xleftarrow[354]{}$ N $\xleftarrow[361]{}$ I.L.
4(n=10,m=4)	Cryst. $\overset{375^*}{\underset{340}{\rightleftarrows}}$ N $\overset{376^*}{\underset{370}{\rightleftarrows}}$ I.L.
4(n=10,m=6)	Cryst. $\overset{372^*}{\underset{316}{\rightleftarrows}}$ N $\overset{373^*}{\underset{369}{\rightleftarrows}}$ I.L.
4(n=10,m=7)	Cryst. $\overset{358}{\underset{331}{\rightleftarrows}}$ N $\overset{366}{\underset{366}{\rightleftarrows}}$ I.L.
4(n=8, m=7)	Cryst. $\overset{355}{\underset{322}{\rightleftarrows}}$ N $\overset{367}{\underset{368}{\rightleftarrows}}$ I.L.
4(n=9, m=7)	Cryst. $\overset{355}{\underset{324}{\rightleftarrows}}$ N $\overset{371}{\underset{371}{\rightleftarrows}}$ I.L.
4(n=12,m=7)	Cryst. $\overset{355}{\underset{327}{\rightleftarrows}}$ N $\overset{364}{\underset{364}{\rightleftarrows}}$ I.L.
4(n=13,m=7)	Cryst. $\overset{362}{\underset{330}{\rightleftarrows}}$ N $\overset{364^*}{\underset{364}{\rightleftarrows}}$ I.L.

Cryst. : crystal phase
I.L. : isotropic liquid
N : nematic phase
S_A : smectic A phase
meso1 , meso2 : unidentified mesophase
* : This temperature was determined by polarizing microscopy observations.

diffraction method is not yet performed. The derivative **3**(*n*=10) showed only one liquid crystalline phase on the cooling. The microscopic texture was a typical fan-shaped one. From the result, it may be considered that the liquid crystalline phase of this compound is a smectic A phase. In the case of the derivative **4**(*n*=10, *m*=1), the DSC results indicated an existence of three liquid crystalline phases in the cooling process. One of them observed in highest temperature region was identified as the nematic one, because the typical schlieren texture and the high fluidity were observed under the polarizing microscope. However, the types of the other two phases can not be determined just as the case of the derivative **2**(*n*=10). In Table 1, the symbol "meso1" is independently defined for the derivative **2**(*n*=10) and **4**(*n*=10, *m*=1). It is not confirmed whether the meso1 phases of these compounds have the same structure or not.

The derivatives **4** showed only one liquid crystalline phase except for the derivative **4**(*n*=10, *m*=1) described above. The melting points of the derivatives **4** are relatively low, not more than 400K, compared with those of the symmetrical type (a) compounds[5].

The results obtained in the case of *n*=10, namely the derivatives **4**(*n*=10, *m*=1, 4, 6, and 7), are described below. The phase transition behavior of the derivative **4**(*n*=10, *m*=1) is already mentioned above. In the cases of the derivatives **4**(*n*=10, *m*=4) and (*n*=10, *m*=6), the typical nematic schlieren texture just as the derivative **4**(*n*=10, *m*=1) was distinctly observed not only on the cooling but also on the heating. However, the DSC results showed that the liquid crystalline phase existed only on the cooling. These results are explained that an endothermic peak corresponding to the clearing point is not independently detected by the DSC because the clearing point is very close to the melting one. The derivative **4**(n=10, m=7) showed the stable enantiotropic nematic phase, and its microscopic texture was the typical schlieren one. It seems that the melting point decreases and the liquid crystalline temperature range expands with increasing m.

The derivatives **4**(n=8, 9, 12, and 13, m=7) gave rise to the stable enantiotropic nematic phase just as the result of the derivative **4**(n=10, m=7) mentioned above. The liquid crystalline temperature range of these derivatives tends to expand with decreasing n, in contrast to the case of n=10 already described.

The member of the derivatives **4** is not so many to discuss the even-odd effect relating to the thermal behavior. However, it is expected that the even-odd effect depending upon n is different from that depending upon m, because the condition of the two flexible chains (n and m) are different from each other. That is, one flexible chain (n) is connected to the 1' position of the ferrocene of which cyclopentadienyl rings may be able to rotate in some degree. In order to discuss this subject, the syntheses of the derivatives **4**, which have various n and m, are now in progress.

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