A Novel Molecular Structure of a Ferrocene Derivative Containing Mesogenic Group, 1,1′-Bis[2-[4-(4-methoxyphenoxycarbonyl)phenoxy]ethoxycarbonyl]ferrocene

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The molecular and crystal structures of 1,1′-disubstituted ferrocene derivative, 1,1′-bis[2-[4-(4-methoxyphenoxycarbonyl)phenoxy]ethoxycarbonyl]ferrocene (bMAF-2) were determined by X-ray diffraction method using the single crystals. The trans conformation (novel "Z" shape) in which the two substituents existed in the opposite directions was found out newly. The structure was different from the cis conformation ("U" shape) and the trans conformation ("S" shape) reported already. It may be one of the most important reasons why bMAF-2 ("Z" shape) shows no liquid crystallinity that the ratio of the width to length is rather large compared with those of other liquid crystalline homologues ("U" shape and "S" shape).

Liquid crystalline compounds have a rod-like molecular shape, basically. If a transition metal introduced into an organic compound containing mesogenic group, it may be expected that the molecule show not only liquid crystallinity but also interesting physical properties such as electro-conductivity. In order to introduce the transition metal, it is convenient to use ferrocene in which an iron atom exists. However, we have some doubt whether the molecular shape is rod-like or not, because ferrocene molecule is bulky. In our laboratory, the relation between the molecular shape and liquid crystallinity has been examined from a structural viewpoint.

Liquid crystalline ferrocene derivative was firstly observed in monosubstituted one.[1] After that, many different kind of ferrocene derivatives, not only the monosubstituted derivatives but also disubstituted ones, have been synthesized from the point of view of liquid crystals. Disubstituted ferrocene derivatives can be classified into three types, 1,2-, 1,3-, and 1,1′-disubstituted ones, according to the position of the substituents. Structure analyses of 1,3- and 1,1′-disubstituted ferrocene derivatives have been carried out by other workers. It has already been reported that the molecular structures of liquid crystalline 1,3-disubstituted ferrocene derivative was "T" shape conformation[2] and that of 1,1′-disubstituted one was "S" shape conformation.[3] But not so many structural results have been reported hitherto.

A series of disubstituted ferrocene derivatives, 1,1′-bis[ω-[4-(4-methoxyphenoxycarbonyl)phenoxy]alkoxycarbonyl]ferrocene (abbreviated hereafter as bMAF-*n*, $n = 2$–12, where n is the number of carbon atoms in the flexible methylene unit) were prepared in our laboratory. The general chemical structure of bMAF-*n* is shown in Figure 1. Characterization of bMAF-*n* was carried out using a differential scanning calorimeter (DSC), a polarizing optical microscope (POM), and a small-angle X-ray diffraction system (SAXD). Nine members of the eleven compounds showed liquid crystallinity. The liquid crystalline phases were identified as a nematic ($n = 3$ and 5–12), a smectic C ($n = 5$–12) and a smectic F or I ($n = 11$ and 12).[4,5]

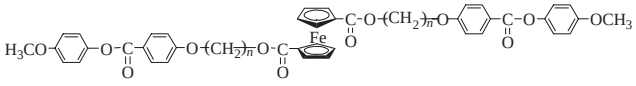

Figure 1. The general structure of bMAF-*n*.

In order to clarify an interrelation between the structure and some physical properties and to discuss a mechanism of the appearance of liquid crystalline phase, we have already determined the crystal structure of bMAF-5. The molecular structure of bMAF-5 was the trans conformation ("S" shape), as was expected in general.[6]

In addition, we have analyzed the crystal and molecular structures of bMAF-10 (which is a homologous compound of bMAF-5) by X-ray diffraction method, and the result was reported in this journal recently.[7] The molecule was assumed to be "U" shape conformation. The "U" shape conformation is sometimes found out in the 1,2-benzene derivatives.[8] But as cyclopentadienylrings in the ferrocene have a rotational freedom in some degree around a molecular axis through the two rings and iron atom, the "U" shape conformation of bMAF-10 is very unique one. The "U" shaped molecular structure of 1,1′-disubstituted ferrocene derivative was reported by other workers already, but water molecules were included in the crystal.[9] Therefore, the "U" shape conformation of bMAF-10 in liquid crystalline 1,1′-disubstituted ferrocene compounds is the first time, as far as we know.

These results obtained suggest that the conformation of bMAF-*n* seems like to depend on the length of the flexible spacer. Therefore, it is expected that bMAF-2 (which is a homologue of bMAF-5 and 10) may show the "S" shape conformation, because the length of the flexible spacer is rather short. In addition, it is interesting in the structure of bMAF-2, because the compound shows no liquid crystallinity. In this study, the crystal and molecular structures of bMAF-2 were determined by X-ray diffraction method.

The sample, bMAF-2, was synthesized in accordance with the method mentioned in our previous paper.[4] The single crystal of the compound was obtained from a solution with a mixed solvent of dichloromethane and ethanol (1:1) by the slow evaporation method. The single crystals are orange in color and plate-like. The sample, which had the approximate dimensions of $0.65 \times 0.26 \times 0.05\,\mathrm{mm}^3$, was mounted on the goniometor.

Figure 2[10] shows the molecular structure of bMAF-2. It is considered that the conformation of 1,1′-disubstituted ferrocene derivatives, of which spacer length is shorter than that of bMAF-5, may assume "S" shape conformation, mentioned above. The molecular structure of bMAF-2 shown in Figure 2 is similar, but not the same, to "S" shape conformation observed in bMAF-5.

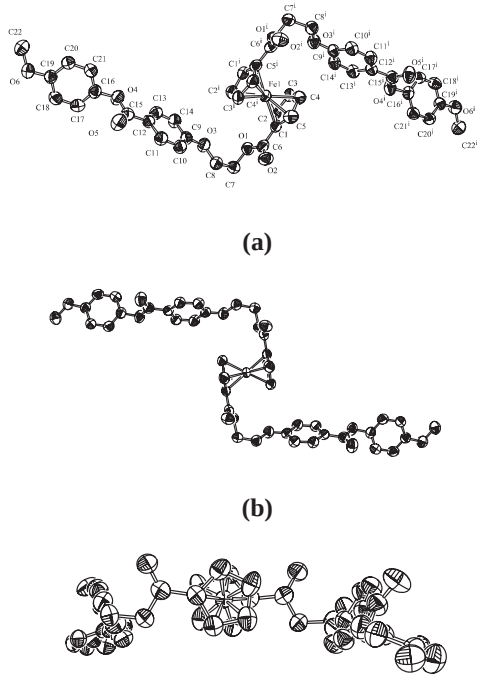

Figure 2. ORTEP-3[11] view of the molecular structure excluding hydrogen atoms in bMAF-2. Thermal ellipsoids are drawn at 50% probability. (a) Showing the crystallographic numbering scheme, (b) side view onto the cyclopentadienyl rings, and (c) overview onto the cyclopentadienyl rings.

This compound revealed very interesting feature. As far as we know, this unique structure of bMAF-2 was novel one. This is the first time in 1,1′-disubstituted ferrocene derivatives containing mesogenic groups. Therefore, this structure is named the "Z" shape conformation by present authors. The skeleton of the methylene chain had *gauche* conformations at C(6)–O(1)–C(7)–C(8) and O(1)–C(7)–C(8)–O(3). Therefore, the methylene chain is bended to ferrocene side. In mesogenic moiety, the dihedral angle of two phenyl rings, (C9–C14)–(C16–C21) was 79.6°(8). This value of the angle is similar to that of monosubstituted ferrocene derivative containing propyl moiety as the flexible spacer. Its value is 77.3°.[12] Such rather large dihedral angles may be regarded as one of the reason why the compound do not show liquid crystallinity as was explained in the paper.

The molecular packing of bMAF-2 in the crystal is shown in Figure 3. In the crystal, the molecules in a layer leaned greatly to *a* axis. This packing closely resemble in that of monosubstituted ferrocene derivative mentioned above.[12] These complicated molecular packing may be another reason why these compounds are non-liquid crystals.

The more detailed discussion of the relation between the molecular and crystal structures and the appearance of liquid crystallinity is now in progress.

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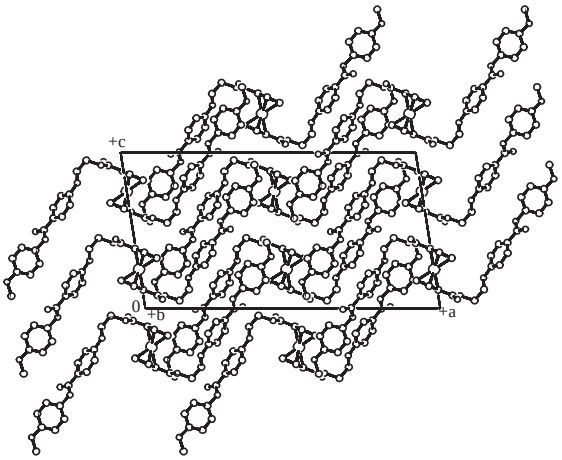

Figure 3. The crystal structure of bMAF-2, the projection of *a*–*c* plane.

References and Notes

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10 Crystal data of bMAF-2: $C_{40}H_{38}FeO_{12}$, fw = 814.62, monoclinic, space group $C2/c$, $a = 27.701(4)$ Å, $b = 9.011(2)$ Å, $c = 15.172(4)$ Å, $\beta = 98.782(2)°$, $V = 3742.5(14)$ Å^3, $Z = 4$, $T = 296(1)$ K, $D_{calcd} = 1.446$ g/cm^3, 4181 reflections measured, 3411 unique ($R_{int} = 0.030$), $R[F^2 > 2\sigma(F^2)] = 0.036$, $wR[F^2 > -3\sigma(F^2)] = 0.067$, and GOF = 1.000. CCDC No. 284166 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
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