Syntheses and Physical Properties of Ferrocene Derivatives (XVII) Crystal Structure of a Liquid Crystalline Ferrocene Derivative, 1,1′-bis[5-[4-(4-methoxyphenoxycarbonyl)phenoxy] pentyloxycarbonyl]ferrocene

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The molecular and crystal structures of 1,1′-disubstituted ferrocene derivative, 1,1′-bis[5-[4-(4-methoxyphenoxycarbonyl)phenoxy]pentyloxycarbonyl]ferrocene (bMAF-5) were determined by X-ray diffraction method using a single crystal. This compound is a liquid crystalline one. As generally expected, the molecular feature is "S" shape in which the two substituents are present in the opposite directions. The $-C_5H_{10}-$ chain introduced into the molecule as a flexible spacer includes two gauche conformations. The gauche conformation plays an important role to make a rod-like shape, which is favorable to show liquid crystallinity.

Keywords: 1,1′-disubstituted ferrocene derivative; crystal structure; ferrocene; liquid crystal

INTRODUCTION

Many liquid crystalline compounds containing ferrocenyl moiety have been synthesized hitherto, because it is expected that these compounds have a possibility of becoming new liquid crystal materials with unique optical, electric and magnetic properties. Ferrocene is one of the metallocenes, and it shows remarkable thermal stability
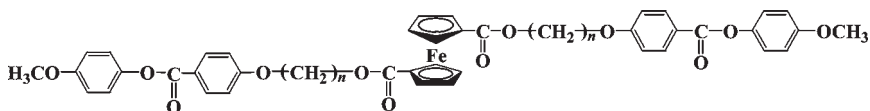
FIGURE 1 The general chemical structure of bMAF-*n*.

and aromaticity. Disubstituted ferrocene derivatives can be classified into three types, 1,2-, 1,3- and 1,1′-disubstituted ferrocene derivatives, according to the substituted position. Some of 1,3- and 1,1′-disubstituted ferrocene derivatives show liquid crystallinity and their structure analyses have been carried out. It has already been reported that the molecular structures of liquid crystalline 1,3-disubstituted ferrocene derivatives and 1,1′-disubstituted ones were "T" shape and "S" shape, respectively [1,2]. "T" shape and "S" shape mean the two substituents exist in the opposite directions.

In our laboratory, a series of disubstituted ferrocene derivatives, 1,1′-bis[ω-[4-(4-methoxyphenoxycarbonyl)phenoxy]alkoxycarbonyl]-ferrocene (abbreviated hereafter as bMAF-*n*, $n = 2 \sim 12$, where *n* is the number of carbon atoms in the methylene unit) were prepared. The general chemical structure of bMAF-*n* is shown in Figure 1. Liquid crystallinity of bMAF-*n* was studied using a differential scanning calorimeter (DSC), a polarizing optical microscope (POM), and a small-angle X-ray diffraction systems (SAXD). 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) [3,4].

The aims of structure analysis of liquid crystalline compounds are to gain understanding of the interrelation between the crystal structure and some physical properties and to discuss the mechanism of an appearance of liquid crystalline phase.

In the present study, the crystal and molecular structures of bMAF-5 was determined by X-ray diffraction method using the single crystals.

EXPERIMENTAL

The objective compound, bMAF-5, was synthesized in accordance with the method mentioned in our previous paper [3]. The single crystal of the compound was obtained from a mixed solvent solution of benzene and heptane (1:3) by the slow evaporation method. The single crystals obtained are orange in color and plate-like. The sample, which had the approximate dimensions of $0.38 \times 0.29 \times 0.03$ mm, was mounted on a goniometer.

All measurements were carried out by Rigaku AFC-5R diffract-ometer operated at 50 kV and 200 mA. The X-ray beam was monochro-matized to Cu-Kα ($\lambda = 1.54178 \text{Å}$) with a graphite single crystal monochromator.

The unit cell parameters were obtained from a least-squares refine-ment using the setting angle of 24 reflections in the range of $18.8° < 2\theta < 30.7°$. The data were collected at $297 \pm 1 \text{K}$ using the ω-scan technique to a maximum 2θ value of $140.2°$.

The 4986 reflections were measured, of which 4037 were unique. The intensity of three representative reflections was measured after every 150 reflections. Over the course of the data collection, the inten-sity of the standards decreased by 1.08%. The data were also corrected for Lorentz and polarization effects and for absorption (integration; minimum and maximum transmission factors were 0.45892 and 0.90623, respectively).

All calculations were performed using the *CrystalStructure* crystal-lographic software package of the Molecular Structure Corporation [5]. The structure was solved by direct methods (SIR92) [6] and expanded using the Fourier technique. All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were refined isotropi-cally. The hydrogen atoms were introduced at their theoretical posi-tions and allowed to ride with the carbon atoms to which they are attached. The final refinement was made by full-matrix least-squares based on 4036 observed reflections ($F^2 > -3.0\sigma(F^2)$). Here, it is better to use all F^2-values for the refinement, but these values sometimes include reflections known to suffer from systematic error. In order to omit the reflections, we used ($F^2 > -3.0\sigma(F^2)$) as a threshold. The refinement was concluded with final reliability factors:

$$R1 = \sum ||F_o| - |F_c|| \Big/ \sum |F_o| = 0.066 \quad \text{for } F^2 > 2.0\sigma(F^2)$$

$$wR = \left[\sum w \left(F_o^2 - F_c^2\right)^2 \Big/ \sum w (F_o^2)^2\right]^{1/2} = 0.143 \quad \text{for } F^2 > -3.0\sigma(F^2)$$

where the weighted scheme $w = 1/[0.0002 F_o^2 + 1.8000\sigma^2(F_o) + 0.5000]/(4F_o^2)$. In addition, *R1* value using normal threshold ($F^2 > 2.0\sigma(F^2)$) based on 1644 observed reflections was also calculated.

Final crystallographic data reported in this manuscript have been deposited with Cambridge Crystallographic Data Centre as sup-plementary publication no. CCDC-249437. Copies of the data can be also obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving. html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: $+44$ 1223 336033; or deposit@ ccdc.cam.ac.uk).
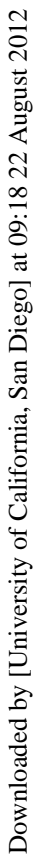
RESULTS AND DISCUSSION

Summarized data regarding collection and refinement of bMAF-5 are shown in Table 1. The molecular conformation with numbering for each atom is presented as an *ORTEP*-3 [7] drawing in Figure 2. The hydrogen atoms are omitted for simplification of Figure 2.

The crystal packing of bMAF-5 is shown in Figure 3 as a projection along the *a* axis. In the crystal, the molecules form the layer structure of herring-bone type and lean greatly to *b* and *c* axis. The molecules are arranged in a head-to-head manner. When it is taken note of one layer, the layer is formed by three layers piled up mesogenic unit, ferrocene part, and mesogenic unit, in that order. That is, three sub-layers existed in one layer. This sub-layers structure may be constructed by an intermolecular interaction between neighboring ferrocene moieties and that between the mesogenic parts.

Some torsion angles chosen arbitrarily are made in Table 2. As shown in Table 2, the torsion angles of (C6−O1−C7−C8) and (C7−C8−C9−C10) were −137.0(12)° and 24.5(19)°. The C−C average distance was 1.43(1)Å, shorter than that of *n*-paraffin (1.54 Å). The length of a flexible chain portion (C7−C11) was 4.456(11) Å. This is also shorter compared with the length of the corresponding *trans* forms (5.08 Å), considering that the length of the−CH_2−CH_2−CH_2−unit of *n*-paraffin is about 2.54 Å. The latter fact is clearly due to the *gauche*

TABLE 1 Summarized Data Regarding Collection and Refinement of bMAF-5

Empirical formula	$C_{50}H_{50}O_{12}Fe$
Formula weight	898.78
Crystal system	Monoclinic
Space group	$P2_1/a$
Lattice parameter	
$a/\text{Å}$	7.653(4)
$b/\text{Å}$	33.852(2)
$c/\text{Å}$	8.941(3)
$\beta/°$	107.43(3)
Volume/Å^3	2210.0(14)
Z value	2
D_{calc}/gcm^{-3}	1.351
Measured reflections	4986
Independent reflections	4037
Observed reflections ($F^2 > -3.0(F^2)$)	4036
$R1$	0.066
wR	0.143
Goodness of fit (S)	1.000

FIGURE 2 *ORTEP*-3 [7] views of the molecular structure excluding hydrogen atoms in bMAF-5. Thermal ellipsoids are drawn at 50% probability. (a) showing the crystallographic numbering scheme, (b) over view onto the cyclopentadienyl rings, (c) side view onto the cyclopentadienyl rings and (d) the projection along the long axis of the molecule.

conformation in the methylene chain. As a result, these two *gauche* conformations give a cavity in which ferrocenyl part just occupies.

The molecular structure of bMAF-5 was S-shaped conformation likely the structure of 1,1′-disubstituted liquid crystalline ferrocene derivatives analyzed already by other workers [2]. As for 1,1′-disubstituted ferrocene derivatives, two kinds of molecule are thought. One is "S" shape in which the two substituents are present in the opposite directions, the other is "U" shape in which the two substituents existed in the same directions. However, since it is more advantageous to be a rod-like molecule in order to show liquid crystallinity generally, it is considered that "S" shape has more possibility to introduce liquid crystal phases than "U" shape. Consequently, the result of this study indicates the molecular structure of bMAF-5 is more advantageous structure to show liquid crystallinity.
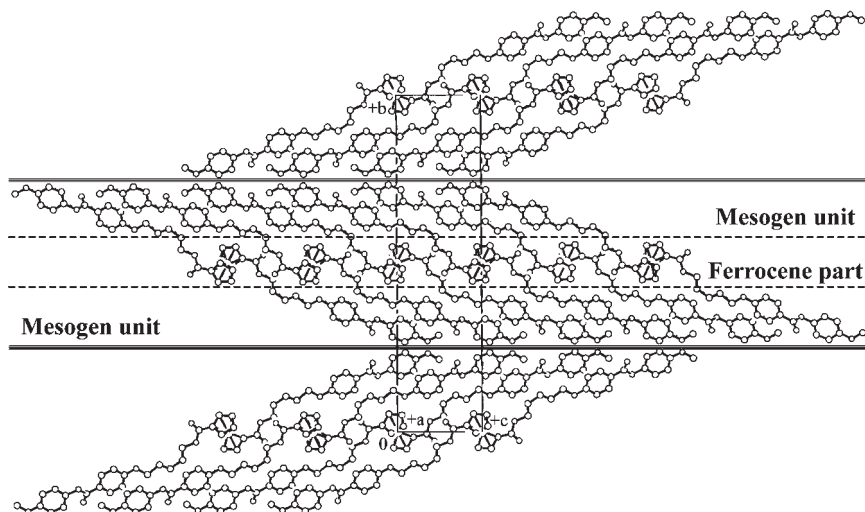
FIGURE 3 The crystal structure of bMAF-5, the projection of *b-c* plane.

The temperature factor of the atoms in the flexible chain is very large as is shown in Figure 2. This means the atoms in the flexible chain vibrates greatly in the crystal. In general, the temperature factor of the atom increases with approaching the end atoms of the molecule. Therefore, *gauche* conformation existing in the flexible chain may not be the most stable state in energy. Here, Figure 4 shows the models assumed that methylene chain has all-*trans* conformation by using Chem3D [8].

In this model, the molecular length is estimated as 45.71 Å, and is almost corresponding to the molecular length 45.020(18) Å which have been obtained by X-ray structure analysis. Comparing the structure

TABLE 2 The Selected Torsion Angles of bMAF-5

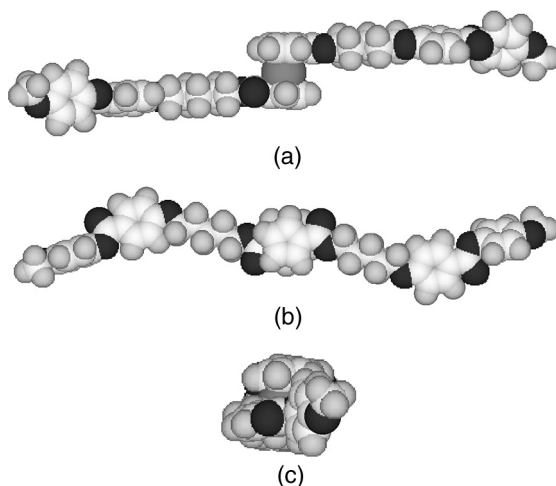| Selected atoms	Torsion angle/°
O(2)–C(6)–O(1)–C(7)	−0.8(12)
C(6)–O(1)–C(7)–C(8)	−137.0(12)
O(1)–C(7)–C(8)–C(9)	−177.1(8)
C(7)–C(8)–C(9)–C(10)	24.5(19)
C(8)–C(9)–C(10)–C(11)	−178.1(7)
C(9)–C(10)–C(11)–O(3)	175.6(7)
C(10)–C(11)–O(3)–C(12)	173.1(6)
O(5)–C(18)–O(4)–C(19)	−0.4(9)

FIGURE 4 The model structure of bMAF-5 including the flexible methylene chain adapted an all-*trans* conformation drawn by Chem3D [8]. (a) side view onto the cyclopentadienyl rings, (b) over view onto the cyclopentadienyl rings and (c) the projection along the long axis of the molecule.

shown in Figure 2(d) and the model structure of Figure 4(c), no significant difference is observed. In addition, there is no big difference in the ratio of the length and breadth of the molecule between the model molecular structure and the actual molecular one. The former has the all-*trans* conformation in methylene chain and the latter has the *gauche* conformation. In the shape of molecule, however, the model structure is slightly bent like "N" shape as is shown in Figure 4(b). On the other hand, the actual structure is more virgulate with two *gauche* conformations. Because typical liquid crystalline compounds are rod-like, the actual structure can be regarded as more advantageous one in order to show liquid crystallinity.

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