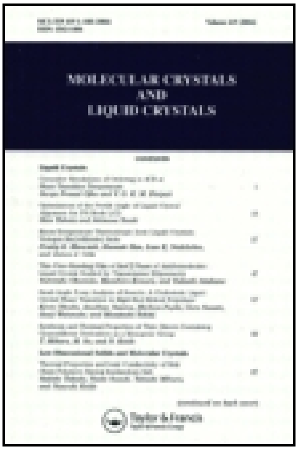

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Synthesis and Physical Properties of Ferrocene Derivatives (XX): Crystal Structure of a Liquid-Crystalline Ferrocene Derivative, 1,1′-bis [9-[4-(4-methoxyphenoxycarbonyl)phenoxy nonyloxycarbonyl]Ferrocene

Naotake Nakamura [a] , Takahiro Nio [a] , Takashi Okabe [a] , Bertrand Donnio [b] , Daniel Guillon [b] & Jean-Louis Gallani [b]

[a] Department of Applied Chemistry, College of Science and Engineering, Ritsumeikan University, Kusatsu, Shiga, Japan

[b] Institut de Physique et Chimie des Matériaux de Strasbourg, Groupe des Matériaux Organiques, Strasbourg, Cedex, France

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Synthesis and Physical Properties of Ferrocene Derivatives (XX): Crystal Structure of a Liquid-Crystalline Ferrocene Derivative, 1,1′-bis [9-[4-(4-methoxyphenoxycarbonyl)phenoxy] nonyloxycarbonyl]Ferrocene

Naotake Nakamura
Takahiro Nio
Takashi Okabe
Department of Applied Chemistry, College of Science and Engineering, Ritsumeikan University, Kusatsu, Shiga, Japan

Bertrand Donnio
Daniel Guillon
Jean-Louis Gallani
Institut de Physique et Chimie des Matériaux de Strasbourg, Groupe des Matériaux Organiques, Strasbourg Cedex, France

Single-crystal X-ray structure analysis has been performed for symmetrical 1,1′-disubstituted ferrocene derivative. This compound exhibits liquid crystallinity as a function of temperature with nematic and smectic liquid-crystalline phases. The X-ray structure analysis revealed that two substituents existed in the same directions, and as such induced the cis conformation ("U" shape) of the molecule. The molecules in the unit cell are arranged in a bookshelf manner. Within each layer, CH-π intermolecular interaction was observed at the substituents between neighboring molecules. It is considered that this interaction plays a predominant role in stabilizing the crystal packing arrangement and the mesomorphism.

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

INTRODUCTION

Liquid-crystalline ferrocene derivatives are representative compounds of the metallomesogens [1]. Because of their unique physical properties,

Address correspondence to Naotake Nakamura, Department of Applied Chemistry, College of Science and Engineering, Ritsumeikan University, 1-1-1, Nojihigashi, Kusatsu, Shiga 525-8577, Japan. E-mail: nakamura@se.ritsumei.ac.jp

liquid crystals containing a transition metal are gaining interest for some applications as photoactive materials (e.g., the fullerene-ferrocene derivative was designed to develop photoactive liquid-crystal switches [2]).

The mesomorphic properties of thermotropic liquid-crystalline ferrocene derivatives depend on the nature, number, and position of the substituents located on the ferrocene. The types of 1,1′-disubstitution are classified into several groups. Molecular structures of opposite and same direction of substitution at the 1,1′-position could be regarded as "S" shape and "U" shape, respectively. The "S" shape seems to create a step in the overall structure, leading to a lack of coplanarity between the substituents in the 1,1′-positions. The deformition of this nature encourages tilted packing arrangements of the molecules as stated by Wulf [3]. Indeed, these systems favor the formation of smectic C phases [4,5]. Recently, we have reported the U shaped molecular structure in 1,1′-disubstituted liquid-crystalline derivatives in the crystalline state [6]. We also reported Z shaped conformation of 1,1′-disubstituted ferrocene derivatives [7]. In 1,3-disubstitution compounds, they have a higher mesogenic character because of their anisometric structure. The liquid-crystalline tendency follows the sequence: $1,3 \geq 1,1' \gg 1,2$-isomeric structures [8].

The understanding of structure–property relationships is important, and a guiding principle based on molecular shapes is applied extensively in the design of novel liquid-crystalline materials. Generally, rod-like molecules assemble into smectic or nematic phases. The exhibiting mesophases are controlled by attractive interactions between neighboring molecules. A lot of different kinds of interactions, such as dipole–dipole, dispersion, hydrogen bonding, $\pi-\pi$, and CH$-\pi$ interaction [9,10], are known. Single-crystal structure analysis is often useful to evaluate and to understand the interactions.

The systematic crystal-structure analyses of liquid-crystalline ferrocene derivatives, monosubstituted ones [11–18] and 1,1′-disubstituted ones [6,7,19] (1,1′-bis [ω-[4-(4-methoxyphenoxycarbonyl)phenoxy]alkyloxycarbonyl]ferrocene, abbreviated hereafter as bMAF-*n*, where *n* is the number of carbon atoms in the methylene unit) have been performed. The general chemical structure of bMAF-*n* is shown in Fig. 1. This article describes the crystal structure of the bMAF-9.

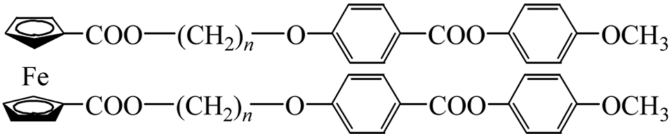

FIGURE 1 General structure of bMAF-*n*.

EXPERIMENTAL

Transparent orange plate-shaped crystals were grown from a mixed solution of 1,2-dichloroethane and ethanol by the slow-evaporation technique at room temperature. The crystal size was $0.50 \times 0.34 \times 0.02\,\mathrm{mm}^3$. The crystal was used for data collection on the Rigaku AFC5*R* four-circle diffractometer with graphite-monochromatized Cu-Kα ($\lambda = 1.54178\,\mathrm{\AA}$) radiation at 50 kV and 200 mA. Lattice dimensions were determined by centering 17 reflections in the theta range 30.9°–38.0°. Intensities of reflection were collected using the $\omega - 2\theta$ scan method at 294 K. Three standard reflections were measured every after 150 to monitor the stability of the experimental conditions. No significant change was observed. A total of 10,956 reflections ($-10 < h < 11$, $-12 < k < 1$, $-33 < l < 33$) were recorded, from which 9,755 unique reflections were used for the structural determination. All reflections were corrected for Lorenz and polarization factors. An absorption correction based on ψ-scan was also applied [20], with maximum and minimum transmission factors of 0.353 and 0.944, respectively. The structure was solved by direct methods using *SIR*-92 [21]. All heavy atoms were refined anisotropically, whereas H atoms were added at their calculated positions and included in the structure factor calculations using a riding model but not refined. The H atoms were allowed to ride on their parent atom with Uiso (H) $= xU$eq (parent), where $x = 1.2$ for all. An extinction correction was applied, and the extinction coefficient [22] was 0.0008(5).

The final refinement was made by full-matrix least-squares based on 9,300 observed reflections ($F^2 > -3.0\sigma(F^2)$). It is better to use all F^2-values for the refinement, but these values sometimes include reflections known to suffer from systematic error. To omit the reflections, we used $F^2 > -3.0\sigma(F^2)$ as a threshold. The final refinement cycles converged to $R = 0.060$, $wR(F^2) = 0.148$, $[w = 1/\sigma_c^2(F_o^2) + (0.027(\mathrm{Max}(F_o^2,\ 0) + 2F_c^2)/3)^2]$, and $S = 1.298$. Maximum shift to e.s.d. ratio for all atoms in the final cycle is 0.0003. Final cycles of the refinement resulted in a residual electron density in the range between -1.08 and $0.59\,\mathrm{e\AA}^{-3}$. All calculations were performed by TEXSAN crystallographic software package of the Molecular Structure Corporation [23]. The atomic scattering factors were taken from the International Tables for Crystallography [24]. The crystallographic data are summarized in Table 1. The Cambridge Crystallographic Data Center, 12 Union Road, Cambridge, CB2 1EZ, UK, contains the supplementary crystallographic data for this structure (CCDC No. 616042).

TABLE 1 Summarized Crystallographic Data and Results of Final Refinement

Parameter	Value
Empirical formula	$C_{58}H_{66}O_{12}Fe$
Formula weight	1010.96
Crystal system	triclinic
Space group	P-1
a/Å	9.148(2)
b/Å	10.865(2)
c/Å	27.694(3)
α/°	80.010(10)
β/°	95.200(10)
γ/°	109.25(2)
Volume Å^3	2557.6(8)
Z value	2
$D_{\mathrm{calc}}/\mathrm{g\,cm^{-3}}$	1.313
Measured reflections	10956
Independent reflections	9755
Observed reflections ($I > -3\sigma(I)$)	9300
Parameters	641
Extinction coefficient	0.0008(5)
R	0.060
$wR(F^2)$	0.148
S	1.298

RESULTS AND DISCUSSION

Molecular Structure

An *ORTEP*-3 view of the bMAF-9 is shown in Fig. 2. The hydrogen atoms are omitted for simplification of the figures. The bond distances and angles are in good agreement with the values for organic compounds containing ferrocenyl and phenyl moieties [6,7,11–19]. Two cyclopentadienyl rings were almost parallel in the ferrocenyl moiety, and the dihedral angles were 3.9(3)°. The torsion angles of C(6)–C(1)–Fe(1)–C(34) and C(5)–Fe(1)–C(30)–C(35) were 16.2(5)° and 17.3(5)°, respectively. When viewed on the top, two cyclopentadienyl rings twist about 36° in staggered conformation. Thus, the ferrocenyl moiety of bMAF-9 is in between eclipsed and staggered conformations. As shown in Fig. 2b, the two substituents are located in the same direction with some divergence. This style resembles the molecular structure of bMAF-10 [6]. The substituents of bMAF-3 [25] have slight different conformation, though it is classified as a "U" type. The structural difference between the two is described later. The average values of the Fe–C and C–C bond distances in bMAF-9 are 2.035(6) Å

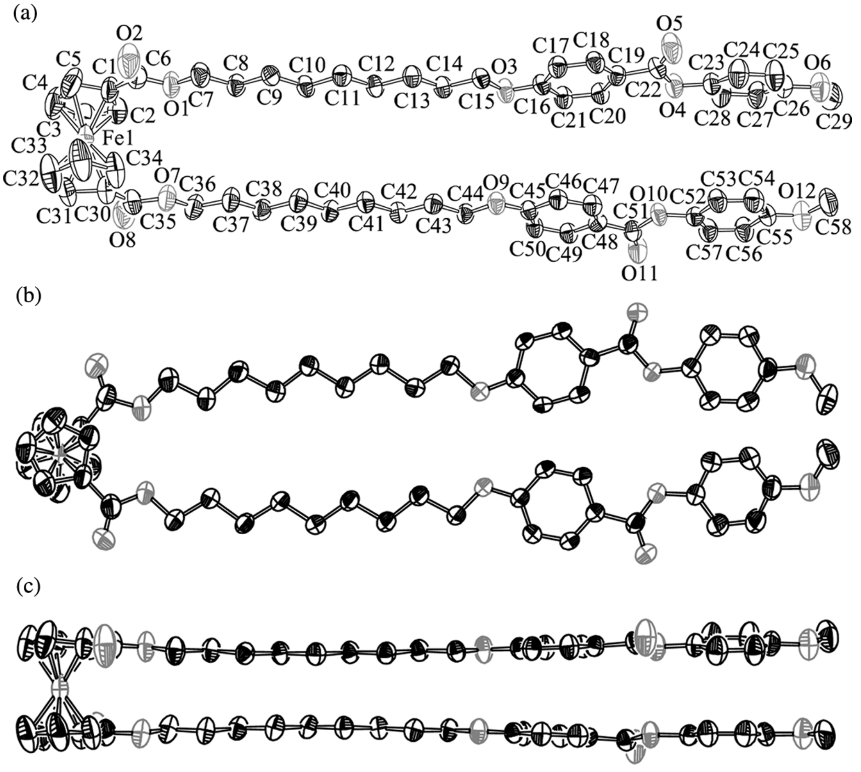

FIGURE 2 *ORTEP*-3 [27] view of the molecular structure of bMAF-9. Thermal ellipsoids are drawn at 50% probability: (a) with the crystallographic numbering scheme, (b) top view onto the cyclopentadienyl rings, and (c) side view onto the cyclopentadienyl rings.

and 1.407(7) Å, respectively. The C−C−C bond angles in the cyclopentadienyl rings are 107.9(5)°. These values agreed, within an experimental error, to those of the ferrocene reported elsewhere [6,7,11–19,26].

The flexible spacers (C7 ∼ C15 and C36 ∼ C44) are regarded as almost all-*trans* conformation with 180° torsion angles differing by less than 5°. The length of each nonyl chain is 10.157(6) Å long, and the length of the C−C−C unit of extended normal paraffin is 2.54 Å long. Thus, the length of the nonyl chains [10.157(6) Å] is nearly equal to those of extended ones (10.16 Å long by 2.54×4). Therefore, it is considered that the structure of the flexible spacers is fully extended. Almost all-*trans* conformations of the flexible spacer have been observed in bMAF-10 [6] and monosubstituted liquid-crystalline ferrocene derivatives [11,13–18].

TABLE 2 Dihedral Angle between Least-Squares Planes of bMAF-9

Plane no.	Least-squares plane	Dihedral angle/°
Plane 1	Substituted Cp-ring (C1 ~ C5)	—
Plane 2	Phenyl ring (C16 ~ C21)	—
Plane 3	Phenyl ring (C23 ~ C28)	—
Plane 4	Substituted Cp-ring (C30 ~ C34)	—
Plane 5	Phenyl ring (C45 ~ C50)	—
Plane 6	Phenyl ring (C52 ~ 57)	—
Plane 1–Plane 2	—	4.7(3)
Plane 2–Plane 3	—	3.6(2)
Plane 1–Plane 4	—	3.9(3)
Plane 4–Plane 5	—	6.9(2)
Plane 5–Plane 6	—	11.2(2)

The dihedral angle between least-square planes of bMAF-9 is represented in Table 2. In bMAF-9, the dihedral angles of two phenyl rings (plane 2–plane 3 and plane 5–plane 6) in the mesogenic group are estimated to be 3.6(2)° and 11.2(2)°, respectively. As shown in Fig. 2c, all of the least-square planes are almost parallel to each other; that is, the *cis* conformation ("U" shape) of bMAF-9 seems to have an adequate coplanarity between Cp rings and the substituents. Thus, the molecular structure of bMAF-9 is effective in showing liquid crystallinity.

The molecular structure of bMAF-9 was "U"-shaped conformation in which the two substituents existed in the same direction. The molecular structure of bMAF-*n* is categorized into three groups by the location of the substituents, as far as we know. One is the "U" conformation reported in bMAF-10 [6] and in this study. The other is the "S" conformation observed for bMAF-5 [19], in which the two substituents existed in opposite directions and formed rod-like structure containing gauche conformations. Both types of bMAF-*n* show liquid crystallinity. Recently, we reported "Z" conformation of bMAF-2 [7], in which the substituents existed in opposite directions and were extremely bent at the flexible spacers. For this reason, the "Z" type did not show liquid crystallinity. As for the 1,1′-disubstituted ferrocene derivatives, the effective structures showing liquid crystallinity are classified into two groups, "S" type and "U" type.

Crystal Structure

Projections of the crystal structure along the *b* and *a* axes are shown in Figs. 3a and b, respectively. From these figures, it is evident that the molecules in the unit cell were arranged in a bookshelf manner and

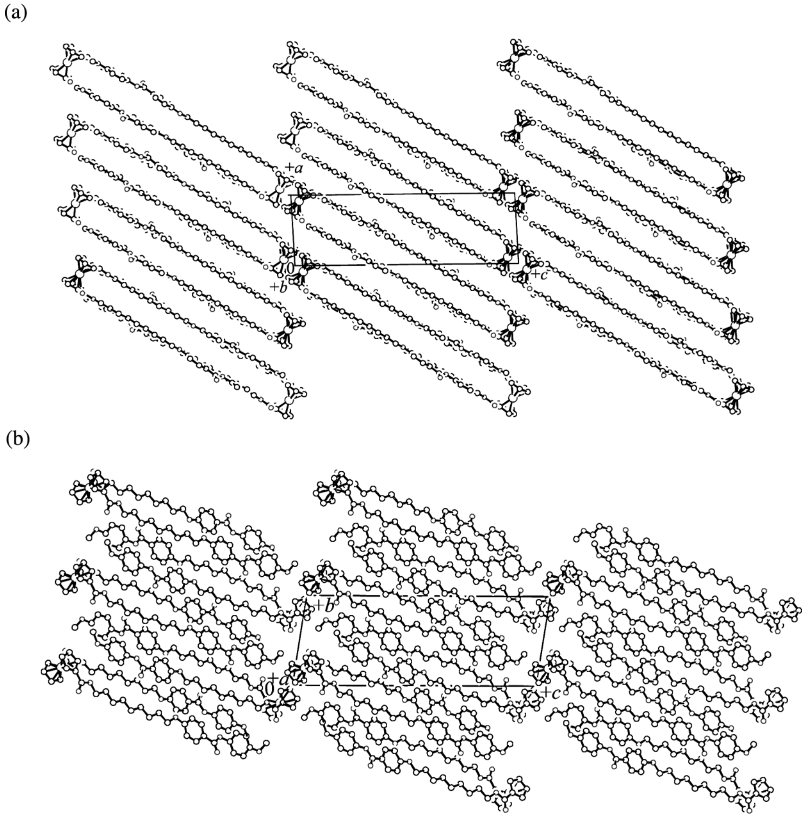

FIGURE 3 Crystal structure of bMAF-9, (a) projection of *a–c* plane and (b) projection of *b–c* plane.

formed a head-to-tail dimer with intercalating structures. The molecular length is estimated as 31.0 Å long. The layer spacing in the mesophase, which has been obtained from X-ray diffraction pattern [5], was found to be 30.1 Å long. Thus, this result indicates that the crystal structure is approximately maintained in the liquid-crystalline phase, as is well known. This fact suggests that the mesophase may be smectic A phase. (In the paper cited here [5], the model molecular length of bMAF-9 was estimated as 58.1 Å long based on "S"-shaped structure. Therefore, the liquid-crystalline phase was supposed to be smectic C in the paper [5]. However, the molecular structure of bMAF-9 assumed to be "U" shaped in this study).

The crystal structure is stabilized by the presence of some intermolecular short contacts of the two substituents. One is the short contact

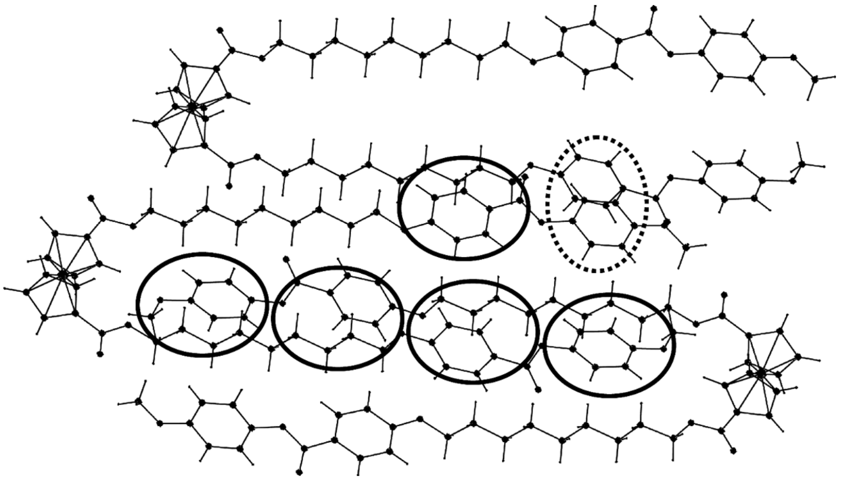

FIGURE 4 Illustration of intermolecular interaction of bMAF-9. The short contacts of methylene chain and benzene ring are indicated by solid circles, and the short contacts of benzene rings are indicated by dashed circles.

of methylene chain and benzene ring (indicated by solid circles in Fig. 4). The distance between the hydrogen atoms (at the C8, C9, C13, C14, C37, C38, C42, and C43 positions) on the nonyl chain and the benzene ring of a neighboring molecule is about 3.00 Å. This value is close to the value of the sum (2.8 Å) of van der Waals radii of a sp^2 carbon atom (1.7 Å) and a C–H bond length (1.1 Å). The other exists in the benzene rings (indicated by a dashed circle in Fig. 4). The distance between the benzene rings is about 3.8 Å. The value is close to the value of the sum (3.4 Å) of that of two sp^2 carbon atoms (1.7 Å). Therefore, it is considered that CH-π and π-π intermolecular interactions [9] exist at the substituents between neighboring molecules within each layer. The CH-π interactions exist only in the layers, whereas the CH-π and π-π interactions are caused in adjacent layers (see Fig. 4). As mentioned previously, the substituents of bMAF-9 were located in the same direction with some divergence. Thus, intermolecular interaction is more attractive than intramolecular. Such intermolecular interaction may render the conformation of Cp rings to be between the eclipsed type and the staggered type. The interaction predominantly made a contribution to stabilization of the crystal-packing arrangement and the mesomorphism. As a result, bMAF-9 shows smectic A phase in addition to the nematic.

On the other hand, no such intermolecular interaction was observed in the crystalline state of liquid-crystalline bMAF-3, whereas intramolecular interactions of two substituents were observed. In accordance with the results of DSC, bMAF-3 shows the nematic phase only [25]. Consequently, the difference of the interactions may play an important role in giving rise to the mesomorphism.

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