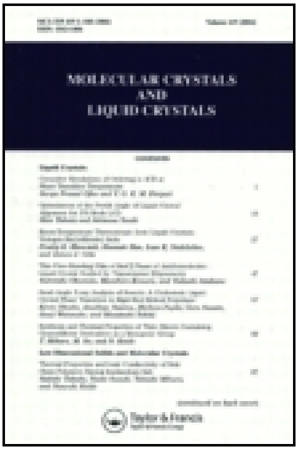

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Synthesis and Physical Properties of Ferrocene Derivatives (XIX): Crystal Structure of a Liquid-Crystalline Ferrocene Derivative, 9-[4-(4-Methoxyphenoxycarbonyl)-phenoxycarbonyl] nonyl 4-Ferrocenylbenzoate

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Synthesis and Physical Properties of Ferrocene Derivatives (XIX): Crystal Structure of a Liquid-Crystalline Ferrocene Derivative, 9-[4-(4-Methoxyphenoxycarbonyl)-phenoxycarbonyl] nonyl 4-Ferrocenylbenzoate

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The molecular and crystal structures of a metallomesogen, 9-[4-(4-methoxyphenoxycarbonyl) phenoxycarbonyl]nonyl 4-ferrocenylbenzoate, have been determined. The space group was monoclinic with the $P2_1/a$, and $Z = 4$. An eclipsed conformation of two cyclopentadienyl rings was observed in the ferrocenyl moiety. The flexible spacer was an almost all-trans conformation. The largest value of the dihedral angle between the two phenyl groups in the mesogenic group was observed throughout all the homologues. This result shows that even if the dihedral angle in the mesogenic group is large, the mesophase can be exhibited by elongating the molecular length. The molecular packing arrangement was similar to those of liquid-crystalline homologues.

Keywords: crystal structure; ferrocene; liquid crystal; metallomesogen; monosubstituted ferrocene derivative

INTRODUCTION

In recent years, research of functional materials that combine liquid crystals with transition metals has been done. They are called metallomesogens. Metallomesogens with terminal metal atoms are not very common, because, as can be deduced from the theory of organic liquid-crystalline compounds, bulky terminal groups are not be conductive to the stabilization of mesophases [1]. Nevertheless, the terminal bulky

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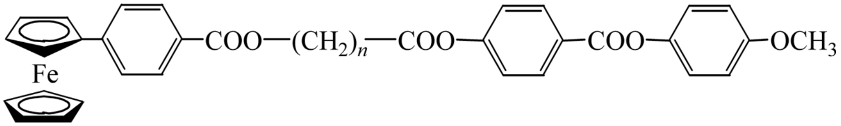

FIGURE 1 General structure of MPAF-*n*.

group can stabilize nematic and smectic phases by improving the molecular structure.

Ferrocene, besides being aromatic, is thermally and chemically stable. Liquid-crystalline ferrocene derivatives are one of the metallomesogens. The monosubstituted ferrocene derivatives are considered as having less or no mesogenity because of the steric effect of the ferrocenyl moiety. In contrast, it is well known that 1,1′- and 1,3-disubstituted ferrocene derivatives are advantageous for exhibiting a mesophase [2]. In our laboratory, however, liquid crystallinity was observed in the monosubstituted ferrocene derivatives by introducing a flexible spacer (alkyl chain) between the ferrocenylbenzoate and mesogenic groups. As is shown, a series of monosubstituted ferrocene derivatives, ω-[4-(4-methoxyphenoxy-carbonyl)phenoxycarbonyl]alkyl 4-ferrocenylbenzoates (abbreviated hereafter as MPAF-*n*, where *n* is the number of carbon atoms in the methylene unit), were synthesized [3]. The general chemical structure of MPAF-*n* is shown in Fig. 1. We have synthesized MPAF-1–11, and MPAF-4, 6, 8–11 exhibited monotropic mesophase, that is, nematic and smectic C phases [3]. In our previous study, even numbered MPAF-*n* compounds better exhibit the mesophase.

By determining the three-dimensional structure of the molecule in the crystal state of liquid-crystalline compounds, it is expected that we can know the molecular interaction in the mesophase. This information is useful for the design of new liquid-crystalline materials. To gain such information, X-ray structure analysis was performed for MPAF-*n*. In our previous work, it was considered that dihedral angles, molecular shapes, and dipole–dipole interactions are the most important factors to exhibiting mesophases.

MPAF-9 is the shortest liquid-crystalline homologue. This article describes the results of molecular and crystal structures of MPAF-9 and also discusses the relationship between the structure and the liquid-crystalline behavior.

EXPERIMENTAL

Orange plates of single crystals were obtained by slow evaporation from a mixed solvent, ethylacetate/ethanol (1/2); the crystal size was $0.60 \times 0.17 \times 0.04\,\mathrm{mm}^3$. Data collection was carried out at 294 K, using the Rigaku AFC5*R* four-circle diffractometer with a Cu-Kα($\lambda = 1.54178$ Å) equipped with a graphite monochromator operated at 50 kV and 200 mA. The number of reflections for cell parameters was 23 ($18.6^\circ < 2\theta < 27.0^\circ$). The data collection was carried out by the ω scan technique. Three standard reflections were measured after every 150 to monitor the stability of the experimental conditions. No significant change was observed. A total of 6,766 unique reflections were measured within the range $-1 < h < 9$, $-1 < k < 12$, $-52 < l < 52$, of which 6,504 were above the significance level of $-3\sigma(I)$. 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. All calculations were performed by TEXSAN crystallographic software package of the Molecular Structure Corporation [4]. All reflections were corrected for Lorenz and polarization factors. An absorption correction based on ψ-scans was also applied, with the ψ-scan; the minimum and maximum transmission factors were 0.503 and 0.859, respectively. The structure was solved by the direct method of SIR-92 [5]. The positions of the hydrogen atoms were inserted from the molecular geometry around the carbon atoms. The H atoms were allowed to ride on their parent atom with Uiso (H) $= xU$eq (parent), where $x = 1.2$ for all. Hydrogen atoms were included in the structure factor calculations but not refined. An extinction correction was applied, and the extinction coefficient [6] was 0.009(2). The atomic scattering factors were taken from the International Tables for Crystallography [7].

RESULTS AND DISCUSSION

Full-matrix least-squares refinement on the structure factors (F^2), with anisotropic temperature factors for the nonhydrogen atoms and isotropic factors for the hydrogen atoms, converged to $R = 0.062$, $wR = 0.185$, $(\Delta/\sigma)_{\max} < 0.001$, and $S = 1.469$. A weighing scheme, $w = [\sigma_c^2(F_o^2) + (0.05(\mathrm{Max}(F_o^2, 0) + 2F_c^2)/3)^2]^{-1}$ was used. Crystallographic details are presented in Table 1. The Cambridge Crystallographic Data Center contains the supplementary crystallographic data, CCDC No. 604731.

Molecular Structure

The ORTEP-3 [8] diagram of the molecular structure of MPAF-9 is shown in Fig. 2. The bond distances and angles were in agreement with those of usual values observed in organic compounds within an

TABLE 1 Summarized Crystallographic Data and Results of Final Refinement

Parameter	Value
Empirical formula	$C_{41}H_{42}O_7Fe$
Formula weight	702.60
Crystal system	monoclinic
Space group	$P2_1/a$
a/Å	8.288(6)
b/Å	10.046(4)
c/Å	42.781(4)
$\beta/^\circ$	90.85(3)
Volume Å^3	3562(3)
Z value	4
$D_{\mathrm{calc}}/\mathrm{gcm}^{-3}$	1.310
Measured reflections	9443
Independent reflections	6766
Observed reflections ($I > -3\sigma(I)$)	6504
Parameters	443
Extinction coefficient	0.009(2)
R	0.062
wR	0.185
S	1.469

experimental error. Some of the anisotropic atomic displacement parameter, C-18 and C-19, are relatively large in this structure analysis. However, the values determined did not have a pronounced effect.

Two cyclopentadienyl rings were parallel in the ferrocenyl moiety, and the dihedral angles were 0.3(7)°. Generally, ferrocenyl moiety of the derivatives often has the eclipsed type in two cyclopentadienyl rings. The cyclopentadienyl rings of MPAF-9 agree with this fact. In addition, disubstituted ferrocene derivatives [9,10] frequently have the staggered conformation while the eclipsed one is found in monosubstituted ferrocene derivatives [11–17] except for MPAF-3 [18] and MPAF-7 [19].

The average values of the Fe–C and C–C bond distances in MPAF-9 are 2.022(6) Å and 1.388(6) Å, respectively. The C–C–C bond angles in the cyclopentadienyl rings are 108.0(6)°. These values agree with the ferrocene reported by Dunitz et al. [20] within the experimental error.

The flexible spacer (C18–C26) is regarded as an almost all-*trans* conformation with 180° torsion angles differing by less than 5°. The length of nonyl chain is 9.987(8) Å long, and the length of the C–C–C unit of extended normal paraffin is 2.54 Å long. Then, the length of the nonyl chain (9.987(8) Å) is nearly equal to the those of extended one

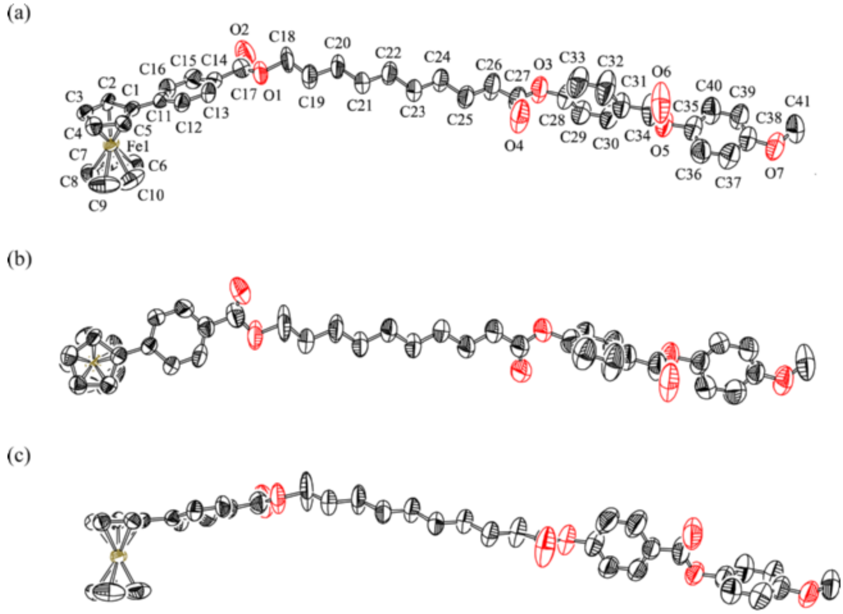

FIGURE 2 ORTEP-3 [8] view of the molecular structure of MPAF-9. Thermal ellipsoids are drawn at 50% probability: a) the crystallographic numbering scheme; b) overview of the cyclopentadienyl rings, and c) side view onto the cyclopentadienyl rings.

(10.16 Å long by 2.54 × 4). Therefore, it is considered that the structure of the flexible spacer is fully extended. Almost all-*trans* conformations of the flexible spacer have been observed in MPAF-2 [12], MPAF-4 [13], the *B* molecule of MPAF-5 [14], MPAF-6 [15], MPAF-7 [19], MPAF-10 [16], and MPAF-11 [17]. This fact suggests that the spacer has almost all-*trans* conformation if the methylene chain is within the range of short length to undecyl.

The molecule has a slightly bent conformation at around the C18 atom (C1–C18–C41). This slightly bent structure may play an important role in giving rise to the mesomorphism described later. Such a bent structure has already been observed in MPAF-2 [12], MPAF-4 [13], MPAF-6 [15], MPAF-10 [16], and MPAF-11 [17].

Almost all of the odd-numbered MPAF-*n* exhibit nonliquid crystallinity except for MPAF-9 and MPAF-11 [17]. It is clear that MPAF-9 is the shortest member to exhibit liquid crystallinity in the odd-numbered MPAF-*n*. Thus, this is an interesting sample because it exhibits mesophase. In the nonliquid-crystalline odd members, each member has some features that are different from those of other

TABLE 2 Dihedral Angle Between Least-Squares Planes of MPAF-9

Plane no.	Least-squares plane	Dihedral angle (°)
Plane 1	Substituted Cp-ring	0.3(7)
Plane 2	Unsubstituted Cp-ring	13.3(2)
Plane 3	Phenyl ring (C11 ~ C16)	88.2(4)
Plane 4	Phenyl ring (C28 ~ C33)	
Plane 5	Phenyl ring (C35 ~ C40)	
Plane 1–Plane 2		
Plane 1–Plane 3		
Plane 4–Plane 5		

liquid-crystalline homologues. The molecular structures of MPAF-1 [11] and MPAF-3 [18] are sharply bent conformations, and MPAF-5 [14] and MPAF-7 [19] contain two crystallographically independent molecules in the unit cell. One of the crystallographically independent molecules (A molecule of MPAF-5 and B molecule of MPAF-7) assumed the bent structure, which is disadvantageous to liquid crystallinity. These results restrain their liquid crystallinity. Therefore, MPAF-9 exhibits liquid crystallinity because there is no restriction.

The dihedral angle between least-square planes of MPAF-9 is represented in Table 2. In MPAF-9, the dihedral angles of two phenyl rings (plane4–plane5) in the mesogenic group are estimated to be 88.2(4)°. This is the largest value of the dihedral angle in the homologue of liquid-crystalline one. The dihedral angle of the two phenyl functions installed into the mesogenic unit in MPAF-*n* is shown in Table 3. It has been reported that the large dihedral angle, which is larger than 70°, prevents the mesophase from being exhibited in MPAF-*n*

TABLE 3 Dihedral Angle of Two Phenyl Functions Installed into the Mesogenic Unit

Compound	Dihedral angle (°)
MPAF-4 [13]	69.4(1)
MPAF-6 [15]	68.7(3)
MPAF-9	88.2(4)
MPAF-10 [16]	65.5(3)
MPAF-11 [17]	45.4(10)
MPAF-1 [11]	6.0(7)
MPAF-2 [12]	77.3(2)
MPAF-3 [18]	49.3(2)
MPAF-5 [14]	(A) 78.5(5), (B) 74.8(5)
MPAF-7 [19]	(A) 72.5(7), (B) 73.2(7)

[12,14,19]. Therefore, such a large dihedral angle was considered to be one of the reasons why liquid crystallinity is not exhibited in those homologues. This result shows that even if the dihedral angle in mesogenic group is large, mesophase can be exhibited by elongating the molecular length.

Crystal Structure

The crystal structures placed onto the projections of the *a*–*c* and *b*–*c* planes are shown in Fig. 3a and b, respectively. The molecules are packed in an antiparallel fashion along the crystallographic *c*-axis. It was reported that, in crystal structure, two molecules faced each other including the ferrocenyl moiety and had become a pair in liquid-crystalline MPAF-*n* [13,15–17]. The results of MPAF-9 correspond with our previous report. As already described, the molecule has a slightly bent conformation around the ester group located in the nearest ferrocenyl moiety. The slightly bent structure and molecular packing arrangement allow compact packing, which is an effective filling of the space. The molecules have a head-to-head arrangement between adjacent layers along the *c*-axis and form a layer structure similar to that of the smectic one.

The *b*–*c* side projection (Fig. 3b) suggests that the conformation of each carbonyl group is important for the packing with neighboring molecules. They are in contact at an uncombined distance of about

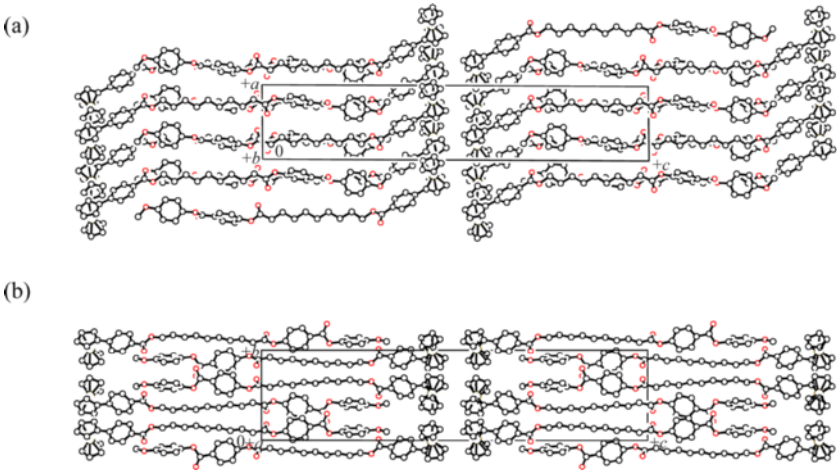

FIGURE 3 Crystal structure of MPAF-9: a) projection of *a*–*c* plane, and b) projection of *b*–*c* plane.

3.8–4.3 Å. The uncombined interatomic distance may cause slight dipole–dipole interaction. These interactions form a network of dipole–dipole interaction, and, as a result, they contribute to the stabilization of liquid-crystalline phases. Therefore, it is possible that this dipole–dipole interaction is one of the important factors for exhibiting liquid crystallinity. These results agree with the other liquid-crystalline MPAF-*n* previously reported [13,15–17].

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