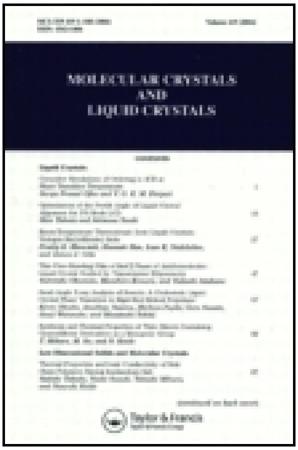

Molecular Crystals and Liquid Crystals

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Synthesis and Physical Properties of Ferrocene Derivatives (XVIII): Crystal Structure of a Liquid-Crystalline Ferrocene Derivative, 10-[4-(4-Methoxyphenoxycarbonyl)phenoxy 4-Ferrocenylbenzoate

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Synthesis and Physical Properties of Ferrocene Derivatives (XVIII): Crystal Structure of a Liquid-Crystalline Ferrocene Derivative, 10-[4-(4-Methoxyphenoxycarbonyl)phenoxycarbonyl] decyl 4-Ferrocenylbenzoate

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The molecular and crystal structures of the title compound, which exhibited smectic C and nematic phases, have been determined by direct methods using single-crystal X-ray diffraction data. The structure was orthorhombic with the space group Pbca and Z = 8. The two cyclopentadienyl rings were an eclipsed conformation, and the flexible spacer was an all-trans conformation, but the molecule was slightly bow-shaped. Additionally, the molecules were packed in an antiparallel fashion, and two molecules had become a pair except for a ferrocenyl moiety. The molecules were in a head-to-head arrangement between contiguity layers and formed a layer structure similar to that of a smectic one. Also, dipole–dipole interaction of carbonyl groups was seen between neighboring molecules.

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

INTRODUCTION

Recently, there has been much interest in the synthesis of metal-containing liquid crystals because of the advantages in combining the properties of liquid crystals and transition metals. Because ferrocene shows remarkable thermal stability and aromaticity, it is easy to make a substitution reaction. A ferrocene derivative containing the mesogenic group is called a metallomesogen.

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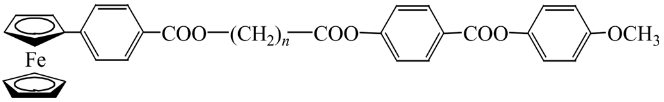

FIGURE 1 General structure of MPAF-*n*.

The monosubstituted ferrocene derivatives are considered to have less or no mesogenity due to the steric hindrance of ferrocene in general. However, it turns out that they can show liquid crystallinity by introducing a flexible spacer (alkyl chain) between the ferrocenylbenzoate and mesogenic groups in our laboratory.

In mesogenic compounds, knowledge of the geometry and packing of the molecule in the crystalline state often helps in explaining the observed phase transition behavior, which depends on a subtle balance of intermolecular interactions. With this aim, an attempt has been made to determine the crystal structures of monosubstituted ferrocene derivatives ω-[4-(4-methoxyphenoxycarbonyl)phenoxycarbonyl]alkyl 4-ferrocenylbenzoate (abbreviated hereafter as MPAF-*n*, where *n* is the number of carbon atoms in the methylene unit). The general chemical structure of MPAF-*n* is shown in Fig. 1.

We have already determined the crystal structures of MPAF-1 [1], 2 [2], 3 [3], 4 [4], 5 [5], 6 [6], 7 [7], and 11 [8]. The molecular structures of MPAF-1 and MPAF-3 were sharply bent and suggest that they show no liquid crystallinity. In fact, they did not show liquid crystallinity [9]. The molecular shapes of MPAF-4, MPAF-6, and MPAF-11 could be regarded as rod-like. Therefore, they show liquid crystallinity and give rise to the mesophase [9]. These results agree with the fact that the rod-like molecular shape is required for the appearance of liquid crystallinity. Although MPAF-2, MPAF-5, and MPAF-7 have similar rod-like forms and crystal structures compared with those of liquid-crystalline MPAF-*n*, they do not exhibit liquid crystallinity. One of the reasons they do not show the liquid-crystalline phase is because the dihedral angle of the phenyl rings in the mesogenic group were relatively large. In MPAF-5 [5] and MPAF-7 [7], another reason was that there was no dipole–dipole interaction of the carbonyl oxygen atoms between the molecules. The crystal structure of MPAF-10 is described and the relation between that structure and liquid-crystalline behavior is also discussed in this article.

EXPERIMENTAL

The crystals of MPAF-10 were obtained from a mixed solvent [ethyl acetate/ethanol (2/1)] solution by the slow evaporation method; the crystal size was $0.60 \times 0.09 \times 0.04\,\mathrm{mm}^3$. Data were collected at 295 K by a Rigaku AFC5*R* four-circle diffractometer using monochromatized Cu-Kα($\lambda = 1.54178\,\text{Å}$), operated at 50 kV and 200 mA. The cell dimensions were obtained from 24 reflections ($18.4^\circ < 2\theta < 26.4^\circ$). Data collection was made by the ω scan technique. Three standard reflections were measured after every 150 in order to monitor the stability of intensity. No significant change was observed. A total of 6,944 unique reflections were measured within the range $-1 < h < 9$, $0 < k < 107$, $-1 < l < 12$, of which 6,922 reflections were above the significant 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.

RESULTS AND DISCUSSION

All calculations were performed using the TEXSAN crystallographic software package from the Molecular Structure Corporation [10]. Corrections were performed with Lorentz and polarization factors and the ψ rotation curve (the minimum and maximum transmission factors were 0.667 and 0.862, respectively). The structure was solved by the direct method of SIR-92 [11] and expanded using the Fourier technique. All hydrogen

TABLE 1 Summarized Crystallographic Data and Results of Final Refinement

Parameter	Value
Empirical formula	$C_{42}H_{44}O_7Fe$
Formula weight	716.62
Crystal system	orthorhombic
Space group	*Pbca*
a/Å	8.176(6)
b/Å	88.253(7)
c/Å	10.139(9)
Volume Å^3	7316(8)
Z value	8
D_{calc}/gcm^{-3}	1.301
Measured reflections	9700
Independent reflections	6944
Observed reflections ($I > -3\sigma(I)$)	6922
Parameters	452
Extinction coefficient	0.0024(4)
R	0.060
wR	0.195
S	1.200

atoms were geometrically fixed and allowed to ride on the corresponding non-H atoms with C−H = 0.95 Å. The H atoms were allowed to ride on their parent atoms with $U_{\mathrm{iso}}(\mathrm{H}) = xU_{\mathrm{eq}}$ (parent), where $x = 1.2$. Hydrogen atoms were included in the structure factor but not refined. An extinction correction was applied, and the extinction coefficient [12] was 0.0024(4). The atomic scattering factors were taken from the International Tables for Crystallography [13]. 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 $R = 0.060$, $wR = 0.195$, $(\Delta/\sigma)_{\mathrm{max}} < 0.001$, $S = 1.200$. A weighing scheme $w = [\sigma_c^2(F_o^2) + (0.05[Max(F_o^2, 0) + 2\ F_c^2]/3)^2]^{-1}$ was used. The crystallographic data are summarized in Table 1. Final data may be obtained from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, U.K. (CCDC No. 298653).

Molecular Structure

Figure 2 represents the ORTEP-3 [14] diagram of the molecular structure of MPAF-10. The bond distances and angles were in agreement with

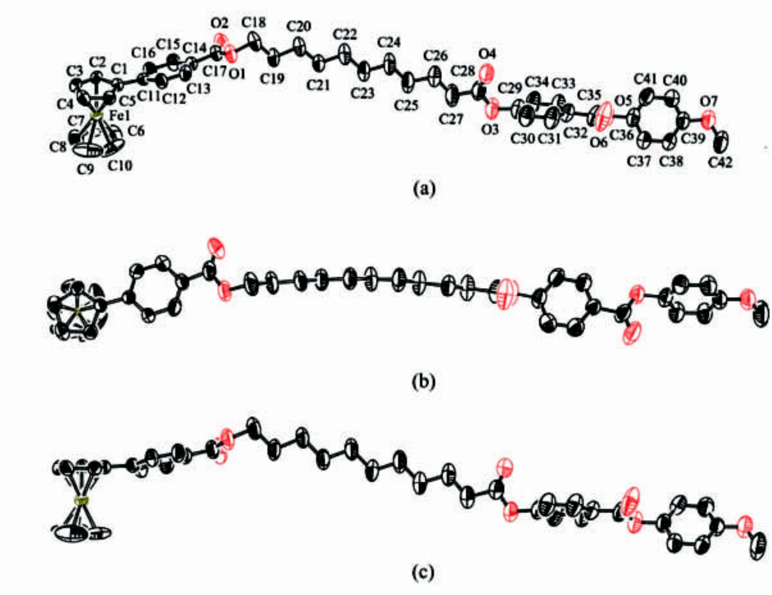

FIGURE 2 *ORTEP*-3 [14] view of the molecular structure of MPAF-10, showing the crystallographic numbering scheme (a), overview onto the cyclopentadienyl rings (b), and side view onto the cyclopentadienyl rings (c).

TABLE 2 Dihedral Angle between Least-Squares Planes of MPAF-10

Plane No.	Least-squares plane	Dihedral angle (°)
Plane1	Substituted Cp-ring	
Plane2	Unsubstituted Cp-ring	
Plane3	phenyl ring (C11 ~ C16)	
Plane4	phenyl ring (C29 ~ C34)	
Plane5	phenyl ring (C36 ~ C41)	
Plane1–Plane2		0.7(5)
Plane1–Plane3		17.5(3)
Plane4–Plane5		65.5(3)

those of the usual values observed in organic compounds within an experimental error.

In the ferrocenyl moiety, two cyclopentadienyl rings were almost parallel, because the dihedral angle was 0.7° as shown in Table 2. Also, the cyclopentadienyl rings could be considered to form the eclipsed type, whereas the ferrocene molecule has the staggered type in two cyclopentadienyl rings. In fact, the staggered one is sometimes observed in disubstituted ferrocene derivatives [15–19], whereas the eclipsed one is found in monosubstituted ferrocene derivatives [1,2,4–6,8] except for MPAF-3 [3] and MPAF-7 [7].

The average values of the Fe-C and C-C bond distances in MPAF-10 are 2.022(7) Å and 1.387(4) Å, respectively. The C−C−C bond angles in the cyclopentadienyl rings are 107.9(6)°. These values were in good agreement with those of ferrocene reported by Dunitz et al. [20] within an experimental error.

In the flexible spacer, the decyl chain (C18–C27) is regarded as an almost all-*trans* conformation with 180° torsion angles differing by less than 5°. It is 11.195(9) Å long. Generally, the length of the C−C−C unit obtained from extended normal paraffin is 2.54 Å long. Using that value, the length of the decyl chain is estimated to be 11.43 Å long by 2.54×4.5. This value (11.43 Å) is nearly equal to the experimental value (11.195 Å). Therefore, it is considered that the structure of the spacer is fully extended. In addition, it has to be noted that the plane of the decyl spacer is coplanar with the ester group in the neighborhood of the mesogenic group. Almost all-*trans* conformations of the flexible spacer have been observed in MPAF-2 [2], MPAF-4 [4], the *B* molecule of MPAF-5 [5], MPAF-6 [6], MPAF-7 [7], and MPAF-11 [8].

The molecule is slightly bent at around the C18 atom (C1—C18—C42). This slightly bent structure may play an important role in giving rise to the mesomorphism described later. Such a bent structure has

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

Compound	Dihedral angle (°)
MPAF-4[4] (LC)	69.4(1)
MPAF-6[6] (LC)	68.7(3)
MPAF-10 (LC)	65.5(3)
MPAF-11[8] (LC)	45.4(10)
MPAF-1[1] (non-LC)	6.0(7)
MPAF-2[2] (non-LC)	77.3(2)
MPAF-3[3] (non-LC)	49.3(2)
MPAF-5[5] (non-LC)	(A) 78.5(5), (B) 74.8(5)
MPAF-7[7] (non-LC)	(A) 72.5(7), (B)73.2(7)}

already been observed in MPAF-2 [2], MPAF-4 [4], MPAF-6 [6], and MPAF-11 [8].

The dihedral angle between least-squares planes of MPAF-10 is represented in Table 2. In the mesogenic group of MPAF-10, the dihedral angle of two phenyl rings is calculated to be 65.5°. Table 3 represents the dihedral angle of two phenyl functions introduced into the mesogenic unit in MPAF-*n*. It has been considered that the value of the dihedral angle in a mesogenic group is smaller than 70° in liquid-crystalline MPAF-*n* [4,6,8]. The value of the dihedral angle in MPAF-10 observed here is 65.5°, which is similar to those of other liquid-crystalline ones.

Crystal Structure

The projections of the *a*–*b* plane and *b*–*c* plane of MPAF-10 are shown in Fig. 3a and b, respectively. The molecules are packed in an antiparallel fashion along the long crystallographic *b*-axis. According to our past report, two molecules faced each other, including the ferrocenyl moiety, and they had become a pair [2,4–8]. In the result of MPAF-10, however, they had become a pair except for the ferrocenyl moiety. As already described, the molecule was slightly bent around the ester group located in the nearest neighbor of the ferrocenyl moiety. The molecular arrangement and slightly bent structure allow for compact packing in the crystal structure, which is an effective occupation of the space. Moreover, the molecules have a head-to-head arrangement between contiguity layers and form a layer structure similar to the smectic one.

According to the *a*–*b* projection (Fig. 3a), it turns out that the conformation of each carbonyl group is important for the packing arrangement. Three carbonyl groups existed in a molecule arranged

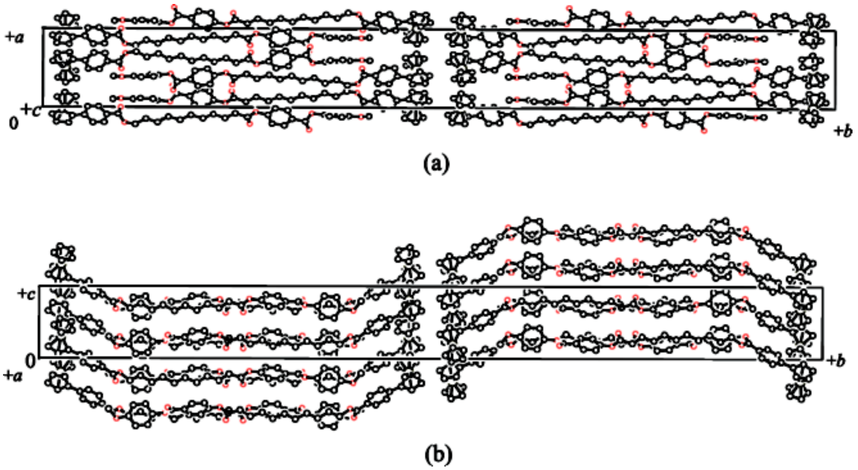

FIGURE 3 Crystal structure of MPAF-10, projection of *a–b* plane (a) and projection of *b–c* plane (b).

almost parallel to the direction of the short axis. They are in contact uncombined distance of about 3.5–5.0 Å. This distance is not long enough because a dipole–dipole interaction occurs. However, the uncombined interatomic distance may cause some amount of 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. Nonliquid-crystalline MPAF-5 [5] and MPAF-7 [7], which are similar to rod-like structures, do not have this interaction. Therefore, it is possible that this dipole–dipole interaction is one of the important factors for liquid crystallinity.

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