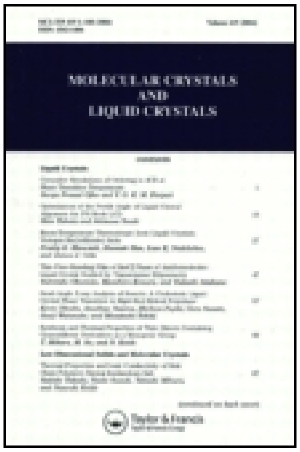

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Syntheses and Physical Properties of Ferrocene Derivatives (VIII) Crystal Structure of a Liquid Crystalline Ferrocene Derivative, ω-[4-(4-methoxyphenoxycarbonyl) phenoxycarbonyl]butyl 4-ferrocenylbenzoate

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Syntheses and Physical Properties of Ferrocene Derivatives (VIII) Crystal Structure of a Liquid Crystalline Ferrocene Derivative, ω-[4-(4-methoxyphenoxycarbonyl) phenoxycarbonyl]butyl 4-ferrocenylbenzoate

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The structure of a monosubstituted ferrocene derivative of which the flexible spacer is located between the ferrocenyl and mesogenic groups, ω-[4-(4-methoxyphenoxycarbonyl)phenoxycarbonyl]butyl 4-ferrocenylbenzoate was determined by the X-ray diffraction method. The —C_4H_8— chain introduced as a flexible spacer is an all-*trans* conformation. The molecule is slightly bent around the ester group to the phenyl ferrocenyl group in order to form a rod-like structure. The molecular geometry is a rod-like feature, and two cyclopentadienyl rings exhibit an eclipsed conformation rather than a staggered one. As a result, this bent structure can lead to efficient packing because it is suitable to make up a bulk of unsubstituted cyclopentadienyl ring, and may play an important role in the appearance of the liquid crystal phase. The molecules are arranged in layers just like the smectic phase of the liquid crystals.

Keywords: Crystal structure; metallocene; ferrocene derivatives; metallomesogen; Liquid crystal

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INTRODUCTION

The liquid crystalline compounds containing transition metal called metallomesogen have been of great interest in recent years. Because the metallomesogen has attracted attention that is expected to show interesting electric, magnetic and chromatic properties.

In our laboratory, two series of monosubstituted ferrocene derivatives were synthesized and studied in regard to the liquid crystallinity of the compounds. One of them is a series of [4-[ω-(cholesteryloxycarbonyl)alkoxycarbonyl]phenyl]ferrocene (abbreviated hereafter as CAPF-*n*, where *n* is the number of carbon atoms in a flexible spacer), and 8 of CAPF-*n* exhibited liquid crystallinity, where $n = 2, 4, 6, 8, 9, 10, 11$ and 15 [1, 2]. Another series is ω-[4-(4-methoxyphenoxycarbonyl)phenoxycarbonyl]alkyl 4-ferrocenylbenzoate (abbreviated hereafter as MPAF-*n*, where *n* is the number of carbon atoms in a methylene unit). The general structure of MPAF-*n* is shown in Figure 1. Only 4 of MPAF-*n* showed liquid crystallinity, where $n = 4, 6, 10$ and 11, whereas 9 kinds of MPAF-*n* were synthesized [3].

X-ray studies on the liquid crystal structure of CAPF-*n* have been made using the powder diffraction method in our laboratory [4], because it was too difficult to obtain the single crystals of these compounds. Recently, three papers describing the crystal structure of the monosubstituted liquid crystalline and related ferrocene derivatives have been published [5–7]. In 1993, the first one was reported by other workers. The crystal structure of CAPF-6 was analyzed using a single crystal and the mechanism of the liquid crystal phase transition was discussed [6]. There are two crystallographically independent molecules in the unit cell. One of them has one *gauche* conformation in the flexible alkyl spacer and as a result the molecule looks rod-like, which is suitable for undergoing the liquid crystal phase transition. In other words, it seems that this conformation may play a very important role in the appearance of the liquid crystal phase. Quite recently, the crystal structure of MPAF-3, which is one of the homologues of the title compounds, was analyzed by present authors [7]. The feature of the molecule is a sharp bent structure. This suggests that it is difficult for MPAF-3 to show liquid

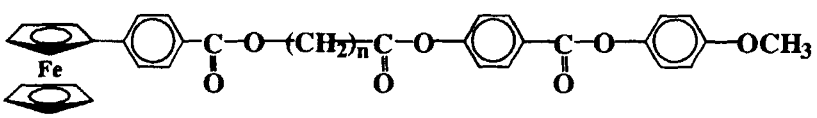

FIGURE 1 General structure of MPAF-*n*.

crystallinity. In fact, MPAF-3, does not show liquid crystallinity as was already reported in our previous paper [3].

In this paper, the crystal structure of MPAF-4 will be presented.

EXPERIMENTAL

The single crystal of the title compound was obtained from a solution with a mixed solvent of benzene and methanol (1:5) by the slow evaporation method. The orange crystals obtained are plate-like having approximate dimensions of $0.4 \times 0.3 \times 0.05$ mm. All measurements were made on a Rigaku AFC-5R diffractometer with graphite monochromatized Cu-Kα radiation ($\lambda = 1.54178$ Å).

The unit cell parameters were obtained by a least-squares refinement of the setting angle of 25 reflections, with 2θ between 18.8 and 26.8°. The data were collected at a temperature of 25 ± 1°C, using the ω-2θ-scan technique to maximize the 2θ value of 120.1°.

5109 reflections were measured, of which 4752 were unique ($R_{\mathrm{int}} = 0.025$). The intensity of three representative reflections were measured after every 150 reflections. Over the course of data collection, the standards decreased by 8.8%. A linear correction factor was applied to the data to account for this phenomenon. The data were corrected for Lorentz and polarization effects and for absorption (Ψ scan; minimum and maximum transmission factors were 0.33 and 1.00, respectively).

The structure was solved by direct methods (SHELX86) [8] and expanded using the Fourier technique. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were introduced at their theoretical positions 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 3544 observed reflections ($I > 3.0\sigma(I)$). The refinement was concluded with final reliability factors:

$$R = \sum(|F_0| - |F_C|) \Big/ \sum |F_0| = 0.043$$

$$R_w = \left(\sum W(|F_0| - |F_C|)^2 \Big/ \sum W{F_0}^2\right)^{1/2} = 0.055$$

where the weighted scheme $W = 1/[\sigma^2(F_0) + 0.00063F_0^2]$.

Final data may be obtained from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge, CB2 1EZ, UK.

RESULTS AND DISCUSSION

Data regarding collection and refinement are summarized in Table I. All calculations were performed using the teXsan crystallographic software package of the Molecular Structure Corporation [9]. Fractional atomic coordinates and equivalent isotropic factors are given in Table II.

The atom labeling along with the molecular conformation is presented in an ORTEP II [10] drawing in Figure 2. The molecular geometry is almost extended and linear in shape. The defined least-squares planes and dihedral angles are given in Table III.

1. Molecular Structure

It might be better to divide this molecular structure into three parts, that is ferrocenyl moiety, flexible spacer and mesogenic group in order to discuss them more exactly.

In ferrocenyl moiety, two cyclopentadienyl rings (plane 1 and plane 2) run parallel to each other with a dihedral angle of 3.17°. Also, the two Cp-rings have an eclipsed conformation rather than a staggered one. This eclipsed conformation is generally found in other monosubstituted ferrocene derivatives [11], while a staggered one is widely observed in disubstituted ferrocene derivatives [12, 13]. The average values of Fe—C and C—C bond distances are 2.04 Å and 1.40 Å, respectively, and all C—C—C bond angles

TABLE I Summarized data regarding collection and refinement

Empirical formula	$C_{36}H_{32}O_7Fe$
Formula weight	632.49
Crystal system	monoclinic
Space group	$P2_1/a$
lattice parameter	
a/Å	7.698(2)
b/Å	10.592(6)
c/Å	36.49(1)
β/°	91.27(2)
Volume/Å^3	2974(1)
Z value	4
D_{calc}/gcm^{-3}	1.412
D_{meas}/gcm^{-3}	1.350
Measured reflections	5109
Independent reflections	4752
Observed reflections ($I > 3.0\sigma(I)$)	3544
R	0.043
R_w	0.055
S	1.51

TABLE II Fractional atomic coordinates and equivalent isotropic temperature factors

Atom	*x*	*y*	*z*	B_{ep}
Fe(1)	0.18309(6)	0.98496(4)	0.06824(1)	3.47(1)
O(1)	0.4626(3)	1.0700(2)	0.26634(6)	4.38(5)
O(2)	0.6125(4)	1.2302(3)	0.24251(7)	5.87(7)
O(3)	0.2296(4)	1.0213(2)	0.45686(6)	5.07(6)
O(4)	0.3453(4)	1.2028(3)	0.43886(7)	6.21(7)
O(5)	0.2128(3)	1.0739(2)	0.62793(6)	4.34(5)
O(6)	0.0361(4)	1.2359(3)	0.61390(7)	5.87(7)
O(7)	0.1260(3)	1.1297(3)	0.77675(6)	5.75(7)
C(1)	0.3889(4)	0.9116(3)	0.09716(8)	3.71(7)
C(2)	0.4422(4)	0.9617(3)	0.06271(9)	4.03(7)
C(3)	0.3525(4)	0.8966(3)	0.03441(9)	4.47(8)
C(4)	0.2423(5)	0.8074(3)	0.0504(1)	4.69(8)
C(5)	0.2642(4)	0.8162(3)	0.08907(10)	4.24(7)
C(6)	0.0699(5)	1.1092(4)	0.1023(1)	5.54(10)
C(7)	0.1354(5)	1.1724(4)	0.0713(1)	6.3(1)
C(8)	0.0466(7)	1.1201(4)	0.0403(1)	6.4(1)
C(9)	−0.0663(6)	1.0304(4)	0.0526(1)	6.1(1)
C(10)	−0.0530(5)	1.0237(4)	0.0899(1)	5.57(10)
C(11)	0.4411(4)	0.9593(3)	0.13379(8)	3.68(7)
C(12)	0.4106(5)	0.8928(3)	0.16572(9)	4.35(8)
C(13)	0.4448(5)	0.9451(3)	0.19985(9)	4.37(8)
C(14)	0.5111(4)	1.0647(3)	0.20329(9)	4.00(7)
C(15)	0.5509(5)	1.1307(4)	0.17150(10)	5.29(9)
C(16)	0.5177(5)	1.0781(4)	0.13777(9)	5.22(9)
C(17)	0.5371(4)	1.1319(3)	0.23882(9)	4.26(8)
C(18)	0.4663(5)	1.1353(4)	0.30088(9)	4.69(8)
C(19)	0.3831(5)	1.0533(4)	0.32899(9)	4.51(8)
C(20)	0.3746(5)	1.1196(4)	0.36556(9)	4.69(8)
C(21)	0.2933(5)	1.0386(4)	0.39473(9)	5.17(9)
C(22)	0.2927(4)	1.1016(3)	0.43145(8)	4.21(8)
C(23)	0.2122(4)	1.0620(3)	0.49330(8)	4.07(8)
C(24)	0.1072(5)	1.1618(3)	0.50164(9)	4.41(8)
C(25)	0.0835(4)	1.1907(3)	0.53792(9)	4.25(7)
C(26)	0.1635(4)	1.1197(3)	0.56562(8)	3.60(7)
C(27)	0.2665(5)	1.0186(3)	0.55643(9)	4.10(7)
C(28)	0.2925(5)	0.9903(3)	0.51983(9)	4.57(8)
C(29)	0.1295(4)	1.1529(3)	0.60419(9)	3.94(7)
C(30)	0.1854(4)	1.0918(3)	0.66566(8)	3.86(7)
C(31)	0.0953(4)	1.0002(3)	0.68336(9)	4.08(7)
C(32)	0.0727(5)	1.0095(3)	0.72093(9)	4.32(8)
C(33)	0.1408(4)	1.1102(3)	0.73973(9)	4.20(7)
C(34)	0.2346(5)	1.2007(3)	0.72144(10)	4.77(8)
C(35)	0.2568(5)	1.1927(3)	0.68431(9)	4.53(8)
C(36)	0.0366(7)	1.0364(5)	0.7965(1)	7.4(1)

in the Cp-rings are 108.0°. These values were in good agreement with those of ferrocene from the paper [14] within an experimental error. The dihedral angle of the substituted Cp-ring (plane 1) and the adjacent phenyl ring (plane 3) is 19.78°, and that of the plane (plane 1) and the neighboring ester

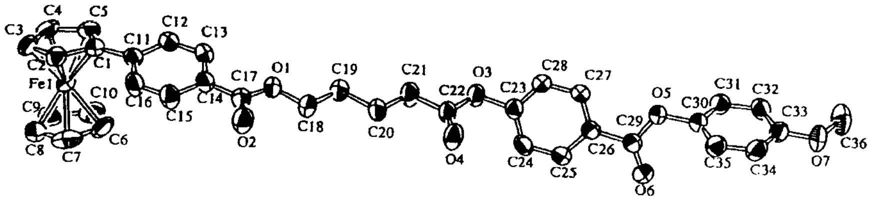

FIGURE 2 ORTEPII (Johnson, 1976) view of the molecular structure, showing the crystallographic numbering scheme. Thermal ellipsoids are drawn at 50% probability.

TABLE III Dihedral angles between least-squares planes

Plane 1	Substituted Cp-ring
Plane 2	Unsubstituted Cp-ring
Plane 3	Phenyl ring (C11~C16)
Plane 4	Phenyl ring (C23~C28)
Plane 5	Phenyl ring (C30~C35)
Plane 6	C(17), O(1), O(2)
Plane 7	C(22), O(3), O(4)
Plane 8	C(29), O(5), O(6)
Plane	*Angle/°*
Plane 1 - Plane 2	3.17
Plane 1 - Plane 3	19.78
Plane 1 - Plane 6	17.40
Plane 4 - Plane 5	69.41
Plane 6 - Plane 7	7.80
Plane 6 - Plane 8	68.86
Plane 7 - Plane 8	61.20

function (plane 6) is 17.40°. Therefore, it is considered that planes 1, 3 and 6 are approximately coplanar.

In the flexible spacer, the —C_4H_8— chain (C18–C21) is regarded as a plane structure with torsion angles differing by less than 1° from the *trans*-conformation (180°) and fully extended plane. The mean values of the C—C bond distance and C—C—C bond angle are 1.49 Å and 120.0°, respectively. The chain length, that is, the spacer length is estimated to be 3.84 Å long. As is well known, the length of the C—C—C unit obtained in the extended normal paraffin is 2.54 Å long. Using this value, the length of the —C_4H_8— chain is calculated to be 3.81 Å long by 2.54×1.5. These values are nearly equal to each other. Therefore, the structure of the spacer is just like that of normal paraffin. In addition to this fact, it has to be noted that the —C_4H_8— spacer is coplanar with both neighbouring ester functions.

In the mesogenic group, the bond distances and angles in the dibenzoate are in agreement with those in other compounds having similar structures already reported [15, 16]. The dihedral angle of two phenyl rings (plane 4 and plane 5) is 69.41 Å and the C26–C29–O5–C30 torsion angle is equal to −177.3(3)°. With respect to similar compounds having a dibenzoate mesogen [15, 16], it is clear that the corresponding dihedral angle indicates an inherent value in each case. The length of the mesogenic group (C22–C33) is calculated as 11.34 Å long.

As a result, the whole molecular length (C3–C36) is estimated to be 27.61 Å long. The molecule is slightly bent at the C17 atom (C1–C17–C36). This slightly bent structure plays a very important role in giving rise to liquid crystallinity.

2. Crystal Structure

The projections of the structure onto the ($x\,0\,z$) and ($0\,y\,z$) planes are shown in Figures 3 and 4 respectively. The mesogenic groups in the molecule are packed anti-parallel along the long crystallographic *c*-axis.

That is, the molecules are arranged in pairs in a head-to-head manner. This molecular configuration allows highly compact packing of the crystal structure, which is the most effective occupation of the space. As is mentioned above, the molecule is slightly bent around the ester group located at the nearest neighbor of the phenyl ferrocenyl group. This slightly bent structure of the molecule also contributes effectively to the highly compact packing of the crystal structure. Therefore, the molecule looks rod-like in shape, which is very suitable for undergoing the liquid crystalline phase transition. As a result, a layer structure was formed in the crystal. The present structure is somewhat similar to that of a smectic one, as is easily

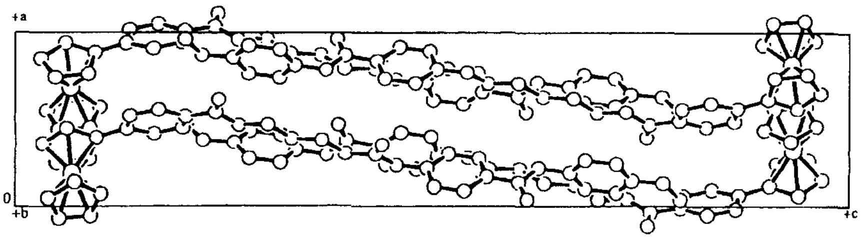

FIGURE 3 Crystal structure of MPAF-4, the projection of the ($x\,0\,z$) plane.

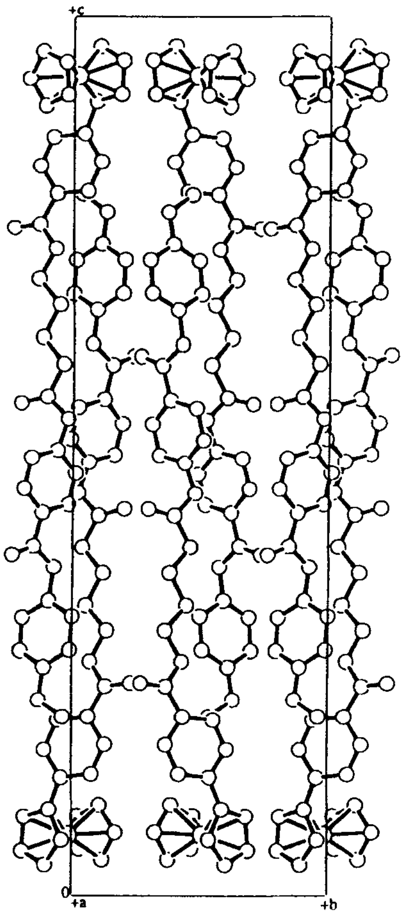

FIGURE 4 Crystal structure of MPAF-4, the projection of the (0*yz*) plane.

understood from Figures 3 and 4, and this crystal structure strongly suggests that the liquid crystal phase of this compound may be smectic.

It is interesting to consider the relation between a space group of the crystal and an appearance of liquid crystallinity. We already analyzed the crystal structures of MPAF-3 [7] and 4. And the structures of MPAF-6 [17], 7 [17], and 11 [18] are not yet completely analyzed, but the space group of these compounds is fixed. According to the results obtained, all compounds which show liquid crystallinity have $P2_1/a$ as the space group, while the compounds which indicate no liquid crystalline phase, that is MPAF-3 and 7, have other space groups, $C2/c$ for MPAF-3 and P-1 for MPAF-7.

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