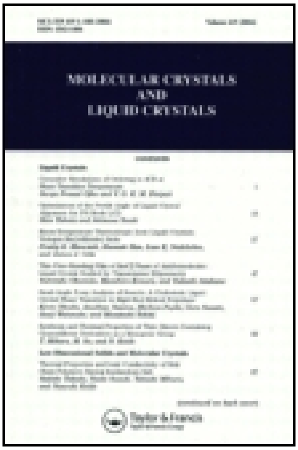

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Syntheses and Physical Properties of Ferrocene Derivatives (IX): Crystal Structure of a Ferrocene Derivative, ω-[4-(4-methoxyphenoxycarbonyl)phenoxy carbonyl]propyl 4-ferrocenylbenzoate

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Syntheses and Physical Properties of Ferrocene Derivatives (IX)

Crystal Structure of a Ferrocene Derivative, ω-[4-(4-methoxyphenoxycarbonyl)phenoxy carbonyl]propyl 4-ferrocenylbenzoate

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The structure of a mono-substituted ferrocene derivative of which the flexible spacer is located between the ferrocenyl and mesogenic groups, ω-[4-(4-methoxyphenoxycarbonyl)phenoxycarbonyl]propyl 4-ferrocenylbenzoate was determined by the X-ray diffraction method. It was found that the two cyclopentadienyl rings in the ferrocene and the —C_3H_6— chain introduced as a flexible spacer exhibited a very interesting conformation. The two cyclopentadienyl rings are a staggered conformation rather than an eclipsed one. This staggered conformation is an unusual structure in mono-substituted ferrocene derivatives, in general. Also, the —C_3H_6— chain includes two *gauche* conformations and makes a bent molecular feature rather than a rod-like one. As a result, the title compound does not exhibit liquid crystallinity.

Keywords: Crystal structure; X-ray diffraction; ferrocene derivative; metallomesogen; liquid crystal

INTRODUCTION

Many kinds of ferrocene derivatives containing a mesogenic group have been synthesized and studied on phase transition phenomena. As ferrocene has an iron atom which is one of the typical transition elements between two cyclopentadienyl (abbreviated hereafter C_p) rings, it is expected that the

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ferrocene derivatives including the mesogenic group exhibit not only liquid crystallinity but also interesting electric, magnetic and chromatic properties. In our laboratory, the ferrocene derivatives having a flexible spacer between the ferrocene and mesogenic group have been investigated using DSC, a polarizing microscope, a X-ray diffractometer and a Mössbauer spectrometer [1 – 10].

Recently, single-crystal structure analysis has been made and an appearance of the liquid crystalline phase has been discussed from a structural point of view [8]. Continuously, the crystal structure of one of the related compounds was analyzed [10]. The sample of the study is ω-[4-(4-methoxyphenoxycarbonyl)phenoxycarbonyl]butyl 4-ferrocenylbenzoate, that is one kind of ω-[4-(4-methoxyphenoxycarbonyl)phenoxycarbonyl]alkyl 4-ferrocenylbenzoate (abbreviated hereafter MPAF-*n*, where *n* is the number of carbon atoms in the alkyl flexible spacer). The general structure of the MPAF-*n* is shown in Figure 1. In 1993, one of the present authors reported that the liquid crystalline phase has been observed in only 4 kinds of MPAF-*n*, which are MPAF-4,6,10 and 11, whereas 9 kinds of MPAF-*n*, which are MPAF-1∼7,10 and 11 have been synthesized [3].

The single-crystal analysis of MPAF-3, of which the liquid crystalline phase was not observed, was carried out by the X-ray diffraction method. In this paper, the exact structure of MPAF-3 will be presented and the liquid crystalline phase transition phenomena of MPAF-*n* will be discussed compared with the structure of the liquid crystalline MPAF-4 [10].

EXPERIMENTAL

The single crystal of the title compound was obtained from a solution with a mixed solvent of benzene and methanol (1 : 7) by the slow evaporation method. The orange crystals obtained are thin-like, having approximate dimensions of 0.6 × 0.3 × 0.05 mm. All measurements were made on a Rigaku AFC-5R diffractometer with graphite-monochromatized Cu-Kα radiation (λ = 1.54178 Å).

The unit cell parameters were obtained by a least-squares refinement of the setting angle of 25 reflections, with 2θ between 19.1 and 27.5°. The data

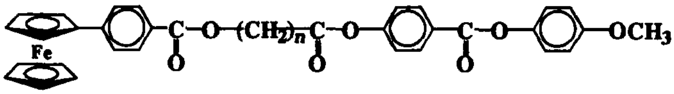

FIGURE 1 General Structure of MPAF-*n*.

were collected at a temperature of 25 ± 1°C using the ω-2θ scan technique to a maximum 2θ value of 120.2°.

4822 reflections were measured, of which 4772 were unique ($R_{\text{int}} = 0.012$). The intensity of three representative reflections were measured after every 150 reflections. Over the course of data collection, the standards decreased by 0.83%. A linear correction factor was not 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 0.95 and 1.00, respectively).

The structure was solved by direct methods (SIR92) [11] 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 3182 observed reflections ($I > 3.0\sigma(I)$). The refinement was concluded with final reliability factors:

$$R = \Sigma(|F_0| - |F_C|)/\Sigma|F_0| = 0.041$$

$$R_w = (\Sigma W(|F_0| - |F_C|)^2/\Sigma WF_0{}^2)^{1/2} = 0.058$$

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 [12]. 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 [13] drawing in Figure 2. The molecular geometry is bent but not an extended shape. The define least-squares planes and the dihedral angles are given in Table III.

This molecular structure could be divided into three parts, that is ferrocenyl phenyl moiety, the flexible spacer and the mesogenic group.

In the ferrocenyl group, two C_p rings (plane 1 and plane 2) are regarded as parallel to each other with a dihedral angle of 1.14°. This angle is very small compared with that of MPAF-4 (3.17°). Also, the two C_p rings occupy the

TABLE I Summarized data regarding collection and refinement

Empirical formula	$C_{35}H_{30}O_7Fe$
Formula weight	618.46
Crystal system	monoclinic
Space group	$C2/c$
Lattice parameter	
a/Å	44.214(9)
b/Å	5.928(3)
c/Å	22.667(4)
β/ °	105.18(1)
Volume/Å^3	5733(2)
Z value	8
D_{calc}/gcm^{-3}	1.433
D_{meas}/gcm^{-3}	1.397
Measured reflections	4822
Independent reflections	4772
Observed reflections ($I > 3.0\sigma(I)$)	3182
R	0.041
R_W	0.058
S	1.43

TABLE II Fractional atomic coordinates and equivalent isotropic temperature factors

atom	x	y	z	B_{eq}
Fe(1)	0.18529(1)	0.4579(1)	0.58851(3)	3.18(1)
O(1)	0.36346(6)	0.6491(5)	0.6218(1)	3.57(6)
O(2)	0.35449(8)	0.9891(5)	0.6564(2)	5.04(8)
O(3)	0.44401(6)	0.1992(5)	0.7436(1)	3.75(6)
O(4)	0.45926(7)	0.5329(5)	0.7140(1)	4.70(7)
O(5)	0.53951(7)	0.3004(5)	1.0019(1)	4.19(7)
O(6)	0.55905(8)	−0.0173(6)	0.9728(1)	5.08(8)
O(7)	0.62338(7)	0.4210(5)	1.2266(1)	4.28(7)
C(1)	0.22678(9)	0.4438(7)	0.6549(2)	3.22(8)
C(2)	0.2149(1)	0.2242(7)	0.6379(2)	3.98(10)
C(3)	0.1851(1)	0.2050(8)	0.6491(2)	4.4(1)
C(4)	0.1781(1)	0.4106(8)	0.6732(2)	4.0(1)
C(5)	0.20350(10)	0.5606(8)	0.6767(2)	3.66(9)
C(6)	0.1879(2)	0.686(1)	0.5236(2)	7.0(2)
C(7)	0.1896(1)	0.467(1)	0.5019(2)	6.6(2)
C(8)	0.1619(2)	0.3586(10)	0.5031(2)	6.2(1)
C(9)	0.1438(1)	0.513(1)	0.5248(3)	6.8(2)
C(10)	0.1599(2)	0.709(1)	0.5373(3)	7.2(2)
C(11)	0.25701(9)	0.5362(7)	0.6505(2)	3.23(8)
C(12)	0.26838(9)	0.7395(7)	0.6771(2)	3.64(9)
C(13)	0.29673(10)	0.8252(7)	0.6724(2)	3.60(9)
C(14)	0.31481(9)	0.7075(7)	0.6418(2)	3.16(8)
C(15)	0.3039(1)	0.5013(7)	0.6162(2)	4.1(1)
C(16)	0.2752(1)	0.4184(8)	0.6192(2)	4.2(1)
C(17)	0.34589(9)	0.8012(7)	0.6412(2)	3.42(9)
C(18)	0.39469(9)	0.7223(7)	0.6212(2)	3.67(9)
C(19)	0.41105(9)	0.5254(8)	0.6021(2)	3.60(9)
C(20)	0.41683(8)	0.3291(7)	0.6469(2)	3.21(9)
C(21)	0.44234(9)	0.3754(7)	0.7042(2)	3.13(8)
C(22)	0.46808(8)	0.1939(7)	0.7986(2)	3.05(8)

TABLE II (Continued)

atom	*x*	*y*	*z*	B_{eq}
C(23)	0.47278(9)	0.3684(7)	0.8397(2)	3.45(9)
C(24)	0.49595(10)	0.3479(7)	0.8940(2)	3.47(9)
C(25)	0.51409(9)	0.1537(6)	0.9061(2)	2.86(8)
C(26)	0.50868(9)	−0.0200(7)	0.8638(2)	3.36(9)
C(27)	0.48534(9)	−0.0024(7)	0.8099(2)	3.24(9)
C(28)	0.53978(9)	0.1289(7)	1.9625(2)	3.34(9)
C(29)	0.56315(9)	0.3160(7)	1.0574(2)	3.40(9)
C(30)	0.5799(1)	0.5136(7)	1.0669(2)	3.66(9)
C(31)	0.60069(9)	0.5547(7)	1.1232(2)	3.48(9)
C(32)	0.60446(9)	0.3964(7)	1.1689(2)	3.20(8)
C(33)	0.58772(9)	0.1937(7)	1.1574(2)	3.55(9)
C(34)	0.56693(9)	0.1536(7)	1.1022(2)	3.34(9)
C(35)	0.6381(1)	0.6310(8)	1.2416(2)	4.5(1)

TABLE III Dithedral 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 (C22∼C27)
Plane 5:	Phenyl ring (C29∼C34)
Plane 6:	C(17), O(1), O(2)
Plane 7:	C(21), O(3), O(4)
Plane 8:	C(28), O(5), O(6)

Plane	Angle/°
Plane 1 – Plane 2	1.14
Plane 1 – Plane 3	9.98
Plane 1 – Plane 6	176.27
Plane 4 – Plane 5	49.32
Plane 6 – Plane 7	81.19
Plane 6 – Plane 8	119.13
Plane 7 – Plane 8	118.98

staggered conformation rather than the eclipsed one. This staggered conformation is rarely seen in other mono-substituted ferrocene derivatives, whereas the staggered one is generally observed in di-substituted derivatives [14, 15]. This very small dihedral angle observed in MPAF-3 may be attributed to the staggered conformation. The average values of the Fe — C and C — C bond distances are 2.04 and 1.40 Å, respectively, and those of all C —C —C bond angles in two C_p rings is 108.0°. These values were in good agreement with those of literature within an experimental error [16]. The dihedral angle of the substituted C_p ring (plane 1) and adjacent phenyl group (plane 3) is 9.98°, and this value is almost the half of that of MPAF-4 (19.78°). Another dihedral angle of plane 1 and the neighboring ester function (plane 6) is estimated to be 176.27°. This fact suggested that the planes 1,3 and 6 are almost in coplanarity.

Two benzoate groups are included in the mesogenic one. The bond lengths of C — C and the C — C — C bond angles of both phenyl groups are ordinary ones observed in many other organic compounds [17], and MPAF-4 has nearly the same values in those [10]. The dihedral angle of the two phenyl groups is 49.32° and the C — C — O — C torsion angle existing between the two phenyl groups is −176.7°. These values are almost the same as the corresponding values of MPAF-4. Therefore, it is considered that the structures of the mesogenic group in MPAF-3 and 4 are quite similar to each other.

It has been noted that the very characteristic structure is observed in the flexible spacer of MPAF-3. The flexible spacer of MPAF-3 is constructed by three carbon atoms: C18, C19 and C20, as is shown in Figure 2. The bond lengths of C18 — C19 and C19 — C20 are 1.495 and 1.520 Å, respectively. These values are quite reasonable. The torsion angle of O1 — C18 — C19 — C20 is −65.0°, whereas those of C17 — O1 — C18 — C19 and O3 — C21 — C20 — C19 are 176.5° and 174.8°, respectively. In other words, the bonds of C17 — O1 and C18 — C19 are approximately parallel to each other and the same geometry is observed in a relation of the C19 — C20 and O3 — C21 bonds. But the spacer is bent at C19, as is easily understood in Figure 2. This structure is a distinctive characteristic. It is considered that this bent structure, not a rod-like one, is strongly influenced by the disappearance of the liquid crystallinity of this compound. By the way, normal torsion angles were observed in the flexible spacer of MPAF-4 which exhibited the liquid crystalline phase.

Projection of the *a*-*c* plane is shown in Figure 3. The ferrocenyl phenyl group is parallel to that of neighboring molecules and the mesogenic moiety is also parallel to that of neighboring molecules, independently. It is a reasonable result that the mesogenic moiety arranges in a parallel fashion. However, the fact that the ferrocenyl phenyl group also arranges in a parallel way suggests that the ferrocenyl phenyl one is able to behave as the mesogenic one. This is possible if we consider that the ferrocenyl phenyl group constructs with direct connection of the cyclopentadienyl ring with the phenyl group. Namely, the ferrocenyl phenyl group may play a role just like the role of the biphenyl one as a mesogen, that is constructed with direct connection of the phenyl group with another phenyl one. From another point of view, the structure is similar to but not the same as that of the herringbone motif of α, ω-disubstituted normal long-chain alkanes with even carbon numbers [18, 19]. It is interestingly evident that the space group

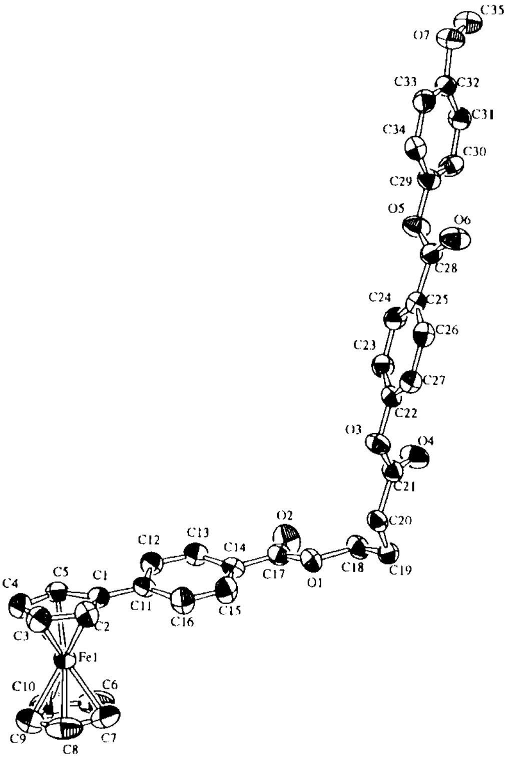

FIGURE 2 *ORTEP* II (Johnson, 1976) view of the molecule, showing the crystallographic numbering scheme. Thermal ellipsoids are drawn at 50% probability.

of MAPF-3 is C2/*c*, while those of MPAF-4 [10] and MPAF-11 [20] are $P2_1/a$, both exhibiting liquid crystallinity. Although this kind of bent structure in MPAF-*n* may be considered as a curious one, the structure of MPAF-3 analyzed in this study is considered to be correct, because the reliability constant, that is the R-factor, is 4.1% as is already shown in Table I, and the value of the goodness of fit indicator, that is the S value in Table I, is 1.43, which is quite a reasonable value.

As is well known, the molecular shape of liquid crystalline compounds is rod-like in general, except the molecules which exhibited a discotic liquid crystallinity. Model structures of the liquid crystalline phase have been proposed by one of the present authors on the basis of X-ray diffraction measurements [5, 7]. In the study, the sample was [4-[ω-(cholesteryloxy-carbonyl)alkoxycarbonyl]phenyl]ferrocene (abbreviated hereafter CAPF-*n*, where *n* is the number of carbon atoms in the alkyl chain as the flexible spacer). Quite recently, the molecular structure and a mechanical liquid

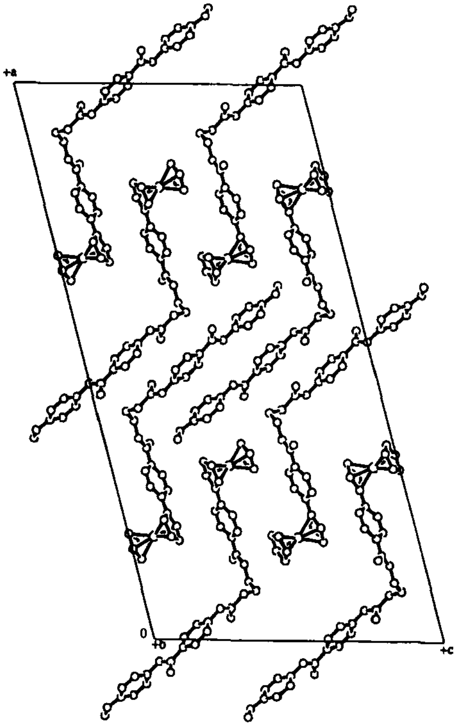

FIGURE 3 Crystal structure of MPAF-3, the projection of the *a-c* plane.

crystalline phase transition model of CAPF-6 [8] were reported. In addition to these papers, the molecular structure of MPAF-4 was analyzed [10]. These structure are regarded as rod-like and similar to each other. Therefore, it is considered that the phase transition mechanism proposed for CAPF-6 is probably applicable to that of MPAF-4. In contrast with this, it is very difficult to apply the same consideration to the liquid crystalline phase transition of MPAF-3 because of the sharp bent structure as is indicated in Figure 2. As a result, MPAF-3 does not exhibit liquid crystallinity.

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