Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Syntheses and Physical Properties of Ferrocene Derivatives (XVI): Crystal Structure of a Liquid Crystalline Ferrocene Derivative, 5-[4-(4-Methoxyphenoxycarbonyl) Phenoxycarbonyl] Pentyl4-Ferrocenylbenzoate

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Version of record first published: 18 Oct 2010

Mol. Cryst. Liq. Cryst., Vol. 383, pp. 27–35

1058-725X/02 $12.00 + .00
DOI: 10.1080/10587250290120305

SYNTHESES AND PHYSICAL PROPERTIES OF FERROCENE DERIVATIVES (XVI): CRYSTAL STRUCTURE OF A LIQUID CRYSTALLINE FERROCENE DERIVATIVE, 5-[4-(4-METHOXYPHENOXYCARBONYL) PHENOXYCARBONYL] PENTYL 4-FERROCENYLBENZOATE

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The crystal structure of a monosubstituted ferrocene derivative, 5-[4-(4-methoxyphenoxycarbonyl)phenoxycarbonyl]pentyl 4-ferrocenylbenzoate was determined by the X-ray diffraction method using a single crystal. The unit cell of the crystal contained two crystallographically unequivalent molecules, A *and* B. *The* $-C_5H_{10}-$ *chain introduced into molecules* A *and* B *as a flexible spacer was an all-*trans *conformation. Both molecules were slightly bent around the ester group located at the nearest neighbor of the ferrocenylbenzoate section, but the shape of the molecules could be regarded as rodlike. This compound was a nonliquid crystalline compound; however, its structure was similar to that of the homologues, which gave rise to smectic liquid crystalline phases.*

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

INTRODUCTION

Metallomesogens, the liquid crystalline compounds containing a transition metal, have been of great interest in recent years, because of their electric, magnetic, and chromatic properties. Ferrocene is one of the metallocenes, and it shows remarkable thermal stability and aromaticity.

Received 2 April 2002; accepted 25 June 2002.

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In our laboratory, a series 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) were prepared. The general chemical structure of MPAF-n is shown in Figure 1. The liquid crystallinity of MPAF-n was studied using a differential scanning calorimeter (DSC), a polarizing optical microscope (POM), wide-angle and small-angle X-ray diffraction systems (WAXD and SAXD, respectively), a dielectric dispersion measurement apparatus, and so on. Some of them (MPAF-4, 6, 8, 9, 10, and 11) exhibited liquid crystallinity [1,2].

The aims of structure analysis of liquid crystalline compounds are to gain an understanding of the interrelation between the crystal structure and some physical properties and to discuss the mechanism of the appearance of the liquid crystalline phase. We have already determined the crystal structures of MPAF-1, 2, 3, 4, 6, 7, and 11. The molecular structures of MPAF-1 [3] and MPAF-3 [4] were sharply bent structures. Because typical liquid crystalline compounds are rodlike, these results suggest that it is difficult for them to show liquid crystallinity. In fact, MPAF-1 and MPAF-3 didn't show liquid crystallinity [1]. On the other hand, the molecular structures of MPAF-4 [5], MPAF-6 [6], and MPAF-11 [7] could be regarded as rodlike. In fact, they have the advantage of showing liquid crystallinity, and they give rise to liquid crystallinity[1]. The remaining MPAF-8, MPAF-9, and MPAF-10 showed liquid crystallinity, while MPAF-5 showed nonliquid crystallinity. But their crystal structures have not been analyzed yet.

In this paper, the crystal structure of MPAF-5 will be presented. The results will be discussed by comparing them with those of MPAF-n, which has already been analyzed.

EXPERIMENTAL

The sample, MPAF-5, was synthesized in accordance with the method mentioned in our previous paper [1]. The single crystal of the compound was obtained from a solution with a mixed solvent of ethyl acetate and ethanol (1:4) by the slow evaporation method. The single crystals obtained are orange in color and platelike. The sample, which had the approximate dimensions of $0.4 \times 0.4 \times 0.3$ mm, was mounted on the goniometer.

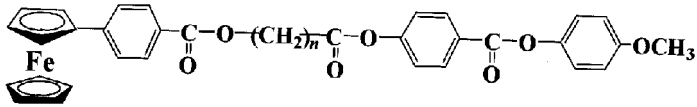

FIGURE 1 General structure of MPAF-n.

All measurements were carried out by a Rigaku AFC-5R diffractometer operated at 50 kV and 200 mA. The X-ray beam was monochromatized to Cu-Kα ($\lambda = 1.54178$ Å) with a graphite single crystal.

The unit cell parameters were obtained from a least-squares refinement using the setting angle of 25 reflections in the range of $19.09^\circ < 2\theta < 27.36^\circ$. The data were collected at 296 $\pm$ 1K using the ω-scan technique to a maximum 2θ value of 140.3°.

The 7403 reflections were measured, of which 6097 were unique ($R_{\text{int}} = 0.017$). The intensities of three representative reflections were measured after every 150 reflections. Over the course of the data collection, the standards decreased by 3.2%. A liner 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 0.851 and 0.999, respectively.)

All calculations were performed using the *TEXSAN* crystallographic software package of the Molecular Structure Corporation [8]. The structure was solved by direct methods (MULTAN88) [9] and expanded using the Fourier technique. All nonhydrogen atoms were refined anisotropically, and all hydrogen atoms were refined isotropically. 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 6084 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. In order to omit the reflections, we used $F^2 > -3.0\sigma(F^2)$ as a threshold. The refinement was concluded with final reliability factors:

$$R = \Sigma(F_o^2 - F_c^2)/\Sigma F_o^2 = 0.050 \qquad \text{for } F^2 > -3.0\sigma(F^2),$$

$$wR = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2} = 0.129,$$

where the weighted scheme $w = 1/[\sigma^2(F_o^2) + \{0.07[\text{Max}(F_o^2, 0) + 2F_c^2]/3\}^2]$. In addition, $R1$ value using normal threshold ($F^2 > 2.0\sigma(F^2)$) based on 4423 observed reflections was also calculated:

$$R1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o| = 0.039 \quad \text{for} \quad F^2 > 2.0\sigma(F^2).$$

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 1. The molecular conformation with numbering for each atom is

TABLE 1 Summarized Data Regarding Collection and Refinement

Empirical formula	$C_{37}H_{34}O_7Fe$
Formula weight	646.52
Crystal system	Monoclinic
Space group	$P2_1$
Lattice parameter	
a/Å	8.860(3)
b/Å	9.955(4)
c/Å	36.092(3)
β/°	97.01(2)
Volume/Å^3	3159(1)
Z value	4
D_{calc}/gcm^{-3}	1.359
Measured reflections	7403
Independent reflections	6097
Observed reflections (F^2 $-3.0(F^2)$)	6084
R	0.050
wR	0.129
Goodness of fit (S)	1.12
Observed reflections ($F^2 > 2.0(F^2)$)	4423
$R1$	0.039

presented in an *ORTEP*II [10] drawing in Figures 2 and 3. The two crystallographically unequivalent molecules, ***A*** and ***B***, exist in the unit cell. As is shown in these figures, these molecules are slightly bent at around C17 and C17′ atoms in MPAF-5, nearly the same as MPAF-*n* (already analyzed). The defined least-squares planes and dihedral angles are given in Table 2.

Molecular Structure

The bond distances and angles are in agreement with those of usual values observed in organic compounds within an experimental error.

In the ferrocenyl moiety, two cyclopentadienyl rings (planes 1 and 2) run parallel to each other with dihedral angles of 0.6(6)° and 0.9(6)° for molecules ***A*** and ***B***, respectively. Also, the two cyclopentadienyl rings in both molecules have an eclipsed conformation rather than a staggered one. The eclipsed conformation of this kind has been observed in MPAF-1, 2, 4, 6, 7 and 11, except for MPAF-3 [4]. In MPAF-5, the average values of Fe-C and C-C bond distances are 2.02(2) Å and 1.39(3) Å for molecule ***A*** and 2.03(2) Å and 1.40(3) Å for molecule ***B***, respectively. C-C-C bond angles in the cyclopentadienyl rings are 108(2)° for both molecules ***A*** and ***B***. These values were in good agreement with those of ferrocene from Dunitz et al. [11] within an experimental error.

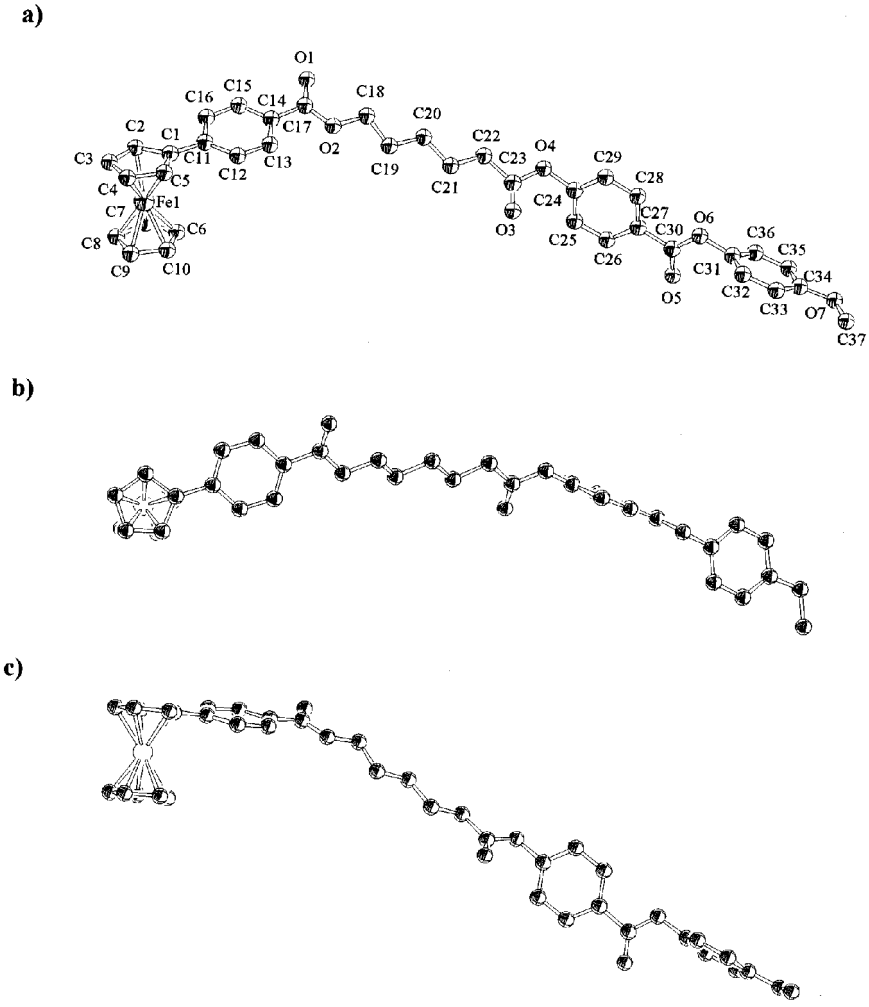

FIGURE 2 *ORTEP*II [10] view of the molecular structure in MPAF-5 (molecule *A*), (a) showing the crystallographic numbering scheme, (b) overview onto the cyclopentadienyl rings, and (c) side view onto the cyclopentadienyl rings.

In the mesogenic group, the dihedral angles of two phenyl rings (planes 4 and 5) are calculated to be 78.5(5)° and 74.8(5)° for molecules *A* and *B*, respectively. These values are relatively large, especially 78.5(5)° for molecule *A*, which is the largest one in those of MPAF-*n* already analyzed. Table 3 shows the dihedral angles obtained from our previous work on MPAF-*n* [3–7, 12]. The average dihedral angle of liquid crystalline MPAF-*n*

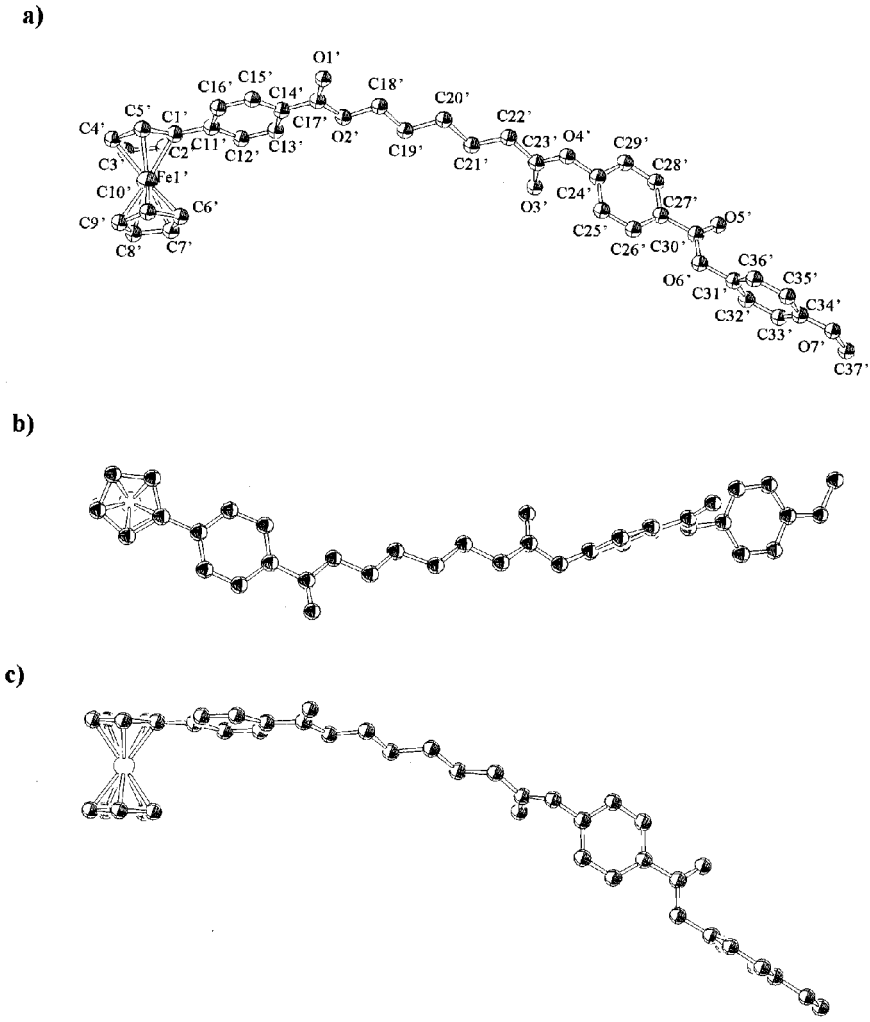

FIGURE 3 *ORTEP*II [10] view of the molecular structure in MPAF-5 (molecule *B*), (a) showing the crystallographic numbering scheme, (b) overview onto the cyclopentadienyl rings, and (c) side view onto the cyclopentadienyl rings.

was 61.21° [5]. As is easily seen, those of rodlike nonliquid crystalline MPAF-2 and MPAF-7 are larger than those of liquid crystalline MPAF-*n*. Probably the large dihedral angle prevents an attractive interaction between the phenyl benzoate groups in the neighboring molecules. Therefore, these large values may be related to the disappearance of liquid crystallinity.

TABLE 2 Dihedral Angles Between Least-squares Planes

	Least-Squares Planes	
Plane No.	*Molecule A*	*Molecule B*
Plane 1	substituted Cp-ring	substituted Cp-ring
Plane 2	unsubstituted Cp-ring	unsubstituted Cp-ring
Plane 3	phenyl ring (C11 ~ C16)	phenyl ring (C11′ ~ C16′)
Plane 4	phenyl ring (C24 ~ C29)	phenyl ring (C24′ ~ C29′)
Plane 5	phenyl ring (C31 ~ C36)	phenyl ring (C31′ ~ C36′)
	Dihedral angle/ °	
Plane	*Molecule A*	*Molecule B*
Plane 1-Plane 2	0.6(6)	0.9(6)
Plane 1-Plane 3	14.0(5)	12.4(5)
Plane 4-Plane 5	78.5(5)	74.8(5)

Crystal Structure

The crystal structures placed onto the projections of the *a*-*c* plane and *b*-*c* plane are shown in Figures 4 and 5. The molecules are packed in an anti-parallel fashion along the long crystallographic *c*-axis. That is, the molecules are arranged in pairs in a head-to-head manner. The molecular arrangement allows compact packing in the crystal structure, which is an effective occupation of the space. As is mentioned above, the molecules are slightly bent around the ester group located at the nearest neighbor of the ferrocenylbenzoate section. This slight bending of the molecular structure also contributes effectively to compact packing of the molecules in the crystal. As a result, a layer structure was formed in the crystal. The present

TABLE 3 Dihedral Angles of Two Phenyl Functions Introduced in Mesogenic Unit

	Dihedral angle/°
MPAF-1	6.0(9)
MPAF-2	77.3(2)
MPAF-3	49.3(2)
MPAF-4	69.4(1)
MPAF-5	(*A*)78.5(5), (*B*)74.8(5)
MPAF-6	68.7(3)
MPAF-7	(*A*)72.5(7), (*B*)73.2(7)
MPAF-11	45.4(10)

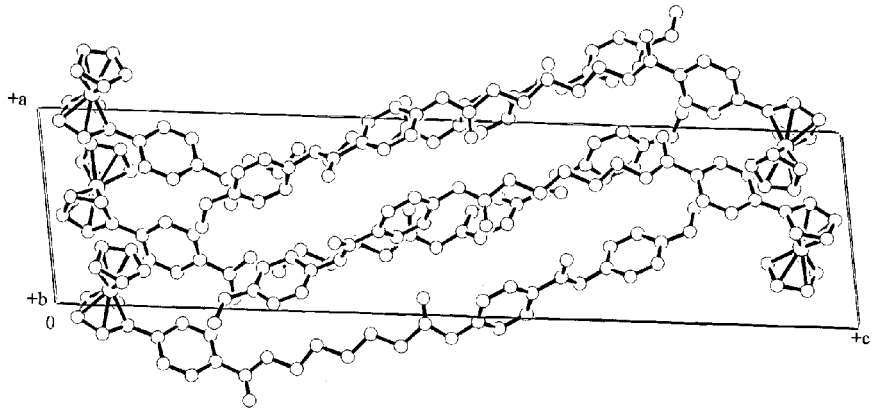

FIGURE 4 Crystal structure of MPAF-5, the projection of the *a*-*c* plane.

structure is somewhat similar to that of the smectic one, as is easily understood from Figures 4 and 5.

In the crystal structures of liquid crystalline MPAF-*n*, carbonyl oxygen atoms induced the dipole-dipole interactions between the neighboring molecules. Depending on the existence of these dipole-dipole interactions, intermolecular attractions and molecular orientation became stronger. In contrast, MPAF-5 and other nonliquid crystalline MPAF-*n* do not have such dipole-dipole interactions. Therefore, it is considered that these interactions affect the appearance of liquid crystallinity.

In addition to the above discussion, one more interesting relation has to be noted. It seems likely that a relation exists between the space group of the crystal and the appearance of liquid crystallinity. The crystal structures

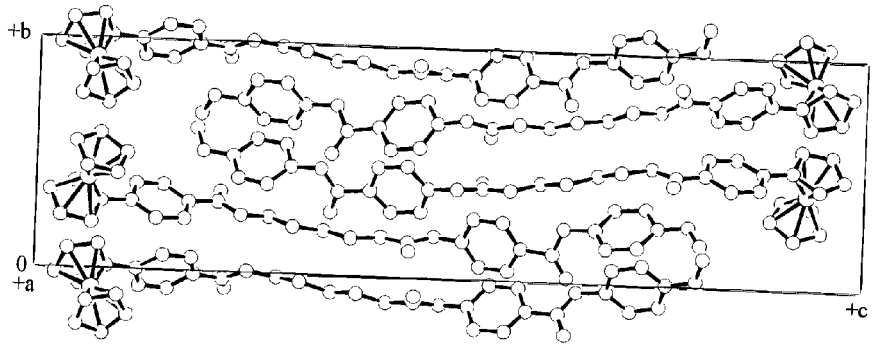

FIGURE 5 Crystal structure of MPAF-5, the projection of the *b*-*c* plane.

of MPAF-1 [3], MPAF-2 [12], MPAF-3 [4], MPAF-4 [5], MPAF-6 [6], MPAF-7 [13] and MPAF-11 [7] have already been analyzed in our laboratory. According to these results, all compounds which show liquid crystallinity have $P2_1/a$ as the space group, while the compounds which have no liquid crystalline phase, that is MPAF-1, MPAF-3 and MPAF-7, have different space groups $C2/c$ for MPAF-1 and MPAF-3, and $P\text{-}\bar{1}$ for MPAF-7. The space group of MPAF-5 analyzed in this study was $P2_1$. This suggests that MPAF-5 shows nonliquid crystallinity. In fact, MPAF-5 gave rise to non-liquid crystallinity. This may be another important point for the appearance of the liquid crystallinity of MPAF-n.

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