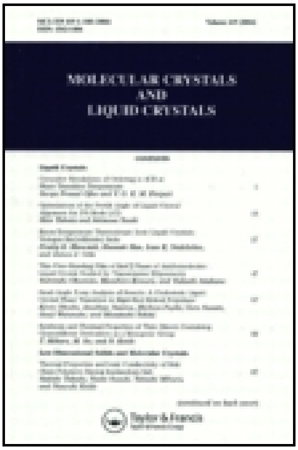

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Syntheses and Physical Properties of Ferrocene Derivatives (XV) Crystal Structure of a Liquid Crystalline Ferrocene Derivative, ω-[4-(4-Methoxyphenoxycarbonyl)Phenoxy Undecyl 4-Ferrocenyl-Benzoate

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Syntheses and Physical Properties of Ferrocene Derivatives (XV) Crystal Structure of a Liquid Crystalline Ferrocene Derivative, ω-[4-(4-Methoxyphenoxycarbonyl)Phenoxycarbonyl] Undecyl 4-Ferrocenyl-Benzoate

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The crystal structure of a liquid crystalline monosubstituted ferrocene derivative, ω-[4-(4-methoxyphenoxycarbonyl)phenoxycarbonyl]-undecyl 4-ferrocenyl-benzoate was determined by the single-crystal X-ray structure analysis. The flexible spacer(undecyl chain) was an all-*trans* conformation. In order to form a rod-like structure, the molecule is slightly bent at the substituted group bonding the ferrocene. Two cyclopentadienyl rings made up an eclipsed type rather than a staggered one. The molecules are arranged in layers just like those in the smectic phase of the liquid crystals. The aspect of dipole-dipole interaction, however, was different from that of other homologues with even number of carbon atoms in the flexible spacer.

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

INTRODUCTION

In our laboratory, many different kinds of metallomesogens were synthesized and investigated in several properties, for example, thermal properties, dielectric properties, crystal structures, Mössbauer effect and so on [1-14]. Especially, a series of monosubstituted ferrocene derivatives, ω-[4-(4-methoxyphenoxycarbonyl) phenoxycarbonyl]alkyl 4-ferrocenylbenzoate (hereafter MPAF-*n*, where *n* is the number of carbon atoms in a methylene unit) were studied from a viewpoint of liquid crystallinity in detail. 9 kinds of MPAF-*n* (*n*=1~7, 10 and 11) were synthesized and MPAF-4, 6, 10 and 11 showed liquid crystallinity [3]. Recently, MPAF-8 and 9 are synthesized and we ascertained liquid crystallinity [15]. The general structure of MPAF-n is given in our previous paper [3].

The molecular structure and crystal one of the liquid crystalline compounds are very important in order to discuss a interrelation between the structures and the several physical properties including liquid crystallinity. Recently, the molecular and crystal structure of MPAF-2 [12], MPAF-3 [11], MPAF-4 [10] and MPAF-6 [13] was reported.

In this paper, the interrelation between crystal structure and liquid crystallinity of MPAF-11 will be described in detail as well as its crystal structure.

EXPERIMENTAL

The sample, MPAF-11, was synthesized in accordance with the established method [3]. The orange plate-like single-crystal of MPAF-11 was obtained by the slow evaporation method employed a solution with a mixed solvent of dichrolomethane and hexane (3 : 1). All measurements were made by a Rigaku

AFC-5R diffractometer with graphite monochromatized Cu-Kα radiation.

Unit cell parameter and an orientation matrix for the data collection were obtained by a least-squares refinement of 25 reflections set the 2θ angle between 41.20 and 47.70 °. The data were collected using the ω-2θ scan technique to maximize the 2θ value of 100.0 ° at the room temperature (25±1°C).

3355 reflections were collected, of which 2678 were unique (R_{int}=0.096). The data were corrected for Lorentz and polarization effects and for absorption (φ scan [16]).

The structure was solved by direct method(SHELEX 86) [17] and expanded using the Fourier technique. The final refinement was made by full-matrix least-squares based on 1447 observed reflections ($I>3.0\sigma(I)$). The refinement was concluded with final reliability factors:

$$R = \Sigma(|F_0| - |F_C|)/\Sigma|F_0| = 0.086$$

$$R_W = (\Sigma W(|F_0| - |F_C|)^2/\Sigma WF_0^2)^{1/2} = 0.098$$

where the weighted scheme $W = 1/[\sigma^2(F_0) + 0.000576F_0^2]$.

All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation [18]. Final data may be obtained from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge, CB2 1EZ, UK.

RESULTS and DISCUSSION

The crystallographic data and the results of final refinement are listed in Table 1. Fractional atomic coordinates and equivalent isotropic factors are given in Table 2.

TABLE 1 The summarized crystallographic data and the results of the final refinement.

Empirical formula	$C_{43}H_{46}O_7Fe$
Formula weight	730.68
Crystal system	Monoclinic
Space group	$P2_1/a$
a / Å	7.956(5)
b / Å	10.301(1)
c / Å	45.844(3)
β / °	94.24(2)
Volume / Å^3	3746(2)
Z value	4
D_{meas} / gcm^{-3}	1.283
Measured reflections	3355
Independent reflections	2678
Observed reflections ($I>3.0\sigma(I)$)	1447
Parameter	460
p-factor	0.0480
Reflections / Parameter	3.15
R	0.086
R_W	0.098
S	2.29

TABLE 2 The fractional atomic coordinates and the equivalent isotropic temperature factors.

Atom	*x*	*y*	*z*	B_{eq}
Fe(1)	0.2842(4)	0.4881(3)	0.44588(6)	4.23(8)
O(1)	-0.242(2)	0.372(2)	0.2944(3)	6.7(5)
O(2)	-0.405(3)	0.516(2)	0.3134(4)	10.3(7)
O(3)	-0.250(2)	0.415(2)	-0.0580(4)	9.0(6)
O(4)	-0.026(5)	0.326(3)	-0.0326(5)	8.4(9)
O(4')	-0.12(1)	0.29(1)	-0.030(1)	6(1)
O(5)	-0.113(2)	0.418(1)	-0.1909(3)	6.4(5)
O(6)	-0.003(9)	0.212(4)	-0.1818(6)	6(1)
O(6')	-0.104(8)	0.208(4)	-0.1828(6)	5(1)
O(7)	-0.062(2)	0.383(1)	-0.3093(4)	7.9(6)
C(1)	0.073(2)	0.394(2)	0.4261(5)	3.2(6)
C(2)	0.199(3)	0.305(2)	0.4345(5)	4.3(6)
C(3)	0.243(3)	0.321(2)	0.4676(5)	4.8(7)
C(4)	0.140(3)	0.413(2)	0.4763(5)	5.9(7)

(TABLE 2 continued)

Atom	x	y	z	B_{eq}
C(5)	0.042(3)	0.455(2)	0.4525(5)	4.3(6)
C(6)	0.364(7)	0.598(5)	0.4158(8)	11(1)
C(7)	0.495(6)	0.523(4)	0.424(1)	11(1)
C(8)	0.512(4)	0.547(3)	0.453(1)	9.4809
C(9)	0.434(6)	0.633(4)	0.4651(7)	9.2891
C(10)	0.333(4)	0.677(2)	0.439(2)	15.8997
C(11)	0.002(2)	0.401(2)	0.3970(5)	3.6(6)
C(12)	0.015(3)	0.312(2)	0.3753(5)	5.0(6)
C(13)	-0.068(4)	0.328(3)	0.3477(5)	6.5(9)
C(14)	-0.189(4)	0.428(3)	0.3438(5)	5.2(8)
C(15)	-0.204(2)	0.512(2)	0.3638(4)	4.9(6)
C(16)	-0.120(3)	0.505(2)	0.3904(5)	5.0(7)
C(17)	-0.280(4)	0.441(3)	0.3168(8)	7(1)
C(18)	-0.342(3)	0.383(2)	0.2660(5)	6.9(8)
C(19)	-0.249(3)	0.335(2)	0.2423(5)	6.1(7)
C(20)	-0.330(3)	0.370(2)	0.2128(4)	7.0(7)
C(21)	-0.240(3)	0.333(2)	0.1860(5)	6.6(7)
C(22)	-0.300(3)	0.386(3)	0.1588(5)	7.9(8)
C(23)	-0.231(3)	0.350(2)	0.1322(6)	7.9(8)
C(24)	-0.284(3)	0.397(2)	0.1025(5)	8.5(9)
C(25)	-0.209(3)	0.353(2)	0.0762(5)	8.7(8)
C(26)	-0.267(3)	0.406(3)	0.0473(6)	9.4(9)
C(27)	-0.199(3)	0.363(3)	0.0212(5)	9.1(9)
C(28)	-0.247(4)	0.417(3)	-0.0076(5)	9.6(9)
C(29)	-0.173(4)	0.383(3)	-0.0342(6)	7(1)
C(30)	-0.197(3)	0.388(3)	-0.0850(6)	7.5(9)
C(31)	-0.122(4)	0.267(3)	-0.0934(6)	8.5(9)
C(32)	-0.104(4)	0.249(2)	-0.1224(6)	9.0(9)
C(33)	-0.123(3)	0.343(3)	-0.1427(5)	5.9(8)
C(34)	-0.203(3)	0.461(3)	-0.1343(5)	7.8(9)
C(35)	-0.229(3)	0.481(2)	-0.1053(6)	7.1(8)
C(36)	-0.105(4)	0.313(3)	-0.1716(6)	7.7(9)
C(37)	-0.098(5)	0.405(2)	-0.2209(5)	5.1(8)
C(38)	0.041(3)	0.352(2)	-0.2326(8)	6.8(9)
C(39)	0.042(4)	0.354(2)	-0.2627(7)	7.3(9)
C(40)	-0.082(4)	0.394(2)	-0.2805(6)	5.7(8)
C(41)	-0.231(3)	0.440(2)	-0.2687(6)	2.9(8)
C(42)	-0.227(3)	0.445(2)	-0.2385(6)	5.9(8)
C(43)	-0.198(4)	0.398(3)	-0.3304(5)	11(1)

In Figure 1, the molecular structure labeling the number of atoms is presented by an ORTEP II [19] drawing. The equivalent isotropic factor in some O atoms indicated the large value as of the time that an approximate structure was decided. Therefore, the atoms of O(4) and O(6) were taken account of the disordered structure. The new atoms, O(4') and O(6'), were located near to O(4) and O(6), respectively. Finally, the values of an occupancy in O(4), O(4'), O(6) and O(6') were to be 0.762, 0.238, 0.482 and 0.518, respectively. All non-hydrogen atoms except O(4), O(4'), O(6) and O(6') were refined anisotropically. The hydrogen atoms introduced at their theoretical positions and the four atoms given above (O(4), O(4'), O(6) and O(6')) were refined isotropically. The molecular geometry is almost extended and linear, in other words, the rod-like feature.

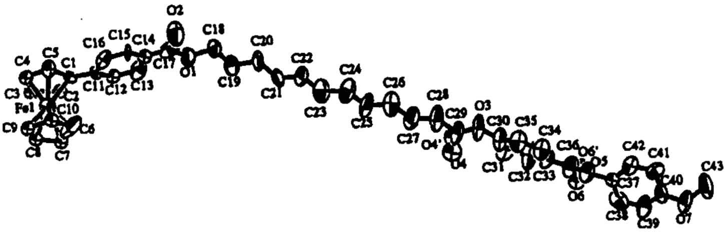

FIGURE 1 ORTEP II view of the molecular structure of MPAF-11 showing the crystallographic numbering scheme with thermal ellipsoids drawn at 50% probability.

Molecular structure

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

In the ferrocenyl moiety, two cyclopentadienyl rings run in parallel conformation to each other with a dihedral angle of 2.32 °. Also, the two cyclopentadienyl rings could be considered to make up an eclipsed type. Ferrocene molecule has the staggered type in two cyclopentadienyl rings [20]. In addition to this fact, the staggered type is widely observed in disubstituted ferrocene derivatives [21-22], while the eclipsed one is found in monosubstituted ferrocene derivatives [8,10,12-13,24] except MPAF-3 [11].

In the flexible spacer, the undecyl chain (C18-C28) is regarded as an all-*trans* conformation with 180 ° torsion angles differing by less than 5 ° and is estimated to be 12.52 Å long. Generally, the length of the C-C-C unit obtained from the extended normal paraffin is 2.54 Å long. Using the value, the length of the undecyl chain is calculated to be 12.70 Å long by 2.54 x 5.0. This value (12.70 Å) is nearly equal to the estimated value (12.52 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 undecyl spacer is coplanar with both those of neighboring ester functions. All-*trans* conformation of the flexible spacer has been observed in MPAF-2 [12], MPAF-4 [10] and MPAF-6 [13].

In the mesogenic group, the bond distances and angles in the phenylbenzoate group are in agreement with those in the homologous [10-13] and other compounds having the phenylbenzoate group [24-25]. The dihedral angle of the two phenyl rings is 48.15 ° and the C33-C36-O5-C37 torsion angle is equal to 179 (2) °. The value of this dihedral angle (48.15 °) is the smallest value compared with those of other MPAF-*n* analyzed its structure already. The values of these dihedral angles in liquid crystalline compounds (MPAF-4, 6 and 11) seem like to decrease with increasing the spacer length [10,13].

The molecule is slightly bent at the C17 atom (C1----C17----C43). This slightly bent structure may play a very important role in giving rise to the liquid crystallinity described later. Such a bent structure has already been observed in MPAF-2 [12], MPAF-4 [10] and MPAF-6 [13]. As a result the whole molecular structure is exceedingly similar to those of MPAF-2 [12], MPAF-4 [10] and MPAF-6 [13].

Crystal structure

The projections of the *a*-*c* plane and *b*-*c* plane are shown in Figure 2 (a) and (b).

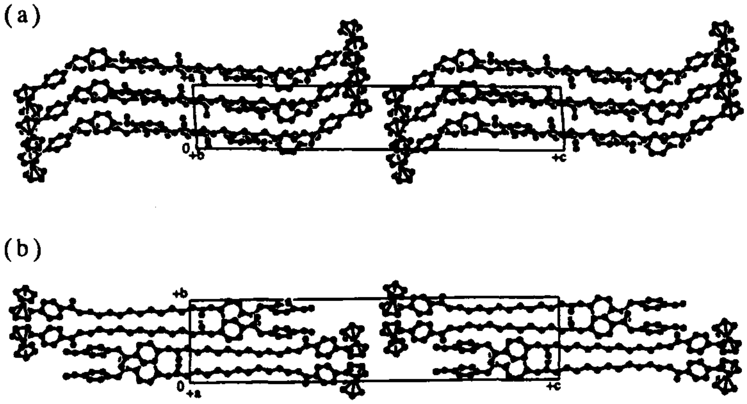

FIGURE 2 Crystal structure of MPAF-11,
(a) the projection of the *a*-*c* plane, (b)the projection of the *b*-*c* plane.

As is already described, the molecule was slightly bent around for the ester group located at the nearest neighbor of the phenylferrocenyl group. Such slightly bent structure contributes effectively to the highly compact packing in the crystal lattice. The mesogenic groups in the molecules are packed in an anti-parallel fashion along the long crystallographic *c*-axis. That is, the two molecules arrayed the anti-parallel form as overlapping conformation, and the overlapping pairs pile up along the short crystallographic axes. As a result, the molecules make up the layer structure just like a smectic manner. This structure is able to lead to the most effective molecular packing.

From the projection of the *b-c* plane (Figure 2 (b)), the position and an orientation of three carbonyl oxygen atoms in one molecule can be discussed from a viewpoint of making up the network of dipole-dipole interactions. Two carbonyl oxygen atoms of three ones orient toward two other carbonyl oxygen ones and the other orients toward the oxygen atom of methoxy group in the neighboring molecule. The interactions in the direction of the molecular short axes arise from not only the mesogenic unit but also the carbonyl oxygen atoms as the dipole-dipole interactions. Generally, the stability of the dipole-dipole interaction in the crystal is expressed by the position and the orientation of the corresponding dipoles. The molecules should pile up the neighboring one in the direction of the molecular short axes by this interaction, strongly and efficiently. It may be considered that this effect may contribute to the appearance of liquid crystallinity and to build up the layer structure in the liquid crystalline phase. The detail of the effect was described in the paper of MPAF-6, already published [13].

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