Crystal Structure of a Liquid Crystalline Ferrocene Derivative, 1,1′-bis[10-[4-(4-methoxyphenoxycarbonyl)phenoxy]decyloxycarbonyl]ferrocene

Naotake Nakamura and Takashi Okabe
Department of Applied Chemistry, College of Science and Engineering, Ritsumeikan University, 1-1-1,Nojihigashi, Kusatsu 525-8577

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The molecular and crystal structures of 1,1′-disubstituted ferrocene derivative, 1,1′-bis[10-[4-(4-methoxyphenoxycarbonyl)phenoxy]decyloxycarbonyl]ferrocene (bMAF-10) were determined by X-ray diffraction method using the single crystals. The structural molecular feature was the *cis* conformation ("U" shape) in which the two substituents existed in the same directions, but not the *trans* conformation ("S" shape) expected in general.

Metallomesogens, the liquid crystalline compounds containing a transition metal, have been of a great interest in recent years, because of their electric, magnetic and chromatic properties. Ferrocene is one of the metallocenes, and it shows a remarkable thermal stability and an aromaticity. Disubstituted ferrocene derivatives can be classified into three types, 1,2-, 1,3-, and 1,1′-disubstituted ferrocene derivatives, according to the substituted position. Some of 1,3- and 1,1′-disubstituted ferrocene derivatives show liquid crystallinity and their structural analyses have been carried out. It has already been reported that the molecular structures of liquid crystalline 1,3-disubstituted ferrocene derivatives and 1,1′-disubstituted ones were "T" shape and "S" shape, respectively.[1,2]

In our laboratory, a series of disubstituted ferrocene derivatives, 1,1′-bis[ω-[4-(4-methoxyphenoxycarbonyl)phenoxy]alkoxycarbonyl]ferrocene (abbreviated hereafter as bMAF-*n*, $n = 2$–12, where *n* is the number of carbon atoms in the flexible methylene unit) were prepared. The general chemical structure of bMAF-*n* is shown in Figure 1. Liquid crystallinity of bMAF-*n* was studied using a differential scanning calorimeter (DSC), a polarizing optical microscope (POM), and a small-angle X-ray diffraction systems (SAXD). Nine members of the eleven compounds showed liquid crystallinity. The liquid crystalline phases were identified as a nematic ($n = 3$, and 5–12), a smectic C ($n = 5$–12) and a smectic F or I ($n = 11$ and 12).[3,4]

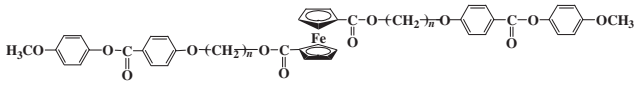

Figure 1. The general structure of bMAF-*n*.

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 a mechanism of the appearance of liquid crystalline phase. We have already determined the crystal structure of bMAF-5. The molecular structure of bMAF-5 was the *trans* conformation ("S" shape), as was expected in general.[5]

In this study, the crystal and molecular structures of bMAF-10 (which is homologous compound of bMAF-5) were determined by X-ray diffraction method. The structural characterization of bMAF-10 is reported below.

The sample, bMAF-10, was synthesized in accordance with the method mentioned in our previous paper. The single crystal of the compound was obtained from a solution with a mixed solvent of benzene and heptane (1:1) by the slow evaporation method. The single crystals obtained are orange in color and platelike. The sample, which had the approximate dimensions of $0.38 \times 0.27 \times 0.03$ mm, was mounted on the goniometer.

All measurements were carried out by Rigaku AFC-5*R* 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 monochrometor.

All calculations were performed using the *CrystalStructure*[6] crystallographic software package of the Molecular Structure Corporation. The structure was solved by direct methods (SIR92)[7] 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 on the carbon atoms to which they were attached. The final refinement was made by full-matrix least-squares based on 9682 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.

Figure 2[8] shows the molecular structure of bMAF-10. This compound revealed interesting feature. Although it is considered that the conformation of liquid crystalline 1,1′-disubstituted ferrocene derivatives is adopted generally "S" shape, the molecular structure of bMAF-10 formed "U" shaped conformation. The "U" shaped structure is very rare in the liquid crystalline molecules including ferrocene derivatives. In the past, D. Demus[9] introduced an example that the "U" shaped structure of 1,2-benzene derivative was reported.[10] Recently, 1,1′-disubstituted ferrocene derivatives with "U" shaped conformation are reported by Ekkehard Lindner.[11] However, a molecule of water existed in this crystal. As far as we know, bMAF-10 showed the "U" shaped conformation for the first time in liquid crystalline 1,1′-disubstituted ferrocene compounds. In consideration of "S" shaped structure of bMAF-5 and a mobility of two cyclopentadienyl rings of the ferrocene molecule, the "U" shaped bMAF-10 is one of the most novel liquid crystalline compounds. In both mesogenic units, carbonyl oxygen atoms between the two phenyl rings had a remarkably large temperature factors and small peaks were found around them. Therefore, these atoms were disordered in further refinement. The disordered atoms were O5, O6, and O12, O13. The occupancy of O5, O6 and O12, O13 was 0.31(2), 0.69(2) and 0.81(3), 0.19(3), respective-

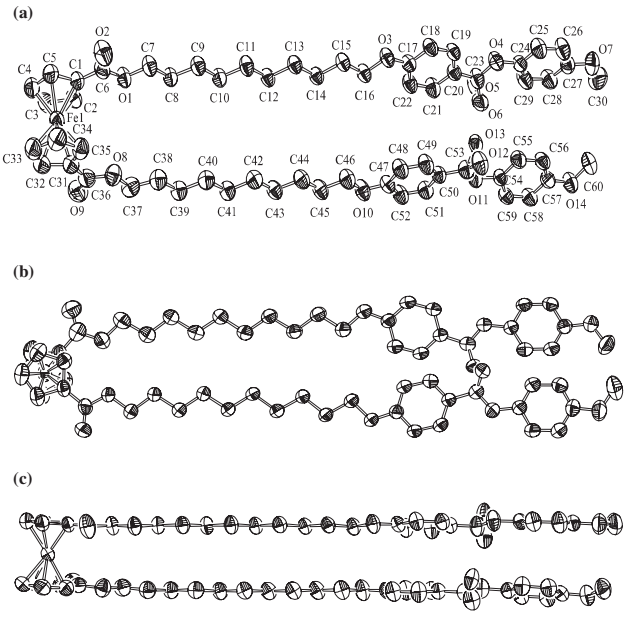

Figure 2. *ORTEP*-3[12] view of the molecular structure excluding hydrogen atoms in bMAF-10. Thermal ellipsoids are drawn at 50% probability. (a) showing the crystallographic numbering scheme, (b) overview onto the cyclopentadienyl rings, and (c) side view onto the cyclopentadienyl rings.

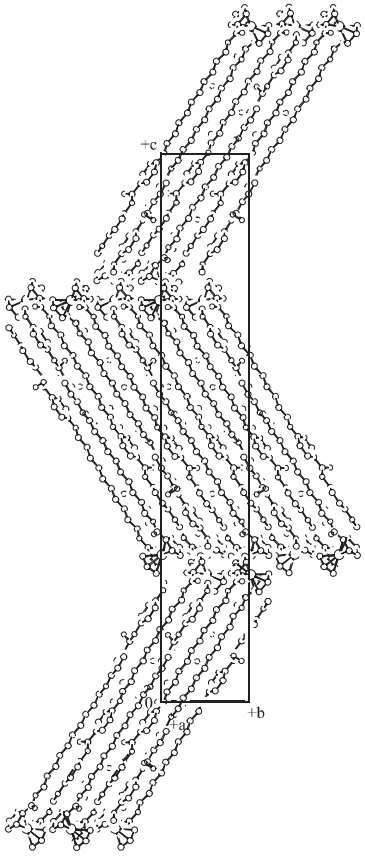

Figure 3. The crystal structure of bMAF-10, the projection of *b*–*c* plane.

ly. The skeleton of the methylene chain had an all-*trans* conformation. In mesogenic moiety, the dihedral angles of two phenyl rings, (C17–C22)–(C24–C29) and (C47–C52)–(C54–C59) were 8.5° (1) and 165.5° (1), respectively.

The crystal packing of bMAF-10 is shown in Figure 3. In the crystal structure, the molecules in a layer leaned greatly to *b* axis. The molecules formed the layer structure of herring-bone type.

Detailed discussion on the structure of the liquid crystalline phase of bMAF-10 is now in progress.

References and Notes

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8 Crystal data of bMAF-10: $C_{60}H_{70}FeO_{12}$, fw = 1039.05, monoclinic, space group $C2/c$, $a = 19.849(5)$ Å, $b = 9.298(5)$ Å, $c = 57.969(6)$ Å, $\beta = 97.31(2)$, $V = 10612.0(64)$ Å^3, $Z = 8$, $T = 296(1)$ K, $D_{calc} = 1.301$ g/cm^3, 11293 reflections measured, 9713 unique ($R_{int} = 0.030$), $R[F^2 > 2\sigma(F^2)] = 0.0460$, $wR[F^2 > -3\sigma(F^2)] = 0.1070$, and GOF = 1.000. Crystallographic data reported in this manuscript have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-229928. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).
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