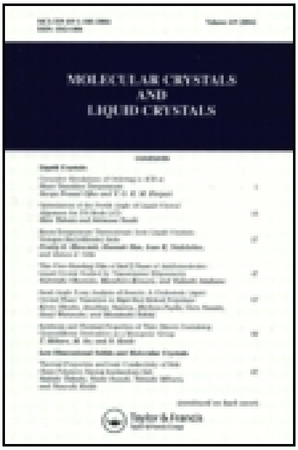

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Syntheses and Physical Properties of Ferrocene Derivatives (IV) A Study on the Smectic Structure of Ferrocene Derivatives Containing a Cholesteryl Group

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Syntheses and Physical Properties of Ferrocene Derivatives (IV) A Study on the Smectic Structure of Ferrocene Derivatives Containing a Cholesteryl Group

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The smectic structure of ferrocene derivatives, [4-[ω-(cholesteryloxycarbonyl)alkoxycarbonyl]phenyl]-ferrocene (abbreviated to CAPF-*n*, $n = 2, 4, 6, 8, 9, 10$, and 11, the carbon number of the frexible alkyl chain), was studied by X-ray diffraction. The structure of CAPF-*n* having a shorter alkyl chain ($n < 9$) was different from that of a longer one. The derivatives containing 2, 4, 6, 8, and 10 carbon atoms in the flexible alkyl chain have a double-layer structure, while the derivatives having 9, 10, and 11 carbon atoms in the alkyl chain showed a quasi single-layer structure. CAPF-10 indicated both the double-layer and the quasi single-layer structures.

Keywords: Ferrocene, liquid crystal, transition metal complex, cholesteryl derivatives

INTRODUCTION

The liquid crystallinity of the monosubstituted ferrocene derivatives containing a cholesteryl group as a mesogenic group has been investigated in our laboratory. Eleven compounds of [4-[ω-(cholesteryloxycarbonyl)alkoxycarbonyl]phenyl] ferrocene (abbreviated to CAPF-*n*, where *n* is the number of carbon atoms in the alkyl chain as a flexible spacer) were prepared. In our previous works using a differential scanning calorimeter and polarizing microscope, it was found that CAPF-2, 4, 6, 8, 9, 10, and 11 showed liquid crystallinity.[1,2] According to the microscopic observations, it was suggested that the liquid crystal phases observed were smectic.

In this paper, the experimental results of X-ray diffraction are described, and the appropriate layer structures of liquid crystalline CAPF-*n* are suggested.

EXPERIMENTAL

All of the compounds studied in this work were synthesized in our laboratory. The synthetic procedure was previously described in detail.[1] The samples for X-ray measurements were prepared as follows. The compound was placed in a very thin-wall glass capillary, was heated to the liquid state, approximately 20°C above its melting point, and then was quickly cooled to room temperature. Immediately following the preparation, the sample was mounted on the top of the goniometer head. All measurements except CAPF-9 were performed at room temperature. Only in the case of CAPF-9, the sample was cooled to 15°C using a new temperature control apparatus,[3] because the clearing point of this sample was relatively low. A small-angle X-ray diffractometer (Rigaku CN203E5) and X-ray camera (Enraf Nonius FR504BS) were used. The camera distance was 100 mm. Monochromated CuKα radiation generated by RIGAKU RU-200 (12 kW) was used.

RESULTS AND DISCUSSION

Figure 1 shows the typical small-angle X-ray diffraction pattern of CAPF-4 which contains two peaks ((A) and (B)). The reflection located at the higher-angle side (B) can be regarded as a second order while the lower-angle side (A) corresponds to an interplaner distance. The patterns of the small-angle X-ray diffraction of the samples studied here were nearly the same each other. This fact indicates the existence of a layer structure in the liquid crystalline phases of CAPF-*n*.

The long spacings observed in the experiments are listed in Table 1 with calculated model molecular lengths of CAPF-*n*, which are estimated from molecular models of CAPF-*n* designed by a personal computer with an aid of a molecular modeling software program using normal bond distances and angles. It is easily understood from Table 1 that the observed long spacing values are divided into two groups. One is associated with CAPF-*n* containing even carbon atoms in the flexible alkyl chain. This group is denoted by Group I. CAPF-9, 10, and 11 are included in another group, that is

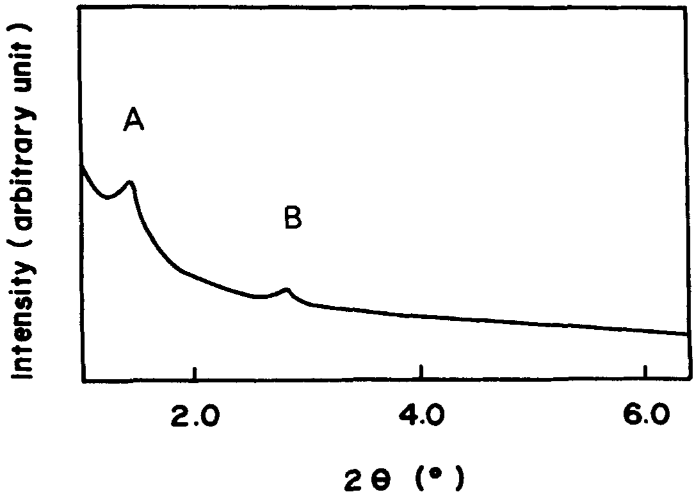

FIGURE 1 X-ray diffraction pattern of CAPF-4.

TABLE 1

List of Long Spacings and Model Molecular Lengths

n	Long spacing (Å) Group I	Long spacing (Å) Group II	Model molecular length (Å)
2	58.6		29.9
4	59.9		32.1
6	64.4		34.4
8	69.8		36.6
9		45.5	36.7
10	70.6	49.5	38.8
11		49.6	39.1

denoted by Group II. It is characteristic point in the result that only CAPF-10 indicates two individual long spacings. This will be discussed later.

The Group I members show about 1.9 times longer compared with the corresponding model molecular length. If the two molecules exist in the layer as a head to head fashion and exist vertically to the layer plane, the long spacing should be more than two times longer than the model molecular length on account of the presence of a molecule–molecule and a layer–layer longitudinal intervals. Therefore, it may be considered that one of possible arrangements in the layer is a tilted double-layer in which the molecules may incline to the layer plane as is shown in Figure 2. Assuming the intervals may be about 6 Å long as is usually observed in ordinary organic crystals constructing the layer structure, a tilt angle in the arrangements is estimated to be about 60°. According to the experimental results of many normal long chain compounds in which smectic like arrangements are often associated, the tilt angle is also about 60°.[4] Therefore, it may be reasonable that the molecular tilt angle in the layer of CAPF-*n* is regarded as 60°. Calculated spacing values obtained from above consideration, which contain the longitudinal intervals, are plotted in Figure 3 with those of experimental ones. Except one from whole experimental results, there is no significant difference between the

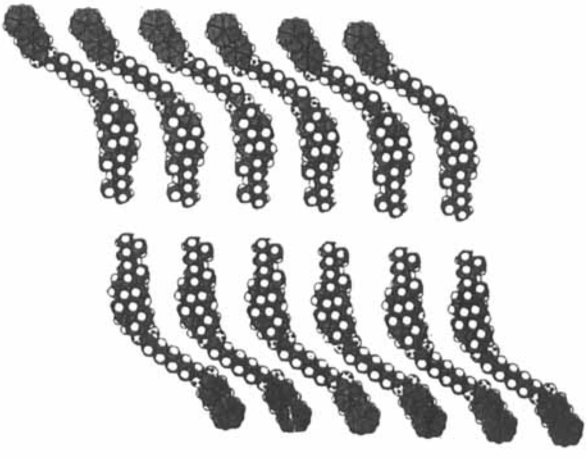

FIGURE 2 Model structure of double-layer of CAPF-8.

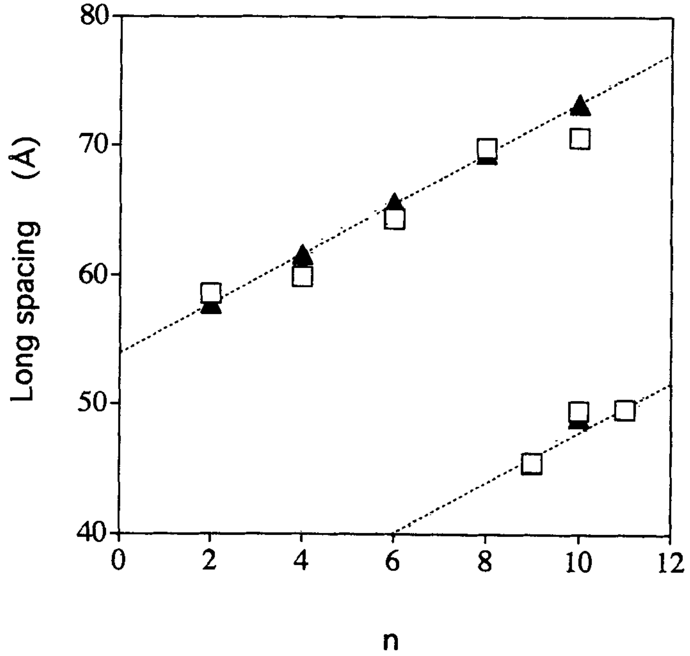

FIGURE 3 Observed and calculated long spacing values of CAPF-*n*. □: Observed values; ▲: Calculated values.

calculated and observed values. Only in the case of CAPF-10, the observed value is a little short compared with that of the calculated one. This may be considered that the flexible alkyl chain in the liquid crystalline phase tends to become mobile gradually with increasing the chain length. In the Group I members, the mobility may be most remarkable in CAPF-10. This remarkable mobility of the flexible alkyl chain might be related to the fact that CAPF-10 showed the two kinds of long spacing, described later again.

Group II is associated with the members containing 9, 10, and 11 carbon atoms in the flexible alkyl chain. The experimental values of long spacing are about 1.3 times longer compared with the corresponding model molecular lengths. This fact suggests that the layer structure may be single-layer, not the double-layer. The interval in this structure is estimated to be about 3–4 Å long, because there is only layer–layer interval. If the molecules are situated vertically on the layer plane, the long spacings observed are a little long even if the longitudinal interval is included. In our previous paper on packing structures of liquid crystalline side-chain polymers containing a cholesteryl group as the mesogenic unit, we proposed a structural model.^{5} The samples studied were methacrylic polymers which were connected with the mesogenic cholesteryl group by the flexible alkyl chain. In the case of the samples having a rather long alkyl chain ($n \geqslant 9$), the flexible alkyl chains of neighboring polymers were able to surround the cholesteryl group. As a result, the molecules were packed in suitable density. It may be possible to apply this discussion to the explanation of the experimental results obtained

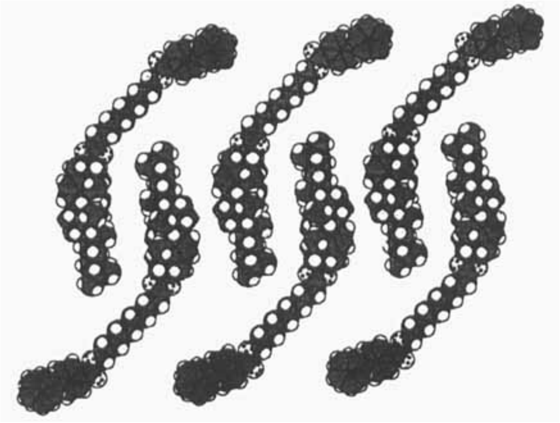

FIGURE 4 Model structure of quasi single-layer of CAPF-9.

in this work. Considering the previous discussion on the packing structure of the polymers and the layer structure model of Group I members shown in Figure 2, we make a proposal. One of an appropriate structural model is shown in Figure 4. In this model arrangement, the tilt angle is 60° and the molecules are packed densely like the packing in the liquid crystalline polymers cited above. The calculated spacing including about 3.5 Å long as the longitudinal interval between the layers, that is about one half of that of Group I members, are plotted in Figure 3 with those of observed ones. There is no big difference between the two. So, it may be considered that the molecular arrangement in the liquid crystalline phases of CAPF-9, 10 and 11 shown in Figure 4 is reasonable. The model proposed here is not the perfect single-layer. Therefore, it is better that the model is called a quasi single-layer structure.

In conclusion, the layer structure of CAPF-n with a shorter flexible alkyl chain ($n < 9$) has a double-layer structure, while that of CAPF-n with a longer alkyl chain ($n > 8$) has a quasi single-layer structure. The reason why the two long spacings are observed in CAPF-10 is considered as follows. As previously discussed from the point of view of the transitional entropy,[2] the liquid crystallinity in CAPF-n with odd carbon atoms in the alkyl chain was first observed in CAPF-9, and CAPF-9 showed a quasi single-layer structure as was described above. This fact indicates that the flexible alkyl chain length first achieves to enough length at $n = 9$ for making the dense arrangement, and the length is able to construct the quasi single-layer structure. Therefore, CAPF-10 is also possible to construct quasi single-layer structure in addition to a double-layer one. The tilt angles of these two structures are nearly the same. So, if one of the molecules in the double-layer structure is slipped to a long axis direction, the quasi single-layer structure will be made. As the result, it may be possible to form two domains, one is double-layer and another is quasi single-layer. External influence, for example a cooling rate from a molten state to the liquid crystalline phase, may play important role to make either a double-layer structure or a quasi single-layer one. The mixed structure of this kind was reported in the structure of polymers cited above, too.[5]

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