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Preliminary communication
Steryl polyfluorobenzoate liquid crystals

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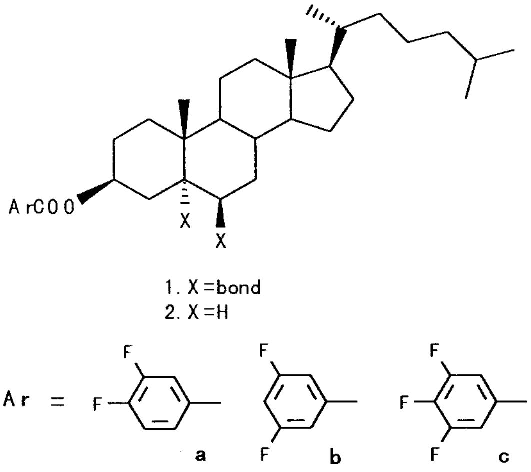
Two series of steryl di- and tri-fluorobenzoate liquid crystals were synthesized and their phase transition behaviours studied by DSC and thermal polarizing microscopy. The results show that while *para*-fluorine substituents stabilize the mesogenicities, *meta*-fluorine substituents slightly depress the mesogenicities.

Fluorinated liquid crystals have attracted much attention since the 1970s owing to their excellent properties for LCD applications. More recently polyfluorination on the aromatic core in mesogenic molecules has been systematically studied. Earlier research of this group showed that lateral polyfluoro-substituted liquid crystals show low melting points to tend to form the nematic phase [1–5]. However, there are few reports on steroidal fluoro-substituted benzoate liquid crystals. Only cholesteryl and cholestanyl monofluorobenzoates have been reported up to now [6–8]. To clarify the effect of polyfluorination on the mesomorphic properties of this kind of liquid crystal material, two series of steryl polyfluorobenzoate liquid crystals, i.e. cholesteryl/cholestanyl di-/tri-fluorobenzoates (**1**, **2**), were synthesized and their phase transition behaviours studied.



The syntheses of the polyfluorobenzoates (**1**, **2**), the details of which will be published elsewhere, started from polyfluorobromobenzenes. The phase transition temperatures of the target compounds were measured visually by optical microscopy using a polarizing microscope (Olympus PM-6) fitted with a heating stage (Mettler FP-80) and a control unit (FP-82); and by differential scanning calorimetry (DSC, Shimadzu DSC-50 calorimeter with a data system, heating and cooling rate 5°C min^{-1}). The phase transition temperatures reported here were the middle values of the transition under the polarizing microscope, and are summarized in the table.

The target compounds are cholesteric liquid crystals. The phase transition temperatures of series **2** are all lower than those of series **1**, since the absence of the 5-double bond in the cholestanyl skeleton reduces the polarizability of the molecule. It is found that in each series, the temperature range of the cholesteric phase of the 3,4-difluorobenzoate (**1a**/**2a**) is the broadest; on the contrary, that of the 3,5-difluorobenzoates (**1b**/**2a**) is the narrowest. The effect of a *p*-F (*para*-fluorine substituent) in stabilizing the mesophase is demonstrated by comparison between compounds **1b**/**1c** (17.2°C difference in cholesteric phase range) and **2b**/**2c** (monotropic/enantiotropic), in which the latter have a higher molecular length–breadth ratio and a more stable Ch phase. On the other hand, the reduction of the length–breadth ratio

Table Phase transition temperatures of the steryl polyfluorobenzoates. Cr = crystal, Ch = cholesteric, I = isotropic.

Compounds	Phase transition temperatures/°C
1a	Cr 154.1 Ch 211.8 I 211.0 Ch 121.4 Recr
1b	Cr 156.9 Ch 160.9 I 159.8 Ch 126.7 Recr
1c	Cr 171.2 Ch 192.4 I 190.1 Ch 129.5 Recr
2a	Cr 139.7 Ch 192.8 I 191.4 Ch 120.0 Recr
2b	Cr 150.3 I 135.9 Ch 119.5 Recr
2c	Cr 155.0 Ch 174.3 I 173.8 Ch 126.2 Recr

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by *m*-F (*meta*-fluorine substituent) is clear from comparison between compounds **1a/1c** (36.5°C difference) and **2a/2c** (33.8°C difference), in which the mesogenicities of the latter are decreased by a higher T_{mp} (melting point) and lower T_{cp} (clearing point).

Furthermore, the relative degree of the effect of *p*-F and *m*-F on the mesomorphic properties can also be found. Comparing with cholesteryl *p*-fluorobenzoate (Cr 152–154 Ch 227 I) [6], the T_{cp} of **1a** is lower, as the *m*-F reduces the molecular length–breadth ratio and polarity. However, in comparison with the unfluorinated parent compound, i.e. cholesteryl benzoate (Cr 145.8 Ch 180.7 I) [9], the T_{mp} and T_{cp} of **1a** are higher. This scenario indicates that for the mesogens, the stabilization of *p*-F is far greater than the depression of *m*-F. The comparison between **1c** and cholesteryl benzoate gives an extreme case, in which one *p*-F improves the thermal stability of the mesophase even though two *m*-F are introduced into the molecule. The same phenomena can be found in the comparison of cholestanyl benzoate (Cr 135 Ch 155 I) [6] with **2a** and **2c**.

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