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Preliminary communication

Steryl polyfluorobenzoate liquid crystals

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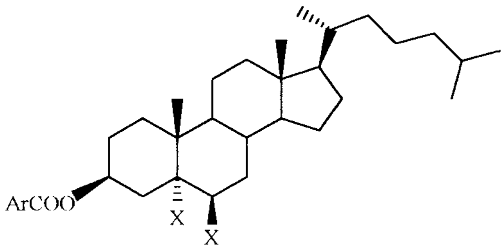
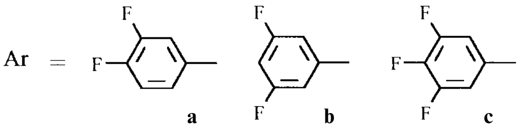
Two series of steryl di- and tri-fluorobenzoate liquid crystal materials were synthesized and their phase transition behaviours studied by DSC and thermal polarizing microscopy. The results show that *para*-fluorine substituents stabilize the mesogenicity whilst *meta*-fluorines depress it to a weak degree.

Fluorinated liquid crystals have attracted much attention since the 1970s owing to their excellent properties for liquid crystal display applications. Polyfluorination on the aromatic core in mesogenic molecules has been intensely studied more recently. Earlier studies of our group indicated that lateral polyfluoro-substituted liquid crystals have low melting points and a tendency to form nematic phases [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 property of this kind of liquid crystal, two series of steryl polyfluorobenzoate liquid crystals, i.e. cholesteryl/cholestanyl di-/tri-fluorobenzoates (**1**, **2**), have now been synthesized and their phase transition behaviour studied.



1. X = bond
2. X = H



The synthesis of the polyfluorobenzoates (**1**, **2**), which will be published elsewhere, was started from the 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 hot stage (Mettler FP-80) and a control unit (FP-82); also by differential scanning calorimetry (DSC, Shimadzu DSC-50 calorimeter with a data system, and a heating and cooling rate of 5°C min^{-1}). The phase transition temperatures reported here in the table were the middle values of the transition under the polarizing microscope.

The target compounds are all cholesteric liquid crystals. The phase transition temperatures of series **2** are lower than the corresponding ones of series **1**, since the absence of a 5-double bond in the steroid skeleton reduces the polarizability of the molecule. It can be found that in each series the temperature range of the cholesteric phase of the 3,4-difluorobenzoates (**1a**/**2a**) is the broadest; on the contrary, that of the 3,5-difluorobenzoates (**1b**/**2b**) is the narrowest. The ability of a *para*-fluorine substituent (*p*-F) to stabilize a mesophase is demonstrated by comparison between compounds **1b**/**1c** (17.2°C difference

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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on the cholesteric phase range) and **2b**/**2c** (monotropic/enantiotropic), in which the latter compounds have a higher molecular length–breadth ratio and a more stable Ch phase. On the other hand, the reduction of the length–breadth ratio by a *meta*-fluorine substituent (*m*-F) is clear by comparison between compounds **1a**/**1c** (36.5°C difference) and **2a**/**2c** (33.8°C difference), in which the mesomorphic thermal stabilities of the latter are decreased by a higher melting point (T_{mp}) and lower clearing point (T_{cp}).

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

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