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## Liquid Crystals

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W. J. Cumming<sup>a</sup>; R. A. Gaudiana<sup>a</sup>

<sup>a</sup> POLAROID Corporation, Cambridge, MA, U.S.A.

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# The effect of fluorocarbon tails on the phase behaviour of some Schiff's base liquid crystals

by W. J. CUMMING and R. A. GAUDIANA\*  
POLAROID Corporation, Cambridge, MA 02139, U.S.A.

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Several new liquid crystalline compounds comprising Schiff's-base cinnamate cores and fluorocarbon alkoxy tails of varying lengths have been synthesized and characterized. The thermal properties of these materials are compared to those of their hydrocarbon analogues. The results show that fluorination stabilizes the crystalline phase, quite unexpectedly destabilizes the  $S_C$  phase, and for two of the compounds produces extraordinarily stable  $S_A$  phases.

## 1. Introduction

There are numerous papers in the literature describing the effect of tail length on phase transitions of all types of liquid crystals. In the course of our work in ferroelectric liquid crystals, we investigated the effect of various types of tails on phase sequence and stability. In a recent publication, we described a study of a series of hydrocarbons, hydrocarbon ethers, and mixed tails, i.e. hybrid tails, containing fluorocarbon/hydrocarbon ethers [1]. The results of that study indicate that the conformation and rotational barriers of the tail portion of a molecule play a key role in determining its liquid crystal behaviour. Specifically, we suggested that the population of *gauche* states in the tail and the rate of conformer interconversion determine phase stability.

Some of the earlier work in the literature on mesogens with fluorocarbon tails compared the effect of trifluoromethyl or pentafluoroethyl tails to the corresponding hydrocarbon tails. With a benzoate core, fluorocarbon tails insert a smectic phase between the crystalline and higher temperature phase [2]. When the core is a Schiff's base, these tails decrease nematic stability [3]. More recently a study of Schiff's base mesogens containing trifluoromethyl or trifluoromethoxy substituent showed that these groups either destabilized the nematic phase or formed smectic phases [4]. The type of phase formed seems to be dominated more by the location and magnitude of the dipolar groups on the core since the fluoro substituents are only one carbon long.

As an extension of our previous work, the present communication describes the synthesis and characterization of a series of fluorocarbon tailed analogues of decyloxybenzylidene-amino-2-methylbutylcinnamate (DOBAMBC). For comparison purposes, every example

in the series, including the hydrocarbon-tailed analogues, has an identical core and head structure, and in those cases where one to one comparisons are made, the tails contain the same number of backbone atoms.

## 2. Results and discussion

Phase transitions and phase sequences of the four fluorocarbon-tailed compounds synthesized for this study along with their hydrocarbon-tailed analogues are graphically illustrated in figure 1 (heating cycle) and (figure 2) (cooling cycle) and figure 3 shows the phase behaviour. While we have included heating and cooling data in bar graphs and compared the data to non-fluorinated analogues, the reader should be cautioned that the data on the non-fluorinated compounds [5–7] is somewhat ambiguous. We use the same data for both heating and cooling due to the fact that the references do not clearly state which part of the heating/cooling cycle the data was obtained from. Our intention is to show graphically the effect of fluorination on these compounds but the uncertainty of the earlier data must be kept in mind when making comparisons.

Referring to the heating cycle, several significant differences in the phase transitions of each of the homologues are immediately evident. First, the crystalline melting points and liquid crystalline isotropic phase transition temperatures of each of the fluorine-containing compounds is significantly higher than the corresponding hydrocarbon analogue. Second, for compounds **II** and **III**, the  $S_A$  phase dominates the LC phase behaviour. In addition, the hydrocarbon-tailed analogues of compound **III** and **IV**, which differ in tail length by one carbon, exhibit three smectic phases, including an  $S_C$  phase. However, the fluorocarbon-tailed compound **III** has only an  $S_A$  phase and compound **IV** has only an 8°C (combined  $S_A$  and  $S_C$ ) smectic range.

\* Author for correspondence.

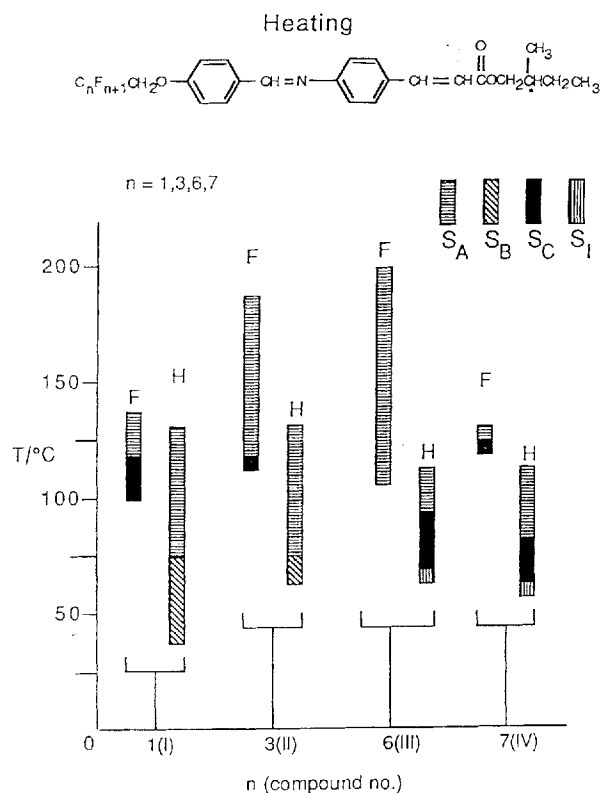


Figure 1. Liquid crystalline phases of compounds I-IV (heating cycle).

In the cooling cycle (figure 2), the isotropic to smectic transition temperatures are lowered by at most 4°C for each of the compounds with the exception of fluoro-tailed compound IV which solidifies directly to the crystalline phase. The phase behaviour of the latter is quite unexpected considering that it differs from compound III by only one CF<sub>2</sub> group and in light of the fact that the hydrocarbon analogues of these two compounds exhibit nearly identical phase behaviour (type, transition temperature and temperature range) to one another.

Compound I (fluorinated) is the only one in the series that exhibits liquid crystalline behaviour typical of the Schiff's base cinnamates.

In a previous paper, we reported the effect of various tail structures on the phase behaviour of smectic liquid crystals. The results showed that the incorporation of hydrocarbon ether tails into liquid crystalline compounds suppresses the crystal/liquid crystal phase transition, relative to hydrocarbon tailed analogues, by destabilizing the crystalline phase but its effect on smectic phase stability varies from compound to compound. It was suggested that these results are directly related to the low rotational barriers of the oxygen/methylene

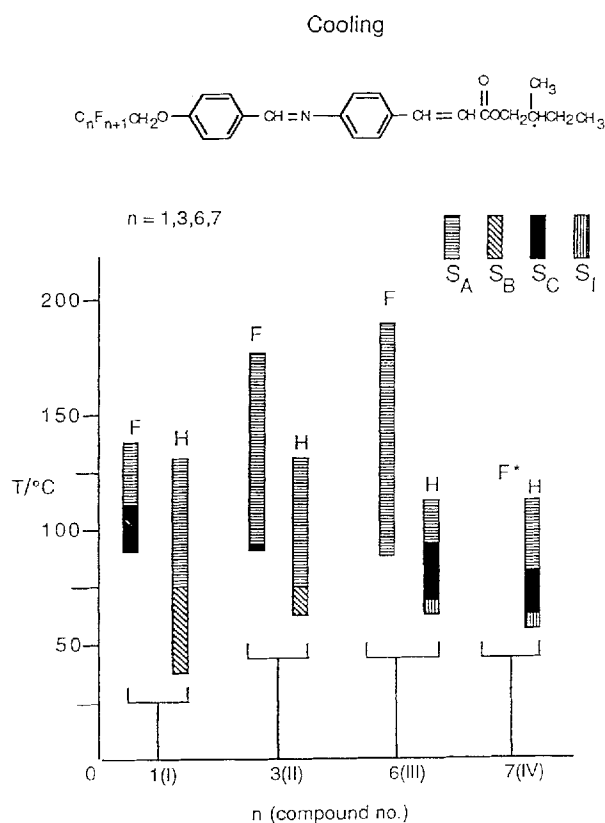


Figure 2. Liquid crystalline phases of compounds I-IV (cooling cycle) (\* = monotropic).

Compound	Phase behaviour
I	$K \xrightarrow{81.2^\circ\text{C}} K \xrightarrow[89^\circ\text{C}]{99.4^\circ\text{C}} S_C \xrightarrow[113^\circ\text{C}]{116.3^\circ\text{C}} S_A \xrightarrow[136.8^\circ\text{C}]{139.4^\circ\text{C}} I$
II	$K \xrightarrow[86.8^\circ\text{C}]{109.5^\circ\text{C}} S_C \xrightarrow[87.5^\circ\text{C}]{114.5^\circ\text{C}} S_A \xrightarrow[177.8^\circ\text{C}]{180^\circ\text{C}} I$
III	$K \xrightarrow[85.5^\circ\text{C}]{106.2^\circ\text{C}} S_A \xrightarrow[188.5^\circ\text{C}]{191.2^\circ\text{C}} \text{Iso}$
IV	$K \xrightarrow[139^\circ\text{C}]{119^\circ\text{C}} S_C \xrightarrow{123^\circ\text{C}} S_A \xrightarrow{131^\circ\text{C}} I$

Figure 3. Phase behaviour of compounds I-IV.

carbon bond which create a high population of rapidly interconverting *gauche* isomers.

The most outstanding feature of those compounds which contain the fluorocarbon/hydrocarbon ether tails is the stabilization of the smectic C phase and the inordinately large effect on all of the compounds con-

taining the fluorocarbon ether tail. Molecular modelling data indicates that the hybrid tails also have a high population of *gauche* conformers, in analogy to hydrocarbon ethers, but that they do not interconvert as rapidly due to the high rotational barriers of the  $\text{CF}_2$  groups and, perhaps, to the comparatively high mass of the perfluorinated segment of the tail.

In the present series of compounds, the bulk of the tail comprises the perfluorinated segment, i.e. each tail has only one  $-\text{OCH}_2-$ . Perhaps in these compounds, phase behaviour is dominated by a low number of *gauche* conformers which interconvert even slower than the hybrid tails which contain three  $-\text{OCH}_2-$  moieties. On heating, the rigidity of the tail stabilizes the crystalline phase, but once the crystal energy is overcome, rigidity seems to enhance the formation of a non-tilted phase ( $S_A$ ). Surprisingly, the more ordered  $S_B$  phase is not formed in any of the present examples even though this phase occurs in two of the hydrocarbon analogues.

### 3. Conclusion

The results of this work indicate that increasing the rigidity of the tail moiety of a liquid crystalline compound has two major effects. First, quite unexpectedly, rigidity greatly enhances the stability of the smectic A phase and concomitantly destabilizes the smectic C phase. Secondly, rigidity stabilizes the crystalline phase.

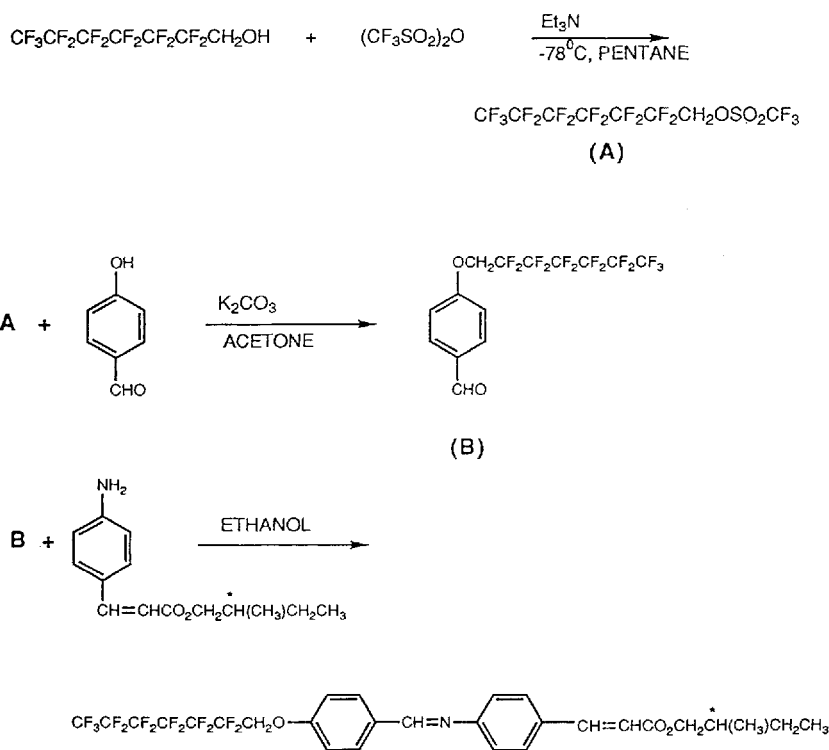
We attribute this phase behaviour to the population and rate of interconversion of *gauche* conformers in these highly fluorinated tails.

### 4. Experimental

All compounds were prepared via the general strategy shown in the scheme. The experimental details for compounds I through IV are given below. (+)-2-methylbutylaminocinnamate was purchased from Kodak Laboratory and Research Products. All materials have satisfactory spectral characteristics (NMR) and elemental analysis (Galbraith) or exact mass. Phase transitions were determined with a Zeiss Universal Microscope fitted with a Leitz Model 350 hot stage. Phase transition temperatures were measured with a Perkin Elmer DSC-7 differential scanning calorimeter in a nitrogen atmosphere at a heating rate of  $10^\circ\text{C min}^{-1}$ ; data reported were obtained from the second heating and cooling cycles. Every sample was run four times to check for thermal stability; no change in  $\Delta H$  or transition temperature was observed for any of the compounds.

#### 4.1. Preparation of 1H,1H-perfluoroheptanoltriflate

8.5 g (0.03 mol) of triflic anhydride are dissolved in 30 ml of pentane and the mixture is placed in the flask of a flamed apparatus consisting of a 100 ml three-necked flask fitted with a dropping funnel, thermometer,



Scheme. General strategy for preparation of compounds I-IV.

mechanical stirrer, drying tube and nitrogen inlet tube. Cool to  $-78^{\circ}\text{C}$  in a dry ice acetone bath. Combine 3 g (0.03 mol) of triethylamine and 10 g (0.029 mol) of 1H,1H-perfluoroheptanol and place in the dropping funnel. Begin dropping the fluoro alcohol-amine mixture into the anhydride with good stirring and at a rate that does not allow the temperature to rise above  $-55^{\circ}\text{C}$ . When addition is complete, stir at  $-78^{\circ}\text{C}$  for 20 min. Replace the dry ice bath with a water ice bath to bring the temperature to  $0^{\circ}\text{C}$ . Transfer to a separatory funnel and extract successively with 30 ml of 5% HC, 30 ml 5%  $\text{NaHCO}_3$  and  $2 \times 30$  ml  $\text{H}_2\text{O}$ . Dry the organic layer over  $\text{Na}_2\text{SO}_4$  for 1–2 h, evaporate the solvent and distil the residue at  $82\text{--}85^{\circ}\text{C}$  at 35 mm. Yield is 11.2g (78%). Store in the freezer under nitrogen.

#### 4.2. Preparation of 4-(1H,1H-perfluoroheptyloxy)-benzaldehyde

Combine 1 g (0.002 mol) of 1H,1H-perfluoroheptanol triflate, 0.26 g (0.0021 mol) of *p*-hydroxybenzaldehyde, 0.55 g of  $\text{K}_2\text{CO}_3$  (0.004 mol) and 10 ml of acetone. Heat to reflux with magnetic stirring for one hour and check by TLC (silica gel,  $\text{CH}_2\text{C}_2$  as solvent), reaction should be essentially complete. Filter, evaporate the solvent, take up in  $\text{CH}_2\text{C}_2$  and filter again. Evaporate to a clear oil and chromatograph on silica gel using  $\text{CH}_2\text{C}_2$  as eluant. Combine appropriate fractions and evaporate to a white solid. Yield 0.74 g. (81%).

#### 4.3. Preparation of (+)-4-(1H,1H-perfluoroheptyloxy)benzylidene-4'-amino-4''-2-methylbutyl cinnamate

In a flask fitted with a magnetic stirrer combine the following: 0.454 g (0.001 mol) of 4-(1H,1H-perfluoroheptyloxy)-benzaldehyde, 0.233 g (0.001 mol) of (+)-2-methylbutyl-*p*-aminocinnamate and 2 ml of absolute ethanol. If after 15 or 20 min no solid has appeared, add a trace of glacial acetic acid. A precipitate should appear very soon. When the solid comes out of solution, stir for an additional 30 min. Filter, wash with ice cold ethanol and let dry. Recrystallize from isopropanol. Weight 0.5 g (75%). Store in the dark under nitrogen.

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