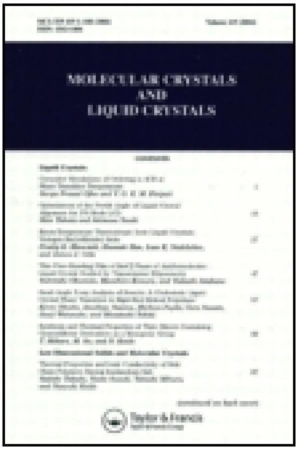


Molecular Crystals and Liquid Crystals

Mesomorphic Properties of a Homologous Series of Liquid Crystals with Short Fluorocarbon Chain

Y. G. Yang [a], G. Tang [a] & J. X. Wen [a]

[a] Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai, China

Version of record first published: 18 Oct 2010

To cite this article: Y. G. Yang, G. Tang & J. X. Wen (2002): Mesomorphic Properties of a Homologous Series of Liquid Crystals with Short Fluorocarbon Chain, Molecular Crystals and Liquid Crystals, 373:1, 25-32

To link to this article: http://dx.doi.org/10.1080/10587250210547

Mol. Cryst. and Liq. Cryst., 2002, Vol. 373, pp. 25-32

Mesomorphic Properties of a Homologous Series of Liquid Crystals with Short Fluorocarbon Chain

Y. G. YANG, G. TANG and J. X. WEN

Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences,
Shanghai, China

A homologous series of short fluorocarbon chain-containing liquid crystals has been synthesized. Several of them show the phase sequence N → SmA → SmC in the cooling process from the isotropic liquid. The mesomorphic properties have been studied by polarizing microscopy and DSC measurements. The thermostability of SmC phases was enhanced along with the lengthening of fluorocarbon chains.

Keywords: Fluorocarbon, liquid crystal, mesomorphic

Earlier work on the materials with either long perfluorocarbon or semiperfluorocarbon chains showed that smectic mesophases were enhanced [1–10]. Compounds with semiperfluorocarbon chains have a tendency to form tilted smectic phases. Due to the existence of strong fluorophobic/fluorophilic self-assembly, only a few of them show the phase sequence N → SmA → SmC [11]. To weaken polyphilic self-assembly and promote nematic phase formation, a homologous series of liquid crystals (**F4–9**) comprising a short fluorinated terminal chain were synthesized. The lateral fluorosubstitution is expected to reduce the melting point of the parent system and to suppress the formation of high-order smectic phases. If the compounds (**F4–9**) exhibit the desired phase types—N; SmA, and SmC—they may be applied as possible hosts for commercial SmC* mixtures to FLC devices.

Received 6 March 2001; accepted 31 May 2001.

The authors gratefully acknowledge the National Natural Science Foundation of China for partial financial support.

Address correspondence to Y. G. Yang, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Lu, Shanghai 200032, China. E-mail: ygyang@pub.sioc.ac.ch

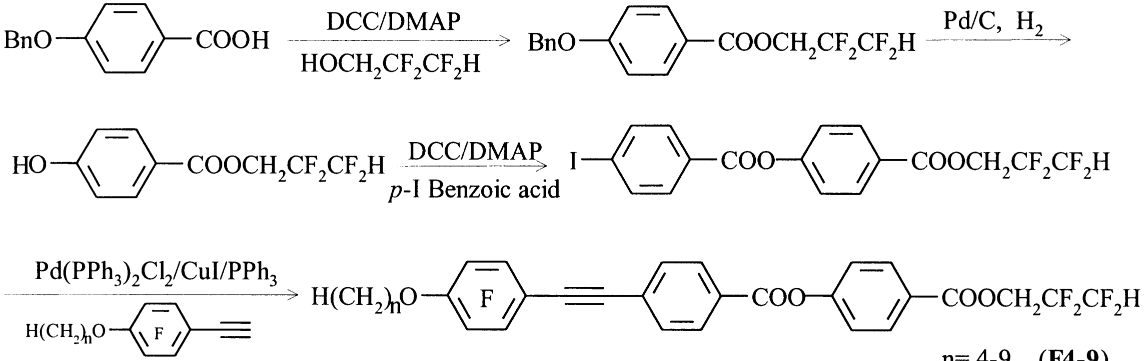
The compounds are synthesized in four steps following the chemical pathway depicted in Scheme 1. The protected acid was esterified with the appropriate alcohol, using dicyclohexylcarbodiimide (DCC) as a dehydrating agent and *N*, *N*-dimethylaminopyridine (DMAP) as a catalyst, in dry tetrahydrofuran solution. Benzyl ether was then converted to the corresponding phenol by the removal of the benzyl protecting group, which was achieved by hydrogenation at room temperature with H_2 atmosphere in the presence of palladium on active carbon in ethyl acetate. After that the phenol was esterified with *p*-iodobenzoic acid using DCC as a dehydrating agent and DMAP as a catalyst, in tetrahydrofuran solution. Finally the coupling reaction between the ester and 4-alkoxytetrafluorophenylacetylene under the catalysis of dichlorobis(triphenylphosphine)palladium(II), triphenylphosphine, and copper(I) iodide in dried triethylamine gave the desired polyfluorinated substituted homologous compound. Yields of 60–70% were achieved and characterization was by MS, elemental analysis, IR, ^{1}H NMR, and ^{19}F NMR spectroscopy.

The phase transition temperatures of the target compounds were measured by optical microscopy using a polarizing microscope (Olympus PM-6) fitted with a heating stage (Mettler FP-80) and a controlling unit (FP-82), and by differential scanning calorimetry (DSC, Shimadzu DSC-50 calorimeter with a data system and heating and cooling rate of 5°C min^{-1}). The transition temperatures reported in this paper were the peak values of the transition on DSC traces and are summarized in Table 1.

All the homologues (**F4–9**) exhibit enantiotropic nematic and smectic A phases. The monotropic smectic C phase was observed for homologues (**F6–F9**). The compound **F9** shows a very narrow nematic phase, which can be found visually by polarized optical microscopy (the temperature range cannot be determined even by polarized optical microscopy). The transition temperatures are plotted against the number of carbon atoms in the alkoxy chain, *n*, in Figure 1. Generally speaking, nematic stability ($T_{\text{N-I}}$) decreases with the increasing of chain length.

To study the effect of lateral fluorosubstitution, homologous series **F4–9** is compared with series **H** [12]. The transition temperatures are plotted against the number of carbon atoms in the alkoxy chain, *n*, in Figure 2. All the homologues of series **H** exhibit enantiotropic SmA and SmC phases, except the cases when $n = 4$ and $n = 16$.

Generally, the melting point and clearing point of the compounds of series **H** are higher than those of the corresponding compounds of series **F**. The nematic phase is more readily formed in series **F** than in series **H** and



n= 4-9. **(F4-9)**

SCHEME 1 The synthesis route of Series **F**.

TABLE 1 Phase transition temperatures of the compounds **F**

Compounds	*n*	*Phase transition temperatures/°C*
F4	4	Cr 117.7 SmA 176.9 N 185.5 I 185.3 N 175.6 SmA 87.5 Recr
F5	5	Cr 120.5 SmA 170.3 N 176.1 I 175.5 N 169.5 SmA 98.7 Recr
F6	6	Cr 104.8 SmA 166.5 N 170.1 I 169.5 N 165.6 SmA 91.0 (SmC 86.5) Recr
F7	7	Cr 104.2 SmA 158.7 N 160.3 I 159.8 N 155.8 SmA 96.6 (SmC 75.2) Recr
F8	8	Cr 99.4 SmA 156.8 N 158.8 I 158.6 N 156.6 SmA 96.7 (SmC 74.5) Recr
F9	9	Cr 104.8 SmA 150.9 I 150.6 SmA 91.0 (SmC 86.5) Recr*

Cr-crystal; N, nematic; SmA, smectic A; SmC, smectic C; I, isotropic; Recr, recrystallization
*The compound **F9** shows very narrow enantiotropic nematic phase for which transition temperatures can not be determined even on OPM.

SmC phases are more favorable in series **H** than in series **F**. The latter may be due to steric effects caused by the protrusion of the fluorosubstituent, which tend to disrupt the side-to-side intermolecular forces of attraction and reduce the melting point and the tendency to form smectic mesophases. Because the fluorine atoms broaden the molecules, the mesomorphic range of the compound in **F** series is narrower than that of the corresponding compound in **H** series.

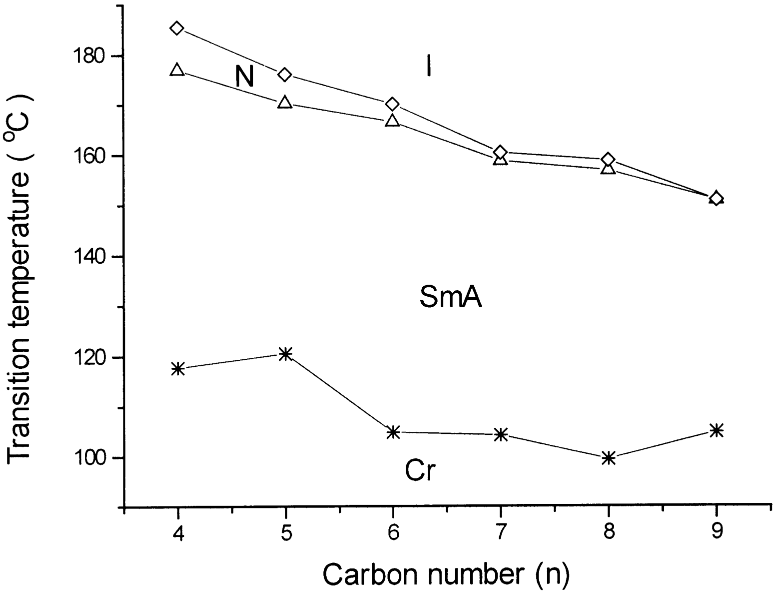


FIGURE 1 Transition temperatures as a function of the number of carbon atoms in the alkoxy chain of compounds **F4–F9**.*, MP; Δ, SmA-N; ◇, N-I transitions.

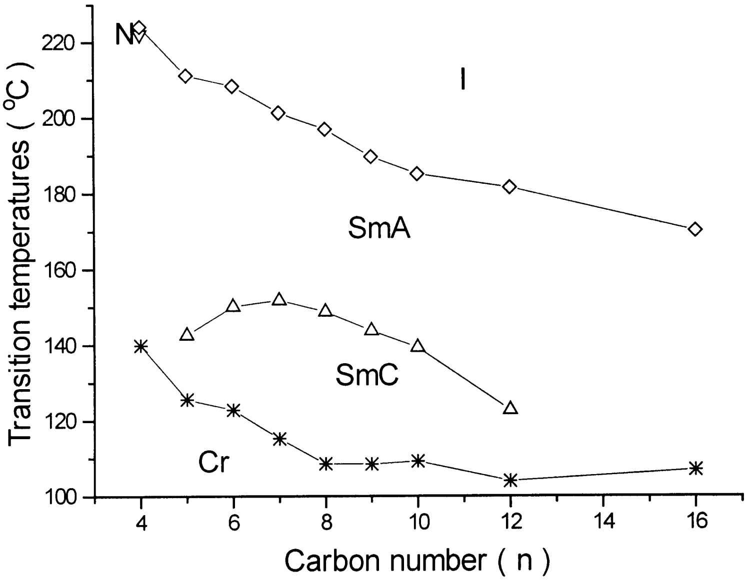
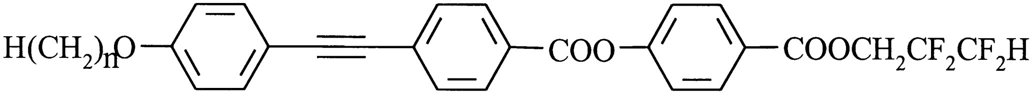


FIGURE 2 Transition temperatures as a function of the number of carbon atoms in the alkoxy chain of compounds **H**. *, MP; Δ, SmC-SmA; ◇, SmA-I; ∇, N-I transitions.

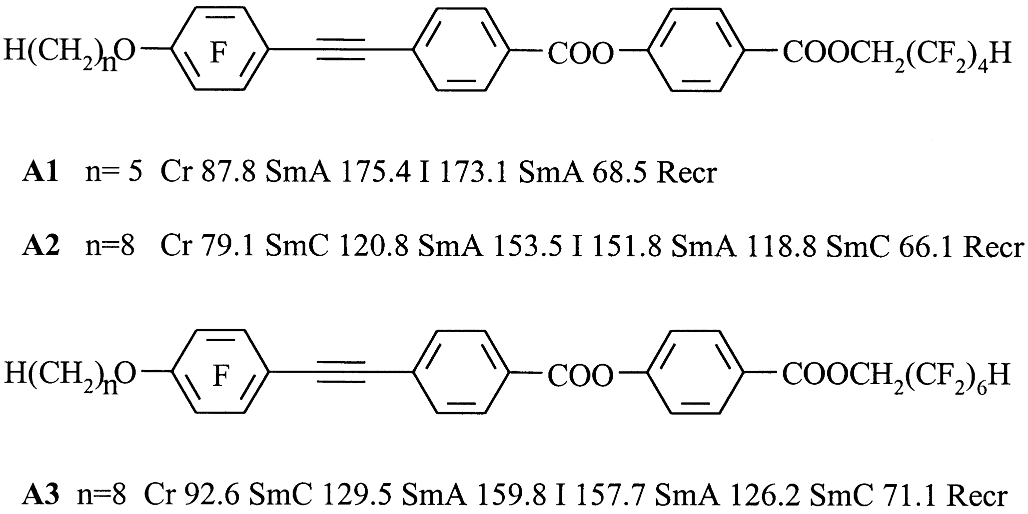
To study the relationship between the mesomorphic properties and the length of the fluorocarbon tails, three other compounds, **A1–A3**, were also synthesized (see Scheme 3). Comparison of **A2** and **A3** with **F8** reveals that as the terminal fluoro-chain is lengthened gradually from -$(CF_2)_2$- to -$(CF_2)_4$- to -$(CF_2)_6$-, the fluorophobic/fluorophilic effect became so strong that the compounds are more favorable to form tilt layer structure with the lengthening of the fluorocarbon tails. But the clearing points of these compounds are nearly the same. Although this may be ascribed to the interaction between the fluorocarbon tails, the lateral-lateral interaction does not change much along with the lengthening of fluorocarbon chains.

The compounds with long terminal fluorocarbon chains often show smectic mesomorphism and do not show nematics [1, 4, 7]. The series in this paper with short fluorocarbon chains show a very broad temperature range and phase sequence of N; SmA and SmC in the cooling process. Unfortunately, SmC phases are monotropic. In the future, the compounds with less fluorosubstituents on the core will be synthesized. Enantiotropic SmC phase might be formed. This kind of liquid crystal might be useful as a host material in ferroelectric LCD in the future.



n= 4-10,12,16. (**H4-10,12,16**)

SCHEME 2 The molecular structure of Series **H**.



A1 n= 5 Cr 87.8 SmA 175.4 I 173.1 SmA 68.5 Recr

A2 n=8 Cr 79.1 SmC 120.8 SmA 153.5 I 151.8 SmA 118.8 SmC 66.1 Recr

A3 n=8 Cr 92.6 SmC 129.5 SmA 159.8 I 157.7 SmA 126.2 SmC 71.1 Recr

SCHEME 3 The molecular structure and mesomorphic properties of compounds **A1–A3**.

REFERENCES

1. B. Q. Chen, Y. G. Yang and J. X. Wen, *Liq. Cryst.*, 24, 539 (1998).
2. P. Kromm, M. Cotrait, J. C. Rouillon, P. Barois and H. T. Nguyen, *Liq. Cryst.*, 2, 121 (1996).
3. P. Kromm, M. Cotrait and H. T. Nguyen, *Liq. Cryst.*, 21, 95 (1996).
4. F. G. Tournilhac, L. Bosio, J. Simon, L. M. Blinov and S. V. Yablonsky, *Liq. Cryst.*, 14, 405 (1993).
5. H. Liu and H. Nohira, *Liq. Cryst.*, 22, 217 (1997).
6. F. Tournilhac, L. M. Blinov, J. Simon and S. V. Yablonsky, *Nature*, 359, 621 (1992).
7. H. T. Nguyen, et al., *Liq. Cryst.*, 10, 389 (1991).
8. G. Johansson, V. Percec, G. Ungar and K. Smith, *Chem. Mater.*, 9, 164 (1997).
9. S. Takenaka, *J. Chem. Soc., Chem. Commun.*, 23, 1748 (1992).
10. H. Okamoto, H. Murai and S. Takenaka, *Bull. Chem. Soc. Jpn.*, 70, 3163 (1997).
11. E. Dietzmann, W. Weissflog, S. Markscheffel, A. Jakli, D. Lose and S. Diele, *Ferroelectrics*, 180 (1–4), 341 (1996).
12. Y. G. Yang, B. Q. Chen and J. X. Wen, *Liq. Cryst.*, 26, 893 (1999).