

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713926090>

Synthesis and liquid crystalline properties of several compounds with semi-fluorocarbon chains

Yong-Gang Yang^a; Jian-Xun Wen^a

^a Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Lu, Shanghai 200032, PR China,

Online publication date: 06 August 2010

To cite this Article Yang, Yong-Gang and Wen, Jian-Xun(2001) 'Synthesis and liquid crystalline properties of several compounds with semi-fluorocarbon chains', *Liquid Crystals*, 28: 11, 1735 – 1737

To link to this Article: DOI: 10.1080/02678290110076380

URL: <http://dx.doi.org/10.1080/02678290110076380>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Preliminary communication

Synthesis and liquid crystalline properties of several compounds with semi-fluorocarbon chains

YONG-GANG YANG* and JIAN-XUN WEN

Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences,
354 Fenglin Lu, Shanghai 200032, PR China

(Received 10 April 2001; accepted 10 May 2001)

Several molecules having long semi-fluoroalkyl chains have been synthesized, and their phase transition temperatures measured by texture observation in a polarizing microscope and DSC. The SmC phase is particularly favoured in this series, especially for compounds with a long semi-fluoroalkyl chain. It was found that when the terminal hydrogen atom of the semi-fluoroalkyl chain of one of the compounds (**D**) was substituted by a chlorine atom, the liquid crystalline sequence and ranges did not change; however, the clearing and melting points and T_{1-SmA} and $T_{SmA-SmC}$ increased by nearly 10°C.

There is a continuing search for new, polar or intermediately polar, liquid crystalline compounds with low viscosity, high thermal stability and chemical inertness. Generally, the core of a liquid crystalline compound consists of a two or three-ring system in order to hold the anisotropy of the molecular structure. However, a large molecular shape is undesirable in applications since it increases the viscosity and melting point. So in recent years much effort has been made to synthesize liquid crystals with a single benzene ring, especially in the field of compounds with semi-perfluorocarbon chains [1–5]. In fact, due to the extremely low surface energy and more rigid molecular structures of perfluorinated alkanes, in comparison with the corresponding perhydrogenated alkanes, the former can also form liquid crystalline phases [6–10]. To study further the mesomorphic properties of compounds with fluorocarbon chains, six compounds have been synthesized, so that subtle modification of the fluorocarbon chain may provide more information on type of compound.

The synthesis of the target molecules is outlined in the scheme. Compound **A** and the methyl esters were prepared by Mistunobu reaction. The esters were hydrolyzed to yield the corresponding acids **B** and **C**. The hydroxyl group of methyl 4-hydroxybenzoate was protected with benzyl chloride and the methyl ester was then hydrolyzed to give the benzoic acid. The protected acid was then esterified with the appropriate alcohol

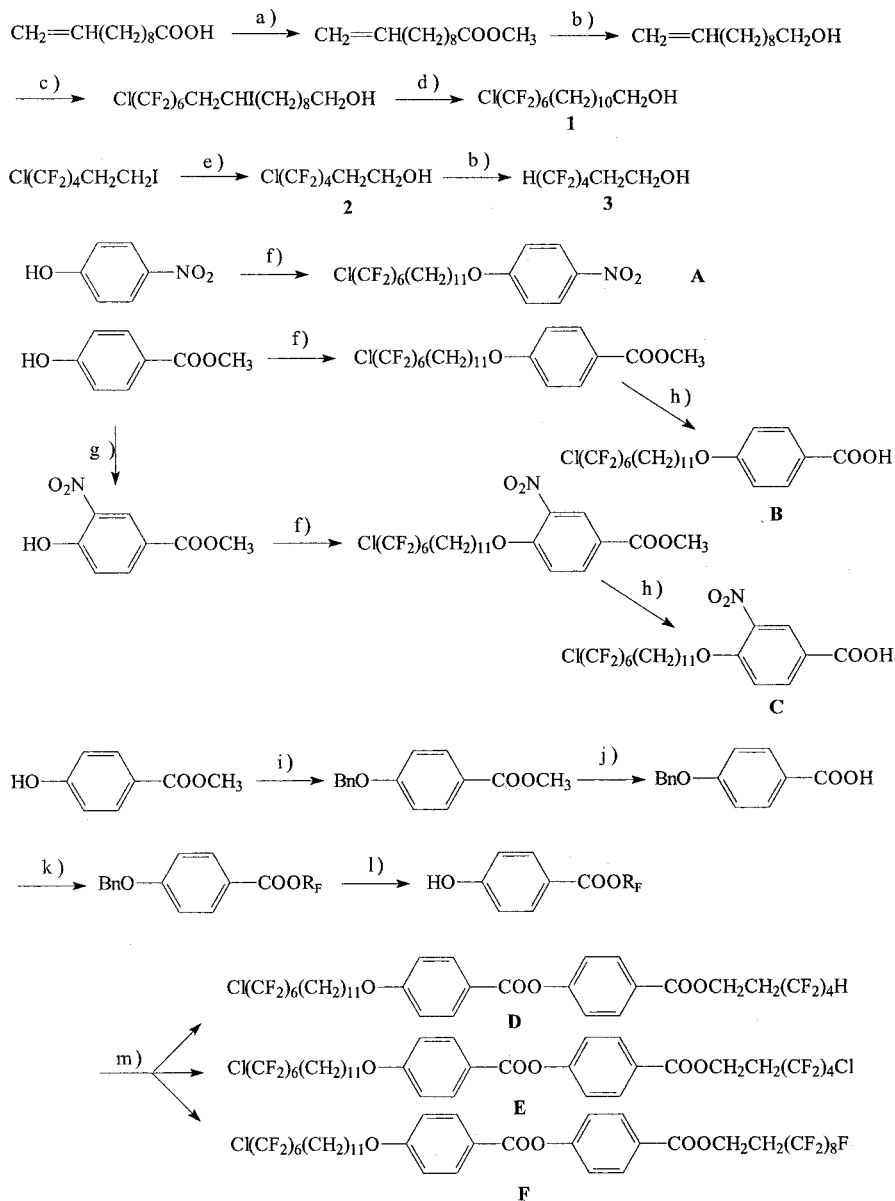
using DCC/DMAP in dry THF solution. The benzyl ether produced was then converted to the corresponding phenol ester by removal of the benzyl protecting group by hydrogenation at room temperature with H₂ in the presence of palladium on active carbon in ethyl acetate. Finally, to obtain compounds **D**, **E** and **F**, the phenol was esterified with the *para*-semi-fluoroalkoxy benzoic acid using DMM/DMAP in dry THF. All the intermediates and the final compounds were characterized by MS, EA, IR, ¹H NMR and ¹⁹F NMR spectroscopy.

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 calorimetry (DSC, Shimadzu DSC-50 calorimeter with a data system, heating and cooling rate 5°C min⁻¹). The transition temperatures reported in this paper were the peak values of the transition from DSC traces, and are summarized in the table.

Table. Transition temperatures of the compounds synthesized.
Cr = crystal, Sm = smectic, I = isotropic, Recr = recrystal.

Compound	Transition temperature/°C
A	Cr 63.9 I 44.3 SmC 44.0 Recr
B	Cr 126.2 SmC 153.3 I 151.2 SmC 121.7 Recr
C	Cr 97.9 SmC 106.3 I 104.6 SmC 77.4 Recr
D	Cr 83.8 I 72.6 SmA 72.0 SmC 70.6 Recr
E	Cr 92.5 I 82.7 SmA 82.2 SmC 79.3 Recr
F	Cr 115.2 I 111.9 SmC 100.0 Recr

*Author for correspondence, e-mail: ygyang@pub.sioc.ac.cn



Scheme. Synthesis route. Reagents and conditions: (a) CH_3OH , H_2SO_4 , C_6H_6 ; (b) LiAlH_4 , THF; (c) $\text{Cl}(\text{CF}_2)_6\text{I}$, $\text{Na}_2\text{S}_2\text{O}_4$, NaHCO_3 , CH_3CN , H_2O ; (d) Zn , CH_3COOH ; (e) SO_3 ; (f) THF, DEAD, PPH_3 , $\text{Cl}(\text{CF}_2)_6(\text{CH}_2)_{11}\text{OH}$; (g) HNO_3 ; (h) (1) NaOH , H_2O , THF; (2) HCl , H_2O ; (i) Na , benzyl chloride, $\text{C}_2\text{H}_5\text{OH}$; (j) (1) NaOH , $\text{C}_2\text{H}_5\text{OH}/\text{H}_2\text{O}$; (2) HCl , H_2O ; (k) DCC/DMAP, R_FOH , THF; (l) H_2 , Pd/C, ethyl acetate; (m) **B**, DCC/DMAP, THF.

The six compounds all have liquid crystalline properties. Compound **A** shows a very short monotropic SmC phase. The acid **B** shows an enantiotropic SmC phase between 126.2 and 153.3°C. Acid **C** has a $-\text{NO}_2$ group at the *meta*-position to the carboxylic acid group; due to this substitution the clearing point of **C** decreases by 47°C and the melting point by 28.3°C. Compounds

D, **E** and **F** are all monotropic liquid crystals. It is found that when the hydrogen atom on the semi-fluoroalkyl terminal chain of compound **D** is substituted by a chlorine atom, the liquid crystalline sequence and ranges do not change, but the clearing point, melting point, $T_{\text{I-SmA}}$ and $T_{\text{SmA-SmC}}$ increase by nearly 10°C. If the hydrogen atom is replaced by a $-(\text{CF}_2)_4\text{F}$ group (see compound **F**),

only the SmC phase is found. The SmC phase appears to be more readily formed with the increasing length of the fluorocarbon chain.

It is very interesting that the subtle change of one atom to another on the terminal semi-fluorocarbon chains can cause so much change in the liquid crystalline properties. Further work in this field is planned.

References

- [1] JOHANSSON, G., PERCEC, V., UNGAR, G., and SMITH, K., 1997, *Chem. Mater.*, **9**, 164.
- [2] TAKENAKA, S., 1992, *J. chem. Soc., chem. Commun.*, 1748.
- [3] OKAMOTO, H., MURAI, H., and TAKENAKA, S., 1997, *Bull. chem. Soc. Jpn.*, 3163.
- [4] OKAMOTO, H., YAMADA, N., and TAKENAKA, S., 1998, *J. Fluorine Chem.*, **91**, 125.
- [5] NISHIKAWA, E., YAMAMOTO, J., and YAKOYAMA, H., 2001, *Chem. Lett.*, 94.
- [6] VINEY, C., RUSSELL, T. P., DEPERO, L. E., and TWIEG, R. J., 1989, *Mol. Cryst. liq. Cryst.*, **168**, 63.
- [7] RABOLT, J. F., RUSSELL, T. P., and TWIEG, R. J., 1984, *Macromolecules*, **17**, 2786.
- [8] RUSSELL, T. P., RABOLT, J. F., TWIEG, R. J., SIEMENS, R. L., and FARMER, B. L., 1986, *Macromolecules*, **19**, 1135.
- [9] VILALTA, P. M., and WEISS, R. G., 1992, *Liq. Cryst.*, **12**, 531.
- [10] VINEY, C., TWIEG, R. J., RUSSELL, T. P., and DEPERO, L. E., 1989, *Liq. Cryst.*, **5**, 1783.