Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Synthesis and Properties of new Halogenated Liquid Crystals

A. I. Pavluchenko [a] , N. I. Smirnova [a] , V. F. Petrov [a b] , Y. A. Fialkov [c] , S. V. Shelyazhenko [c] , M. Schadt [d] & R. Bucheker [d]

[a] Organic Intermediates & Dyes Institute, Moscow, 103787, Russia

[b] Samsung Electronics Co., Ltd., P.O. Box 37, Suwon, 449-900, Korea

[c] Institute of Organic Chemistry, Ukrainian Academy of Sciences, Kiev, Ukraine

[d] F. Hoffman La Roche Ltd., CH-4002, Basel, Switzerland

Version of record first published: 04 Oct 2006.

To cite this article: A. I. Pavluchenko , N. I. Smirnova , V. F. Petrov , Y. A. Fialkov , S. V. Shelyazhenko , M. Schadt & R. Bucheker (1995): Synthesis and Properties of new Halogenated Liquid Crystals, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 265:1, 41-45

To link to this article: http://dx.doi.org/10.1080/10587259508041676

Mol. Cryst. Liq. Cryst. 1995, Vol. 265, pp. 41–45
Reprints available directly from the publisher
Photocopying permitted by license only

SYNTHESIS AND PROPERTIES OF NEW HALOGENATED LIQUID CRYSTALS

A.I. Pavluchenko, N.I. Smirnova, V.F. Petrov*
Organic Intermediates & Dyes Institute, Moscow 103787, Russia.
Y.A. Fialkov#, S.V. Shelyazhenko#
Institute of Organic Chemistry, Ukrainian Academy of Sciences, Kiev, Ukraine.
M. Schadt**, R. Bucheker**
** F.Hoffman La Roche Ltd., CH-4002 Basel, Switzerland.

ABSTRACT
Several new classes of low polar, low viscous and optically weak anisotropic two- and three-ring halogenated liquid crystals containing terminal group -OCF_2Cl are presented. Their material properties are investigated and compared with those of other halogenated liquid crystals.

INTRODUCTION

Halogenated liquid crystals have been extensively studied during last decade owing to their suitability for various electro-optical display applications/1-5/. Here, we introduce a number of new difluorochloro-methoxy derivatives.

RESULTS AND DISCUSSION

Mesomorphic and Physico-Chemical Properties

The procedures for measuring phase transition points, as well as dielectric and optical characteristics of liquid crystalline materials, are described in detail in Reference 6. Phase transition temperatures of synthesized compounds are given in Table 1 along with dielectric anisotropy $\Delta\varepsilon$ and optical anisotropy Δn obtained by extrapolation from the corresponding values of mixtures with ZLI-1132 (Merck). As follows from Table 1 and the data presented in /4/, the replacement of the terminal group $OCHF_2$ by the OCF_2Cl leads to the slight increasing of melting points, decreasing of the clearing temperatures, optical and dielectric anisotropies. In some cases this replacement causes the disappearance of the smectic phase that could be very useful for the development of the wide temperature range liquid crystalline materials.

* Present address: Samsung Electronics Co., Ltd., P.O. Box 37, Suwon 449-900, Korea.

Experimental

Example 1. Preparation of 4-Difluorochloromethoxy-4'-(4-trans-propyl-cyclohexyl)-diphenyl (1)

Solution of 0.05 mol of 4-(4-trans-propylcyclohexyl)brombenzene in 50 ml of THF is added drop by drop to a boiling mixture of 0.05 gram-atom of magnesium in 25 ml of THF. When the adding is over the reaction mixture is boiled for 1 hour, cooled and added drop by drop to a mixture of 0.05 mol of 4-difluorochloromethoxybromobenzene and 0.9 g of $PdCl_2$ (dppf) in 30 ml pf THF at 0 °C. After 30 min, the reaction mixture is boiled for i hour, then is decomposed by a saturated aqueous solution of NH_4Cl at room temperature. The organic phase is separated, the aqueous layer is extracted by the benzene. The combined organic layer and the benzene extract are dried by $MgSO_4$, filtered and the solvent is evaporated. The residue is purified by the column chromatography on SiO_2 (L 40/100), h = 15 sm, hexane-eluent. The solvent is distilled of, the residue is recrystallized from the alcohol. The required product is obtained with 30 - 35% yield.

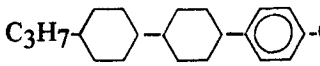
Tc-s = 96.0 °C, Ts-n = 112.0 °C, Tn-i = 123.0 °C.

Found, %: C 69.81; H 6.54; F 10.21;

$C_{22}H_{25}F_2ClO$

Calculated, %: C 69.74; H 6.65; F 10.03

Compounds (a) and (b) are prepared similarly.



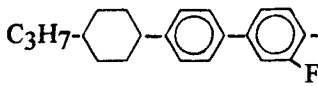
(a)

Tc-n = 82.0 °C, Tn-i = 133.0 °C.

Found, %: C 68.79; H 8.34; F 9.61;

$C_{22}H_{31}F_2ClO$

Calculated, %: C 68.65; H 8.12; F 9.87



(b)

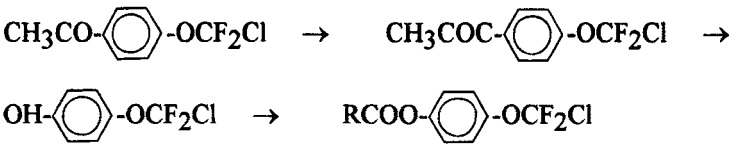
Tc-n = 43.0 °C, Tn-i = 75 °C

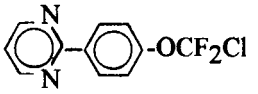
Found, %: C 66.70; H 6.01; F 14.12;

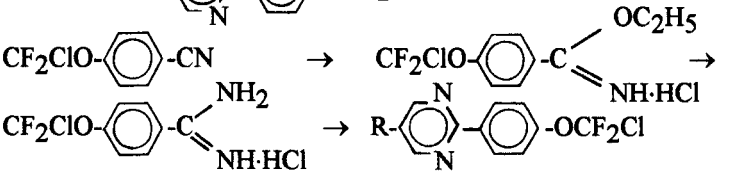
$C_{22}H_{24}F_3ClO$

Calculated, %: C 66.58; H 6.10; F 14.36

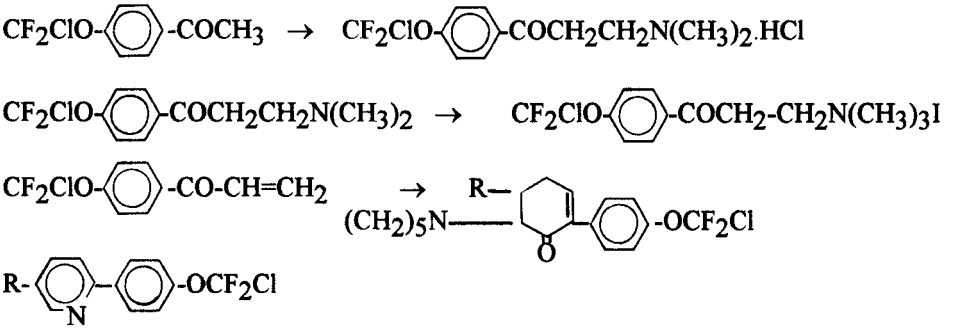
The esters are obtained using the general synthetic scheme:



Compounds  are obtained using the following synthetic scheme:



Synthesis of pyridine derivatives is performed according to the general scheme:



Preparation of 2-(4-difluorochloromethoxyphenyl)-6-substituted-5,6,7,8-tetrahydroquinoline derivatives.

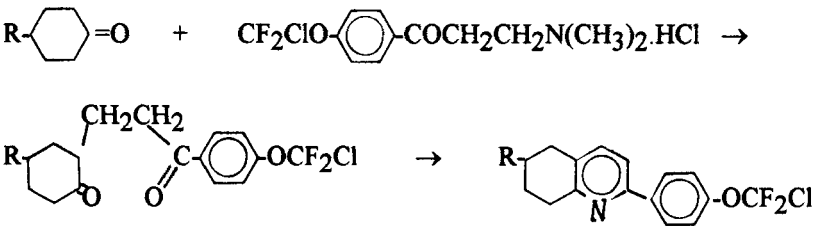
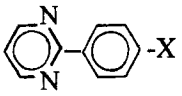
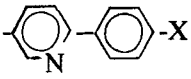
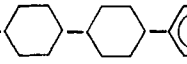
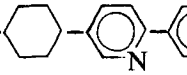
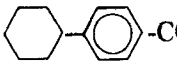
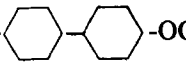
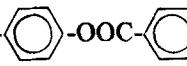
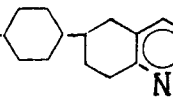
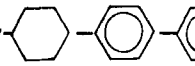
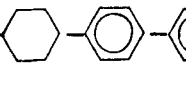
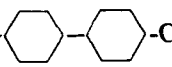
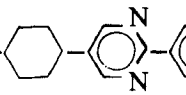


Table 1. Physico-chemical properties of new liquid crystalline compounds.

No	Material, X = OCF_2Cl	Tc-s, c-n, c-i, °C	Ts-n, °C	Tn-i, °C	ΔH, kcal mol	Δε 20 °C	Δn 20 °C
1.	C_3H_7-  -X	44.9				13.1	0.125
2.	C_5H_{11}-  -X	36.0					
3.	C_3H_7-  -X	82.0		133.0		7.5	0.100
4.	C_4H_9-  -X	79.5	121.7	130.3	5.7	12.2	0.134
5.	C_5H_{11}-  -X	113.0		150.0	8.7	13.8	0.125
6.	C_3H_7-  -X	62.2	91.0	150.5	7.2	4.4	0.094
7.	C_3H_7-  -X	50.4					
8.	C_5H_{11}-  -X	101.4	113.5	164.5	5.1	10.3	0.125
9.	C_3H_7-  -X	96.0	112.5	123.0		9.2	0.154
10.	C_3H_7-  -X	43.0		75.0		11.5	0.123
11.	C_5H_{11}-  -X	62.6		113.6		6.2	0.090
12.	C_4H_9-  -X	30.0	130.6	135.2		16.1	0.142

CONCLUSION

The discussed new liquid crystalline compounds represent a new, promising class of liquid crystals whose characteristics allow to consider them as the most suitable components to be used for the development of liquid crystalline materials for display applications.

REFERENCES

1. E. Bartmann, D. Dorsch, U. Finkenzeller, Mol.Cryst.Liq.Cryst., **204**, 77(1991).
2. H. Takatsu, K. Takeuchi, M. Sasaki, et al., Mol.Cryst.Liq.Cryst., **206**, 159(1991).
3. Y. Goto, T. Ogawa, S. Sawada, et al., Mol.Cryst.Liq.Cryst., **209**, 1(1991).
4. A.I. Pavluchenko, N.I. Smirnova, V.F. Petrov, et al., Ibid, **209**, 225(1991).
5. S.-T. Wu, D. Coates, E. Bartmann, Liquid Crystals, **10**, 635(1991).
6. M.F. Grebyonkin, V.F. Petrov, V.V. Belyaev, et al., Mol.Cryst.Liq.Cryst., **129**, 245(1985).