Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl18

Synthesis and Properties of Liquid Crystals with Fluorinated Terminal Substituents

A. I. Pavluchenko [a], N. I. Smirnova [a], V. F. Petrov [a], Yu. A. Fialkov [b], S. V. Shelyazhenko [b] & L. M. Yagupolsky [b]

[a] Organic Intermediates and Dyes Institute, Moscow, 103787, USSR

[b] Institute of Organic Chemistry, Kiev, USSR Ukrianian Academy of Sciences

Version of record first published: 24 Sep 2006.

To cite this article: A. I. Pavluchenko , N. I. Smirnova , V. F. Petrov , Yu. A. Fialkov , S. V. Shelyazhenko & L. M. Yagupolsky (1991): Synthesis and Properties of Liquid Crystals with Fluorinated Terminal Substituents, Molecular Crystals and Liquid Crystals, 209:1, 225-235

To link to this article: http://dx.doi.org/10.1080/00268949108036197

Mol. Cryst. Liq. Cryst., 1991, Vol. 209, pp. 225–235
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

Synthesis and Properties of Liquid Crystals with Fluorinated Terminal Substituents

A. I. PAVLUCHENKO,† N. I. SMIRNOVA† and V. F. PETROV†

† *Organic Intermediates and Dyes Institute, Moscow 103787, USSR*

and

YU. A. FIALKOV,‡ S. V. SHELYAZHENKO‡ and L. M. YAGUPOLSKY‡

‡ *Institute of Organic Chemistry, Kiev, USSR Ukrianian Academy of Sciences.*

(Received July 26, 1990)

The paper reports synthesis of LC derivatives of different chemical classes containing terminal groups —$OCHF_2$, —OCF_3, —$SCHF_2$, —OC_nF_{2n+1} and —C_nF_{2n+1} and indicates their phase transition points and physico-chemical properties.

Keywords: synthesis, physical-chemical properties, fluorinated terminal groups

INTRODUCTION

The overwhelming majority of modern LCDs are based on the twist-effect[1] and require adequate LC materials of positive dielectric anisotropy ($\Delta\varepsilon = \varepsilon_{||} - \varepsilon_{\perp} > 0$). The most common way to obtain LC compounds with light positive $\Delta\varepsilon$ is to introduce polar groups such as —CN, —NCS and F into the terminal position of the LC molecule.

This paper presents synthetic scheme and physico-chemical properties of LC derivatives of different chemical classes containing terminal groups —$OCHF_2$, —OCF_3, —$SCHF_2$ and —OC_nF_{2n+1} and —C_nF_{2n+1}.

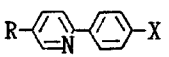
RESULTS AND DISCUSSION

Experimental

The pyridine derivatives were obtained using the following general synthetic scheme[2]: diene condensation of the corresponding enamine with 1-acryloyl-4-substituted benzene, followed by reaction of the resulting 3-alkyl-6-(4-P-phenyl)-3,4-dihydro-

TABLE I

Physico-chemical properties of Liquid Crystalline compounds

Formula	R	X	Mesophase(s), °C	$T_{cl.}$, °C	$\Delta\varepsilon$,	Δn,	ν, mm²/s,
1	2	3	4	5	6	7	8
	C_3H_7	OCF_3	C22.0S65.1I	-45	13.2	0.134	
		$OCHF_2$	C14.2S37.5I	4	17.7	0.160	11.3
		NCS	C64.0S_A99.0I				
		CN	C43.4N43.8I	41.5	29.4	0.239	42.0
	C_5H_{11}	OCF_3	C18.6S_B38.5S_A52.4I	-24	11.8	0.074	
		$OCHF_2$	C26.0S43.6I	-9	15.9	0.125	12.0
		$SCHF_2$	C2.5I	-17	22.9	0.133	9.0
		NCS	C34.0S_A98.5I	67	15.5	0.220	18.0
		CN	C33.6N43.5I	42	18.9	0.214	50.0
		F	C28.1I	24	9.8	0.074	
		C_6F_{13}	C81.1S_B(74.6)I	49	0.7	0.142	
		C_6H_{13}	C15.0S_A33.0I				
	C_7H_{15}	OCF_3	C24.0S44.3I	-17	8.3	0.060	
		$OCHF_2$	C22.1S46.1I				

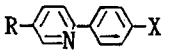
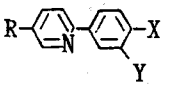
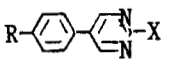
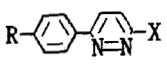
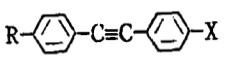
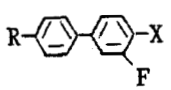
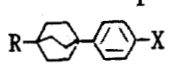
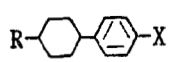
1	2	3	4	5	6	7	8
	C_7H_{15}	OC_7F_{15}	C53.1S_A111.7I				
		OC_7H_{15}	C24S_H31.5S_G40.3S_F 53.0S_C76.6I				
		NCS	C26.1S_A99.2I				
	C_7H_{15} Y=F	OC_7F_{15}	C32.5S_A86.1I	37	7.0	0.040	
	C_7H_{15} Y=F	OC_7H_{15}	C28.1S_A49.1I	2	4.2	0.113	
	CH_3SCH_2 Y=H	OCF_3	C42.5I				
	$CH_2{=}CH(CH_2)_2$ Y=H	OCF_3	C14.3S42.9I				
	$CH_2{=}CH(CH_2)_2$ Y=H	$OCHF_2$	C32.2S42.9I				
	$C_2H_5{-}\underset{\displaystyle CH_3}{\overset{\displaystyle *}{C}}H$ Y=H	$OCHF_2$	C54.5I				
	C_8H_{17} Y=F	$OCHF_2$	C15I				

TABLE I (*continued*)

Formula	R	X	Mesophase(s), °C	$T_{cl.}$, °C	$\Delta\varepsilon$,	Δn,	ν, mm²/s,
1	2	3	4	5	6	7	8
	C_5H_{11}	$SCHF_2$	C50.8I	-17	14.7	0.134	39.0
		CN	$C96.0S_A(93.5)N109I$				
	C_5H_{11}	$OCHF_2$	C86.6I	-22	10.9		
		$SCHF_2$	C95.0I	-40	9.4		
	C_5H_{11}	$OCHF_2$	C28.1S37.8I	28	8.8	0.180	
	C_8H_{17}	OC_7F_{15}	$C53.0S_A64.2I$				
	C_7H_{15}	$OCHF_2$	C10.8N31.6I	26	3.8	0.063	14.0
	C_3H_7	$OCHF_2$	C-14.9I	-40	8.3	0.044	5.0
		$SCHF_2$	C12.5I	-56	10.6	0.044	18.5
		CN	C43.0N45.0I		13.5	0.130	
	C_7H_{15}	$OCHF_2$	C7.0I	1	5.6	0.055	8.0

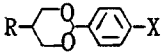
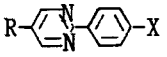
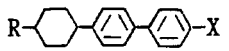
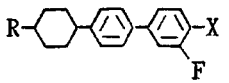
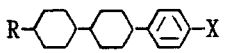
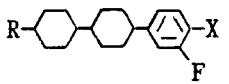
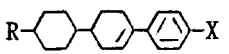
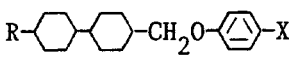
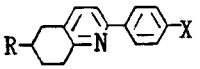
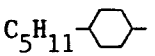
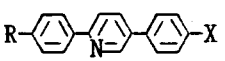
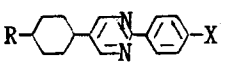
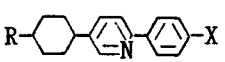
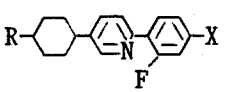
1	2	3	4	5	6	7	8
	C_3H_7	OCF_3	C36.3S_B(35)I				
		$OCHF_2$	C29.1I	-14	17.2	0.093	
	C_5H_{11}	OCF_3	C23.6S_B34.9I	-24	10.0	0.040	
		$OCHF_2$	C23.0S(4.0)N(8.0)I	-36	14.6	0.044	9.0
		$SCHF_2$	C42.5I	-29	16.1	0.050	
		CN	C57.0N(48)I		32.0	0.140	
	C_7H_{15}	$OCHF_2$	C24.6S(22.7)N24.3I	21	9.6	0.044	12.4
	C_3H_7	OCF_3	C43.1S48.2I	-17	18.9	0.134	
		$OCHF_2$	C40.1I				
		$SCHF_2$	C53.2I	-16	26.9	0.149	
	C_5H_{11}	OCF_3	C32.0S_A45.2I	-6	18.5	0.094	
		$OCHF_2$	C20.1S24.0I	-5	20.6	0.123	
		$SCHF_2$	C43.1I	-16	22.7	0.130	
		CN	C71N(53.3)I		34.0	0.220	55.0
	C_8H_{17}	$OCHF_2$	C26.3S31.6I	-3	13.0	0.104	
		OC_9F_{19}	C65.1S_A115.1I				

TABLE I (*continued*)

Formula	R	X	Mesophase(s), °C	$T_{cl.}$, °C	Δε,	Δ*n*,	*ν*, mm²/s,
1	2	3	4	5	6	7	8
	C_5H_{11}	$OCHF_2$	C69.5S119.6N167.5I	137	9.7	0.154	28.0
		$SCHF_2$	C56.2S94.7N114.0I	105	11.4	0.174	
		CN	C96.0N222.0I		12.0	0.190	
	C_3H_7	$OCHF_2$	C82.0S121.1N169.4I	156	10.2	0.170	
	C_3H_7	$OCHF_2$	C50.5N118.4	110	12.3	0.139	
	C_3H_7	$OCHF_2$	C50.8S69.2N172.2I	155	8.3	0.114	23.0
	C_5H_{11}	$OCHF_2$	C35.0N148.2I	123	11.2	0.090	26.0
	C_3H_7	$OCHF_2$	C36.7S96.4N167.7I	165	8.9	0.154	
	C_5H_{11}	$OCHF_2$	C52.0S76.7N142.5I	139	7.2	0.094	

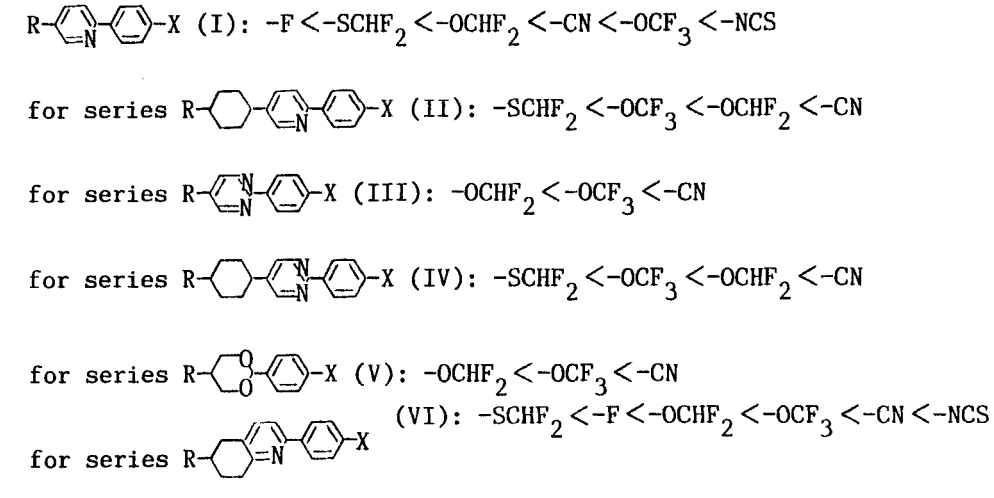
1	2	3	4	5	6	7	8
	C_5H_{11}	OCF_3	C57.5N63.2I	33	13.3	0.104	
		$OCHF_2$	C61.8N(59.1)I	64	10.1	0.130	
		$SCHF_2$	C40.9I	6	16.0	0.130	
		CN	C96.2N98.0I	106	19.6	0.214	
		NCS	C92.0S104.0N115.1	107	15.3	0.254	
		F	C65.0N(55.1)I	31	10.7	0.113	74.0
		$OCHF_2$	C121.0N204.1I	179	10.9	0.190	
	C_5H_{11}	$OCHF_2$	$C58.1S_1173.7S_2$ 235.5I	159	10.9		
	C_4H_9	OCF_3	C57.0S161.3I	134	16.6	0.146	
		$OCHF_2$	C91.4S152.0N176.6I	155	18.2	0.149	
		$SCHF_2$	C69.1S111.1N131.4I	125	14.4	0.184	
	C_4H_9	OCF_3	C35.1S149.2N154.8I	107	10.6	0.123	
		$OCHF_2$	C57.1S135.7N165.3I	111	13.8	0.154	
	C_4H_9	$OCHF_2$	C39.6S78.3N136.4I				

2-*N*-pyperidine-2H-pyrans with hydroxylamine hydrochloride. Similarly, derivatives of 5,6,7,8-tetrahydroquinoline were prepared. The dioxane derivatives were synthesized by common procedure from corresponding *p*-substituted aldehydes.[3,4] The pyrimidine derivatives were obtained from corresponding *p*-substituted benzamidine hydrochloride using the general synthetic scheme. The compound's structures were confirmed by NMR analysis. The element analysis proved satisfactory for all derivatives.

Mesomorphic and Physico-Chemical Properties

Procedures for measuring phase transition points, as well as dielectric, optical and viscous properties of liquid crystal compounds, are described in detail in Reference 5. Phase transition temperatures for the synthesized compounds are given in Table I along with clearing points, dielectric anisotropy $\Delta\varepsilon$, optical anisotropy Δn and kinematic viscosity ν (at 20°C) obtained by extrapolation from the corresponding values for mixtures with ZLI-1132, as well as the same parameters for some known compounds taken from literature.

As follows from Table I, clearing points for pyridine derivatives of general formula (I) grow depending on the type of the terminal substituent as follows:



Replacement of the —CN group by $—OCF_3$, $—OCHF_2$ or $—SCHF_2$ results in lower melting points, while introduction of $—C_nF_{2n+1}$ and OC_nF_{2n+1} leads to a significant growth of clearing points and disappearance of polymorphism.

Table II gives measured values $\varepsilon_{\|}$, $\varepsilon_{\perp}$ and $\Delta\varepsilon$ for the series $—OCHF_2$ and $—SCHF_2$ derivatives belonging to different chemical classes.

In Table III values of dielectric constant $\varepsilon_{isotr.}$ are given measured in the isotropic phase at $T = T_{cl.}$ for the fifth homolog series of polar derivatives having different chemical structures.

$$\varepsilon_{isotr.} \approx \varepsilon_{av.} = \frac{2\varepsilon_{\perp} + \varepsilon_{\|}}{3}$$

Study of dielectric properties in the isotropic phase allows the increase of number of compared substances by adding nonmesomorphic compounds as well as those having only a smectic phase.

As follows from Tables I–III, for the compounds whose dielectric properties were measured, a correlation with their calculated counterparts is observed permitting us to include in the comparative analysis of dielectric characteristics those liquid crystals for which calculation is the only possible way to evaluate their properties. According to Maier and Meier,[6] dielectric anisotropy of LCs with polar molecules depends on polarizability of the molecule, magnitude of dipole moment, degree of ordering S and angle between dipole moment and axis of maximal polarizability of the molecule. Tables I–III show that for definite chemical structure

TABLE II

Dielectric constants of some polar compounds

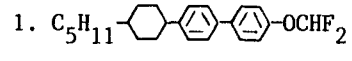
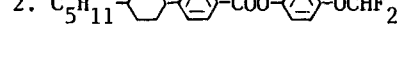
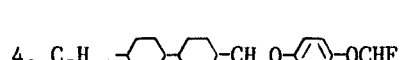
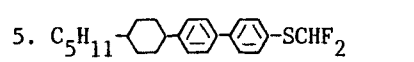
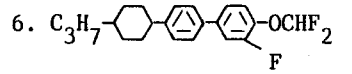
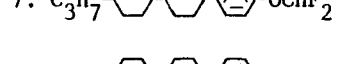
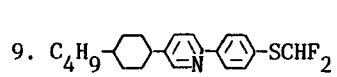
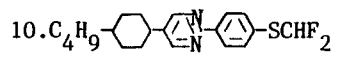
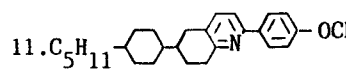
N Formula	$\varepsilon_{\parallel}$	$\varepsilon_{\perp}$	$\Delta\varepsilon$	$\tau = T/T_{cl.}$, K
1. 	6.8	3.3	3.5	0.88
2. 	12.1	4.8	7.3	0.85
3. 	6.5	4.8	2.5	0.85
4. 	6.2	3.8	2.4	0.85
5. 	7.4	3.6	3.8	0.95
6. 	8.7	4.6	4.1	0.95
7. 	5.0	2.8	2.2	0.85
8. 	6.9	3.3	3.6	0.85
9. 	11.1	5.7	5.4	0.95
10.	10.5	5.0	5.5	0.95
11.	8.4	4.0	4.4	0.85

TABLE III

Permittivity results for some polar compounds.

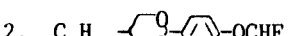
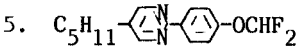
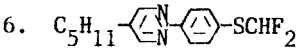
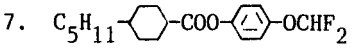
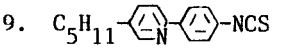
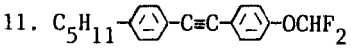
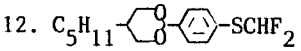
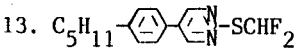
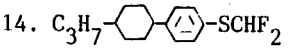
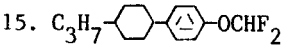
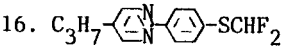
N	Formula	$\varepsilon_{isotr.}$, $T = T_{cl.}$
1.		5.9
2.		11.2
3.		10.5
4.		11.6
5.		10.1
6.		10.6
7.		6.4
8.		17.4
9.		9.2
10.		8.5
11.		5.7
12.		10.6
13.		12.7
14.		6.4
15.		6.3
16.		11.3

TABLE III (*continued*)

N Formula	$\varepsilon_{isotr.}$, T = $T_{cl.}$
17. C_5H_{11}-(Pyr)-(Ph)-CN	12.4
18. C_5H_{11}-(Pyr)-(Ph)-$SCHF_2$	8.8
19. C_5H_{11}-(Pyr)-(Ph)-$OCHF_2$	7.9
20. C_5H_{11}-(Pyr)-(Ph)-F	5.2

of LC, its dielectric anisotropy as a rule decreases in the same sequence as values of dipole moments for terminal groups —CN, —NCS, —$OCHF_2$, —OCF_3 and F diminish: 4.05 D, 3.59 D, 2.46 D, 2.36 D and 1.47 D, respectively.[7,8]

The data given in Table I show that replacement of —CN group by terminal substituents —OCF_3, —$OCHF_2$, —$SCHF_2$ or —C_nF_{2n+1} results in lower values of optical anisotropy and kinematic viscosity.

CONCLUSION

The discussed LC compounds with fluorinated terminal substituents represent a new, promising class of liquid crystals whose characteristics allow to consider them as most suitable components to be used for developoment of liquid crystal materials.

Acknowledgment

The authors are grateful to MERCK (Germany) for providing a sample of ZLI-1132.

References

1. M. Schadt and W. Helfrich, *Appl. Phys. Lett.*, **18**, 127 (1971).
2. A. I. Pavluchenko, G. V. Purvanyatskas, N. I. Smirnova and V. V. Titov, *Zh. Org. Khim.*, V.XXII, No. 7, 1524 (1986).
3. L. M. Yagupolsky and V. I. Trotskaya, *Zh. Obshch. Khim.*, **30**, No. 3, 3129 (1960).
4. Yu. A. Fialkov and S. V. Shelyazhenko, Inventor's Cert. 1085971, USSR, MKI CO7C 47/575, *Otkryt. Izobret.*, No. 14, 79 (1984).
5. M. F. Grebyonkin, V. F. Petrov, V. V. Belyaev *et al.*, *Mol. Cryst. Liq. Cryst.*, **129**, 245 (1985).
6. W. Maier and G. Meier, *Z. Naturforsch.*, **16a**, 262 (1961).
7. V. I. Minkin, O. A. Osipov and Y. A. Zhdanov, Dipole Moments in Organic Chemistry, Plenum, New York, 1970.
8. A. E. Lutskii, E. M. Obukhova, V. V. Prezhdo *et al.*, *Teor. Eksp. Khim.*, **6**, 834 (1970).