Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

New Mesogenic Compounds with a Large Dielectric Anisotropy

A. V. Ivashchenko [a] , E. I. Kovshev [a] , V. T. Lazareva [a] , E. K. Prudnikova [a] , V. V. Titov [a] , T. I. Zverkova [a] , M. I. Barnik [a] & L. M. Yagupolski [a]
[a] Organic Intermediates and Dyes Institute, 103787, Moscow, U.S.S.R.
Version of record first published: 14 Oct 2011.

To cite this article: A. V. Ivashchenko , E. I. Kovshev , V. T. Lazareva , E. K. Prudnikova , V. V. Titov , T. I. Zverkova , M. I. Barnik & L. M. Yagupolski (1981): New Mesogenic Compounds with a Large Dielectric Anisotropy, Molecular Crystals and Liquid Crystals, 67:1, 235-240

To link to this article: http://dx.doi.org/10.1080/00268948108070893

Mol. Cryst. Liq. Cryst., 1981, Vol. 67, pp. 235–240
0026–8941/81/6704–0235$06.50/0

Printed in the U.S.A.

New Mesogenic Compounds with a Large Dielectric Anisotropy

A. V. IVASHCHENKO, E. I. KOVSHEV, V. T. LAZAREVA, E. K. PRUDNIKOVA, V. V. TITOV, T. I. ZVERKOVA, M. I. BARNIK and L. M. YAGUPOLSKI

Organic Intermediates and Dyes Institute, 103787, Moscow, U.S.S.R.

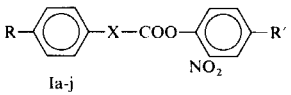
(*Received August 12, 1980*)

Mesomorphic 2-nitrophenyl benzoates and cinnamates as well as 4-cyanophenyl 4′-perfluoroalkyl-, 4′-perfluoroalkoxy- and 4′-monohydropherfluoroalkoxy benzoates have been synthesised. The mesomorphic properties of the fluorinated derivatives are compared with those of the corresponding hhdrogenous derivatives.

INTRODUCTION

Electro-optical effects in liquid crystals[1] determine the technological significance of mesophases in display production. The principle of operation of such displays is based mainly on an orientational action of the external electric field on a macroscopically ordered layer of liquid crystal with a positive or negative dielectric anisotropy. The effectiveness of LC applications in electro-optical devices depends to a considerable extent on the possibility of controlling the sign and magnitude of the dielectric anisotropy, since those properties determine mainly the type of electro-optical effect and its threshold.

We have synthesised two new series of esters with a large negative (I) and positive (II) dielectric anisotropy whose general formulae are:

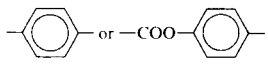


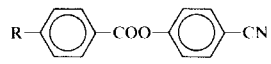
Ia-j

R = alkyl or alkoxy

R′ = alkyl

X = single bond or =CH=CH—





IIa-f

R = perfluoroalkyl or perfluoroalkoxy or $HF_2C(CF_2)_3O$

The large magnitudes of the dielectric constants of the compounds I and II are determined by the strongly dipolar nitro and cyano groups.

EXPERIMENTAL

Transition temperatures (Tables I and II) were measured by optical microscopy using a polarising microscope (Polam L–211) fitted with a Mettler FP–52 heating stage and FP–5 control unit. Measurement of the dielectric constants of the esters I (Figure 1) and their solutions in a LC matrix (Figures 1 and 2, Table I) were carried out using cells presenting flat capacitors of

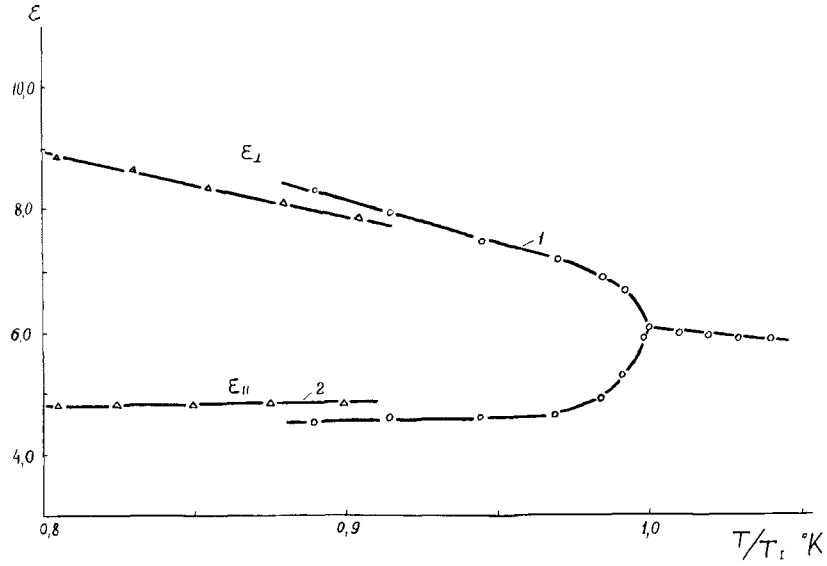


FIGURE 1 Temperature dependences of the dielectric permittivities of compounds Ia (1) and Ii (2) (temperatures are given in °K).

1 cm^2 × 160. Dielectric permittivities in the frequency range from 200 Hz to 30 kHz were measured by a bridge method, the accuracy being approximately 3% for $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$.

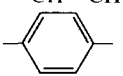
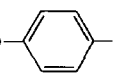
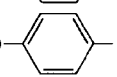
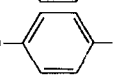
A mixture of azoxybenzenes was used as the LC matrix; temperature range from −5 to 74°C, $\varepsilon_{\parallel}$ 4.85, $\varepsilon_{\perp}$ 5.25 (ε_a − 0.4 at 20°C).

4-Alkyl-2-nitrophenyl benzoates (Ia-j)

a) A solution of 4-alkylphenol (0.1 mol) in acetic acid (20 ml) was added

TABLE I

Phase transition temperatures for the 4-alkyl-2-nitrophenyl esters (I); their dielectric constants and the clearing points of their solutions in a LC matrix*

Compound index		R	R′	X	Phase transition temperatures (°C) T_N	T_I	ε_z (calculated)	Solution in LC matrix $\varepsilon_{\parallel}$	$\varepsilon_{\perp}$	ε_z	T (°C)	Clearing point (°C)
I	a	C_3H_7	C_7H_{15}	—		34–35	−4,9	4,88	5,73	−0,85	20,5	
	b	C_4H_9	C_7H_{15}	—		20	−4,7	4,94	5,77	−0,83	21,0	
	c	C_7H_{15}	C_7H_{15}	—		oil	−4,3	4,80	5,59	−0,79	21,0	
	d	C_3H_7	$C_6H_{13}O$	—		33–34	−4,5	4,92	5,73	−0,81	21,0	56,5
	e	C_7H_{15}	$C_6H_{13}O$	—		30–31	−5,9	4,85	5,80	−0,95	20,5	64,3
	f	C_7H_{15}	C_7H_{15}	—CH=CH—		32–33	−4,8	4,83	5,67	−0,84	20,0	66,2
	g	C_3H_7	C_6H_{13}		84–85	91–92	−5,4	4,80	5,70	−0,90	20,0	77,6
	h	C_3H_7	C_7H_{15}	—COO— 	120–121	120–121	−4,4	4,82	5,62	−0,80	21,0	79,1
	i	C_4H_9	C_7H_{15}	—COO— 	77–78	128–129	−4,4	4,84	5,64	−0,80	21,5	80,1
	j	C_7H_{15}	C_7H_{15}	—COO— 	62–63	123–124	−4,7	4,80	5,63	−0,83	21,5	82,6

* mixture (2:1) of 4-metiioxy-4′-butylazoxybenzenes and 4-heptanoyloxy-4′-butylazoxybenzenes.

TABLE II

Phase transition temperatures for the 4-cyanophenyl 4′-substituted benzoates (II).

Compound index		R	Phase transition temperature (°C) T_S	T_N	T_I	R	Phase transition temperature (°C) T_N	T_I
II	a	C_4F_9	(79)		82	C_4H_9	(41,1)	66
	b	C_4F_8HO	74	—	94			
	c	C_4F_9O	80	—	128	C_4H_9O	92	104
	d	$C_5F_{11}O$	(136)	(142)	143	$C_5H_{11}O$	87	96
	e	C_6F_{13}	100	—	124	C_6H_{13}	(44,4)	48,6
	f	$C_7H_{15}O$	104	—	128	$C_7H_{15}O$	71,6	82

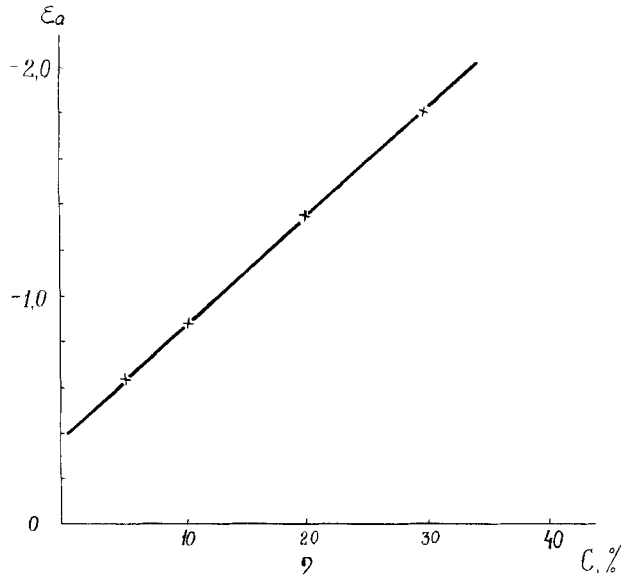


FIGURE 2 Dependence of the dielectric anisotropy of the LC matrix on the concentration of compound Ig.

with stirring to cooled (5–7°C) nitric acid (20 ml, *d* 1.35) at a rate such that the reaction temperature was kept below 10°C. After 30 min stirring at 10°C, the reaction mixture was diluted and shaken with ether; the extract was washed with water until neutral, dried with anhydrous sodium sulfate and distilled in vacuum.

2-Nitro-4-propylphenol: b.p. 90–92°C (1 mm);

2-nitro-4-butylphenol: b.p. 98–100°C (1 mm);

2-nitro-4-heptylphenol: m.p. 35–6°C (crystallized) from ethanol; separated by steam distillation). The elemental analysis data for the 2-nitro-4-alkylphenols were in agreement with calculated values.

b) The 4-substituted benzoyl chloride (0.01 mol) was added with stirring to a cooled solution of the 2-nitro-4-alkylphenol (0.01 mol) in pyridine (20 ml) at a rate such that the reaction temperature was kept below 20°C. After 14 hours at 20°C, the mixture was poured into water, acidified with hydrochloric acid (to pH 3); the precipitate was then separated by filtration, washed with water, a 10% solution of sodium carbonate, and again with water. The dried solid was crystalized 2–3 times from ethanol (with charcoal). If an oily product was formed, it was extracted into methylene chloride, the solution was dried with calcium chloride, and the product crystallised from ethanol (with charcoal) after removal of the solvent. All compounds Ia-j (Table I) gave satisfactory data on elemental analysis.

4-Perfluoroalkyl(alkoxy)benzoic acids have been synthesized by methods previously used for lower homologues.[2] The esters IIa-f have been prepared by reaction of the corresponding acid chlorides with 4-cyanophenol in pyridine.[3] (Table II).

DISCUSSION

Looking at Table I, we can see that the 4-alkyl-2-nitrophenyl 4-alkyl(alkoxy)-benzoates (Ia-e) and cinnamates (1f) melt at low temperatures and do not exhibit nematic phases, whereas the biphenyl derivative (Ig) and the 4-(4′-heptylbenzoyloxy)benzoic acid esters (Ih-j) form nematic liquid crystals. Introduction of these compounds (10%) into the LC matric leads to an enlargement in the absolute value of the dielectric anisotropy by 0.4–0.55 with a clearing point lowering of 7–16° for compounds Ia-f and an increase in clearing point the compounds Ig-j, as expected.

As we can see from Figure 1, the ε_a value of the solution of Ih in the LC matrix varies approximately proportionaly to the component ratio. Taking this fact into account and measuring dielectric constants for 10% solutions, we have calculated effective values of the dielectric anisotropies of compounds 1a-f (Table I) that were found to be equal to -4.3 to -5.9.

The similarity of the ODA values of the two ring compounds Ia-f and the three ring compounds Ig-j may be due to the lower ordering of the former in the LC matrix. It is necessary to note that direct measurements of the dielectric constants of compounds Ig, i were used to obtain approximate data relating to ambient temperature and that this gives values which somewhat differ from those calculated from 10% solution data. These differences may be explained by the different packings of the molecules of the pure compound in the nematic phase and in its solutions.

Looking at Table II, we can see that the mesophase thermal stabilities of the 4-cyanophenyl 4′-perfluoroalyl(alkoxy)benzoates are higher than those of their hydrogenous analogues.[2] As for previous fluorine containing compounds,[2] these derivatives exhibit smectogenic properties.

References

1. L. M. Blinov, *Electro- and Magneto-optics of Liquid Crystals*, "Nauka", Moscow, 1978.
2. V. V. Titov, T. I. Zverkova, E. I. Kovshev, Yu. N. Fialkov, S. V. Shelazhenko, and L. M. Yagupolski, *Mol. Cryst. Liq. Cryst.*, **17**, 1 (1978).
3. A. I. Ismailov and V. A. Salimova, *Zh. Obshch. Khim.*, **4**, 85 (1968).
4. V. V. Titov, E. I. Kovshev, A. I. Pavluchenko, V. T. Lazareva, and M. F. Grebenkin. *J. Phys.* (*Paris*), **36**, 381 (1975).