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Synthesis and Mesomorphism of Aryl *p*-Fluoralkyl(alkoxy)benzoates

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The mesomorphic *p*-alkoxyphenyl and *p*-phenylene *p*-trifluoromethyl-, *p*-trifluoromethoxy-, *p*-pentafluoroethoxy, and *p*-difluoromethoxy-benzoates were prepared, and their transition temperatures measured. The mesomorphic properties of the compounds were compared with those of their hydrogen analogues.

INTRODUCTION

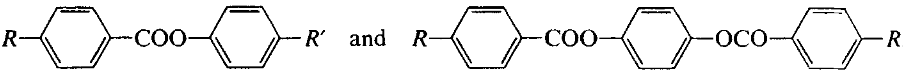
The mesomorphic properties of liquid crystals as known depend strongly on the nature of terminal groups. The effects of such groups as halogen, nitro, cyano, amino and some others have been discussed in details in monography.[1] A terminal alkyl (alkoxy, alkanoyloxy) group is a characteristic unit of most liquid crystalline structures and influences strongly the thermal and structural properties of mesomorphic compounds.

So, there are general regularities for liquid crystals with different central units when increasing the number of methylene groups in the alkyl chain: an appearance of smectic properties, alternation of clearing points, lowering (for compounds with high clearing points) or increasing (for compounds with low clearing points) of a mesophase thermal stability, etc. These facts illustrate a considerable role of terminal alkyl groups in the behaviour of mesomorphic compounds.

Therefore, we have an interest in the study of liquid crystals with fluorinated alkyls as terminal groups. The replacement of hydrogen atoms at fluorine ones must cause a change of intermolecular interaction and consequently mesomorphic properties owing to geometric and electronic factors.

Only two Schiff's bases containing fluorine in the alkyl chain were known at the time of this study. They were synthesized by condensation of *p*-trifluoromethylaniline with *p*-hexyloxybenzaldehyde or terephthalaldehyde[2] and had lower thermal stabilities of their nematic phases in comparison with their hydrogen analogues. This fact was separately due to a broadening of this molecule and the weakening of lateral intermolecular interactions.

We have studied the influence of the replacement of hydrogen atoms in alkyl chains by fluorine ones on the mesomorphic properties of *p*-fluoroalkyl(alkoxy)benzoic acid esters



where $R = CF_3, OCHF_2, OCF_3, OC_2F_5$, and $R' = OC_5H_{11}, OC_6H_{13}$.

RESULTS AND DISCUSSIONS

All synthesized compounds (Tables I, II), with the exception of *p*-alkoxyphenyl *p*-trifluoromethylbenzoates (Compounds III, IV) form mesophases. In most cases (with the exception of Compounds IX, XIII, XIV) their mesophase thermal stabilities are lower than in the case of appropriate hydrogen analogues; the difference makes up ~ 100° for Compounds XVIII and XIX). All mesomorphic fluoroderivatives have 20–50° lower melting points than the hydrogen analogues; this points out the weakening of intermolecular interactions in the crystalline state.

Perfluoroalkylated derivatives have a tendency to form a smectic mesophase in contrast to their hydrogen and difluoromethyl analogous (Compounds VII, VIII, XIII).

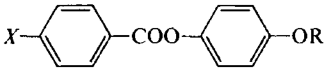
These results testify to the possible advantages of fluorinated liquid crystals, especially in search of low temperature smectic mesophases, though appropriate derivatives of other classes must be obtained to make possible a prognostication of the properties of fluorinated liquid crystals.

EXPERIMENTAL

p-Amyloxyphenol and *p*-hexyloxyphenol[3,4] as well as *p*-fluoralkyl(alkoxy)-benzoic acids[5-8] were obtained by known methods and had constants corresponding to published data. Transition temperatures of the compounds were determined with a MIN-8 polarizing microscope equipped with a Mettler FP-5 apparatus.

TABLE I

4-Alkoxyphenyl 4-alkyl(alkoxy)benzoates



Compound index	X	R	S[b] °C	N[c] °C	I[d] °C	Found (%) C	Found (%) H	Formula	Required (%) C	Required (%) H	Ref.
I	CH_3	C_5H_{11}	61	—	63	76.3	7.3	$C_{19}H_{22}O_3$	76.5	7.4	
II	CH_3	C_6H_{13}	—	—	81	76.7	7.8	$C_{20}H_{24}O_3$	76.9	7.7	
III	CF_3	C_5H_{11}	—	—	79	64.5	5.6	$C_{19}H_{19}F_3O_3$	65.0	5.5	
IV	CF_3	C_6H_{13}	—	—	84	65.7	6.2	$C_{20}H_{21}F_3O_3$	65.6	6.0	
V	CH_3O	C_5H_{11}	—	68	73			$C_{19}H_{22}O_4$	—	—	9
VI	CH_3O	C_6H_{13}	—	55	79	—	—	$C_{20}H_{24}O_4$	—	—	9
VII[a]	CHF_2O	C_5H_{11}	—	61	56	65.0	5.7	$C_{19}H_{20}F_2O_4$	65.1	5.8	
VIII	CHF_2O	C_6H_{13}	—	56	58	66.0	6.2	$C_{20}H_{22}F_2O_4$	65.9	6.1	
IX	CF_3O	C_5H_{11}	47	—	92	62.2	5.1	$C_{19}H_{19}F_3O_4$	61.9	5.2	
X	CF_3O	C_6H_{13}	43	110	138	63.0	5.6	$C_{20}H_{21}F_3O_4$	62.8	5.5	
XI	C_2H_5O	C_5H_{11}	—	94	102	—	—	$C_{20}H_{24}O_4$	—	—	9
XII	C_2H_5O	C_6H_{13}	—	83	98	—	—	$C_{21}H_{26}O_4$	—	—	9
XIII	C_2F_5O	C_5H_{11}	76	—	107	57.6	4.5	$C_{20}H_{19}F_5O_4$	57.4	4.6	
XIV	C_2F_5O	C_6H_{13}	61	94	102	58.4	5.0	$C_{21}H_{21}F_5O_4$	58.3	4.5	

[a] Monotropic liquid crystal.

[b] S—Transition into smectic state,

[c] N—Transition into nematic state,

[d] I—Transition into isotropic liquid

TABLE II

p-Phenylene bis-4-alkyl(alkoxy)benzoates

Compound index	*X*	S °C	N °C	I °C	Found (%) C	Found (%) H	Formula	Required (%) C	Required (%) H	Ref.
XV	CH_3	—	220	228	76.6	5.4	$C_{22}H_{18}O_4$	76.3	5.2	
XVI	CF_3	174	—	221	58.2	2.7	$C_{22}H_{12}F_6O_4$	58.2	2.7	
XVII	CH_3O	—	222	300	—	—	$C_{22}H_{18}O_6$	—	—	10
XVIII	CHF_2O	—	175	200	58.7	4.0	$C_{22}H_{14}F_4O_6$	58.7	3.9	
XIX	CF_3O	135	162	193	54.5	2.7	$C_{22}H_{12}F_6O_6$	54.3	2.5	
XX	C_2H_5O	—	226	287	—	—	$C_{24}H_{22}O_6$	—	—	11
XXI	C_2F_5O	199	257	263	49.2	2.5	$C_{24}H_{12}F_{10}O_4$	49.2	2.2	

4-Alkoxyphenyl 4-fluoroalkyl(alkoxy)benzoates and *p*-phenylene bis-4-fluoroalkyl(alkoxy)benzoates

A solution of the appropriate phenol (0.003 mole) or hydroquinone (0.0016 mole) in 7 ml of dry pyridine was added at 0°C to a stirred acid chloride (0.0033 mole). After keeping overnight at 25°C, the mixture was poured into 10 ml of concentrated hydrochloric acid and 50 g of ice. The precipitate was separated by filtration, washed by water, a solution of sodium hydrocarbonate and water, and recrystallized from hexane or benzene to achieve constant transition points (Tables I and II).

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