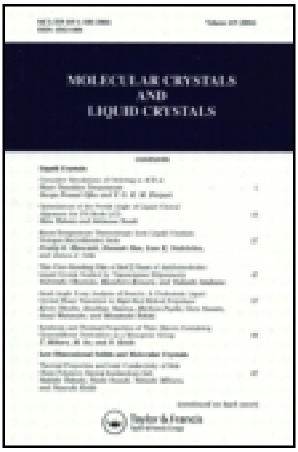

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Liquid Crystalline Properties of *p*-*n*-alkoxybenzylidene-*p*-fluoroaniline

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Thermodynamic data referring to a new homologous series of fluorinated alkoxy-benzylidene-anilines are presented. Phase diagrams show the presence of smectic A and/or B phases determined by thermal microscopy and X-ray diffraction techniques. Interdigitated structures are not present in these smectic phases. Trends in clearing temperatures are briefly discussed in comparison with those for the *p*-alkoxybenzylidene-*p'*-alkoxy-anilines in order to clarify the role of the fluorine atom.

INTRODUCTION

Recently it has been shown that smectic solvents are able to exert stereochemical and catalytic effects on reactions with severe orientational demand in the transition state, because of the enforced anisotropy of all diffusions of the reactant molecules by ordered solvent structures.[1–8]

Regarding to this it is important the synthesis and the thermodynamic characterization of new cheap and easy preparation compounds able of giving smectic phases at relatively low temperatures and large stability ranges.

The introduction of a fluorine atom into organic molecules has given a great number of new compounds[9] where the fluorine shows a special role to promote smectic phases because it is the smallest substituent with the highest electronegativity. With regard liquid crystals, particularly, the introduction of fluorine atoms in 2-2' position into diphenyle nucleous has been used to value the steric effect of substituents on the angle torsion and therefore on the thermic behaviour of mesomorphic compounds obtained.[10,11]

The introduction of the fluorine atom in the side chain of thermotropic liquid crystals has been used to promote mesophases having high dielectric anisotropy[12] to utilize in electrooptic display.

In any case the effect of the fluorine substitution on the transition temperatures of thermotropic liquid crystals is not univocal, but it depends on the examined compound.

The literature reports data in which the substitution of a hydrogen atom with a fluorine atom causes an increase of the transition temperatures[13] data, in which this substitution causes a decrease.[14]

In previous papers we have reported the synthesis and the thermodynamic characterization of several series of mesomorphic *p-p′*-dialkoxy-benzylidene-anilines.[15] It is well-known that the introduction of the fluorine atoms influences the ability of thermotropic liquid crystals to give smectic polymorphism. The appearance of a smectic phase as consequence of the introduction of a fluorine atom into at least one of the benzylidene-aniline rings was reported in Reference 16, and refers to molecules in which the substituent in the para position of the aniline-ring is a $—OCF_3$ group.

In order to obtain compounds with smectic B phases, and using our past experience in the thermotropic liquid crystals derived from the benzylideneaniline, we have synthetized a new series of compounds with general formula:

$$F—C_6H_4—N{=}CH—C_6H_4—O—C_nH_{2n+1} \qquad (a)$$

where $n = 1–8$ represents the compounds reported as A–H in Table I. Only high pressure investigation has been carried out on compound C, to the best of our knowledge.[17]

With respect to compounds studied previously[15] the alkoxy chain of the aniline ring has been substituted with a fluorine atom. The consequence of this substitution is a large decrease in clearing temperature, and the appearance of smectic polymorphism.

EXPERIMENTAL

All products were synthetized by standard methods from equivalent quantities of amine and aldehyde.

The reagents were dissolved in anhydrous benzene and refluxed for several hours. The water of reaction was removed azeotropically and the crude products so obtained were purified by several crystallizations from anhydrous ethanol.

A Mettler TA processor equipped with a DSC-20, previously calibrated in terms of temperature and energy, using indium as standard, was used for the measurements. Several DSC scans were carried out for each sample.

The transition temperatures were observed using a Galileo polarizing microscope with a 20 × 0.22 objective and Mettler FP 52 microfurnace for sample temperature control. Special care was taken to ensure clear observation.

RESULTS AND DISCUSSION

Data obtained by Differential Scanning Calorimetry (DSC) and Thermal Microscopy (TM), for the compounds examined are collected in Table I.

The transition temperatures reported for compound C refer to TM measure-

TABLE I

Thermodynamic data for compounds A–H

Compound	Transition	T (°C)	ΔH(cal/mol)	ΔS(cal/mol* °K)
A	K—I	64.0	3898	11.6
B	K—I	72.3	5060	14.6
	I—N	57.2	4587	14.1
	N—SB	50.5		
	SB—K	n.d.		
C	K—I	63.4	6877	20.4
	I—SB	55.9	1910	5.9
	SB—K	48.0	3193	10.7
D	K—I	66.6	6540	19.3
	I—N	60.1	150	0.46
	N—SB	58.5	1650	4.98
	SB—K	50	4450	13.8
E	K—K2	48.5	437	1.36
	K2—SB	53.9	5050	15.4
	SB—I	59.2	1930	5.8
	I—SB	58.8	1883	5.7
	SB—K2	n.d.		
F	K—SB	52.1	5479	16.8
	SB—SA	56.6	690	2.09
	SA—N	61.3	679	2.03
	N—I	62.8	130	0.39
	I—N	62.5	150	0.45
	N—SA	61.0	770	2.31
	SA—SB	56.3	715	2.17
	SB—K	n.d.		
G	K—K2	56.0	6700	20.20
	K2—SA	58.4		
	SA—I	62.3	1197	3.6
	I—SA	62.2	1056	3.2
	SA—SB	57.2	639	1.9
	SB—K2	37.5	4790	15.4
	K2—K	n.d.		
H	K—SA	62.2	7974	23.8
	SA—I	65.2	1073	3.2
	I—SA	64.6	1081	3.2
	SA—SB	55.1	650	1.9
	SB—K	47.8	7097	22.1

n.d.: not detected.

ments. Enthalpies ΔH and transition entropies ΔS are reported in cal/mol and cal/mol*K respectively.

In order to establish possible thermal hysteresys phenomena, several DSC scans were carried out, but no differences was found between the first and following thermal cycles. Data referring to monotropic transitions were obtained by the procedure reported in Reference 15.

Figure 1 shows the polymorphic schemes referring to the compounds examined.

In order to clarify the role of the fluorine atom in the *p*-position, it is convenient to discuss the present data in comparison with those for previously examined series of general formula:

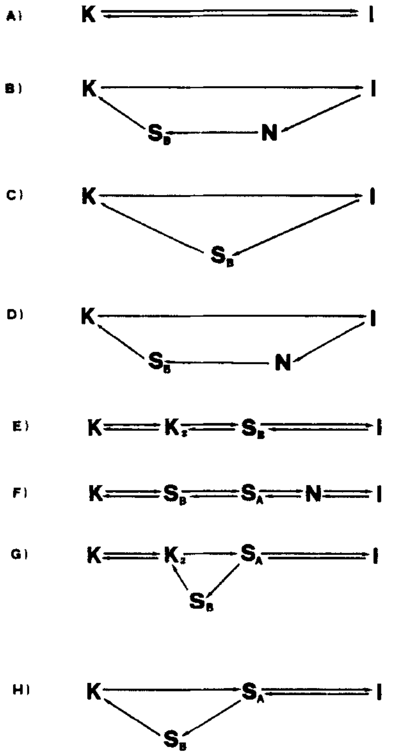

FIGURE 1 Polymorphic schemes of the studied compounds.

$$H_5C_2—O—C_6H_4—N{=}CH—C_6H_4—O—C_nH_{2n+1} \qquad \text{(b)}$$

Figure 2 shows the trend in the clearing temperatures when plotted against the number of carbon atoms in the *p*′-alkoxy chain of the fluorinate compounds and those of the b) series.

It is evident the effect of the substitution of the *p*-alkoxy group of the aniline moiety with the fluorine atom in this class of compounds respect to compounds of b) series.

The comparison between the results referring to the two series suggests the following considerations: i) *p*-fluoro derivatives (series a) exhibit clearing temperatures at much lower temperature range than compounds of b) series; ii) smectic phases appear at a shorter alkoxy chain length in the *p*-fluoro derivatives than in the other series. The features for the compounds of former type are considered to be due to the decrease of the terminal intermolecular attraction resulting from the lack of the polar oxygen atom in the substituent of aniline moiety. In fact smectic stability increases when terminal attraction decrease and lateral interaction becomes relatively predominant[18]; iii) if we consider the present series a), it can see that the length of *p*′-alkoxy chain of the benzylidene moiety play a determinant role on the nature of the mesophase due to the interaction between adjacent molecules.

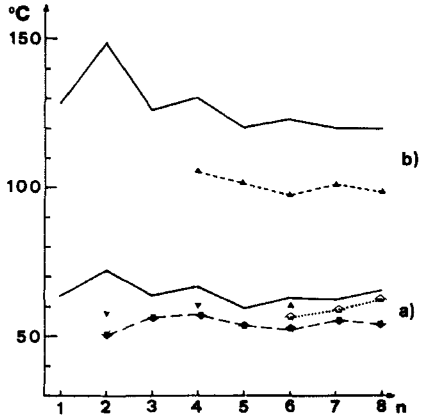

FIGURE 2 Effect of the chain length on the transition temperatures: a) series: full line refer to clearing temperature; ▲ ▼ are the temperature of appearance of the Nematic phase, on heating and on cooling (monotropic phase) respectively; ◆ ◆ are the temperature of appearance of the Smectic B phase on heating and on cooling (monotropic phase) respectively; ◇ is the temperature of appearance of the Smectic A phase on heating. b) series: full line refer to clearing temperature; dashed line refer to solid-nematic transition.

In particular the compound A, where the p'-alkoxy- group is a methoxy, shows no mesophases; compounds B, C and D, do not show stable mesophases; but only monotropic ones, and finally compounds E, F, G and H having p'-alkoxy chains longer than the previous ones, show stable mesophases. iv) Curves of clearing temperatures of the fluorinated compounds, related to an odd-numbered chain length (total C and O atoms) of the substituent of the benzylidene moiety lie always above those related to an even-numbered chain length. This usual behaviour for compounds of this kind can be explained by assuming a head-to-tail molecular arrangement in which central C═N bondings of neighboring molecules are in the same direction. Moreover, it can be noted that the "odd" compounds, except the compound H, show nematic mesophases, while the other compounds, the "even" ones, except the first, show smectic mesophases as more stable phase at high temperature before the clearing.

If we refer to the simple molecular scheme reported in Figure 3 it can be seen that the terminal situation of neighbouring molecules with terminal bonds lying on the same direction of the molecular axis, makes easier molecular creep and promotes a nematic phase. Moreover, in this situation, the favoured intermolecular interaction causes a greater clearing temperature with respect to "even" compounds, as reported in Figure 2.

The nature of smectic phases, enantiotropic and monotropic ones, (Table I) was determined by TM and X-ray diffraction techniques. The layer thickness in both SA and SB phases appears coincident with the molecular lengths obtained using standard bond lengths and bond angles for benzene ring and the lateral chain assumed in all-trans conformation.

The central bond lengths of the benzylidenaniline framework, bond and torsion angles, as well as C—F lengths were optimized using AM1 method as reported in

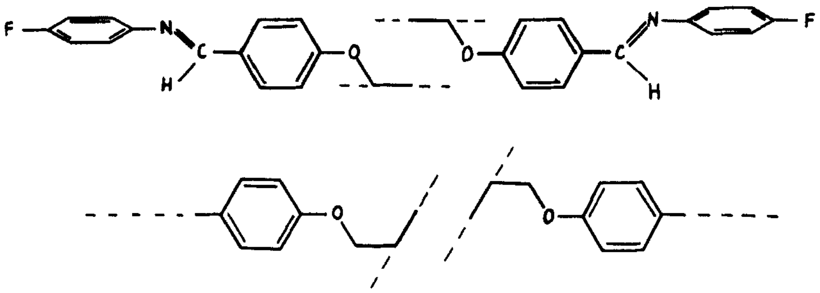

FIGURE 3 Terminal situation of neighbouring molecules referring to the B, D, F, H (upper scheme) and A, C, E, and G (lower scheme).

Reference 19. In the evaluation of the total molecular length, the Van der Waals radii of the terminal atoms, H and F, were taken into account, too. From these results we can deduce that in the smectic phases the molecules are, on the average, perpendicular to the smectic layers, and interdigitate structures should be excluded.

In conclusion a new series of fluorinated liquid crystals was synthesized. Thermodynamic behaviour, phase diagrams and structural information, evidence the determining role of the fluorine atom to promote smectic phases. In particular, referring to the aim reported in the introduction the compounds E and F, which give stable and not interdigitated smectic B phases, could be tested as solvents able to exert stereochemical effects on polymerization reactions.

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