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Fluorinated Analogues of Liquid Crystals 1. Analogues of 4-Methoxybenzylidene-4'-Butylaniline with Perfluorinated Alkyl- and Alkoxy-Groups

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FLUORINATED ANALOGUES OF LIQUID CRYSTALS 1. ANALOGUES OF 4-METHOXYBENZYLIDENE-4'-BUTYLANILINE WITH PERFLUORINATED ALKYL- AND ALKOXY-GROUPS

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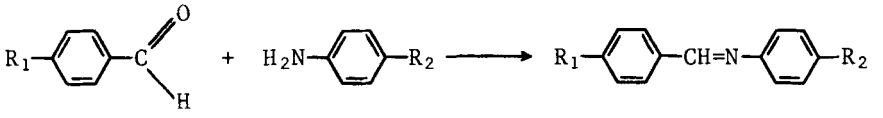
Abstract For the first time the MBBA analogues comprising of perfluorinated methoxy- and/or n-butyl groups have been synthesized and their mesomorphic properties have been studied. It has been shown that introduction of fluorine atoms into at least one of the substituents causes the appearance of a smectic mesophase, and that the compound comprised of both CF_3O and n-C_4F_9- groups possesses no mesomorphic properties.

4-Methoxybenzylidene-4'-n-butylaniline (MBBA) is one of the most thoroughly studied compounds of the Schiff's base series;[1] [2] it forms a nematic mesophase within the temperature range of 22-48°C.[3]

Recently the series of 4-alkoxybenzylidene-4'-trifluoromethylanilines has been synthesized and studied.[4] The 4-methoxy derivative, which can be considered as a lower homologue of MBBA, proved to be a non-mesomorphic compound. With elongation of the alkoxy-group, beginning at C_3, the smectic B phase appears and it has been noticed that compounds of this series promote smectic A phase formation in binary liquid crystal systems.

It was of interest to obtain the fluorinated analogues of MBBA and to make clear the effect that substitution of hydrogen atoms by fluorine (both in the alkyl- and alkoxy-

groups) has on the mesomorphic properties of the compounds. The synthesis of these substances has been carried out by condensing equimolar amounts of the aldehydes with aniline derivatives in absolute ethanol.



(I) (II) (III)a-c

(I)a $R_1 = CH_3O$, (I)b $R_1 = CF_3O$;
(II)a $R_2 = C_4H_9$-n, (II)b $R_2 = C_4F_9$-n;
(III)a $R_1 = CF_3O$, $R_2 = C_4H_9$-n; (III)b $R_1 = CH_3O$, $R_2 = C_4F_9$-n; (III)c $R_1 = CF_3O$, $R_2 = C_4F_9$-n.

The 4-trifluoromethoxybenzaldehyde ((I)b, $R_1 = CF_3O$) was obtained according to ref[5], and 4-n-perfluorobutylaniline ((II)b, $R_2 = C_4F_9$) by condensing n-perfluorobutyl iodide[6] with 4-iodoacetanilide in DMSO according to ref[7] with subsequent hydrolysis of the acetyl derivative with hydrochloric acid in alcohol. The purification of the fluorinated MBBA analogues was carried out by multiple fractional distillation in vacuum or by crystallization to constant temperatures for the phase transitions. The purity of compound (III)a was checked by analytical glc. Only analytically pure materials were used throughout the investigation, and the yields, properties, and analytical data for the compounds prepared are presented in Table 1.

The structures of the substances (III)a-c were confirmed by their ^1H NMR spectra (Table 2) as well as by ultraviolet (Figure 1) and infrared spectroscopic data. The absorption maxima in the electronic spectra are in agreement with those specified for MBBA[8] and other compounds of the Schiff's base type.[9]

While investigating the mesomorphic properties of the fluorinated MBBA analogues it has been found that compounds comprised of at least one fluorinated substituent, ie, the OCF_3 (III)a group or C_4F_9 (III)b, form not nematic but smectic mesophases with temperature ranges K 38°, S 54°, I and K 78°, S 94°, I respectively. The mesophases formed by compounds (III)a-b appear to possess the confocal texture on melting the crystals, and the mosaic or polygonal texture

Compound	Yield %	Boiling temperature (P mm)	Analysis results		
			Obtained % F	Formula	Calculated % F
(II)b	80	84-85° (3 mm)†	54.52 54.67	$C_{10}H_6F_9N$	54.98
(III)a	70	149.150° (0.3 mm)	17.24 17.36	$C_{18}H_{18}F_3NO$	17.75
(III)b	74.5	-	39.29 39.42	$C_{18}H_{12}F_9NO$	39.85
(III)c	80.7	130° (0.3 mm)	46.76 46.91	$C_{18}H_9F_{12}NO$	47.20

TABLE 1

† n_D^{20} 1.4180; acetyl derivative has mp 99°C. Obtained %: F 48.35, 48.40. $C_{12}H_8F_9NO$. Calculated %: F 48.44.

Compound	δCH	δCH_3O	δC_6H_4	$\delta CH_2-C_3H_7$	
				δCH_2	δC_3H_7
MBBA	8.53	4.06	8.10-7.20	2.86	1.50
(III)a	8.33	-	8.10-7.10	2.63	1.63
(III)b	8.46	4.00	8.00-7.10	-	-
(III)c	8.50	-	8.00-7.20	-	-

TABLE 2 Data from the ^1H NMR spectra of MBBA and its fluorinated analogues (III)a-c.

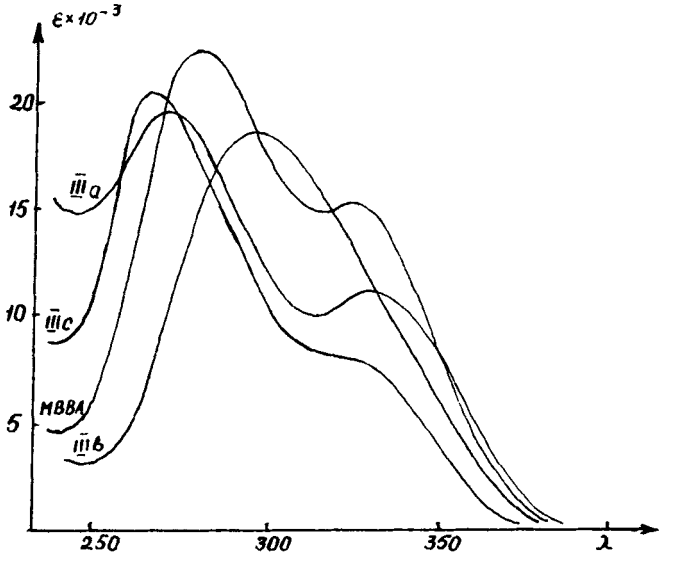


FIGURE 1 Electronic spectra of $R_1C_6H_4-CH=N-C_6H_4R_2$:
$R_1 = CF_3O$, $R_2 = C_4H_9$-n (III)a
$R_1 = CH_3O$, $R_2 = C_4F_9$-n (III)b
$R_1 = CF_3O$, $R_2 = C_4F_9$-n (III)c
$R_1 = CH_3O$, $R_2 = C_4H_9$-n (MBBA)

on cooling the isotropic liquid (Figure 2).

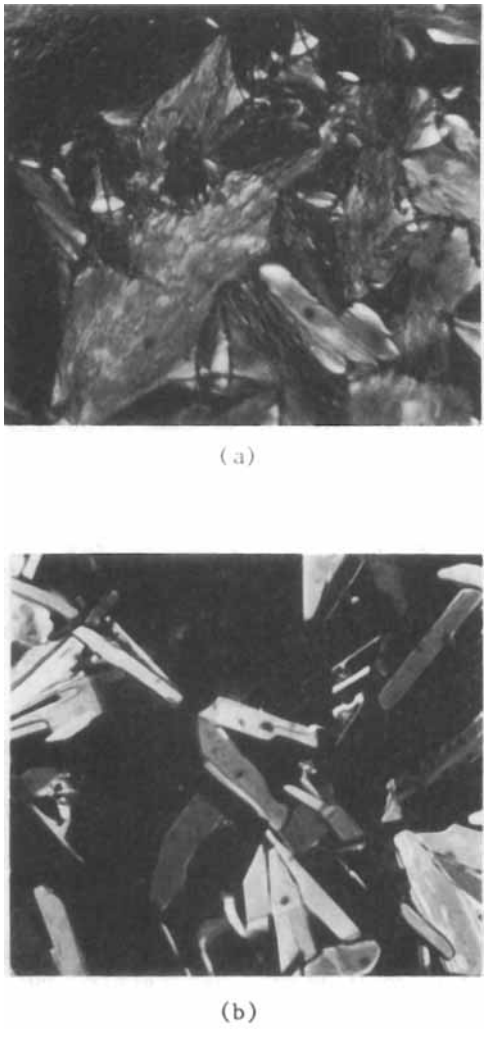


FIGURE 2 Photomicrograph of 4-methoxybenzylidene-4'-perfluorobutylaniline at 85°C (a): 4-trifluoromethoxybenzylidene-4'-butylaniline at 45°C (b).

It is interesting to notice that substance (III)c containing both fluorinated groups is non-mesomorphic and has the lowest melting temperature of this series (mp 28°C).

Comparing the transition temperatures for compounds (III)a-b with those for MBBA, one can see that substitution of hydrogen atoms by fluorine in the side chains causes rises in these temperatures. Moreover, the greatest effect is observed when fluorine is introduced into the alkyl group.

These surprising effects which substitution of hydrogen atoms by fluorine atoms in the side chains of the MBBA molecule have on the mesomorphic properties are apparently caused by changes in the packing of the molecules in the crystals as well as by changes in the character of the intermolecular interactions. Furthermore, the introduction of the fluorine atoms into the CH_3O- and C_4H_9- substituents considerably alters their electronic nature; this in turn influences the conformations of the compounds formed.[10,11,12]

We shall continue investigations of the fluorinated analogues of MBBA to make clear the nature of the effects discovered. We propose to synthesize and study the properties of a wider series of compounds, including partially fluorinated systems. In this work, the smectic phases detected will be carefully investigated and classified.

Experimental The investigation of the mesomorphic properties was carried out using a Kofler hot stage with a Reichert polarizing microscope. The ^1H NMR spectra were recorded using a "Tesla BS-467" instrument of 60 MHz frequency with the GMDS internal standard. The ultra-violet spectra were recorded using a "Specord UV-VIS" spectrometer (heptane as solvent), and infrared spectra by means of a UR-20 instrument (CCl_4 as solvent, concentration 0.1 mol/l). Analytical gas chromatography was carried out using a "TSVET-4" instrument with a flame ionization detector (inertial carrier - spherochrome; mobile phase - polymethylsiloxan-4 (11% of carrier weight); carrier gas - nitrogen at 24 ml/min; program 150-250°C).

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