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NEW LIQUID CRYSTAL DERIVATIVES OF THIAZOLE

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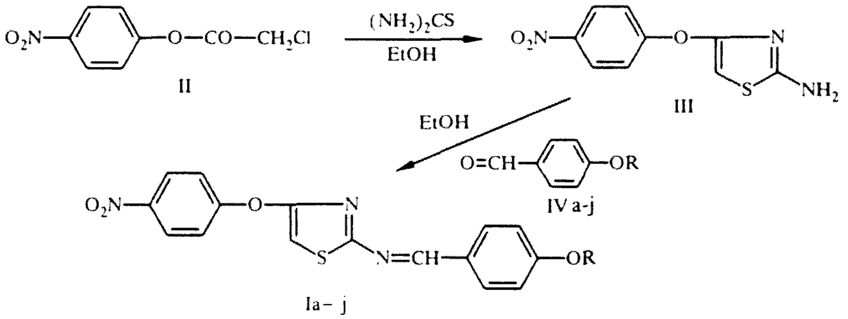
2-(4′-Alkoxybenzylidenamino)-4-(4-nitrophenoxy)thiazoles, which possess monotropic mesomorphism of the nematic type over the range 68-160°C, have been synthesized.

Liquid crystals are currently widely used in science and technology [1, 2]. The prospects for their practical utilization has stimulated the study of the physical behavior of compounds with liquid crystal properties, in particular to improve the characteristics of apparatus based on them. The possibilities of theoretical and practical investigation of the liquid crystalline state have not yet been exhausted. This is particularly true of the synthesis of model compounds and the establishment of the connection between their chemical structures and the stability of the mesophases.

In a continuation of our work on the synthesis and the influence of molecular structure on the type, stability, and temperature range of the mesophases of azomethines containing different heterocyclic units [3, 4], we synthesized for the first time 2-(4′-alkoxybenzylidenamino)-4-(4-nitrophenoxy)thiazoles (Ia-j) according to the following scheme:



I, IV a R = CH_3, b R = C_2H_5, c R = C_3H_7, d R = C_4H_9, e R = C_5H_{11}, f R = C_6H_{13}, g R = C_7H_{15}, h R = C_8H_{17}, i R = C_9H_{19}, j R = $C_{10}H_{21}$

Sodium 4-nitrophenoxide was quantitatively acylated with chloroacetyl chloride in alkaline media to give 4-nitro-O-chloroacetylphenol (II). Reaction of the latter with thiourea in absolute ethanol gave 2-amino-4-(4-nitrophenoxy)thiazole (III). Compounds Ia-j were obtained by condensation of the thiazole III with aromatic aldehydes IVa-j in absolute ethanol in the presence of a trace of piperidine.

The composition and structure of the compounds synthesized were confirmed by ^1H NMR spectroscopy and elemental analysis. The ^1H NMR spectra of compounds Ia-j contained signals at 0.5-0.9 (CH_3), 1.2-1.9 (CH_2, excluding OCH_2), 3.5-4.2 (OCH_2) and 6.7-7.9 ppm (Ar). The singlets corresponding to the hydrogen atoms of the thiazole ring and the azomethine group occur at 7.1-7.2 and 9.7-9.8 ppm respectively.

Mesomorphism of the nematic type over the temperature range from 68° to 160°C is characteristic for compounds Ia-j. The translucence temperature increases unevenly as the length of the aliphatic chain benzylidene unit increases, showing a tendency to increase in the series IIb-d, Ie-h, and Ii,j, reaching its maximum value for compounds Id and Ih. The mesophase exists over a wide temperature range for compounds Id and Ig, reaching a maximum value of 89°C for Ig. Monotropic mesomorphism is characteristic for all of the compounds synthesized.

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TABLE 1. Properties of the Compounds Synthesized, Ia-j

Compound	Molecular formula	(Found, %)/(Calculated, %)			Phase transitions*		Yield, %
		C	H	N	T_N, °C	T_I, °C	
Ia	$C_{17}H_{13}N_3O_4S$	57.71 57,46	3.96 3,69	11.58 11,82	80	135	57
Ib	$C_{18}H_{15}N_3O_4S$	58.83 58,53	4.18 4,09	11.06 11,38	78	121	55
Ic	$C_{19}H_{17}N_3O_4S$	59.34 59,52	4.28 4,47	10.66 10,96	76	133	62
Id	$C_{20}H_{19}N_3O_4S$	60.22 60,44	4.56 4,82	10.38 10,57	70	159	57
Ie	$C_{21}H_{21}N_3O_4S$	61.22 61,30	5.01 5,14	10.06 10,21	68	108	49
If	$C_{22}H_{23}N_3O_4S$	61.86 62,10	5.34 5,45	9.75 9,88	84	122	59
Ig	$C_{23}H_{25}N_3O_4S$	62.64 62,85	5.45 5,73	9.38 9,56	73	151	60
Ih	$C_{24}H_{27}N_3O_4S$	63.26 63,56	5.82 6,00	9.12 9,26	94	160	61
Ii	$C_{25}H_{29}N_3O_4S$	64.06 64,22	6.14 6,25	8.68 8,99	99	136	55
Ij	$C_{26}H_{31}N_3O_4S$	64.72 64,84	6.38 6,49	8.58 8,72	78	141	50

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*T_N) Temperature at which the nematic modification exists.

T_I) Transition temperature to the isotropic liquid.

EXPERIMENTAL

^{1}H NMR spectra of $CHCl_3$ containing HMDS as internal standard were recorded with a Tesla BS-487B (80 MHz) spectrometer. Temperatures of phase transitions were measured with an MIN-10 polarizing microscope with a thermal attachment in an increasing temperature regime. The purity of all the compounds described were monitored by TLC on aluminum oxide with 1:1 toluene–chloroform as eluant.

Properties of the compounds obtained are given in Table 1.

4-Nitro-O-chloroacetylphenol (II). Chloroacetyl chloride (12.4 g, 0.1 mole) was added dropwise to a vigorously stirred to a solution of 4-nitrophenol (16.1 g, 0.1 mole) in aqueous sodium hydroxide (2 M, 100 cm^3) and the reaction mixture was kept for 3 h at room temperature. The precipitate of compound II was filtered off, washed with water and recrystallized from ethanol. Yield 17.3 g (81%). mp 94-95°C. Found, %: C 44.82, H 3.00, N 6.72. Calculated, $C_8H_6ClNO_4$, %: C 44.57, H 2.81, N 6.50.

2-Amino-4-(4-nitrophenoxy)thiazole (III). A mixture of compound II (10.8 g, 0.05 mole), thiourea (3.8 g, 0.05 mole), and absolute ethanol (125 cm^3) was boiled for 8 h, the solvent was evaporated, and the residue was neutralized with 20% aqueous sodium carbonate. The precipitate was filtered off and recrystallized from water to give compound III, yield 6.8 g (63%), mp 89-90°C. Found, %: C 45.87, H 3.16, N 17.84. Calculated, $C_9H_7N_3O_3S$, %: C 45.57, H 2.97, N 17.71.

2-(4'-Alkoxybenzylidenamino)-4-(4-nitrophenoxy)thiazoles (Ia-j). A mixture of compound III (1 g, 4.2 mmole) and an aldehyde (IVa-j, 4.2 mmole) in absolute ethanol (30 cm^3) was boiled for 4 h in the presence of a catalytic amount of piperidine. The product (Ia-j), which precipitated on cooling, was recrystallized from water.

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