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NOVEL MESOMORPHIC SCHIFF BASES

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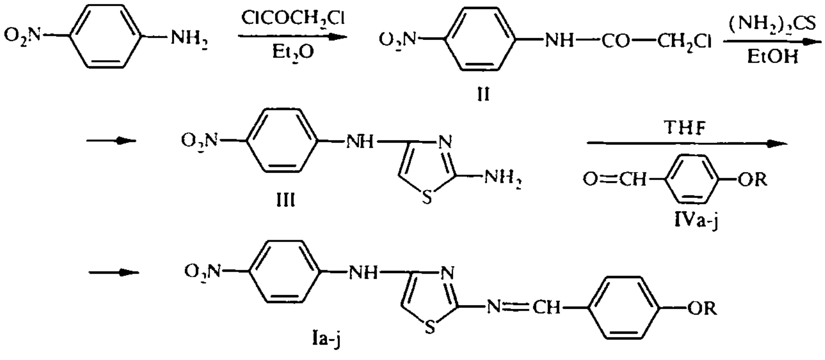
2-(4-Alkoxybenzylideneamino)-4-[(4-nitrophenyl)amino]thiazoles have been synthesized. They show nematic type enantiotropic mesomorphism in the range 41-184°C.

Continuing our work on the synthesis and investigation of the effect of molecular structure on the type, stability, and temperature range for azomethine mesophases containing the thiazole ring [1, 2], we have now synthesized 2-(4-alkoxybenzylideneamino)-4-[(4-nitrophenyl)amino]thiazoles (Ia-j) by 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 = $C_{10}H_{21}$

Compounds Ia-j were prepared from 4-nitroaniline which was chloroacetylated in diethyl ether and the N-chloroacetyl-4-nitroaniline (II) formed was then treated with thiourea in absolute alcohol to give N-(2-aminothiazol-4-yl)-4-nitroaniline (III). The product was then condensed with 4-alkoxybenzaldehydes (IVa-j) in dry tetrahydrofuran in the presence of a catalytic amount of piperidine.

The composition and structure of the synthesized azomethines was confirmed by PMR spectral and elemental analytical data. Thus the PMR spectra of Ia-j show proton signals at 0.6-1.0 (CH_3); 1.0-2.6 (CCH_2); 3.7-4.2 (OCH_2); and 6.3-8.4 ppm (Ar). The singlet signals for the thiazole ring proton and the azomethine group appear at 7.1-7.3 and 9.8-9.9 ppm respectively.

Compounds Ia-j show typical nematic type mesomorphism in the range 41-184°C. With increase in the aliphatic chain length in the benzylidene component, the temperature of clearing increases smoothly, reaches a maximum value at $n = 6$, and then changes unevenly. Compounds Ia-h are typified by the existence of mesophases over a broad temperature range, the maximum value of which reaches 95°C (for compounds Ia and If). All of the indicated compounds show enantiotropic mesomorphism, moreover the liquid crystalline state is preserved even on cooling the crystalline modification.

EXPERIMENTAL

PMR Spectra were recorded on a Tesla BS-487B (80 MHz) in $CDCl_3$ with HMDS internal standard. The phase transition temperatures were measured using a MIN-10 polarizing microscope with the thermo accessory in the heating mode.

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TABLE 1. Parameters for Compounds Synthesized Ia-j

Compound	Empirical formula	Found, % / Calculated, %			Phase transitions*		Yield, %
		C	H	N	T_{nem}, °C	T_{iso}, °C	
Ia	$C_{17}H_{14}N_4O_3S$	57,46 57,62	3,80 3,98	15,65 15,81	41	136	87
Ib	$C_{18}H_{16}N_4O_3S$	58,46 58,68	4,24 4,38	15,06 15,21	60	138	86
Ic	$C_{19}H_{18}N_4O_3S$	59,44 59,67	4,52 4,74	14,32 14,65	62	142	56
Id	$C_{20}H_{20}N_4O_3S$	60,42 60,59	4,96 5,08	14,02 14,13	105	148	54
Ie	$C_{21}H_{22}N_4O_3S$	61,32 61,44	5,28 5,40	13,45 13,65	115	180	60
If	$C_{22}H_{24}N_4O_3S$	62,06 62,24	5,54 5,70	13,08 13,20	89	184	78
Ig	$C_{23}H_{26}N_4O_3S$	62,80 62,99	5,76 5,98	12,66 12,78	73	158	65
Ih	$C_{24}H_{28}N_4O_3S$	63,46 63,69	6,40 6,24	11,88 12,38	62	130	69
Ii	$C_{25}H_{30}N_4O_3S$	64,08 64,35	6,32 6,48	11,96 12,01	110	145	66
Ij	$C_{26}H_{32}N_4O_3S$	64,82 64,97	6,58 6,71	11,54 11,66	94	136	67

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*$T_{nem.}$) Temperature for existence of a nematic modification; $T_{iso.}$) transition temperature to the isotropic liquid.

The identification and purity of all of the compounds described were controlled by TLC on aluminium oxide using the system chloroform–toluene (1:1).

Parameters for the compounds prepared are given in Table 1.

N-Chloroacetyl-4-nitroaniline (II). Chloroacetyl chloride (12.4 g, 0.11 mole) was added dropwise with vigorous stirring to a solution of 4-nitroaniline (13.8 g, 0.1 mole) in diethyl ether (100 ml). The reaction mixture was held for 3 h at room temperature. The precipitated product was filtered and washed with water and then ether to give II (20.4 g, 95%) with mp 156-157°C.

N-(2-Aminothiazol-4-yl)-4-nitroaniline (III). A mixture of II (14.2 g, 0.06 mole) and thiourea (4.6 g, 0.06 mole) in absolute ethanol (100 ml) was refluxed for 8 h, solvent distilled off, and the residue neutralized with aqueous sodium carbonate (20%). The precipitate was filtered and recrystallized from water to give III (12.6 g, 81%) with mp 140-141°C. Found, %: C 45.64; H 3.28; N 23.48. $C_9H_8N_4O_2S$. Calculated, %: C 45.76; H 3.41; N 23.71.

2-(4-Alkoxybenzylideneamino)-4-[(4-nitrophenyl)amino]thiazoles (Ia-j). A mixture of III (1 g, 0.0042 mole) and aldehyde IVa-j (0.0042 mole) in dry tetahydrofuran (30 ml) was refluxed for 4 h in the presence of a catalytic amount of piperidine. The precipitate was cooled and the product Ia-j filtered and crystallized from ethanol.

REFERENCES

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