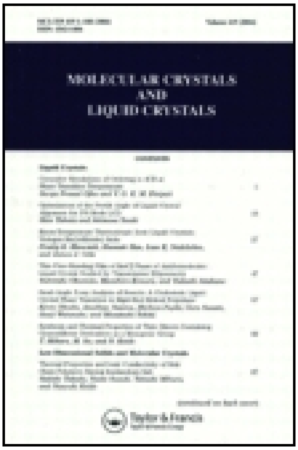

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Nematic Liquid Crystals Containing Pyridine and Benzazole Rings

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Nematic Liquid Crystals Containing Pyridine and Benzazole Rings

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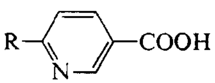
The liquid crystalline 6-alkoxynicotinic acids were prepared, and their transition temperatures measured. The isomeric 5-alkoxypicolinic acids are not mesomorphic. A series of 2,6- and 2,5-disubstituted benzazoles were also synthesized. The effects of a molecule geometry, central linkages and a heteroatom on the mesomorphic properties of these compounds are discussed.

INTRODUCTION

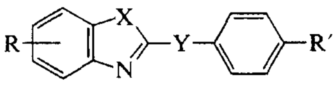
Most nematic liquid crystals as known at that time are derivatives of benzene, naphthalene and biphenyl. Mesomorphic compounds with heterocyclic nuclei are not still numerous, although they are of interest because of greater possibilities in the variations of direction and magnitude of their permanent dipole moments, and in consequence of that in the variations of sign and magnitude of their dielectric anisotropy.

Several classes of heterocyclic compounds have been synthesized earlier; these are derivatives of pyridine[1–4] (mostly Schiff bases), quinoline,[5] diazines.[6–11] Some representatives of benzazole and benzoxazole[12,13] are also known. Recently a great number of liquid crystalline derivatives of 5-membered heterocycles was reported by H. Schubert.[14]

We have investigated the mesomorphic behaviour of 6-alkoxynicotinic acids (A) and benzazoles (B), i.e., the 2,5- and 2,6-disubstituted benzoxazoles



A



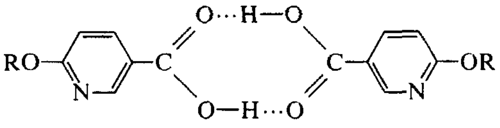
B

and benzthiazoles, where Y is azomethyne, ethylene, esteric, azo-group or simple linkage.

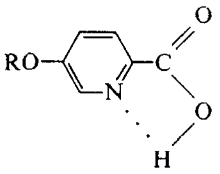
RESULTS AND DISCUSSION

The 5-alkoxypicolinic acids (I) were prepared by alkylation of the 5-hydroxypicolinic acid in alcohol solution in the presence of the base. The 6-alkoxynicotinic acids (II) were accessible by the reaction of the 6-chloronicotinic acid with sodium alkylates (Table I).

As compared to appropriate benzene derivatives, the substitution of the benzene ring for the pyridinic one causes the lowering of melting points (Figure 1). Only the higher homologues of compounds II form an enanthiomorphic mesophase with a narrow temperature range. Their lower homologues are monotropic, and the 5-alkoxypicolinic acids do not form a mesophase. The mesomorphic behavior of the 6-alkoxynicotinic acids (II) is undoubtedly due to the formation of dimers (C),[15] whereas an absence of mesomorphic properties of compounds I is possibly caused by their stronger intramolecular coordination (D).[16] A low thermal stability of the acids II (N–I transition points are ~60° lower than in the case of their benzene analogues) is apparently due to an existence of the H···N type hydrogen linkage resulting in the partial destroying of the liquid crystalline order (E).



C



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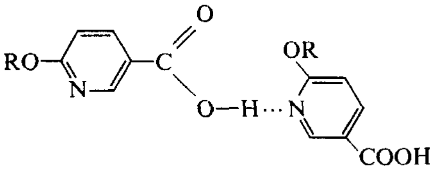


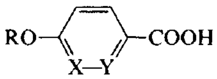
E

There is little information on mesomorphic properties of heterocyclic compounds containing two different heteroatoms. We have synthesized a number of disubstituted benzoxazoles and benzthiazoles and compared their mesomorphic properties.

The substituted 2-(*p*-alkoxybenzylideneamino)benzthiazoles (III–VI) were obtained by condensation of the appropriate 2-aminobenzthiazoles with the *p*-alkoxybenzaldehydes in the presence of the *p*-toluenesulphonic acid. The reaction of aldehydes with the 2-methylbenzthiazoles in the presence of the zinc chloride leads to the formation of the appropriate styrylbenzthiazoles

TABLE I

Substituted pyridinecarboxylic acids



Compound index	X	Y	R	C–N °C	N–I °C	Found (%) C	Found (%) H	Found (%) N	Formula	Required (%) C	Required (%) H	Required (%) N	Yield (%)
Ia	CH	N	C_4H_9	95.0	—	61.7	6.7	6.7	$C_{10}H_{13}NO_3$	61.5	6.7	7.2	20.0
IIa	N	CH	C_4H_9	93.6	(86.7)[a]	61.9	6.6	7.0	$C_{10}H_{13}NO_3$	61.5	6.7	7.2	44.7
XXIIa[b]	CH	CH	C_4H_9	147.0	160.0	—	—	—	—	—	—	—	—
Ib	CH	N	C_5H_{11}	94.5	—	63.1	7.2	6.6	$C_{11}H_{15}NO_3$	63.1	7.2	6.7	18.0
IIb	N	CH	C_5H_{11}	95.4	—	63.4	7.2	6.3	$C_{11}H_{15}NO_3$	63.1	7.2	6.7	43.0
XXIIb[b]	CH	CH	C_5H_{11}	124.0	151.0	—	—	—	—	—	—	—	—
Ic	CH	N	C_6H_{13}	80.3	—	64.4	7.3	6.0	$C_{12}H_{17}NO_3$	64.6	7.7	6.3	23.2
IIc	N	CH	C_6H_{13}	93.2	(90.8)[a]	64.4	7.9	6.3	$C_{12}H_{17}NO_3$	64.6	7.7	6.3	53.3
XXIIc[b]	CH	CH	C_6H_{13}	105.0	153.0	—	—	—	—	—	—	—	—
Id	CH	N	C_7H_{15}	95.0	—	65.4	7.6	5.7	$C_{13}H_{19}NO_3$	65.8	8.1	5.9	28.5
IId	N	CH	C_7H_{15}	88.5	89.5	65.9	8.3	5.7	$C_{13}H_{19}NO_3$	65.8	8.1	5.9	40.2
XXIId[b]	CH	CH	C_7H_{15}	92.0	146.0	—	—	—	—	—	—	—	—
IIe	N	CH	C_8H_{17}	87.8	93.3	66.7	8.2	5.8	$C_{14}H_{21}NO_3$	66.9	8.4	5.6	56.4
XXIIe[b]	CH	CH	C_8H_{17}	101.0	147.0	—	—	—	—	—	—	—	—

[a] Monotropic transition.

[b] Data for comparison from Ref. 17.

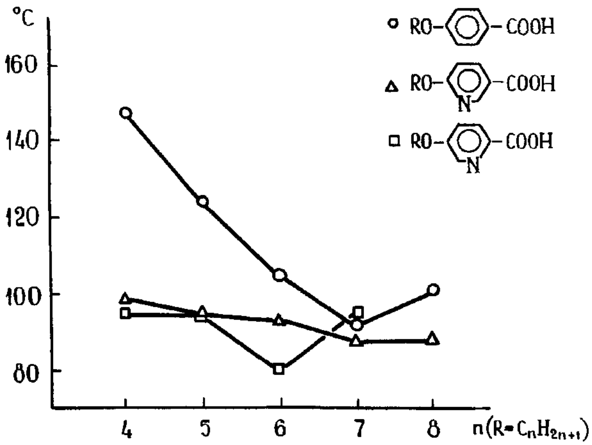


FIGURE 1 Plot of the melting points against the number of carbon atoms (*n*) in the *n*-alkyl chain of the carboxylic acids.

(VII, VIII). By the action of the phosphorus pentachloride on the 6-methoxythiazole-2-carboxylic acid and by the subsequent reaction of the formed acid chloride with phenols the phenyl esters (IX) were obtained. The aza-compounds (X–XII) were obtained by diazoreaction of the 2-aminobenzthiazoles, by coupling of the diazonium salts with the phenol, and by subsequent acylation of the intermediate hydroxyderivatives. The condensation of the zinc 2-amino-5-methoxyphenylmercaptide with the *p*-alkoxybenzaldehydes leads to the appropriate phenylbenzthiazoles (XIII).

Their benzoxazole isologues (XIV, XVI, XVIII, XX) were obtained by condensation of the *o*-aminophenol with aldehydes in the presence of the *p*-toluenesulphonic acid, and by the subsequent oxydation of intermediate Schiff bases with the lead tetraacetate. The styrylbenzoxazoles (XV, XVII, XIX, XXI) were obtained by condensation of the *p*-alkoxycinnamic acids with the *p*-aminophenols in the presence of the polyphosphoric ester.

As it was expected, the melting points of the obtained compounds do not obey to formal regularities while their clearing points have a distinct odd–even alternation when compounds with the odd number of atoms in the chain, including an oxygen, have a greater mesophase thermal stability as one can see at the diagram for the benzthiazole Schiff bases III (Figure 2).

An introduction of the hydroxy group into orto-position to the methyne group (compounds IIId, f) leads to an increase of the melting and clearing points that is apparently due to the association of molecules. The substitution of the methoxy group in the 6th position for the butoxy group (compound V) does not cause a considerable change of the mesophase transition tempera-

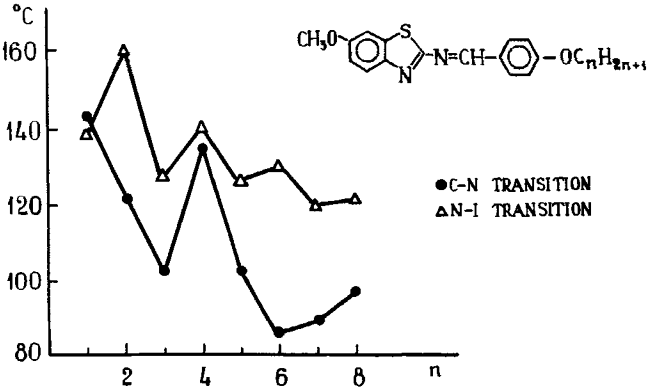
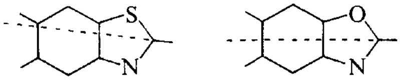


FIGURE 2 Plot of the transition temperatures against the number (n) of carbon atoms in the n-alkyl chain of the 2-(p-alkoxybenzylideneamino)-6-methoxybenzthiazoles.

tures whereas the transition points are very sensible to the changes in the benzene part of molecule.

It should be noted that the 5-methoxy substituted styrylbenzthiazoles (VIIIa, b) as well as the appropriate Schiff bases do not exhibit the mesomorphism whereas both series 5- and 6-substituted benzoxazoles (XVb; XVIIa, b; XIXb; XXIb) possess the liquid crystalline properties, the 5-substituted derivatives having greater mesophase thermal stability than their 6-isomers. Such differences of mesomorphic properties of isomeric benzazoles are apparently due to the different length of the carbon–sulfur (1.74 Å in thiophene), carbon–oxygen (1.41 Å in furane) and carbon–nitrogen (1.42 Å in pyrrole) linkages as schematically shown in the figure where a broken line means a direction of a long molecular axis. As one can see, a molecule linearity depends strongly on a lateral group position and on a

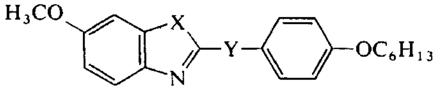


heteroatom. A different geometry of molecules is an essential factor influencing the mesophase thermal stability. Another factor causing the greater thermal stability of mesophases forming by the 6-substituted benzthiazoles in comparison with their benzoxazole analogs is a difference in a degree of aromatization of azole cycles that is a degree of conjugation of heteroatom p-electrons with π-electrons of cycle.

A comparison of liquid crystals differing by central groupment shows that their mesophase thermal stability decreases in series vinyl > azomethyne > simple linage > ester group (Table II). The most obtained benzazoles have a positive sign of dielectric anisotropy as follows from the Table V with typical examples.

TABLE II

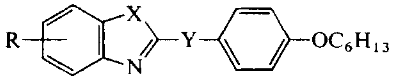
Comparison of influence of central linkage and heteroatom on the mesophase thermal stability.



Y	N–I (X = S)	N–I (X = O)	N–I (X = O, 5-OCH_3)
N=CH	130.1	—	—
CH=CH	165.0	83.7	124.7
COO	105.3	—	—
Simple linkage	119.2	40.6	69.5

TABLE III

Dielectric anysotropy of benzazoles ($\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp}$).



Compound	R	X	Y	°C	$\Delta\varepsilon$
VIIb	6-OCH_3	S	CH=CH	100	+0.45
XIIb	6-OCH_3	S	Simple linkage	104	−0.20
XVb	5-CH_3	O	CH=CH	100	+1.06
XVIIb	5-OCH_3	O	CH=CH	100	+1.25
XIXb	6-CH_3	O	CH=CH	85	+0.27

EXPERIMENTAL

Transition temperatures were determined with a MIN-8 polarizing microscope equipped with a Mettler FP-52 heating stage. All compounds were purified with a thin layer chromatography until satisfactory elemental analyses were achieved.

5-Alkoxypicolinic acids (I)

A mixture of 90% alcohol (15 ml), 5-hydroxypicolinic acid (0.0095 mole), potassium hydroxide (0.019 mole) and alkyl iodide (0.012 mole) were refluxed on a steam bath for 12–20 h. The solvent was distilled off under reduced pressure. The solid was dissolved in water and reprecipitated with 10% HCl at pH5. The resulting crude I was recrystallised from petroleum ether (Table I).

6-Alkoxynicotinic acids (II)

6-Chloronicotinic acid (0.0317 mole) was added to a stirred solution of sodium alcoholate (0.07 mole) in 50 ml of appropriate alcohol. The mixture was refluxed on an oil bath under stirring for 10 h. Isolated as described for I acids II were recrystallised from hexane (Table I).

5(or 6)-Substituted 2-(*p*-alkoxybenzylideneamino)benzthiazoles (III–VI)

A mixture of *p*-alkoxybenzaldehyde (0.01 mole), 5(or 6)-substituted 2-aminobenzthiazole (0.009 mole), *p*-toluenesulfonic acid (0.1 g) and 100 ml of benzene was refluxed for 2 h with a Dean–Stark column. The solvent was removed and the resulting solid was recrystallised from ethyl alcohol–hexane mixture (1 : 1) (Table IV).

2-*p*-Alkyl(or alkoxy)styryl-6(or 5)-methoxybenzthiazoles (VII, VIII)

A mixture of aldehyde (0.01 mole), 2-methyl-6(or 5)methoxybenzthiazole (0.01 mole) and anhydrous zinc chloride (0.2 g) was heated in a sealed tube for 5 h at 195–200°C. After cooling a melt was triturated with aqueous ammonia and extracted with benzene. The benzene solution was chromatographied on alumina, and a residue after evaporation of benzene was recrystallised from hexane (Table IV).

p-Alkoxy(or alkyl)phenyl 6-methoxybenzthiazole-2-carboxylates (IX)

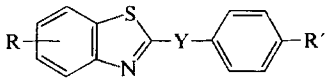
A mixture of 6-methoxybenzthiazole-2-carboxylic acid (0.01 mole) and phosphorus pentachloride (0.01 mole) was heated for 2 h on a steam bath. Anhydrous benzene (50 ml), *p*-alkoxy(or alkyl)phenol (0.01 mole) and pyridine (0.01 mole) were added, and the heating was continued for 4 h. The benzene solution was washed with 5% hydrochloric acid and water, and chromatographied with benzene on alumina. After evaporation of the eluate, a residue was recrystallized from hexane (Table IV).

2-*p*-Acyloxyphenylazo-6-alkoxy(or cyano)benzthiazoles (X–XII)

A solution of sodium nitrite (0.02 mole) in 2 ml of water was added dropwise at −5°C to a stirred solution of 6-alkoxy(or cyano)-2-aminobenzthiazole in 10 ml of 85% formic acid, 4 ml of glacial acetic acid and 8 ml of concentrated sulfuric acid. After cooling at −5°C for 5 h, the solution was added dropwise at 0°C to the solution of phenol (0.02 mole) and 26 g of sodium carbonate in 300 ml of water and 40 ml of 0.5% sodium hydroxide.

TABLE IV

Substituted benzthiazole liquid crystals



Compound index	R	Y	R′	C–N °C	N–I °C	Found (%) C	Found (%) H	Found (%) N	Formula	Required (%) C	Required (%) H	Required (%) N	Yield (%)
IIIa	6-OCH_3	N=CH	OCH_3	143.0	(138.0)	64.4	4.9	9.3	$C_{16}H_{14}N_2O_2S$	64.1	4.7	9.4	57
b	6-OCH_3	N=CH	OC_2H_5	121.5	160.0	65.4	5.3	8.9	$C_{17}H_{16}N_2O_2S$	65.4	5.2	8.9	50
c	6-OCH_3	N=CH	OC_3H_7	102.0	127.0	66.3	5.5	8.6	$C_{18}H_{18}N_2O_2S$	66.2	5.5	8.6	63
d	6-OCH_3	N=CH	2-OH-4-OC_3H_7	129.2	154.9	63.1	5.2	8.2	$C_{18}H_{18}N_2O_3S$	63.1	5.3	8.2	60
e	6-OCH_3	N=CH	OC_4H_9	134.1	140.1	66.8	5.7	8.3	$C_{19}H_{20}N_2O_2S$	67.0	5.9	8.2	54
f	6-OCH_3	N=CH	2-OH-4-OC_4H_9	151.2	159.4	64.1	5.7	7.6	$C_{19}H_{20}N_2O_3S$	64.0	5.6	7.8	36
g	6-OCH_3	N=CH	OC_5H_{11}	102.2	126.0	67.9	6.1	7.9	$C_{20}H_{22}N_2O_2S$	67.8	6.2	7.9	57
h	6-OCH_3	N=CH	OC_6H_{13}	86.0	130.1	68.7	6.7	7.5	$C_{21}H_{24}N_2O_2S$	68.5	6.5	7.6	46
i	6-OCH_3	N=CH	OC_7H_{15}	89.5	120.0	69.2	6.6	7.2	$C_{22}H_{26}N_2O_2S$	69.1	6.8	7.3	53
j	6-OCH_3	N=CH	OC_8H_{17}	97.0	122.0	69.3	6.9	7.1	$C_{23}H_{28}N_2O_2S$	69.6	7.1	7.1	63
IVa	5-OCH_3	N=CH	OC_4H_9	—	88.3	67.1	6.0	8.2	$C_{19}H_{20}N_2O_2S$	67.0	6.0	8.2	49
b	5-OCH_3	N=CH	OC_6H_{13}	—	83.2	68.8	6.2	7.6	$C_{21}H_{24}N_2O_2S$	68.5	6.6	7.6	30
Va	6-OC_4H_9	N=CH	OC_3H_7	109.0	129.6	68.4	6.3	7.4	$C_{21}H_{24}N_2O_2S$	68.4	6.6	7.6	54
b	6-OC_4H_9	N=CH	OC_6H_{13}	76.0	128.7	70.6	7.2	6.8	$C_{24}H_{30}N_2O_2S$	70.2	7.3	6.8	55
VIa	6-CN	N=CH	OC_3H_7	181.0	(174.0)	67.3	5.0	13.0	$C_{18}H_{15}N_3OS$	67.3	4.7	13.0	32
b	6-CN	N=CH	OC_6H_{13}	131.5	164.1	69.3	6.1	11.8	$C_{21}H_{21}N_3OS$	69.4	5.8	11.6	37

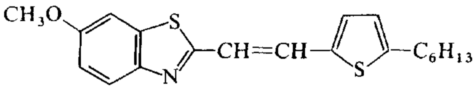
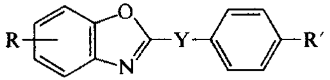
VIIa	6-OCH$_3$	CH=CH	OC$_3$H$_7$	122.0	162.7	70.3	5.9	4.0	$C_{19}H_{19}NO_2S$	70.1	5.9	4.3	30
b	6-OCH$_3$	CH=CH	OC$_6$H$_{13}$	103.0	165.0	71.9	6.5	3.6	$C_{22}H_{25}NO_2S$	71.9	6.8	3.8	28
c	6-OCH$_3$	CH=CH	C$_3$H$_7$	109.6	126.0	73.5	6.2	4.3	$C_{19}H_{1}NOS$	73.7	6.2	4.5	34
d	6-OCH$_3$	CH=CH	C$_6$H$_{13}$	84.4	116.3	75.4	7.3	3.8	$C_{22}H_{25}NOS$	75.2	7.2	4.0	23
e				74.6	(43.2)	67.1	6.4	3.9	$C_{20}H_{23}NO_2S$	67.2	6.5	3.9	31
VIIIa	5-OCH$_3$	CH=CH	OC$_3$H$_7$	—	102.4	70.0	5.8	4.2	$C_{19}H_{19}NO_2S$	70.1	5.9	4.3	22
b	5-OCH$_3$	CH=CH	OC$_6$H$_{13}$	—	89.9	72.1	6.7	3.6	$C_{22}H_{25}NO_2S$	72.0	6.8	3.8	27
IXa	6-OCH$_3$	COO	OC$_3$H$_7$	140.3	(107.0)	62.6	4.7	3.9	$C_{18}H_{17}NO_4S$	62.9	5.0	4.1	40
b	6-OCH$_3$	COO	OC$_6$H$_{13}$	104.6	105.3	65.4	6.0	3.4	$C_{21}H_{23}NO_4S$	65.4	6.0	3.6	31
c	6-OCH$_3$	COO	C$_6$H$_{13}$	91.3	(66.2)	68.4	6.1	3.4	$C_{21}H_{23}NO_3S$	68.3	6.3	3.8	24
Xa	6-OCH$_3$	N=N	OCOC$_5$H$_{11}$	115.0	143.8	62.3	5.5	10.9	$C_{20}H_{21}N_3O_3S$	62.6	5.5	10.9	49
XIa	6-OC$_4$H$_9$	N=N	OCOC$_4$H$_9$	109.5	127.0	64.2	6.1	10.2	$C_{22}H_{25}N_3O_3S$	64.2	6.1	10.2	48
b	6-OC$_4$H$_9$	N=N	OCOC$_5$H$_{11}$	107.0	131.8	64.7	6.4	9.7	$C_{23}H_{27}N_3O_3S$	64.9	6.4	9.9	51
c	6-OC$_4$H$_9$	N=N	OCOC$_6$H$_{13}$	105.8	119.7	65.5	6.5	9.6	$C_{24}H_{29}N_3O_3S$	65.6	6.6	9.6	49
XIIa	6-CN	N=N	OCOC$_5$H$_{11}$	—	217.6	63.0	4.7	14.8	$C_{20}H_{18}N_4O_2S$	63.5	4.8	14.8	30
b	6-OC$_4$H$_9$	N=N	OCOC$_6$H$_{13}$	—	213.5	64.2	5.6	14.4	$C_{21}H_{20}N_4O_2S$	64.3	5.1	14.3	31
XIIIa	6-OCH$_3$	Simple linkage	OC$_3$H$_7$	133.8	(110.8)	68.1	5.6	4.6	$C_{17}H_{17}NO_2S$	68.2	5.7	4.7	36
b	6-OCH$_3$	Simple linkage	OC$_6$H$_{13}$	105.5	119.2	70.2	6.6	3.0	$C_{20}H_{23}NO_2S$	70.3	6.8	4.1	34

TABLE V

Substituted benzoxazole liquid crystals



Compound index	R	Y	R′	C–N °C	N–I °C	Found (%) C	H	N	Formula	Required (%) C	H	N	Yield (%)
XIVa	5-CH_3	Simple linkage	OC_3H_7	—	93.0	76.7	6.4	4.8	$C_{17}H_{17}NO_2$	76.4	6.4	5.2	75
b	5-CH_3	Simple linkage	OC_6H_{13}	79.6	(67.6)	77.7	7.0	4.5	$C_{20}H_{23}NO_2$	77.6	7.5	4.5	63
XVa	5-CH_3	CH=CH	OC_3H_7	—	117.0	78.0	6.6	4.6	$C_{19}H_{19}NO_2$	77.8	6.6	4.7	65
b	5-CH_3	CH=CH	OC_6H_{13}	91.5	122.9	79.0	7.2	4.0	$C_{22}H_{25}NO_2$	78.8	7.5	4.2	71
XVIa	5-OCH_3	Simple linkage	OC_3H_7	—	84.2	72.2	6.3	4.8	$C_{17}H_{17}NO_3$	72.1	6.0	4.9	56
b	5-OCH_3	Simple linkage	OC_6H_{13}	77.7	(69.5)	73.8	6.7	4.1	$C_{20}H_{23}NO_3$	73.8	7.1	4.3	49
XVIIa	5-OCH_3	CH=CH	OC_3H_7	120.5	(116.2)	73.5	6.1	4.4	$C_{19}H_{19}NO_3$	73.8	6.2	4.5	74
b	5-OCH_3	CH=CH	OC_6H_{13}	87.5	124.7	74.9	7.1	3.7	$C_{22}H_{25}NO_3$	75.2	7.2	4.0	72
XVIIIa	6-CH_3	Simple linkage	OC_3H_7	—	106.8	76.2	6.4	5.0	$C_{17}H_{17}NO_2$	76.4	6.4	5.2	47
b	6-CH_3	Simple linkage	OC_6H_{13}	94.8	(49.0)	77.3	7.3	4.4	$C_{20}H_{23}NO_2$	77.6	7.5	4.5	48
XIXa	6-CH_3	CH=CH	OC_3H_7	—	102.7	77.5	6.3	4.8	$C_{19}H_{19}NO_2$	77.8	6.5	4.8	73
b	6-CH_3	CH=CH	OC_6H_{13}	85.5	90.4	78.8	7.5	3.8	$C_{22}H_{25}NO_2$	78.8	7.5	4.2	75
XXa	6-OCH_3	Simple linkage	OC_3H_7	—	76.0	72.2	6.5	4.7	$C_{17}H_{17}NO_3$	72.1	6.0	4.9	48
b	6-OCH_3	Simple linkage	OC_6H_{13}	70.6	(40.6)	73.8	7.0	4.1	$C_{20}H_{23}NO_3$	73.8	7.1	4.3	46
XXIa	6-OCH_3	CH=CH	OC_3H_7	—	104.0	73.5	6.2	4.3	$C_{19}H_{19}NO_3$	73.7	6.2	4.5	74
b	6-OCH_3	CH=CH	OC_6H_{13}	86.8	(83.7)	75.0	7.0	3.7	$C_{22}H_{25}NO_3$	75.2	7.2	3.9	74

After stirring for 2.5 h at 0°C the mixture was acidified with hydrochloric acid. A deposited precipitate of *p*-hydroxyphenylazo-6-alkoxy(or cyano)benzthiazole was collected, dried at 100°C under reduced pressure and used without further purifying. Acyl chloride (0.005 mole) was added at 0°C to the solution of above hydroxy derivative (0.005 mole) in 10 ml of anhydrous pyridine. After keeping overnight at 25°C, the mixture was poured into 10% glacial hydrochloric acid, filtered, and a solid was recrystallised from hexane-ethyl alcohol mixture (3 : 1) (Table IV).

2-*p*-Alkoxyphenyl-6-methoxybenzthiazoles (XIII)

p-Alkoxybenzaldehyde (0.16 mole) was added dropwise to a stirred suspension of zinc 2-amino-5-methoxyphenylmercaptide in 150 ml of hot glacial acetic acid. The mixture was heated for 15 min under reflux and poured into water. The precipitate of XIII was recrystallised from hexane (Table IV).

2-*p*-Alkoxyphenyl-5 (or 6)methyl (or methoxy)benzoxazoles (XIV, XVI, XVIII, XX)

A mixture of the appropriate *o*-aminophenol (0.01 mole), *p*-alkoxybenzaldehyde (0.01 mole) and *p*-toluenesulfonic acid (0.1 g) in 100 ml of benzene was refluxed with a Dean–Stark column for 4 h. After distilling of the solvent, the residue of Schiff base was recrystallised from ethyl alcohol–hexane mixture (5 : 1). A benzenic solution of above Schiff base (0.005 mole) was shaken for 30 min with plumb tetraacetate (0.01 mole). A solid was filtered, and the solution was chromatographied on alumina. After evaporation of benzene, the residue was recrystallised from hexane (Table V).

2-*p*-Alkoxystyryl-6-(or 5)methyl (or methoxy)benzoxazoles (XV, XVII, XIX, XXI)

p-Alkoxycinnamic acid (0.015 mole) was added at 100°C to a mixture of appropriate aminophenol (0.01 mole) and polyphosphoric ester. After heating for 30 min at 100°C, the mixture was cooled, decomposed with 50 ml of glacial water and neutralized with sodium acid carbonate. A precipitate was recrystallised from hexane (Table V).

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