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New Heterocyclic Liquid Crystalline Compounds

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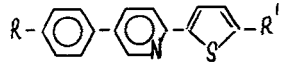
Mesomorphic derivatives of 2-substituted 5-*p*-alkyl(alkoxy or cyano)phenylpyridines, 1,4-disubstituted piperidines, and ethyl 5-*p*-alkylphenylthiophene-2-carboxylates have been synthesised and their liquid crystal properties compared with those of analogous benzene and cyclohexane derivatives. Intermediates in the pyridine derivative synthesis 2-thienyl- and 2-furylpyridines—have been found to be mesomorphic too. Some piperidine compounds containing the cyano group in the benzene ring exhibit a large (over +30) positive dielectric anisotropy.

INTRODUCTION

Up to now, a great number of mesomorphic compounds containing heterocyclic units has been synthesised,[1] and interest in such structures constantly grows. This is not only because of the greater possibilities with heterocycles for the design of new mesogenic molecules, but also because introduction of heteroatoms can cause considerable changes of polarity, polarisability, and sometimes the geometry of a molecule, so influencing greatly the type of mesophase, the phase transition temperatures, and the dielectric and other properties of the mesogens.

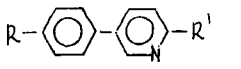
Following on our investigations in this direction, we have synthesised new, potentially mesogenic heterocyclic compounds in the series A – F:

A

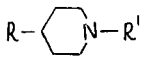


B

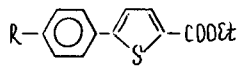
Paper presented at the 8th International Liquid Crystal Conference, Kyoto, Japan, June 30–July 4, 1980.



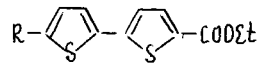
C



D



E



F

The compounds A and B, containing two heterocycles, were intermediates in the synthesis of the compounds C, but they were found to be mesomorphic themselves.

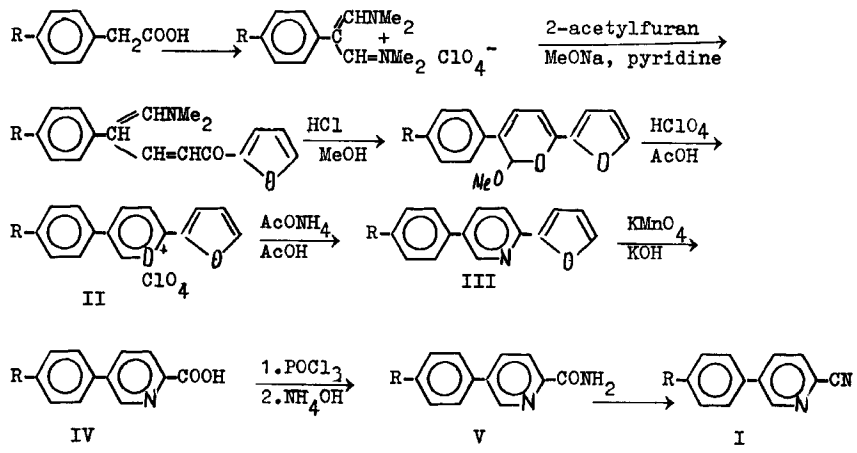
Such a choice of heterocyclic structures was not caused by the search for liquid crystalline compounds with properties useful for applications. Our aim was to find out the alterations in mesomorphic and sometimes dielectric properties of some well known mesogens when changing the benzene or cyclohexane ring to a pyridine (compounds C) or an *N*-substituted piperidine (compounds D) ring. When synthesising the latter compounds, we have taken into account that the geometry of exocyclic bonds from hetero-atoms must be equivalent to that for equatorial substitution on a cyclohexane ring (e.g., tetrahydropyran-*trans*-oxides,[2] equatorially substituted 1-piperidines[3]).

It was also of interest to check the mesogenic possibilities of the new thiophene-containing systems (compounds E and F). The results obtained can be useful in further searches for applicable mesogens; for example, the lower melting points of piperidine derivatives, in comparison with analogous cyclohexanes, may be taken into account.

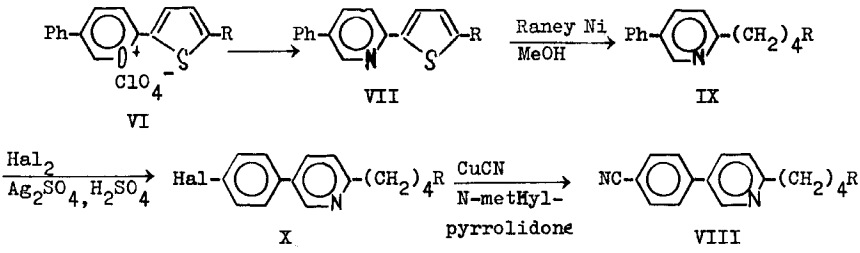
EXPERIMENTAL

Phase transition temperatures have been measured using a MIN-8 polarising microscope fitted with a Mettler FP–52 heating stage and FP–5 control unit. Electronic absorption spectra have been recorded using a Hitachi EPS–3T spectrophotometer; IR spectra from 400–4000 cm^{-1} have been recorded using a UR–20 spectrophotometer. Dielectric constants have been measured by the bridge method in a cell 1 cm^2 × 200 μ. A magnetic field of 7 kG has been used to orient the liquid crystals. PMR spectra have been registered using a Varian 100 D spectrophotometer. Satisfactory elemental analyses have been obtained for all substances with the exception of compounds XIc,d which are difficult to crystallise and oxidise rapidly in air. β-Phenyl-substituted pyridines are difficult compounds to prepare, and we have rejected some methods described in the literature on account of their complexity or the low yields of intermediate products obtained. We propose a new synthetic

path to 2-cyano-5-arylpyridines (I) presented by the following scheme:



Approximately the same scheme, with the intermediate formation of the thienylpyrylium perchlorate (VI), has been used by us to synthesise the intermediate thienylpyridines (VII) which have then been transformed into the 3-*p*-cyanophenylpyridines (VIII) according to the scheme:



Phase transition temperatures for the pyridine derivatives and the intermediates are listed in Table I and II.

Substituted piperidines (XI) have been obtained by dialkylation of amines and anilines with substituted 1,5-dibromopentanes synthesised in their turn from aldehydes according to the following scheme:

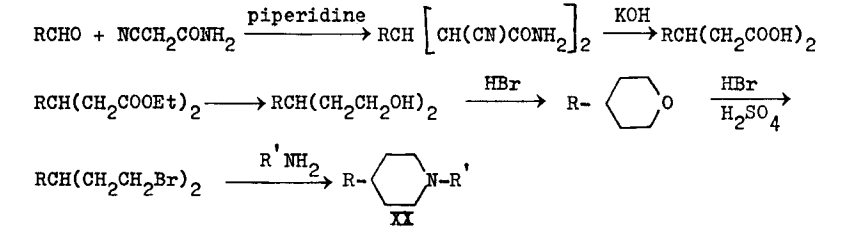


TABLE I

Phase transition temperatures (°C) for compounds I–V

	II	III		IV	V		I		
R	m.p.	C–S	S–I	m.p.	C–S	S–I	C–S(C–N)	S–N(S–I)	N–I(m.p.)
a C_4H_9	114	75	96	160	174	196	—	—	64
b C_5H_{11}	146	65	106	164	160	183	—	—	73
c C_6H_{13}	119	55	103	160	176	180	58	—	44*
d C_7H_{15}	151	48	107	159	164	180	66	—	56*
e C_8H_{17}	127	42	102	158	172	180	61	58*	—
f C_4H_9O	176	106	136	178	190	212	97	—	81*
g $C_5H_{11}O$	164	62	133	167	190	204	69	—	82
h $C_6H_{13}O$	172	76	133	161	190	189*	80	–	90
i $C_7H_{15}O$	166	63	136	162	134	192	62	86	91
j $C_8H_{17}O$	157	54	137	160	148	192	84	97	—

* Monotropic liquid crystal

TABLE II

Phase transition temperatures (°C) for compounds VI–VIII, X

	VI	VII	X	VIII	
R	m.p.	m.p.	m.p.	C–S	S–I
H	196	108	68 (X = I)	—	—
C_2H_5	142	86	67 (X = I); 48 (X = Br)	52	26*
C_5H_{11}	138	92	44 (X = Br)	42	54

* Monotropic liquid crystal.

TABLE III

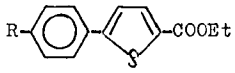
Phase transition temperatures (°C) for the compounds XI

R	R'	m.p.	cl.p.	type of mesophase
a C_4H_9O-⟨⟩-	C_7H_{15}	38-40	-	-
b C_4H_9O-⟨⟩-	C_8H_{17}	50	-	-
c C_6H_{13}	C_4H_9-⟨⟩-	20	44	S_B
d C_6H_{13}	C_4H_9O-⟨⟩-	40	78	S_B
e C_6H_{13}	NC-⟨⟩-	28-30	12-13[X]	N
f C_4H_9O-⟨⟩-	NC-⟨⟩-	86	106	N
g C_4H_9O-⟨⟩-	C_4H_9-⟨⟩-	70	132	S_B

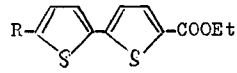
[X] Monotropic liquid crystal

The types of mesophase and the phase transition temperatures for compounds XI are listed in Table III.

Ethyl thiophene-2-carboxylates (XII) (Table IV) have been synthesised as described earlier[4] by condensation of 3-chloro-3-arylpropene-2-ylidene-1-dimethylammonium perchlorate with ethyl thioglycolate in 60% yield.



XII



XIII

The 2,2′-bithienyl derivative (XIII; R=C_9H_{19}) has been obtained from 2,2′-bithienyl by acylation, hydrogenation to 5-nonyl-2,2′-bithienyl, acetylation, and oxidation of the acetyl derivative into 5-nonyl-2,2′-bithienyl-5′-carboxylic acid (which forms a nematic phase between 112° and 162°); this acid has been transformed into compound XIII by esterification.

TABLE IV

Phase transition temperatures (°C) for the compounds XIII

	R	C–S	S–I
a	C_4H_9O	87	86
b	$C_5H_{11}O$	72	90
c	$C_6H_{13}O$	60	82
d	$C_7H_{15}O$	86	82*
e	$C_8H_{17}O$	72	84
f	C_7H_{15}	84	47*

* Monotropic liquid crystal.

DISCUSSION

In contrast to the analogous biphenyl derivatives, the compounds I(R=alkyl) have comparatively high melting points. Their clearing points are however approximately 15° higher. The higher homologues exhibit monotropic liquid crystal properties, whereas the lower members are not mesomorphic. On the contrary, the melting points of the compounds I (R=alkoxy) increase, in comparison with the benzene analogues, to a smaller degree than their clearing points. In consequence of this, the compounds I (R=alkoxy) exhibit enantiotropic liquid crystal properties. The intermediate furylpyridines (III) and picolinic acid amides (V) are purely smectic. We have studied some of the compounds III by DSC and revealed several smectic

phases whose types were not investigated. Typical examples are:

$$\text{IIId: C} \xrightarrow{48} \text{S}_1 \overset{100}{\leftrightarrow} \text{S}_2 \overset{103}{\leftrightarrow} \text{S}_3 \overset{107}{\leftrightarrow} \text{Iso}$$

$$\text{IIId + IIIj mixture (1:1), C} \xrightarrow{34.8} \text{S}_1 \overset{105.6}{\leftrightarrow} \text{S}_2 \overset{109.5}{\leftrightarrow} \text{S}_3 \overset{120}{\leftrightarrow} \text{Iso}$$

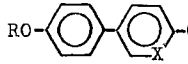
The acids IV, in contrast to the analogous benzene derivatives, do not exhibit mesomorphic properties. We suppose that such a behaviour is caused by the existence of intermolecular hydrogen bonds which prevent a linear dimer formation, in an analogous manner to that for 5-alkoxypicolinic acids.[5] This fact is confirmed by the IR spectra of the acids IV (in carbon tetrachloride) which contain an intense absorption band at 3340 cm^{-1} (stretching vibration of the H—O bond) and a narrow intense band at 1772 cm^{-1} (stretching vibration of the carbonyl group).

Figure 1 shows the result of measurements of the dielectric constants ($\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$) for 3-*p*-aloxyphenyl-6-cyanopyridines (Figure 1a) in comparison with the values for 4-alkoxy-4′-cyanobiphenyls (Figure 1b) as a function of reduced temperature (T/T_{cl}, where T = temperature of measurement, T_{cl} = clearing point in °K).

The dependencies $\varepsilon_{\parallel}$ (T) and $\varepsilon_{\perp}$ (T) are typical for nematic liquid crystals with a large positive dielectric anisotropy (PDA) ε_a. The $\varepsilon_{\parallel}$ (T) dependence curve for 3-*p*-heptyloxyphenyl-6-cyanopyridine has a fracture caused by the transition of the liquid crystal from the nematic state into a smectic on cooling. The large PDA value is due to the large permanent dipole of the terminal cyano group acting along the main molecular axis. It is however essential to consider the contribution of the permanent dipole of the pyridine nitrogen, since this dipole is tilted to the main molecular axis and will contribute both to the parallel ($\varepsilon_{\parallel}$) and the perpendicular ($\varepsilon_{\perp}$) dielectric constants that are measured experimentally. From data cited in Table V for the $\varepsilon_{\parallel}$, $\varepsilon_{\perp}$, and ε_a values of three members of the homologous series of cyanophenylpyridines

TABLE V

Dielectric constants for the compounds



at $T/T_{cl} = 0.98$

R	X	$\varepsilon_{\parallel}$	$\varepsilon_{\perp}$	ε_a
C_5H_{11}	CH	16.7	8.2	+8.5
	N	23.2	13.8	+9.4
C_6H_{13}	CH	15.8	7.8	+8.0
	N	19.7	11.4	+8.3
C_7H_{15}	CH	15.0	7.5	+7.5
	N	19.5	11.2	+8.3

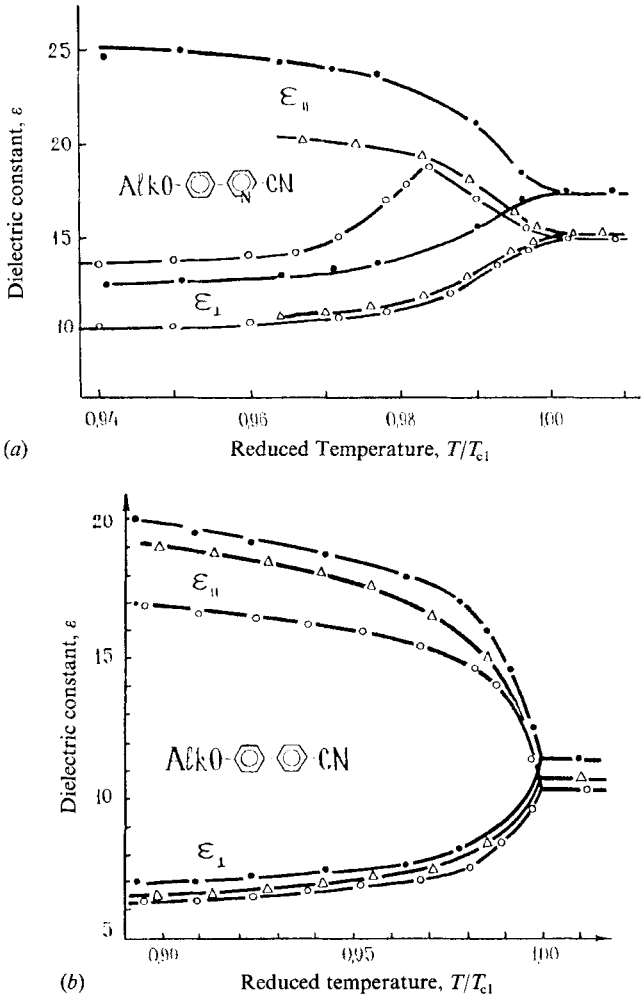


FIGURE 1 Dependencies of the dielectric constants $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ on reduced temperature for the 3-*p*-alkoxyphenyl-6-cyanopyridines (Figure 1(a) and 4-alkoxy-4′-cyanobiphenyls (Figure 1(b)). ● Alk = C_5H_{11}; △ Alk = C_6H_{13}; ○ Alk = C_7H_{15}.

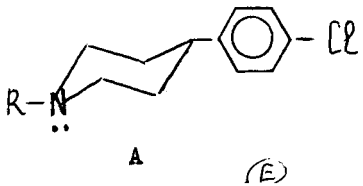
and cyanobiphenyls at the same reduced temperatures, we can see in fact that replacement of the benzene ring by the pyridine ring does cause increases in both $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$. The values of ε_a for the compounds I are therefore insignificantly higher than those for the analogous benzene derivatives.

Of three of the synthesised compounds VIII, the butyl homologue (R=H) is not mesomorphic, the hexyl derivative (R=C_2H_5) exhibits a monotropic

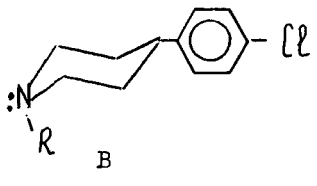
smectic phase, and only the nonyl derivative ($R=C_5H_{11}$) forms an enantiotropic smectic phase with a narrow temperature range.

The 1,4-disubstituted piperidines (XI) (Table III) turn rapidly yellow; this low chemical stability prevents their practical use despite the good dielectric properties of piperidines with a cyano substituent in benzene ring (XIe,f).

It is known that the valence angle between the bonds of nitrogen is close to that of the tetrahedral carbon (near 106°). Therefore, as in the case of the cyclohexanes, an exocyclic bond N—C bond can be axial or equatorial. According to published data,[6] compounds of type XIa,b contain about 90% of the equatorial (A) and about 10% of the axial (B) conformational isomers.

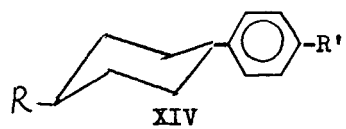


A (E)



B

According to Eliel *et al.*,[7] the equatorial conformation is dominant for a "cyclohexyl-aryl" bond, its content being up to 99%. Thus, in the case of the piperidines XIa,b, the proportion of diequatorial isomer responsible for a linear structure of the molecule and the mesogenic properties cannot be over 89%. The absence of liquid crystal properties in these compounds would appear to be caused by the presence of about 11% of non-linear conformers. Synthesised by us, the alkylphenylcyclohexanes (XIV) too do not exhibit mesomorphic properties.



XIV

$R=C_3H_7$, C_5H_{11}, C_6H_{13}, C_7H_{15}

$R'=C_2H_5$, C_6H_{13}

They have been synthesised according to.[8]

A different behaviour is observed for compounds XIc,d, where the nitrogen atom is adjacent to the benzene ring ($R=p\text{-}XC_6H_4$). These compounds exhibit a smectic mesophase to 44°C (XIc, $X=C_4H_9$) and 78°C (XId, $X=C_4H_9O$). The axial position of the pair of electrons on the nitrogen is more advantageous owing to the conjugation with the π-elektrons of the aromatic ring. On account of this, both a geometric (increase of the content of equatorial conformer with respect to the N–Ar bond) and an electronic (increase of the anisotropy of polarisability due to more extended conjugation) factor contribute to the appearance of mesomorphic properties. As in other series of mesomorphic compounds, replacement of an alkyl substituent (XIb) by an alkoxy group (XId) leads to an increase in the molecular polarisability

and consequently to a raising of the smectic phase thermal stability. While comparing textures of the phases of the compounds XIc,d with those of known liquid crystals, we concluded that they exhibit smectic B phases like most cyclohexane derivatives.

The three-ring piperidine derivative XIg has an even larger smectic temperature range.

Introduction of the nematogenic cyano group into the *para*-position of the benzene ring (two-ring piperidine derivative XIe) gives a monotropic nematic phase only (at 12–13°C), whereas the analogous 4-hexyl-1-*p*-cyanophenylcyclohexane exhibits an enantiotropic nematic phase with a large temperature range.[9] This appears to be due to a strengthening of the dipole-dipole interactions in the crystal lattice, induced by the axially located lone pair of nitrogen electrons. In this way, an increase in the melting point occurs and the appearance of a monotropic phase. The dielectric anisotropy of compound XIe, measured in mixtures with azoxybenzenes (isomers of 4-methoxy-4′-butylazoxybenzene and 4-heptanoyloxy-4′-butylazoxybenzene in a ratio of 2:1) at 20°C has been found to be equal to +35 (in comparison with +10 for phenylcyclohexanes). Such an increase in ε_a is caused by enhancement of the longitudinal dipole due to the electron donating alkylamino group located in the *para*-position of the benzene ring with respect to the cyano group.

On increasing the "geometric anisotropy" of the molecule (XIf), an enantiotropic nematic mesophase appears. The dielectric anisotropy of this compound is equal to +34 at 20°C (in mixtures) and +14 at 85°C (pure compound).

There is a little possibility of comparing transition temperatures with analogous phenylcyclohexane and biphenyl derivatives. Some approximate examples are listed in Table VI.

The compounds XII (Table IV) form a monotropic or a narrow enantiotropic smectic phase with a mesophase thermal stability 30° lower than that in the case of analogous biphenyl derivatives. Our suggestion that in the case of the 2,2′-bithienyl derivative (XIII), the molecule will be more linear, has not been justified. This compound is not mesomorphic, and the corresponding acid (C–N 112°C, N–I 162°C) has a clearing point 90° lower than that of the analogous 4-nonylbiphenyl-4′-carboxylic acid. The nitrile corresponding to this acid exhibits monotropic liquid crystal properties, with a melting point of 60°C and a clearing point near −5°C. It seems that bithienyl derivatives have a planar *trans*-conformation in the solid state only. Indeed, according to UV spectral data, the conformation of this compound in solution corresponds to a tilt of the two rings (with respect to the central bond) equal to 23 ± 10°. According to PMR spectra, the equilibrium between the *cis*- and *trans*-isomers of compound XIII is approximately 2:1.

TABLE VI

Phase transition temperatures (°C) for the poperidine derivatives XI and their carbocyclic analogues

Compound	T_S	T_N	Cl.p.	Ref.
C_6H_{13}-(Py)-CN	-	(12)	28-30	
C_6H_{13}-(Ph)-(Ph)-CN	25	42	47	9
C_6H_{13}-(Ph)-(Ph)-CN	-	13.5	27	10
C_4H_9O-(Ph)-(Py)-CN	-	86	106	
C_5H_{11}-(Ph)-(Ph)-(Ph)-CN	130	-	239	11
C_6H_{13}-(Py)-C_4H_9	20	-	44	
C_6H_{13}-(Ph)-C_6H_{13}	isotropic liquid			
C_6H_{13}-(Py)-OC_4H_9	40	-	78	
C_6H_{13}-(Ph)-OC_6H_{13}	66	-	84	12
C_4H_9O-(Ph)-(Py)-C_4H_9	70	-	132	
C_4H_9-(Ph)-(Ph)-(Ph)-C_4H_9	86	-	107	12
C_4H_9-(Ph)-(Ph)-(Ph)-C_4H_9	208	-	218	12

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