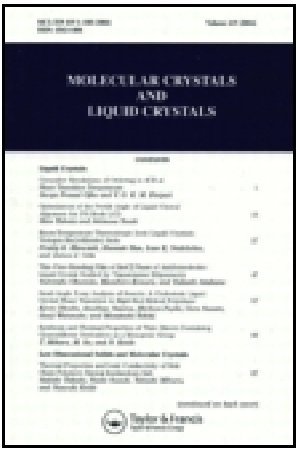

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A Study of the Structure: Mesogenic Behaviour Relationship in Three Types of Liquid Crystals (6-n-Alkoxy-3-Pyridinecarboxaldehyde Derivatives, 5-n-Alkoxy-2-Pyridinecarboxaldehyde Derivatives and 4-n-Alkoxybenzaldehyde Derivatives) Using Spectroscopic and Semi-Empirical Methods of Calculation (MNDO)

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A Study of the Structure: Mesogenic Behaviour Relationship in Three Types of Liquid Crystals (6-*n*-Alkoxy-3-Pyridinecarboxaldehyde Derivatives, 5-*n*-Alkoxy-2-Pyridinecarboxaldehyde Derivatives and 4-*n*-Alkoxybenzaldehyde Derivatives) Using Spectroscopic and Semi-Empirical Methods of Calculation (MNDO).

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Our aim in this paper is to make a comparative study of the mesogenic properties of liquid crystalline compounds derived from 6-*n*-alkoxy-3-pyridinecarboxaldehydes, 5-*n*-alkoxy-2-pyridinecarboxaldehydes and 4-*n*-alkoxybenzaldehydes. The relationship between molecular structure and mesogenic properties was determined using spectroscopic techniques (U.V. and ^{1}H NMR) and semi-empirical methods of calculation (MNDO). The results have proved to be of interest in that a relation can be seen to exist between the dipole moment of the molecules and the net partial charges of the atoms and the type of mesophase formed.

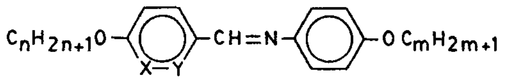
Keywords: mesogenic properties, molecular structure

INTRODUCTION

The synthesis and study of the mesogenic properties of compounds derived from 6-*n*-alkoxy-3-pyridinecarboxaldehydes (6-*n*-alkoxynicotinaldehydes) and 5-*n*-alkoxy-2-pyridinecarboxaldehydes (5-*n*-alkoxypicolinaldehydes) have been described in previous papers.[1,2,3]

The presence of pyridinic rings instead of benzenic rings has two fundamental advantages. In the first place, a permanent dipolar moment is introduced in the molecules without modifying their molecular breadth and secondly, an increase in electronic polarizability, provided the lone pair of electrons in the heterocycle nitrogen atom can be delocalized.[4] These effects probably depend on the position of the heteroatom in the ring.

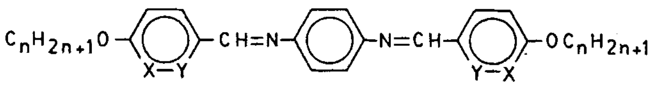
In this paper a comparative study is made of the mesomorphic properties of the different types of heterocyclic and carbocyclic compounds synthesized (imines, diimines and azines).



(I) X=N, Y=CH

(II) X=CH, Y=N

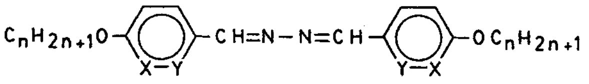
(III) X=Y=CH



(IV) X=N, Y=CH

(V) X=CH, Y=N

(VI) X=Y=CH



(VII) X=N, Y=CH

(VIII) X=CH, Y=N

(IX) X=Y=CH

$n = 2, 4, 6, 8, 10$ $m = 2, 8, 14$

A study of the structural and electronic properties using spectroscopic techniques (U.V. and ^1H NMR) and semi-empirical calculations (MNDO) respectively was carried out in order to determine the relation between the molecular structure of the compounds and their mesogenic behaviour.

EXPERIMENTAL

Synthesis

The synthesis of the compounds in series I, II, IV, V, VII, VIII and IX used in this study has been described in previous papers.[1,2,4]

Data corresponding to the two carbocyclic series, III and VI, were partly taken from the literature (series III: n = 2, 4, 6, 8, 10, m = 2[6,7]; series VI: m = 2, 4[8]) and partly determined by us. Some of the compounds synthesized have not been previously described in the literature.

Techniques

The transition temperatures were determined using a Perkin-Elmer DSC-2. The apparatus was calibrated by measuring the known melting points of benzoic acid (121.2°C), indium (156.6°C) and tin (231.9°C).

Optical observations were made using a Reichert-Thermovar HT1-B11 polarizing microscope equipped with a heating stage.

^{1}H NMR spectra were obtained with a Bruker Wp-80CW using $CDCl_3$ solutions and TMS as internal reference.

U.V. spectra were obtained with a Perkin-Elmer 200 instrument.

MNDO calculations were made using a Digital VAX 11/780 computer.

RESULTS AND DISCUSSION

Comparative study of 6-*n*-alkoxy-3-pyridylmethylene-4′-*n*-alkoxyanilines (series I), 5-*n*-alkoxy-2-pyridylmethylene-4′-*n*-alkoxyanilines (series II), and 4-*n*-alkoxybenzylidene-4′-n-alkoxyanilines (series III)

The optical and thermal data for series I, II and III are listed in Table I.

As can be observed, smectic mesophases tend to appear more frequently in compounds belonging to series I, whereas the nematic mesophase predominates in series II and III. It can also be seen that the compounds in series I exhibit smectic polymorphism (S_A, S_C, S_B, S_G) whilst in series II and III the smectic mesophase shown by compounds is basically of type C (with the exception of compound n = 2, m = 8 which forms an S_A mesophase in both series).

TABLE I

Optical and thermal data for imines (series I, II and III).

		Series I		Series II		Series III	
n	*m*	Trans.	T^a(°C)	Trans.	T^a(°C)	Trans.	T^a(°C)
2	2	C_1—I	91.0	C—N	132.6	C—I^a	149.0
		C_2—N	84.0	N—I	139.2	I—N^b	143.0
4	2	C_1—I	87.9	C_2—N	89.5	C—N^a	105.5
		C_2—I	85.0	N—I	117.2	N—I	129.5
		I—N^b	84.4				
6	2	C—I	90.5	C—N	73.9	C—N^a	97.5
		I—N	86.8	N—I	112.2	N—I	122.5
8	2	C_1—N	76.5	C—N	53.6	C—N^a	99.0
		N—I	83.1	N—I	110.1	N—I	119.0
10	2	C—N	80.3	C—S_A	63.6	C—N^a	103.2
		N—I	81.9	S_A—N	79.4	N—I	117.0
				N—I	108.2	N—S_A^{b}	94.0
2	8	C—I	91.2	C—N	65.1	C—N	92.5
		I—S_A^{b}	88.7	N—I	108.9	N—I	117.5
4	8	C—S_A	79.3	C—N	62.8	C—N	98.8
		S_A—I	92.6	N—I	103.6	N—I	114.2
6	8	C_1—S_G	66.1	C—S_C	48.6	C_1—S_C	92.6
		C_2—S_G	65.0	S_C—N	61.5	C_2—S_C	86.7
		C_3—S_G	61.0	N—I	104.9	S_C—N	102.3
		S_G—S_C	68.8			N—I	113.4
		S_C—S_A	80.5				
		S_A—I	93.0				
8	8	C_1—S_G	63.7	C—S_C	51.2	C—S_C	102.6
		C_2—S_G	61.0	S_C—N	87.7	S_C—N	110.9
		C_3—S_G	62.2	N—I	106.4	N—I	113.6
		S_G—S_C	68.4				
		S_C—S_A	84.6				
		S_A—I	93.0				
10	8	C—S_G	67.7	C—S_C	52.9	C_1—S_C	95.0
		S_G—S_C	69.6	S_C—N	99.5	C_2—S_G	89.1
		S_C—S_A	84.0	N—I	105.5	S_G—S_C	94.7
		S_A—I	92.4			S_C—I	113.1
2	14	C—I	90.4	C—N	83.5		
		I—S_A^{b}	88.6	N—I	99.6		
4	14	C—S_A	88.6	C—N	61.8		
		S_A—I	91.0	N—I	94.4		
		S_A—S_B^{b}	78.8				
6	14	C_1—S_A	82.1	C—S_C	63.2		
		C_2—S_C	80.9	S_C—N	76.6		
		S_C—S_A	82.0	N—I	96.7		
		S_A—I	91.5				
		S_C—S_G^{b}	79.4				
8	14	C_1—S_C	85.2	C—S_C	65.9		
		C_2—S_G	79.8	S_C—N	94.2		
		C_3—S_G	81.7	N—I	99.7		
		S_G—S_C	83.7				
		S_C—I	92.6				
10	14	C_1—S_C	86.3	C_1—S_C	66.2		
		C_2—S_G	81.7	C_2—S_C	50.2		
		S_G—S_C	86.1	S_C—I	102.7		
		S_C—I	92.4				

[a] Data of literature (Refs. 6, 7).

[b] Monotropic transition.

Figures 1 and 2 show the melting points and clearing temperatures respectively of the three series of imines.

It is apparent that the imines derived from the heterocyclic aldehydes have lower melting points and clearing temperatures than those derived from benzaldehyde.

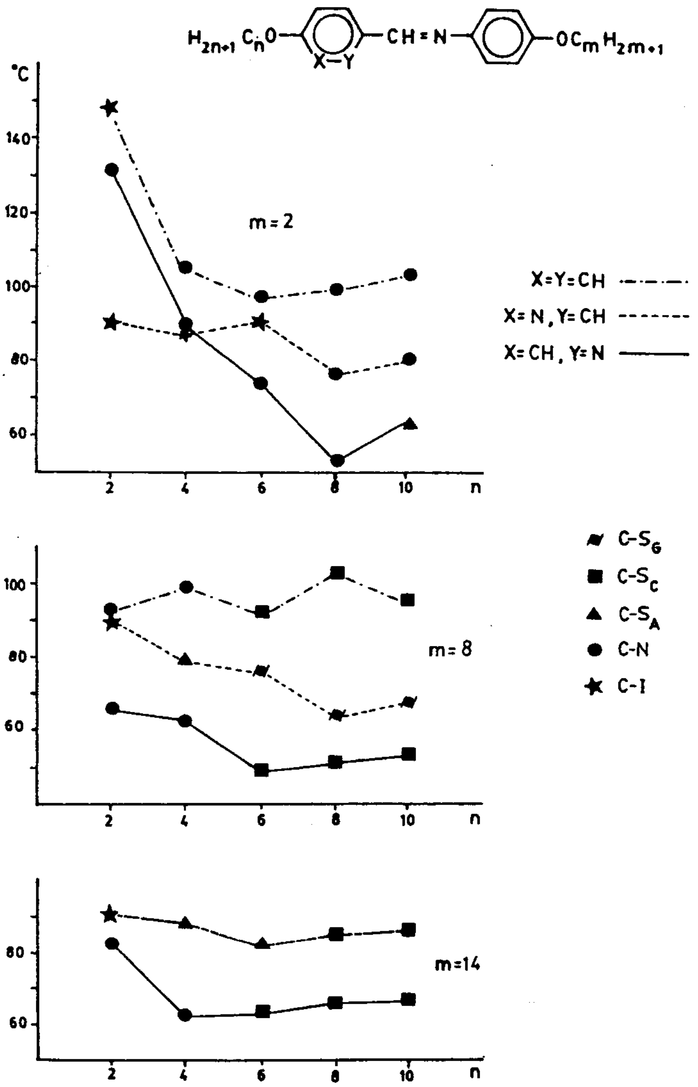


FIGURE 1 Melting points as function of alkyl chain length, for compounds of series I, II and III.

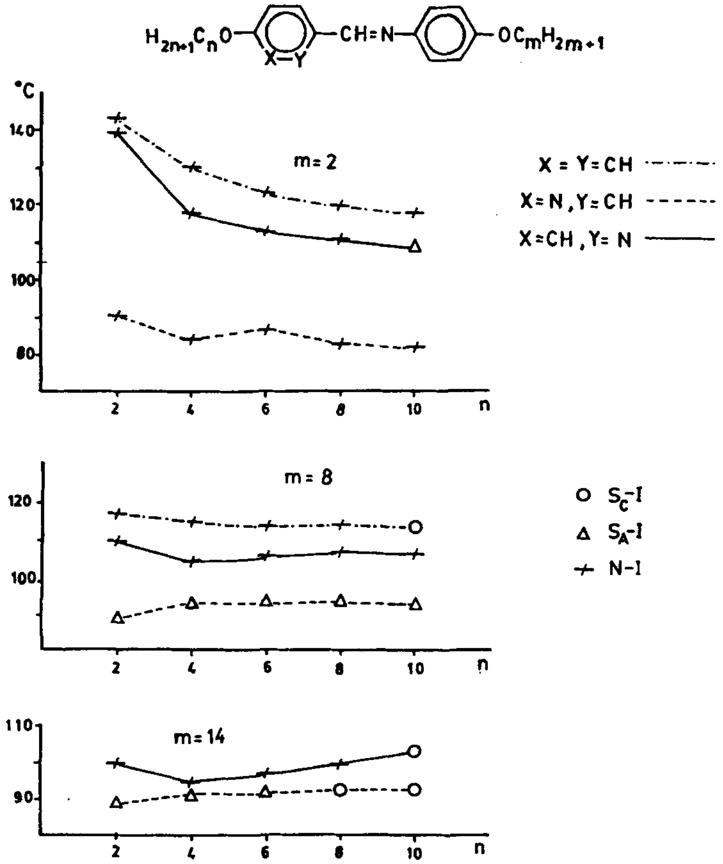


FIGURE 2 Clearing temperatures as function of alkyl chain length, for compounds of series I, II and III.

Unless they have very short terminal chains, picolinic derivatives (series II) show lower melting points than nicotinic analogues (series I) and in all cases, have higher clearing points. The former also exhibit wider mesophase ranges than either nicotinic or carbocyclic derivatives.

Comparative study of bis-(6′-*n*-alkoxy-3′-pyridylmethylene)-1,4-phenylenediamines (series IV), bis-(5′-*n*-alkoxy-2′-pyridylmethylene)-1,4-phenylenediamines (series V) and bis-(4′-n-alkoxybenzylidene)-1,4-phenylenediamines (series VI)

Table II shows the optical and thermal data for the compounds in series IV, V and VI.

TABLE II

Optical and thermal data for diimines (Series IV, V and VI).

	Series IV		Series V		Series VI	
n	Trans.	T^a(°C)	Trans.	T^a(°C)	Trans.	T^a(°C)
2	C—S_A	156.8	C_3—N	188.4	C—N[a]	202.5
	S_A—N	219.4	N—I	dec.	N—I	dec.
	N—I	272.9				
4	C—S_A	132.1	C—N	153.3	C—N[a]	186.5
	S_A—N	232.4	N—I	278.9	N—I	297.5
	N—I	236.2				
	S_A—S_B[b]	126.1				
6	C_1—S_G	99.6	C—S_B	122.4	C—S_H	154.6
	C_2—S_G	98.2	S_B—N	132.6	S_H—S_G	159.6
	C_3—S_G	96.9	N—I	243.0	S_G—S_F	166.4
	S_G—S_C	116.5			S_F—S_C	167.0
	S_C—S_A	171.0			S_C—N	186.0
	S_A—I	214.0			N—I	254.9
8	C_2—S_G	98.3	C_1—S_H	61.2	C—S_H	114.7
	S_G—S_C	114.5	C_2—S_H	55.2	S_H—S_G	143.4
	S_C—S_A	184.0	S_H—S_G	100.2	S_G—S_F	150.4
	S_A—I	195.8	S_G—S_C	121.2	S_F—S_I	155.3
			S_C—N	158.4	S_I—S_C	165.3
			N—I	223.1	S_C—N	204.3
					N—I	233.4
10	C_1—S_G	105.3	C—S_G	89.9	C—S_H	117.8
	C_2—S_G	104.2	S_G—S_C	95.5	S_H—S_G	138.6
	S_G—S_C	111.7	S_C—N	173.4	S_G—S_I	142.2
	S_C—S_A	177.0	N—I	202.1	S_I—S_C	161.0
	S_A—I	180.0	S_G—S_H[b]	87.2	S_C—N	206.5
					N—I	216.8

[a] Data of literature (Ref. 8).
[b] Monotropic transition.

As with the imines, it can be seen that compounds derived from nicotinaldehyde (series IV) tend to show smectic mesophases whilst those in series V and VI clearly exhibit nematic mesophases.

In all three series, however, compounds with long terminal chains show smectic polymorphism.

It can also be seen from the optical data, that in series IV, orthogonal mesophases (S_A in all cases studied) predominate, but only tilted mesophases appear in series V and VI.

In Figure 3 the melting and clearing temperatures for series IV, V and VI are represented in terms of the length of the alkoxy chain.

Mesogenic behaviour similar to that described for the mono-imines can be observed, with melting points and clearing temperatures being lower for heterocyclic derivatives than for benzenic ones.

In the case of the heterocyclic compounds the melting points are lower for picolinic compounds (series V) when the chain is long and

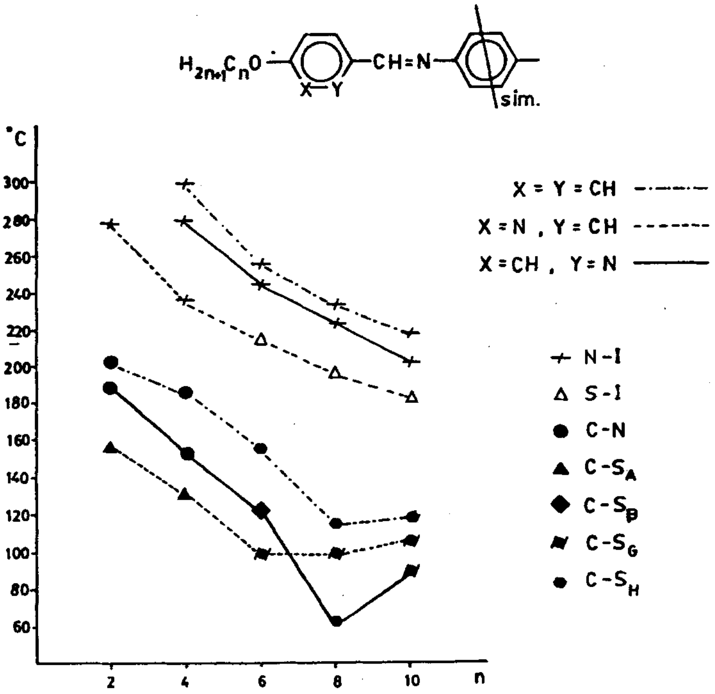


FIGURE 3 Melting and clearing temperatures as function of alkyl chain length, for compounds of series IV, V and VI.

higher when the chain is short. The picolinic derivatives were found to have higher clearing points than the nicotinic analogues in all the cases studied. The compounds with the widest mesophase ranges were those derived from picolinaldehyde (series V).

Comparative study of bis-(6-*n*-alkoxy-3-pyridylmethylene)hydrazines (series VII), bis-(5-*n*-alkoxy-2-pyridylmethylene)hydrazines (series VIII) and bis-(4-*n*-alkoxybenzylidene)hydrazines (series IX).

Table III shows the optical and thermal data for the compounds in series VII, VIII and IX.

As can be observed, the compounds in series VII, with the exception of $n = 4$, do not exhibit mesogenic properties whilst the compounds in series VIII and IX show enantiotropic mesomorphism (usually nematic) in all the cases studied.

In Figure 4 we can see that the melting points are lower for the

TABLE III

Optical and thermal data for azines (Series VII, VIII and IX)

n	Trans.	T[a](°C)	Trans.	T[a](°C)	Trans.	T[a](°C)
2	C—I	173.4	C—N	163.0	C—N	172.6
			N—I	210.6	N—I	198.2
4	C—I	136.4	C—N	110.6	C—N	146.3
	I—N[a]	124.0	N—I	175.2	N—I	168.7
6	C—I	131.6	C—N	103.9	C—N	126.8
			N—I	159.4	N—I	151.4
8	C—I	130.9	C—S_C	102.0	C—N	131.0
			S_C—N	109.2	N—I	140.8
			N—I	151.0		
10	C—I	121.7	C—S_C	96.2	C—S_C	123.2
			S_C—N	125.0	S_C—N	124.6
			N—I	143.1	N—I	135.5

[a] Monotropic transition

compounds in series VIII and are similar to those for compounds in the other two series (VII and IX).

On the other hand, the clearing points for the compounds in series VIII are higher than those in series IX, indicating much wider mesophase ranges for the compounds derived from the picolinaldehyde.

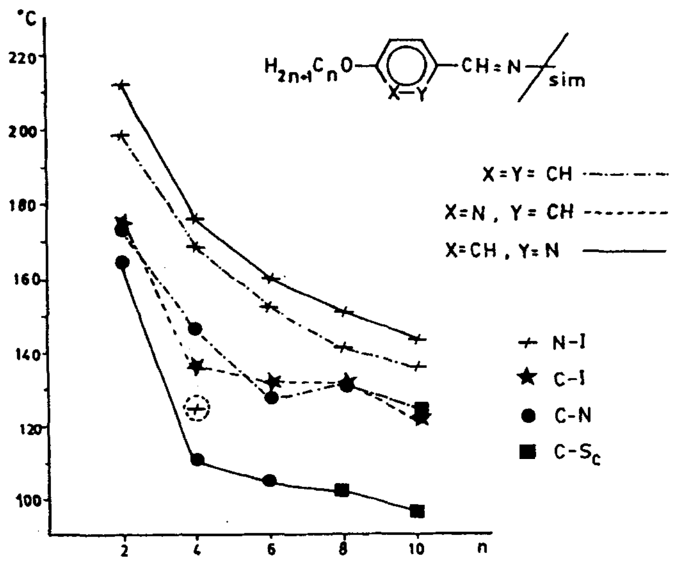


FIGURE 4 Melting and clearing temperatures as function of alkyl chain length, for compounds of series VII, VIII and IX.

RELATION BETWEEN STRUCTURE AND MESOGENIC ACTIVITY

X-ray studies of benzylideneaniline[9] show that the benzenic ring linked to the carbonyl group and the central core are practically coplanar, whereas the ring linked to the amine part is considerably twisted in relation to the central core, the torsion angle being 55.2°. X-ray studies of the anisaldazine[10] indicate that the benzenic rings make an angle with the central core of 4.2° and −3.3° respectively, which would suggest a practically planar structure of the molecules.

With these geometrical data in mind, we made spectroscopic studies of U.V. and ^1H NMR with one compound from each of the series studied in this paper (imines, diimines and azines) with a view to investigating the electronic properties of the molecules and to finding a relationship between structure and mesogenic activity. The most relevant data are gathered in Tables IV and V. Semiempirical calculations of molecular orbitals (MNDO) were also made.

For the sake of simplicity and in order to reduce the calculation time, it was found necessary to use the model molecules which are shown with their simplified nomenclature in Figure 5. The molecules were allowed to move freely in all cases until total optimization had been attained.

The most interesting data (extracted from the theoretical calculations) for the study of the mesogenic properties are set out in Table VI.

From the U.V. data in Table IV it can be deduced that with imines, as well as diimines the compounds derived from picolinaldehyde are those which have a greater extension of the conjugation if we observe

TABLE IV

U.V. data

Compound[a]	Solvent	$\lambda_1(\mathrm{lg}\ \epsilon)$	$\lambda_2(\mathrm{lg}\ \epsilon)$	$\lambda_3(\mathrm{lg}\ \epsilon)$
Im(Nic)C_8C_8	*n*-pentane	271.5(4.29)	330(4.26)	340(4.25)
Im(Pic)C_8C_8	*n*-pentane	288(4.27)	329(4.23)	338(4.24)
Im(Ben)C_8C_8	*n*-pentane	281(4.35)	330(4.27)	338(4.26)
Di(Nic)$_2$(C_8)$_2$	cyclohexane	277(4.41)	354(4.52)	
Di(Pic)$_2$(C_8)$_2$	cyclohexane	291(4.43)	356(4.50)	
Di(Ben)$_2$(C_8)$_2$	cyclohexane	285(4.46)	358(4.55)	
Az(Nic)$_2$(C_8)$_2$	*n*-pentane	317(4.72)	329(4.71)	342^{sh}
Az(Pic)$_2$(C_8)$_2$	*n*-pentane	315(4.69)	325(4.67)	339^{sh}
Az(Ben)$_2$(C_8)$_2$	*n*-pentane	320(4.60)	331(4.61)	346^{sh}

[a] Im = Imine, Di = Diimine, Az = Azine, Nic = Nicotinic, Pic = Picolinic, Ben = Benzenic, C_8 = Terminal chain C_8H_{17}.

TABLE V

NMR data

Compound[a]	δ_A[b]	δ_B[c]	δ_C[d]
Im(Nic)C_6C_8	8.36	4.29	7.15
Im(Pic)C_6C_8	8.53	4.02	7.24
Im(Ben)C_6C_8	8.34	3.95	7.16
Di(Nic)$_2$(C_{10})$_2$	8.43	4.35	7.23
Di(Pic)$_2$(C_{10})$_2$	8.58	4.03	7.31
Di(Ben)$_2$(C_{10})$_2$	8.42	4.01	7.23
Az(Nic)$_2$(C_6)$_2$	8.54	4.35	
Az(Pic)$_2$(C_6)$_2$	8.64	4.04	
Az(Ben)$_2$(C_6)$_2$	8.57	3.96	

[a] Im = imine, Di = diimine, Az = azine, Nic = nicotinic, Pic = picolinic, Ben = benzenic, C_x = terminal chain.

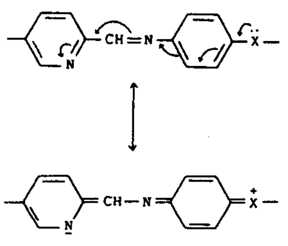
[b] δ_A corresponds to the proton or protons of the central core (CH=N imines, CH=N— —N=CH diimines and CH=N—N=CH azines).

[c] δ_B corresponds to the protons of the methylene group linked to the oxygen atom of the terminal chain.

[d] δ_C corresponds to the protons ortho of the aniline or *p*-phenylenediamine ring in imines and diimines.

the variation of the λ_1, which enables us to predict greater anisotropy of the polarizability for compounds of this kind (λ_2 and λ_3 in the case of the imine compounds and λ_2 in the diimines do not show an appreciable variation).

It should be remembered that the heteroatom in a pyridinic ring behaves in many ways like a nitro group in a benzenic ring. In picolinaldehyde derivatives, this behaviour makes an interaction by resonance possible between the nitrogen in the ring and the π-system of the central core given that both are in the *ortho* position.



On the other hand nicotinaldehyde derivatives, in which the heterocyclic nitrogen is in a *meta* position in relation to the central core, show a reduced extension of the conjugation, confirmed by the λ_1 value which is even lower than those of the benzenic derivatives.

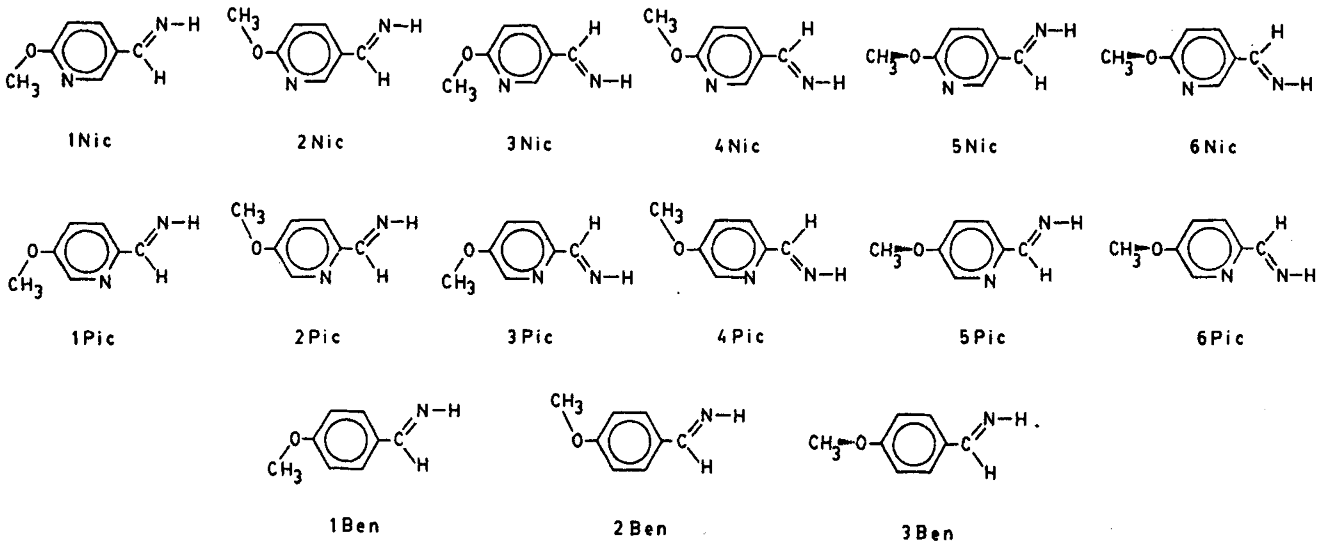


FIGURE 5 Model molecules and their simplified nomenclature used for the MNDO studies.

TABLE VI

MNDO Calculation data

Comp.	δ^{0} [a]	θ^{0} [b]	μ(D)[c]	$\mu_{\parallel}$(D)[c]	$\mu_{\perp}$(D)[c]	α^{0}_{μ} [d]	ΔH Kcal/mole[e]	%[f]	q_2-q_3[g]	q_3-q_4[g]	q_4-q_5[g]	q_5-q_6[g]	q_6-q_7[g]	q_7-q_2[g]
1Nic	177.0	−0.1	1.35	−0.19	1.33	97.7	3.44	22.06	−0.31	0.43	−0.56	0.41	−0.23	0.26
2Nic	174.8	180.4	1.16	0.10	1.15	85.1	7.91	0.01	−0.31	0.37	−0.50	0.46	0.30	0.28
3Nic	−3.0	0.3	2.06	−0.17	2.05	94.7	3.37	24.86	−0.34	0.47	−0.57	0.40	−0.20	0.24
4Nic	−0.8	179.7	4.52	−0.07	4.52	90.9	8.19	0.01	−0.34	0.40	−0.50	0.45	−0.26	0.25
5Nic	186.6	1.1	1.36	−0.19	1.34	98.0	3.41	23.20	−0.31	0.44	−0.57	0.40	−0.22	0.26
6Nic	−19.8	0.8	2.06	−0.22	2.05	96.1	3.29	29.90	−0.34	0.47	−0.57	0.47	−0.19	0.23
1Pic	142.1	−7.3	1.90	1.30	1.39	46.8	9.31	11.01	0.19	−0.17	−0.11	0.14	−0.04	−0.04
2Pic	173.0	177.2	2.02	1.79	0.94	27.6	9.24	12.40	0.20	−0.23	−0.06	0.20	−0.09	−0.02
3Pic	−121.8	26.6	1.56	1.11	1.10	44.6	9.08	16.25	0.21	−0.19	−0.09	0.12	0.01	−0.06
4Pic	−4.5	177.6	4.58	1.56	4.30	70.1	11.97	0.12	0.17	−0.19	−0.06	0.19	−0.04	−0.07
5Pic	185.9	99.5	1.40	0.86	1.10	52.1	9.11	15.14	0.25	−0.26	−0.01	0.09	0.01	−0.08
6Pic	−110.2	95.1	1.35	0.61	1.21	63.1	8.48	44.78	0.25	−0.26	0.01	0.07	0.04	−0.11
1Ben	171.4	−0.3	2.89	0.64	2.82	77.2	2.90	13.17	−0.13	0.16	−0.30	0.26	−0.14	0.15
2Ben	170.3	178.4	1.02	0.74	0.70	43.5	2.76	16.68	−0.12	0.10	−0.26	0.32	−0.20	0.16
3Ben	248.4	93.8	0.82	0.37	0.73	116.8	1.91	70.15	−0.06	0.06	−0.19	0.19	−0.07	0.07

[a] Twist angle between the aromatic ring plane and central core plane.

[b] Twist angle between the aromatic ring plane and terminal chain plane.

[c] Total dipolar moment (μ); Dipolar moment component parallel to the long axis of the molecule ($\mu_{\parallel}$); Dipolar moment component perpendicular to the long axis ($\mu_{\perp}$).

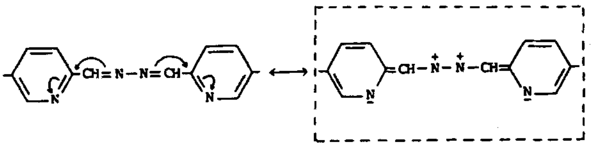
[d] Angle between the dipolar moment and the long axis of the molecule.

[e] Formation heat.

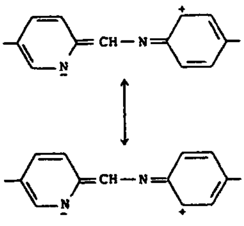
[f] Relative population of each conformer of a molecule.

[g] Difference of the net atomic charges between neighbouring atoms of the aromatic ring. Atoms in model molecules are numbered clockwise beginning with the carbon atom linked to the central core (q_z).

In the case of the azines, the λ_1 is lower for the picolinic derivatives than for the benzenic homologues, in all probability because the effects of the heteroatoms could be in opposition to each other thus producing a resonant form with a destabilizing influence on the conjugation between the two heterocyclic rings.



The ^{1}H NMR data (see Table V) confirm the greater degree of conjugation through the central core in the picolinic compounds, the protons in the aniline or *p*-phenylenediamine ring in the *ortho* position in relation to the central core being more deshielded in the picolinic imines and diimines than in the nicotinic and benzenic analogues. This could be attributed to the possible existence of the following resonant structures:



Mesomeric forms of this kind cannot exist in the case of nicotinic and benzenic compounds.

Looking at the data obtained from the theoretical study by semi-empirical MNDO calculations (Table VI) it is noticeble that this method tends to overestimate steric interactions, a fact already well known.

This is confirmed by the 1,3 methyl-hydrogen interaction in the methoxy group, where conformers of the nicotinic molecules with the methoxy group in the *cis* position in relation to the nitrogen atom of the heterocycle, are far more stable (ΔH_f approximately 3 Kcal/mole) than when the methoxy group is in the *trans* position (ΔH_f approximately 8 Kcal/mole), whereas in the picolinic and benzenic molecules the conformers are more stable when the methoxy group is out of plane with the aromatic ring by an appreciable twist angle.

This overestimation of steric interactions is what persuaded us to leave the geometrical characteristics obtained by the semi-empirical calculations out of the discussion. Instead, our attention will be centred on two fundamental aspects concerning the electronic characteristics of the molecules.

In the first place, the dipole moment of the nicotinic molecules is practically perpendicular to the principal axis (α_μ close to 90°), whereas in the picolinic and benzenic molecules the angle between the dipolar moment and the principal axis is smaller (see Table VI).

Secondly, if the values of the net charge differences of adjacent atoms in the nicotinic, picolinic and benzenic rings are compared, it can be seen that these differences are greater in the case of nicotinic rings, which seems to point to the existence of higher values for the partial dipoles in the nicotinic molecules.

These two factors, taken together, should cause an increase in intermolecular dipolar attractions (especially the lateral ones) in nicotinic derivatives and could account for their more marked tendency towards smectic mesomorphism. The fact that the nematic phase predominates in the picolinic and benzenic derivatives could be related to the higher value of the dipole moment component parallel to the principal axis in these compounds. In these two series a smectic C phase also appears for compounds with long chains, which is probably due to the fact that in the layered structure typical of smectic mesophases, the molecules are ordered in such a way that their dipoles are orientated in a direction likely to maximize dipole–dipole attractive forces.

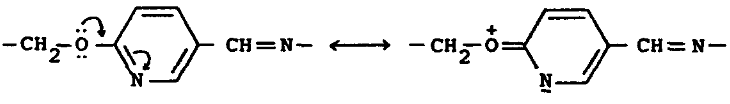
Consequently in molecules with the dipole moment perpendicular to the principal axis the existence of orthogonal smectic mesophases (S_A, S_B etc.) is possible, as can be observed in the case of the nicotinic derivatives (Tables I and II).

Molecules with the dipolar moment forming an oblique angle with the axis, generally form tilted smectic mesophases (S_C, S_G, S_H, etc.) as well as a nematic mesophase, as in the case of picolinic and benzenic derivatives (Tables I, II and III).

The fact that the melting temperatures for heterocyclic derivatives are lower than those for their carbocyclic analogues can be attributed either to the lower symmetry of the pyridine ring compared to benzene or to repulsions between electron pairs of nitrogen and/or oxygen atoms.

The lower melting points of the nicotinic derivatives compared to picolinic ones, for short chains, may be due to better interannular conjugation in the picolinic derivatives.

The higher melting points of the nicotinic derivatives for long chains may be related to the fact that when the chains are lengthened the melting points of picolinic derivatives decrease because of steric hindrance, while in the nicotinic derivatives the effect of steric hindrance is reduced because of the better extension of the electronic conjugation to the terminal chain, which increases intermolecular electrostatic attraction. This view appears to be supported by the higher values for δ_B (Table V) for the nicotinic derivatives, which points to the participation of the lone pairs of electrons on the oxygen atom in the π-system of heterocycle, with the consequent deshielding of the methylenic protons adjacent to the oxygen atom.



The fact that the clearing points of the heterocyclic derivatives (imines and diimines) are lower than those of their carbocyclic analogues can be attributed to the same factors which cause the melting points to be lower. The picolinic azines exhibit higher clearing points than the benzenic ones, possibly due to greater anisotropy of the polarizability of the former. The higher clearing points of the picolinic derivatives in comparison with nicotinic ones can also be put down to the greater anisotropy of the polarizability. In contrast to what happens with the melting points, the effect of the conjugation between the aromatic rings and the alkoxylic chain is reduced here because of the increased disorder of the chain, with the conjugation through the central core playing an important role.

The absence of mesogenic properties in the nicotinic azines is not easy to explain, although it could be caused by repulsion between lone pairs of electrons of heteroatoms in neighbouring molecules leading to a considerable decrease in these intermolecular interactions which cause mesomorphism to appear.

CONCLUSIONS

Generally speaking, heterocyclic derivatives show lower melting and clearing temperatures than their carbocyclic analogues. (The exception being the azines, where the picolinic compounds have higher clearing temperatures than the benzenic derivatives).

The imines and diimines derived from 6-*n*-alkoxynicotinaldehydes show a marked tendency towards smectic behaviour (especially of type A), whereas the 5-*n*-alkoxypicolinaldehyde and 4-*n*-alkoxybenzaldehyde derivatives show nematic behaviour and in the case of those with long chains form tilted smectic mesophases (S_C . . . etc.) also.

This is supported by the theoretical MNDO calculations from which it can be seen that the nicotinic derivatives have a dipolar moment approximately perpendicular to the molecular axis and have high partial dipoles. In the picolinic and benzenic derivatives the dipole moment lies at an oblique angle with the molecular axis.

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