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New Liquid Crystalline Pyridine Derivatives

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NEW LIQUID CRYSTALLINE PYRIDINE DERIVATIVES

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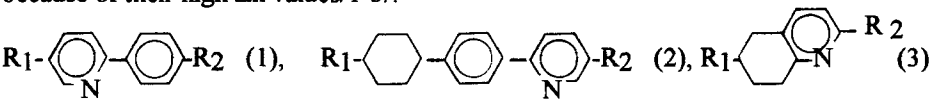
ABSTRACT

Several new classes of mesogenic heterocyclic liquid crystals with different terminal groups are presented. Their material properties are investigated and compared with those of 2,5-disubstituted pyridine derivatives. New compounds are found to exhibit broader temperature ranges and higher transition temperatures than their analogs. Data also reported on our structural investigations (X-ray scattering) which revealed the correlation with physico-chemical properties of new 2,6-disubstituted pyridine derivatives.

1.INTRODUCTION

The 2,5-disubstituted pyridine derivatives (1) and (2) respectively have been recognised for more than ten years as extremely useful materials for electro-optical display devices, principally because of the suitability of their mesomorphic ranges for the displays and because of their high Δn values/1-3/.



Since the temperature in which display devices now need to operate can extend to 150° C, there is a need to raise the upper temperature limit of commercial liquid crystalline mixtures without adversely influencing other properties.

With this aim we synthesized new series of 2,6-disubstituted pyridine derivatives (3) and compared their physico-chemical properties with those of compounds (1-2).

2.RESULTS AND DISCUSSION

Experimental

The 2,6-disubstituted pyridine derivatives were obtained using the following general synthetic scheme/4/. The compound's structures were confirmed by NMR analysis. The elemental analysis proved satisfactory for all derivatives.

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Mesomorphic and Physico-Chemical Properties

Procedures for measuring phase transitions, as well as dielectric properties of liquid crystalline compounds, are described in detail in Reference 5. Phase transitions for the synthesized and some well known compounds are given in Tables I - III. As follows from these Tables, replacement of the pyridine ring by the 5,6,7,8-tetrahydroquinoline fragment results in higher phase transition temperatures and broadering of the of the mesomorphic ranges. Table IV shows that the dielectric properties of compared compounds are similar with the exception of those for compounds 35 and 41 when the change of the sign of $\Delta\varepsilon$ caused by the conformational changes occurs.

X-ray diffraction studies

The study of the nematic phase by small angle X-ray scattering yields the information about the characteristic sizes of the structures at the molecular and supermolecular levels/6-7/, which significantly influence their physico-chemical properties/7-8/.

X-ray scattering was investigated on an automatic ADP-1 X-ray diffractometer by the method described previously/7/, one or two peaks being observed. From their location and shape, the layered structure periods d and correlation length ξ were calculated. The X-ray diffraction parameters obtained are presented in Table V (subscripts 1 and 2 refer respectively to the monomeric and dimeric waves/7/). The correlation lengths of different compounds were compared at the reduced temperatures (the period of the layered structure is almost independent of the temperature). The upper part of Table V refers to highly polar liquid crystals - cyanoderivatives whose characteristic feature is dimerization processes/9/, as a result of which fluctuations of the local smectic order in the nematic phase may be observed in the monomeric (not always) and dimeric density waves.

Analysis of the periods of the layered structure d_1 and d_2 (Table V) shows that the monomeric density wave d_1 is fully correlated with the geometrical length of the molecule. Comparison of the values of d_1 for compounds 43 and 45 shows that the increase in the length of the molecule caused by replacing the pyridine ring by the 5,6,7,8-tetrahydroquinoline fragment is accompanied by an increase in the period d_1. The period d_2 reflects the characteristic size of the dimers of the compounds under consideration. It can be seen from the Table V, the replacement of the pyridine ring by the 5,6,7,8-tetrahydroquinoline fragment leads to the greater relative increase in the length of the single molecule d_1 than for dimer d_2, which indicates an appreciable overlap of the rigid molecular sceletons in forming of the dimer.

Table I. Phase Transition Points (°C)

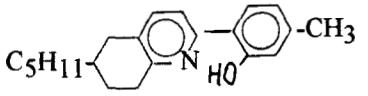
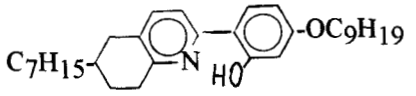
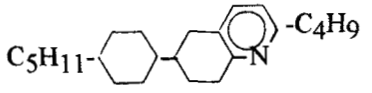
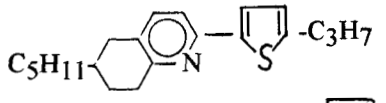
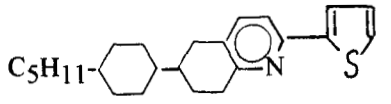
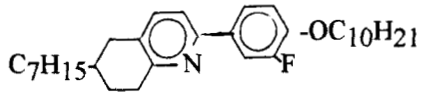
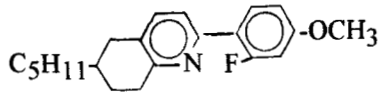
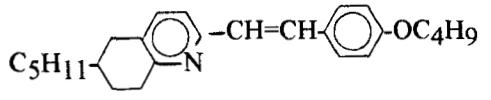
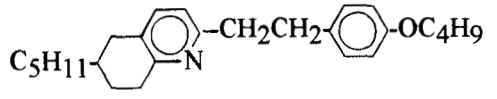
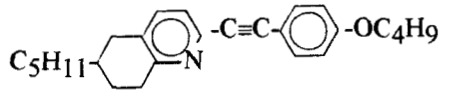
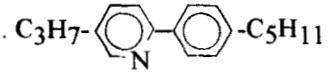
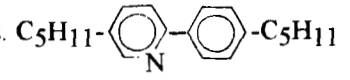
No	Chemical structure	Tc-s, Tc-n, Tc-i	Ts-n, Ts-i	Tn-i
1	2	3	4	5
1.		88.0	120.0	136.0
2.		73.0	165.0	
3.		33.0	(20.0)	
4.		34.0		
5.		149.0		
6.		49.0	80.0	
7.		65.0		(55.0)
8.		120.0		138.5
9.		42.6		(29.2)
10.		110.5		124.0
11.		20.0	(5.0)	
12.		33.0	(30.7)	

Table I (Continued)

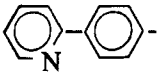
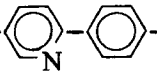
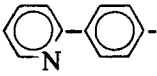
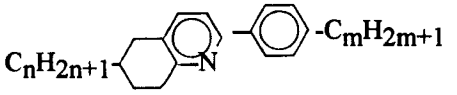
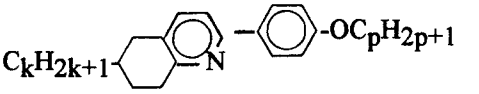
1	2	3	4	5
13.	C_7H_{15}-  -C_5H_{11}	31.0	46.5	
14.	C_3H_7-  -OC_6H_{13}	50.0	72.0	
15.	C_5H_{11}-  -OC_5H_{11}	55.0		62.0

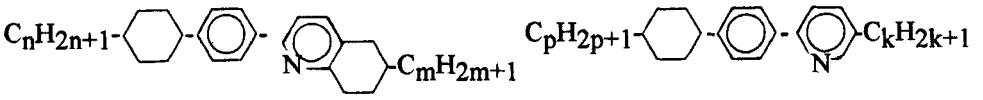
Table II. Phase Transition Points (°C)





No	n	m	Tc-n, c-s	Ts-n, s-i	Tn-i	No	k	p	Tc-n, c-s	Ts-n, s-i	Tn-i
16	5	7	37.0	76.0		26	1	10	73.0		
17	3	3	63.0		(59)	27	3	5	59.0		90.0
18	3	5	55.4		66.0	28	3	6	82.0		95.0
19	3	2	70.0		(41)	29	5	5	87.0		99.0
20	5	5	43.0	72.7	73.6	30	6	5	85.0	87.0	99.0
21	7	7	22.0	84.0		31	5	6	66.0	84.0	102.4
22	5	9	21.0	73.5		32	7	3	93.0		(92)
23	7	9	33.0	83.0		33	7	10	85.0	102.0	
24	7	5	24.0	82.0							
25	5	1	81.0	(74.6)							

Table III. Phase Transition Points (°C)



No	n	m	Tc-s, c-n	Ts-n	Tn-i	No	p	k	Tc-s	Ts-n	Tn-i
34	3	3	95.0	108.0	220.0						
35	3	4	82.0	100.0	208.0						
36	3	5	96.0	116.0	209.0	40	3	5	47.0	95.0	176.5
37	2	3	86.0	92.0	201.0	41	2	3	51.0	94.0	157.8
38	5	1	88.0		181.0						
39	5	3	90.0	132.0	196.0	42	5	3	37.0	93.5	174.0

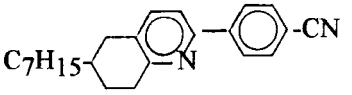
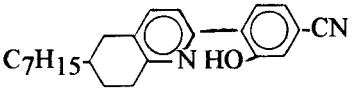
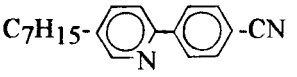
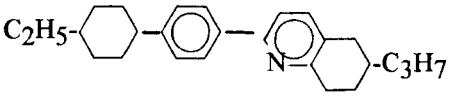
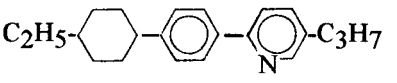
Table IV. Dielectric Properties

No	ε	ε	Δε	ΔT, °C
18	3.98	3.17	+0.21	5
18	3.46	3.16	+0.30	10
27	3.52	3.53	-0.01	5
27	3.48	3.55	-0.07	10
28	3.34	3.36	-0.02	5
28	3.51	3.38	-0.07	10
31	3.19	3.23	-0.04	5
31	3.18	3.25	-0.07	10
15	3.90*	4.55*	-0.65*	
8	3.41	3.40	+0.01	5
8	3.43	3.41	+0.02	10
41	3.39	3.62	-0.23	60
35	3.14	2.76	+0.38	100
39	3.00	2.70	+0.30	70

ΔT = Tn-i - Tmeas.

* $\tau = 0.95 = T/Tn\text{-}i, K$

Table V. X-ray Structural Parameters Of The Nematic Phase Of Liquid Crystals

No	Material	d_1, Å	d_2, Å	ξ_1, Å	ξ_2, Å	ΔT, °C
43		20.2	29.3	33	60	10
44			28.8		122	30
45		18.0	27.3	37	83	10 /7/
37		21.6		70		40
41		19.5		48		40 /10/

The introduction OH-group in α-position of phenyl ring leads to the diappearance of the local smectic fluctuations on the monomeric density wave (compounds 43 and 44).
For weakly polar compounds, X-ray diffraction parameters are quoted in the lower part of Table V (compounds 37 and 41). As before reported in /10/, only the monomeric density wave is observed for them with a characteristic period d_1. It can be seen that d_1 for compound 37 is the same. Their higher value of d_1 reflects the increasing in the molecular length.

3.CONCLUSION

The results obtained permit a soundly choice of particular synthesized compounds as components of a liquid crystalline material for display applications on the basis of their phase transition temperatures, the correlation length ξ characterizing the smectogenic nature related to the viscoelastic properties/10/, the period d_2 related to the ratio of the elastic constants K_3/K_1/7/.

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