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Synthesis and Properties of 5-Alkyl-2-(4-Cyanophenyl)Pyridines†

M. F. GREBYONKIN, V. F. PETROV, V. V. BELYAEV, A. I. PAVLUCHENKO, N. I. SMIRNOVA, E. I. KOVSHEV, V. V. TITOV and A. V. IVASHCHENKO

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The synthesis, physico-chemical and electro-optical properties of new nematic liquid crystal materials with a positive dielectric anisotropy—the 5-alkyl-2-(4-cyanophenyl)-pyridines—are reported. The transition temperatures, transition enthalpies, dielectric, optical, and visco-elastic properties, and also the threshold voltages and response times of the twist-effect have been measured for 2–7 homologues and binary mixtures of 5-alkyl-2-(4-cyanophenyl)pyridines (PR) containing the pentyl and heptyl components in the molar proportion 40:60. The results obtained are compared with the properties of 4-cyano-4′-n-alkyl-biphenyls (CB) and 5-n-alkyl-2-(4-cyanophenyl)pyrimidines (PY).

INTRODUCTION

Modern liquid crystalline materials (LCM) are multicomponent mixtures of liquid crystal compounds belonging to different chemical classes. The LCM for the twist effect contain cyano-derivatives that assure a positive dielectric anisotropy of the mixture.

A great number of liquid crystal cyano-derivatives of different chemical classes are known.[1] Among them the 4-cyano-4′-n-alkoxybiphenyls, 4-cyano-4′-n-alkylbiphenyls,[2] 5-n-alkyl-2-(4-cyanophenyl)pyrimidines[3] and *trans*-4-alkyl-(4-cyanophenyl)-cyclohexanes (PCH)[4] are well known and commonly used. Physico-chemical and electro-optical properties of these compounds are presented in particular in refs. 5–15. The choice of suitable cyano-

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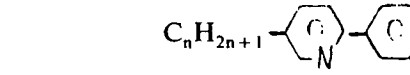
derivatives depends on the properties of the LCM needed. CB and PY materials are used in the low threshold voltage LCM and in LCM for multiplex drive displays.[13,14] PCH materials are used for LCM with a low viscosity and a wide temperature range.[15]

Because of the increasing diversification in applications of LCM, it is necessary to have other LCM with new properties or new combinations of properties. For this purpose a search for new liquid crystal cyano-derivatives is taking place.

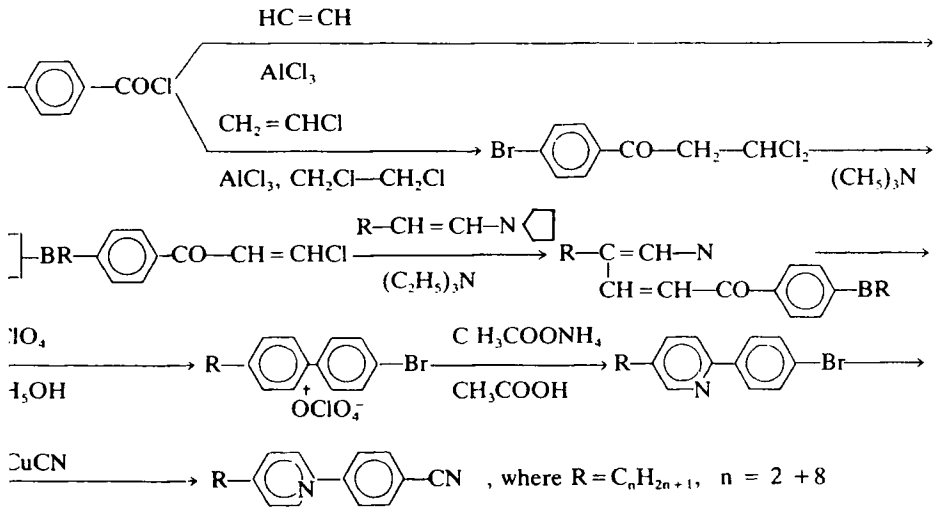
Previously[16] the cyano-derivatives—the 5-alkyl-(4-cyanophenyl)-pyridines (PR) were reported by some of us. None we describe the synthesis and the physico-chemical and electro-optical properties of these compounds.

EXPERIMENTAL

5-Alkyl-2-(4-cyanophenyl)pyridines of formula (1)



have been prepared according to the following scheme:



p-Bromophenyl β-chlorovinyl ketone is obtained[17] from *p*-bromobenzoyl chloride in 70% yield, or without separation of the intermediate product,[18] in 82% yield. *N*-1-Alkenylpiperidines are obtained from aliphatic aldehydes and piperidine on addition of 1 mole of aldehyde to a stirred mixture of 2,2 mole of piperidine and 1 mole of anhydrous potassium carbonate at 5°C followed by distillation.[19] 5-Alkyl-2-(4-bromophenyl)pyridines are obtained according to the well known[20] method of synthesis of 2,5-disubstituted pyridines that consists of the interaction of *N*-1-alkenylpiperidines with *p*-bromophenyl β-chlorovinyl ketone in the presence of triethylamine in hexane. The reaction products, 4-piperidinyl-3-alkyl-1-*p*-bromobenzoyl-1,3-butadienes are washed with cooled hexane and water, and then cyclised without purification to yield 5-alkyl-2-*p*-bromophenylpyrilium perchlorates using $HClO_4$(54%): EtOH(2:1) at ambient temperature (1,5 litres of mixture for 1 mole).

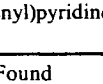
The pyrilium salt precipitated (yield 60–70%) is washed with water, dried and transformed into the 5-alkyl-2-(4-bromophenyl)-pyridine by boiling with ammonium acetate solution.[21]

The reaction product is separated, distilled *in vacuo* and recrystallized from acetone.

Transition temperatures, yields and elemental analysis data for 5-alkyl-2-(4-bromophenyl)pyridines are presented in Table I.

5-Alkyl-2-(4-cyanophenyl)pyridines are obtained by one hour heating of 1 mole of the 5-alkyl-2-(4-bromophenyl)pyridine with 1.2 mole of cuprous cyanide at 210–250°C. The product of the reaction is distilled *in vacuo*. The yield of PR is 90–95%. The product is recrystallized from ethanol and hexane. Transition temperatures, melting

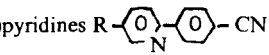
TABLE I

5-Alkyl-2-(4-bromophenyl)pyridines R-  -Br

R	$T_{m.}$, °C	$T_{cl.}$, °C	Yield %	Found C	Found H	Found N	Formula	Calculated C	Calculated H	Calculated N
C_2H_5	83	—	80	59.41	4.59	5.60	$C_{13}H_{12}BrN$	59.56	4.61	5.34
C_3H_7	93.5	—	75	60.75	5.01	5.11	$C_{14}H_{14}BrN$	60.88	5.10	5.07
C_4H_9	76	65.5*	72	61.90	5.40	4.63	$C_{15}H_{16}BrN$	62.08	5.55	4.82
C_5H_{11}	84	66*	77	63.12	5.74	4.56	$C_{16}H_{18}BrN$	63.16	5.96	4.60
C_6H_{13}	66	70	75	63.88	6.48	4.51	$C_{17}H_{20}BrN$	64.15	6.33	4.40
C_7H_{15}	73	72*	74	65.11	6.48	4.28	$C_{18}H_{22}BrN$	65.06	6.67	4.21
C_8H_{17}	49	70	78	66.19	6.96	4.01	$C_{19}H_{24}BrN$	65.89	6.98	4.04

*Monotropic transition

TABLE II

5-Alkyl-2-(4-cyanophenyl)pyridines R-  -CN

R	$T_{m.}$, °C	T_{cl}, °C	Yield %	Found C	Found H	Found N	Formula	Calculated C	Calculated H	Calculated N	ΔH_m kjoules/mole
C_2H_5	69.3	35.7*	92	80.93	5.72	13.38	$C_{14}H_{12}N_2$	80.74	5.80	13.45	17.05
C_3H_7	43.4	43.8	95	81.15	6.41	12.58	$C_{15}H_{14}N_2$	81.04	6.34	12.60	16.71
C_4H_9	32.3	26.5*	93	81.54	6.69	11.70	$C_{16}H_{16}N_2$	81.32	6.82	11.82	22.23
C_5H_{11}	33.6	43.5	90	81.90	6.73	11.34	$C_{17}H_{18}N_2$	81.56	7.24	11.18	20.92
C_6H_{13}	29.0	32.5	95	81.66	7.57	10.47	$C_{18}H_{20}N_2$	81.77	7.26	10.59	25.73
C_7H_{15}	30.9	47.0	95	82.27	7.74	9.94	$C_{19}H_{22}N_2$	81.97	7.96	10.06	25.50
C_8H_{17}	39.5	43.0	90	82.08	8.36	9.48	$C_{20}H_{24}N_2$	82.14	8.27	9.57	

*Monotropic transition

enthalpies determined by the DSC method, and the elemental analysis data for the PR materials are presented in Table II. The structure of the product obtained was proved using IR, UV and PMR spectroscopy.

A comparison of the PR, PY, and CB materials shows that the clearing points (T_{cl}) of PR are higher than those of CB, but are less than T_{cl} of PY. The compounds PR and CB have comparable nematic ranges that are considerably higher than those of the compounds PY. Physico-chemical and electro-optical properties of individual compounds PR, as well as of their mixtures, have been studied. The corresponding parameters of CB mixtures (BDH, UK) and PY mixtures (Hoffmann-LaRoche, Switzerland) have been also investigated to obtain comparitive data.

The dielectric constants of LCM are investigated[22] by measuring the capacity of a flat capacitor filled with a liquid crystal. The orientation of the liquid crystal layer is achieved by a magnetic field. The constant K_{11} is obtained from the Fréedericksz transition threshold on reorientation of the planar layer of the LCM in the sandwich cell by an electric field.[23,24] The measurement of the complete phase delay on the reorientation of the LCM layer from the planar orientation to the field-induced homeotropic alignment allows one to determine the value of the birefrigence Δn. A coefficient of the rotational viscosity γ_1 is obtained from measurement of the relaxation time of the phase delay of the planar LCM layer when it is reoriented by the external electric field.[24] The activation energy is estimated from the measurement of the temperature dependence of γ_1, using the relationship $\gamma_1 = SA \exp(E/K_B T)$ where K_B = Boltzmann constant, S

= order parameter, A = pre-exponential factor. The ratio of the elastic constants K_{33}/K_{11} is obtained from the optical properties of the cell with homeoplanar surface orientation.[25]

A kinematic viscosity ν is measured using an Ostvald-type viscometer.

Electro-optical properties of the twist-effect were obtained using an electro-optical cell of 12 to 13 μ thickness, with later recalculation of the response times τ to a thickness $d = 10$ μ, according to $\tau \sim d^2$. A polymer coat on the electrodes rubbed in one definite direction gives the planar orientation of the LCM layer. As a light source, a helium-neon laser was used (normal incidence of the laser beam to the cell, crossed polarizers, the vector of polarization of the incident light being perpendicular to the director of the liquid crystal at the nearest electrode). The threshold voltage of the twist-effect (U_{90}) corresponds to a light transmission level of the cell of 0.9 (initial transmission is equal to 1.0). The saturation voltage of the twist-effect (U_{10}) corresponds to a transmission level equal to 0.1. The time off of the twist-effect (τ_{off}) is defined as the time from the moment when the voltage V applied to cell is switched off to the moment of achievement of the transmission level of 0.9. The time on ($\tau_{on'}$) (with delay) is defined as the time from the moment when the voltage is applied to the cell to the moment of achievement of the transmission level of 0.1; the time on (τ_{on^2}) (without delay) is defined as the time from the moment of achievement of the transmission level of 0.9 to the moment of achievement of the transmission level of 0.1 when the voltage is applied to the cell. The cell is thermostated with an accuracy of ± 0.2 °C.

DISCUSSION

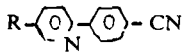
Direct measurement of the anisotropic properties was possible only for those PR homologues that have a broad temperature range of the nematic mesophase (C_5, C_7). However the estimation of values for all homologues is very important from the point of view of their practical use as LCM. Therefore the following procedure has been used. If it was possible, direct measurements for some homologues (C_5, C_7 and C_6) have been made taking advantage of supercooling. In addition, binary mixtures of all homologues with 4-cyano-4′-n-pentylbiphenyl (1:1 mole) have been made. These mixtures have a sufficiently broad nematic temperature range for successful measurements of the properties. The values of the parameters for all PR homologues were

calculated from those of binary mixtures and pure CB5 using the additive rule.† The results obtained are presented in Tables III and IV, where results measured directly have the index meas. and those calculated have the index calc. Some values are given at +25°C and others at a reduced temperature $\tau = 0.95$ ($\tau = T/T_{cl}$). A good correspondence between the values of the physico-chemical and electro-optical parameters measured and calculated has been found for the C_5, C_6, and C_7 homologues. This fact gives us a basis for analyzing the properties of all the PR homologues with a sufficient degree of reliability. The odd-even alternation for all parameters is observed, and the changes in the parameters are practically the same as for CB[13,27,28] and PCH materials.[26,29] The clearing temperatures for odd homologues are considerably higher than those for even members. For even homologues the values of $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ are greater. The dependence of $\Delta\epsilon = \epsilon_{\parallel} - \epsilon_{\perp}$ on alkyl chain length is nevertheless practically monotonous; the $\Delta\epsilon$ value decreases with increasing of n. The birefringence Δn at the same reduced temperature is less for even homologues; this corresponds to the odd-even alternation of clearing temperature due to different contributions of the dispersion interactions parallel and perpendicular to the molecular axis.[30] The elastic constants K_{11} are greater for odd members of the homologues series; this leads to considerably lower values of the threshold voltage and saturation voltage for odd members than for even members (Table IV). The rotational viscosity coefficient γ_1 is greater for even members than for odd members; this corresponds to data on γ_1 for CB[31] and data on dynamic viscosity for PCH.[26] This leads to greater relaxation times of the twist-effect for even members in comparison with odd members (Table IV). To describe the temperature dependence of the rotational viscosity the approximation mentioned earlier was used because it describes the experimental data better than the approximation of Diogo and Martins.[32,33] According to ref. 32, the activation energy should be proportional to the clearing temperature T_{cl}, i.e., the activation energy for odd homologues should be less than for even homologues, as is observed for CB materials.[31] However, for PR materials, the reverse situation is observed—the activation energy is greater for even homologues. Possibly in this case the suggestion of

†Binary mixtures of all the PR homologues with PR5 would be preferable for calculation of the parameters for the various homologues, as has been done for the PCH series.[26] However, the additive-rule is well fulfilled for mixtures of PR and CB, apparently because of the comparable molecular structures of the components. At the same time, the additive rule for the clearing temperatures of binary mixtures of the cyano-derivatives of the different chemical classes is not fulfilled in many cases.[12]

TABLE III

Properties of the 5-alkyl-2-(4-cyanophenyl)pyridines

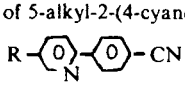


R	$T_{cl.}$, °C calc.	$\epsilon_{\parallel}$, meas.	τ = 0.95 calc.	$\epsilon_{\perp}$, meas.	τ = 0.95 calc.	$\Delta\epsilon$, meas.	τ = 0.95 calc.	γ_1 Poise 25°C	τ = 0.95	E/K_B 10^3K	$K_{11}.10^7$ dyne 25°C	τ = 0.95	Δn τ = 0.95
C_2H_5	35.7		38.2		13.3		24.9						
C_3H_7	41.0		35.0		9.7		25.3						
C_4H_9	26.5*		34.5		13.1		21.4						
C_5H_{11}	42.0	28.7	28.5	10.9	10.7	17.8	17.8	1.28	1.03	3.50	6.75	6.54	0.176
C_6H_{13}	30.3	27.2	26.6	12.0	11.3	15.2	15.3	0.98	2.34	5.75	3.75	5.30	0.163
C_7H_{15}	45.7	25.0	25.0	9.2	10.0	15.8	15.0	2.15	1.47	4.60	8.95	7.50	0.172

*Monotropic transition

TABLE IV

Electrooptical data of 5-alkyl-2-(4-cyanophenyl)-pyridines



R	U_{90}, V, 25°C		U_{10}, V, 25°C		$\tau_{off.}$, 25°C, ms		U, V
	meas.	calc.	meas.	calc.	meas.	calc.	
C_2H_5		0.56		0.84		68	2.5
C_3H_7		0.86		1.05		59	2.5
C_4H_9		0.62		1.00		153	2.5
C_5H_{11}	0.96	0.93	1.52	1.54	91	90	2.5
C_6H_{13}		0.67		1.05		173	2.5
C_7H_{13}	1.23	1.20	1.67	1.67	106	110	2.5

proportionality of the activation energy to the enthalpy of transition N → I, but not to the temperature of transition T_{cl} is right. In fact, in the PR series, the transition enthalpy for the 6th member is greater than for the 5th and 7th members; this is in accordance with the change of the activation energy E in the homologues series.

Thus when it is necessary to obtain a LCM with a high value of T_{cl} and fast response times, odd members of the homologous series should be preferably chosen, but in the case of the necessity for a LCM with low driving voltages, the even members should be preferred. Naturally the dependence of parameters on over-all alkyl chain length should be taken into consideration. For example the threshold voltage and response times *increase* with lengthening of the alkyl chain.

The comparative characteristics of PR, CB and PY materials

The properties of the cyano-derivatives of the different chemical classes are conveniently compared using binary mixtures of 5th and 7th homologues (40:60 mole) of every class. In this case a sufficient width of nematic range of the mixtures as well as a definite molecular structure are assured.

The properties of the cyano-derivatives of different chemical classes can be found elsewhere.[5-12] The physico-chemical and electro-optical properties of binary mixtures PR and for comparison of CB and PY materials measured under the same conditions are presented in Tables V and VI. It is easy to see that in many cases the properties of PR are intermediate between those of CB and PY, because one can consider the molecular structure of PR as intermediate between the molecular structures of CB and PY. PR derivatives have higher values

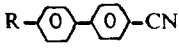
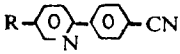
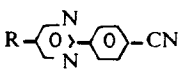
TABLE V

Properties of biphenyl, pyridine and pyrimidine cyano-derivatives.

LC	$T_{cl.}$, °C	γ_1, Poise 25°C	E/K_B 10^3K	$K_{11}.10^7$ dyne 25°C $\tau = 0.95$	$\tau = 0.95$	K_{33}/K_{11} $\tau = 0.95$	$\epsilon_\perp$ $\tau = 0.95$	$\Delta\epsilon$ $\tau = 0.95$	$\Delta\epsilon/\epsilon_\perp$ $\tau = 0.95$	Δn $\tau = 0.95$
R-⟨0⟩-⟨0⟩-CN	39.0	1.10	4.12	7.65	8.01	1.37	5.50	+ 11.7	2.08	0.184
R-⟨0⟩(N)-⟨0⟩-CN	44.2	1.84	4.00	7.98	6.90	1.25	10.7	+ 16.6	1.55	0.175
R-⟨0⟩(N,N)-⟨0⟩-CN	51.2	1.90	3.78	10.24	8.03	1.06	8.65	+ 19.6	2.26	0.174

TABLE VI

Electro-optical data for biphenyl, pyridine, and pyrimidine cyano-derivatives

LC	U_{90}, V	U_{10}, V	U, V	τ_{on^1}, ms	τ_{off}, ms	τ_{on^2}, ms	T_{meas}, °C
	1.30	1.78	3/2.5	85/115	70/65	20/30	25
	1.08	1.54	3/2.5	75/130	105/95	20/40	25
	1.07	1.48	3/2.5	70/110	90/80	20/35	25

of their clearing temperatures and dielectric anisotropy and lower values of their threshold voltage for the twist-effect than CB. The viscosity, threshold voltage, and response times of PR are comparable with the same properties of PY, but PR derivatives have broader nematic ranges; this is very useful when LCM with a broad range nematic phase are needed. The experiments show that PR derivatives can be successfully used to create LCM with a high level of multiplexibility.

Examples of LCM containing PR derivatives as components

Some LCM have been developed on the basis of the 5-alkyl-2-(4-cyanophenyl)pyridines. The composition and properties of the LCM are presented in Table VII. PR materials give the possibility of creating LCM (A) with low threshold voltage and wide temperature range for static driving, and LCM (B, C) with comparatively low threshold voltage for multiplex driving. For comparison, the properties of E7 (BDH, UK) are presented in this Table.

CONCLUSION

New liquid crystalline pyridine derivatives—the 5-alkyl-2-(4-cyanophenyl)pyridines—have been synthesized and the physicochemical and electro-optical properties of the C_2 to C_7 homologues have been studied. The properties of these PR materials are compared with those of corresponding derivatives of pyrimidine and biphenyl. PR have higher values of T_{cl} and dielectric anisotropy than CB, and broader nematic ranges than PY. It has been shown that PR may be successfully used in LCM for low voltage electro-optical devices both with static and multiplex driving.

TABLE VII

Properties of liquid crystal materials

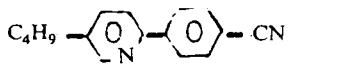
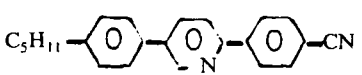
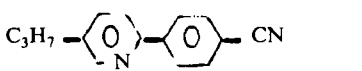
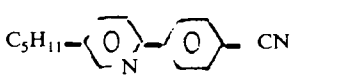
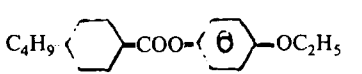
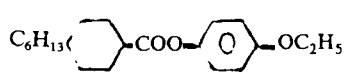
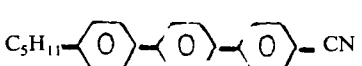
LCM	Composition	weight %	T_m, °C	T_{cl}, °C	meas., °C	U_{90}, V	U_{10}, V	U V	τ_{on1}, ms	τ_{off}, ms	τ_{on2}, ms	υ20°C cSt
A		34.6	− 7	78	+ 25	1.18	1.65	3	135	120	30	78
		40.17										
		25.23			0			3	925	770	615	
B		25	− 10	67	+ 25	1.34	1.81	3	110	68	30	66
		34										
		18			0			3	645	400	185	
		12										
		11										

TABLE VII

(continued)

LCM	Composition	weight %	T_m, °C	T_{cl}, °C	$_{meas.}$, °C	U_{90}, V	U_{10}, V	U V	τ_{on1}, ms	τ_{off}, ms	τ_{on2}, ms	υ20°C cSt
	C_3H_7–Pyr–Ph–CN	20	− 10	67	+ 25	1.45	1.85	3	125	60	35	58
	C_5H_{11}–Pyr–Ph–CN	30										
C	C_6H_{13}–Ph–COO–Ph–OC_2H_5	15			0			3	680	310	185	
	C_5H_{11}–Ph–Pyr–Ph–CN	10										
	C_4H_9–Ph–COO–Ph–OC_2H_5	25										
E7			− 10	60	+ 25	1.34	2.20	3	135	70	30	44

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