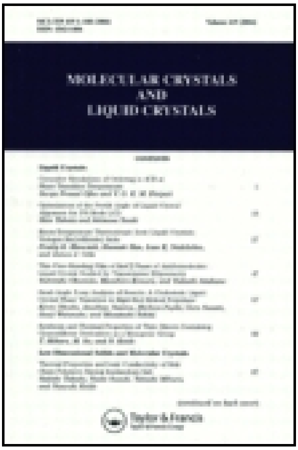

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Liquid Crystalline 4-Alkylamino-4'-Cyanobiphenyls

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Liquid Crystalline 4-Alkylamino-4′-cyanobiphenyls

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A number of mesomorphic 4-alkylamino-4′-cyanobiphenyls were synthesized. These compounds melt at higher temperatures and form nematic and smectic A state with higher thermal stability than that of analogous 4-alkoxy-4′-cyanobiphenyls. 4-Octylamino-4′-cyanobiphenyl is characterized by a significantly higher dielectric anisotropy in comparison with its 4-octyloxy analogue, in the nematic state, but not in the smectic state. Density data and refractometric indices of several 4 substituted 4′-cyanobiphenyls are presented; refractometric data confirm higher polarizability of 4-alkylamino-4′-cyanobiphenyls as compared with their 4-alkoxy analogues.

A number of mesomorphic 4-alkylamino-4′-cyanobiphenyls were synthesized and their transition temperatures were determined. Optical and dielectric properties of some compounds were investigated.

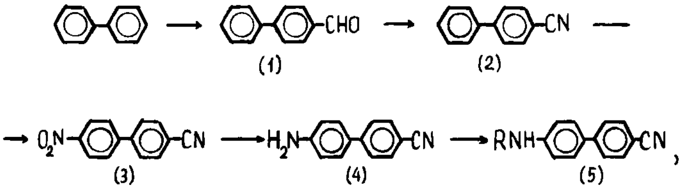
INTRODUCTION

It is known from the literature[1-4] that the introduction of alkylamino group into a molecule of polar liquid crystal instead of alkoxy group increases the value of positive dielectric anisotropy, however little numerical data about the properties of such compounds are available.

We have found that 4-alkylamino-4′-cyanobiphenyls form mesomorphic state with higher thermal stability than that of analogous 4-alkoxy-4′-cyanobiphenyls.[5] In order to compare the influence of alkylamino groups with that of alkoxy groups on physical properties of polar liquid crystals, the dielectric, optical anisotropy and viscosity of some compounds were measured.

RESULTS AND DISCUSSION

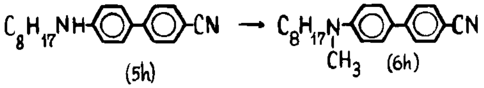
The synthesis of 4-monoalkylamino-4′-cyanobiphenyls was performed according to the scheme:



where $R = C_I - C_{IO}$ alkyl group.

The 4-formylbiphenyl (*I*) was obtained by an action of *I*,I-dichloromethylbutylether on biphenyl in the presence of titanium tetrachloride[6] and converted into 4-cyanobiphenyl (2) by the action of hydroxylamine hydrochloride in pyridine in the presence of acetic anhydride.[7] The nitration of (2) was performed in acetic anhydride by the action of fuming nitric acid or the action of a mixture of nitric and sulphur acids. In both cases the 4-nitro-4′-cyanobiphenyl (3) was obtained with only 40–43% yield, the by-product of this reaction step being 2-nitro-4′-cyanobiphenyl, which after hydrolysis yielded 2-nitro-biphenyl-4′-carboxylic acid, described earlier.[8] The reduction of (3) was carried out in a usual way (stannic chloride in the mixture of hydrogen hydrochloride and acetic acid or iron powder in hydrogen hydrochloride); the 4-amino-4′-cyanobiphenyl (4) was isolated with 70% yield. The alkylation reaction was carried out in boiling iso-propyl alcohol with alkyl bromides in the presence of sodium iso-propylate. Both initial compound (4) and products of dialkylation were always present in the reaction mixture, so the desired 4-alkylamino-4′-cyanobiphenyls (5) could be isolated and purified only by means of column chromatography on alumina.

4-(N-Octyl-N-methylamino)-4′-cyanobiphenyl (6h) was obtained by methylation of 4-octylamino-4′-cyanobiphenyl (5h):



The microanalysis data and transition temperatures of obtained compounds are presented in Table I.

As is seen from Table I, 4-alkylamino-4′-cyanobiphenyls exhibit higher temperatures of transition to the isotropic state than the corresponding 4-alkoxy-4′-cyanobiphenyls[5] and considerably higher melting points; as a result, most of obtained compounds are only monotropic ones. A smectic A

TABLE I

4-Alkylamino-4'-cyanobiphenyls, $C_nH_{2n+1}—N(R)—C_6H_4—C_6H_4—CN$

		Found, %			Calculated, %			Transition temp., °C			
Nr.	*nR*	C	H	N	C	H	N	C	Sm	N	I
5*a*	1 H	80.6	5.9	13.5	80.7	5.8	13.4	·196.5	—	—	·
5*b*	2 H	81.1	6.3	12.5	81.0	6.3	12.6	·165.0	—	—	·
5*c*	3 H	79.4	6.6	12.1	81.3	6.8	11.9	·105.5	—	(·100.5)	·
5*d*	4 H	81.1	6.7	11.0	81.6	7.2	11.2	·113.5	—	(·98.5)	·
5*e*	5 H	81.6	7.4	10.5	81.8	7.6	10.6	·86.5 81.5[a]	—	·89.5	·
5*f*	6 H	81.3	7.9	10.0	82.0	7.9	10.0	·105.5	—	(·96.0)	·
5*g*	7 H	81.7	8.1	9.6	82.2	8.2	9.6	·92.5	—	(·79.5)	·
5*h*	8 H	82.4	8.6	9.2	82.3	8.6	9.1	·68.0	·82.0	·92.0	·
5*i*	9 H	82.4	8.8	8.8	82.5	8.8	8.7	·84.0	·84.5	·87.5	·
5*j*	10 H	82.7	8.9	8.3	82.6	9.0	8.4	·84.0	·86.0	·94.5	·
6*h*	8 CH_3	82.2	8.3	8.9	82.5	8.7	8.8	·97.0	—	(·74.0)	·

[a] Intersolid phase transition.

mesophase is formed in compounds (5) beginning from the 4-octylamino derivative. The type of smectic mesophase was determined by the miscibility with 4-octyloxy-4'-cyanobiphenyl test. The introduction of the second small alkyl (methyl) radical to the nitrogen atom decreases the thermal stability of mesophase by 18° while the melting point increases (compound Nr. 6h in Table I). An analogous decrease of the thermal stability of mesophase caused by introduction of the second alkyl radical was observed in 4-alkylaminobenzoic acids.[4]

The kinematic viscosities of 4-alkylamino-4'-cyanobiphenyls are higher than that of 4-alkoxy-4'-cyanobiphenyls (Table II).

TABLE II

The kinematic viscosity (η) of 4-substituted-4'-cyanobiphenyls, $C_8H_{17}—X—C_6H_4—C_6H_4—CN$

	X = —NH—		X = —O—	
Temp., °K	η, cSt	Phase	η, cSt	Phase
368	7.0	Isotr.	3.4	Isotr.
365	7.5		3.7	
363	8.0		3.9	
358	8.0	Nemat.	4.3	
355	8.6		4.7	
353	—	Smect.	5.2	
348	—		5.0	Nemat.
343	—		6.4	

The dielectric permittivities ($\epsilon_{\parallel}$ and $\epsilon_{\perp}$) and dielectric anisotropy ($\Delta\epsilon$) of 4-octylamino-4′-cyanobiphenyl are presented in Table III and compared with those of 4-octyloxy-4′-cyanobiphenyl. As is seen from Table III, 4-alkylamino-4′-cyanobiphenyl is characterized by a significantly higher dielectric anisotropy in the nematic state than its 4-alkoxy analogue. There is the opposite situation in the smectic state: almost zero dielectric anisotropy indicating almost ideal antiparallel orientation of neighboring molecules is characteristic to the alkylamino derivative and the values of the dielectric permittivities close to the ones obtained in the nematic state in the case of alkoxy derivative. We don't know what is the nature of this striking difference in the dielectric anisotropies in the smectic state between the classes of compounds of close structure, especially taking into consideration that the enthalpy of *Sm A* − *N* transition in both cases has the values that are almost equal and less than 0.02 kcal/mole.

Density and refractometric data (corresponding to the wavelength 632,8 nm) for the homologous 4-alkylamino-4′-cyanobiphenyls, compared with those of 4-pentyloxy-4′-cyanobiphenyl, are presented in Table IV.

Refractometric data confirm higher polarizability of 4-alkylamino-4′-cyanobiphenyls to compare with their 4-alkoxy analogues.

EXPERIMENTAL

The transition temperatures were measured on the differential scanning calorimeter Perkin-Elmer DSC-2. Viscosities were measured by the capillary method, dielectric permittivity values were obtained in samples oriented by 6.4 kOe magnetic field. Refraction indices were measured according to[9] and cor-

TABLE III

The low-frequency (10 kHz) dielectric permittivities of 4-substituted-4′-cyanobiphenyls, C_8H_{17}—X—C_6H_4—C_6H_4—CN

$T_R = \frac{T°K}{T_{N\text{-}I}°K}$	X = —NH—				X = —O—			
	$\epsilon_{\parallel}$	$\epsilon_{\perp}$	$\Delta\epsilon$	Phase	$\epsilon_{\parallel}$	$\epsilon_{\perp}$	$\Delta\epsilon$	Phase
1.02	14.9	—	—	Isotr.	9.8	—	—	Isotr.
1.01	14.8	—	—		9.6	—	—	
0.99	23.8	9.6	14.2	Nemat.	13.7	6.6	7.1	Nemat.
0.98	24.7	8.9	15.8		13.9	6.3	7.6	
0.97	3.03	2.88	0.15	Smect.	14.0	6.1	7.9	
0.96	2.88	2.78	0.10		12.7	5.8	6.9	Smect.
0.95	2.77	2.72	0.05		12.6	5.7	6.9	
0.94	2.70	2.68	0.02		12.6	5.7	6.9	
0.93	2.46	—	—	Solid.	12.5	5.6	6.9	
0.92	2.43	—	—		2.96	—	—	Solid.

TABLE IV

Refractometric indices and density of 4-substituted-4′-cyanobiphenyls, $C_nH_{2n+1}—X—C_6H_4—C_6H_4—CN$

n	—X—	$T_R = \frac{T°K}{T_{N\text{-}I}°K}$	n_e	n_{is}	n_o	ρ, g/ccm
5	—O—	1.01		1.599		1.029
		0.99	1.669		1.548	1.034
		0.98	1.687		1.538	1.036
		0.97	1.698		1.532	1.041
		0.96	1.704		1.528	1.047
5	—NH—	1.01		1.647		1.017
		0.99	1.758		1.584	1.029
		0.98	1.773		1.576	1.032
		0.97	1.783		1.570	1.034
		0.96	1.793		1.566	1.037
7	—NH—	1.01		1.626		0.994
		0.99	1.726		1.567	1.004
		0.98	1.739		1.561	1.007
		0.97	1.750		1.555	1.010
		0.96	1.759		1.551	1.013
8	—NH—	1.01		1.611		0.985
		0.99	1.717		1.559	0.995
		0.98	1.733		1.553	0.997
		0.97	1.745		1.549	1.000
		0.96	1.755		1.544	1.004
9	—NH—	1.01		1.605		0.974
		0.99	1.698		1.553	0.983
		0.98	1.713		1.547	0.986
		0.97	1.725		1.541	0.989
		0.96	1.735		1.536	0.992

respond to the wavelength 632.8 nm. Densities were measured in a two-capillary picnometer.

4-Nitro-4′-cyanobiphenyl. 4-Cyanobiphenyl (0.2 mole) was dissolved in acetic anhydride (200 ccm), cooled to 0°C. Fuming nitric acid (84 ccm, $d_4^{20} = 1.50$) was added dropwise under stirring and maintaining the temperature at 0–20°C, after that the reaction mixture was stirred for 20 min at room temperature and poured into cold water. The precipitate was filtered off and crystallized from a propyl alcohol and acetone mixture (1:1), yielding 19.3 g (43%) of bright-yellow product with m.p.200-1°C.

Found, %: *N* 12.49. $C_{13}H_8N_2O_2$. Calcd., %: *N* 12.64.

4-Amino-4′-cyanobiphenyl. Concentrated hydrochloric acid (90 ccm) and stannic chloride (0.4 mole) were added to 4-nitro-4′-cyanobiphenyl, dissolved in 300 ccm iso-propyl alcohol. The mixture was heated under reflux for 10 min, cooled, made alkaline by adding concentrated solution of potassium hydroxide, extracted with benzene. The solvent was evaporated, the residue was crystallized from iso-propyl alcohol. 13.6 g (yield 70%) of product with m.p. 186–8°C was obtained.

Anal. calcd. for $C_{13}H_{10}N_2$: *N*%, 14.42. Found: *N*%, 14.56.

4-Alkylamino-4'-cyanobiphenyls. 4-Amino-4'-cyanobiphenyl (0.021 mole) and the appropriate n-alkyl bromide (0.031 mole) were added to the solution of sodium iso-propylate obtained from sodium (0.021 mole) and 15 ccm iso-propyl alcohol. The mixture was heated under reflux for 10 hours, poured into water, extracted with benzene. The solvent was evaporated, the residue was fractionated by column chromatography on alumina, using diethyl ether-hexane mixture (1:2) as eluent. The first product, eluted from the column, was 4-(N,N-dialkylamino)-4'-cyanobiphenyl ($R_f = 0.84$), the next one was 4-(N-alkylamino)-4'-cyanobiphenyl ($R_f = 0.68$). This fraction was collected, evaporated and crystallized from iso-propyl alcohol. The yield of colorless or light yellowish product was 20–30%.

4-(N-Octyl-N-methylamino)-4'-cyanobiphenyl. The alkylation of 4-N-octylamino-4'-cyanobiphenyl with methyl iodide was carried out in the way analogous to the alkylation of 4-amino-4'-cyanobiphenyl. The product was purified by column chromatography (the fraction with $R_f = 0.84$) and crystallized from iso-propyl alcohol, yield 68%.

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