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Liquid Crystalline 4-Cyanobiphenyl-4-Alkylaminobenzoates†

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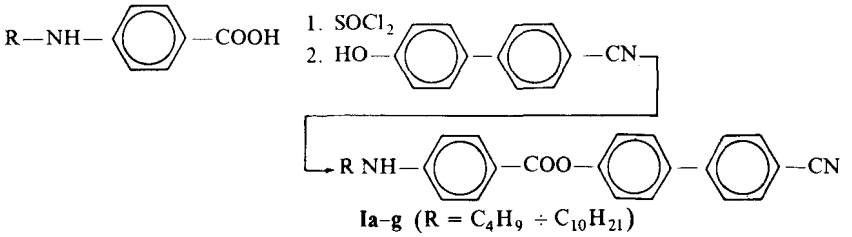
The mesomorphic and dielectric properties of homolo new compounds 4-cyanobiphenyl-4-alkylaminobenzoates are presented.

It is known (1), that 4-cyanophenyl-4′-alkylaminobenzoates are characterized by very high values of positive dielectric anisotropy, but exhibit only deep monotropic isotropic-nematic transition.

In this study, mesomorphic 4-cyano-4′-oxybiphenyl 4-alkylaminobenzoates (I) have been synthesized and their dielectric properties examined. These compounds were obtained by treatment of 4-cyano-4′-hydroxybiphenyl with 4-alkylaminobenzoyl chlorides prepared from the corresponding acids, without additional purification according to the following scheme:



Ia–g (R = $C_4H_9 \div C_{10}H_{21}$)

The 4-alkylaminobenzoic acids were obtained by alkylation of *p*-aminobenzoic acid with alkyl bromides in water medium. The yields of product isolated after recrystallization from ethanol were 40–50%. The phase transition temperatures for the 4-alkylaminobenzoic acids prepared by this method agree with the values reported in the literature (1).

†Presented at the IX Int. Liquid Crystal Conference, Bangalore, 1982.

The compounds **Ia–e** formed only nematic mesophase and exhibited higher melting temperatures and considerably higher temperatures for the nematic-isotropic transition in comparison with analogous derivatives of 4-cyanophenol (1). The compounds **If** and **Ig** form both smectic A and nematic mesophases (see Table I). Because of their high melting temperatures, the dielectric properties of compounds I were estimated by the measurement of the dielectric permittivities for a solution of **Ic** in the low-polar liquid crystal, 4-butyloxyphenyl-4′-pentylbicyclo-/2.2.2/octylcarboxylate (nematic range C 43° N to 102° I). The results are given in Table II.

These results show that compounds I possess a higher positive dielectric anisotropy than the 4-cyanobiphenyl-4′-alkoxybenzoates, but noticeably lower than the 4-cyanophenyl-4′-alkylaminobenzoates or 4-alkylamino-4′-cyanobiphenyls do (2). However, their application for preparation of mixtures with a high positive dielectric anisotropy is limited by their high melting temperatures.

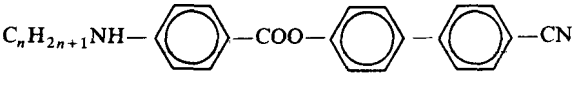
EXPERIMENTAL

Synthesis of 4-cyano-4′-hydroxybiphenyl 4-alkylaminobenzoates (Ia – g)

4-Alkylaminobenzoic acid (0.02 mol) was dissolved in toluene (75 ccm) at 80 °C and a solution of thionyl chloride (0.04 mol) in toluene (15 ccm) added. The reaction mixture was allowed to cool to 30 °C. The resultant solution of 4-alkylaminobenzoyl chloride was added to a

TABLE I

The phase transition temperatures, yields and elemental analysis data for 4-cyano-4′-hydroxybiphenyl 4-alkylaminobenzoates



Compound	n	Yield, %	The phase transition temp., in °C			Found, %			Empirical formula	Calculated, %		
			C–S_A	S_A–N	N–I	C	H	N		C	H	N
Ia	4	38	182	—	250	77.01	5.84	7.36	$C_{24}H_{22}N_2O_2$	76.97	5.93	7.48
Ib	5	41	156	—	260	77.15	6.03	6.89	$C_{25}H_{24}N_2O_2$	77.28	6.24	7.21
Ic	6	36	147	—	225	77.48	6.34	6.77	$C_{26}H_{26}N_2O_2$	77.57	6.52	6.98
Id	7	43	155	—	255	78.36	6.27	6.57	$C_{27}H_{28}N_2O_2$	78.60	6.85	6.78
Ie	8	34	165	—	237	78.51	6.98	6.41	$C_{28}H_{30}N_2O_2$	78.82	7.10	6.56
If	9	41	159	169	224	78.72	7.29	6.15	$C_{29}H_{32}N_2O_2$	79.04	7.33	6.36
Ig	10	32	158	185	214	79.01	7.52	5.96	$C_{30}H_{34}N_2O_2$	79.24	7.55	6.16

TABLE II

The temperature dependence of dielectric permittivity for 4-butyloxyphenyl-4′-pentylbicyclo/2.2.2/octylcarboxylate (A) and the 10% solution of compound (**Ic**) in 4-butyloxyphenyl-4′-pentylbicyclo/2.2.2/octylcarboxylate (B)

	A				B			
T/T_{NI}	$\epsilon_{\parallel}$	$\epsilon_{\perp}$	ϵ_{is}	$\Delta\epsilon$	$\epsilon_{\parallel}$	$\epsilon_{\perp}$	ϵ_{is}	$\Delta\epsilon$
1.02			3.30				5.76	
1.01			3.31				5.80	
0.995	3.10	3.48		−0.38	5.56	4.48		1.08
0.990	3.05	3.53		−0.48	5.54	4.38		1.16
0.985	3.03	3.56		−0.53	5.50	4.34		1.15
0.980	3.01	3.58		−0.57	5.47	4.30		1.17
0.975	3.00	3.59		−0.59	5.44	4.27		1.17
0.970	3.00	3.62		−0.62	5.40	4.26		1.14

The extrapolation of measured values to the properties of the pure (**Ic**) gives following values for $T/T_{NI} = 0.97$: $\epsilon_{\parallel} = 29.70$, $\epsilon_{\perp} = 10.02$, $\Delta\epsilon = 19.68$.

solution of 4-cyano-4′-hydroxybiphenyl (0.02 mol) in dry pyridine (10 ccm). After 30 min at room temperature, the reaction mixture was poured into a saturated aqueous solution of sodium bicarbonate. The organic layer was separated, washed twice with water, dried over anhydrous magnesium sulfate. Then 2/3 of the toluene was evaporated and the residue filtered through a layer of alumina using a mixture of diethyl ether and hexane (1 : 1) as the eluent. The yields, the phase transition temperatures and elemental analysis data are presented in Table I.

A 10% solution of 4-cyano-4′-hydroxybiphenyl 4-hexylaminobenzoate in 4-butyloxyphenyl-4′-pentylbicyclo/2.2.2/octylcarboxylate was used for the investigation of dielectric properties of this material. This mixture is nematic at 38–91°C. The values for components of the dielectric permittivity $\epsilon_{\parallel}$ (parallel to the longitudinal axis of the molecule), $\epsilon_{\perp}$ (perpendicular to this axis) and $\Delta\epsilon$ (dielectric anisotropy) of 4-butyloxyphenyl-4′-pentylbicyclo/2.2.2/octylcarboxylate and this prepared mixture are shown in Table II. The measurements were carried out in the magnetic field of 0.72 *T* at frequency 10 kHz.

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