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Synthesis and mesomorphic properties of cyano derivatives of 2-(4-carbohydroxy-3-halogenphenyl)-5-alkyl-1,3,2-dioxaborinanes

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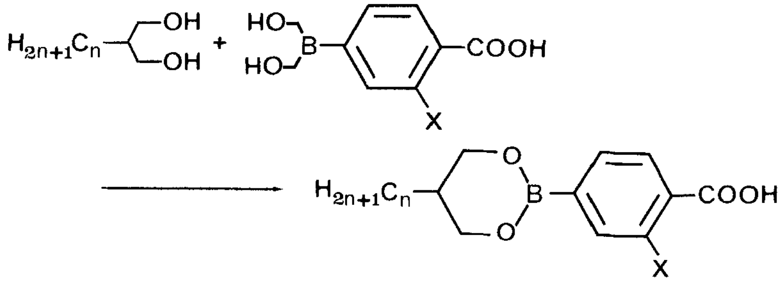
Cyano derivatives of 2-(4-carbohydroxy-3-halogenphenyl)-5-alkyl-1,3,2-dioxaborinane have been synthesized. These compounds are characterized by low nematic–isotropic transition temperatures and a high positive dielectric anisotropy; they are promising for use in liquid-crystalline mixtures intended for high information electrooptic display devices.

1. Introduction

It has been shown that compounds containing a 1,3,2-dioxaborinane fragment form liquid-crystalline phases and are characterized by a higher positive dielectric anisotropy in comparison with analogous derivatives of 1,3-dioxane [1–4]. In order to continue these investigations we have synthesized other cyano derivatives (**IIa–w**, **IIIa**) by the reaction of 2-alkyl-1,3-propanediols with 4-carbohydroxy-3-halogenphenylboric acids and then by the conversion of the resultant 2-(4-carbohydroxy-3-halogenphenyl)-5-alkyl-1,3,2-dioxaborinanes (**Ia–g**), and we have studied their mesomorphic properties and dielectric anisotropy. It was supposed that incorporation of halogen atoms into positions ortho to the carboxy and nitrile groups would allow us to obtain compounds not only with lower nematic–isotropic transition temperatures but also with a considerably higher positive dielectric anisotropy in comparison with the unsubstituted analogues.

2. Results and discussion

2-[4-(4′-cyano-3-halogenphenyloxycarbonyl)-3-halogenphenyl]-5-alkyl-1,3,2-dioxaborinanes (**IIa–w**) were synthesized by reaction of the acid chlorides with 4-hydroxy-3-halogenbenzonitriles in the presence of pyridine. The 2-(4-cyano-3-halogenphenyl)-5-alkyl-1,3,2-dioxaborinanes (**IIIa**) were obtained by treatment of the acid chlorides (**Ia–g**) with aqueous ammonia and by subsequent dehydration of the amides in the presence of thionyl chloride.



Ia–g

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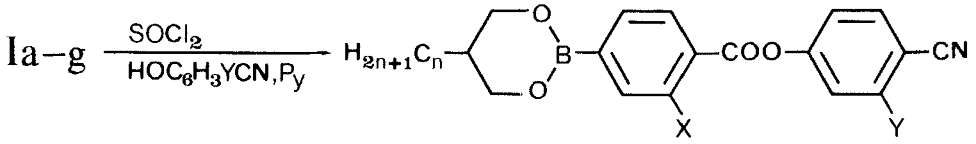
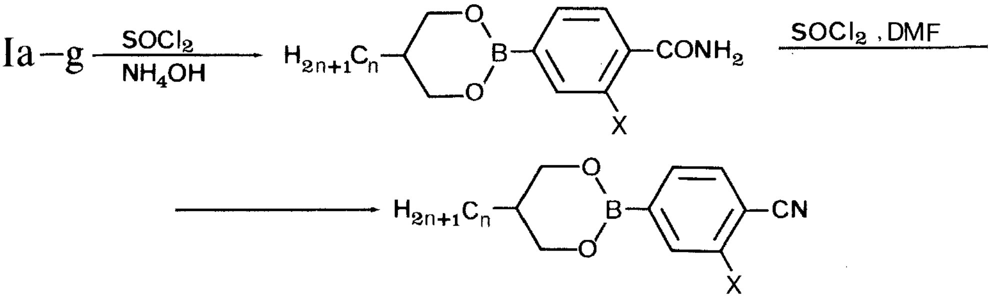


IIa–w



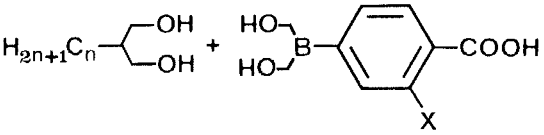
IIIa

n = 3–7; *X*, *Y* = H, F, Cl. The yields and transition temperatures are given in tables 1 and 2.

The composition and structure of the compounds obtained (**Ia–g**, **IIa–w**, **IIIa**) were confirmed by the results of elemental analysis as well as infrared and proton NMR spectroscopy. Thus, in the proton NMR spectra of the esters (**IIa–i**), proton signals of dioxaborinane and aryl fragments were observed within the ranges 3·53–4·23 ppm and 7·27–8·13 ppm, respectively. NMR signals within the range 3·53–4·20 ppm correspond to the analogous protons of nitriles. In the infrared spectra of compounds **IIa–i** and **IIIa**, an intense signal at 2225 cm^{-1} corresponds to the stretching of the nitrile group.

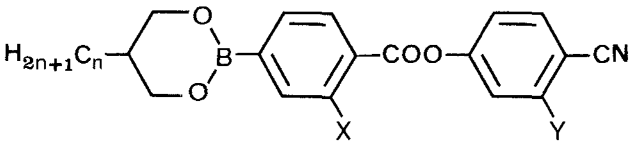
The investigations of the mesomorphic properties and dielectric anisotropy of the 1,3,2-dioxaborinanes synthesized as well as the electrooptic and dynamic parameters of the liquid-crystalline mixtures containing these compounds showed that they are more promising for use in electrooptic display devices in comparison with the analogous derivatives of *trans*-4-alkylcyclohexylbenzene and *trans*-2-phenyl-5-alkyl-1,3-dioxane.

Table 1. Yields and transition temperatures of the 2-(4-carbohydroxy-3-halogenphenyl)-5-alkyl-1,3,2-dioxaborinanes (**Ia–g**).



Compound	*n*	*X*	Yield/%	Melting point or nematic range °C
Ia	3	F	88	186
Ib	3	Cl	73	183
Ic	4	F	82	164–169
Id	5	F	76	156–174
Ie	5	Cl	69	118–123
If	6	F	64	158–167
Ig	7	F	72	147–169

Table 2. Yields, transition temperatures and dielectric anisotropy of 2-[4-(4′-cyano-3-halogenphenyloxycarbonyl)-3-halogenphenyl]-5-alkyl-1-1,3,2-dioxaborinanes (**IIa**–**w**).



Compound	*n*	*X*	*Y*	Yield/%	Nematic range or melting point °C	Dielectric anisotropy†
IIa	3	F	H	67	89–174	38
IIb	3	Cl	H	51	109–114	29
IIc	3	H	F	75	126–173·5	–
IId	3	F	F	83	103–143·5	83
IIe	3	Cl	F	72	78	–
IIf	3	F	Cl	86	111	58‡
IIg	4	F	H	76	95–168	31
IIh	4	H	F	57	103–164	–
IIi	4	H	Cl	58	115–116	–
IIj	4	F	Cl	74	104	–
IIk	4	F	F	79	64–143	–
IIl	5	F	H	64	94–167	–
IIm	5	Cl	H	68	93–109	–
IIn	5	H	F	47	82–109	–
IIo	5	H	Cl	62	106–117	–
IIp	5	F	Cl	68	105	–
IIq	5	F	F	60	63–142	46
IIr	5	Cl	F	73	59–74	–
IIs	5	Cl	Cl	73	86	–
IIt	6	F	H	72	87–157	–
IIu	6	F	F	62	68–131	–
IIv	7	F	H	65	95–153	–
IIw	7	F	F	57	71–131	–

† The dielectric anisotropy was measured at a temperature 60°C below T_{NI}.
‡ Extrapolated value.

Table 3. Electrooptic parameters of the liquid-crystalline mixtures†.

Compound in mixture	Threshold voltage V	Saturation voltage V	ΔU/V
4-Cyano-3-fluorophenyl ester of 4-*trans*-(4′-pentylcyclohexyl) benzoic acid	2·24	2·96	0·72
2-[4-(4′-Cyano-3-fluorophenyloxycarbonyl)phenyl]-5-pentyl-1,3-dioxane	2·12	2·81	0·69
IIn	1·94	2·58	0·64
IIq	1·50	1·89	0·39
IIIa	1·51	1·90	0·39

† The mixtures were composed of 55 wt% of the 4-ethoxyphenyl ester of *trans*-4-butylcyclohexane-carboxylic acid, 25 wt% of the 4-ethoxyphenyl ester of *trans*-4-hexylcyclohexanecarboxylic acid and 20 wt% of the compounds indicated in the first column of the table.

4-Cyano-3-fluorophenylderivatives of 1,3,2-dioxaborinane are characterized by low nematic–isotropic transition tempertures (60–70°C) and high positive dielectric anisotropies reaching 80. This allows for liquid-crystalline compositions with a small threshold voltage, which are superior than the analogous compositions containing the derivatives of 1,3-dioxane and can be used for producing high information display devices (see table 3).

3. Experimental

The infrared spectra of 0·1 M solutions of the compounds in carbon tetrachloride were recorded with a SPECORD IR-75 spectrophotometer. The proton NMR spectra of 10 per cent solutions in carbon tetrachloride with hexamethyldisiloxane as an internal standard were recorded with a TESLA BS-467. The transition temperatures were determined with a thermometer or a Perkin–Elmer DSC-2 differential scanning calorimeter.

The measurements of the electrooptic parameters of the mixtures were performed at 20°C in twisted nematic cells with a 10 μm spacer.

3.1. *Preparation of the 2-[4-(4′-carbohydroxy-3-halogenphenyl)]-5-alkyl-1,3,2-dioxaborinanes* (**Ia–g**)

A mixture of 0·05 mol of 2-alkyl-1, 3-propanediol and 0·05 mol of 4-carbohydroxy-3-halogenphenylboric acid in 50 ml of acetone was boiled for three to four hours and cooled. The precipitated crystals were filtered off and recrystallized from a minimum amount of acetone.

3.2. *Preparation of the 2-[4-(4′-cyano-3-halogenphenoxycarbonyl)-3-halogenphenyl]-5-alkyl-1,3,2-dioxaborinanes* (**IIa–w**)

A mixture of 0·05 mol of the 2-(4-carbohydroxy-3-halogenphenyl)-5-alkyl-1,3,2-dioxaborinanes, 0·006 mol of pyridine and 0·06 mol of thionyl chloride in 50 ml of anhydrous diethylether was stirred for one hour. Then 0.6 mol of 4-hydroxy-3-halogenbenzonitrile and 0·01 mol of pyridine were added. The mixture was left overnight and filtered. The residue obtained after the solvent had been removed was recrystallized from hexane and ethyl alcohol. The positive dielectric anisotropy of the obtained compounds are presented in table 2.

3.3. *Preparation of the 2-(4-cyano-3-fluorophenyl)-5-propyl-1,3,2-dioxaborinane* (**IIIa**)

A mixture of 0·007 mol of 2-(4-carbohydroxy-3-fluorophenyl)-5-propyl-1,3,2-dioxaborinane and 0·03 mol of thionyl chloride was boiled in a reversecooler flask for an hour. The residue obtained after the solvent had been removed was treated with 15 ml of aqueous ammonia. The precipitated crystals were filtered off, washed with water, air dried and then dissolved in 10 ml of dimethylformamide and 0·8 ml of thionyl chloride, held for 1 hour and poured into aqueous sodium bicarbonate. The product was extracted with diethylether, washed with water and dried with anhydrous sodium sulphate. The residue obtained after the solvent had been removed was recrystallized from ethyl alcohol; yield 36 per cent, mp 45°C. The extrapolated value of the positive dielectric anisotropy (from mixtures of this compound with 4-ethoxyphenyl esters of *trans*-4-alkylcyclohexanecarboxylic acids) is equal to 56.

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