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Synthesis, mesomorphic properties and potential applications of aryl esters of 4-*n*-alkylcyclohexene-1-carboxylic acids in electrooptic displays

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The reaction of 4-substituted phenols with 4-*n*-alkylcyclohexene-1-carbonyl chlorides, which differ in the position of their double bond in the ring, has yielded the corresponding esters. Investigation of their mesomorphic properties including the electrooptic parameters of mixtures containing these compounds show that aryl esters of acids containing the double bond in the second position of the cyclohexene fragment are the most promising for use as components of liquid crystal mixtures.

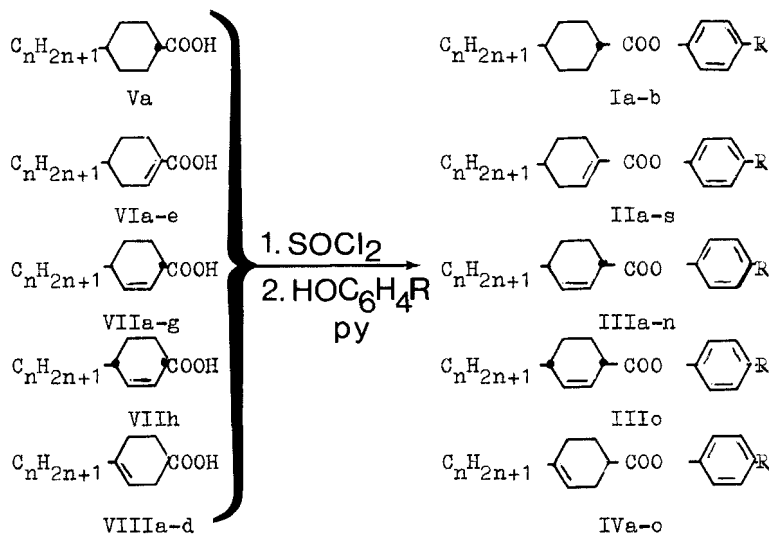
1. Introduction

The use of liquid crystal materials in various electrooptic display devices (electronic watch displays, calculators, digital displays, etc), which are characterized by their small sizes and low power consumption has resulted in extensive experimental data on the synthesis and investigation of their mesomorphic properties and their mixtures. The results obtained allowed certain regularities in the change of electrooptic and dynamic parameters of liquid crystal displays (for example, the threshold voltage, the saturation voltage, and the time characteristics), which depend on the physical properties of the liquid-crystal materials (such as the viscosity, the dielectric anisotropy and the elastic constants), to be ascertained and to elaborate rules for the use of liquid crystals in the display devices. However the dependence of the physical properties of liquid crystals and their mixtures upon the molecular structure is still insufficiently studied.

2. Results and discussion

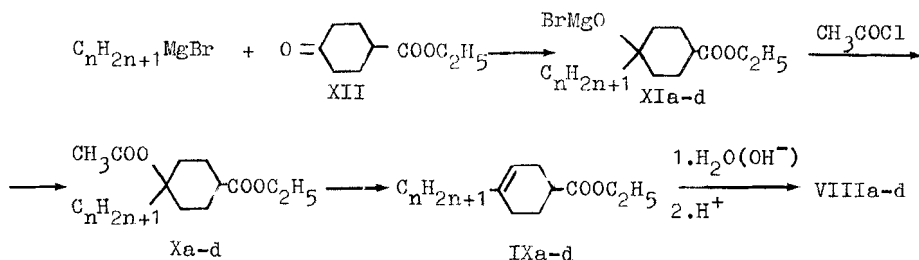
Mesomorphic 1,4-disubstituted cyclohexene, as well as similar cyclohexane, derivatives are promising candidates for use in liquid crystal mixtures intended for electrooptic displays. These compounds are characterized by low melting points, wide mesomorphic ranges and high values of the positive dielectric anisotropy [1]. In order to continue the investigation of the mesomorphic properties of 1,4-disubstituted cyclohexenes and to ascertain the regularities in the change in their transition temperatures depending on the double bond position in the cyclohexene fragment, as well as the variation of certain parameters of liquid crystal mixtures containing these compounds, we have prepared the esters (I *a, b*; II *a-s*; III *a-o*; IV *a-o*) by the reaction of trans-4-*n*-alkylcyclohexane-1-carboxylic (V *a*), 4-*n*-alkyl-1-cyclohexene-1-carboxylic (VI *a-e*) cis- and trans-4-*n*-alkyl-2-cyclohexene-1-carboxylic (VII *a-g, h*), 4-*n*-alkyl-3-cyclohexene-1-carboxylic (VIII *a-d*) acids with thionyl chloride and 4-substituted phenols in the

presence of pyridine. Their mesomorphic properties and the possibility of using them as components for liquid-crystal mixtures for electrooptic displays were also studied.



$n = 1-8$, $R = \text{OC}_4\text{H}_9$, OC_5H_{11} , CN , $\text{C}_6\text{H}_4\text{CN}$, $\text{COOC}_6\text{H}_4\text{CH}_3$, $\text{COOC}_6\text{H}_4\text{C}_2\text{H}_5$, $\text{COOC}_6\text{H}_4\text{C}_4\text{H}_9$, $\text{COOC}_6\text{H}_4\text{C}_5\text{H}_{11}$.

4-*n*-alkyl-1-cyclohexene-1-carboxylic acids (VI *a-e*) were synthesized either by dehydrobromination of 1-bromo-4-*n*-alkylcyclohexane-1-carboxylic acids prepared by the Hell-Volhard-Zelinsky method from trans-4-*n*-alkylcyclohexane-1-carboxylic acids [2], or by alkaline hydrolysis of *N*-(1-trichloromethyl-4-*n*-alkylcyclohexyl-1) morpholines (the products of the reaction of *N*-(4-*n*-alkyl-1-cyclohexenyl-1) morpholines with trichloroacetic acid [3]). Cis- and trans-4-*n*-alkyl-2-cyclohexene-1-carboxylic acids (VIII *a-h*) were prepared by the reduction of the corresponding 4-alkylbenzoic acids [4]. 4-*n*-alkyl-3-cyclohexene-1-carboxylic acids (VIII *a-d*) were obtained by alkaline hydrolysis of esters (IX *a-d*). These were prepared as the pyrolysis products of 4-*n*-alkyl-4-acetyloxycyclohexane-1-carboxylic acids (X *a-d*) synthesized by the interaction of alkylmagnesium bromides with the ethyl ester of 4-*n*-cyclohexanone-1-carboxylic acid (XII) and followed by the decomposition of their magnesium derivatives (XI *a-d*) using acetyl chloride



The synthesis of 4-*n*-alkyl-3-cyclohexene-1-carboxylic acids (VIII *a-d*), except for 4-methyl-3-cyclohexene-1-carboxylic acid (VIII *a*), by condensation of 2-alkyl-1,3-butadienes with acrylic acid, or its ester was less effective than the method described. 2-alkyl-1,3-butadienes are almost inaccessible, unstable and, in case of the reaction with acrylic acid or its ester, form a considerable quantity of polymer products, which reduce the yield and impede the separation of adducts (VIII *a-d*, IX *a-d*).

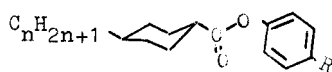
Trans-4-*n*-alkylcyclohexane-1-carboxylic acids (*Va*) were obtained by catalytic hydrogenation of acid (*VIIa*) in the presence of 10 per cent palladium on carbon.

The composition and structure of the acids (*VIa-e*, *VIIa-g, h*, *VIIIa-d*) and aryl esters (*IIa-s*, *IIIa-n, o*, *IVa-o*) were confirmed by the results of elemental analysis as well as infrared and proton N.M.R. spectra. Thus, in the proton spectra of acids (*VIa-e*), a multiplet signal at 6.64 p.p.m. is observed, which is characteristic of the proton located at the double bond of the cyclohexene ring. The corresponding proton of acids (*VIIIa-d*) and of esters (*IVa-o*) is characterized by a signal at 5.18 p.p.m. in their N.M.R. spectra. In the proton spectra of *cis*- and *trans*-4-*n*-alkyl-2-cyclohexene-1-carboxylic acids (*VIIa-g, h*) and their esters (*IIIa-h, o*), the protons located at the double bond give a singlet at 5.60 p.p.m., which after addition of a shift reagent tris[3-(trifluoromethyloxymethylene)-*d*-camphorate]europium for the *trans*-acids (*VIIa-d*) and their esters (*IIIa-n*) is split into two doublets with a coupling constant of 11 Hz, while for the *cis*-acid (*VIIh*) and ester (*IIIo*) splitting into a number of poorly resolved multiplets is observed.

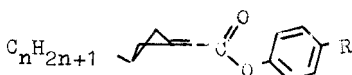
It should be noted that the configuration of *trans*- and *cis*-4-*n*-alkyl-2-cyclohexene-1-carboxylic acids (*VIIa-g, h*) was inferred by the presence of liquid-crystalline properties in the esters of the *trans*-acid (*IIIa-n*) with their rod-shaped molecules, as well as by the absence of such properties in an ester of the *cis*-acid (*IIIo*), since the pseudo-axial position of the alkyl group excludes the possibility of their rod-like form. The esters (*IIa-s*, *IIIa-n, o*, *IVa-o*) give the signals of aromatic protons in the N.M.R. spectra within the range 6.47-8.13 p.p.m.

The infrared spectra of the esters (*IIa-s*, *IIIa-n, o*, *IVa-o*), contains intense bands at 1735, 1765 and 1700 cm^{-1} corresponding to the stretching vibrations of the ester carbonyls. The stretching vibrations of the nitrile group of the esters is located at 2230 cm^{-1} .

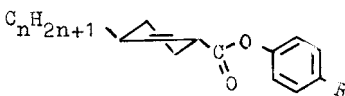
The investigation of the liquid-crystalline properties of the compounds (*IIa-s*, *IVa-o*) and their comparison with the similar parameters of aryl esters of *trans*-4-*n*-alkylcyclohexane-1-carboxylic acids [5-7] (see tables 1-3) shows that the appearance of the double bond in the 1st or 3rd positions of the ring in relation to an ester fragment causes a large distortion of the rod-like shape of the molecule. This is accompanied by a considerable narrowing of the mesophase (nematic) range (reduced by 50°C), and also by a lowering of the melting point in the esters of 4-*n*-alkyl-3-cyclohexene-1-carboxylic acids (*IVa-o*) and its increase for the esters of 4-*n*-alkyl-1-cyclohexene-1-carboxylic acids (*IIa-n*)



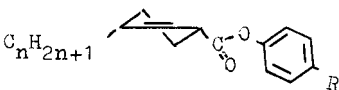
(Esters of *trans*-4-*n*-alkylcyclohexane-1-carboxylic acids).



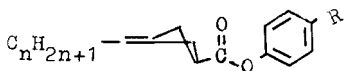
(Esters of 4-*n*-alkyl-1-cyclohexene-1-carboxylic acids).



(Esters of *trans*-4-alkyl-2-cyclohexene-1-carboxylic acids).



(Esters of *cis*-4-*n*-alkyl-2-cyclohexene-1-carboxylic acids).



(Esters of 4-*n*-alkyl-3-cyclohexene-1-carboxylic acids).

Table 1. Constants, yields, data of the elementary analysis of aryl esters (II *a-s*).

No.	<i>n</i>	<i>R</i>	Yield (per cent)	Liquid crystal range ($T_{CN}-T_{NI}$) or the melting point, °C
1	2	3	4	5
<i>a</i>	3	OC ₄ H ₉	39	44
<i>b</i>	3	OC ₃ H ₁₁	42	36
<i>c</i>	4	OC ₄ H ₉	36	34-39
<i>d</i>	5	OC ₄ H ₉	47	45-51
<i>e</i>	3	CN	56	71
<i>f</i>	3	C ₆ H ₄ CN	62	109-224
<i>g</i>	4	CN	73	57
<i>h</i>	4	C ₆ H ₄ CN	67	113-223
<i>i</i>	5	CN	56	42-44
<i>j</i>	5	C ₆ H ₄ CN	64	104-218
<i>k</i>	8	CN	43	44.5-52
<i>l</i>	8	C ₆ H ₄ CN	52	87-185
<i>m</i>	1	COOC ₆ H ₄ CH ₃	45	142
<i>n</i>	1	COOC ₆ H ₄ C ₂ H ₅	60	96-169
<i>o</i>	3	COOC ₆ H ₄ C ₃ H ₁₁	43	67-173
<i>p</i>	3	COOC ₆ H ₄ C ₄ H ₉	49	69-170
<i>q</i>	4	COOC ₆ H ₄ C ₃ H ₅	38	104-175
<i>r</i>	5	COOC ₆ H ₄ C ₂ H ₅	37	99-181
<i>s</i>	5	COOC ₆ H ₄ C ₃ H ₁₁	47	67-177

Table 2. Constants, yields, data of the elementary analysis of aryl esters (III *a-n*).

No.	<i>n</i>	<i>R</i>	Yield (per cent)	Liquid crystal range ($T_{CN}-T_{NI}$) or the melting point, °C
1	2	3	4	5
<i>a</i>	3	OC ₄ H ₉	70	21-46
<i>b</i>	6	OC ₄ H ₉	52	24-46.5
<i>c</i>	3	CN	37	(9) 17
<i>d</i>	1	C ₆ H ₄ CN	58	85.5-168.5
<i>e</i>	2	C ₆ H ₄ CN	53	58-189
<i>f</i>	3	C ₆ H ₄ CN	44	59-203
<i>g</i>	4	C ₆ H ₄ CN	42	42.5-197
<i>h</i>	5	C ₆ H ₄ CN	56	48.5-189
<i>i</i>	6	C ₆ H ₄ CN	46	44-186
<i>j</i>	7	C ₆ H ₄ CN	43	65-185
<i>k</i>	8	COOC ₆ H ₄ CH ₃	49	77-148
<i>l</i>	1	COOC ₆ H ₄ C ₂ H ₅	42	53-162
<i>m</i>	2	COOC ₆ H ₄ C ₃ H ₁₁	46	50.5-134
<i>n</i>	3	COOC ₆ H ₄ C ₃ H ₁₁	42	48-166

The high melting points for the esters (II *a-s*) are probably due to the conjugation of the double bond in the cyclohexene ring with the ester fragment resulting in strong intermolecular interactions. The mesophase range in the aryl esters of the *trans*-4-*n*-alkyl-2-cyclohexene-1-carboxylic acids (III *a-n*), whose molecules are close to rod-like,

Table 3. Constants, yields, data of the elementary analysis of esters (IV *a-o*).

No.	<i>n</i>	<i>R</i>	Yield (per cent)	n_D^{20}	Liquid crystal range ($T_{CN}-T_{NI}$) or the melting point, °C
1	2	3	4	5	6
<i>a</i>	3	OC ₄ H ₉	43	—	8
<i>b</i>	3	OC ₅ H ₁₁	38	—	5
<i>c</i>	4	OC ₄ H ₉	63	—	20
<i>d</i>	3	CN	62	1.5238	—
<i>e</i>	3	C ₆ H ₄ CN	20	—	63-172
<i>f</i>	4	CN	47	1.5196	—
<i>g</i>	5	C ₆ H ₄ CN	34	—	64-165
<i>h</i>	1	COOC ₆ H ₄ CH ₃	42	—	75-142
<i>i</i>	1	COOC ₆ H ₄ C ₂ H ₅	58	—	58-165
<i>j</i>	3	COOC ₆ H ₄ C ₄ H ₉	63	—	61-144
<i>k</i>	3	COOC ₆ H ₄ C ₅ H ₁₁	56	—	39-163
<i>l</i>	4	COOC ₆ H ₄ C ₂ H ₅	32	—	48-146
<i>m</i>	4	COOC ₆ H ₄ C ₄ H ₉	36	—	45-146
<i>n</i>	4	COOC ₆ H ₄ C ₅ H ₁₁	43	—	41-140
<i>o</i>	5	COOC ₆ H ₄ C ₂ H ₅	27	—	70-142

differs only slightly from that of the corresponding esters of the trans-4-*n*-alkylcyclohexane-1-carboxylic acids. However these compounds are characterized by low melting points and this makes them potentially useful for use as components in liquid crystal mixtures.

The investigation of the electrooptic and dynamic parameters of mixtures composed of 4-*n*-pentyl-4'-cyanobiphenyl and the aryl esters of 4-*n*-alkylcyclohexene-1-carboxylic acids showed that mixtures containing esters of alkylcyclohexenecarboxylic acids had lower threshold voltages and saturation voltages and higher switch-on and switch-off times in comparison with those containing the corresponding esters of trans-4-*n*-alkylcyclohexane-1-carboxylic acids (see table 4).

Among the compounds differing by the position of the double bond in the ring, esters of 4-*n*-alkyl-3-cyclohexene-1-carboxylic and 4-*n*-alkyl-1-cyclohexene-1-carboxylic acids are the least promising for practical applications, Their use is limited by the absence of liquid crystal properties or by a narrow nematic range in esters (IV *a-o*), rather high melting points in esters (II *a-s*), as well as by higher switch-on and switch-off times. In addition the voltage-contrast characteristic for the mixtures containing these compounds exhibited a low slope in comparison with those containing esters of trans-4-*n*-alkyl-2-cyclohexene-1-carboxylic acids.

3. Experimental

The infrared spectra of 0.1 M solutions of compounds in carbon tetrachloride were recorded with a SPECORD IR-75 spectrophotometer. The proton N.M.R. spectra of 10 per cent solutions in carbon tetrachloride with hexomethyldisiloxane as an internal standard were recorded with a TESLA BS-467 spectrometer. The transition temperatures were determined visually or with a Perkin-Elmer DSC-2 differential scanning calorimeter. Textures of different phases were studied with a polarizing microscope. The purity of the compounds was determined chromatographically.

Table 4. Electrooptic parameters of the liquid crystal mixtures†.

	III/										II n				IV i					
	I b	15	20	25	10	15	20	25	10	15	20	25	10	15	20	25	10	15	20	25
Ester and its contents in the mixtures, (per cent)	10	15	20	25	10	15	20	25	10	15	20	25	10	15	20	25	10	15	20	25
Threshold voltage/V	1.3	1.36	1.44	1.49	1.18	1.29	1.32	1.36	1.18	1.28	1.29	1.34	1.17	1.20	1.24	1.30				
Saturation voltage/V	1.72	1.78	1.84	1.96	1.60	1.72	1.76	1.85	1.60	1.72	1.74	1.86	1.60	1.65	1.72	1.82				
Switch-on time/ms	32	40	45	55	42	50	60	70	50	60	70	80	45	55	62	75				
Switch-off time/ms	140	140	140	140	150	150	150	150	150	150	150	150	150	150	150	150				
Viscosity	27.5	32.8	36	38.5	27.8	33	38	42	32.8	39.4	44	49	29.5	38	42.3	48				

† The mixtures are composed of 4-*n*-pentyl-4-cyanobiphenyl and one of the esters (I b, II n, III l, IV i).

Table 5. Electrooptic parameters of the mixtures†.

Ether	IV <i>g</i>			III <i>h</i>			II <i>j</i>		
	20	35	50	20	35	50	20	35	50
Measurement temperature/°C	20	35	50	20	35	50	20	35	50
Threshold voltage V_{10}	1.46	1.38	1.33	1.61	1.55	1.5	1.58	1.51	1.45
V_{50}/V	1.83	1.74	1.69	1.93	1.86	1.8	1.95	1.86	1.78
Saturation voltage V_{90}/V	2.44	2.39	2.36	2.43	2.34	2.30	2.54	2.41	2.32
Slope of the current-contrast curve/ P_{50}	0.253	0.26	0.27	0.2	0.2	0.2	0.234	0.232	0.227
Switch-on time/ms	—	110	—	—	100	—	—	—	—
Switch-off time/ms	—	75	—	—	65	—	—	—	—

† The mixtures are composed of 65 wt % 4-*n*-pentyl-4'-cyanobiphenyl and 35 wt % of one of the esters (II *j*, III *h*, IV *g*).

Measurements of the electrooptic parameters of mixtures were performed at a temperature of $20^\circ \pm 0.5^\circ\text{C}$ in twisted nematic cells with a $10\ \mu\text{m}$ spacer using parallel polarizers.

4-*n*-butoxyphenylester of 4-propyl-3-cyclohexene-1-carboxylic acid (IV *a*). 0.05 mol of 4-*n*-propyl-3-cyclohexene-1-carbonyl chloride, 0.06 mol 4-*n*-butoxyphenol and 0.01 mol pyridine in 50 ml of anhydrous diethylether were mixed for 6 h, washed with water and dried using anhydrous sodium sulphate. The residue after the solvent had been removed was crystallized from ethyl alcohol. Yield 43 per cent, m.p. 8°C . Found (per cent): C 75.85, H 8.72, $\text{C}_{20}\text{H}_{28}\text{O}_3$. Calculated (per cent): C 75.95, H 8.86.

The other esters (II *a-s*; III *a-n, o*; IV *a-o*) were obtained in a similar way; their transition temperatures are presented in tables 1-3.

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