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Synthesis and mesomorphic properties of some 3-substituted-4-cyanophenyl esters, 4'-cyano-3-substituted-4-biphenyl esters of 4-(trans-4-alkylcyclohexyl) benzoic, 4-alkyl-3-substituted biphenyl-4'-carboxylic, trans-4-alkylcyclohexanecarboxylic and 4-alkylbenzoic acids and electrooptic parameters of liquid-crystalline mixtures containing these compounds

V. S. Bezborodov[a]; V. I. Lapanik[a]; P. V. Adomenas[b]; R. Sirutkaitis[b]
[a] A. N. Sevchenko Institute of Applied Physical Problems, Minsk, Byelorussia [b] Vilnius University, Vilnius, Lithuania

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Synthesis and mesomorphic properties of some 3-substituted-4-cyanophenyl esters, 4′-cyano-3-substituted-4-biphenyl esters of 4-(*trans*-4-alkylcyclohexyl) benzoic, 4-alkyl-3-substituted biphenyl-4′-carboxylic, *trans*-4-alkylcyclohexanecarboxylic and 4-alkylbenzoic acids and electrooptic parameters of liquid-crystalline mixtures containing these compounds

by V. S. BEZBORODOV*†, V. I. LAPANIK†, P. V. ADOMENAS‡ and R. SIRUTKAITIS‡

† A. N. Sevchenko Institute of Applied Physical Problems,
Kurchatova 7, Minsk, 220064, Byelorussia
‡ Vilnius University, Naugarduko 24, Vilnius, 232044, Lithuania

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The reaction of *trans*-4-alkylcyclohexanecarboxylic acid chlorides, 4-alkylbenzoic, 4-(*trans*-4-alkylcyclohexyl)-benzoic, 4-alkyl-3-substituted biphenyl-4′-carboxylic acids (**I**) with 4-hydroxy-3′-substituted benzonitriles (**IIa-d**) and 4-hydroxy-3′-substituted-4′-cyanobiphenyls (**IIe** and **g**) has produced the corresponding esters (**IIIa-v**). The mesomorphic properties of the esters and electrooptic and dynamic parameters of the mixtures containing these compound have been studied. It has been shown that the liquid-crystalline mixtures containing 4-cyano-3-substituted-4′-biphenyl esters of 4-alkylbenzoic and *trans*-4-alkylcyclohexanecarboxylic acids have higher threshold voltages and saturation voltages in comparison with the analogous mixtures containing 4-cyano-3-substituted phenyl esters of 4-(*trans*-4-alkylcyclohexyl)benzoic acids.

1. Introduction

Mesomorphic compounds with high positive dielectric anisotropies are an integral part of liquid-crystalline mixtures for electrooptic display devices now widely available. Such compounds ensure not only a director response to an electric field but also allow (depending on their polarity and concentrations) liquid-crystalline mixtures to be obtained with parameters which are optimim for specific device applications. However, the compounds with high dielectric anisotropy are not always suitable as components of liquid-crystalline mixtures. This can result from a high nematic–isotropic transition or by the absence of the mesomorphic properties, by poor miscibility or strong molecular interactions between non-polar and polar components of mixtures, leading to a viscous nematic phase and unsatisfactory electrooptic parameters of the liquid-crystalline compositions.

In order to continue the investigation [1–5] of the liquid-crystalline properties of compounds that are characterized by a positive dielectric anisotropy we have obtained 3-substituted-4-cyanophenyl esters of 3-(*trans*-4-alkylcyclohexyl)benzoic, 4-alkyl-3-substituted biphenyl-4′-carboxylic acids, 4-cyano-3-substituted biphenyl esters

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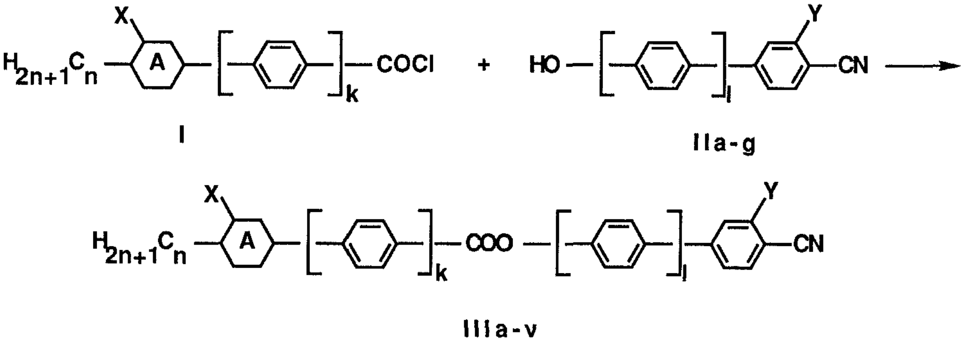
* Author for correspondence.

of *trans*-4-alkylcyclohexanecarboxylic and 4-alkylbenzoic acids. We have proposed, taking into consideration a weakening of the molecular interactions when lateral substituents are introduced into the molecules of mesomorphic compounds, that the derivatives of 4-cyano-3-bromophenyl will have a lower nematic–isotropic transition temperature than the corresponding fluoro-derivatives, and liquid-crystalline mixtures containing these compounds will be characterized by low threshold voltages and steeper voltage–contrast characteristics.

2. Results and discussion

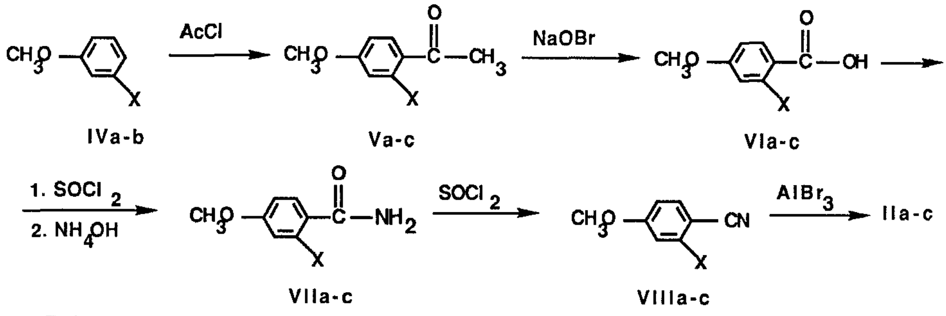
3-Substituted-4-cyanophenyl esters of 4-(*trans*-4-alkylcyclohexyl)benzoic, 4-alkyl-3-substituted biphenyl-4-carboxylic acids, 4-cyano-3-substituted biphenyl esters of *trans*-4-alkylcyclohexanecarboxylic and 4-alkylbenzoic acids (**IIIa–v**) were prepared by the interaction of chlorides of *trans*-4-alkylcyclohexanecarboxylic, 4-alkylbenzoic, 4-(*trans*-4-alkylcyclohexyl)benzoic, 4-alkyl-3-substituted biphenyl-4′-carboxylic acids (**I**) with 4-hydroxy-3-substituted benzonitriles (**IIa–d**) and 4-hydroxy-3-substituted-4′-cyanobiphenyls (**IIe and g**) and 4-hydroxy-3-substituted-4′-cyanobiphenyls (**IIe and g**).



IIIa-v

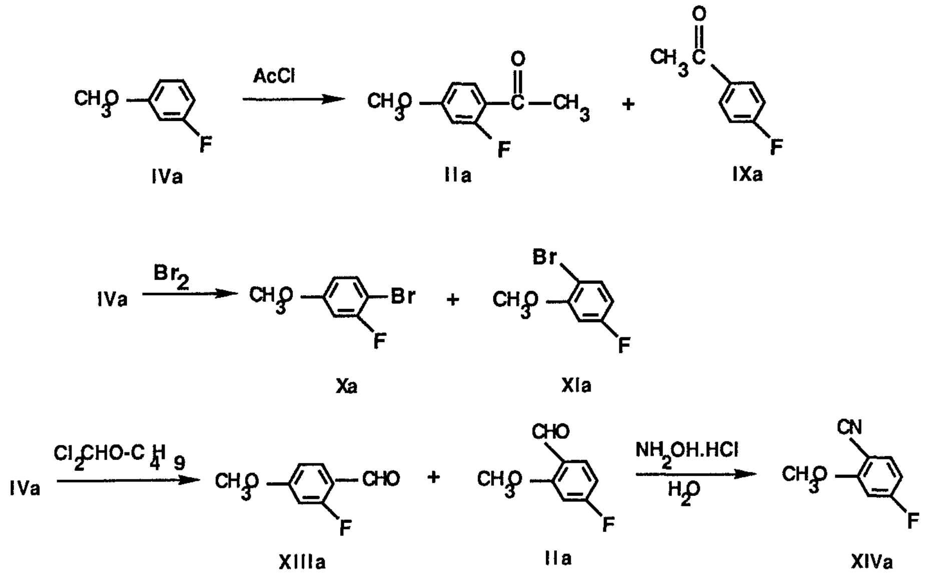
$n=4, 5, 6$; $X=\mathrm{H, Cl, CH_3}$; A = benzene ring (B), cyclohexane ring (C); $k=0$ or 1; $l=0$ or 1; $Y=\mathrm{H, F, Cl, Br, CH_3}$.

3-Fluoro-4-cyanophenol (**IIa**), 3-chloro-4-cyanophenol (**IIIb**) and 3-bromo-4-cyanophenol (**IIc**) were obtained from the corresponding *m*-halogenoanisoles (**IVa–c**) by acetylation and oxidation of the synthesized ketones (**Va–c**) with hypobromites of alkaline metals and by conversion of the acids (**VIa–c**) into the corresponding amides (**VIIa–c**) and then nitriles, the demethylation of the latter with aluminium bromide or chloride and boron tribromide yields the phenols (**IIa–c**).



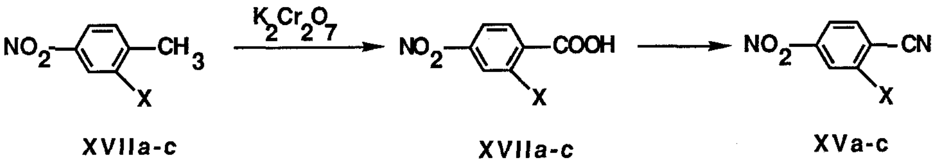
a = F, b = Cl, c = Br.

In this case the overall yield of fluorophenol (**IIa**) is 18 per cent and somewhat lower than that of chlorophenol (**IIb**) (23 per cent) and bromophenol (**IIc**) (21 per cent). This may be related to the fact that 4-fluoro-2-methoxyacetophenone is formed along with the main product 2-fluoro-4-methoxyacetophenone (**IVa**) in the course of acetylation of *m*-fluoranisole, contrary to other *m*-halogenoanisoles. It should be noted that not only the acetylation of *m*-fluoroanisole but also its bromination and formylation are accompanied by the formation of by-products; the yield of acetophenone (**IXa**) not exceeding 15 per cent during the acetylation, the yield of the analogous isomer (**XIa**) being no less than 25 per cent during the bromination and the yield of (**XIIa**) being in a prevailing quantity during the formylation. Therefore while the necessary product (**IIa**) was isolated after the cyanation of the bromides (**Xa**, **XIa**) and the demethylation of the nitriles, 4-fluoro-2-methoxybenzonitrile (**XIVa**) was obtained after the treatment of the formylation product.

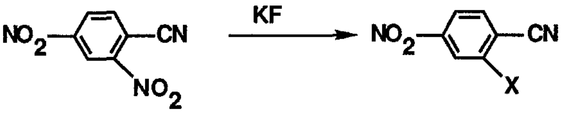


It is known [6] that the nitro-group of the esters of 4-nitrobenzoic acids is easily substituted by an alkyloxy group during the reaction with alkaline metal alcolates. Of some interest was the investigation of the possibility of an analogous substitution of the nitro-group in 4-nitro-3-halogenobenzonitriles (**XVa–c**) which, in contrast to *m*-halogenoanisoles, can be obtained without using a rather undesirable decomposition of diazonium salts.

4-Nitro-3-halogenobenzonitriles (**XVa–c**) were synthesized by oxidation of the corresponding toluenes (**XVIa–c**) and then by successive conversion of the acids (**XVIIa–c**) into nitriles.



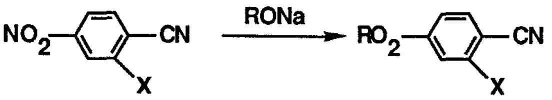
4-Nitro-2-fluorobenzonitrile was also obtained by treatment of 2,4-dinitrobenzonitrile with potassium fluoride [2].



XVIII

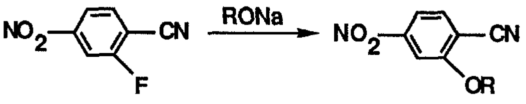
XVa

The investigations showed that the highest yield of substitution products (80–90 per cent) is observed for the chloro-derivative (**XVb**) during reaction of 4-nitro-2-halogenobenzonitriles (**XVa–c**) with alcolates of alkaline metals and alkaline alcohol. 4-Alkyloxy-2-brombenzonitriles (**VIIIc**) were formed with a yield of 30–35 per cent while another substitution product, 4-nitro-2-alkyloxybenzonitrile (**XIX**), was obtained when 4-nitro-2-fluorobenzonitrile (**XVa**) was refluxed with the alkaline metal alcolates, the yield being 20–25 per cent.



XVa,b

VIIIa,b



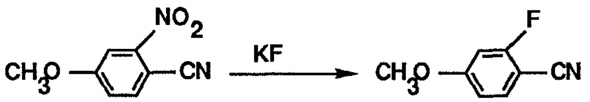
XVa

XIX

$R = CH_3, C_2H_5$

Therefore, the corresponding fluorophenol (**IIa**) can be obtained from the nitro derivative (**XVa**) only by a further reduction of the nitro group, by diazotization of the amino group and then by decomposition of the diazonium tetrafluoroborate.

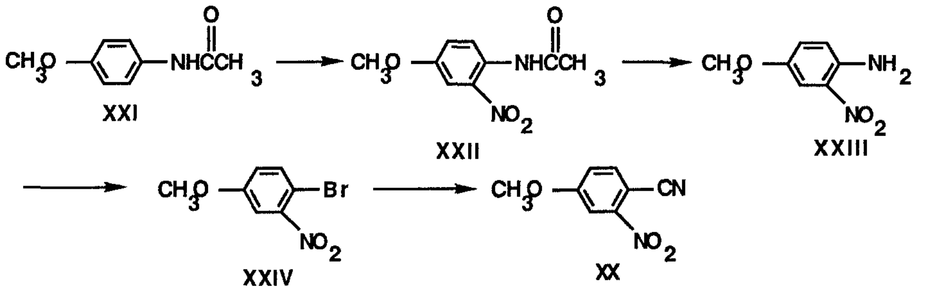
Since the optimization of the methods for obtaining 3-fluoro-4-cyanophenol (**IIa**) is of obvious interest, other possible ways of obtaining this compound or its semi-products were considered. It was found that the treatment of 4-methoxy-2-chlorobenzonitrile (**VIIIb**) with potassium fluoride at an elevated temperature in the presence of a catalyst does not yield the corresponding fluoro-derivative (**VIIIa**) while an analogous reaction with 4-methoxy-2-nitrobenzonitrile (**XX**) yields only 20 per cent of 4-methoxy-2-fluorobenzonitrile (**VIIIa**). It should be noted that the reaction of 2,4-dinitrobenzonitrile (**XVIII**) with potassium fluoride forms the substitution product (**XVa**) with a higher yield:



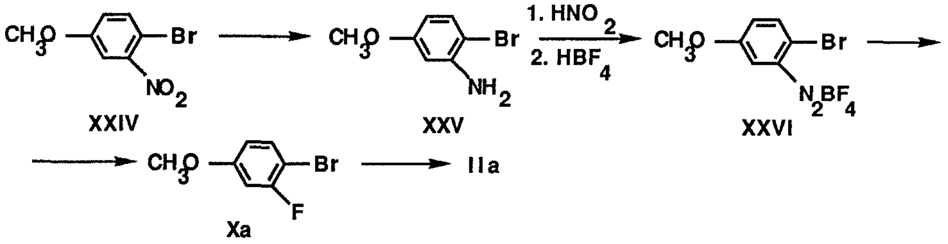
XX

VIIIa

4-Methoxy-2-nitrobenzonitrile (**XX**) was synthesized from 4-methoxyacetanylide (**XXI**) by nitration, alkaline hydrolysis of the nitro compound (**XXII**) and by conversion of the substituted aniline (**XXIII**) into the bromide (**XXIV**) and then into the nitrile:

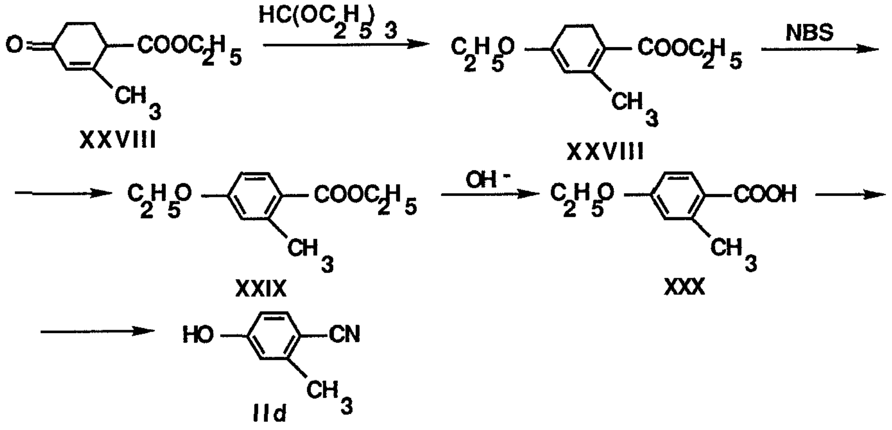


It should be noted that the reduction of 4-methoxy-2-nitrobromobenzene (**XXIV**), diazotization of the aniline (**XXV**) and decomposition of the diazonium tetrafluoroborate (**XXVI**) yields the previously considered bromide (**Xa**) and then the fluorophenol (**IIa**):

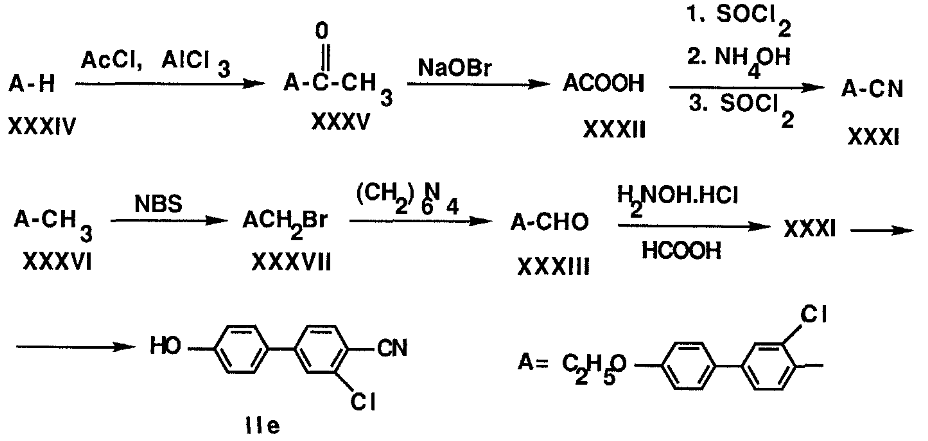


Using analogous conversions, 4-methoxy-2-fluorobenzonitrile (**VIIIa**) can be synthesized from 3-nitro-4-methoxyphenol, as well. However, this method as well as the previous one is characterized by a low total yield of the product and is more time consuming than the method for obtaining the phenols (**Ia–c**) from *m*-halogenoanisoles (**IVa–c**) [1].

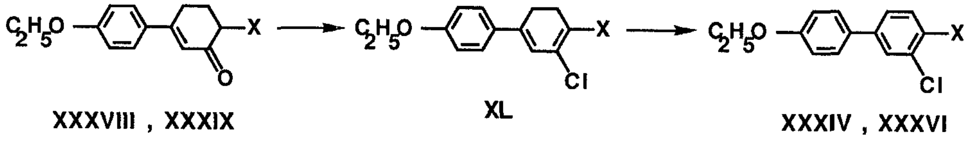
4-Hydroxy-2-methylbenzonitrile (**IId**) was synthesized in a similar way from 3-methylphenol or from ethyl 2-methylcyclohex-2-ene-4-one-1-carboxylate (**XXVII**) [7] by reaction with triethylorthoformate and *N*-bromosuccinimide, by subsequent alkaline hydrolysis of the ethyl ester of 4-ethoxy-2-methylbenzoic acid (**XXIX**) and then by conversion of 4-ethoxy-2-methylbenzoic acid (**XXX**) into its nitrile using the methods considered previously:



4′-Hydroxy-3-chloro-4-cyanobiphenyl (**IIe**) was synthesized by de-alkylation of 4-ethoxy-3-chloro-4-cyanobiphenyl (**XXXI**) obtained from the corresponding acid (**XXXII**) or the aldehyde (**XXXIII**). The acid (**XXXII**) was obtained by acetylation of 4′-ethoxy-3-chlorobiphenyl (**XXXIV**) and then by oxidation of the ketone (**XXXV**), while the aldehyde (**XXXIV**) was obtained by bromination of 4′-ethoxy-3-chloro-4-methylbiphenyl (**XXXVI**) and then by conversion of the benzylbromide (**XXXVII**) according to the method of Sommelet.



The biphenyls (**XXXIV** and **XXXVI**) were synthesized from the corresponding 3-(4-ethoxyphenyl)-cyclohex-2-enones (**XXXVIII** and **XXXIX**) by refluxing them with phosphorus pentachloride in inert solvents. In this case the yield of 4′-ethoxy-3-chlorobiphenyl (**XXXIV**) does not exceed 10–15 per cent while the yield of the biphenyl (**XXXVI**) reaches 60–70 per cent. When the reaction temperature is lowered or the reaction time is reduced the yield of the methylbiphenyl decreases. In this reaction the mixture of compound (**XXXVI**) with 4-(4-ethoxyphenyl)-2-chloro-1-methylcyclohex-1,3-diene (**XL**) is formed, the latter compound is obtained with a yield of 65 per cent without an aromatization product admixture by reaction of the ketone (**XXXIX**) with Wilsmeyer's complex. When the ketone (**XXXIX**) reacts with the complex of thionyl chloride and dimethylformamide the intermediate diene formed is easily aromatized up to biphenyl.



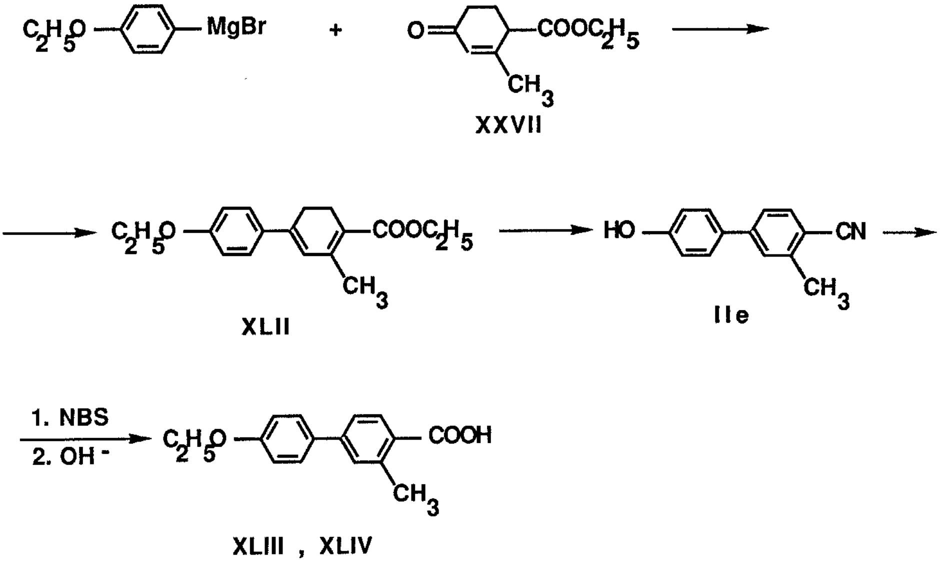
$X = H$ (**XXXVIII** and **XXXIV**), CH_3(**XXXIX**, **XL** and **XXXVI**).

It should be noted that, in contrast to the methylcyclohexenone (**XXXIX**), 3-(4-ethoxyphenyl)cyclohex-2-enone (**XXXVIII**) is formylated with Wilsmeyer's complex. However, the formyl group enters the second position of the cyclohexene ring, leading to the formation of 4-ethoxy-2-formyl-3-chloro-biphenyl (**XLI**) with a yield of 10–15 per cent.

Other attempts to introduce the formyl group into the sixth position of the cyclohexene ring also failed. The formylation of the ketone (**XXXVIII**) with ethyl formate in the presence of alkali metal alcolates leads, as shown earlier [8], to a mixture of products whereas 3-(4-ethoxyphenyl)cyclohex-2-enone does no actually react with the dimethylacetal of dimethylformamide.

3-(4-Ethoxyphenyl)cyclohex-2-enones (**XXXVIII** and **XXXIX**) were obtained by the reaction of 4-ethoxyphenylmagnesium bromide with 3-butoxycyclohex-2-enones.

4'-Ethoxy-3-methylbiphenyl-4-carboxylic acid (**XLIV**), from which 4-hydroxy-3-methyl-4-cyanobiphenyl was obtained according to the scheme considered earlier (**IIe**) [7], was synthesized by the reaction of 4-ethoxyphenylmagnesium bromide with the ethyl 2-methylcyclohex-2-ene-4-one-1-carboxylate (**XXVII**), by an aromatization of the obtained product (**XLII**) with *N*-bromosuccinimide and by hydrolysis of the ethyl ester (**XLIII**).



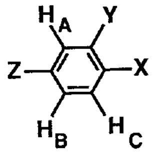
The initial acids (**I**) were obtained from the corresponding hydrocarbons.

The composition and structure of the compounds obtained were confirmed by elemental analysis and by IR and proton NMR spectra. The NMR spectra of the alkyloxy(nitro)benzonitriles and their derivatives are presented in table 1.

In the NMR spectra of the 4-ethoxy-3-chlorobiphenyls (**XXXV** and **XXXVI**), a quartet signal of the α-methylene protons of the ethoxy groups is located at 3·86 ppm (7 Hz). The signals from the aromatic protons of these and the final products (**IIIa–v**) are observed in the proton NMR spectra within the ranges 6·58–7·50 and 7·00–8·12 ppm, respectively. In the NMR spectra of 4-(4-ethoxyphenyl)-2-chloro-1-methylcyclohex-1,3-diene (**XL**), a singlet signal at 1·76 ppm belongs to the protons of the methyl group. The singlet signal of the methyl group protons of 4-ethoxy-3-methyl-4-cyanobiphenyl (**XV**) is observed in the spectrum at 2·50 ppm. In spectra of the derivatives of 4-(*trans*-4-alkylcyclohexyl)benzoic acids (**IIIa–d**) the signals of the cyclohexane fragment are observed within the range 1·3–2·69 ppm. In the IR spectra of the esters the intense bands at 1705 and 2230 cm^{-1} correspond to the stretching vibrations of the carboxyl group and the cyano group, respectively.

The investigation of the liquid-crystalline properties of the compounds (**IIIa–v**) showed that the incorporation of halogen atoms into the position ortho to the nitrile group in comparison with the unsubstituted analogue is accompanied by a lowering of the nematic–isotropic transition temperature by 19°C and 25°C for the fluoro-derivatives (**IIIb** and **IIIg**); by 21°C and 13°C for the chloro-derivatives (**IIIe** and **IIIh**);

Table 1. Data extracted from the proton NMR and IR spectra of the compounds.

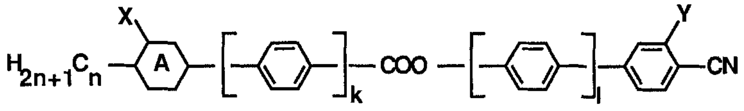


			Chemical shifts, (ppm) of hydrogen			Spin–spin coupling constants			Chemical shifts of substituents/ ppm	IR absorption bands positions/cm^{-1}
Z	*Y*	*X*	H_A	H_B	H_C	J_{BC}/Hz	J_{AB}/Hz	J_{BC}/Hz		
CH_3O	F	CN	(6·64–6·83)		7·43–7·60	–	–	–	3·87 (CH_3O)	2215 (CN)
F	CH_3O	CN	(6·65–6·83)		7·48–7·65	–	–	–	3·96 (CH_3O)	2235 (CN)
HO	F	CN	(6·71–6·88)		7·46–7·64	–	–	–		2220 (CN)
CH_3O	Cl	CN	6·98	6·85	7·29	8·29	2·4	0·5	3·85 (CH_3O)	2225 (CN)
CH_3O	Br	CN	7·17	7·94	7·56	8·5	2·4	0·5	3·88 (CH_3O)	2230 (CN)
NO_2	Cl	CN	9·03	8·90	8·54	8·8	2·5	0·5		–
CH_3O	NO_2	Br	7·33	6·96	7·55	8·9	2·8	–	3·85 (CH_3O)	–
CH_3O	NO_2	CN	7·87	7·52	8·01	8·7	2·6	0·3	4·07 (CH_3O)	2230 (CN)
NO_2	C_2H_5O	CN	(8·34–8·07)		6·87	9·2	–	–	4·14, 1·47 (C_2H_5O)	–
C_2H_5O	CH_3	CN	(6·83–7·23)		7·68	9·0	–	–	2·50 (CH_3)	–

by 7°C and 6°C for the bromo-derivatives (**IIId** and **IIIj**); and by 26°C and 25°C for the methyl-derivatives (**IIIl** and **IIIk**) and leads to an insignificant narrowing of the nematic range by 4°C and 14°C for the fluoro-derivatives (**IIIb** and **IIIg**) and to a drastic narrowing of the nematic range for compounds containing cumbersome substituents: by 50°C and 74°C for chloro-derivatives (**IIIe** and **IIIh**) and 83°C and 101°C for the bromo-derivatives (**IIId** and **IIIj**). It should be noted, that the incorporation of a chlorine atom or a methyl group into the position ortho to the nitrile group of the esters (**IIIp** and **u**) in comparison with the unsubstituted analogues [9] is accompanied only by a narrowing of the nematic range by 106°C and 84°C, respectively which is larger than for the analogous change for the esters (**IIIe** and **IIIl**) (see table 2).

The correlation of the electrooptic parameters of the liquid-crystalline mixtures containing compounds (**IIIa–k** and **IIIp–r**) (see table 3) showed that the esters (**IIIa–k**) are the most promising for use as components of liquid-crystalline mixtures intended for electrooptic display devices. These compounds (**IIIa–k**) give liquid-crystalline mixtures with lower threshold and saturation voltages. The 3-fluoro-4-cyanophenyl esters (**IIIb–g**) allow us to obtain mixtures with better parameters. The mixtures containing these fluoro-derivatives (**IIIb** and **g**) are characterized by the lowest threshold (2·21 V and 2·01 V) and saturation voltages (2·96 V and 2·90 V) and steeper voltage-contrast characteristics.

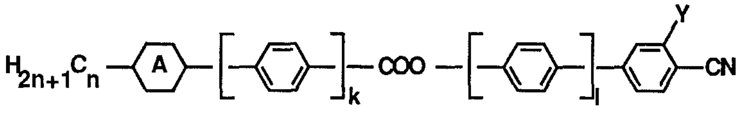
Table 2. Yields and transition temperatures and nematic ranges of the esters (**IIIa–v**)



IIIa-v

							Yield	Transition temperatures/°C							
Compound	*n*	*X*	*A*	*k*	*l*	*Y*	%	C		S		N		I	Δ*T*/°C
IIIa	5	H	C	1	0	H	70	●	109			●	218	●	109
IIIb	5	H	C	1	0	F	67	●	90			●	195	●	105
IIIc	5	H	C	1	0	Cl	52	●	88			●	147	●	59
IIId	5	H	C	1	0	Br	44	●	102			●	128	●	26
IIIe	5	H	C	1	0	CH_3	46	●	83			●	135	●	52
IIIf	5	H	B	1	0	H	71	●	111			●	229	●	118
IIIg	5	H	B	1	0	F	64	●	86			●	190	●	104
IIIh	5	H	B	1	0	Cl	42	●	98			●	142	●	44
IIIi	5	Cl	B	1	0	Cl	36	●					104	●	0
IIIj	5	H	B	1	0	Br	48	●	105			●	122	●	17
IIIk	5	H	B	1	0	CH_3	57	●	86			●	146	●	60
IIIl	5	CH_3	B	1	0	H	42	●	107			●	164	●	57
IIIm	6	H	B	1	0	H	49	●	103			●	213	●	110
IIIn	6	Cl	B	1	0	H	48	●	66	●	107	●	143	●	77
IIIo	6	Cl	B	1	0	Cl	37	●					74	●	0
IIIp	4	H	C	0	1	Cl	38	●	77			●	133	●	56
IIIq	4	H	C	0	1	CH_3	49	●	76			●	154	●	78
IIIr	5	H	C	0	1	CH_3	59	●	92			●	158	●	66
IIIs	5	H	B	0	1	Cl	53	●					129	●	0
IIIt	5	H	B	0	1	CH_3	36	●	98			●	146	●	48
IIIu	6	H	B	0	1	Cl	59	●					120	●	0

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



IIIa-v

Compound	*n*	*A*	*k*	*l*	*Y*	Threshold voltage/V	Saturation voltage/V	Δ*U*/V
IIIa	5	C	1	0	H	2·80	4·00	1·20
IIIb	5	C	1	0	F	2·24	2·96	0·72
IIIc	5	C	1	0	Cl	2·25	3·37	1·12
IIId	5	C	1	0	Br	2·23	3·35	1·12
IIIe	5	C	1	0	CH_3	2·66	3·38	0·72
IIIf	5	B	1	0	H	2·74	3·90	1·16
IIIg	5	B	1	0	F	2·01	2·90	0·89
IIIh	5	B	1	0	Cl	2·32	3·36	1·04
IIIk	5	B	1	0	CH_3	2·67	3·41	0·74
IIIp	4	C	0	1	Cl	2·87	3·92	1·05
IIIq	4	C	0	1	CH_3	3·21	4·06	0·85
IIIr	5	C	0	1	CH_3	3·28	4·18	0·90

†The compositions of the liquid-crystalline mixtures are 25 per cent 4-ethoxyphenyl *trans*-4-butylcyclohexylcarboxylate, 55 per cent 4-ethoxyphenyl *trans*-4-hexylcyclohexanecarboxylate and 20 per cent of the compound under investigation.

It should be noted that the liquid-crystalline mixtures containing the less polar methyl derivatives (**IIIe** and **IIIk**) are characterized by higher values of the threshold (2·66 V and 2·67 V) and saturation voltages (3·38 V and 3·41 V), but have steeper voltage–contrast characteristics. It can result from a considerable weakening of the anisotropic molecular interactions which are responsible for orientational order in the nematic phase, after a methyl group is incorporated in a position ortho to the nitrile group.

Thus, the results obtained show, that our supposition is not yet confirmed. An increase in the volume of a halogen atom, which is in a position ortho to the nitrile group does not lead to a fall in the nematic–isotropic transition temperature or an increase of the threshold and saturation voltages of the liquid-crystalline mixtures containing these compounds. From the esters (**IIIa**–**v**), the 3-fluoro-4-cyanophenyl derivatives (**IIIb** and **g**) are the most promising for use as components of liquid-crystalline mixtures for electrooptic display devices. These compounds are characterized by a nematic–isotropic transition temperature 20°C lower than the unsubstituted analogues (**Ia** and **IIa**), have a wide nematic range in contrast to other esters (**IIIa**–**v**) and allow us to obtain liquid-crystalline mixtures with low threshold and saturation voltages. A subsequent increase in the size of the substituents (chloro derivatives and bromo derivatives) is accompanied only by a great narrowing of the nematic range and an increase of the threshold and saturation voltages of the liquid-crystalline mixtures containing these compounds.

3. Experimental

The infrared spectra of 0·1 M solutions of the compounds dissolved in carbon tetrachloride were recorded on a SPECORD IR-75 spectrophotometer. The proton

NMR spectra of 10 per cent solutions in carbon tetrachloride or perdeuteroacetone with hexamethyldisiloxane as an internal standard were recorded with a TESLA BS-467 or a TESLA BS-56&A spectrometer. The textures of different phases and the transition temperatures were determined with a polarizing microscope. The measurement of the electrooptic parameters of the mixtures was performed at room temperature in twisted nematic cells with a 10 μm spacer, a thin polyamide layer was used to obtain homogeneous oriented samples.

3.1. *4-Methoxy-2-fluorobenzonitrile* (**VIIIa**)

0·3 mol of bromide was added drop by drop while stirring to a solution of 0·3 mol of *m*-flouroranisole in 50 ml of chloroform. After the addition the mixture was refluxed for 2 h, washed with a 15 per cent sodium hydroxide solution and with water and dried with anhydrous sodium sulphate. The solvent being removed the residue was distilled and the fraction with the boiling point 210–220°C (760 mm Hg) was collected. The bromide obtained (0·24 mol) was mixed with 0·28 mol of copper cyanide in 35 ml of dimethylformamide, refluxed with stirring for 8 h, cooled, diluted with 100 ml of diethyl ether, washed with 25 per cent ammonium hydroxide and water and dried with anhydrous sodium sulphate. The residue obtained after the solvent had been removed was recrystallized from hexane. Yield 34 per cent; mp 58–59°C; [1] mp 58–60°C.

3.2. *4-Methoxy-2-chlorobenzonitrile* (**VIIIb**)

A mixture of 0·1 mol of 4-nitro-2-chlorobenzonitrile obtained from 4-nitro-2-chlorobenzoic acid and 0·2 mol of potassium hydroxide in 250 ml of methanol was refluxed for 20 h and diluted with 1 l of water. The precipitated crystals were filtered off, washed with water and recrystallized from 2-propanol. Yield 83 per cent; mp 76°C.

The following compounds were obtained in a similar way: 4-ethoxy-2-chlorobenzonitrile (**VIIIb**), yield 75 per cent mp 60°C; 4-ethoxy-2-bromobenzonitrile (**VIIIc**), yield 31 per cent mp 65°C; and 4-nitro-2-ethoxybenzonitrile (**XIX**), yield 13 per cent, mp 98°C.

3.3. *4-Methoxy-2-bromobenzonitrile* (**VIIIc**)

4-Methoxy-2-bromobenzoic acid obtained from *m*-bromoanisole was converted into 4-methoxy-2-bromobenzonitrile using the methods described in [4]. Yield 52 per cent; mp 78°C.

3.4. *2-Fluoro-4-cyanophenol* (**IIa**)

A mixture of 0·15 mol of 4-methoxy-2-fluorobenzonitrile and 0·25 mol of anhydrous aluminium chloride in 200 ml of benzene was refluxed for 15 h and poured into 300 ml of a 10 per cent hydrochloric acid solution. The organic layer was diluted with 100 ml of diethyl ether, washed with water and dried with anhydrous sodium sulphate. The residue obtained after the solvent had been removed was crystallized from a mixture of toluene and hexane (3:1). Yield 67 per cent , mp 118°C.

The following compounds were obtained in a similar way: 3-chloro-4-cyanophenol (**IIb**), yield 70 per cent, mp 162°C; 3-bromo-4-cyanophenol (**IIc**), yield 54 per cent, mp 164°C; 4-cyano-3-methylphenol (**IId**), yield 45 per cent, mp 136°C; and 4-hydroxy-3-methyl-4-cyanobiphenyl (**IIg**), yield 78 per cent, mp 152°C.

3.5. *4′-Ethoxy-3-chloro-4-methylbiphenyl* (**XXXVI**)

A mixture of 0·1 mol of 3-(4-ethoxyphenyl)-6-methylcyclohex-2-enone and 0·1 mol of phosphorous pentachloride in 100 ml of hexane was refluxed for 4 h, cooled and poured into 250 ml of a 20 per cent sodium hydroxide solution. The organic layer was separated, washed with water to neutral, dried with anhydrous sodium sulphate and then filtered through a layer of alumina. The residue obtained after the solvent had been removed was crystallized from 2-propanol, yield 64 per cent, mp 99°C.

3.6. *4-Hydroxy-3-chloro-4-cyanobiphenyl* (**IIe**)

A mixture of 0·02 mol of 4-ethoxy-3-chloro-4-cyanobiphenyl and 0·04 mol of anhydrous aluminium chloride in 100 ml of toluene was stirred for 4 h at 60°C and poured into 250 ml of a 5 per cent hydrochloric acid solution. The organic layer was diluted with 100 ml of diethyl ether, washed with water and dried with anhydrous sodium sulphate. The residue obtained after the solvent had been removed was crystallized from toluene. Yield 54 per cent, mp 206°C.

3.7. *3-Fluoro-4-cyanophenyl 4-*(trans-*4-pentylcyclohexyl*) *benzoate* (**IIIb**) [1]

A mixture of 0·05 mol of 4-*trans*-4-pentylcyclohexyl)benzoic acid chloride, 0·06 mol of 3-fluoro-4-cyanophenol and 0·1 mol of pyridine in 100 ml of anhydrous diethyl ether was stirred for 6 h, washed with water and dried with anhydrous sodium sulphate. The residue obtained after the solvent had been removed was crystallized from 2-propanol. Yield 67 per cent; T_{CN} = 90°C and T_{NI} = 195°C. The other esters presented in table 1 were obtained in a similar way.

References

[1] Kelly, S. M., 1984, *Helv. chim. Acta*, **67**, 1572.
[2] Sasaki, M., Takeuchi, K., Sato, H., and Takatsu, H., 1984, *Molec. Crystals liq. Crystals*, **109**, 169.
[3] Kelly, S. M., and Schad, H., 1984, *Helv. chim. Acta*, **67**, 1580.
[4] McDonnell, D. G., Raynes, E. P., and Swith, R. A., 1989, *Liq. Crystals*, **6**, 515.
[5] Gerber, P. R., and Schadt, M., 1982, *Z. Naturf.* (*a*), **37**, 179.
[6] Bradscher, Ch. K., Brown, F. C., and Porfer, H. K., 1954, *J. Am. chem. Soc.*, **76**, 2357.
[7] Bezborodov, V. S., Lapanik, V. I., Petrovitch, A. E., and Polozov, G. I., 1986, *J. org. Chem.* (in Russian), **22**, 1482.
[8] Labidalle, S., Jean, E., and Moskowitz, H., 1981, *Tetrahedron Lett.*, **22**, 2869.
[9] Gray, G. W., and McDonnell, D. G., 1979, *Molec. Crystals liq. Crystals*, **53**, 147.