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Synthesis and mesomorphic properties of some derivatives of 2-methylcyclohex-2-ene-4-one-1-carboxylic and *cis*-2,6-dimethyl cyclohex-2-ene-4-one-1-carboxylic acids

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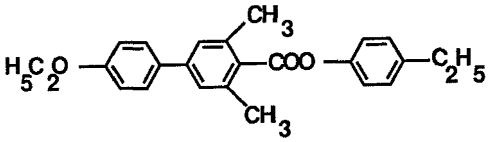
Mesomorphic derivatives prepared from ethyl esters of 2-methylcyclohex-2-ene-4-one-1-carboxylic and *cis*-2,6-dimethylcyclohex-2-ene-4-one-1-carboxylic acids have been synthesized. It has been shown that the compounds obtained are characterized by a lower nematic–isotropic transition temperature (10–20°C) and a considerably narrower nematic range in comparison with the analogous derivatives of 4-alkylcyclohex-3-ene-carboxylic and *trans*-4-alkylcyclohexane-carboxylic acid.

1. Introduction

Liquid-crystalline compounds containing lateral substituents in comparison with the unsubstituted analogues have, as a rule, a lower transition temperature and are promising for producing liquid-crystalline mixtures, the liquid-crystalline range of which includes temperatures below 0°C. With some exceptions [1, 2], the liquid-crystalline properties of derivatives of cyclohexene, cyclohexane and biphenyl containing lateral methyl groups are still insufficiently studied. In this connection some liquid-crystalline derivatives of 4′-ethoxy-3,5-dimethylbiphenyl-4-carboxylic acid (**I**). 4′-hydroxy-3-methyl(-5-*Y*)-4-cyanobiphenyl (**II, III**) and esters of *trans*-4-alkyl-*cis*-2-methylcyclohexane-1-*n*-carboxylic acid (**IV, V**), *trans*-4-alkyl (4-methoxyphenyl)-*trans*-2-methylcyclohexane-1-*n*-carboxylic acid (**VI, VII**), 4-alkyl-*cis,cis*-2,6-dimethylcyclohex-3-ene-1-*n*-carboxylic acid (**VIII, IX**) and of *trans*-4-alkyl-*cis,cis*-2,6-dimethylcyclohexane-1-*n*-carboxylic acid (**X**) were synthesized in order to continue previous investigations [3, 4].



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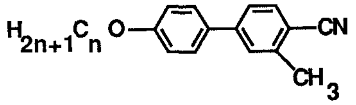

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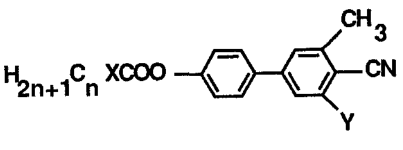

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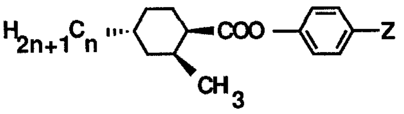
*Author for correspondence.



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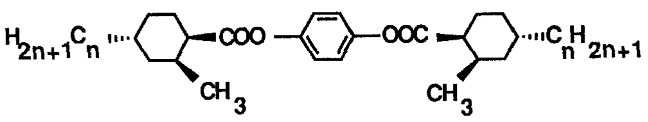

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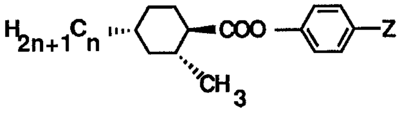

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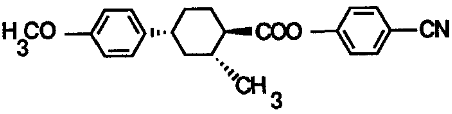

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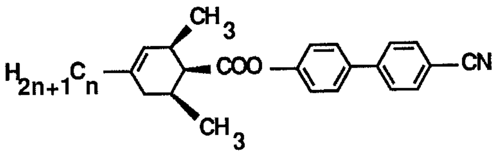

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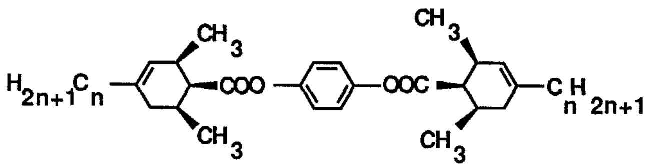

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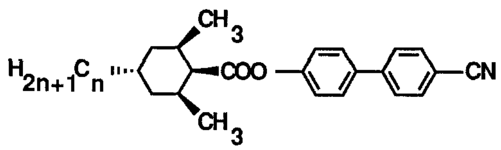


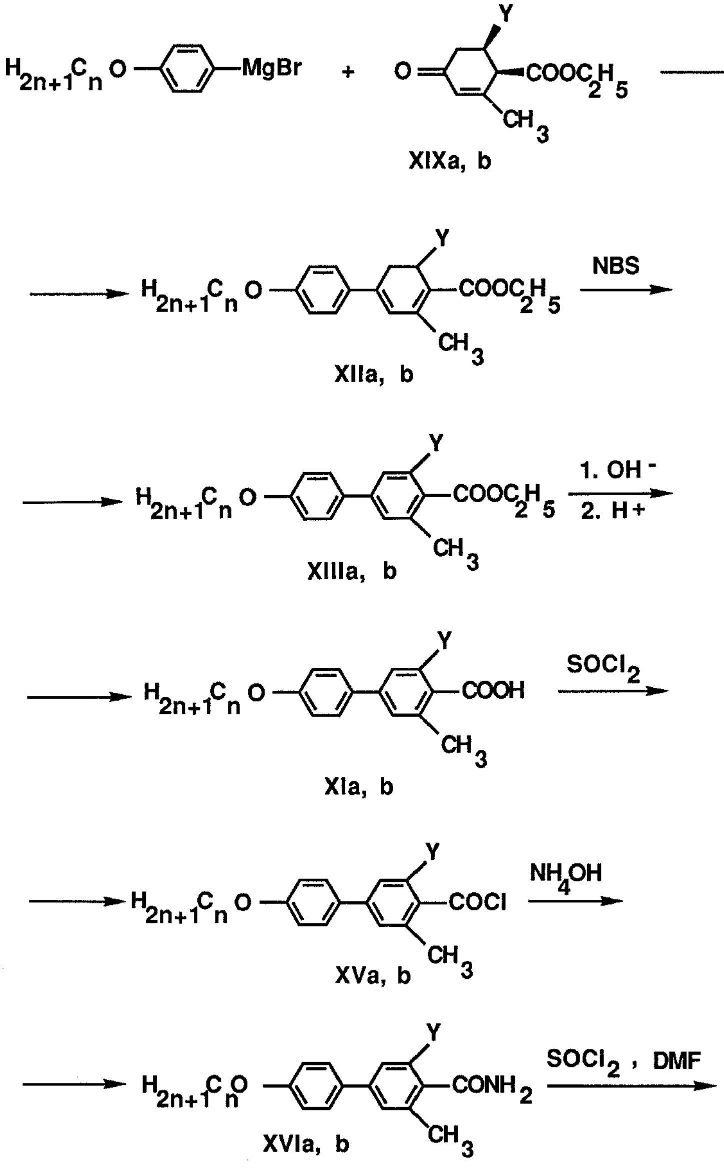
(X)

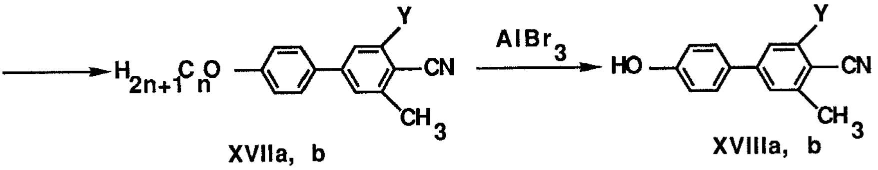
$n = 3$–8; $Z = OC_4H_9$, OC_6H_{13}, C_6H_5, C_6H_4CN; $X = C_6H_4$, *trans*-1,4-cyclohexyl; $Y = H$, CH_3.

2. Results and discussion

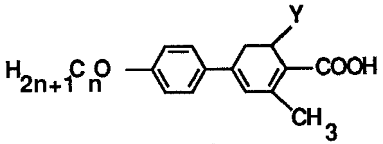
4′-Ethoxy-3,5-dimethylbiphenyl-4-carboxylic and 4′-alkyloxy-3-methylbiphenyl-4-carboxylic acids (**XIa** and **b**) were synthesized by dehydrobromination of the products from the reaction of ethyl esters of 4-(4-ethoxyphenyl)-2,6-dimethylcyclohexa-1,3-diene-1-carboxylic and 4-(4-alkyloxyphenyl)-2-methylcyclohexa-1,3-diene-1-carboxylic acids (**XIIa** and **b**) with *N*-bromosuccinimide, and then by alkaline hydrolysis of ethyl esters (**XIIIa** and **b**) of 4′-ethoxy-3,5-dimethylbiphenyl-4-carboxylic and 4′-alkyloxy-3-methylbiphenyl-4-carboxylic acids.

4′-Hydroxy-3-methyl-4-cyanobiphenyl and 4′-hydroxy-3,5-dimethyl-4-cyanobiphenyl (**XVIIIa** and **b**) were obtained by dehydration of the amides of these acids (**XVIa** and **b**) and by subsequent dealkylation of the alkyl ethers (**XVIIa** and **b**). The esters (**XIIa** and **b**) were synthesized by the reaction of ethyl esters of 2-methylcyclohex-2-ene-4-one-1-carboxylic and *cis*-2,6-dimethylcyclohex-2-ene-4-one-1-carboxylic acids (**XIXa** and **b**) with 4-alkyloxyphenylmagnesium bromides. Additionally, it was established that the yield of esters does not exceed 40–50 per cent after decompostion of the magnesium derivatives using hydrochloric acid or 20 per cent sulphuric acid. In the process of the decomposition the esters are partially hydrolyzed to form 4-(4-alkyloxyphenyl)-2,5-dimethylcyclohexa-1,3-diene-1-carboxylic acids (**XXa** and **b**), and boiling the acids with thionyl chloride immediately yields the corresponding biphenylcarboxylic acid chlorides (**XVa** and **b**).



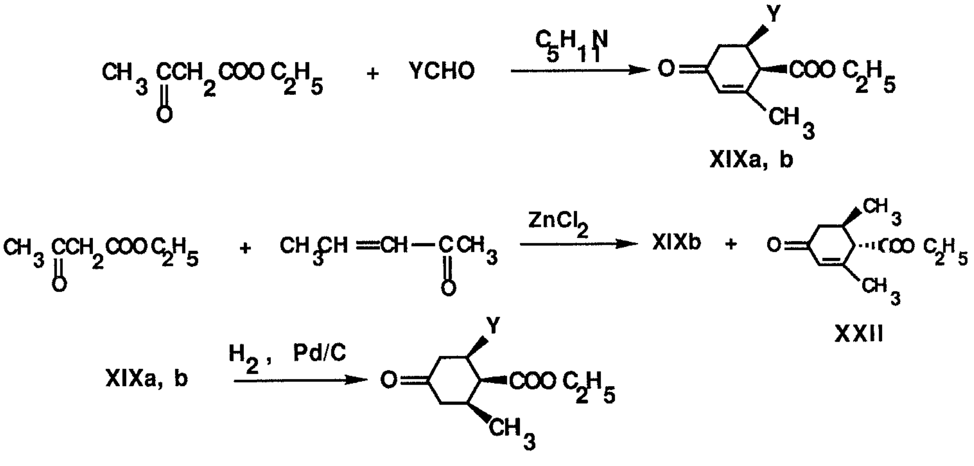


XVIIa, b XVIIIa, b



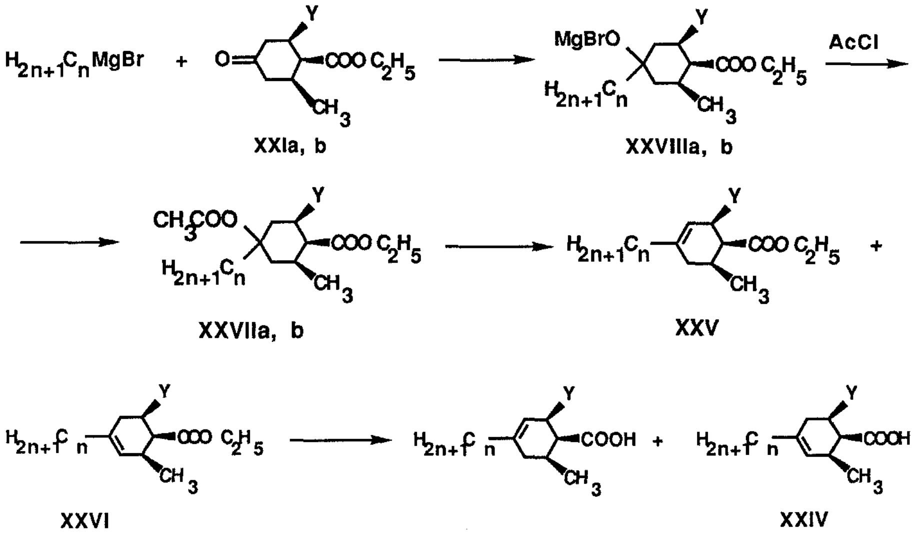
XXa, b $n = 1, 2$; $Y = H(a)$; $CH_3(b)$

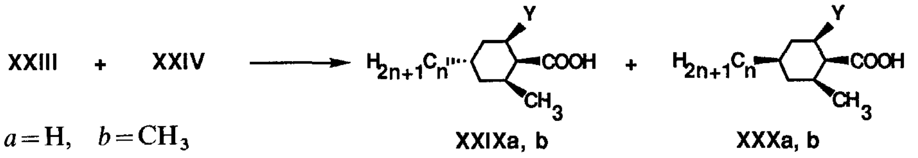
The ethyl esters of 2-methylcyclohex-2-ene-4-one-1-carboxylic and *cis*-2,6-dimethylcyclohex-2-ene-4-one-1-carboxylic acids (**XIXa** and **b**), (catalytic hydrogenation of which in the presence of palladium on carbon results in saturated esters (**XXIa** and **b**), were obtained by interaction of acetoacetic esters with paraformaldehyde or acetaldehyde [5]. It should be noted that the *trans* isomer (**XXII**) is formed concurrently with the ethyl ester of *cis*-2,6-dimethylcyclohex-2-ene-4-one-1-carboxylic acid in an equal quantity during cyclization of the adduct of methylpropenylketone to acetoacetic ester in the presence of zinc chloride.



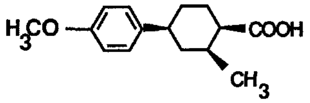
$Y = H, CH_3$

4-Alkyl-*cis*-2-methylcyclohex-3-(4)-ene-1-carboxylic, 4-alkyl-*cis*,*cis*-2,6-dimethylcyclohex-3-ene-1-carboxylic acids (**XXIII** and **XXIV**) were obtained by alkaline hydrolysis of the pyrolysis products (**XXV** and **XXVI**) of the ethyl esters of 4-alkyl-4-acetyloxy-*cis*, *cis*-2,6-dimethylcyclohexane-1-carboxylic acids (**XXVIIa** and **b**) synthesized by reaction of alkylmagnesium bromides with ethyl esters (**XXIa** and **b**) and further by decomposition of the magnesium derivatives (**XXVIIIa** and **b**) using acetyl chloride. *trans*-4-Alkyl-*cis*-2-methylcyclohexane-1-carboxylic and *trans*-4-alkyl-*cis*, *cis*-2,6-dimethylcyclohexane-1-*n*-carboxylic acids (**XXIXa** and **b**) which were separated by crystallization out of the solution of mixtures in hexane from the *cis* isomers (**XXXa** and **b**) simultaneously formed with them, were synthesized by subsequent catalytic hydrogenation of the unsaturated acids (**XXIII** and **XXIV**) in the presence of palladium on carbon.





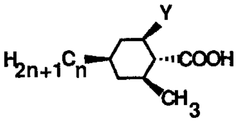
cis-4-(4-Methoxyphenyl)-*cis*-2-methylcyclohexane-1-*n*-carboxylic acid (XXXI) was obtained in a similar way from the mixture of the ethyl esters of 4-(4-methoxyphenyl)-*cis*-2-methylcyclohex-3-ene-1-carboxylic acids formed in an equal quantity during dehydration of the product of reaction of 4-methoxyphenylmagnesium bromide with the ethyl ester of *cis*-2-methylcyclohexane-4-one-1-carboxylic acid.



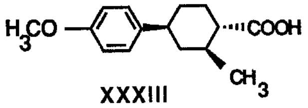
XXXI

It should be noted that in contrast to hydrogenation of the unsaturated acids (**XXIIIa** and **b**; **XXIVa** and **b**) the corresponding *trans* isomer is not formed in this case.

The *trans* acids (**XXXIIa** and **b**; **XXXIII**) and their chlorides were obtained by isomerization of the *cis* acids (**XXXa** and **b**; **XXXXI**) in boiling thionyl chloride.



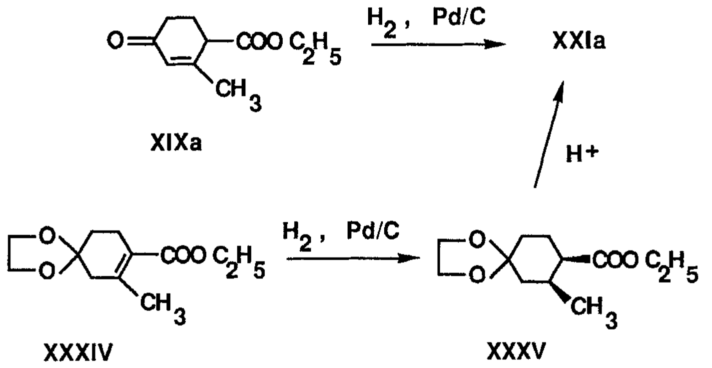
XXXIIa, b

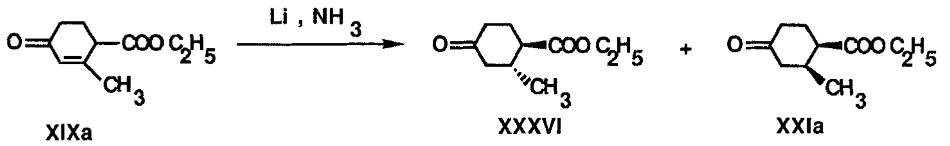


$Y=H, CH_3$ XXXIII

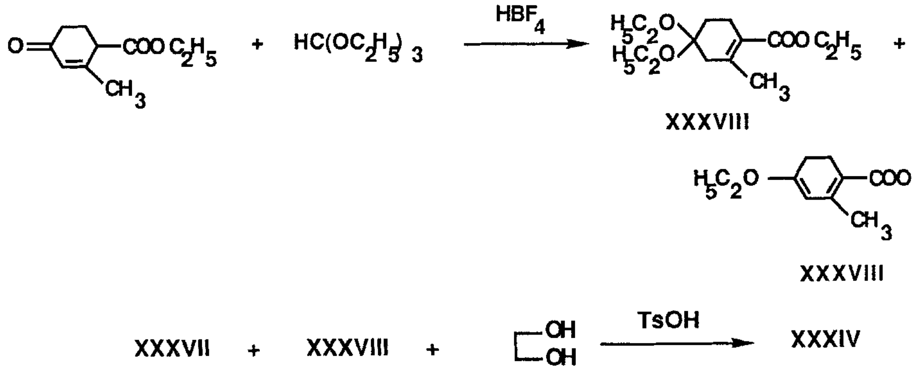
In order to confirm the configuration of the ester substituents (**XXIa** and **b**), the ketone (**XXIa**) was obtained by hydrogenation of the ethyl ester of 4,4-ethylenedioxy-2-methylcyclohex-1-ene-1-carboxylic acid (**XXXIV**) and then by treatment of the ester (**XXXV**) using dilute hydrochloric acid.

A mixture of isomers was obtained when the ketone (**XIXa**) was reduced using lithium in liquid ammonia:





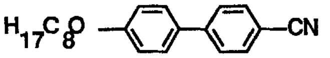
It was not possible to synthesize the ethyl ester of 4,4-ethylenedioxy-2-methylcyclohex-1-ene-1-carboxylic acid (**XXXIV**) by acetalization of the ketone (**XIXa**) using ethylene glycol because the ethylene ketal with the unchanged position of the double bond in the cycle is formed in the course of the reaction. The ethylene ketal was obtained by reaction of ethylene glycol with a mixture of the ethyl esters of 4,4-diethoxy-2-methylcyclohex-1-ene-1-carboxylic (**XXXVII**) and 4-ethoxy-2-methylcyclohexa-1,3-diene-1-carboxylic (**XXXVIII**) acids (formed in a proportion depending on the conditions for performing the reaction when the ketone (**XIXa**) reacts with triethylorthoformate in the presence of fluoroboric acid):



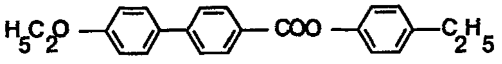
The esters (**I** and **III**–**X**) were usually obtained by reaction of the acid chlorides with 4-substituted phenols in the presence of bases and pyridine.

The composition and structure of the compounds were confirmed by the results of elemental analysis as well as infrared and proton NMR spectra. Thus, in the proton NMR spectrum (δ, ppm) of the ester (**XIXc**) a doublet at 0·95 ($J=7$ Hz) belongs to the signals from the protons of the methyl group located at the sixth carbon atom of the cyclohexene ring. In the proton spectrum a doublet at 0·93 with a spin–spin interaction constant of 4·5 Hz corresponds to the analogous fragment of a *trans* isomer (**XXII**). The proton signals of the methyl groups of the saturated esters (**XXIa** and **b**) are observed in the NMR spectra at 0·86 ($J=7$ Hz) and at 0·93 ($J=7$ Hz) respectively. In the proton NMR spectrum of the mixture of the esters (**XXa**; **XXXVI**) the signals within the ranges of 2·0–3·0 and 0·82–0·93 correspond to the protons of the cyclohexane fragment and the methyl group. In the proton NMR spectrum of the ethyl ester of 4-ethoxy-2-methylcyclohexa-1,3-diene-1-carboxylic acid (**XXXVIII**) two quartet signals of the methylene protons of the ethoxy groups at 3·70 and 4·00 ($J=7$ Hz) are observed along with a singlet signal of an olefin proton at 4·77. Quartet signals of the methylene protons of the ethoxy groups of the ester (**XXXVII**) are observed at 3·37, 4·77 and 4·54 ($J=7$ Hz). Singlets at 3·80 and 3·76 in the proton NMR spectra of the esters (**XXXIV** and **XXXV**) correspond to the signals of protons in dioxalane fragments. The signals of protons of the methyl groups of the biphenyl derivatives (**I**, **II**, **III**, **XIIIa** and **b** and **XVIIa** and **b**) are observed in the proton NMR spectra in the form of singlets at 2·50. Multiplet signals of the olefin protons of the acids (**XXIIa** and **b** and **XXIVa** and **b**) and the esters (**VIII** and **IX**) are seen in the NMR spectra at 5·12. Doublet signals at 0·85 ($J=7$ Hz) belong to the methyl groups of the *trans* acids (**XXIXa** and **b**). Doublet signals at 0·98 and 0·99, with a spin–spin interaction constant of 7 Hz indicating the axial and equatorial position in the ring of the methyl group and carboxy group, respectively, correspond to the protons of the analogous fragments of the *cis* isomers (**XXXa** and **b** and **XXXI**). In the proton NMR spectra of the arylesters of the *trans* and *cis* acids (**IV**–**VII** and **X**) typical doublets are observed at a weaker field of 0·97 and 1·08 ($J=7$ Hz). Doublet signals of hydrogen atoms of the methyl group of *trans*-4-(4-methoxyphenyl)-*trans*-2-methylcyclohexane-1-*n*-carboxylic acid (**XXXIII**) and esters (**VI** and **VII**) are observed at 0·90 and 0·98 but they are characterized by a smaller spin–spin coupling constant ($J=5$ Hz) confirming the equatorial position of this fragment in the ring.

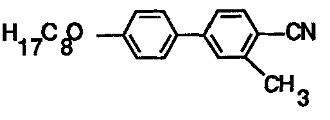
The investigation of the mesomorphic properties of the derivatives of 4′-hydroxy-3-methyl-4-cyanobiphenyl (**II**) and 4′-hydroxy-3,5-dimethyl-4-cyanobiphenyl (**III**) showed (see table 1) that incorporation of methyl groups into the position ortho to the nitrile group seems to cause a weakening of the anisotropic intermolecular interactions and to disturb an antiparallel arrangement of molecules in the mesophase. As a result, the nematic–isotropic transition temperature is reduced and the nematic range decreases sharply and disappears for 4′-*n*-octyloxy-3-methyl-4-cyanobiphenyl (**II**, $n=8$). The ethylphenyl ester of 4′-ethoxy-3,5-dimethylbiphenyl-4-carboxylic acid (**I**) is not a liquid crystal.



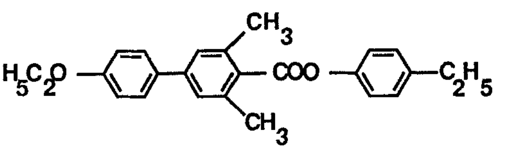
C 54·5°C S 67°C N 80°C I



C 148°C N 229°C I

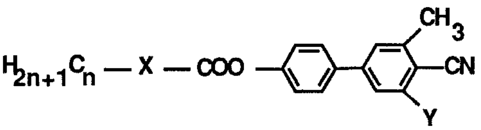


(**II**, $n=8$) C 44°C I



(**I**) C 168°C I

Table 1. Yields and transition temperatures for the compounds (III).

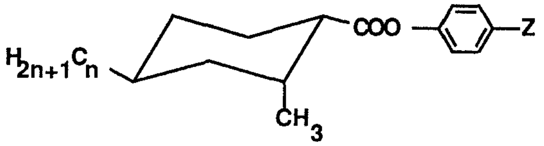


				Transition temperatures/°C					
n	*X*	*Y*	Yield/%	C		N		I	
3	C_6H_4	H	54	●	93	●	166	●	
4	C_6H_4	H	62	●	88	●	148	●	(110–242)
5	C_6H_4	H	68	●	98	●	146	●	(109–237·5)
6	C_6H_4	H	47	●	71	●	137	●	(91–229·6)
4	C_6H_{10}	H	49	●	76	●	154	●	(79·8–141·9)
5	C_6H_{10}	H	59	●	92	●	158	●	(85·2–240·8)
5	C_6H_4	CH_3	43	●			86	●	

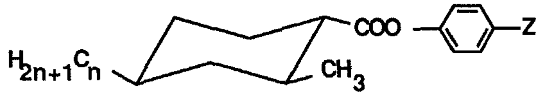
The transition temperatures of the analogues without the methyl substituent are given in parenthesis.

It follows from a comparison of the electrooptic parameters of the liquid-crystalline mixtures presented in table 2 that the mixtures containing the esters (**III**) are characterized by higher values of switch-on and switch-off times, threshold voltage and saturation voltage in comparison with the mixtures containing the analogous derivatives of 4′-hydroxy-4-cyanobiphenyl.

The comparison of the liquid-crystalline properties of the esters (**IV**–**X**) and the analogous derivatives of *trans*-4-alkylcyclohexane-1-carboxylic acids show that in this case, too, the incorporation of a methyl group reduces the nematic–isotropic transition temperature and sharply decreases the nematic range; the nematic–isotropic transition temperature of the esters containing a methyl group in the axial position of the cyclohexane ring (A) (**IV**) is lower than that of the esters with the equatorial position for this group (B) (**VI**).

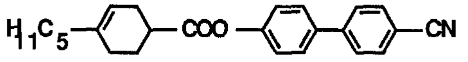


(A)

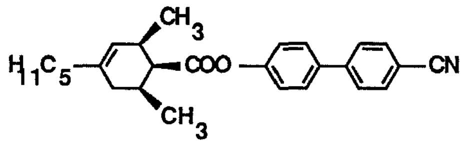


(B)

This results because of a considerably greater broadening of the molecules in the former case (A) (see tables 3 and 4). When another methyl group is incorporated, the nematic range decreases further,



C 64°C N 165°C I



C 69°C N 103°C I

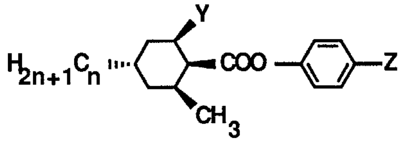
Table 2. Electrooptic parameters of the liquid-crystalline mixtures.

Mixture no.	4′-pentyl-4-cyanobiphenyl/%	4-pentylphenyl anisate/%	4′-cyanobiphenyl-4-yl 4-hexylbenzoate/%	4′-cyano-3′-methylbiphenyl-4-yl 4-hexylbenzoate/%	Threshold voltage/V	Saturation voltage/V
1	70	30	0	0	0·95	2·3
2	63	27	10	0	0·75	2·1
3	63	27	0	10	1·25	2·4

The applied voltage is 3 V.

leading to the disappearance of liquid-crystalline properties in a number of cases (for example esters **IX**). It should also be noted that the mesophase formation temperature of these compounds is not always lower, but in some cases it is even higher than that of the analogous compounds which do not contain methyl groups in ring systems (see table 1). Thus, a reduction of the nematic range, a significant lowering of the transition temperatures upon incorporation of methyl groups into cyclic systems and the difficulty of synthesizing the isomers of 4-alkyl-2-methyl-(2,6-dimethyl)-cyclohexanecarboxylic acids considerably reduce the utility of the compounds as components in liquid-crystalline compositions intended for electrooptic display devices.

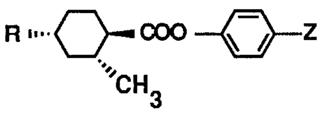
Table 3. Transition temperatures and yields of esters (**IV**, **X**).



n	*Y*	*Z*	Yield/%	C	Transition temperatures/°C	N		I	
3	H	OC_6H_{13}	54	●			44	●	(34–72)
3	H	C_6H_5	58	●			65	●	
4	H	OC_6H_{13}	61	●			41	●	(25–70)
4	H	$OOCC_6H_9(CH_3)C_4H_9$	38	●	81	●	128	●	(134–215)
4	H	C_6H_5	52	●	64	●	78	●	
5	H	OC_4H_9	47	●			43	●	(49–81)
6	H	OC_4H_9	51	●			54	●	(34–75)
6	H	OC_6H_{13}	55	●			38·5	●	(34–77)
3	H	C_6H_4CN	47	●	69	●	184	●	(94–258)
4	H	C_6H_4CN	51	●	88	●	187	●	(80–242)
5	H	C_6H_4CN	58	●	73	●	183	●	(89–246)
6	H	C_6H_4CN	53	●	69	●	191	●	(84–227)
5	CH_3	C_6H_4CN	36	●	93	●	147	●	

The nematic range of the analogues without the methyl substituent is given in parentheses.

Table 4. Transition temperatures and yields of the esters (**VI** and **VII**).



R	*Z*	Yield/%	C	Transition temperatures/°C	S		N		I	
$CH_3OC_6H_4$	CN	76	●	147			●	168	●	(167–232)
C_3H_7	C_6H_5	27	●					83	●	
C_3H_7	C_6H_4CN	35	●	79			●	187	●	(94–258)
C_5H_{11}	C_6H_4CN	23	●	66	●	77	●	196	●	(89–246)

The nematic range of the analogues without the methyl substituent is given in parentheses.

3. Experimental

The infrared spectra of 0·1 M solutions of the substances in carbon tetrachloride were recorded with a SPECORD IR-75 spectrophotometer. The proton NMR spectra of 10 per cent solutions in carbon tetrachloride and in deuterioacetone with hexamethyldisiloxane as an internal standard were recorded with a TESLA BS-467 spectrometer. The textures of different phases and the transition temperatures were determined with a polarizing microscope.

3.1. *Ethyl 2,6-dimethyl-4-(4-ethoxyphenyl)-cyclohexa-1,3-diene carboxylate* (**XIIb**)

0·2 mol of the ester (**XIXb**) in 100 ml of anhydrous ester was added, with vigorous stirring, to the Grignard reagent obtained from 0·2 mol of *n*-bromophenetole in 200 ml of anhydrous ester. After the addition, the mixture was boiled for half an hour and cooled. The complex formed was decomposed using aqueous ammonium chloride. The ester layer was washed with water and dried with anhydrous sodium sulphate. The residue obtained after the solvent had been removed was used in subsequent reactions. Yield 65 per cent; oil.

When the complex was decomposed with a 20 per cent solution of sulphuric acid, 4-(4-ethoxyphenyl)-2,6-dimethylcyclohexa-1,3-diene-1-carboxylic acid (**XXb**) (yield 20 per cent), which was purified by crystallization from acetone, was formed simultaneously with the ester (**XIIb**) (yield 30 per cent). The transition temperatures are C 55°C N 184°C I.

The following compounds were obtained in similar ways.

Ethyl 2-methyl-4-(4-methoxyphenyl)-cyclohexa-1,3-diene-1-carboxylate (**XIIa**), yield 51 per cent; mp 56°C.

4-(4-Methoxyphenyl)-2-methylcyclohexa-1,3-diene-1-carboxylic acid (**XXa**), yield 35 per cent, transition temperatures C 177°C N 218°C I.

4-(4-Ethoxyphenyl)-2-methylcyclohexa-1,3-diene-1-carboxylic acid (**XXa**), yield 21 per cent, transition temperatures C 191°C N 220°C I.

3.2. *4′-Ethoxy-3,5-dimethylbiphenyl-4-carboxylic acid* (**XIb**)

A mixture of 0·1 mol of ethyl 4-(4-ethoxyphenyl)-2,6-dimethylcyclohexa-1,3-diene-carboxylate, 0·11 mol of *N*-bromosuccinimide and catalytic quantities of benzoyl peroxide in 200 ml of carbon tetrachloride was boiled for 4 h, cooled and filtered. The filtrate was washed with water and dried using anhydrous magnesium sulphate. The residue obtained after the solvent had been removed was mixed with 0·16 mol of potassium hydroxide in 150 ml of isopropyl alcohol and boiled for 6 h. The reaction mixture was poured into 300 ml of water and filtered. The filtrate was acidified with dilute hydrochloric acid. The isolated crystals were filtered off, washed with water and recrystallized from butan-2-one. Yield 50 per cent and mp 179°C.

4′-Methoxy-3-methylbiphenyl-4-carboxylic acid (**XIa**) was obtained in a similar way. Yield 75 per cent, transition temperatures C 202°C N 226°C I.

3.3. *4′-Methoxy-3-methylbiphenyl-4-carboxamide* (**XVIa**)

0·05 mol of the acid in 10 ml of thionyl chloride was boiled for 3 h. The excess of thionyl chloride was removed at a reduced pressure and aqueous ammonia was added to the residue. The precipitated crystals were filtered off, washed with water and recrystallized from butan-2-one. Yield 80 per cent; mp 234°C.

4-Ethoxy-3-methylbiphenyl-4-carboxamide (**XVIa**) was obtained in a similar way. Yield 75 per cent; mp 250°C.

3.4. *4′-Methoxy-3-methyl-4-cyanobiphenyl* (**XVIIa**)

0·07 mol of thionyl chloride was added to 0·03 mol of amide in 20 ml of dimethylformamide. The mixture was held at room temperature for 2 h, poured into aqueous sodium carbonate and extracted with ether. The ether solution was washed with water and dried using anhydrous sodium sulphate. The residue obtained after the solvent had been removed, was crystallized from propan-2-ol. Yield 75 per cent; mp 97°C.

4′-Ethoxy-3-methyl-4-cyanobiphenyl (**XVIIa**) was obtained in a similar way, yield 60 per cent; mp 88°C.

3.5. *4′-Hydroxy-3-methyl-4-cyanobiphenyl* (**XVIIIa**)

The mixture of 0·02 mol of cyanobiphenyl (**XVIIa**) and 0·05 mol of anhydrous aluminium bromide in 100 ml of toluene was stirred at a temperature of 60°C for 5 h and poured into hydrochloric acid solution. The organic layer was washed with water and dried using anhydrous sodium sulphate. The residue obtained after the solvent has been removed was recrystallized from butan-2-one. Yield 78 per cent, mp 152°C.

4′-Hydroxy-4-cyano-3,5-dimethylbiphenyl (**XVIIIb**) was obtained in a similar way. Yield 23 per cent; mp 193°C.

3.6. *4′-n-Octyloxy-3-methyl-4-cyanobiphenyl* (**II**)

A mixture of 0·005 mol of hydroxybiphenyl (**XVIIIa**), 0·0075 mol of 1-bromooctane and 0·0075 mol of potassium hydroxide was boiled for 2 h in 15 ml of isopropyl alcohol, diluted with water and extracted with ether. The ether extract was washed with water and dried using anhydrous sodium sulphate. The residue obtained after the solvent had been removed was recrystallized from hexane. Yield 45 per cent; mp 44°C.

3.7. *4′-Cyano-3′-methylbiphenyl-4-yl 4-hexylbenzoate* (**III**)

A mixture of 0·05 mol of 4-hexylbenzoyl chloride, 0·06 mol of 4-hydroxy-3′-methyl-4′-cyanobiphenyl and 0·01 mol of pyridine in 50 ml of anhydrous diethyl ether was stirred for 6 h, washed with water, dried using anhydrous sodium sulphate. The residue obtained after the solvent had been removed was crystallized from isopropyl alcohol. Yield 50 per cent, transition temperatures C 71°C N 137°C I.

Some other esters were obtained in a similar way and their transition temperatures are presented in table 1.

3.8. *Ethyl 4-ethoxy-2-methylcyclohexa-1,3-diene-1-carboxylate* (**XXXVIII**)

0·45 mol of the ester (**XIXa**) was added to a mixture of 1·1 mol of triethyl orthoformate, 3 ml of fluoroboric acid and 15 ml of ethyl alcohol. The reaction mixture was stirred for 3 h, treated with potassium hydroxide and filtered. The residue obtained after the unreacted reagents had been removed was distilled under vacuum. Yield 90 per cent; bp 173°C (35 mm Hg); n_D^{20} 1·5148.

3.9. *Ethyl 4,4-diethoxy-2-methylcyclohex-1-ene-1-carboxylate* (**XXXVII**)

The reaction mixture obtained by addition of 15 ml of ethyl alcohol to 0·45 mol of the ether (**XIXa**), 1·1 mol of triethyl orthoformate and 3 ml of fluoroboric acid was stirred for 4 h, treated with potassium hydroxide and filtered. The residue obtained after the unreacted reagents had been removed was distilled in a vacuum. Yield 85 per cent; bp 182°C (30 mm Hg); n_D^{20} 1·4816.

3.10. *Ethyl 4,4-ethylenedioxy-2-methylcyclohex-1-ene-1-carboxylate* (**XXXIV**)

A mixture of 0·25 mol of ethyl 4-ethoxy-2-methylcyclohexa-1,3-diene-1-carboxylate (**XXXVIII**), 0·35 mol of ethylene glycol, a catalytic quantity of *p*-toluenesulphonic acid in 80 ml of toluene was boiled for 5 h during slow removal of ethyl alcohol. The product was washed with water and dried using anhydrous sodium sulphate. The residue obtained after the solvent has been removed was distilled. Yield 79 per cent; bp 175°C (25 mm Hg); n_D^{20} 1·4821.

3.11. *Ethyl 4,4-ethylenedioxy-*cis*-2-methylcyclohexane-1-carboxylate* (**XXXV**)

0·2 mol of the ester (**XXXIV**) in 100 ml of isopropyl alcohol was hydrogenated in the presence of 1 g of 10 per cent palladium on carbon until hydrogen absorption stopped. The catalyst was separated, the alcohol was removed and the residue was distilled. Yield 92 per cent; bp 171°C (25 mm Hg); n_D^{20} 1·4643.

3.12. *Ethyl* cis*-2-methylcyclohexan-4-one-1-carboxylate* (**XXIa**)

0·2 mol of the ester (**XXXV**) in a mixture of 50 ml of ethyl alcohol, 10 ml of water and 5 ml of concentrated hydrocholoric acid was stirred for 2 h, diluted with water and extracted using diethyl ether. The ester solution was washed with water and dried using anhydrous sodium sulphate. The residue obtained after the solvent had been removed was distilled. Yield 90 per cent; bp 148–150°C (30 mm Hg); n_D^{20} 1·4609.

3.13. *Ethyl* cis,cis*-2,6-dimethylcyclohexan-4-one-1-carboxylate* (**XXIb**)

0·2 mol of the ester (**XIXb**) in 100 ml of isopropyl alcohol was hydrogenated in the presence of 1 g of 10 per cent palladium on carbon until hydrogen absorption stopped. The catalyst was separated, the alcohol was removed and the residue was distilled. Yield 92 per cent; bp 135°C (20 mm Hg); n_D^{20} 1·4539.

3.14. *4-Pentyl-*cis,cis*-2,6-dimethylcyclohex-3-ene-1-carboxylic acid* (**XXIII**)

0·28 mol of the ester (**XXIb**) in 100 ml of diethyl ether was added during vigorous stirring to the Grignard reagent solution prepared from 0·3 mol of 1-bromopentane and 0·3 g atoms of magnesium in 500 ml of anhydrous diethyl ether and then acetyl chloride was added after stirring for 1·5–2 h. The reaction mixture was left overnight and subsequently treated with dilute hydrochloric acid. The organic layer was washed with water and dried with anhydrous sodium sulphate. The residue obtained after the solvent had been removed was heated to 350°C, and the pyrolysis products, which distilled below a temperature of 250°C and under a pressure of 100 mm Hg, were collected. The distillate obtained was boiled in an alkaline alcohol solution for 5–6 h, diluted with water and acidified with dilute hydrochloric acid. The isolated oil-like substance was extracted with diethyl ether, washed with water and dried with anhydrous sodium sulphate. The residue obtained after the solvent had been removed was distilled. Yield 56 per cent; bp 170–180°C (3 mm Hg). The acid obtained was used in subsequent syntheses without purification. The unsaturated acids were obtained in a similar way.

3.15. cis *and* trans*-4-Propyl-*cis*-2-methylcyclohexane-1-*n*-carboxylic acid* (**XXIXa and XXXa**)

0·1 mol of the acid (**XXIII**) in 50 ml of isopropyl alcohol was hydrogenated in the presence of 1 g of 10 per cent palladium on carbon until hydrogen absorption stopped. The catalyst was separated, the alcohol was removed and the residue was dissolved in hexane and cooled to −50°C. The separated crystals of the *cis* isomer were filtered off and recrystallized from hexane again. Yield 20 per cent; mp 66°C.

The *trans* isomer was separated by column chromatography of the residue using silica gel (eluent diethyl ether–hexane; 1 : 16). Yield 9 per cent; n_D^{20} 1·4593.

The following compounds were obtained in a similar way: *trans*-4-butyl-*cis*-2-methylcyclohexane-1-*n*-carboxylic acid, yield 19 per cent, mp 70°C; *cis*-4-butyl-*cis*-2-methylcyclohexane-1-*n*-carboxylic acid, yield 8 per cent, mp 32°C; *trans*-4-pentyl-*cis*-2-methylcyclohexane-1-*n*-carboxylic acid, yield 24 per cent, mp 72°C; *cis*-4-pentyl-*cis*-2-methylcyclohexane-1-*n*-carboxylic acid, yield 12 per cent, mp 29°C; *trans*-4-hexyl-*cis*-2-methylcyclohexane-1-*n*-carboxylic acid, yield 17 per cent, mp 13°C; *cis*-4-hexyl-*cis*-2-methylcyclohexane-1-*n*-carboxylic acid, yield 24 per cent, mp 44°C and *trans* -4-pentyl-*cis,cis*-2,6-dimethylcyclohexane-1-*n*-carboxylic acid, yield 15 per cent, mp 63°C.

3.16. cis-*4-(4-Methoxyphenyl)-*cis*-2-methylcyclohexane-1*-n-*carboxylic acid* (XXXI)

0·12 mol of 4-methoxyphenylmagnesium bromide in 150 ml of diethyl ether was added with stirring to 0·1 mol of ethyl *cis*-2-methylcyclohexane-4-one-1-carboxylate in 250 ml of anhydrous diethyl ether. After addition the reaction mixture was stirred for 30 min and decomposed with dilute hydrochloric acid. The organic layer was washed with water and the diethyl ether was removed. The residue obtained was boiled in 100 ml of isopropyl alcohol in the presence of 0·2 mol of potassium hydroxide for 4 h, then diluted with water and extracted with diethyl ether. The aqueous layer was acidified with hydrochloric acid. The isolated mixture of the acids was extracted with ether, washed with water and dried with anhydrous sodium sulphate. The residue obtained after the solvent had been removed was hydrogenated in 50 ml of isopropyl alcohol in the presence of 1 g of 10 per cent palladium on carbon. The catalyst was isolated, the solvent was removed and the residue was crystallized from the hexane. The yield calculated on the initial ester is 28 per cent, the melting point is 96°C.

3.17. trans-*4-(4-Methoxyphenyl)-*trans*-2-methylcyclohexane-1*-n-*carboxylic acid* (XXXIII)

0·01 mol of *cis* acid (**XXXI**) was boiled in 25 ml of thionyl chloride for 8 h. The excess of thionyl chloride was removed, the residue was dissolved in 10 ml of dioxane, poured into an aqueous alkaline solution and filtered. The filtrate was acidified with concentrated hydrochloric acid. The separated oil-like substance was extracted with diethyl ether washed with water and dried with anhydrous sodium sulphate. The residue obtained after the solvent had been removed was crystallized from hexane. Yield 64 per cent, transition temperatures C 97°C N 152°C I. Isomerization of the *cis* acids (**XXXa** and **b**) was performed in a similar way. The *trans* acid chlorides obtained were further used without purification.

3.18. *4-Cyanophenyl* trans-*4-(4-methoxyphenyl)-*trans*-2-methylcyclohexane-1*-n-*carboxylate* (VII)

0·01 mol of the acid chloride of acid **XXXIII**, 0·01 mol of 4-hydroxybenzonitrile and 0·04 mol of pyridine in 50 ml of anhydrous diethyl ether were stirred for 6 h and filtered. The solvent was removed and the residue was recrystallized from isopropyl alcohol. Yield 67 per cent. The esters (**IV–X**) were obtained in a similar way.

References

[1] Ferrato, J. P., 1983, U.S. Patent 4406814.

[2] Pohl, L., Scheuble, B., Hittich, R., Eidenschink, R., Kurmeier, H.-A., and Wachtler, A., 1986, DE 3510432 A1.

[3] Karamysheva, L. A., Roitman, K. W., Agafonova, I. F., Torgova, S. J., Geyvandova, N. P., and Bumagin, N. A., 1989, *The 8th Liquid Crystal Conference of Socialist Countries*, A46.

[4] Bezborodov, V. S., Konovalov, V. A., Lapanik, V. I., and Minko, A. A., 1989, *Liq. Crystals*, **4**, 209.

[5] McAndrew, B. A., 1979, *J. chem. Soc. Perk. Trans. 1*, p. 1837.