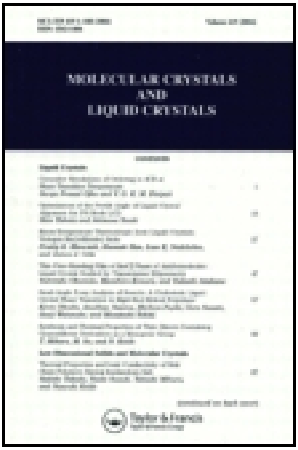

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Mesomorphism and Dielectric Properties of Phenyl 4 -Alkylbiphenyl-4′ -Carboxylates and Phenyl 4 (4-Alkylphenyl) cyclohexanecarboxylates

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Mesomorphism and Dielectric Properties of Phenyl 4-Alkylbiphenyl-4′-Carboxylates and Phenyl 4(4-Alkylphenyl) cyclohexanecarboxylates

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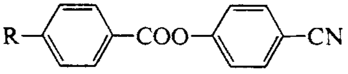
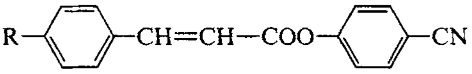
4-Alkylbiphenyl-4′-carboxylic and trans-4(4-alkylphenyl)cyclohexanecarboxylic acids have been synthesized. Their *p*-cyanophenyl esters formed only nematic mesophase in a wide temperature range, and *p*-hexyloxyphenyl esters—both smectic and nematic mesophases. The replacement of the benzene ring in carboxylic part of molecule by the 1,4-disubstituted trans-cyclohexane ring leads to decrease of nematic thermal stability and all dielectric constants.

INTRODUCTION

p-Cyanophenyl *p*-alkylbenzoates (I)[1] and *p*-alkylcynnamates (II)[1] are the nematic liquid crystals (LC) with a considerable positive dielectric anisotropy, therefore this compound may be used in various electrooptical devices which utilise field orientational effects. In order to study an influence of introduction in I of supplementary benzene or cyclohexane ring on mesomorphic and dielectric properties we have synthesized a number of *p*-cyanophenyl 4-alkylbiphenyl-4′-carboxylates (III), trans-4(4-alkylphenyl)-cyclohexanecarboxylates (IV) and their hexyloxy analogues (V) and (VI).



I



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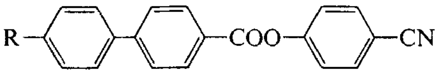

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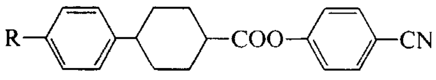

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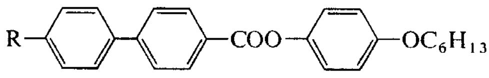

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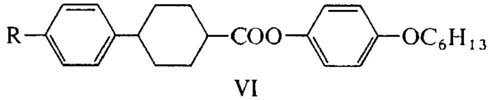

VI

RESULTS AND DISCUSSION

4-Alkylbiphenyl-4′-carboxylic acids (VII) and trans-4(4-alkylphenyl)-cyclohexanecarboxylic acids (VIII) were obtained from biphenyl as follows:

$$\mathrm{Ph{-}Ph} \xrightarrow[\mathrm{AlCl_3}]{\mathrm{RCOCl}} p\text{-}\mathrm{RCOC_6H_4{-}Ph} \xrightarrow[\mathrm{KOH}]{\mathrm{N_2H_4}} p\text{-}\mathrm{RCH_2C_6H_4{-}Ph} \xrightarrow[\mathrm{AlCl_3}]{\mathrm{AcCl}}$$

$$p\text{-}\mathrm{RCH_2C_6H_4{-}C_6H_4Ac}\text{-}p' \xrightarrow{\mathrm{NaOBr}} \underset{\mathrm{(VII)}}{p\text{-}\mathrm{RCH_2C_6H_4{-}C_6H_4COOH}\text{-}p'} \xrightarrow[\mathrm{AmOH}]{\mathrm{Na}}$$

$$\underset{\mathrm{(VIII)}}{p\text{-}\mathrm{RCH_2C_6H_4{-}C_6H_{10}COOH}\text{-}p'}$$

a) $R = n\text{-}C_4H_9$; b) $R = n\text{-}C_5H_{11}$; c) $R = n\text{-}C_6H_{13}$.

The transition temperatures of the synthesized compounds are listed in the Tables I and II.

The acids (VII) form smectic and nematic mesophases similarily to the known 4-alkyloxybiphenyl-4′-carboxylates,[2] but the alkyl derivatives (VII) demonstrated the lowering of the melting and clearing points (lower 53, 48, 33 and 4, 12, 7°, respectively). The trans-configuration of the acids (VIII) is considered from their mesomorphic properties and from mesomorphism their esters (IV) and (VI). The acids (VIII) have only smectic mesophase which texture is similar to the texture of the trans-4-alkylcyclohexanecarboxylic acids[3] and some other cyclohexane derivatives.[4] The esters (III) and (IV) have only nematic mesophase.

The replacement of benzene ring in esters (III) by cyclohexane ring leads to decrease of the melting (about 25–30°) and clearing (about 55°) points (Table II). The nematic thermal stabilities of the compounds (II), (III) and (IV) were compared with clearing points of the esters (I) (Table II). It was

TABLE I

The transition temperatures for compounds V–VIII

Compound index	Transition temperature, °C		
	C–S	S–N	N–I
Va	108.2–108.9	163.5	190.7
Vb	97.7; 103.6	166.0	182.9
Vc	88.8–89.2; 107–108.0	166.8–168.6	176.5–178.5
VIa	92–96; 124.8	134.2–135.0	145.9
VIb	124.4; 125.5	138.7	141.9
VIc	121.5	139.8–140.0	142.0
VIIa	175.0	235.0	271.0
VIIb	165.0	230.0	261.0
VIIc	162.0	233.0	259.0
VIIIa	137.0	—	203.0
VIIIb	132.7	—	199.6
VIIIc	130.1	—	201.0

TABLE II

Transition temperatures for esters $R—C_6H_4—X—COO—C_6H_4—CN$

Compound index	R	X	Transition temperature, °C		Mesomorphic range	$T^X = (N\text{–}I)^X - (N\text{–}I)^I$
			C–N	N–I		
Ia	C_5H_{11}	—	—	55.4[a]	−9	—
IIa	C_5H_{11}	CH=CH	74.5	118.5	44	63
IIIa	C_5H_{11}	C_6H_4	105–106.0	212.0	106	157
IVa	C_5H_{11}	C_6H_{10}	82.7–84.2	160.3	77	105
Ib	C_6H_{13}	—	44.4	48.6	4	—
IIb	C_6H_{13}	CH=CH	73.0	107.4	34	52
IIIb	C_6H_{13}	C_6H_4	101.7–102.6	213.3	111	164
IVb	C_6H_{13}	C_6H_{10}	78–79.0	155–156	77	106
Ic	C_7H_{15}	—	44.0	56.5	12.5	—
IIc	C_7H_{15}	CH=CH	57.8	109.8	52	54
IIIc	C_7H_{15}	C_6H_4	101.4–102.3	208.8	107	153
IVc	C_7H_{15}	C_6H_{10}	68.8–70.8	153.2–153.7	83	97

[a] Monotropic LC, m.p. 64.4°C.

seen that the introduction of supplementary benzene ring (esters III) leads to the considerable increase of the mesophase thermal stability (about 160°), as well as introduction of cyclohexane ring (IV, about 100°) and ethylene group (II, about 60°).

The greatest effect is caused by the introduction of benzene rings because of increase of the geometric anisotropy and the anisotropy of polarizability. The cyclohexanic moiety therefore have the greater influence on the nematic thermal stability than the more polarizable double bond. This fact suggests that the geometric anisotropy is more important in determination of the mesophase stability than the anisotropy of polarizability. The conclusion on paramount importance of geometry in determining the stabilities of nematic mesophases was made early by investigation the esters of terephtalic acid and their alicyclic analogues.[5]

The esters III have $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ similar to the dielectric constants of the esters II (Table III).

The magnitudes $\varepsilon_{\parallel}$ for some other liquid crystals having the *p*-cyano-group (azomethines,[6] cyanobiphenyls[7]) are also very high. It is surprising therefore that the significant lowering take place if the benzene ring (esters III) substitutes for the cyclohexanic one (esters IV). One can explain this phenomenon by the considerable decrease of the dipole moment in the partly hydrogenated esters (6.4D—for IIIc and 5.0D—for IVc).

TABLE III

Dielectric properties of the esters $R—C_6H_4—X—COO—C_6H_4—R'$

Compound index	R	R′	X	Temperature of measure, °C	$\varepsilon_{\parallel}$	$\varepsilon_{\perp}$	$\Delta\varepsilon$
IIIa	C_5H_{11}	CN	p-C_6H_4	144.4	19.0	6.1	+12.9
IIIb	C_6H_{13}	CN	p-C_6H_4	144.0	19.3	5.9	+13.4
IIIc	C_7H_{15}	CN	p-C_6H_4	144.0	18.4	5.4	+13.0
IVa	C_5H_{11}	CN	p-C_6H_{10}	95.0	10.4	4.2	+6.2
IVb	C_6H_{13}	CN	p-C_6H_{10}	95.0	12.4	5.0	+7.4
IVc	C_7H_{15}	CN	p-C_6H_{10}	95.0	11.5	4.7	+6.8
Vc	C_7H_{15}	OC_6H_{13}	p-C_6H_4	171.0	3.30	3.47	−0.17
VIc	C_7H_{15}	OC_6H_{13}	p-C_6H_{10}	142.0	2.75	2.88	−0.13

p-Hexyloxyphenyl 4-alkylbiphenyl-4′-carboxylates (V) and 4(4-alkylphenyl)cyclohexanecarboxylates (VI) (Table I) have nematic and one or more smectic mesophases, smectic temperature range increasing with increase of the terminal substituent length in the carboxylic part of the molecule. The hydrogenation of the esters (V) lowers a nematic thermal stability of the esters (VI). The melting points and the smectic mesophase thermal stability of the esters (VI) increased respecting to the esters (V).

The esters (V) and (VI) have a small negative dielectric anisotropy (Table III). The hydrogenation of the one benzene ring leads to decrease all dielectric constants also as for esters (IV).

Thus the substitution of aromatic esters (III) and (V) for the partly hydrogenated esters (IV) and (VI) leads to the destabilization of the nematic mesophase and to lowering of all dielectric constants.

EXPERIMENTAL

IR spectra of the acids (VIII) were measured on the spectrophotometer UR-20 in the tablets with KBr. Dielectric constants of LC were determined by the bridge method for layers of 160 μ thickness. A magnetic field of 7 kG was used to align the LC. The cell capacitance was measured by the AC bridge at 1000 Hz; the accuracy was estimated to be $\pm 5\%$. The dipole moments were determined by the Debay method in the solution. Transition temperatures were measured using a Mettler FP-52 apparatus with a polarising microscope. Analytical data for compounds (III–VIII) are given in Table IV.

TABLE IV

Elemental analyses for compounds of type III–VIII

Compound index	Found (%)			Formula	Required (%)		
	C	H	N		C	H	N
IIIa	81.1	6.0	3.2	$C_{25}H_{23}NO_2$	81.3	6.3	3.8
IIIb	81.7	6.6	3.5	$C_{26}H_{25}NO_2$	81.5	6.5	3.6
IIIc	81.8	6.5	3.2	$C_{27}H_{27}NO_2$	81.6	6.8	3.5
IVa	80.7	7.6	3.4	$C_{25}H_{29}NO_2$	80.0	7.7	3.4
IVb	80.2	7.7	3.2	$C_{26}H_{31}NO_2$	80.2	7.9	3.6
IVc	79.5	7.4	3.3	$C_{27}H_{33}NO_2$	80.4	8.2	3.5
Va	81.5	7.8	—	$C_{30}H_{36}O_3$	81.1	8.1	—
Vb	81.4	8.4	—	$C_{31}H_{38}O_3$	81.2	8.3	—
Vc	80.9	8.7	—	$C_{32}H_{40}O_3$	81.3	8.5	—
VIa	80.2	9.1	—	$C_{30}H_{42}O_3$	80.0	9.3	—
VIb	80.2	9.1	—	$C_{31}H_{44}O_3$	80.2	9.5	—
VIc	80.3	9.5	—	$C_{32}H_{46}O_3$	80.3	9.6	—
VIIa	80.4	7.4	—	$C_{18}H_{20}O_2$	80.6	7.5	—
VIIb	80.6	7.3	—	$C_{19}H_{22}O_2$	80.8	7.7	—
VIIc	80.8	7.6	—	$C_{20}H_{24}O_2$	81.1	8.1	—
VIIIa	79.4	9.0	—	$C_{18}H_{26}O_2$	78.8	9.5	—
VIIIb	78.9	9.6	—	$C_{19}H_{28}O_2$	79.2	9.7	—
VIIIc	80.1	10.0	—	$C_{20}H_{30}O_2$	79.5	9.9	—

4-n-Alkylbiphenylketons and *4-n-alkylbiphenyls* were obtained by the known methods.[8]

4-Acetyl-4′-alkylbiphenyls (yield of 25–63%) and *4-alkylbiphenyl-4′-carboxylic acids* (VII) (yield of 75%) were obtained similarly to alkoxy analogous.[9]

4-(4-n-Alkylphenyl)cyclohexanecarboxylic acids (VIII) Hydrogenation of the acids (VII) was realized accordingly to the method.[10] The acids (VIII) were recrystallized from alcohol until the constant melting and clearing points were achieved (Table I), yield of 40%. IR-spectra of compounds (VIII) resemble one another and have the following absorbtion bands: 3000, 2930, 2850, 1710, 1525, 1460, 1430, 1300–1320, 1270, 1130, 1020, 960, 930, 840, 540–550 cm^{-1}.

Preparation of esters (III–VI) These esters were prepared by acilation of corresponding phenols with the acid chlorides in pyridine[11] or in benzene in the presence equimolar quantity of triethylamine,[12] yield of 60%.

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