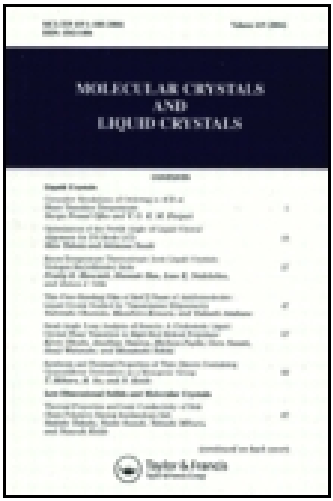

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Nematic Phase Formed by V-Shaped Molecules

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Nematic Phase Formed by V-Shaped Molecules

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In the paper there are presented synthesis and properties of new banana-shaped molecules that are ester resorcinol derivatives. The compounds with lateral alkyl substituent at the 4-position of the resorcinol ring exhibit the liquid crystalline nematic phase. Some of the synthesised compounds are able to induce the anticlinic S^*_{CA} phase that proves their bent molecular shape.

Keywords: liquid crystal; banana phases

INTRODUCTION

Mesogenic compounds with banana-shaped molecules are intensively studied in the recent years.[1-9] We present here synthesis and properties of several series of V-shaped molecules. Our compounds are ester resorcinol derivatives with mono- or di-substituted branches. The banana molecule branches are formed from two phenyl rings joint by

the imino (-N=CH-), ethyleno (-CH=CH-) or etheral ($-CH_2-O-$) bridges and terminated with long alkoxy chains (mainly dodecyloxy and pentadecyloxy). Additionally at the lateral 4-position of the resorcinol ring n-alkyl or ester moieties was attached. For the substances with the n-propylo, n-pentylo, n-hexylo and n-heptylo lateral substituents the nematic phase appears. For comparison, compounds with non-symmetric ester branches were also obtained.

EXPERIMENTAL

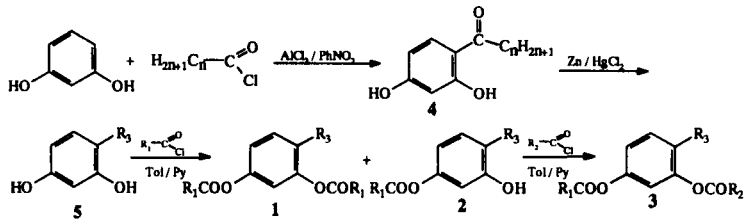
The mesophases were identified in microscopic observation of liquid crystalline texture. A Zeiss Jenapol-U polarising microscope equipped with a Mettler FP82HT hot stage was used. Phase transition temperatures were determined using a Perkin Elmer DSC 7 calorimeter.

The molecular structure of the compounds synthesised was confirmed by NMR spectra (Varian Unity Plus spectrometer operating at 200 MHz for ^1H NMR and at 125 MHz for ^{13}C NMR). The progress of the reaction and the purity of the final products were monitored by thin layer chromatography (Merck 60 silica gel glass plates). Column chromatography was carried out at atmospheric pressure using silica gel (230-400 mesh, Merck). Elemental analyses and NMR spectra obtained for all the compounds were fully consistent with the required structure, but only representative examples of these results are quoted.

SYNTHESIS

The synthetic route to the 4-alkylresorcinol derivatives with identical or different ester branches is outlined in Scheme. We have already described procedure for synthesis of 3-[4-(4-alkoxybenzylideneamino) benzoyloxy]-4-alkylphenyl-4-(4-alkoxybenzylideneamino)benzoate having two symmetric branches with the imino joint [9]. Synthesis of 4-[(4'-alkoxyphenoxy)methyl]-1-benzenecarbonyl chloride with the

etheral linking and 4-[(4'-alkoxybiphenoxy)methyl]-1-benzenecarbonyl chloride is common. Trans 4-alkoxy-4'-carboxystilbenes with the ethyleno linking were obtained according to description by S. Vaday at all.[10] Reaction between 4-substituted resorcinol and related chlorides results in the bent-shape molecules of type **1, 2, 3.**



Scheme

1-(2,4-dihydroxyphenyl)-1'-propanone **(4).** Resorcinol (10 g, 0.1 mol) was dissolved in nitrobenzene (150 cm^3) and anhydride aluminium chloride (36 g, 0.27 mol) was added. To the stirred and cooled solution propanoic chloride (9.3 g, 0.1 mol) was added drop by drop. The temperature could not rise more than 8 ^0C. The stirring was continued for 25 h. The reaction mixture was poured into water (1000 cm^3) and conc. hydrochloric acid (150 cm^3). Nitrobenzene was distilled with water vapour. The residue was dissolved in chloroform and dried over anhydrous magnesium sulphate. The solvent was evaporated under reduced pressure and the resulting solid was purified by column chromatography on silica gel with chloroform as eluent to afford final compound (10.0 g, 0.06 mol) with 65% yield.

4-propylresorcinol **(5)** To zinc amalgamate a mixture of water (30 cm^3), conc. hydrochloric acid (30 cm^3) and a solution of the compound **4** (8.3 g, 0.05 mol) in ethanol (15 cm^3) was added. The obtained mixture was stirred vigorously and refluxed for 10 h. The heating was stopped and toluene (25 cm^3) was added. The stirring was continued for a further few minutes. The zinc precipitate was filtered out. From the

filtrate the organic layer was separated, which was washed with water and dried over anhydrous magnesium sulphate. The crude product was purified by column chromatography with 5% (v/v) methanol in chloroform as eluent to give compound **5** with 73% yield.

4-propylo-1,3-phenylene bis[4'-(4''-n-dodecyloxyphenoxymethyl)-benzoates] **(3)** and ***3-hydroxy-4-propylo-1-phenylene-4'-(4''-n-dodecyloxyphenoxymethyl)-benzoate*** **(2)** To the compound **5** (1 g, 6.6 mmol) dissolved in dry toluene (100 cm^3) and pyridine (7 cm^3) 4-[(4'dodecyloxyphenoxy)methyl]-1-benzoatecarbonyl chloride (obtained in the well known procedure) (6.5 g, 15.23 mmol) was added all at once. The reaction mixture was heated on a water bath for 8 h; then the solvents were evaporated and residue was chromatographed on silica gel, eluting with chloroform. Two products were obtained: compound **1** (2.8 g; yield 45%) and **2** (1 g, yield 30%). For compound **1**: ^1H NMR ($CDCl_3$) δ 8.23-8.17 (m, 4 H), 7.61-7.54 (m, 4H), 7.33 (d, 1H, J=9.0 Hz), 7.13-7.08 (m, 2H), 6.94-6.80 (m, 8H), 5.12 (s, 4H), 3.90 (t, 4H, J=6.5 Hz), 2.58 (t, 2H, J=7.0 Hz), 1.79-1.67 (m, 4H), 1.47-1.16 (m, 38H), 0.97-0.85 (m, 9H). Elemental analysis for $C_{61}H_{80}O_8$: calc. C 77.87, H 8.51; found C 77.50, H 8.40. For compound **2**: ^1H NMR ($CDCl_3$) δ 8.19 (d, 2H, J=8.2 Hz), 7.56 (d, 2H, J= 8.0 Hz), 7.14 (d, 1H, J=8.2 Hz), 6.93-6.80 (m, 4H), 6.75-6.67 (m, 2H), 5.12 (s, 2H), 4.97 (s, 1H), 3.90 (t, 2H, J=6.5 Hz), 2.58(t, 2H, J=7.7 Hz), 1.79-1.56 (m, 4H), 1.42-1.26 (m, 18 H), 0.99 (t, 3H, J=7.0 Hz), 0.88 (t, 3H, J=6.3 Hz). Elemental analysis for $C_{35}H_{46}O_5$: calc. C 76.92, H 8.42; found C 76.60, H 8.35.

The non-symmetric resorcinol derivatives were obtained from the mono-substituted compounds **2** in the way similar to the preparation of the compound **1**.

RESULTS AND DISCUSION

For the studied substances the phase transition temperatures and thermal effects are gathered in TABLE 1A and B.

The groups of the compounds with the n-propyl, n-pentyl, n-hexyl and n-heptyl lateral moiety and with the symmetric branches containing the imino –C=N– linking exhibit the monotropic nematic phase. It appears 60 – 20 °C below the melting temperature and is stable at room temperature. The highest clearing point of the nematic phase is observed for the longest lateral n-heptyl chain (see TABLE 1A). When the lateral chain is extended the examined compounds do not display a distinct odd–even effect. The substances with the n-butyl lateral substituent do not form liquid crystalline phases.

When the internal linking in the banana branches is exchanged into the ethyleno- or etheral- groups the mesogenic properties disappear although the isotropic phase could be easily supercooled to room temperature.

The resorcinol derivatives with the substituted ester groups or short alkyl moieties (ethyl and methyl) at 4-position do not reveal mesogenic phases. The application of two non-symmetric branches in the resorcinol derivatives does not induce mesogenity either (TABLE 1A). The compounds containing only one ester branch exhibit the calamitic phases (N, S_A, S_C, S_G). In this case the *para*-substituted chains form the long molecular axis, around which the molecules rotate.

In order to confirm the molecular shape of the synthesised substances their ability to induce the anticlinic S^*_{CA} phase was checked.[11] Small amount (1 – 2 % w.g.) of the examined substance was added to the matrix (R(-)2-octyl-4'-(4''-tridecyloxybiphenyl-4-yloxymethyl)benzoate, which forms the ferroelectric S^*_C phase.[12] This matrix compound belongs to a homologous series that exhibits ferroelectric (FE) S^*_C as well as antiferroelectric (AF) S^*_{CA} phases, thus some ability to form the anticlinic AF phase is preserved. The studied dopants induce the AF phase regardless of their ability to form

TABLE 1A. Phase sequences, phase transition temperatures (°C) and enthalpies (in parenthesis, J g^{-1}) for compounds of type 1, 2, and 3.

R_3	R_1	R_2	Phase sequences
H	$H_{31}C_{15}O$–ϕ–CH=N–ϕ–(CO)-	R_1	Cry-112.3 (84.7)-I
	$H_{25}C_{12}O$–ϕ–O–CH_2–ϕ–(CO)-	R_1[e]	Cry-138.3 (91.0)-I
	$H_{25}C_{12}O$–ϕ–O–CH_2–ϕ–(CO)-	H[f]	Cry-127.8 (100.1)-I
	H_3C-CO-O–ϕ–CH=N–ϕ–(CO)-	R_1	Cry-200.8 (69.6)-I
	H_2N–ϕ–(CO)-	R_1	Cry-191.9 (112.0)-I
	O_2N–ϕ–(CO)-	R_1	Cry-184.1 (88.7)-I
CH_3	$H_{25}C_{12}O$–ϕ–CH=N–ϕ–(CO)-	R_1[e]	Cry-109.7 (64.0)-I
	$H_{31}C_{15}O$–ϕ–CH=N–ϕ–(CO)-	R_1[e]	Cry-109.4 (56.0)-I
C_2H_5	$H_{25}C_{12}O$–ϕ–CH=N–ϕ–(CO)-	R_1[e]	Cry-80.9 (84.9)-I
C_3H_7	$H_{25}C_{12}O$–ϕ–CH=N–ϕ–(CO)-	R_1[e]	Cry-86.2 (67.9)-N-24.7[a]-I
	$H_{31}C_{15}O$–ϕ–CH=N–ϕ–(CO)-	R_1[e]	Cry-92.6 (76.9)-N-26.5[a]-I
	$H_{25}C_{12}O$–ϕ–O–CH_2–ϕ–(CO)-	R_1[e]	Cry-77.0 (111.3)-I
	$H_{25}C_{12}O$–ϕ–O–CH_2–ϕ–(CO)-	H	Cry-166.7-I
C_4H_9	$H_{25}C_{12}O$–ϕ–CH=N–ϕ–(CO)-	R_1[e]	Cry-89.7 (53.0)-I[b]
	$H_{31}C_{15}O$–ϕ–CH=N–ϕ–(CO)-	R_1[e]	Cry-81.5 (62.0)-I[b]
C_5H_{11}	$H_{25}C_{12}O$–ϕ–CH=N–ϕ–(CO)-	R_1[e]	Cry-77.9 (53.9)-N-35.6 (0.5)-I
	$H_{31}C_{15}O$–ϕ–CH=N–ϕ–(CO)-	R_1[e]	Cry-75.8 (63.6)-N-37.4 (0.7)-I
C_6H_{13}	$H_{25}C_{12}O$–ϕ–CH=N–ϕ–(CO)-	R_1	Cry-74.0 (43.4)-N-43.6 (0.7)-I[b]

C_7H_{15}	$H_{31}C_{15}O$–ϕ–CH=N–ϕ–(CO)-	R_1	Cry-74.8 (90.6)-N-44.0 (0.8)-I[b]
	$H_{25}C_{12}O$–ϕ–CH=N–ϕ–(CO)-	R_1[e]	Cry-75.1 (46.3)-N-50.5 (0.6)-I
	$H_{31}C_{15}O$–ϕ–CH=N–ϕ–(CO)-	R_1[e]	Cry-73.9 (74.6)-N-49.0 (0.5)-I
-COO-CH_3	$H_{25}C_{12}O$–ϕ–CH=N–ϕ–(CO)-	R_1[e]	Cry-112.0 (55.9)-I
	$H_{31}C_{15}O$–ϕ–CH=N–ϕ–(CO)-	R_1	Cry-107.8 (78.7)-I
-COO-C_2H_5	$H_{25}C_{12}O$–ϕ–CH=N–ϕ–(CO)-	R_1[e]	Cry-101.5 (6.1)-I
-COO-C_4H_9	$H_{25}C_{12}O$–ϕ–CH=N–ϕ–(CO)-	R_1[e]	Cry-62.5 (34.4)-I[b]
	$H_{31}C_{15}O$–ϕ–CH=N–ϕ–(CO)-	R_1	Cry-99.2 (34.9)-I[b]
	$H_{31}C_{15}O$–ϕ–CH=N–ϕ–(CO)-	H	Cry-77.8 (67.3)-I

TABLE 1B. $R_3 = C_6H_{13}$.

R_1	R_2	phase sequences
O_2N–ϕ–(CO)–	R_1[f]	Cry-75.9 (52.0)-I
O_2N–ϕ–(CO)–	-(CO)-CH=CH–ϕ–$OC_{12}H_{25}$	Cry-45.1 (77.5)-I
H_2N–ϕ–(CO)–	R_1	Cry-143.6 (76.8)-I
$H_{31}C_{15}O$–ϕ–CH=N–ϕ–(CO)-	H	Cry-120.2 (30.6)-S_C-161[a]-S_A-191.7 (14.3)-I
$H_{33}C_{16}O$–ϕ–CH=N–ϕ–(CO)-	-(CO)–ϕ–F	Cry-73.7 (77.2)-S_C-55.0 (4.1)-I
$H_{25}C_{12}O$–ϕ–CH=CH–ϕ–(CO)-	R_1[e]	Cry-96.7 (52.8)-I
$H_{25}C_{12}O$–ϕ–CH=CH–ϕ–(CO)-	H	Cry-108.5 (11.0)-S_C-*200*[a]-S_A[d]
$H_{29}C_{14}O$–ϕ–CH=CH–ϕ–(CO)-	-(CO)–ϕ–$OC_{10}H_{21}$[f]	Cry-65.0 (26.0)-I
$H_{29}C_{14}O$–ϕ–CH=CH–ϕ–(CO)-	-(CO)–ϕ–F[f]	Cry-77.4 (61.2)-S_C-84.1 (4.9)-I
$H_{25}C_{12}O$–ϕ–CH=CH–ϕ–(CO)-	-(CO)-CH_2-CH_3[f]	Cry-91.4 (90.6)-S_C-101.3 (1.5)-N-109.8 (1.6)-I
$H_{21}C_{10}O$–ϕ–(CO)-	-(CO)–ϕ–N=CH–ϕ–$OC_{15}H_{31}$[f]	Cry-68.4 (93.7)-I
$H_{25}C_{12}O$–ϕ–O-CH_2–ϕ–(CO)-	R_1[f]	Cry-57.3 (81.2)-I
$H_{25}C_{12}O$–ϕ–O-CH_2–ϕ–(CO)-	H	Cry-113.4 (89.8)-S_C-130.1[a]-S_A-147.8 (22.8)-I
$H_{25}C_{12}O$–ϕ–ϕ–O-CH_2–ϕ–(CO)-	R_1[f]	Cry-113.6 (151.4)-I
$H_{25}C_{12}O$–ϕ–ϕ–O-CH_2–ϕ–(CO)-	H	Cry-107.6 (38.0)-S_G-95.1[a]-N-128.8 (1.0)-I

[a]from microscopy, [b]stable at room temperature, [d]decomposition, [e]induce AF phase, [f]not induce AF phase

liquid crystalline phases. The most effective are the compounds that have the long symmetric branches with the imino or ethyleno internal joints (see TABLE 1). The dopants with the etheral linking inside induce anticlinic S^*_{CA} phase more reluctantly. The compounds containing anti-symmetric or short branches do not influence the structure of FE phase. It points that the long stiff branches with the π-conjugated bond system are necessary to prevent the banana shape of the molecules.

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