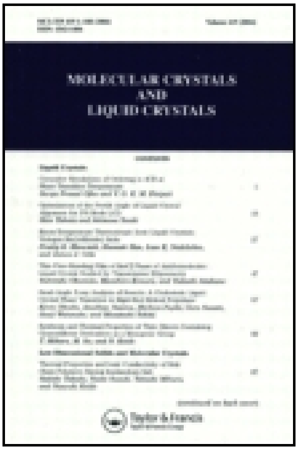

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Ortho Cyano Substituted Negative Dielectric Anisotropic Liquid Crystals

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Ortho Cyano Substituted Negative Dielectric Anisotropic Liquid Crystals†

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A homologous series of 2′-cyano-4′-*n*-alkylphenyl-4-*n*-alkylbiphenylcarboxylates and 4-*n*-alkylcyclohexyl-p-benzoates were synthesized by treating 2′-cyano-4′-*n*-alkyl substituted phenols with 4-n-alkyl substituted biphenyl carboxylic acids and cyclohexyl benzoic acids. The method of synthesis was discussed. All these compounds were nematogenic in character and their phase transition temperatures were examined. A wide range of mesomorphism was observed in almost all the homologous series. IR, NMR and dielectric property of these compounds were studied. The negative dielectric anisotropic property of these liquid crystalline compounds makes them suitable for application in positive GH display devices.

INTRODUCTION

Many aromatic benzoates, biphenyls, phenylcyclohexanes and other compounds substituted with cyano groups in the para position of the benzene ring have found important uses as positive dielectric anisotropic nematogens in mixtures used in twisted nematic display devices. Their method of preparation has already been extensively investigated. However, liquid crystals with relatively strong negative dielectric anisotropy and wide phase transition temperature have scarcely been studied, although negative dielectric anisotropic liquid crystals can be widely used in guest host effect, dynamic scattering effect and cholesteric to nematic phase change effect devices. In recent years, G. W. Gray[1] and T. Inukai[2] have reported that esters with one cyano group or two cyano groups substituted in the ortho position of the phenol or hydroquinone moiety can exert a strong negative

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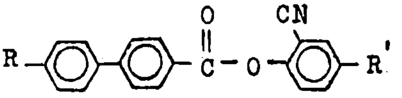
[†] Presented at the Ninth International Liquid Crystal Conference, Bangalore, December 1982.

effect on the dielectric anisotropy. We have, therefore, prepared a number of mono- or dicyano substituted esters in order to meet the requirements of manufacturing positive color display devices of GH effect. In this paper we will only report the mono cyano substituted esters.

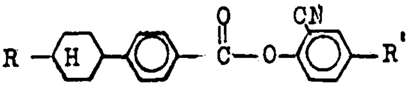
RESULTS AND DISCUSSION

A series of 2-cyano *n*-alkyl substituted biphenyl carboxylates and cyclohexyl benzoates have been synthesized with the following structural formula:



(I)

$R{=}n{-}C_5H_{11}, n{-}C_6H_{13}$
$R'{=}n{-}C_4H_9, n{-}C_5H_{11}, n{-}C_6H_{13}, n{-}C_7H_{15}$



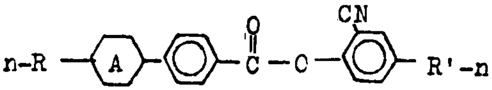
(II)

$R{=}n{-}C_7H_{15}$
$R'{=}n{-}C_4H_9, n{-}C_7H_{15}$

The melting points and transition temperatures of these esters are listed in Table I.

TABLE I

Thermal data of the 2-cyano substituted esters

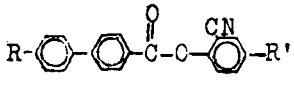


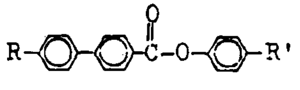
Ring A	n-R	n-R′	Transition Temperature (°C) C-N	Transition Temperature (°C) N-I
Benzene	C_5H_{11}	C_4H_9	80	98
Benzene	C_5H_{11}	C_5H_{11}	85	105
Benzene	C_5H_{11}	C_6H_{13}	56	102
Benzene	C_5H_{11}	C_7H_{15}*	46	102
Benzene	C_6H_{13}	C_5H_{11}	78	99
Benzene	C_6H_{13}	C_6H_{13}	45	92
Benzene	C_6H_{13}	C_7H_{15}	63	98
Cyclohexane	C_7H_{15}	C_4H_9	56	110
Cyclohexane	C_7H_{15}	C_7H_{15}	49	94

*G. W. Gray reported the mesomorphic range as 45-101 °C

TABLE II

Comparison of phase transition temperatures of biphenyl carboxylates with or without cyano substitution





R	R′	C-N(°C)	N-I(°C)	C-S(°C)	S-N(°C)	N-I(°C)
n-C_5H_{11}	n-C_4H_9	80	98	104	144	174
n-C_5H_{11}	n-C_5H_{11}	85	105	93	145	175
n-C_5H_{11}	n-C_6H_{13}	56	102	93	145	163

By comparing the mesomorphic range of 4′-*n*-alkylphenyl 4-*n*-alkyl biphenyl carboxylates[3] with the corresponding 2′-cyano substituted biphenyl esters (see Table II), we found that the introduction of ortho cyano group reduces the phase transition temperatures and renders the compound to be nematogenic instead of smectic-nematic as in most of the biphenyl esters without cyano substitution.

The dielectric data of 2′-cyano substituted esters were presented in Table III. It was shown that, due to the permanent dipole moment acting perpendicular to the molecular long axis as a result of the presence of an ortho cyano group on the benzene ring, the ester compounds are much more negative than their counterparts without cyano substitution. There is no remarkable difference in $\Delta\varepsilon$ between the cyclohexyl benzene carboxylates and biphenyl carboxylates, although the alkyl terminals are not quite alike.

TABLE III

Dielectric data for 2′-cyano substituted esters*

Ring A	R	R′	Dielectric anisotropy	Measuring temperature (°C)
Benzene	C_5H_{11}	C_4H_9	−1.28	82
Benzene	C_5H_{11}	C_5H_{11}	−1.42	89
Benzene	C_5H_{11}	C_6H_{13}	−1.69	65
Benzene	C_5H_{11}	C_7H_{15}	−1.82	55
Benzene	C_6H_{13}	C_5H_{11}	−1.70	82
Benzene	C_6H_{13}	C_6H_{13}	−1.69	64
Benzene	C_6H_{13}	C_7H_{15}	−1.61	65
Cyclohexane	C_7H_{15}	C_4H_9	−1.66	65
Cyclohexane	C_7H_{15}	C_7H_{15}	−1.68	50

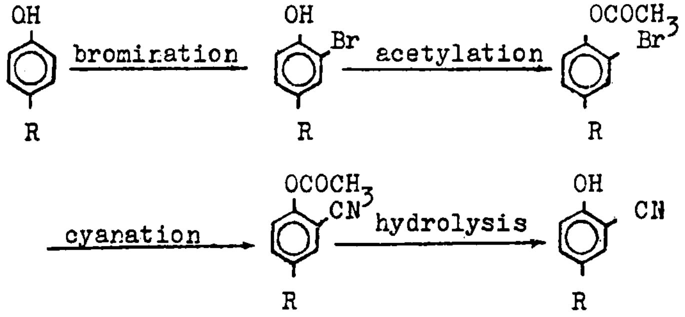
*We measured the dielectric anisotropy of these esters between the nematic range, i.e. just above the melting point of these compounds.

EXPERIMENTAL

All the compounds synthesized gave satisfactory IR, NMR and elemental analysis. The transition temperatures were measured using a Reichert Polarizing microscope equipped with a programmable heating stage. Infrared spectra were recorded on a Specord 75 IR, ^{1}HNMR spectra were obtained on a EM-360L 60 MHZ NMR Spectrometer. Dielectric measurements were carried out at the magnetic field strength of 8000–9000 Gauss with a capacitance bridge in the frequency of 1 KHZ.

Preparation of 2-cyano 4-*n*-alkyl phenol

The following scheme represents the reaction pathway used to prepare the 4-*n*-alkyl 2-cyano phenols:



The experimental procedures are shown as follows:

Bromination A solution of dibromodioxane reagent (35.2 g., Br_2, 0.22 mole in dioxane 20 cm^3) was added dropwise at room temperature to a stirred solution of *p*-*n*-heptyl phenol (42.3 g., 0.22 mole) in dioxane (80 cm^3). Forty five minutes after completion of addition, the obtained pale yellow solution was stirred for 4 h at room temperature, then poured into ice water to liberate the oil layer. The upper aqueous layer was extracted with ether, and the combined organic layer was washed with water and dried over Na_2SO_4. After removal of ether the crude residue was distilled under vacuum to give 43 g (72%) of product, b. p. 111°C/0.28 mm Hg.

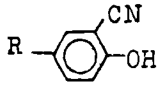
Acetylation Acetyl chloride (15.7 g., 0.2 mole) was added dropwisely during 20 minutes to the stirred ice-water cooled solution of 2-Bromo 4-*n*-heptylphenol (48.8 g., 0.18 mole) in dry pyridine (60 cm^3). The mixture was stirred at room temperature for further 3 h and then poured into ice water. The aqueous layer was separated from the oil layer and extracted with ether. The combined organic layer was washed successively with 3% hydrochloric acid, sodium bicarbonate solution and water, and finally dried over Na_2SO_4. After removal of ether, the acetate was distilled under vacuum. (121 ~ 124°C/0.3 mm Hg). The yield was 50 g., (90%).

Cyanation Copper (I) cyanide (9.85 g., 0.11 mole) was added to a stirred solution of 2-bromo-4-heptylphenyl acetate (25 g., 0.08 mole) in dried dimethylformamide (70 cm^3). The mixture was refluxed for 7 h at 152°C. After cooling, the reaction mixture was added to a solution of ferric chloride (32 g., 0.2 mole), concentrated hydrochloric acid (8 cm^3) and water (54 cm^3) and the mixture was stirred at 65 ~ 70°C for 20 min. The crude product was extracted with ether, and the extract washed with water and dried over Na_2SO_4. After removal of ether the residue was distilled under vacuum to give two fractions. The first fraction consists of the expected cyano acetate and the second fraction was the hydrolyzed product 2-cyano 4-heptyl phenol, boiling at 157°C/0.5 mm Hg.

Hydrolysis 2-Cyano 4-heptyl phenylacetate (3 g., 0.01 mole) was heated with ethanol (8 cm^3), water (2 cm^3) and sodium hydroxide (0.8 g., 0.02 mole) under reflux for 1 h, ethanol was removed and water (10 cm^3) was added again to dissolve the precipitate. Neutralized with hydrochloric acid (6N) to slightly acidic, then extracted with ether twice (60 cm^3). The ether extract was washed with water until neutral and dried over Na_2-SO_4. Ether was removed and the crude product (1.7 g.) was recrystallized together with the above mentioned hydrolyzed fraction (7.7 g) from benzene and petroleum ether (b. p. 60–80°C) (1:4) mixture to afford a white crystalline solid. mp. 81°C. After purification the total yield was 6.2 g. (46%).

TABLE IV

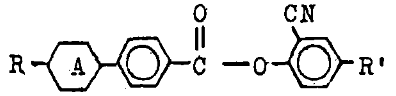
Melting points, yields and analytic data of 2-cyano 4-*n*-alkyl phenols



R	mp (°C)	Yield (%)	Analytic data N%	
			Cal.	Found
C_4H_9	59	58	8.00	8.08
C_5H_{11}	80	18	7.41	7.38
C_6H_{13}	68	34	6.90	7.10
C_7H_{15}	81	46	6.50	6.50

TABLE V

Yields and analytical data of 2′-cyano 4′-*n*-alkyl phenyl-4-*n*-alkyl biphenyl carboxylates and 4-*n*-alkyl cyclohexyl benzoates



Ring A	R	R′	Yield (%)	Analytical data (%)					
				Found			Calculated		
				C	H	N	C	H	N
Benzene	C_5H_{11}	C_4H_9	64	81.62	7.26	3.34	81.8	7.3	3.29
Benzene	C_5H_{11}	C_5H_{11}	58	82.16	7.63	3.20	82.0	7.52	3.19
Benzene	C_5H_{11}	C_6H_{13}	60	81.50	7.80	3.09	82.12	7.73	3.20
Benzene	C_5H_{11}	C_7H_{15}	72	82.41	7.89	3.02	82.30	7.92	2.99
Benzene	C_6H_{13}	C_5H_{11}	77	82.09	7.95	3.08	82.10	7.72	3.09
Benzene	C_6H_{13}	C_6H_{13}	68	81.74	7.92	3.11	82.22	7.92	3.00
Benzene	C_6H_{13}	C_7H_{15}	65	82.20	7.75	2.97	82.40	7.72	3.00
Cyclohexane	C_7H_{15}	C_4H_9	80	80.88	9.02	3.08	81.05	8.93	3.05
Cyclohexane	C_7H_{15}	C_7H_{15}	76	81.30	9.24	2.58	81.44	9.38	2.80

The above procedures were also applicable to butyl, amyl and hexyl phenols.

Preparation of 2′-cyano-4′-heptylphenyl-4-hexylbiphenyl carboxylate

The 4-*n*-alkylbiphenyl acids were prepared from biphenyl, followed by alkylation, acetylation and hydrolysis.

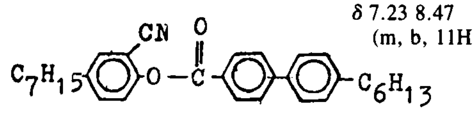
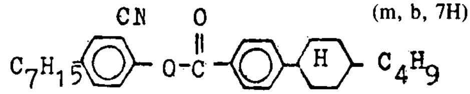
4-*n*-alkylcyclohexyl benzoic acid was synthesized from cyclohexene according to the method of Tsinghua University.[4]

The following procedure for the preparation of 2′-cyano 4′-*n*-heptylphenyl 4-*n*-hexylbiphenylcarboxylate exemplifies the method used.

4-Hexylbiphenyl acid (4.2 g, 0.015 mole) in toluene (8 cm^3) was heated with exclusion of moisture, with freshly distilled thionyl chloride 3.6 g (0.03 mole) at 90–100°C for 2 h. The excess thionyl chloride was removed by distillation. The residual acid chloride was then diluted with toluene (3 cm^3). Whilst stirring a solution of 2-cyano 4-*n*-heptyl phenol (3.26 g, 0.215 mole) in dry toluene (2.5 cm^3) and dry pyridine (4.2 cm^3) was added dropwise. After the addition, the stirred mixture was heated under reflux with the exclusion of moisture for 3 h. Then distilled out the toluene and added H_2O (60 cm^3) to the reaction mixture, the separated organic layer was extracted with ether twice (150 cm^3), washed to neutral and dried over Na_2SO_4. Ether was removed and the residue (5 g) was chromatographed on a column of silica gel eluting with benzene: *n*-hexane (1 : 1). The fractions

TABLE VI

Selected NMR data for cyanoesters

Compound	Aromatic protons	Aliphatic protons
	δ 7.23 8.47 (m, b, 11H)	δ 2.66 (t, 4H) 1.35 (m, b, 18H) 0.90 (t, 6H, 2 X CH_3)
	δ 7.35 8.18 (m, b, 7H)	δ 2.68 (t, 2H) 1.29 ~ 2.01 (m, b, 26H) 0.94 (t, 6H, 2 X CH_3)

Solvent CCl_4

containing the ester were combined and crystallized several times from absolute ethanol to afford the pure 2′-cyano 4′-*n*-heptyl phenyl 4-*n*-hexyl biphenyl carboxylate (4.5 g) as white needles, yield 65%.

The yields and analytical data for the final products are listed in Table V.

IR and 'H NMR data for the esters

The infrared spectrum for the 2′-cyano 4′-*n*-heptyl phenyl 4-hexylbiphenyl carboxylate was consistent with the product: νmax (KCl) 2230 (CN, medium band), 1730 (ester, C = 0 strong band (cm^{-1}. Its spectral data exemplify the 2′-cyano substituted esters as a whole, only when the phenyl group is replaced by a cyclohexane ring, the νc = 0 shifted towards higher frequency from 1730 to 1770 cm^{-1}.

The 'H NMR spectroscopic data for the representative examples of the esters prepared are given in Table VI.

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