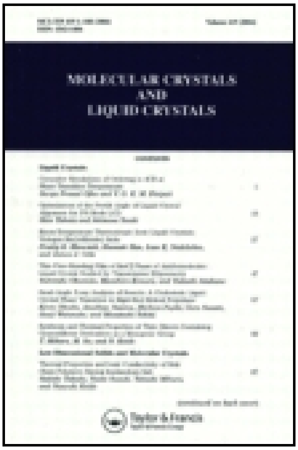

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Synthesis of Three Ring Ester Liquid Crystals

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Synthesis of Three Ring Ester Liquid Crystals

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Eleven compounds of general structure R—X—Y—COO—Z—R′, where X, Y and Z are either phenyl or *trans* cyclohexyl rings, were synthesized and their liquid crystalline properties were evaluated. The isomerization methods for *cis*-4-alkyl cyclohexanol to the *trans* isomer and for 4′-alkylphenyl-4-*cis*-cyclohexanecarboxylic acid to its *trans* isomer are discussed. The *trans* isomers were isolated and purified by preparative HPLC. The structure assignments were confirmed by carbon 13 NMR.

INTRODUCTION

Dual-frequency addressable liquid crystals have found uses in fast color switches[1] and highly multiplexable matrix applications[2,3] due to the control possible over the dielectric behavior and threshold voltages of the materials. The manipulation of these properties depends primarily on the custom tailoring of the dielectric relaxation frequency of the components. Many ester liquid crystals with the general structure R—X—Y—COO—Z—R′ where X, Y and Z are phenyl or *trans* cyclohexyl were evaluated with respect to frequency dependence of their dielectric constants in mixtures.[4]

Since phenyl and *trans*-cyclohexyl rings are so different in terms of electronic distribution, polarizability and flexibility, we hope by arranging these rings at different positions one could change the relaxation frequency.

Out of eight possible arrangements of these rings (Figure 1) three are commercially available from E. M. Laboratories. (These were shown by commercial names under the structures.) In this paper we will describe the synthesis of the other five possible ring arrangements and their liquid crystalline properties.

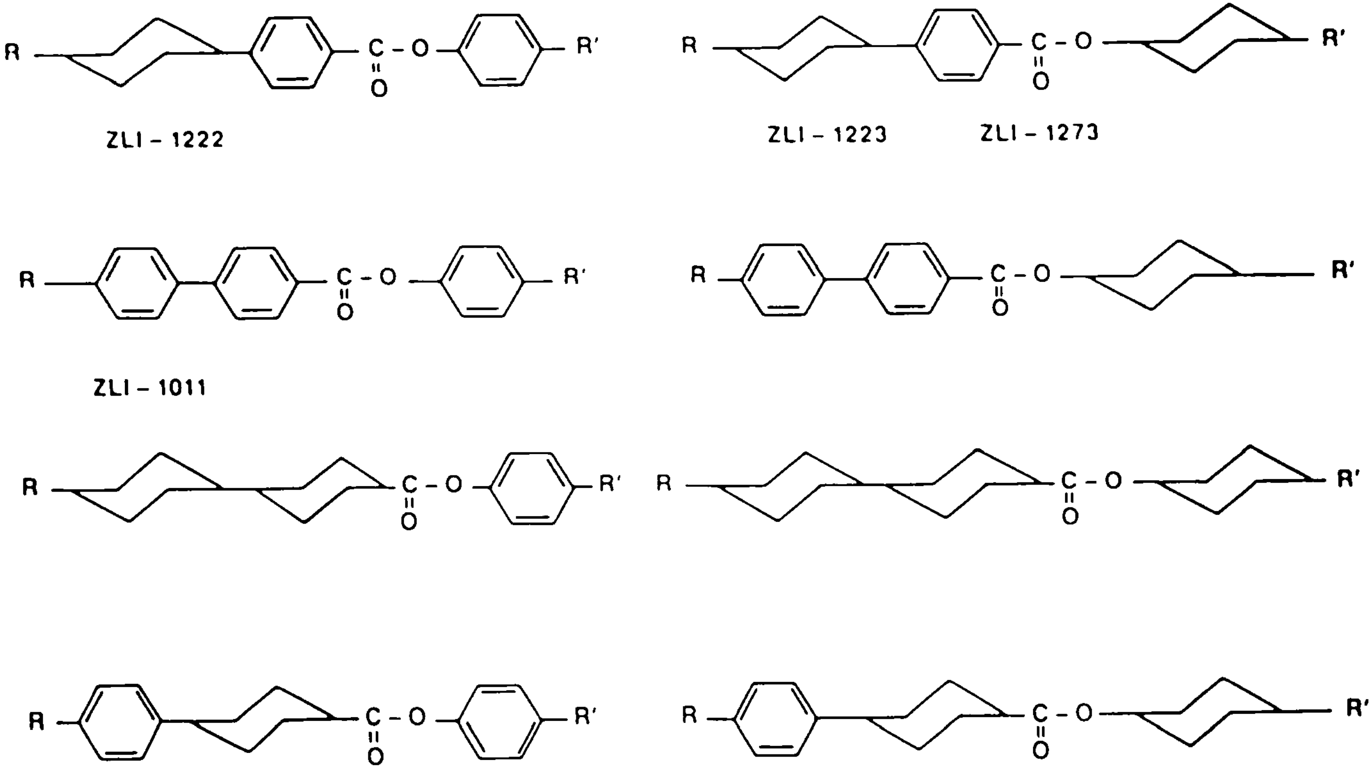


FIGURE 1

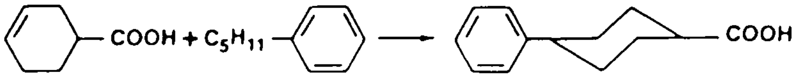
SYNTHESIS

The esterification reactions are easily carried out in high yield by reaction of the acid cholorides with the substituted phenols or cylohexanols.

The synthesis of 4-n-alkyl-biphenyl-4′-carboxylic acid chloride was reported by Chan S. Oh.[5] The 4′-n-alkyl-4-cyclohexyl cyclohexane carboxylic acid was obtained by acid catalysed hydrolysis of commerical available cyclohexylcyclohexane (CCH) liquid crystals such as ZLI-1185 (E. M. Labs). The synthesis of 4-(p-n-alkylphenyl) cyclohexane carboxylic acid was more involved.

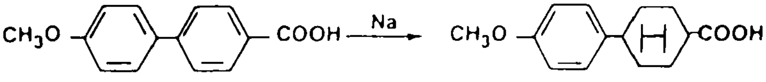
Sugita Kyoto, *et al.*,[6] reported using 3-cyclohexane carboxylic acid to react with benzene to form *trans* 4-phenylcyclohexane carboxylic acid as a major product.

A complex mixture resulted from this method using pentylbenzene as starting material. One of the major products was *trans* 4-phenylcyclohexane carboxylic acid, due to elimination of the pentyl group in the presence of aluminium trichloride.



Separation of several other isomerization products was not attempted.

W. S. Johnson, *et al.*[7] reported the synthesis of 4(P-methoxyphenyl) cyclohexane carboxylic acid by sodium reduction of 4-(P-methoxyphenyl) benzoic acid in isoamyl alcohol.



When this method was applied to p-pentylphenylbenzoic acid an oily product was obtained. The carbon 13 NMR spectrum of this crude product showed that the product is a mixture of *cis* and *trans* isomers. The isomers were separated into reasonably pure *cis* and *trans* isomers by preparative HPLC. The C-13 NMR spectra showed chemical shift of carboxylic carbon at 176ppm in *cis*-isomer and 182ppm in *trans*, the carbon attached to it then at 63ppm in *cis* and 43ppm in *trans*-isomer respectively. The ratio is about 70% *cis* and 30% *trans* isomer. Since we need only the *trans* acid it is important to isomerize the *cis* isomer into *trans* in good yield. Inukai Takashi, *et al.*,[8] reported a method for conversion of *cis*-alkylcyclohexane carboxylic acid to the *trans* isomer by heating with sodium methoxide in N-methyl pyrrolidinone. We found that their method also works with *cis*(4-n-alkylphenyl) cyclohexane carboxylic acid. Takashi heated the reactant to 200°C for ten hours which produced some decomposition but the yield was still acceptable with alkylcyclohexane carboxylic acid. In our case, the decomposition became so serious that a lot of tar was formed. Since the mechanism of this isomerization must be ionic in nature, the reaction time could be minimized as long as the temperature is high enough. After heating at 205°C for one hour, we obtained up to 90% isomerization. We also obtained equally good results with pentylcyclohexane carboxylic acid.

The hydrogenation of p-alkylphenol on rhodium catalyst gives a mixture of *cis* and *trans* alkylcyclohexanol with a ratio of about 60% *cis* and 40% *trans* isomers (determined by carbon 13 NMR). The two isomers were separated by preparative HPLC and the *cis* isomer was isomerized to *trans* using the method of W. G. Dauben, *et al.*,[9] and E. L. Eliel, *et al.*[10] The *cis* isomer was refluxed in isopropanol with aluminium triisopropoxide and a catalytic amount of acetone for 72 hours, and a mixture of about 80% *trans* isomer was obtained, as confirmed by carbon 13 NMR. The chemical shift of the carbon attached to the hydroxy group is 67ppm in *cis* and 71ppm in *trans*-isomer.

RESULTS

Eleven compounds were thus synthesized; their structure and thermal data are summerized in Table 1.

These esters were added to test mixtures defined in a previous paper.[4] The dielectric anisotropies are plotted against frequency in Figures 2 and 3. We can see that the arrangement of the three rings do have a significant influence on the cross-over frequency, with R—PH—PH—COO—PH—R′ (18kHZ) having the highest cross-over frequency and the R—CY—CY—COO—PH—R′ (8kHZ) the lowest.

TABLE I

$R—X—Y—CO_2—X—R'$

Tek No.	X	Y	Z	R	R′	K → S (°C)	→ N (°C)	→ I (°C)	Yield (%)
2029	CY	CY	CY	C_5H_{11}	C_5H_{11}	44		187	25
2032	CY	CY	PH	C_5H_{11}	C_5H_{11}		172	187	30
2042	CY	CY	PH	C_3H_7	C_5H_{11}	31	150	185	30
2043	CY	CY	PH	C_3H_7	C_7H_{15}	46	153	176	35
2044	CY	CY	PH	C_3H_7	C_3H_7	60	143	195	33
2045	PH	PH	CY	C_5H_{11}	C_5H_{11}		71	152	46
2046	PH	PH	CY	C_5H_{11}	C_7H_{15}		71	136	45
2047	PH	CY	PH	C_5H_{11}	C_3H_7	80	99	135	42
2048	PH	CY	PH	C_5H_{11}	C_5H_{11}	71	110	125	41
2049	PH	CY	CY	C_5H_{11}	C_5H_{11}	54	110	122	38
2050	PH	CY	CY	C_5H_{11}	C_7H_{15}	57		123	35

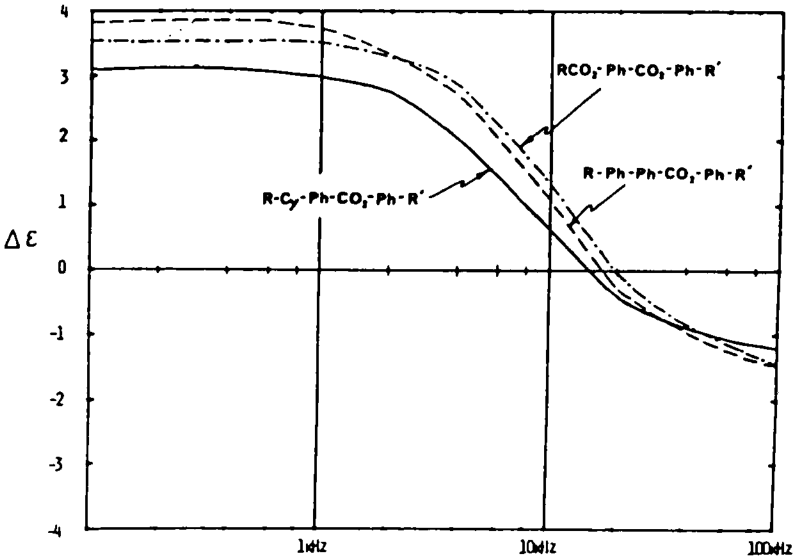


FIGURE 2

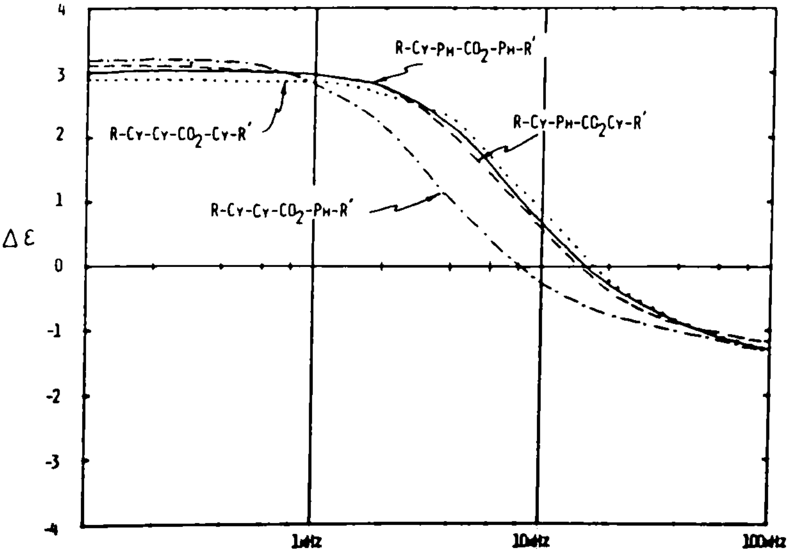


FIGURE 3

When these esters are incorporated into mixtures the parallel and perpendicular dielectric constants and the cross-over frequency can be adjusted to suit specific applications. This will be discussed as part of a later publication.

EXPERIMENTAL METHODS

The final products were purified on a Waters 500A preparative chromatograph using a silica gel column. The pure products were identified by their proton and carbon-13 NMR spectra obtained on a JEOL FX-900 Spectrometer and by IR spectroscopy.

The purity of the products was checked by HPLC using a Perkin-Elmer Series 10 liquid chromatograph.

The synthesis procedures using *trans*-4-n-pentylcyclohexyl 4′-n-pentylphenyl-*trans*-4-n-cyclohexanoate as an example are as follows:

Preparation of 4(4′-n-pentylphenyl) cyclohexane carboxylic acid: Isoamyl alcohol (45ml) was added to sodium (50 g) and heated to reflux. A hot solution of 3 g pentylbiphenyl acid in isoamyl alcohol was added to the sodium-alcohol mixture through a funnel as quickly as possible. The mixture was kept at reflux for 2 hours. It was poured over ice and acidified with dilute sulfuric acid, extracted with toluene. The organic layer was dried over magnesium sulfate and concentrated under vacuum. An oily product (3 g) was obtained. The Carbon-13 NMR spectrum showed it to consist of about 80% *cis* and 20% *trans* 4(4′-n-pentylphenyl)cyclohexane carboxylic acid.

Preparation of pure *trans* 4(p-n-pentylphenyl)cyclohexane carboxylic acid: The crude oily product of the previous reaction (4.5g) was dissolved in N-methylpyrrolidinone (120 ml), and sodium methoxide (15g) was added. The mixture was heated to reflux and the low boiling fraction was distilled out until the temperature rose to 205°C. The heating was continued for one hour under reflux. The mixture was poured over 500ml crushed ice acidified by 20% hydrochloric acid. The *trans* acid precipitate was filtered, washed with water, dried under vacuum and recrystallized with methanol. A yield of 4g (89%) was obtained.

Preparation of *trans*-4-n-pentyl-cyclohexanol: 4-n-pentylphenol (19g) dissolved in 150 ml methanol. A 5% rhodium on alumina catalyst (1 g) was added to the above solution. The reaction mixture was hydrogenated at about 50 psi hydrogen pressure on a Parr hydrogenation apparatus until the absorption of hydrogen had stopped, which took about 5 hours. The catalyst was filtered out, and the solution was concentrated under vaccuum to remove methanol. The residue was dissolved in 150 ml of isopropyl alcohol. Aluminum isopropoxide (12 g) and methyl-ethyl ketone (0.5 ml) were added. The mixture was refluxed for 70 hours. The mixture was concentrated under vacuum to remove all solvents. The residue was carefully dissolved in ice cold dilute hydrochloric acid, and was extracted by methylene chloride. The organic solution was dried over magnesium sulfate, and concentrated to remove methylene chloride. The carbon-13 NMR spectrum showed it to consist of about 80% *trans* and 20% *cis* 4-n-pentylcyclohexanol. The mixture was dissolved in a 1:4 mixture of ethyl acetate and hexane. The solution was injected into a normal phase preparative column. The same solvent system was used as the mobile phase.

Pure *trans*-4-n-pentylcyclohexanol (14 g) was obtained. The *cis* isomer and *cis-trans* mixture could be combined and run through the isomerization procedure again.

Preparation of *trans*-4-n-pentylcyclohexyl 4′-n-pentyl phenyl *trans*-4-n-cyclohexanoate: *trans*-4-(p-n-pentylphenyl) cyclohexane carboxylic acid (2.0 g) was dissolved in 50 ml toluene, to which thionyl chloride (10 ml) was added. The mixture was boiled under reflux for 4 hours. It was then concentrated under vacuum to remove excess thionyl chloride. The residue was dissolved in 20 ml toluene, and 4-n-pentylcyclohexanol (1.5 g) was added. Pyridine (2 ml) was added slowly into the reaction mixture with stirring. The mixture was stirred at room temperature for 24 hours. After dilution by toluene it was washed by 10% hydrochloric acid, twice by water, dried over magnesium sulfate, filtered and concentrated. The residue was dissolved in a 1:8 mixture of ethyl acetate and hexane, injected into a normal phase preparative HPLC column using the same solvent system for the mobile phase. The compound corresponding to the main peak was separated out and recrystallized from methanol. A yield of 1.2 g of *trans*-4-n-pentylcyclohexyl 4′-n-pentylphenyl-*trans*-4-cyclohexanoate (38%) was obtained. The mother liquor was not treated.

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