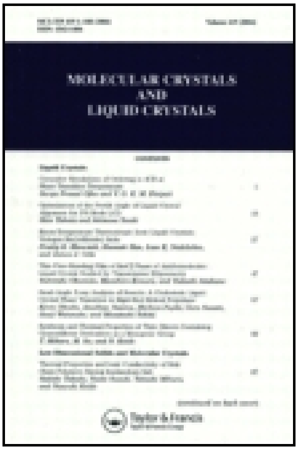

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Liquid Crystals With a Chiral Core: Cyclohexene Carboxylates

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Liquid Crystals with a Chiral Core: Cyclohexene Carboxylates

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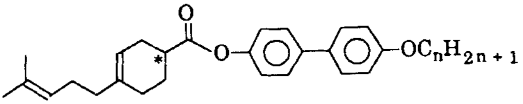
A series of new liquid crystals containing a cyclohexene ring have been synthesized and characterized. The cyclohexene ring is formed by the Diels-Alder reaction between myrcene and methyl acrylate, and has a chiral center. Hydrolysis of the resulting methyl ester into the corresponding acid and esterification of the latter with 4-hydroxy-4′-*n*-alkoxybiphenyl yields a homologous series of liquid crystals with the structure:



The compounds thus prepared are racemic mixtures. The lower members of this series (n = 1 and 2) have a large nematic range, and the higher members (n = 3–10) have multiple smectic phases in addition to the nematic phase. When (1R,2S,5R)-(−)-menthyl acrylate was used instead of methyl acrylate in the Diels-Alder synthesis, optically active compounds with 40% enantiomeric excess were obtained.

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INTRODUCTION

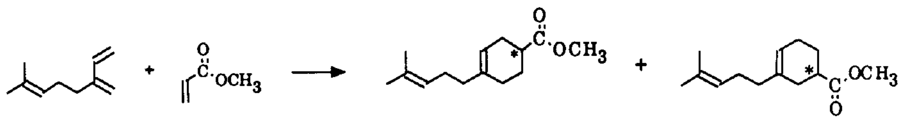
Most thermotropic liquid crystals contain a "rigid" mesogenic core which is composed of benzene, cyclohexane, or heterocyclic rings, sometimes with a bridging linkage. The first liquid crystals containing a cyclohexene ring were reported by Osman and Revesz in 1982.[1] More recently, a series of liquid crystals derived from the three isomers of cyclohexene carboxylic acid were reported by Bezborodov *et al.*[2] In the mean time, two 3-cyclohexenecarboxylates were synthesized independently in one of our laboratories.[3]

Since the cyclohexene ring is non-planar, its contribution to the mesogenic properties of a compound would be similar to that of the cyclohexane ring. However, there is a significant difference in molecular symmetry: 1,4-disubstituted cyclohexenes have at least one asymmetric carbon. This opens the interesting possibility of introducing a chiral center in the mesogenic core of a liquid crystal molecule. Then the branching out of the aliphatic chain caused by the incorporation of the chiral center into the chain can be avoided and the mesomorphic character of the compounds may be enhanced. Actually, cholesterol esters belong to this category, but the fused ring system imparts some undesirable physical properties such as high viscosity to the compounds. Therefore, some applications of liquid crystalline cholesterol esters are rather limited. A few compounds with a chiral center in non-fused rings in the mesogenic core have been reported.[4,5] Unfortunately, they have only monotropic liquid crystalline phases.

The synthetic routes reported by Bezborodov *et al.*[2] for cyclohexenecarboxylic acids are rather elaborate, and the compounds obtained are racemic mixtures. In a previous report by Fung *et al.*[3] 3-cyclohexenecarboxylic acid was prepared by a simple Diels-Alder reaction using myrcene, an inexpensive terpene, as the starting material. Although the liquid crystals synthesized are also racemic mixtures, optically active compounds can be prepared by using optically pure menthyl acrylate in the Diels-Alder reaction to provide optical induction. The synthetic procedures and the properties of a series of racemic 3-cyclohexenecarboxylates and those of two optically active compounds are reported here.

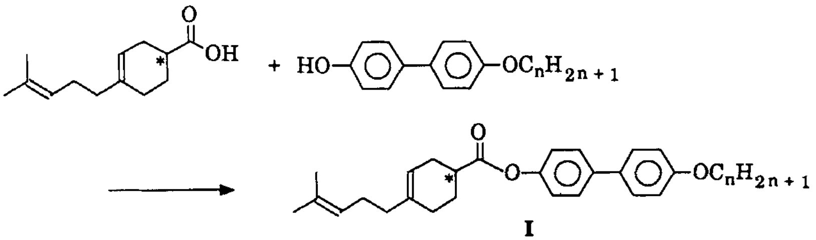
EXPERIMENTAL

The Diels-Alder reaction between myrcene and the dienophile methyl acrylate has been discussed previously.[3] The reaction is highly regioselective, and the *para*/*meta* product ratio is 95:5 when aluminum chloride is used as a catalyst:



95 : 5

The reaction product, after vacuum distillation, is hydrolyzed to give the corresponding acid, which is then reacted with 4-*n*-alkoxy-4′-hydroxybiphenyl to yield the desired compound:



I

I = 4′-*n*-alkoxybiphenyl 4-(4-methyl-3-pentenyl)-3-cyclohexenecarboxylate.

The procedures for the synthesis and purification have been given in detail previously,[3] and they are not repeated here. These procedures are not enantiospecific, and yield racemic mixtures. In order to synthesize optically active 4-alkenyl-3-cyclohexene-carboxylic acid, we used the method of asymmetric induction, which is described herein.[6,7]

The starting dienophile menthyl acrylate was prepared in the following way.[8] A solution of 9.5 g (0.11 mole) of acryloyl chloride and 11.7 g (0.11 mole) of triethylamine in 50 ml of anhydrous diethyl ether was cooled in an ice bath, and a solution of 15.7 g (0.1 mole) of (1R,2S,5R)-(−)-menthol in 50 ml of anhydrous diethyl ether was added dropwise. Triethylammonium hydrochloride was precipitated immediately. After the addition was complete, the reaction mixture was refluxed for 2 hr. The ether solution was filtered and washed successively with 10% aqueous sodium bicarbonate and saturated sodium chloride. The ether layer was dried over anhydrous sodium sulfate. The solvent was removed by rotary evaporation and the residue was distilled to yield 13.7 g (65%) of menthyl acrylate, b.p. 94–96°C/3 mmHg (lit. b.p. 102–104°C/11 mmHg).[8] In order to obtain a homogeneous reaction solution in the asymmetric Diels-Alder reaction between myrcene and the optically active menthyl acrylate, diethyl aluminum chloride was used as the Lewis acid catalyst instead of aluminum chloride. The reaction mixture was stirred for 24 hr at 4°C. After working up as usual, the pure product was obtained by distillation at reduced pressure (b.p. 174°C/0.1 mmHg; 63% yield). The menthyl ester had a rotation of $[\alpha]^{23} = (-)24.9$ ($c = 8$, dioxane). The ratio of the resulting diastereo isomers was determined by ^{13}C-NMR, and found to be about 7:3, or 40% diastereomer excess. The chemical shifts of the olefinic carbons in the cyclohexene ring are 118.98 and 137.33 ppm for one isomer, and 118.94 and 137.42 ppm for another. To hydrolyze the menthyl acrylate, it was refluxed in 4% ethanolic potassium hydroxide solution for 2 days. The solution was neutralized to obtain the acid, which had a rotation of $[\alpha]^{23} = (+)20.4$ ($c = 2$, chloroform). This value is equal to 39% of the specific rotation of (+)-4-*n*-pentyl-3-cyclohexenecarboxylic acid,[6] and is consistent with the result obtained from the ^{13}C NMR spectrum of the diastereomeric precursor, (1R,2S,5R)-(−)-menthyl acrylate. This is an indication that no appreciable racemerization occurred during the saponification. Further esterification of the acid with 4-hydroxy-4′-*n*-octyloxybiphenyl or 4-hydroxy-4′-cyanobiphenyl yielded the desired optically active liquid crystals. For 4′-*n*-octyloxybiphenyl 4-(4-methyl-3-pentenyl)-3-cyclohexenecarboxylate (**II**), the chemical shifts δ (ppm) of ^{13}C-NMR ($CDCl_3$) are 174.49, 158.74, 149.77, 138.50, 137.49, 132.72, 131.50, 128.03, 127.57, 124.12, 121.68, 118.68, 114.78, 68.09, 39.57, 37.52, 31.80, 29.35, 29.28, 29.22, 27.64, 27.59, 26.38, 26.05, 25.67, 25.50, 22.64, 17.68, and 14.07. For 4'-cyanobiphenyl 4-(4-methyl-3-pentenyl)-3-cyclohexenecarboxylate (**III**), the chemical shifts δ (ppm) of ^{13}C-NMR ($CDCl_3$) are 174.21, 151.30, 144.66, 137.48, 136.56, 132.51, 131.44, 128.16, 127.55, 124.03, 122.20, 118.72, 118.51, 110.93, 39.43, 37.44, 27.54, 27.47, 26.30, 25.60, 25.39, and 17.62.

RESULTS AND DISCUSSION

The alkyl chain in **I** contains a double bond and a methyl branch as found in myrcene. If additional steps are used to synthesize 2-*n*-alkylbutadienes as the starting material in the Diels-Alder reaction, compounds with non-branched alkyl chains can be prepared. Alternatively, they can also be synthesized by more elaborate procedures.[2,9] It is known that liquid crystals with alkenyl side chains are chemically and photochemically stable as long as the double bond is not conjugated.[10–14] Some of the alkenyl liquid crystals, especially those having a double bond between the third and fourth carbon atoms in the chain, have some interesting properties which are advantageous for liquid crystal displays, such as a reduced k_{33}/k_{11} ratio and increased dielectric anisotropy.[10–14] Thus, the homologous compounds **I** may be useful components in preparing eutectic mixtures for liquid crystal displays.

As far as the branched methyl group at the end of the chain is concerned, it is not unreasonable to expect that it would cause less disturbance to the molecular ordering in the liquid crystalline phases than branching groups in the middle of an aliphatic chain. Actually, the major effect of the end-branched methyl group seems to raise the melting point, but does not change the clearing point considerably. For example, the clearing temperature for the racemic mixture **II** (n = 8 in **I**) is 144°C (Table I), while that of a similar compound with a 3-*n*-pentyl chain instead of the 4-methyl-3-pentenyl chain on the cyclohexene ring is 148.5°C.[9] Another

TABLE I

Transition temperatures (°C) of compounds in series I

n	K	S_{X2}	S_{X1}	S_C	S_A	N	I
1	81	-	-	-	-	157	
2	99	-	(70)	(84)	-	165	
3	97	-	(90.5)	100	-	150	
4	86	(84)	107	122	-	156	
5	78	-	106	124	-	148	
6	79	94	113	132	133	150	
7	73	97	113	132	133	144	
8	73	102	116	136	137	144	
9	72	97	114	132	135	138	
10	78	104	118	136	139	140	

example is the racemic mixture of **III**, which is similar to **I** except that there is a cyano group instead of an alkoxy group attached to the biphenyl ring. It has a nematic range from 93° to 152°C[3] compared with the nematic range of 64–165°C for the straight-chain alkyl analog, 4′-cyanobiphenyl 4-*n*-pentyl-3-cyclohexenecarboxylate.[2] Again, the increase of the melting point is considerably more than the lowering of the clearing point. However, it must be pointed out that in both of these examples, we have compared compounds with a 4-methyl-3-pentenyl group to compounds with an *n*-pentyl group because the corresponding unbranched 3-pentenyl compounds are not available. The actual effect of the different chains on the mesomorphic properties may be due to a combination of the double bond and the branched methyl group in the alkenyl chain rather than due to the methyl group alone.

The transition temperatures of the racemic mixtures of the homologous series **I** are given in Table I. For $n = 1$ and 2, there is only one mesomorphic phase with a fairly wide nematic range of about 70°C. Smectic phases exist for compounds with $n \geqslant 3$, and the phase behavior is unusually rich for the higher members of this series, especially for $n \geqslant 8$. The existence of many smectic phases is apparently due to the presence of the cyclohexene ring. The 4-methyl-3-pentenyl chain does not seem to play an important role in causing the rich phase behavior, because a compound analogous to **II** except with an *n*-pentyl chain instead of the alkenyl chain has an essentially identical phase sequence.[9] Judging from the pattern appearing under the polarizing microscope, the phase labelled S_{X1} is probably a smectic F phase, and the phase labelled S_{X2} is probably S_G. The melting points for $n = 8$ and 10 from solid to S_{X2} could not be clearly determined by microscopic evaluation. The transition temperatures listed in Table I were determined from DSC measurements, except for those of the monotropic phases, which were determined from polarizing microscope observations. Actually the compounds with $n = 4$ and 9 have another monotropic phase, which is probably S_H. It appears at 91°C and 97°C, respectively, for these two compounds, and is not listed in Table I. These phase identifications are tentative and must be confirmed by X-ray diffraction studies.

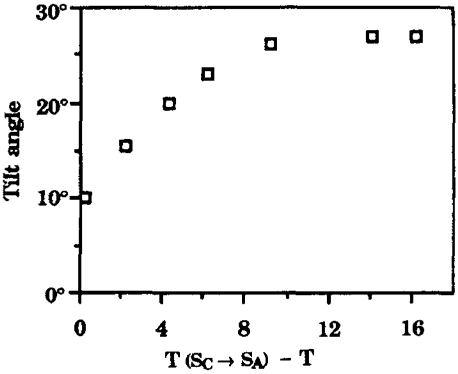


FIGURE 1 The tilt angle of 4′-*n*-octyloxybiphenyl 4-(4-methyl-3-pentenyl)-3-cyclohexenecarboxylate (**II**) (40% ee) in its SmC* phase as a function of temperature.

As stated in the Introduction, our foremost interest in the synthesis of cyclohexenyl liquid crystals is to prepare optically active compounds with a chiral center in the mesogenic core. Optically pure liquid crystals containing a cyclohexene ring can be synthesized by carrying out enantiospecific conversion of a natural product, such as β-pinene, into 4-alkyl-3-cyclohexenecarboxylic acid.[9] On the other hand, when asymmetric induction[6,7] is used in the Diels-Alder reaction as described above, the cyclohexene adduct synthesized has an enantiomeric excess (ee), and the final liquid crystal products are optically active. Although the optical activity of the products obtained is lower than that synthesized from β-pinene, the synthetic procedures are much simpler. Thus, the use of (1R,2S,5R)-(−)-menthyl acrylate instead of methyl acrylate as the starting dienophile yielded products with 40% ee. Attempts were made to increase the ee by using (−)-8-phenylmenthyl acrylate, but no obvious improvement was obtained.

One of the incentives in preparing the optically active cyclohexenecarboxylates was to obtain ferroelectric liquid crystals with high spontaneous polarization (Ps) to be used in surface-stabilized ferroelectric liquid crystal displays.[15] The reasoning

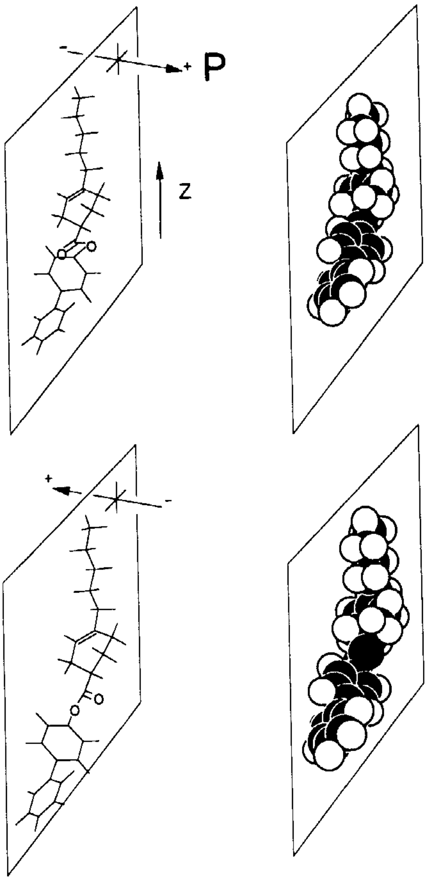


FIGURE 2 Stick and space-filling models of biphenyl 4-*n*-pentyl-3-cyclohexenecarboxylate.

for this is that the molecular segments about the chiral center in the "rigid" core would have more restricted rotation and therefore possibly larger average lateral dipole moments. The optically active compound **II** does have a SmC* phase (Table I), and its tilt angle is quite normal (Figure 1). Unfortunately, its value of Ps is extremely small, being less than 0.4 nC/cm^2 over the entire SmC* range. When it is extrapolated to a 100% optically active compound, the value of Ps would not be more than 1 nC/cm^2. This small polarization can be rationalized as follows. Figure 2 shows stick and space-filling models of the principal configurations expected for the core and tail attached to the cyclohexene ring relative to the smectic C tilt plane indicated by the parallelograms. As is generally the case with thermotropic smectic C materials, we expect the tail to be less tilted than the core relative to the layer normal direction **z**, vertical in Figure 2.[16] Tripos force field calculation of the preferred configuration about the first C—C bond connecting the cyclohexene ring to the tail yields the result shown, in which the plane containing an all-*trans* chain would be normal to the best plane of the cyclohexene ring. In this configuration the small dipole associated with the chiral carbon is in the tilt plane and will not contribute to **P**. The other potential source of dipole moment is the carbonyl adjacent to the chiral carbon. However, the two Tripos preferred configurations shown have nearly the same energy and molecular shape, but opposite carbonyl dipole moment relative to the tilt plane, with the signs indicated. These would be expected to occur with nearly equal probability to yield a small polarization.

Although the small Ps value of the chiral smectic C compound is disappointing, the chiral nematic compound **III** could be useful for the formulation of eutectic liquid crystal mixtures for supertwist nematic LC display devices.[17] The reason for this is that it has a large nematic range and can be easily synthesized, and the double bond at the 3-position of the alkenyl chain might increase the dielectric anisotropy and lower the elastic constant ratio of liquid crystalline compounds.[10–14]

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