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The Synthesis and Liquid Crystal Behavior of *p*-Benzotrifluoride Compounds III

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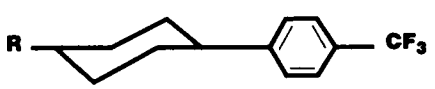
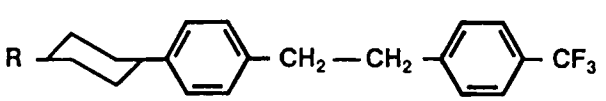
Two compounds with the general structure R—CY—CY—CH_2—CH_2—Ph—CF_3 were synthesized where CY is a 1,4 disubstituted *trans* cyclohexyl ring, and R is a *n*-alkyl group. The synthesis procedure is discussed and structural assignments confirmed by proton and carbon 13 NMR spectroscopy. Liquid crystal behavior was evaluated by DTA and polarized microscope. We discovered that the two compounds have smectic and nematic phases and can be used in fast switching liquid crystal mixtures.

INTRODUCTION

In our previous papers[1,2] we discussed the liquid crystal behavior of alkyl cyclohexyl benzotrifluoride.



Although the turn off time of a liquid crystal mixture was shortened by using them as additives the amount that could be added was limited, because they do not have any liquid crystal phase by themselves. We also discussed the introducing of another phenyl ring and an ethylene linkage into the molecule to give it a longer center core as well as flexibility. Some of the compounds with the structure



do have mesophases as expected, but only with the less important smectic I phase. Therefore the amounts that can be added in a nematic liquid crystal mixture are still limited.

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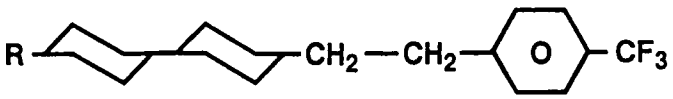
It would be ideal if we could make a compound which has a nematic liquid crystal phase while still maintaining the low viscosity and high dipole moment of a benzotrifluoride compound. Since a cyclohexyl ring is more flexible and less likely to give an induced dipole moment than a phenyl ring, we thought it would be interesting to substitute a cyclohexyl ring for a phenyl ring. Therefore we synthesized two compounds with the following structure:

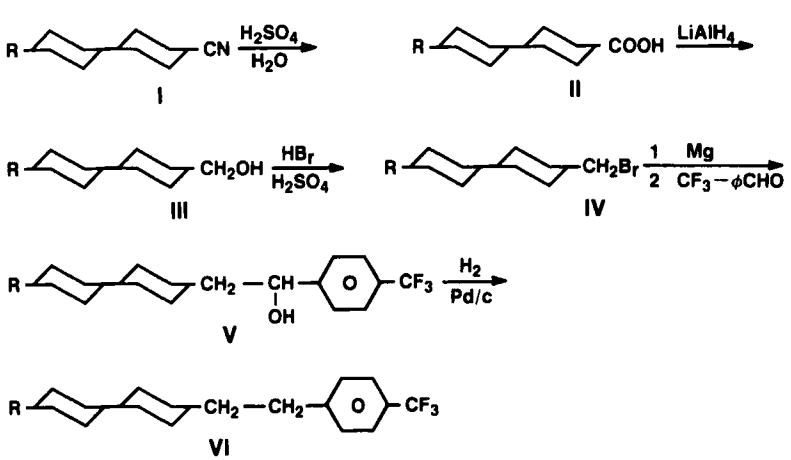


They were both shown to have nematic liquid crystal phases as well as smectic phases.

SYNTHESIS

The general method of introducing an ethylene linkage used by Carr[3] and Takatsu[4] could not be used in our case. Because of the exclusive *meta* directing property of the trifluoromethyl group, the reaction between cyclohexyl acetyl chloride and trifluoromethylbenzene will only give us a bent molecule. We tried the Grignard reaction of trifluoro methyl phenyl magnesium bromide wtih alkylbicyclohexyl acetonitrile and with the acetyl chloride without success. The Wittig reaction successfully used in our synthesis of alkylcyclohexylphenylethyl-*p*-benzotrifluoride was also tried. The formation of the quaternary phosphonium salt from the cyclohexyl carbobromide needs a higher temperature, but since there is no phenyl ring to stabilize the ylide, the next reaction only gives an extremely low yield. Although we could see by carbon 13 NMR that there was some ethylene compound present, it is not a practical preparation method.

After many failures the 4-*n*-alkyl*trans*,*trans*bicyclohexylethyl-*p*-benzotrifluorides were eventually prepared by the following sequence of reactions:



The commercially available CCH compound(I) was hydrolysized to the acid(II) which was then reduced by lithium aluminum hydride to the 4-*n*-alkyl-*trans*,*trans*-bicyclohexyl-4′-carbinol(III). III was converted to the bromide by heating in concentrated hydrobromic acid with a few drops of sulfuric acid as catalyst. The bromide(IV), in THF was made into the Grignard agent which could be added to *p*-trifluoromethyl-benzaldehyde to form the benzyl alcohol(V). V was hydrogenated using 1:2 THF-methanol as solvent to give the final compound.

RESULTS AND DISCUSSION

Two compounds were synthesized; their structure and phase transition temperatures (observed on cooling from isotropic liquid under polarized microscope) are listed in Table I. Both have smectic and nematic phases. Differential thermal analysis charts (data collected heating) are shown in Figure 1. The compound Tek# 2138 is a monotropic liquid crystal, thus the transition temperatures on heating and cooling are different. The phase identifications will be discussed in detail in the experimental section.

Since both compounds have nematic phases they are much more useful for making nematic liquid crystal mixtures. The behavior of compound Tek# 2138 is very interesting. In fact within the smectic temperature range Tek# 2138 does respond to electrical pulses of positive and negative amplitudes. This property is being explored further in our studies.

EXPERIMENTAL

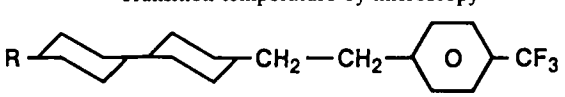
A. Synthesis

The compounds were purified on a Waters 500A preparative HPLC instrument. The structures of the products were established by their carbon 13 and proton nmr spectra taken on a Jeol FX 90Q Fourier transform nmr spectrometer and by IR spectroscopy. The purity of the final products was checked on a Perkin-Elmer series 10 analytical HPLC instrument.

Using: 4-(4*n*-pentyl-*trans*,*trans*-bicyclohex-4′-ylethyl)benzotrifluoride (Tek# 2126) as an example the synthetic procedure used is described below.

TABLE I

Transition temperature by microscopy[a]



Tek#	R group	Isotropic–nematic	Nematic–smectic	Smectic–Cryst
2126	Pentyl	123 C	100 C	55 C[b]
2144	Propyl	110.3 C	104.6 C	51.7 C

[a]Phase transition temperature observed on cooling.
[b]Cryst-Cryst transition at 38.3 C.

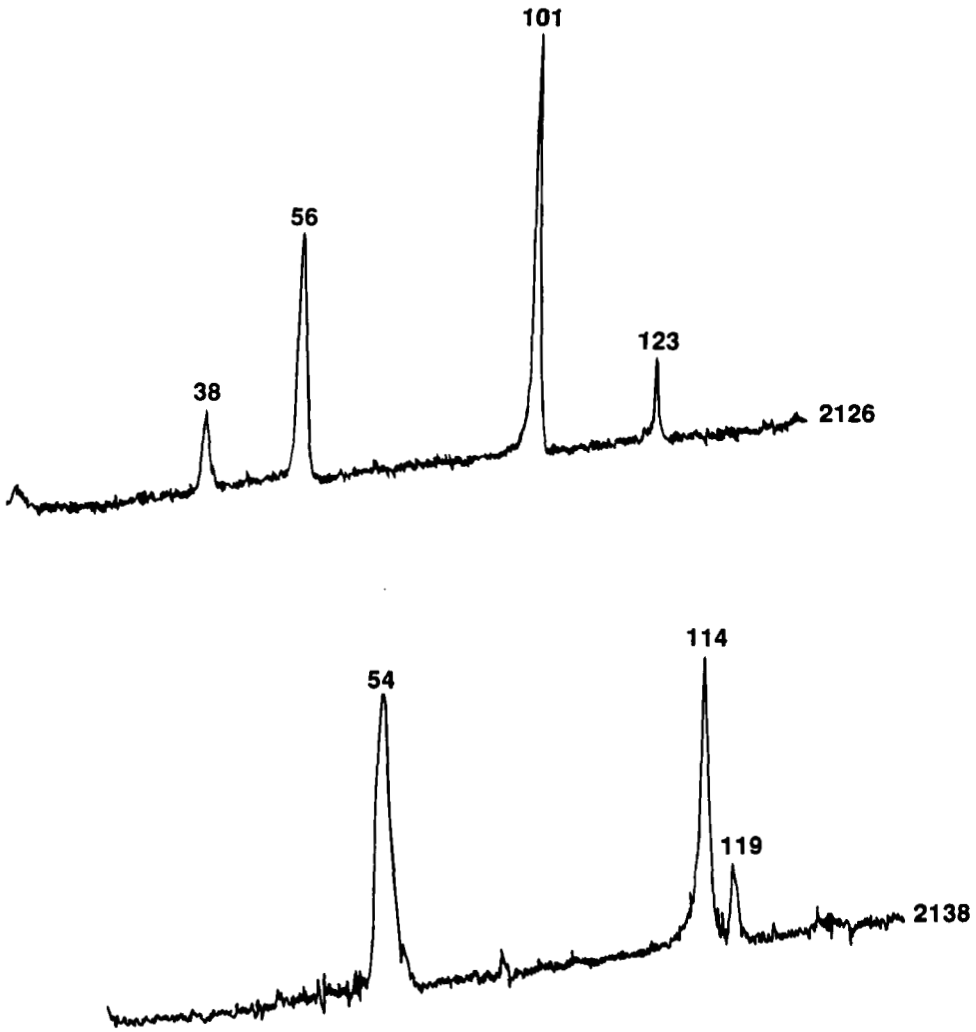


FIGURE 1 DSC thermograms (all data collected on heating).

4-n-*Pentyl*-trans,trans-*bicyclohexyl-4'-carbinol.* 4-*n*-Pentyl-*trans,trans*-bicyclohexyl-4'-carbonitrile (EM S-1185) (5 g = 0.019 mol) was hydrolyzed by heating for 5 h with 42 ml of sulfuric acid and 50 ml water. The mixture was diluted by 100 ml of ice, and the acid was collected by filtration. The white powder was washed by water and dried in vacuum. The acid II was dissolved in 200 ml of tetrahydrofuran (THF), and lithium aluminum hydride (1.6 g = 0.038 moles) was added slowly in small portions. The mixture was stirred at room temperature over night. It was cooled by an ice bath and methanol was added slowly to decompose the excess hydride. The mixture was acidified with dilute hydrochloric acid and extracted twice by methylene chloride. The solution was washed with water, dried over

magnesium sulfate, filtered and the filtrate was concentrated in vacuum to give III 4.1 g (80.3%) of the carbinol. The carbon 13 nmr spectrum showed that it was pure enough to be used in the next reaction. (Carbon 13 nmr: 68.5 (hydroxy carbon), 43.5, 40.8, 38.03, 37.5, 33.7, 32.3, 30.2, 29.9, 29.55, 26.7, 22.7, 14.04.)

4-n-*pentyl*-trans,trans-*bicyclohexy-4'-carbobromide.* The carbinol (4.1 g = 0.0154 mol) was added to a mixture of 120 ml hydrobromic acid (48%) and 0.5 ml concentrated sulfuric acid. The mixture was heated for 10 h, poured onto ice and extracted by methylene chloride. The methylene chloride solution was washed by water, dried over magnesium sulfate and filtered. The filtrate was concentrated in vacuum. The residue was dissolved in a 1:5 mixture of ethyl acetate and hexane, injected onto a normal phase preparative HPLC column using the same solvent system as the mobile phase. The compound corresponding to the first peak was collected and concentrated in vacuum to give the pure bromide IV 4.2 g. (83%). (Carbon 13 nmr: 43.25, 43.1, 40.52, 40.37, 37.93, 37.45, 33.64, 32.23, 32.03, 30.13, 29.5, 26.67, 22.67, 14.04.)

2-(4-n-*pentyl*-trans,trans-*bicyclohex-4'yl)-1-(4-trifluorom ethylphenyl)ethanol.* A few drops of ethylene dibromide were added to magnesium string (0.3 g = 0.0144 moles) in 30 ml tetrahydrofuran. The mixture was stirred for 10 min, then heated to about 50°C, and a solution of the bromide (IV) (4.2 g = 0.0128 mol) in 30 ml tetrahydrofuran was added dropwise. The mixture was kept at gently boiling for four h, and then allowed to cool down to room temperature. Trifluoromethylbenzaldehyde (2.5 g = 0.0144 mol) in 20 ml tetrahydrofuran was added dropwise and the mixture was stirred at room temperature for 24 h. Water was added to decompose the magnesium complex followed by dilute hydrochloric acid to make it acidic. It was extracted by ether and the ether solution dried over magnesium sulfate, filtered and the filtrate concentrated in vacuum. The residue was dissolved in a mixture of 20% ethyl acetate in hexane and injected onto a normal phase preparative chromatography column. The same solvent system was also used as the mobile phase. Two major peaks were obtained. The first corresponded to 3 g of product and the nmr spectra indicated that it might be a mixture of hydrocarbons; no further study was done on it. The second corresponded to 1 g of product and the carbon 13 nmr spectrum (Figure 2) shows that it is the desired hydroxy compound V (18.5%). (Carbon 13 nmr: 149.4, 128.96, 126.04, 125.65, 125.45, 125.31, 125.11, 118.19, 71.67 (hydroxy carbon), 47.29, 43.49, 43.39, 38.03, 37.54, 34.62, 34.32, 33.74, 33.2, 32.33, 30.18, 30.03, 29.89, 26.72, 22.72, 14.09.)

4-(4-n-*pentyl*-trans,trans-*bicyclohexyl-ethyl)benzotrifluoride.* The hydroxy compound (V) (1 g = 0.00236 mol) was dissolved in a mixture of 50 ml tetrahydrofuran and 120 ml of methanol. Palladium on charcoal (5%, 0.7 g) was added as catalyst. The mixture was hydrogenated at 55 psi for 24 hours, filtered and the filtrate concentrated in vacuum. The residue was crystallized from methanol to give 0.75 g (77.9%) of pure compound VI. Figure 3 is the carbon 13 nmr of this compound. (Carbon 13 nmr: 147.34, 128.62, 127.35, 125.45, 125.26, 125.11, 124.92, 43.54, 39.05, 38.08, 37.64, 33.79, 33.59, 33.3, 32.33, 30.23, 30.08, 26.72, 22.77, 14.09.)

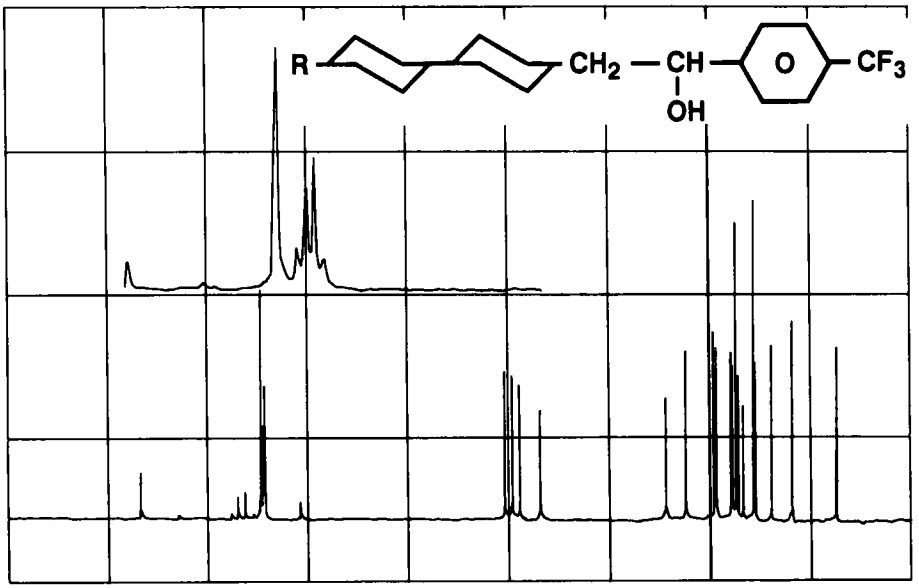


FIGURE 2 Carbon 13 NMR spectrum of compound V.

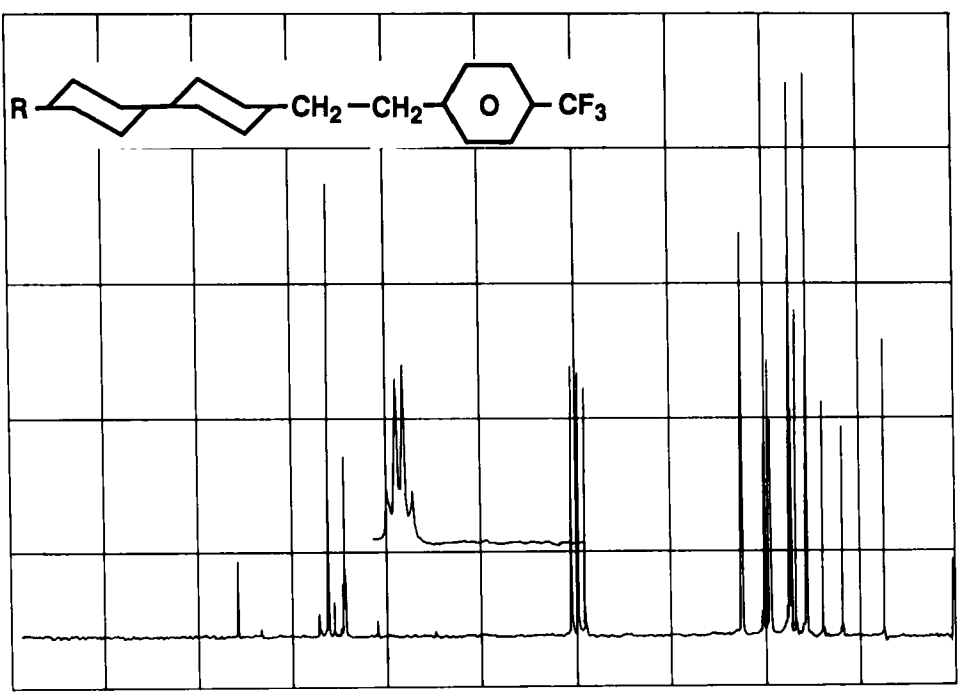


FIGURE 3 Carbon 13-NMR spectrum of Tek# 2126.

B. Liquid crystalline study

Transition temperatures for heating were determined by differential thermal analysis (Perkin-Elmer DTA 1700 and system 7/4 controller). The temperatures were interpolated from the thermal charts and are within 1°C. Phase transitions for heating and cooling were then observed between crossed polarizers using a Mettler FP 80 calorimeter with microstage and an Olympus polarizing microscope. Using Tek# 2126 as an example the observation is as follows. Three intermediate textures were observed between 35°C and 123°C.

The low temperature texture (I) is barely discernible from the crystalline texture. The other two textures are easily distinguished on heating, the texture in the 55–100°C range is a mosaic texture with uniform monodomains with various birefringence colors including black (crossed polarizers). This texture is usually associated with SmB. From 100 to 123°C the threaded nematic texture is observed. The polymorphism for 2126 is thus

$$\text{Cryst} \rightarrow \text{I} \rightarrow \text{SmB} \rightarrow \text{N} \rightarrow \text{Is}$$

The large transition enthalpy of I → SmB and the similarity in the texture between cryst and I suggest that I is a crystalline modification rather than a smectic mesophase. The photomicrographs of Tek# 2126 are shown in Figure 4.

Sb → I transition

Crystalline

FIGURE 4 Photomicrographs of 2126 (textures observed on cooling).

Nematic → SbL

Sb mosaic texture

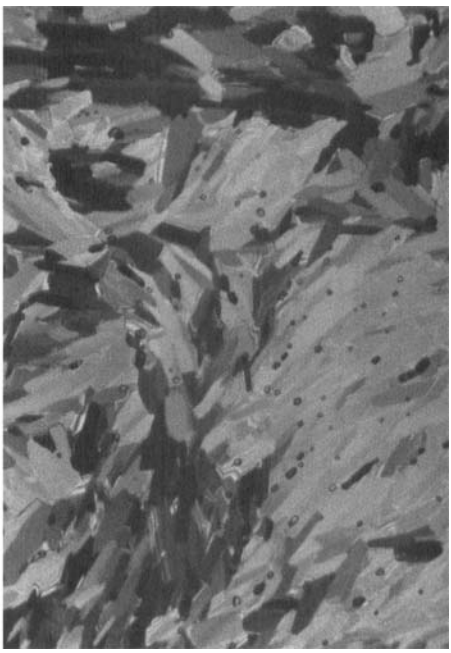


Figure 4 (*continued*)

Acknowledgments

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