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The Synthesis and Liquid Crystal Behavior of p-Benzotrifluoride Compounds II

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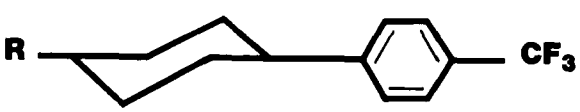
Four compounds with the general structure R—X—Y—CH_2—CH_2—Ph—CF_3 were synthesized, where X is a 1,4 disubstituted trans-cyclohexyl ring, Y is a phenyl ring, and R is a *n*-alkyl group. The synthetic procedure is discussed and the structural assignments were confirmed by NMR spectroscopy. The liquid crystal behavior of these compounds was evaluated by DSC and polarizing microscopy. They might be used in fast switching liquid crystal mixtures.

INTRODUCTION

In a previous paper,[1] we discussed the synthesis and liquid crystal behavior of alkyl cyclohexyl benzotrifluorides.



When they were used in liquid crystal mixtures, the turn off time of that mixture was shortened and also less dependent on the cell thickness. Unfortunately none of them exhibit a liquid crystal phase, limiting the amount that could be used in a liquid crystal mixture. If we compare their structure with the structure of commonly used PCH liquid crystal materials, we can see that the cyano compounds can form antiparallel dimers.[2,3] This dimer would have a longer rigid center core, and this might be the reason why they do have liquid crystal phases. This tendency for dimer formation should be much less in the cyclohexyl benzotrifluorides, and consequently they melt directly into isotropic liquids. If this is the case, introducing another cyclohexyl or phenyl ring should be helpful for liquid crystal phase formation. However, a three ring core will make the compound too rigid and this might increase the melting point and the viscosity. Considering that there is a certain flexibility remaining in the dimer, we reasoned that we should introduce a

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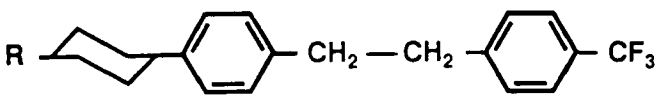
certain flexibility into the molecule as well. The dimethylene linkage was first introduced to liquid crystal molecules by Carr, Gray and McDonnell.[4] As pointed out by Takatsu,[5,6] compounds with such a linkage usually have a low viscosity, because the linkage keeps the molecule straight but flexible.

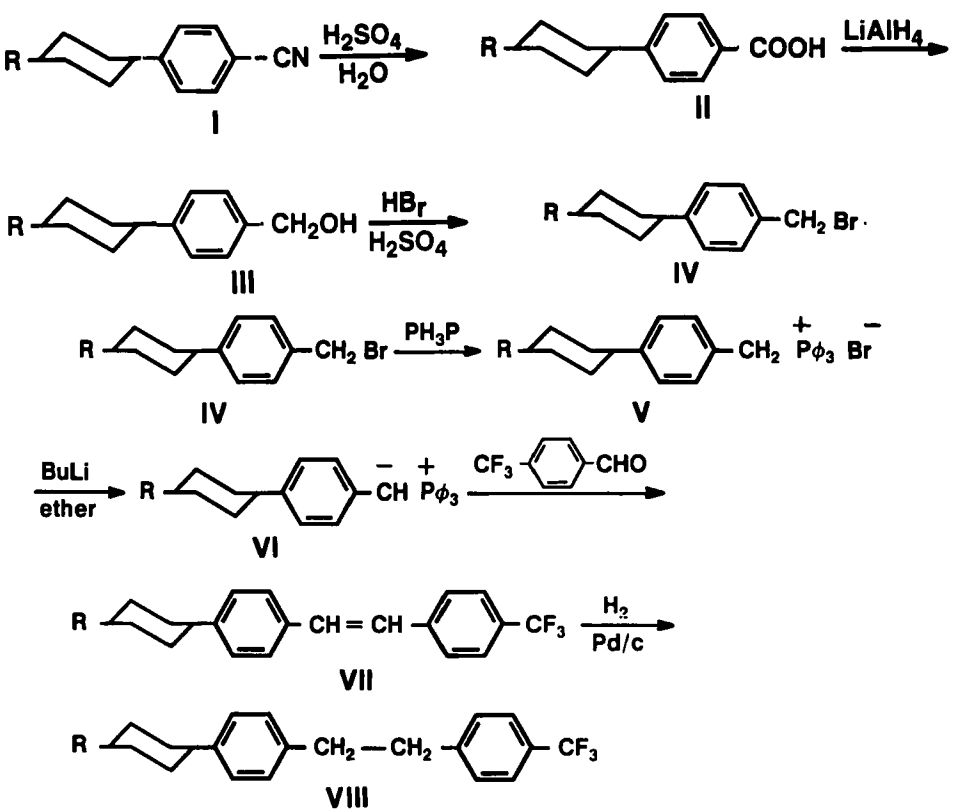
We have now synthesized a series of compounds with the structure



and studied their liquid crystal behavior.

SYNTHESIS

The 4-(2-(4-(trans-4-*n*-alkylcyclohexyl)phenyl)ethyl)benzotrifluorides were prepared according to the following scheme:



The alkylcyclohexyl benzylbromide (IV) obtained from the commercially available PCH compound (I) was reacted with triphenylphosphine to form the quaternary phosphonium salt (V) in almost quantitative yield. This was treated with butyllithium in a typical Wittig procedure[7] involving interaction with 4-trifluoromethyl-

benzaldehyde to give the ethylene compound (VII). The double bond was then saturated by hydrogenation to give the product (VIII).

RESULTS AND DISCUSSION

Four homologous 4-(2-(4-(*trans*-4-*n*-alkylcyclohexyl)phenyl)ethyl)-*p*-benzotrifluorides were prepared. Their structures and the phase transition temperatures obtained by DSC are summarized in Table I.

Only one compound Tek #2146 had two peaks on the DSC thermogram (63.7° and 76.8°C) collected at first heating. The mesophase is a highly ordered smectic phase with a mosaic type mixture which we believe to be a smectic I phase.

EXPERIMENTAL

A. Synthesis

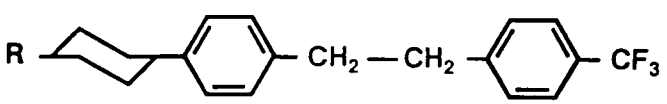
The compounds were purified using a Waters 500A preparative HPLC instrument. The structures of the products were established by their carbon 13 and proton NMR spectra (Jeol FX 90Q Fourier transform nmr spectrometer) and by IR spectroscopy. The purity of the final products was checked using a Perkin-Elmer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

Using compound Tek# 2143 as an example the synthetic procedure is described below.

4-(*trans*-4-*n*-heptylcyclohexyl)benzyl alcohol (III):

4-(*trans*-4-*n*-heptylcyclohexyl)benzonitrile (EM S-1115) (5 g = 0.018 moles) was hydrolyzed by refluxing for 5 h with sulfuric acid (42 ml) and water (50 ml). The mixture was diluted by 100 g of ice, and the acid was collected by filtration. The white powder was washed with water and dried in vacuum. The acid II was dissolved in tetrahydrofuran (200 ml), 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 then cooled by an ice bath and methanol was added slowly to

TABLE I



Tek#	R group	Transition	Temp	ΔH(Kcal/mol.)
2143	pentyl	Cryst—I	86.1	6.12
2144	heptyl	Cryst—I	78.3	6.23
2145	propyl	Cryst—I	96.1	4.73
2146	butyl	Cryst—SmI	63.7	2.10
		SmI—I	76.8	3.57

decompose the excess of hydride. The mixture was acidified with dilute hydrochloric acid and extracted twice with methylene chloride. The solution was washed with water dried over magnesium sulfate, filtered and the filtrate was concentrated in vacuum to give the alcohol III, 4.1 g (80.3%). The carbon 13 NMR spectrum showed that it was pure enough to be used in the next reaction. (carbon 13 NMR 146.9, 138.5, 127.1, 126.8 (*para*-disubstituted phenyl ring), 64.6 (benzyl alcohol), 44.4, 37.5, 34.5, 33.7, 32, 30.1, 29.5, 27.1, 22.8, 14.1)

4-(*trans*-4-*n*-heptylcyclohexyl)benzyl bromide (IV):

The alcohol (4.1 g = 0.015 moles) was mixed with 48% hydrobromic acid (120 ml). The mixture was heated for 10 h, poured onto ice and extracted with 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, and injected on a normal phase preparative HPLC column. The same solvent system was used 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 148.3, 135.2, 128.9, 127.3 (disubstituted phenyl ring), 44.3, 37.2, 37(benzyl bromide), 34.4, 33.6, 32, 30, 29.4, 27, 22.7, 14.)

1-(4-(*trans*-4-*n*-heptylcyclohexyl)phenyl)-2-(4-trifluoromethylphenyl)ethene (VII):

The bromide (3.5 g = 0.011 moles) was dissolved in toluene (120 ml), triphenylphosphine (4 g = 0.015 moles) was added with stirring and the mixture was heated for 6 hours. After cooling to room temperature, the white precipitate was filtered off, washed by toluene and dried in vacuum. The yield was almost quantitative (6.43 g 100%). This was dispersed in anhydrous ether (75 ml) and a 1.55 M solution of butyllithium in hexane (8 ml = 0.0124 moles) was added. The color of the mixture changed to blood red almost instantly. After stirring for 2 h at room temperature 4-trifluoromethylbenzaldehyde (2.5 g = 0.0144 moles) was added. The color of the mixture changed to light brown and a white precipitate formed. The mixture was heated for 4 h and stirred at room temperature over night. More ether was added and the mixture was filtered. The ether solution was washed with water, dried over magnesium sulfate, decolorized by charcoal and concentrated under vacuum. A residue of about 8 g was obtained.

The residue (2 g) was dissolved in a 1:5 mixture of ethyl acetate and hexane, and injected on a normal phase preparative HPLC column. The same solvent system was used as the mobile phase. The compound corresponding to the first peak was collected and concentrated under vacuum to give compound V, 0.9 g (20%).

1-(4-(*trans*-4-*n*-heptylcyclohexyl)phenyl) 2-(4-trifluoromethylphenyl)ethane (VIII):

The ethene (0.9 g = moles) was dissolved in a 1:3 mixture of tetrahydrofuran and absolute ethanol 60 ml and 0.7 g palladium on charcoal (10% palladium) added as catalyst. This mixture was hydrogenated at 55 psi for 48 h, filtered and the filtrate concentrated in vacuum. The residue was recrystallized from ethanol to

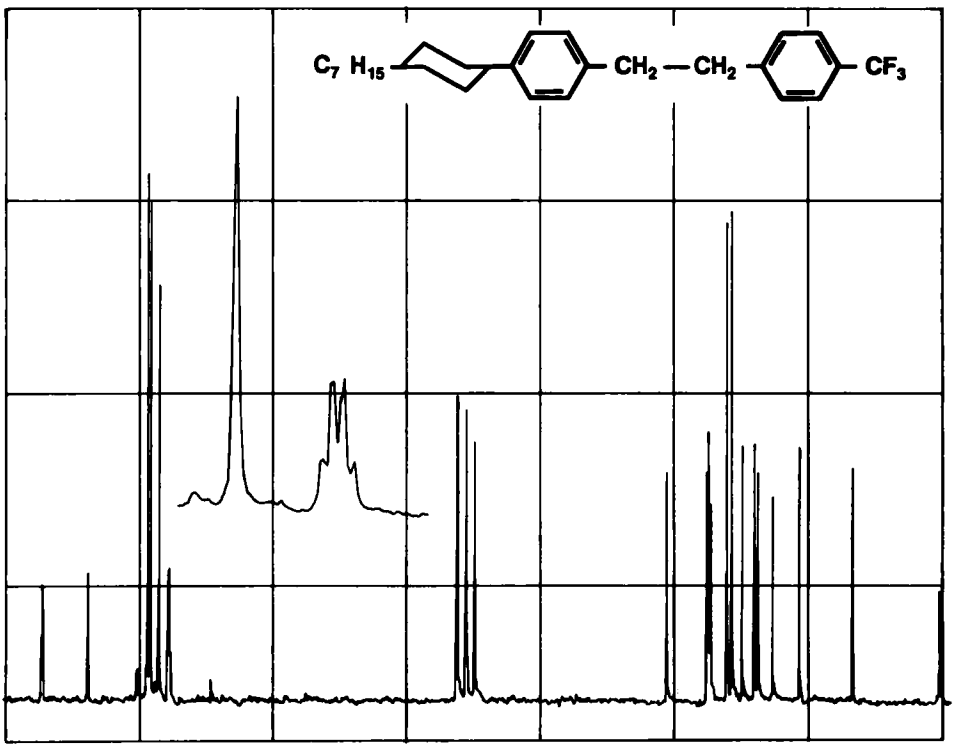


FIGURE 1 Carbon 13-NMR spectrum of Tek# 2144.

give 0.45 g (50%) of pure compound. Figure 1 is the carbon 13 NMR spectrum of Tek# 2143. (The upper spectrum is a ten times expansion of the 125 ppm area, and shows the quartet from the long range fluorine coupling.) Peaks are (145.8, 138.4, 128.8, 128.3, 126.9, 125.4(a quartet), 44.3, 37.7, 37.4, 37.1, 34.5, 33.7, 32, 30.1, 29.5, 27.1, 22.8, 14.1.).

B. Liquid crystal study

The transition temperatures and phase identification were made by observing the materials under a polarizing microscope. A Mettler FP 80 heating stage, with a temperature accuracy of ±0.1°C, and an Olympus polarizing microscope were used. The latent heats of transitions were determined by Differential Scanning Calorimetry using a Perkin-Elmer DSC-2 calorimeter calibrated against Indium standard. The scanning rates were in 2–10°C/minute range and the sensitivity was 5 mcal/°C.

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