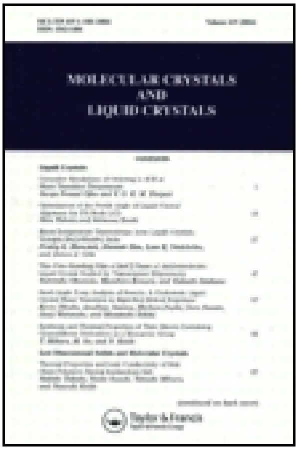

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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

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To cite this article: Jason C. Liang & Satyendra Kumar (1987): The Synthesis and Liquid Crystal Behavior of p-Benzotrifluoride Compounds I, Molecular Crystals and Liquid Crystals, 142:1-4, 77-84

To link to this article: http://dx.doi.org/10.1080/00268948708084594

Mol. Cryst. Liq. Cryst., 1987, Vol. 142, pp. 77–84
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Printed in the United States of America

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

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(*Received April 15, 1986; in final form July 3, 1986*)

Three compounds with the R—X—Y—CF_3 structure were synthesized where X is a *trans* cyclohexyl ring, Y is a benzene ring and R is an alkyl group. The structure assignments were confirmed by carbon 13 NMR and the compounds were purified by preparative liquid chromatography. The separation of *cis* and *trans* isomers of 1-p-trifluorophenyl-4-alkyl-cyclohexanol is also discussed. Although these compounds do not have a liquid crystalline phase themselves, a liquid crystal mixture containing them shows a much faster turn off speed than materials without them.

Keywords: benzotrifluoride, trifluoromethyl, time response, TN cell

INTRODUCTION

Liquid crystals have become widely used materials for information displays. For these applications, strongly polar compounds of positive dielectric anisotropy are required. The cyano group is the most commonly used functional group to introduce a large dipole moment. As pointed out by Hp. Schad *et al.*,[1,2] such cyano liquid crystal compounds exhibit an antiparallel molecular association and thus possess a reduced effective dipole moment. In order to decrease the degree

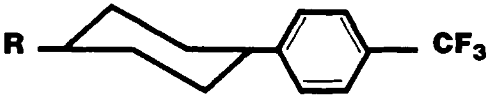

FIGURE 1

of such association and to increase the positive dielectric anisotropy even more, a fluorine atom was introduced at the ortho position of the cyano group by Hp. Schad and S. M. Kelly.[3] Fluorine was also used by H. Takatsu *et al.*[4] in their studies of low viscosity liquid crystals suitable for high level multiplexed LCDs.

The trifluoromethyl group is a very stable and very strong electron-withdrawing functional group. Since sterically it is a bulkier group than cyano group, the tendency of antiparallel molecular association should be smaller than for cyano compounds. Therefore, it would be interesting to introduce a trifluoromethyl group into liquid crystal molecules and to study their behavior. We chose alkyl cyclohexyl benzotrifluorides for our study as shown in Figure 1.

SYNTHESIS

Since ordinary substitution reactions such as nitration and halogenation take place exclusively in the meta position of benzotrifluoride, the readily obtained meta substituted derivatives have been extensively investigated and used in pharmaceutical industry. However, we need the para substituted derivatives to maintain the straight rod like structure of the liquid crystal molecules.

p-Bromobenzotrifluoride was synthesized by R. G. Jones.[5] He made p-aminobenzotrifluoride from p-nitro benzotrifluoride which could be made from p-nitrotoluene through bromination and fluorination. By the well known diazonium transformation (the Sandmeyer reaction) the amino compound was converted into phenol, fluoride, chloride, bromide, and iodide. This is a rather long synthesis route. We have taken a more direct path following the sequence of reactions shown in Figure 2.

By using a strong visible light, the free radical bromination of p-bromotoluene was achieved in a high yield. However, the nucleophilic fluorination reaction condition used by Jones with a 90% yield in his case gave us a very poor yield with p-bromobenzotribromide. In order to fluorinate the less positive carbon in p-bromobezotribromide, an-

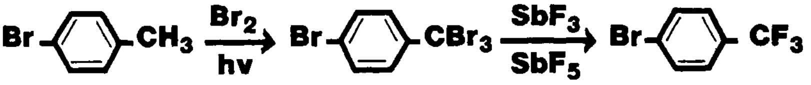

FIGURE 2

timony pentafluoride was used as catalyst. The yields lie in the 45–65% range depending on the amount of antimony pentaflouride used.

The sequence of reactions used to prepare the final compounds is shown in Figure 3.

Due to the strong electron withdrawing effect of the trifluoromethyl group, p-bromobenzotrifluoride did not react with magnesium in ether under general conditions. However, by using tetrahydrofuran as the solvent at an elevated temperature and by using ethylene dibromide as initiating agent, the grignard reagent of p-trifluoromethyl phenyl was obtained. 4-Alkyl-cyclohexanone was prepared by catalytic hydrogenation of p-alkylphenol and oxidation of the cyclohexanol.

The addition of the p-trifluoromethylphenyl grignard reagent to the alkylcyclohexanone gave a mixture of two isomers, A and B which could be separated by preparative liquid chromatography in a 2:1 ratio. The assignment of structures A and B was based upon the following information:

1) The hydroxy group in structure A has a high probability of occupying the axial position, but in structure B it is more likely to be in the equatorial position. Therefore, in a carbon 13 NMR spec-

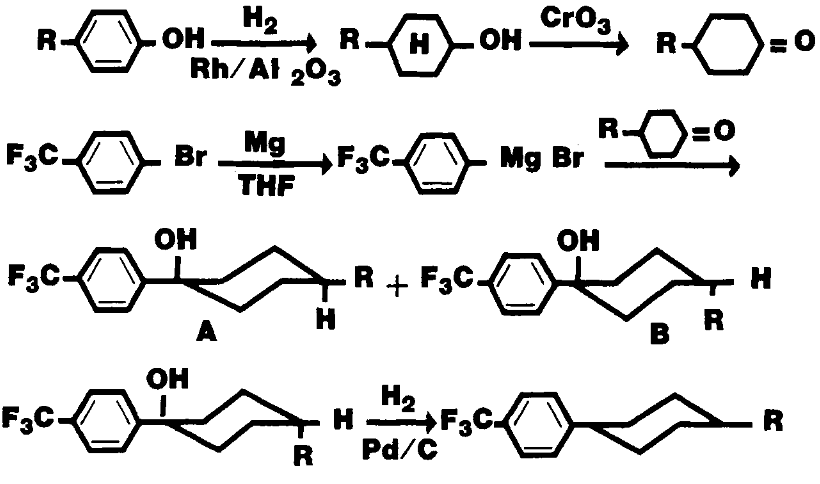

FIGURE 3

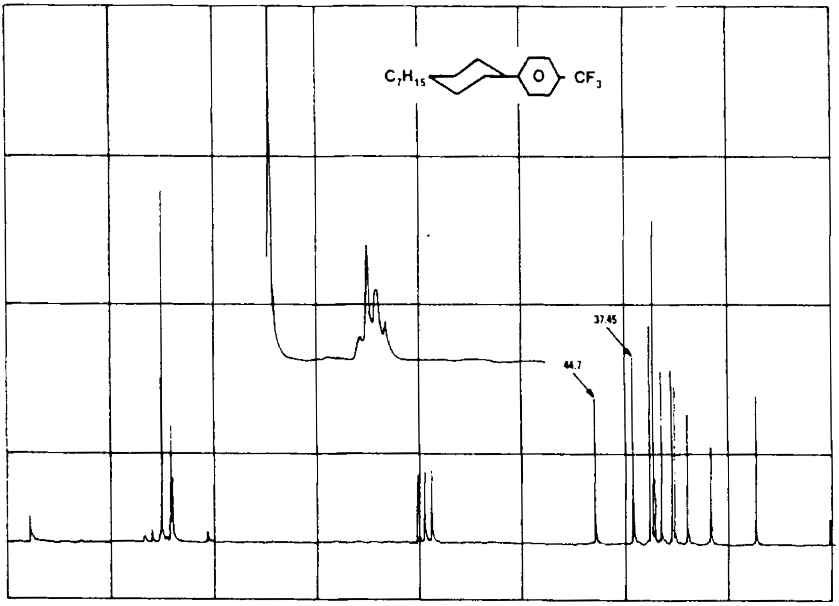

FIGURE 4 *trans* heptyl cyclohexyl benzotrifluoride.

trum, the chemical shift of the carbon atom attached to the hydroxy group would be more down field in structure B than in A.

2) The hydroxy group in structure B would be more exposed to the absorbent surface than in A. Therefore, in a normal phase chromatography, B should have a longer retention time than A (3.217 min. for B, 2.264 min. for A, by using unmodified silica gel column and 5% acetonitrile in methylene chloride-hexane mobile phase).

3) Catalytic hydrogenolysis of isomers A and B over palladium/charcoal gave the *cis* and *trans* alkylcyclohexyl benzotrifluorides, respectively. Since palladium catalysts usually cause inversion of configuration, the *trans* isomer should come from the reduction of structure B. Figure 4 is the carbon 13 NMR spectra for *trans*-heptylcyclohexyl-benzotrifluoride obtained from structure B. For comparison the spectra of the *cis* isomer was shown in Figure 5.

Unfortunately, the desired *trans* compound comes from the minor component of the isomeric mixture of the hydroxy compound. R. Eidenschink *et al.*(6) reported that the *cis* isomer obtained from the reaction between phenylmagnesium bromide and alkylcyclohexanone could be hydrogenated over Raney nickel with retention of configuration and to form *trans* alkylcyclohexyl benzene. We tried to hydrogenate compound A with Raney nickel, but after more than 100

TABLE I

R-X-Y-CF_3

Tek # R	X	Y	MP	Mesophase
2123 n-pentyl	cyclohexyl	phenyl	23°C	none
2124 n-heptyl	cyclohexyl	phenyl	34°C	none
2128 methylbutyl	cyclohexyl	phenyl	< -5°C	none

hours hydrogenation at 50 psi and room temperature no reaction occurred. R. Eidenschink and L. Pohl[7] reported a method for isomerizing *cis* alkylcyclohexylbenzene to *trans* isomer by using potassium t-butoxide. Only a mixture of decomposition products was isolated using this method. No further investigation was attempted.

RESULTS AND DISCUSSION

Three compounds were synthesized, their structure, and melting points are listed in Table I. Although they do not exhibit liquid crystalline phases by themselves, they could be used as dopants in liquid crystal

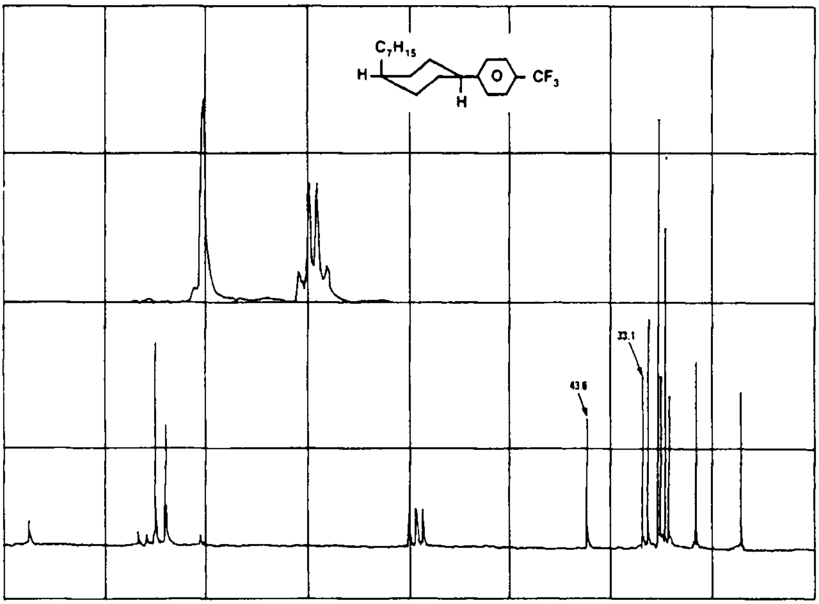

FIGURE 5 *cis* heptyl cyclohexyl benzotrifluoride.

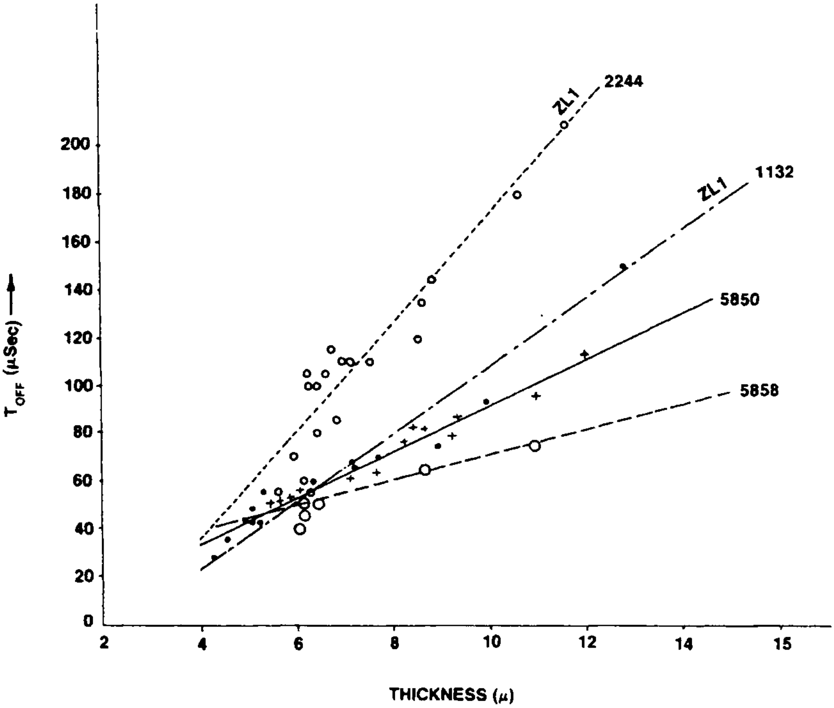

FIGURE 6 Time response of various materials in TN cell.

materials. Figure 6 shows the relationship between turn off time (T_{off}) and cell thickness of two commercially available liquid crystal materials (ZLI 1132 and 2244 from E. Merck) and two Tek materials made in our laboratory. There is 5% of *trans* 4-n-heptyl cyclohexyl benzotrifluoride in the material Tek #5858. We can see that 5858 not only is faster than any other material but also less dependent on the cell thickness. Therefore it is a significantly better liquid crystal material for display applications.

EXPERIMENTAL

Part A synthesis

The compounds were purified on a water 500A preparative HPLC instrument. The structures of the products were established by their carbon 13 and proton NMR spectra taken on a Jeol FT 90 Q Fourier Transform NMR spectrometer and by IR spectroscopy. The purities of the final products were checked using a Perkin-Elmer series 10 HPLC instrument. Using heptylcyclohexyl benzotrifluoride as an example the synthesis method is as follows:

p-Bromobenzotribromide. p-Bromotoluene (30 g = 0.1754 moles) was heated to 120°C and illuminated by a GE EJA 150 W 21 V lamp. Bromine (85 g = 0.532 moles) was added dropwise over a period of 30–40 minutes, while the temperature was increased to 180°C. The heating and illuminating was continued for 15 minutes, the mixture was cooled and recrystallized from hexane to give 43 g (60.1%) of the tribromide compound (carbon 13 NMR 146, 2*131, 2*128, 124.5, 34.3 ppm).

p-Bromobenzotrifluoride. p-Bromobenzotribromide (43 g = 0.1054 moles) was mixed carefully with antimony trifluoride (22 g = 0.123 moles), a few drops of antimony pentafluoride was added and the mixture was heated quickly for distillation. Water was added to the distillate and the mixture extracted with methylene chloride. The methylene chloride solution was dried over magnesium sulfate and fractionally distilled. The fraction boiling at 153–155°C was collected, to give 14 g (59%) of bromobenzotrifluoride (carbon 13 NMR quartet 142, 129.5, 117.2, 105 quartet 127.1, 126.9, 126.8, 126.7 ppm).

1-p-trifluoromethanylphenyl-4-transcyclohexanol. A few drops of ethylene dibromide was added to magnesium string (0.7 g = 0.0288 moles) in 50 ml tetrahydrofuran. The mixture was stirred for 15 minutes, then heated to about 50°C, and a solution of p-bromobenzotrifluoride (4.5 g = 0.02 moles) in 50 ml tetrahydrofuran was added dropwise. The mixture was kept at about 50°C for three hours, and cooled in an ice bath. A solution of heptylcyclohexanone (4.5 g = 0.023 moles) in 50 ml tetrahydrofuran was added dropwise and the mixture was stirred overnight at room temperature. 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 to dryness. The residue was disolved in a mixture of 20% ethyl acetate in hexane and injected on a normal phase preparative chromatography column. This solvent system was also used as the mobile phase and three peaks were obtained. They represent unreacted ketone, product A (3 g), and product B (1.5 g = 21.9%).

trans 4-n-Heptylcyclohexyl-p-benzotrifluoride. Product B (1.5 g = 0.0044 moles) was dissolved in 200 ml methanol and 1 g palladium on charcoal added as catalyst. This mixture was hydrogenated at 50 psi for 48 hours, filtered and the filtrate concentrated in a vacuum. The residue was recrystallized from methanol to give 0.7 g (48.8%) of pure compound: m.p. 34°C. (carbon 13 NMR 151.9, 127.2, quartet 125.45, 125.31, 125.11, 124.96, 44.7, 37.4, 34.2, 33.5, 32, 30, 29.4, 27, 22.8, 14 ppm.)

Part B liquid crystalline study

Liquid crystal material Tek#5858 containing 5% of *trans* heptylcyclohexyl benzotrifluoride was made according to the principle described by R. Hubbard and J. Liang.[8] The time response measurements were made using $\pi/2$ twist cells. The cells were made using ITO coated glass plates with evaporated silicon oxide alignment layer. The thickness of these cells varied from one end to another. Selected locations on these wedge cells were marked, and cell thickness measured using an optical interferometer with a precision of 0.1 μm. The time response at the marked locations was measured by observing the transmission of green light under polarizing microscope with the polarizer and analyzer parallel. The on state voltage was adjusted to give 95% of the maximum transmission (fully on). This minimized the optical bounce. The measured Toff was the time from 90% to 10% transmission level. The results are plotted in Figure 6.

Acknowledgment

The authors wish to thank Dr. Michel Bayard for reviewing the manuscript and making valuable comments.

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