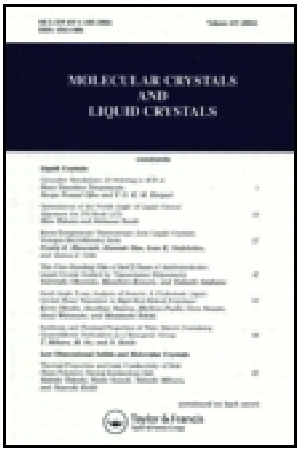

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Synthesis and Liquid Crystalline Phases of Pyridazine Derivatives III

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Synthesis and Liquid Crystalline Phases of Pyridazine Derivatives III

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Eight compounds with the general structure R—X—Y—O—R′ were sythesized where X is a phenyl ring, Y is a 3,6 disubstituted pyridazine ring, R is a n-alkyl or n-alkoxy group and R′ may be either a n-alkyl group or a branched alkyl group containing a chiral center. The synthesis procedures are discussed. Structural assignments for these compounds were confirmed by proton and carbon 13 NMR. Their liquid crystalline behavior was evaluated by DTA and polarizing microscopy. We discovered that all of the n-alkyl compounds have smectic phases, but a branch in the alkyl group will make the compound melt directly into the isotropic liquid, except for 3 p-octyloxyphenyl 6 (R) 1′methylheptyloxy pyridazine which, interestingly, does have smectic phase.

Keywords: synthesis, pyridazine, smectic, negative dielectric anisotropy

INTRODUCTION

Dual-frequency addressable liquid crystals have found uses in fast color switches[1] and highly multiplexable matrix applications.[2,3] Most of these liquid crystals have a fairly good positive dielectric anisotropy at low frequencies, but the negative dielectric anisotropy at high frequencies is usually poor. Therefore it is important to synthesize dopants that can improve the negative dielectric anisotropy. Because of the strong dipole moment perpendicular to the molecular axis, 3,6 disubstituted pyridazine compounds should be very useful for this purpose.

A series of 3-aryl 6-alkyl pyridazines were synthesized in our laboratory, but unfortunately most of these compounds do not exhibit liquid crystal phases. Later, a cyclohexane ring was introduced into the center core. These compounds did exhibit liquid crystal phases and were discussed in our previous papers,[4,5] but the study of pyridazine derivatives would not be completed if alkoxy pyridazine compounds were not included. H. Zaschke et al.[6] have already reported the preparation of 3-alkoxy-6- (alkylphenyl) pyridazines but no phase identifications were made. We felt that it was worthwhile to synthesize some similar compounds again and study their liquid crystalline behavior. We also thought that it would be interesting to introduce a chiral center into the molecule to see if we could make cholesteric liquid crystals with a negative dielectric anisotropy. Therefore a series of compounds with a general structure of R—X—Y—O—R′ where X is a phenyl ring Y is a 3,6 disubstituted pyridazine ring VIII were synthesized and their liquid crystalline behavior studied.

SYNTHESIS

These compounds were prepared by the route shown in Figure 1. The ether II was prepared using the well known Williamson Synthesis. A Friedel-Crafts acylation of this compound with succinic anhydride gave the 3-oxo acid III. Cyclization of this acid using the method of Zaschke et al.[6] gave the dihydropyridazine IV followed by dehydrogenation with selenium dioxide to the pyridazine VI using the method of Kumagoi.[7] Conversion of this phenol to the chloride VII with phosphorous oxychloride followed by alkoxylation gave the dialkoxypyridazine VIII.

Figure 2 is the Carbon 13 NMR spectrum for compound III. Spectra for compounds IV (Figure 3) and VI (Figure 4) clearly show that the two carbons in the aliphatic area have migrated downfield to the aromatic region, confirming the proposed structures for these compounds. The carbon 13 NMR spectrum of the final compound is shown in Figure 5. Seven additional homologs were prepared in the same manner. A typical synthesis example is given in the detailed experimental section below.

EXPERIMENT

The structure of the products was established by their carbon 13 and proton NMR spectra taken on a Jeol FX 90Q Fourier transform NMR

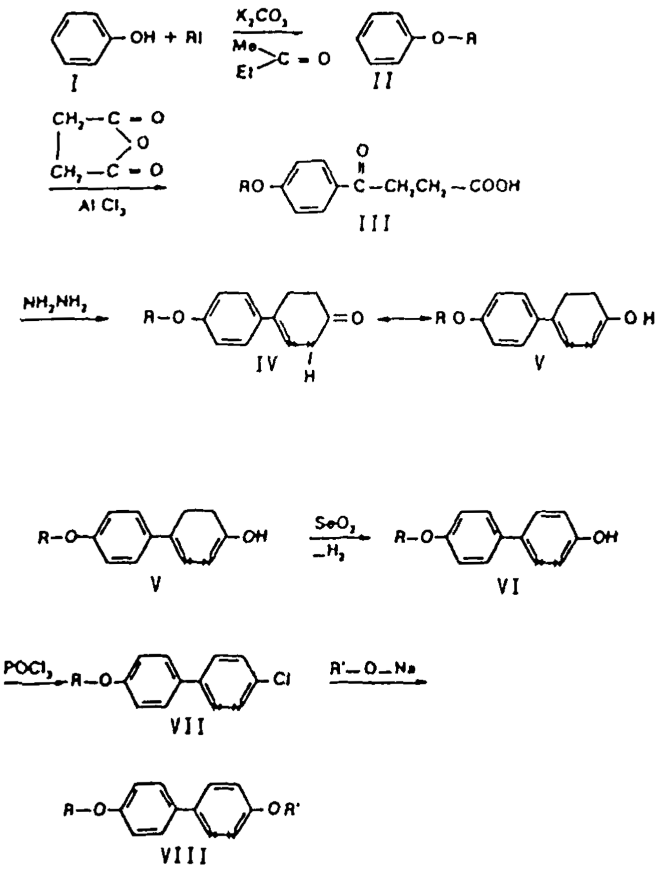


FIGURE 1

spectrometer and by IR spectroscopy. The purity of the final products was checked on a Perkin-Elmer series 10 analytical HPLC instrument.

Using 3 *p*-octyloxyphenyl 6 (R) 1'methylheptyloxy pyridazine as an example the synthesis method is as follows:

octyloxybenezene II: A solution of phenol (6g = 0.064 moles) and idooctane (13.5 g = 0.056 moles) in 200 ml. methyl ethyl ketone containing finely ground potasium carbonate (30 g = 0.22 moles) was refluxed for 12 hours. The insoluble salts were removed by filtration and the filtrate concentrated *in vacuo*. The residue was dissolved in toluene, washed with dilute sodium hydroxide solution, twice with water, dried over anhydrous magnesium sulfate, filtered

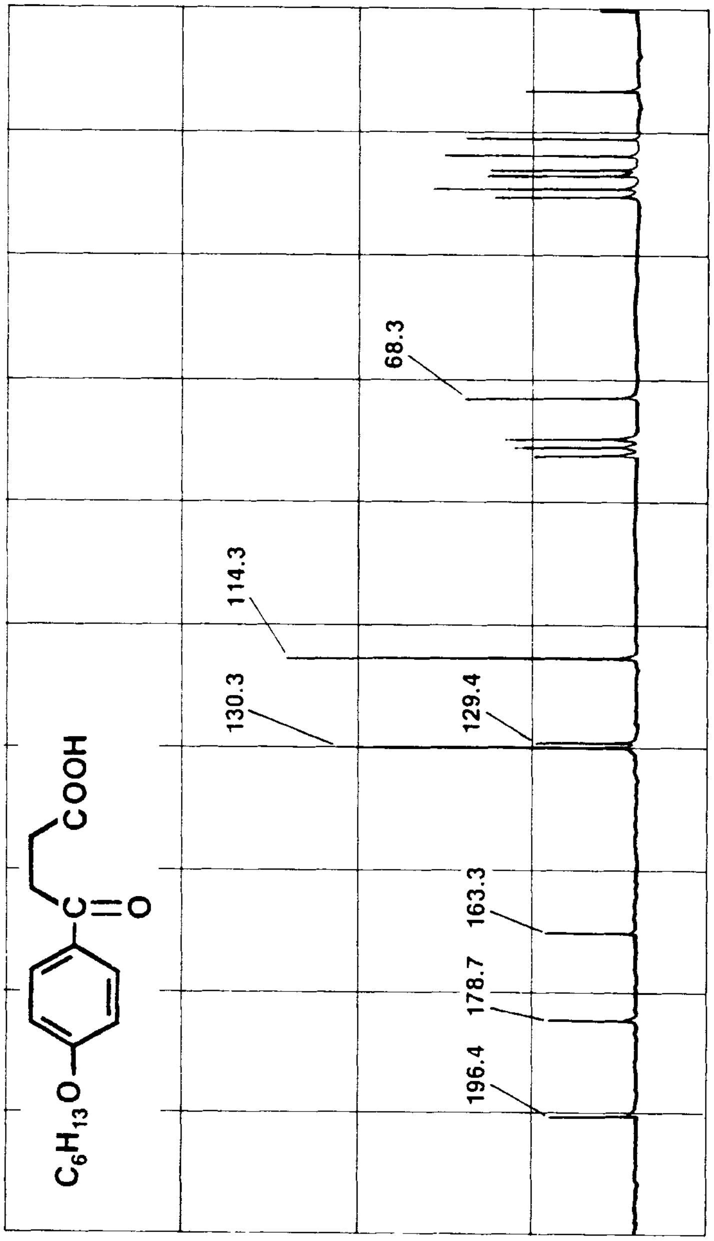


FIGURE 2

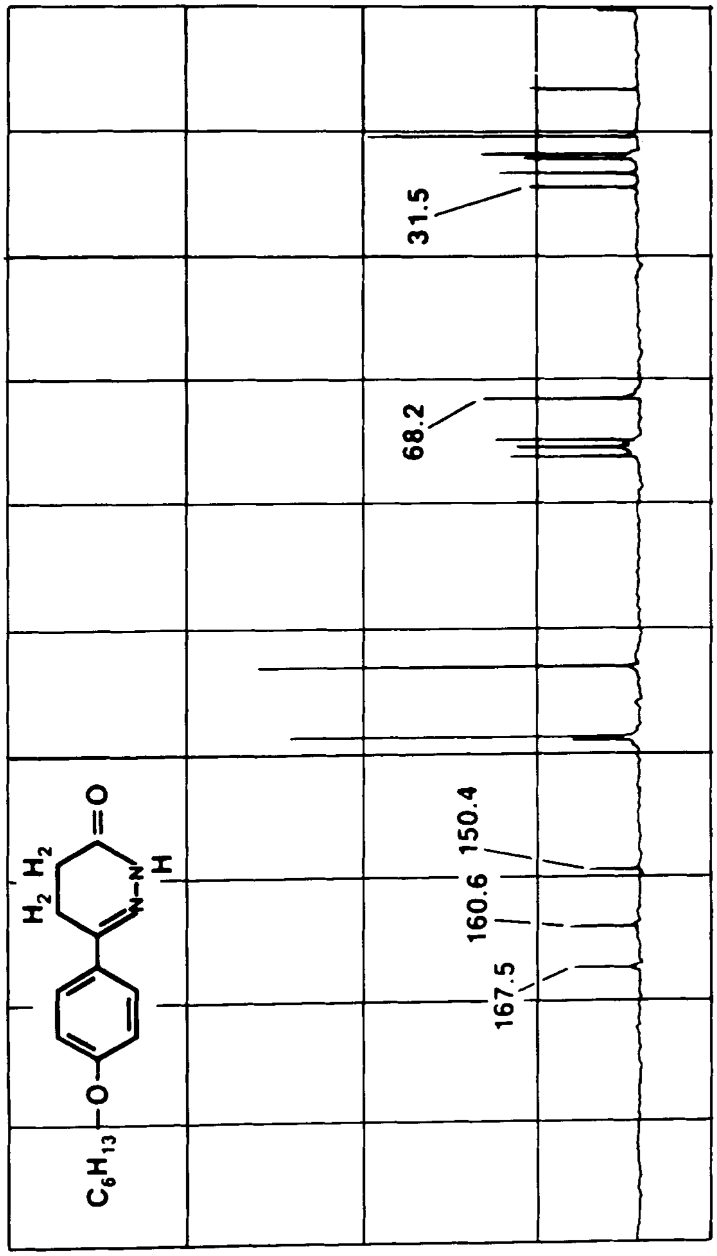


FIGURE 3

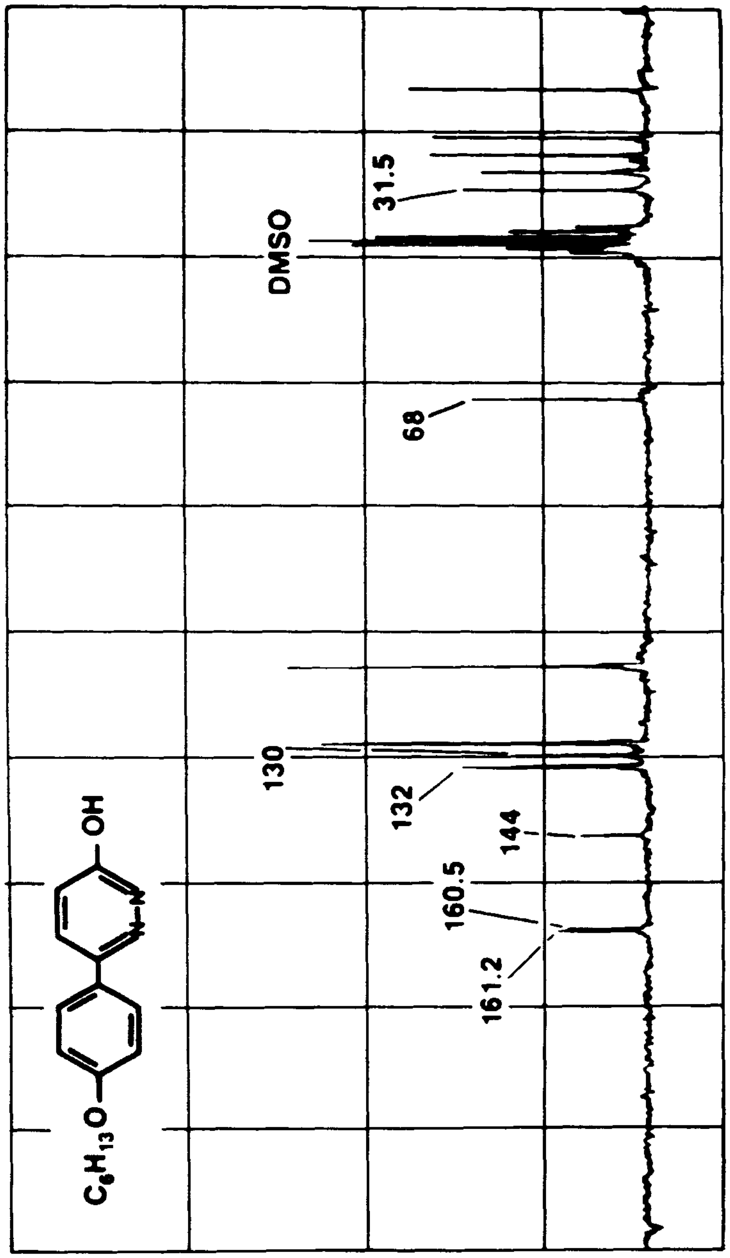


FIGURE 4

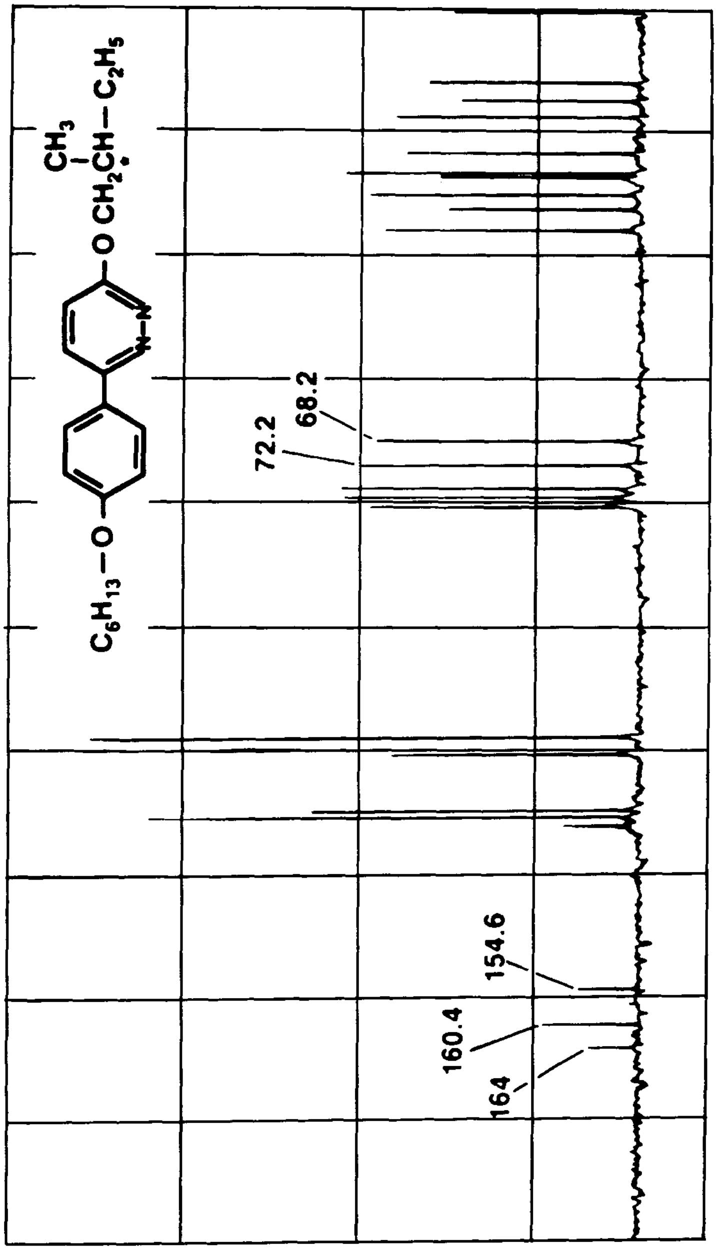


FIGURE 5

and the filtrate concentration *in vacuo* to give 11.4g (98%) of the ether II. This material was used in the next reaction without further purification.

4-octyloxybenzoylpropionic acid III: Succinic anhydride (5.95 g = 0.0595 moles) was added to a stirred solution of anhydrous Aluminum trichloride (16 g = 0.12 moles) in 80 ml nitromethane. To this solution was added dropwise a solution of octyloxybenzene (11.4 g = 0.055 moles) in 40 ml of nitrobenzene. This solution was stirred at room temperature for two hours and then poured slowly onto ice. The resulting precipitate was collected by filtration, washed with water and then 15 ml. of hexane and dried *in vacuo* to give 11.5g (68.3%) of the acid III. A carbon 13 NMR spectrum showed that this material was the desired acid and pure enough to be used in the next reaction without further purification. The purity of this material was analyzed by HPLC using a Perkin Elmer 5 micron C18 reversed phase column, 254 μm wave lenth UV detecter, and an Interactive Microware data acquisition system. Water (13%) in acetonitrile was used as mobile phase. The major peak area for the crude material was 97.45%. After the material was redispersed in hexane and washed, the peak area was increased to 99.73%.

3-p-octyloxyphenyl 6(3H)pyridazinone IV: Octyloxybenzoyl propionic acid (11.5 g = 0.38 moles) and 10 ml Hydrazine monohydrate in 100 ml acetic acid was refluxed for 5 hours. The solution was diluted with 150 ml. water and kept at 0–5°C overnight. The crude product was removed by filtration, washed with water and dried *in vacuo* to give 10.3 g (89.7%) of 3 Octyloxybenzoyl 4,5 dihydro 6(3H)pyridazinone IV. This material was used without further purification in the next reaction.

3-p-octyloxyphenyl 6-hydroxy pyridazine VI: The above crude product (10.3 g = 0.034 moles) was added to a solution of selenium dioxide (7.5 g = 0.068 moles) in 90 ml dioxane and 10 ml water, and refluxed for 5 hours. The black precipitate was removed by filtration. The filtrate was concentrated *in vacuo* and the residue mixed with 80 ml methanol. The mixture was refluxed for 30 min. to reduce the unreacted selenium dioxide. The hot solution was filtered, cooled slowly and kept at 0–5°C overnight. The white crystals were collected by filtration, and dried *in vacuo* to give 9g (87.9%) of the hydroxypyridazine VI. Carbon 13 NMR showed this material was pure.

3 octyloxyphenyl 6 chloropyridazine VII: The hydroxypyridazine VI (9 g = 0.3 moles) and 15 ml phosphorus oxychloride were heated to 80°C for 4 hours. The mixture was poured onto ice and carefully stirred to hydrolyze the unreacted phosphorus oxychloride. The crude product was collected by filtration, dissolved in toluene and the organic solution washed with water, decolorized with charcoal and filtered. The filtrate was concentrated *in vacuo*. Hexane was added to the residue and the precipitate collected by filtration, washed with hexane and dried *in vacuo* to give 6.5 g (68%) of the chloropyridazine VII. Carbon 13 NMR showed this was pure enough to be used in the next reaction.

3-*p*-octyloxyphenyl-6-(R)1'methylhepyloxypyridazine VIII: Sodium (0.5 g = 0.022 moles) was added to a solution of (R)(—)2-octanol (0.5 g = 0.0038 moles) in 5ml dried toluene and this mixture stirred for two hours until no additional hydrogen gas was released. A solution of chloropyridazine (0.6 g = 0.0019 moles) in 30 ml of toluene was added and the mixture refluxed for two hours. This solution was washed with water, dried over magnesium sulfate, decolorized by charcoal filtered and the filtrate concentrated *in vacuo*. The residue was recrystallized from hexane to give 0.5 g (63.8%) of 3-octyloxyphenyl-6-(R)-1' methylheptyl pyridazine VIII (0.5 g). Carbon 13 NMR showed that this was pure compound.

LIQUID CRYSTALLINE BEHAVIOR

Thermal behavior was studied using a differential thermal analyzer (Perkin Elmer DTA 1700 and system 7/4 controller). Phase identifications at the transition temperatures were made using an Olympus polarizing microscope with a Mettler FP80 calorimetric heating stage and controller. Materials in this series which showed mesophase behavior had the morphology Cr—Sa—Is, with the exception of 2109. The intermediate phase of 2109 (74 to 82°C) appeared to be smectic B. A small domain mosaic texture appears on heating from the solid phase and large crystal-like domains formed on cooling from the isotropic melt. When held in the intermediate temperature range the large domains gradually settled into a mosaic texture with no interference colors. DTA thermograms are shown in Figure 6 and are summarized in Table I.

Although these materials do not exhibit a nematic phase, they may still prove useful as dopents. Since they do not destroy the nematic

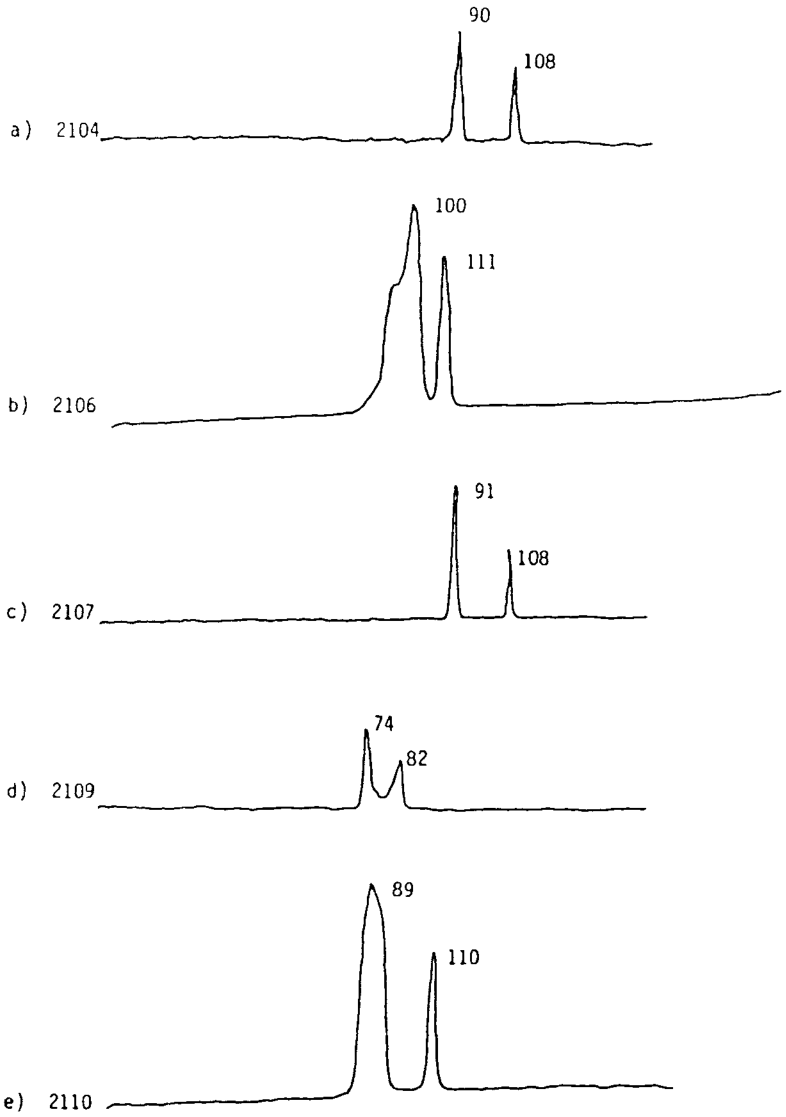
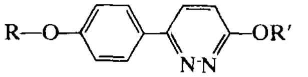


FIGURE 6 DTA Thermograms of those materials with an intermediate phase.

phase when dissolved into a nematic mixture, some improvement might be seen in the overall negative dielectric anisotropy. We might explore their actual effects on the switching properties of liquid crystals in future studies.

TABLE I

Table of chemical structures and transition temperatures.



Tek #	R	R′	C–S	S–1	Range of S
2104*	C_6H_{13}	C_6H_{13}	90°	108°	18°
2105	C_6H_{13}	$CH_2CH\genfrac{}{}{0pt}{}{CH_3}{C_2H_5}$		No Mesophase	
2106	C_8H_{17}	C_4H_9	100°	111°	11°
2107	C_8H_{17}	C_6H_{13}	91°	108°	17°
2108	C_8H_{13}	$CH\genfrac{}{}{0pt}{}{CH_3}{C_6H_{13}}$		No Mesophase	
2109	C_8H_{17}	$CH\genfrac{}{}{0pt}{}{CH_3}{C_6H_{13}}$	74°	82°	8°
2110	C_8H_{17}	$C_{10}H_{21}$	89°	110°	21°
2101	C_3H_7 (without oxygen)	$CH_2CH\genfrac{}{}{0pt}{}{CH_3}{C_2H_5}$		No Mesophase	

* Material with Tek$_7$ 1D #2104 was first described by H. Zaschke et al.

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