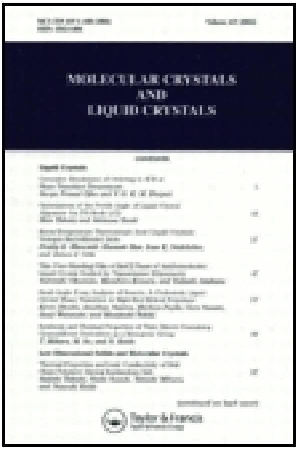

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Synthesis and Liquid Crystalline Phases of Pyridazine Derivatives 1

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Synthesis and Liquid Crystalline Phases of Pyridazine Derivatives I

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Seven pyridazine compounds were synthesized. The compounds have a general structure R—X—Y—PZ—R′, where PZ is 3, 6 disubstituted pyridazine ring, X and Y are either *trans* cyclohexyl or phenyl rings, R and R′ are n-alkyl groups. The structure assignments were confirmed by carbon 13 nmr. Their liquid crystalline properties were evaluated. All of them have mesophases with a broad temperature range.

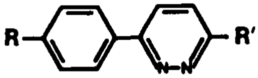
INTRODUCTION

Pyridazine derivatives, due to their lateral permanent dipole moments in the pyridazine ring, should exhibit large negative dielectric anisotropies. This could be a very valuable property for dual-frequency addressable liquid crystals.

3-(4-alkyl-cyclohexyl)-6-alkyl pyridazines were presented by M. Schadt et al.[1] Their compound (5PZH3) is monotropic, melts at 66°C and has a nematic-isotropic transition at 12°C.

3 (2-*trans*-4-pentylcyclohexyl)ethyl) 6-propylpyridazine were also synthesized by P. Martin and T. Georg.[2] But only a melting point of 64.2°C was mentioned in the report.

A series of 3-aryl-6-alkylpyridazines with the structure of



have been synthesized in our laboratory, but unfortunately most of these compounds do not exhibit a liquid crystalline phase. They melt to isotropic liquids directly.

As pointed out by W. Schafer et al.,[3] cyclohexane compounds usually have lower melting points and higher clearing points than corresponding phenyl compounds, therefore inserting the non-planar and somewhat flexible cyclohexane ring in some positions may have an advantageous effects on the phase transitions. A series of pyridazine compounds with three ring rigid central cores was synthesized and their liquid crystalline behavior was studied. The compounds have the general structure R—X—Y—PZ—R′ where PZ is a pyridazine ring X and/or Y could be either phenyl or cyclohexyl rings.

SYNTHESIS

J. Levisalles[4] reported a method for synthesizing 3-phenyl-6-methylpyridazine. We discovered that by modifying his method we could make R—X—Y—PZ—R′ compounds in good yield with an easy purification. We also discovered that, when preparative HPLC is used to purify the final product, it is not necessary to purify most of the intermediates. This makes this synthetic route even more attractive, as described in Figure 1.

Reaction of a nitrile with a Grignard reagent is a well known synthetic route to ketimines which are easily hydrolyzed to give ketones (I → II) as reviewed by F.C. Schaefer.[5]

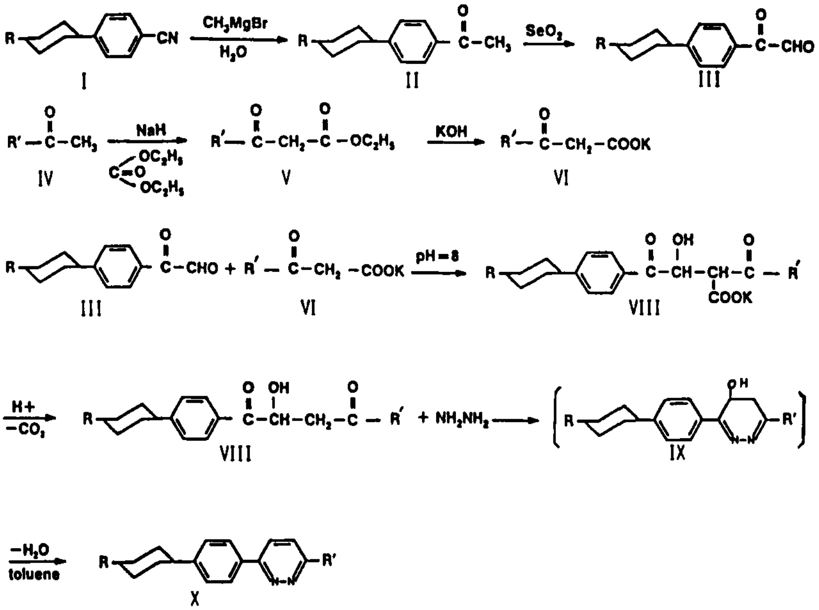


FIGURE 1

The preparation of ethyl 3-oxo-octanoic acid was reported by S. Soloway et al.,[6] and its hydrolysis into potassium salt was reported by M. Schechter et al.[7] (IV—VI)

The selenium dioxide oxidation of acetophenone to glyoxal (II→III) was reported by H. Riley.[8] In our case however, the molecular weight is high, therefore purification by distillation is impossible. We found out that purification is not necessary if we purify the final product by HPLC.

The condensation reaction (III + VI → VII) is also well known,[9] but with the large molecules we can not expect a good yield without a suitable solvent. Dioxane is very appropriate in this case since it can dissolve the organic compounds as well as mix with the water solution of the keto acid salt. The cyclization reaction (VIII → X) was achieved by refluxing VIII and hydrazine in toluene as reported by J. Levisalles. Seven compounds were synthesized, their structure, yield and phase transition temperatures are listed in table 1.

LIQUID CRYSTALLINE BEHAVIOR

The differential scanning calorimetry charts for this series are shown in Figure 2. As can be seen they all have many phase transitions

TABLE 1

R—X—Y—PZ—R′

TEK NO.	R	X	Y	R′	C→S (°C)	S→N (°C)	N→I (°C)	YIELD (%)
2111	C_5H_{11}	CY	PH	C_3H_7	113	195	201	19.8
2112	C_7H_{15}	CY	PH	C_3H_7	103	195	197	18.7
2113	C_7H_{15}	CY	PH	C_5H_{11}	68	197	200	17.4
2114	C_5H_{11}	CY	PH	C_5H_{11}	110	•	205	19.2
2116	C_5H_{11}	CY	CY	C_5H_{11}	66		210	11.5
2120	C_5H_{11}	CY	PH	C_8H_{17}	53		199	20.4
2121	C_7H_{15}	CY	PH	C_8H_{17}	75		195	21.2

CY = CYCLOHEXYL PH = PHENYL P2 = PYRIDAZINE

• MONOTROPIC NEMATIC PHASE APPEARS WHEN COOLING

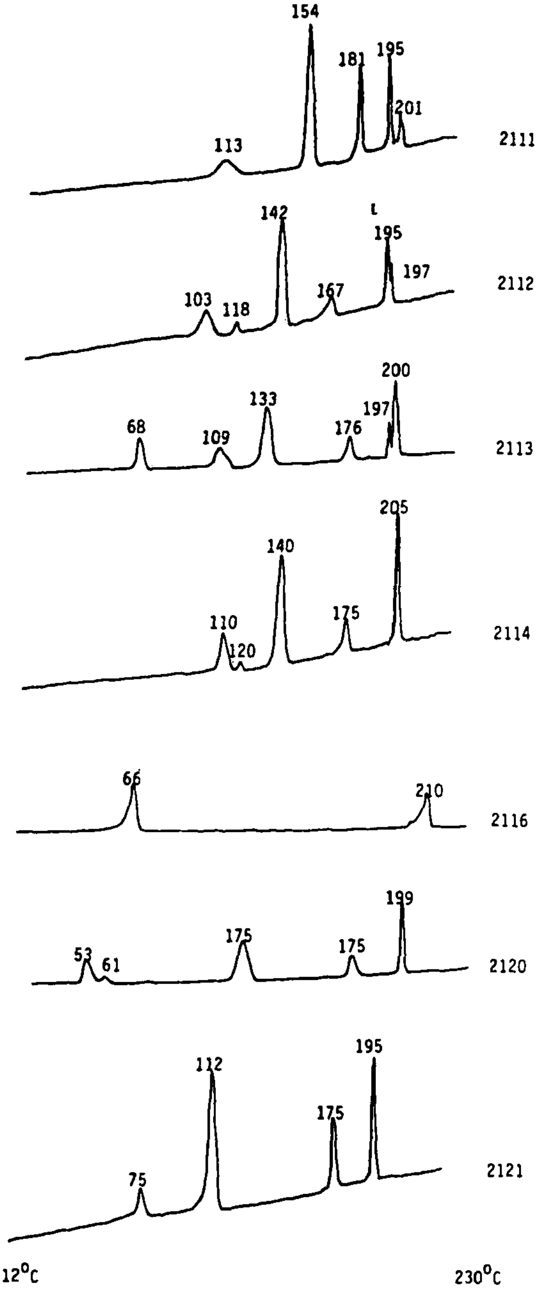


FIGURE 2 D.S.C. Thermograms (All data collected at first heating)

except 2116 which exhibits a much simpler morphology. The phase identifications will be discussed in detail in the experimental section.

EXPERIMENTAL

Part A. synthesis

The final compounds were purified on a Water 500A preparative HPLC instrument. The structure of the products was 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 3-(4'-pentyl-cyclohexyl)-*p*-phenyl)-6-pentyl-pyridazine as an example, the general synthesis procedure used is described below.

(4-(4'-pentyl-cyclohexyl)-acetophenone:

trans-4-pentyl-(4-cyanophenyl)-cyclohexane (EM S114) 5 g. was dissolved in 100 ml. anhydrous ether. While stirring under nitrogen, an ether solution of methyl magnesium bromide (2.85 m.) 30 ml. was added slowly. The mixture was stirred over night at room temperature. Water was added, followed by 20 ml. 10% hydrochloric acid. The ether solution was separated out, washed twice by water, dried over magnesium sulfate and concentrated. The crude product was recrystallized by methanol. A pure compound (3.8 g.) as indicated by NMR was obtained Mp 63-65°C. An additional 1.15 g. of product was recovered from the mother liquor with a lower melting point 59–63°C, (yield 92.8%) carbon 13 NMR 197.6 (ketone), 153.5, 135.2, 128.5, 127 (*para* disubstituted phenyl ring), 47.1 (methyl), 41, 38, 37.6, 36.5, 31.5, 27.9, 20, 14.2 Ppm.

3-((4'-n-pentyl-cyclohexyl)-phenyl)-6-n-pentyl-pyridazine:

Selenium dioxide 0.45 g., water 3 ml., and dioxane 30 ml. were mixed, stirred and heated until the white crystals dissolved. 4-(4'-n-pentyl-cyclohexyl) acetophenone 1.2g. was added to the mixture which was boiled under reflux for three hours. After the mixture had been cooled, the black precipitate was removed by filtration and the yellow filtrate was diluted with 80 ml. dioxane and mixed with the aqueous solution of the potassium 3-oxo-octanoate 5 ml. (made from 5 ml. ethyl 3-oxo-octanoate and 2.4 g. potassium hydroxide in 20 ml. water, hydrolysis for 4 days at 0.5°C and then saturated by carbon dioxide to adjust the pH). The reaction mixture was kept at 0–5°C for four days. Then 10 ml. 20% hydrochloric acid were added, and the mixture was extracted by 80 ml. toluene. The toluene solution was washed twice with water, dried over magnesium sulfate and filtered. Hydrazine monohydrate (1.5 ml.) was added to the toluene filtrate and the mixture was boiled under reflux for 3 hours. The toluene solution was washed twice with water, dried over magnesium sulfate and concentrated. The residue was dissolved in a 1:3 mixture of ethyl acetate and hexane, injected in a normal phase preparative HPLC column using the same solvent system for the mobile phase. The compound corresponding to the main peak was separated out and recrystallized from hexane. About 0.32 g. (yield 19.2%) was obtained, carbon 13 NMR 162, 157.3, 149.8, 134.1, 127.5, 126.8, 126.5, 123.6, 44.6, 37.4, 34.3, 33.6, 32.3, 31.5, 29.2, 26.7, 22.7, 22.5, 14.1, 13.9 ppm. The mother liquid was not treated. The purity was checked by analytical HPLC instrument (Perkin-Elmer series 10, using 5 micro C18 reverse phase column, 90% methanol-water for the mobile phase). Only one peak was observed.

Part B. liquid crystalline study

Transition temperatures were established using a differential thermal analyzer (Perkin Elmer DTA 1700 and system 7/4 controller). The temperatures were interpolated from the thermal charts and are within ± 1°C. Phase identifications were made using a Mettler FP 80 calorimeter with microscope stage and an Olympus polarizing microscope.

The typical thermal behavior for this series may be characterized by the scheme:

cryst—II—I—Sb—Sa—N—I

The large transition enthalpy of I,II → SmB and the absence of observable texture changes below this point lead us to believe that I and II may be crystalline modifications. In this case, the melting points of these materials are higher than those reported in Table 1.

Tek No.	2111	2112	2113	2114	2120	2121
C→S (°C)	154	142	133	140	175	112

Figure 3 shows the Sb, Sa, N, and the unidentified texture for 2111.

A) Nematic

B) Smectic A

C) Smectic B

D) Unidentified Smectic Phase

FIGURE 3 Photomicrographs of 2111 (Textures observed on cooling)

See Color Plate I located in this volume.

All of the compounds behave in a similar manner except 2116, which has only a single mesophase, smectic B, throughout its temperature range.

Finally, we would like to make the following remarks: 1) The nematic phase transition in 2113 and 2114 is monotropic; it only occurred when the isotropic phase was cooling. 2) No nematic phase was observed in 2120 and 2121.

RESULTS AND DISCUSSION

All six compounds have liquid crystalline phases which may cover a very broad temperature range. The most interesting thing is that when we substituted the center phenyl ring with a cyclohexyl ring (as in 2116) the phase transitions were dramatically simplified from as many as five phases to a single smectic B phase. We suspect that this property was caused by the absence of a phenyl ring. We will pursue this point in another paper.

These compounds can be used as negative anisotropy additives in dual frequency addressable as well as other liquid crystal devices.

Acknowledgments

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