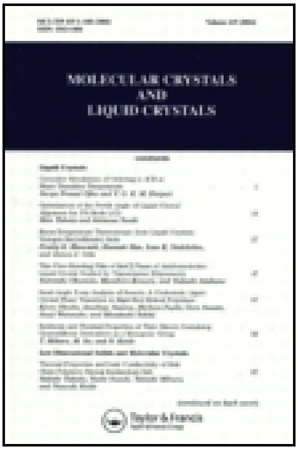

Molecular Crystals and Liquid Crystals

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# Heteroaromatic Salts Exhibiting Thermotropic Liquid Crystalline Properties

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# HETEROAROMATIC SALTS EXHIBITING THERMOTROPIC LIQUID CRYSTALLINE PROPERTIES

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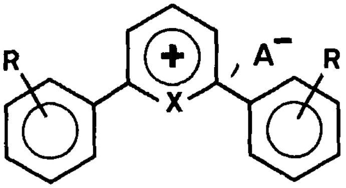
Abstract: We present a new class of thermotropic liquid crystals in which the rigid part of the molecules are constituted of heteroaromatic cations (1,2-dithiolium, pyrylium and thiopyrylium).

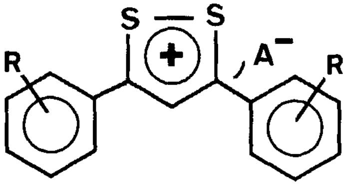
## INTRODUCTION

In previous work we described mesomorphic properties of pyrylium, 1, and thiopyrylium, 2, salts[1-2]. We showed that introduction of long chain substituants ($C_nH_{2n+1}$ or $OC_nH_{2n+1}$) on the aromatic rings induces ($n \geqslant 9$) mesomorphic behavior.
We now describe a new class of thermotropic liquid crystals in which the cationic part is constructed of 3,5-diaryl 1,2-dithiolium, 3. We will compare the mesomorphic properties of the dithiolium salts with pyrylium and thiopyrylium ones.



1 X = O

2 X = S



3

$A^- = ClO_4^-, Cl^-, I^-, PF_6^-$

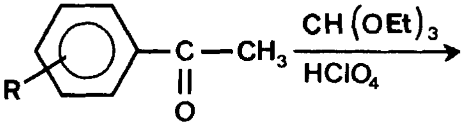
$R = OC_nH_{2n+1}, C_nH_{2n+1}$

# RESULTS

## 1. Synthesis

Compounds 1, 2 and 3 were obtained according to following schemes :

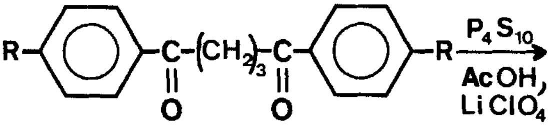
Pyrylium salts[1] : Heterocyclisation of substituted acetophenones :



1 R = $C_nH_{2n+1}$

$OC_nH_{2n+1}$

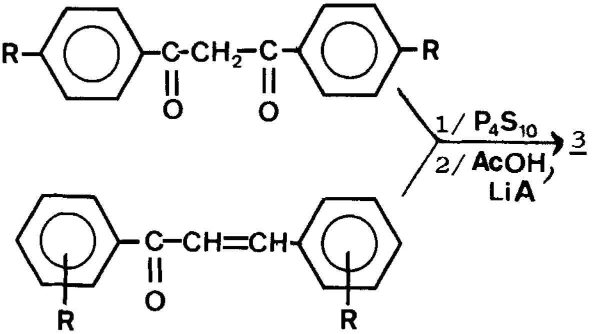
Thiopyrylium salts[3] : Starting from $\delta$-diketones :



2 R = $C_nH_{2n+1}$

$OC_nH_{2n+1}$

1,2-dithiolium salts[4] : Starting from β-diketones or chalcones



$R = OC_nH_{2n+1}$

$A^- = ClO_4^-, Cl^-, PF_6^-$

In the case of pyrylium and dithiolium salts our attempts to synthesize 3, 5-, 3', 5'-alkoxy substituted compounds were unsuccessful.

## 2. Mesomorphic properties

Tables 1, 2 and 3 summarize data concerning phase transitions of the studied salts.

TABLE 1 : Salts 2 $A = ClO_4$

| R | n | crystal(s) | mesophase(s) | I |
|---|---|---|---|---|
| $p\text{-}OC_nH_{2n+1}$ | 9 | ● 68 ● | 76 ● | 161 ● |
|  | 12 | ● | 98 ● | 179 ● |
| $p\text{-}C_nH_{2n+1}$ | 9 | ● 64 ● | 90 ● | 124 ● |
|  | 12 | ● | 114 ● 108 ● | 146 ● |

Transition temperatures in °C; ● indicates existence of corresponding phase.

TABLE 2 : Salts 3

| R | n | A | crystal | | mesophase | | a) I |
|---|---|---|---|---|---|---|---|
| p-$OC_nH_{2n+1}$ | 5 | Cl | ● | | | 149 | ● |
| | 8 | Cl | ● | | | 105 | ● |
| | | $ClO_4$ | ● | | | 185 | ● |
| | 9 | Cl | ● | 143 | ● | 193 | ● |
| | | $ClO_4$ | ● | | ↗b) | 195 | ● |
| | | $PF_6$ | ● | 140 | ● c) | 180 | ● |
| | 10 | Cl | ● | 138 | ● | 173 | ● |
| | | $ClO_4$ | ● | 175 | ● | 190 | ● |
| | | $PF_6$ | ● | 145 | ● | 225 | ● |
| | 12 | Cl | ● | 141 | ● | 196 | ● |
| | | $ClO_4$ | ● | 170 | ● | 213 | ● |
| | | $PF_6$ | ● | 161 | ● | 200 | ● |
| m-$OC_nH_{2n+1}$ | 10 | $ClO_4$ | ● | | ↗d) | 133 | ● |

Transition temperatures in °C; ● indicates existence of corresponding phase. a) partial or total decomposition ; b) ↘I → $S_A$ monotrope at 183° ; c) $S_A$ phase in equilibrium with I ; d) ↘I → $S_A$ monotrope at 120° ; $S_A$ → K at 84,5°C ; ↗ means by heating, ↘ means by cooling.

TABLE 3 : Salts 1 , A = $ClO_4^-$

| R | n | $K_1$ | | $K_2$ | | $K_3$ | | $M_1$ | | $M_2$ | | I |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| p-$OC_nH_{2n+1}$ | 8 | ● | 79 | ● | | | | | | | 176.5 | ● |
| | 9 | ● | 82.5 | ● | 115 | ● | 129 | ● | 137 | ● | 162 | ● |
| | 12 | ● | 124 | | | ● | 113 | ● | | | 157 | ● |
| m-$OC_nH_{2n+1}$ | 7 | ● | 89 | ● | 95 | | | ● | | | 150.5 | ● |
| | 8 | ● | | | 97.5 | | | ● | | | 148.5 | ● |
| | 9 | ● | | | 98 | | | ● | | | 148 | ● |
| | 10 | ● | | | 105.5 | ● | 104 | ● | 145.5 | ● | 149 | ● |
| | 12 | ● | 76 | ● | 96 | ● | 127 | ● | | | 147 | ● |
| p$C_nH_{2n+1}$ | 5 | ● | 116 | ● | | | | | | | 151 | ● |
| | 8 | ● | 128.5 | | | | | ● | | | 161 | ● |
| | 9 | ● | 117 | | | | | ● | | | 152 | ● |
| | 12 | ● | 119.5 | | | | | ● | | | 147 | ● |

Transition temperatures in °C; ● indicates existence of corresponding phase.

In the case of pyrylium salts, ortho substituted compounds are not mesomorphic[1].

## DISCUSSION

Mesomorphic properties are observed, in the case of compounds substituted in para position by $OC_nH_{2n+1}$, for n ≥ 9, whatever the nature of cation (pyrylium, thiopyrylium and dithiolium). After microscopic investigations, the mesophases were identified as smectic A.

In the case of dithiolium salts, for compounds substituted in the para position by alkoxy groups, transitions K $\rightarrow$ $S_A$ and $S_A$ $\rightarrow$ I take place at lower temperatures for $Cl^-$ than for $ClO_4^-$ anions. In the same way, the range of the mesophase is larger for $Cl^-$ than for $ClO_4^-$ anions.

In all three types of cations associated with perchlorate anions, the range of the mesophases depends on the nature of the heterocycles. Otherwise, the thermal stability of the mesophase is greater for thiopyrylium derivatives than for dithiolium and pyrylium ones (see tables 1, 2 and 3).

Transition temperatures $S_A \rightarrow I$ are higher for dithiolium salts than for other kinds of studied salts. In each series, this transition changes only by a few degrees upon increasing the length of the chains.

In the case of meta alkoxy substituted compounds, the transitions $K \rightarrow S_A$ and $S_A \rightarrow I$ appear at lower temperatures than for para substituted ones.

For alkyl substituted compounds, the transition $S_A \rightarrow I$ takes place at lower temperatures than in the case of corresponding alkoxy compounds.

Polymorphism is often observed in the case of pyrylium salts (see table 3).

## CONCLUSION

By this work, we proved that it was possible to obtain thermotropic liquid crystals ($S_A$) in which the rigid part of the molecule is constituted by a flat polarizable organic cation. Owing to their ionic properties, new applications may be possible.

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