

This article was downloaded by:

On: 29 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713618290>

SULFUR CONTAINING HETEROAROMATIC LIQUID CRYSTALLINE SALTS

H. Strzelecka^a; M. Veber^a; C. Jallabert^a

^a ESPCI, CNRS, UA958, Paris, France

To cite this Article Strzelecka, H. , Veber, M. and Jallabert, C.(1991) 'SULFUR CONTAINING HETEROAROMATIC LIQUID CRYSTALLINE SALTS', *Phosphorus, Sulfur, and Silicon and the Related Elements*, 59: 1, 247 — 250

To link to this Article: DOI: 10.1080/10426509108045734

URL: <http://dx.doi.org/10.1080/10426509108045734>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

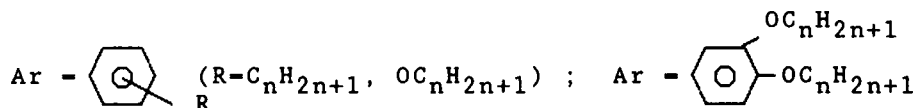
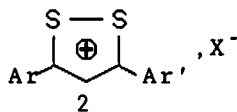
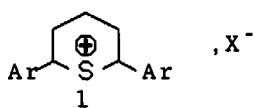
SULFUR CONTAINING HETEROAROMATIC LIQUID CRYSTALLINE SALTS

H. STRZELECKA, M. VEBER and C. JALLABERT
 ESPCI, CNRS, UA958, 10 rue Vauquelin, 75231 Paris, France

Abstract The series of liquid crystals in which the rigid part is constituted by heteroaromatic cation (thiopyrylium, 1-2-dithiolium) have been synthesized. The nature of the mesophases depends on the number of flexible substituents grafted on the cationic units. Lamellar (S_A) mesophases are obtained with two or three chains. With four paraffinic substituents columnar order (D_H) appears.

INTRODUCTION

Generally, the rigid part of thermotropic liquid crystals is neutral, we have shown the possibility to obtain liquid crystalline species in which the central rigid part is constituted of an organic polarisable cation (pyrylium, thiopyrylium, 1,2-dithiolium)^{1,2} In this paper we describe the synthesis and the properties of sulfur containing heteroaromatic salts **1** and **2** bearing mesogenic flexible substituents.



Ar = Ar' symmetrical

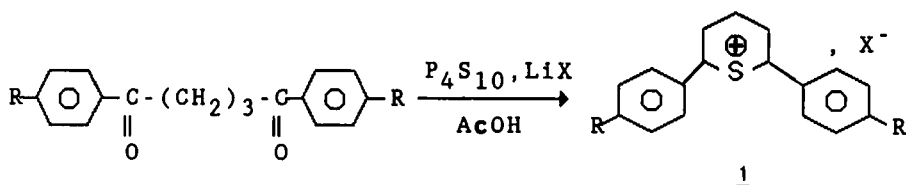
Ar \neq Ar' non symmetrical

We tried to determine the influence of various structural parameters on the mesomorphic properties of obtained species :

- the nature of the cation
- the nature of the anion
- the nature of the flexible substituents
- the position of the substituents on the phenyls
- the number of the flexible substituents
- the length of the chains

SYNTHESIS

Diaryl-2,6 thiopyrylium salts 1 were obtained by heterocyclization of δ -diketones :



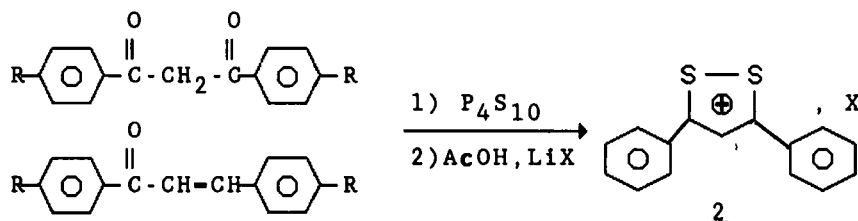
We found that acetic acid can be used as solvent. In this case the salt 1 is isolated as a single product.^{1c}

In fact the action of P_4S_{10} on δ -diketones such as dibenzoyl propane in refluxing acetic acid leads to thiopyrylium salt which has been isolated as perchlorate by metathesis at the end of the reaction (yield : 20-30%).

When the reaction was performed in the presence of alkaline or alkaline earth perchlorates the yield was considerably increased (yield : 70-80%).

The perchlorates can be replaced by tetrafluoroborates with equal efficiency. This positive salt effect was interpreted^{1c}.

Diaryl-3,5 dithiolium salts 2 were obtained starting from β -diketones or chalcones^{1e} :



As a general rule the yield of salts 2 are superior starting from β -diketones, but the chalcones being easier to prepare.

Recently a series of non symmetrical tetrafluoroborates 2 has been synthesized starting from

isomeric chalcones (ArC-CH=CH-Ar' or Ar'-C-CH=CH-Ar).

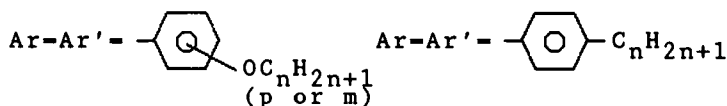
MESOMORPHIC PROPERTIES

Optical observations, DSC studies and X-ray diffraction measurements were performed for both series of salts.

Compounds with lamellar structure (S_A)

Compounds with two substituents :

Salts 1 and 2 ($Ar=Ar'$) in which the phenyls are substituted, in meta or para position, by alkyl or alkoxy groups

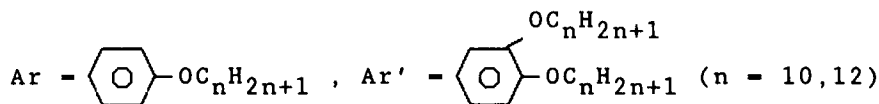


are S_A for $n \geq 9$, whatever the nature of the anion ($X=\text{ClO}_4$, BF_4 , Cl , PF_6).

Ortho isomers do not exhibit mesomorphic behaviours. For data concerning the phase transitions, see refs. 1d-e

Compounds with three substituents :

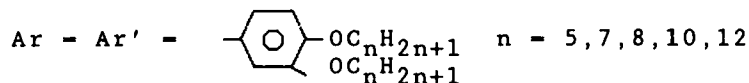
Non symmetrical dithiolium salts 2 exhibit also S_A behaviour. 1f



Compounds with columnar structure

Salts with four alkoxy chains² :

The series of tetrafluoroborates 2 was prepared, in which each phenyl is substituted by two alkoxy chains in meta and para positions :



Optical observations, DSC studies and X-ray diffraction measurements are consistent with a columnar hexagonal mesomorphic order in the case of these salts.

It is the first time that D_h mesophases are observed in the case of heteroaromatic salts with only four flexible chains. In the mesophase, the cations are probably associated forming dimers.^{2b}

CONCLUDING REMARKS

We have developed general approaches for the heterocyclization of various carbonyl derivatives leading to thiopyrylium and dithiolium salts.

Several of them exhibit liquid crystalline properties.

Some relationships between molecular structure and mesomorphism of studied salts were established.

The nature of mesophase depends of the number of flexible chains.

It should be mentioned that the thiopyrylium salts 1 are useful intermediates for synthesis of liquid crystalline conductors³. Dithiolium salts 2, with relatively short chains are shown to yield Langmuir-Blodgett films⁴.

Other applications of these materials will be presented later.

REFERENCES

1. a) V. Gionis, R. Fugnitto, H. Strzelecka and P. Barny, Mol. Cryst. Liq. Cryst., **95**, 351 (1983).
 b) G. Sigaud, F. Hardouin, H. Gasparoux, V. Gionis, M. Veber and H. Strzelecka, Mol. Cryst. Liq. Cryst., **92**, 217 (1983).
 c) V. Gionis and H. Strzelecka, Synth. Comm., **14**, 775 (1984).
 d) Veber, C. Jallabert, H. Strzelecka, V. Gionis and G. Sigaud, Mol. Cryst. Liq. Cryst., **137**, 373 (1986).
 e) M. Veber, C. Jallabert and H. Strzelecka, Synth. Comm., **17**, 693 (1987).
 f) M. Veber, C. Jallabert, H. Strzelecka, O. Julien and P. Davidson, Liquid Crystals 1990 inpress.
2. a) H. Strzelecka, C. Jallabert and M. Veber, Mol. Cryst. Liq. Cryst., **156**, 355 (1988).
 b) H. Strzelecka, C. Jallabert, M. Veber, P. Davidson, A.M. Levelut, J. Malthête, P. Weber and G. Sigaud, Mol. Cryst. Liq. Cryst., **161**, 403 (1988).
3. R. Kormann, L. Zuppiroli, V. Gionis and H. Strzelecka, Mol. Cryst. Liq. Cryst., **133**, 283 (1986) (and references therein).
4. M. Vandevyver, J. Richard, A. Barraud, M. Veber, C. Jallabert and H. Strzelecka, J. Chim. Phys. **85**, 385 (1988).