

This article was downloaded by:

On: 26 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



Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713926090>

Synthesis and X-ray study of new columnar heteroaromatic salts

P. Davidson^a; C. Jallabert^b; A. M. Levelut^a; H. Strzelecka^b; M. Veber^b

^a LA 2, Laboratoire de Physique des Solides, Université Paris-Sud, Orsay, France ^b ESPCI, UA 429, Paris Cedex 05, France

To cite this Article Davidson, P. , Jallabert, C. , Levelut, A. M. , Strzelecka, H. and Veber, M.(1988) 'Synthesis and X-ray study of new columnar heteroaromatic salts', *Liquid Crystals*, 3: 1, 133 – 137

To link to this Article: DOI: 10.1080/02678298808086357

URL: <http://dx.doi.org/10.1080/02678298808086357>

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.

PRELIMINARY COMMUNICATIONS

Synthesis and X-ray study of new columnar heteroaromatic salts

by P. DAVIDSON†, C. JALLABERT‡, A. M. LEVELUT†, H. STRZELECKA‡
and M. VEBER‡

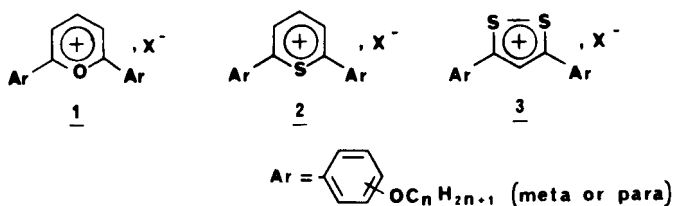
†LA 2, Laboratoire de Physique des Solides, Université Paris-Sud, Bâtiment 510,
91405 Orsay, France

‡ESPCI, UA 429, 10, rue Vauquelin, 75231 Paris Cédex 05, France

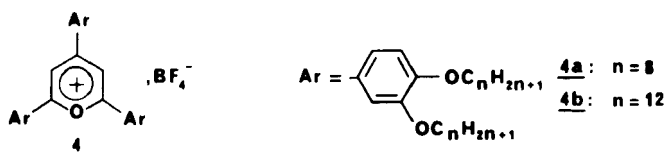
(Received 23 March 1987; accepted 26 July 1987)

The synthesis of 2,4,6-triarylpyrylium tetrafluoroborates substituted by six long alkyloxy chains ($n = 8$ and 12) is described. These salts exhibit a discotic mesophase from room temperature to 200°C . X-ray diffraction experiments on powder and oriented samples show that this phase is an ordered hexagonal columnar phase, D_{ho} .

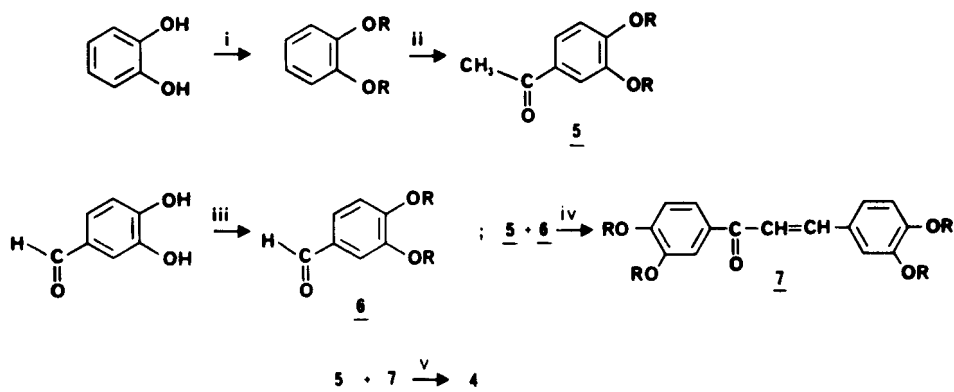
We have described several series of thermotropic liquid crystals in which the central rigid part consists of heteroaromatic cations such as pyrylium **1**, thiopyrylium **2** and dithiolium **3** [1].



Each phenyl ring is substituted with long alkyloxy chains ($n \geq 8$); the observed mesophases are smectic A (S_A). Here we report the synthesis and structural properties of 2,4,6-triarylpyrylium tetrafluoroborates **4**, the aryls being substituted in the 3 and 4 positions by alkyloxy groups.



We had expected that the presence of six alkyloxy groups might induce a columnar disc-like structure [2]. The salts **4** were obtained according to the scheme



(i) Alkylation by RX under solid-liquid phase transfer conditions, without solvent [3]; (ii) CH_3COCl , AlCl_3 , solvent CH_2Cl_2 ; (iii) RX, K_2CO_3 , DMF at 80°C ; (iv) NaOH catalyst, EtOH at 60°C [4]; (v) modified Katritzky procedure [5]: **5** and **7** are in a molecular ratio of 1:2:1, Ac_2O , HBF_4 (35 per cent) at 100°C for 5 h.

The salts **4** were purified by recrystallization from ethyl acetate or dichloroethane, and characterized by I.R., N.M.R. and U.V.-visible spectroscopy. These salts were quite difficult to purify as it seems that they dissolve in many non-volatile solvents.

Microscopic observations, performed in polarized light on a variable-temperature stage, revealed some uniaxial homeotropic domains of hexagonal shape. These are mesophase domains growing in the isotropic liquid.

Powder X-ray diffraction patterns were recorded at different temperatures with a classical Guinier camera. A linearly collimated X-ray beam of wavelength $\lambda = 1.541 \text{ \AA}$ (Cu K_α) was obtained by reflection from a quartz monochromator. The sample was held in a Lindemann glass tube (0.5 mm diameter) and was heated in an air stream.

For both compounds **4a** and **4b** the powder diffraction patterns show some sharp reflections at small angles and two diffuse rings at wide angles; they are therefore characteristic of discotic columnar phases [2 (b)]. Moreover, the small-angle reflections can be indexed in terms of a hexagonal two-dimensional lattice, and so their mesophases belong to the D_{ho} type. The powder patterns also allow us to measure accurately the parameter a for the three-dimensional lattice and its evolution with temperature (see figure 2 and the table). However, the two compounds exhibit slightly different thermal behaviour; compound **4a** has a discotic columnar structure from room temperature to about 200°C , at which it starts to decompose. Compound **4b** gives a more complicated X-ray pattern between room temperature and 40°C . At 40°C a transition takes place, also leading to a columnar discotic phase which is stable

The structural parameters for compounds **4a** and **4b**.

Compound	$a/\text{\AA}$	$c/\text{\AA}$	Calculated density/ g cm^{-3}	$V_{\text{CH}_2}/\text{\AA}^3$	Calculated chain length/ \AA	Trans-trans chain length/ \AA
4a	26.45	3.4	0.94	~ 30	~ 6.2	~ 10
4b	30.70	3.4	0.90	~ 30	~ 8.4	~ 15

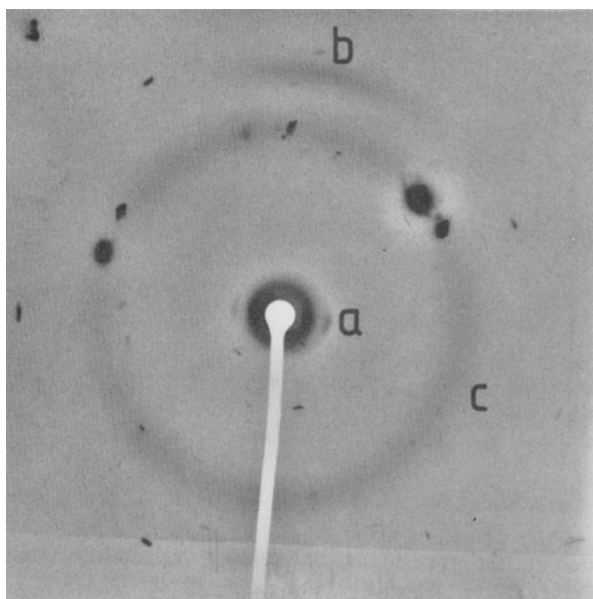


Figure 1. X-ray diffraction pattern of an oriented sample of compound **4b** taken at room temperature in the mesophase. The strong Bragg spots are due to the mica substrate. The film-sample distance was 67 mm.

until decomposition starts at approximately 200°C. Upon cooling from either 200°C or 40°C, the columnar phase B is preserved until room temperature is reached. The X-ray pattern of the low-temperature phase is still characteristic of a mesophase, and studies are under way to elucidate its structure. According to a technique described elsewhere [6], oriented samples were obtained by spreading both compounds with a spatula onto mica single-crystal sheets. The columns are aligned in the stretching direction; there is a symmetry of revolution around this axis, which we call the meridian. X-ray diffraction experiments were made with a monochromatic beam (Cu K_α) from a doubly bent graphite pyrolytic crystal. Samples were held in an oven, itself placed in an evacuated camera. The X-ray patterns are characteristic of hexagonal, ordered columnar mesophases, as already inferred from the powder diffraction patterns. At small angles and in a plane perpendicular to the meridian, two sharp reflections are observed in the ratio 1 : √3 for compound **4a** and three sharp reflections in the ratio 1 : √3 : 2 for compound **4b**.

These Bragg peaks ('a' in figure 1) show that the columns stack themselves on a two-dimensional hexagonal lattice with parameter *a*. At wide angles, along the meridian and perpendicular to it, a diffuse line ('b' in figure 1) is found, corresponding to the ordered stacking of the cores in a column with a stacking periodicity of *c* = 3.4 Å. This value is one of the smallest observed in columnar phases; for classical compounds such as the hexa alkyloxy derivatives of triphenylene [7], *c* = 3.6 Å. Our value should be compared instead with some metallophthalocyanines [8], for which *c* = 3.4 Å, and with the stacking periodicity of TTF (*c* = 3.47 Å) in the TTF-TCNQ one-dimensional conductor system [9]. The correlation length along the column is about 200 Å at room temperature. At wide angles, an isotropic diffuse ring ('c' in figure 1) corresponding to a scattering vector of $(2 \sin \theta)/\lambda = 1/4.5 \text{ \AA}^{-1}$ is observed;

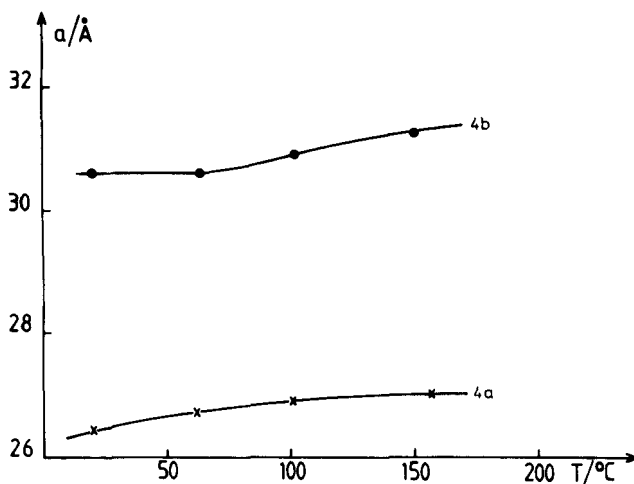


Figure 2. Variation of the hexagonal lattice parameter a with temperature T .

this is characteristic of the melted state of the alkyloxy chains. The table gives values of the structural parameters for compounds **4a** and **4b**.

Let us denote by $V_c = \frac{1}{2}\sqrt{3}a^2C$ the volume of the cell, by V_{al} the volume of the aliphatic chains, by V_{ar} the volume of the aromatic core and by $V_{BF_4^-}$ the volume of the BF_4^- anion. We can measure the aromatic core radius ($\approx 7 \text{ \AA}$) on Dreiding stereomodels and deduce the BF_4^- radius from ionic radii; we obtain $V_{ar} \approx 525 \text{ \AA}^3$ and $V_{BF_4^-} \approx 100 \text{ \AA}^3$. We can then estimate $V_{al} = V_c - V_{ar} - V_{BF_4^-}$, and define an average volume per methylene group, $V_{CH_2} = V_{al}/n_{CH_2}$, where n_{CH_2} is the number of aliphatic carbon atoms in the cell. The calculated value for V_{CH_2} , 30 \AA^3 , is slightly larger than the value of 28 \AA^3 found for other classical discotic compounds [10]. This difference may be caused by the influence of some impurities dissolved in the phase, as we did not take impurity volume into account. The calculated chain length is much smaller than their size in a trans-trans configuration. This is in agreement with the melted chain image.

The variation of the hexagonal lattice parameter a with temperature has been measured on powder diffraction patterns, and is shown in figure 2: a is seen to increase slowly with temperature, as is observed for many other discotic compounds. However, we noticed that the salts **4** first produced had a high impurity content and showed a different behaviour. For such salts, a strong decrease with temperature was observed as the impurities are expelled from the phase. Thus, the results in figure 2 indicate a low impurity content.

As compared with the organic cations, the BF_4^- anions do not scatter X-rays very much since they do not have so many electrons. Indeed, we do not see their contribution in the X-ray patterns, and we need to use other experimental methods to gain information about them.

References

- [1] (a) GIONIS, V., FUGNITTO, R., STRZELECKA, H., and LE BARNY, P., 1983, *Molec. Crystals liq. Crystals*, **95**, 351. (b) SIGAUD, G., HARDOUIN, F., GASPAROUX, H., GIONIS, V., VEGER, M., and STRZELECKA, H., 1983, *Molec. Crystals liq. Crystals Lett.*, **92**, 217. (c) GIONIS, V., and STRZELECKA, H., 1984, *Synth. Commun.*, **14**, 775. (d) VEGER, M., JALLABERT, C., STRZELECKA, H., GIONIS, V., and SIGAUD, G., 1986, *Molec. Crystals liq. Crystals*, **137**, 373. (e) VEGER, M., JALLABERT, C., and STRZELECKA, H., 1987, *Synth. Commun.* (in press).

- [2] DESTRADE, C., GASPAROUX, H., FOUCHER, P., NGUYEN HUU TINH, MALTHETE, J., and JACQUES, J., 1983, *J. Chim. phys.*, **80**, 137, and references therein. LEVELUT, A. M., 1983, *J. Chim. phys.*, **80**, 149.
- [3] BARRY G., BRAM, G., DESCOTES, G., LOUPY, A., PIGEON, P., and SANSOULET, J., 1982, *Tetrahedron Lett.*, **23**, 5407.
- [4] WATTANASIN, S., and MURPHY, W. S., 1980, *Synthesis*, **8**, 647.
- [5] KATRITZKY, A. R., SCHWARTZ, O. A., ABDEL RAMMAN, A. E., and LEAHY, D. E., 1984, *J. heter. Chem.*, **21**, 1673.
- [6] LEVELUT, A. M., MALTHETE, J., and COLLET, A., 1986, *J. Phys., Paris*, **47**, 351.
- [7] LEVELUT, A. M., 1979, *J. Phys. Lett., Paris*, **40**, 281.
- [8] PIECHOKI, C., SIMON, J., SKOULIOS, A., GUILLON, D., and WEBER, P., 1982, *J. Am. chem. Soc.*, **104**, 5245.
- [9] KISTENMACHER, T. J., PHILLIPS, T. E., and COWAN, D. O., 1974, *Acta crystallogr. B*, **30**, 763.
- [10] CAYUELA, R., 1986, Ph.D. thesis, Bordeaux, p. 91.