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The Smectic a Phases of Some Long Chain Substituted Diaryl-2,6 Pyrylium and Thiopyrylium Salts

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THE SMECTIC A PHASES OF SOME LONG CHAIN SUBSTITUTED DIARYL-2,6 PYRYLIUM AND THIOPYRYLIUM SALTS.

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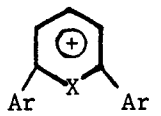
We report on the characterization of smectic A phases in pyrylium perchlorates. Different models of the layered structure are discussed.

INTRODUCTION

The synthesis of diaryl-2,6 pyrylium and thiopyrylium perchlorates in which aryls contain mesogenic long chain alkyl or alkoxy groups at different positions has been previously reported[1,2] :



, ClO_4^-

X = O or S $R = C_nH_{2n+1}$ or

Ar =  $R = O\,C_nH_{2n+1}$

Among them some are known to produce mesomorphic phases which has initiated an effort of characterization. This paper is devoted to confirm the S_A nature of a mesophase that occurs in three salts.

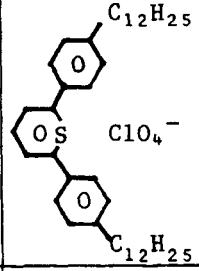
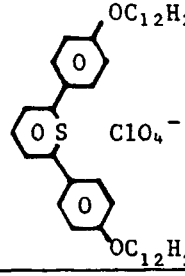
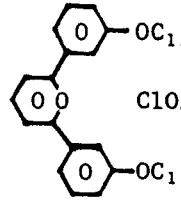
EXPERIMENTAL

Two thiopyrylium 1, 2 and one pyrylium 3 salts have been investigated by DSC, polarizing microscopy and X-ray diffraction on powder samples. Their chemical structures are given in the table 1.

The clearing temperatures together with the corresponding entropies of transitions and the range of mesophases are indicated in this table. Other thermodynamical data regarding the transitions occuring at lower temperatures have been previously listed in the ref.1. From the table 1 we can note the weak value for the smectic to isotropic entropy (ΔS_{S-I}) compared to what is usually observed for that kind of transition : a

common ΔS_{S_A-I} lies in the range 3-7 cal.mole^{-1} K^{-1} [3]. This remark is of interest for the following discussion. No important shift is noticeable on the DSC traces upon heating compared to cooling.

TABLE I

Comp. N°		T Cr-S	$T_{S_A \rightarrow I}$ °C	$\Delta S_{S_A \rightarrow I}$ cal.K^{-1}mole^{-1}
1		115 Cr S_A	150	1.2
2		100 Cr S_A	185	1.2
3		98 Cr-S_2	147	1.2

All three salts present the same fan-shaped texture with homeotropic parts indicative of an uniaxial medium. A typical microscopic texture is shown on the figure 1 for compound 2.

The X-ray patterns confirm the smectic character of these mesophases : at small angles one observes a sharp reflection arising from the modulation of the layers and at wide angles a diffuse scattering gives evidence for a liquid like order

within the layers.

These experimental facts all together classify these mesophases as smectic A ones.

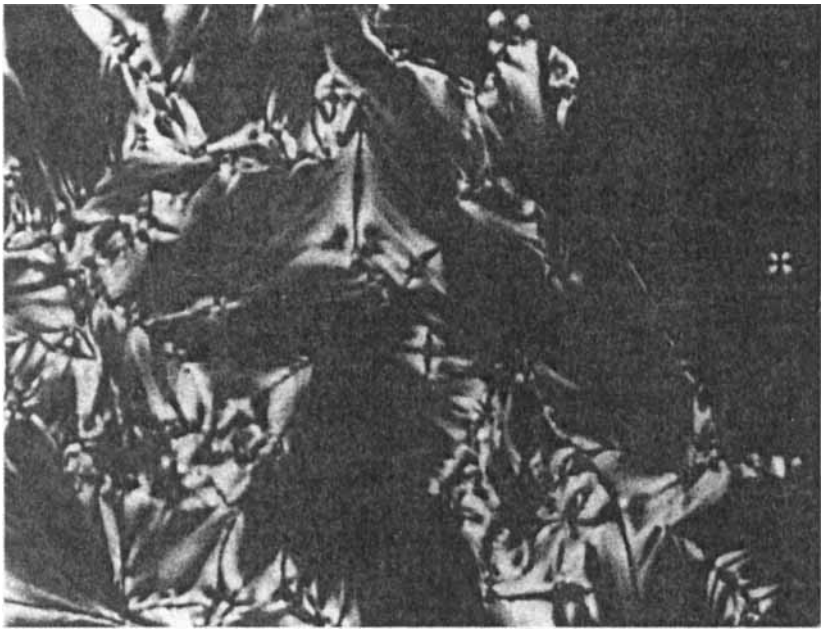


Figure 1

DISCUSSION

What structural model would be consistent with these experimental results ?

One can suggest three different molecular arrangements able to fit the experimental measurement for the layer thickness in the case ot the compound 3 for example.

In the first one, each aliphatic chain is located on opposite sides of the pyrylium heterocycle : the chains are partially melted which results in a length of 34 Å for the overall molecule itself directly comparable to the experimental layer thickness : 32 Å. The molecules would then be packed parallel one to each other inside classical smectic A layers

(Fig.2). The principal argument against this model is the great repulsive forces of charges. In addition considering the amphiphilic properties of these compounds (see below), this model appears very unlikely : the layers do not present the ionic interfaces required for an amphiphilic behavior.

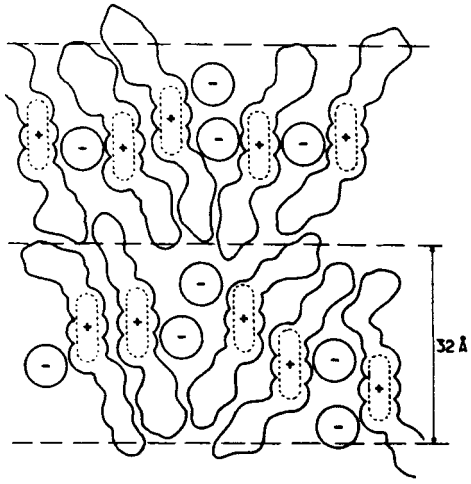


Figure 2

. The second and third possibilities imply another conformation for the molecules : the two chains lie on the same side of the ionic core (Fig.3).

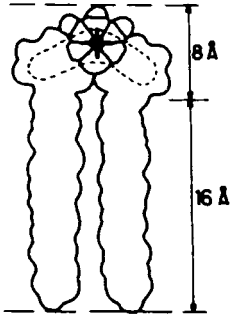


Figure 3

One can then postulate two cases :

i. Either all trans chains with an almost complete overlapping of these aliphatic tails which leads to a periodicity of the structure in close agreement with the experimental parameter (Fig.4). This model is similar to the description of the smectic A phase of pyridinium salts proposed by Sudhölter et coll.[4].

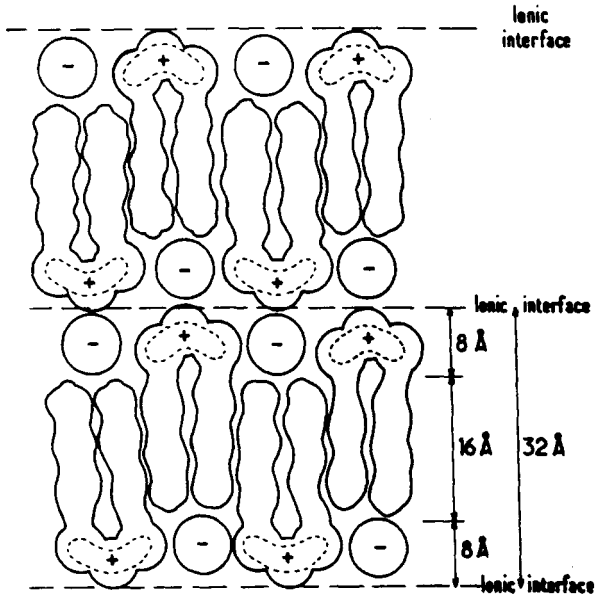


Figure 4

ii. Or entirely melted chains without interpenetration at all which provides bilayers comparable to the structure of the L_α phases in lyotropic systems[5] (Fig.5).

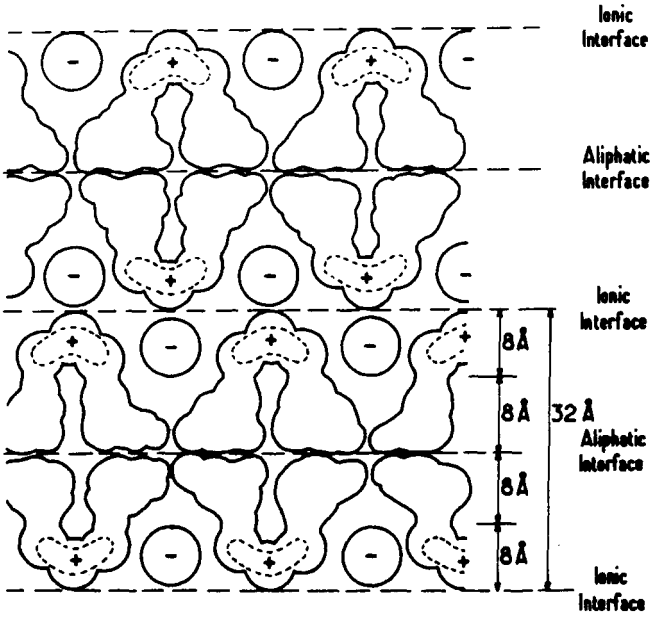


Figure 5

How to decide whether one model or the other is preferable ?

We already mentioned that the entropies for the $S_A - I$ transitions for these compounds are much lower than for usual rod-like molecule. We propose to interpret this difference by a more or less complete melting of the aliphatic chains. For an usual non polar rod-like molecule one can consider that the probability is high to have trans conformations in its aliphatic tails : typically the experimentally measured layer spacing is close to the length of the molecular model in its most extended form[6]. Now if we compare the $S_A - I$ entropies for two successive homologues in a given series[3], the difference is about 0.2 cal. K^{-1} per CH_2 group which can be assumed to figure a rough evaluation of the melting entropy for one C-C bond in the chain.

Starting from an all trans conformation including twelve CH_2 and assuming that the first ones (say 3) keep always a blocked conformation, it is necessary to add 1.8 cal. $K^{-1}(9 \times 0.2)$ to melt this stretched chain. Thus considering the pyrylium salt with two C_{12} chains, the situation with all trans conformations would require an additional entropy : 3.6 cal.K^{-1} per mole (1.8×2) for melting which added to the experimental value : 1.2 cal.K^{-1}.$mole^{-1}$ for the S_A-I transition (table I) leads to a hypothetic transition entropy : 4.8 cal.$mole^{-1}$.K^{-1} for the transition from a smectic A in which the molecules would be in their most extended form ; this values falls in the classical range for a smectic A to isotropic transition (see above). Thus we conclude that the chains are highly melted in the smectic A phases of the pyrylium salts which explains the difference in the $S_A - I$ entropies. This point favours the model of the figure 5.

Another observation sustains this point of view : the rather large variations of the layer thickness with regard to the temperature (table 2) which seems to indicate that two chain ends participate to this evolution. For this reason an interpenetration of the chains might be less efficient in the increase of the layer spacing with decreasing temperature. The extreme deformation of the chains required to accomodate the size of the molecular model to the experimental layer thickness in the case of the figure 5 implies a large lateral extension of the volume occupied by the aliphatic parts.

TABLE II

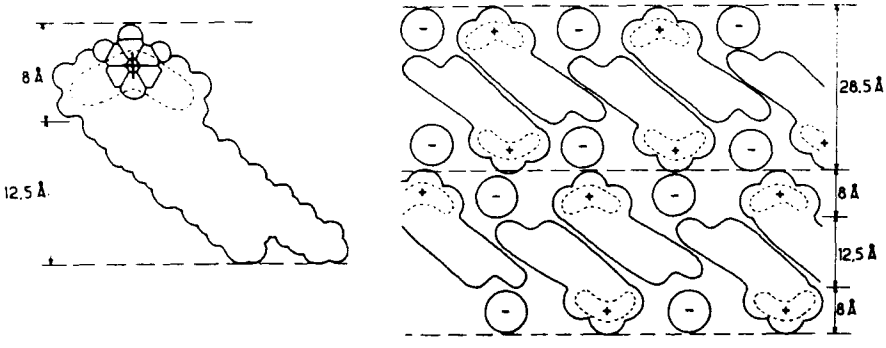
Variation of the layer spacing with the temperature for the compound 3

Phase	T °C	Layer spacing Å
S_A	145.5	31.6
	139.5	32.2
	133.5	32.8
	127.5	33.3
S_2	120	29.3

Further on, the same mesomorphism is observed without significant shifts of the temperatures of transition whatever the solvent used for the recrystallization is, acetic acid, ethanol or acetonitrile. This is a good evidence for the thermotropic character of the existing mesophases. Of course, this does not rule out the possibility to induce a lyotropic state by adding some polar solvent (acetic acid) to the pure compound as suggested by some experiments[7]. On the other hand the thermotropic polymorphism seems unlikely if the chains are strongly interpenetrated as in the model of the figure 4 : one would expect that "ionic impurities" are needed to decorrelate the ionic interfaces when the aliphatic ones are missing. Nevertheless it should be remarked that the compound 3 presents a highly ordered lamellar phase at lower temperature. Although its nature is not yet definitely determined, the layer thickness (from X-ray diffraction) in this phase seems to indicate that the average molecular axis is tilted with regard to the plane of the layers. A model in which there are an impeded rotation of the chains around the C-O bonds and an almost complete overlapping of the aliphatic parts fits very well the experimental layer spacing (Fig.6) : if this geometry is somewhat kept in the high temperature smectic A phase, the structure of the figure 4 would not be completely misleading.

To summarize : our experimental observations in the S_A phase are rather well described by the model of the figure 5, the chains being highly melted, but may be they are little interdigitated too. In order to fill the excess volume due to the

counterion we expect effects on the specific volume to be greater than in the S_A structures of non ionic amphiphilic compounds.



a b

Figure 6

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