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Nature of the mesophase of a conducting charge transfer complex : neither discotic nor calamitic

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Résumé. — Nous décrivons la structure de la mésophase d'un complexe conducteur à transfert de charge constitué de TCNQ et d'un donneur portant quatre longues chaînes paraffiniques. Les hétérocycles du donneur restent empilés dans la mésophase; leur distance moyenne est courte (3,6 Å). La présence des chaînes aliphatiques favorise la formation d'une structure lamellaire, les piles de donneur restant localisées dans les couches et étant vraisemblablement séparées entre elles dans chaque couche par le TCNQ. Ainsi l'organisation de cette mésophase est-elle intermédiaire entre celle des smectiques et celle des phases en colonnes.

Abstract. — We describe the structure of the mesophase of a conducting charge transfer complex formed by a donor substituted by four long paraffinic chains and TCNQ as acceptor. In the mesophase the donor cores remain in stacks with a short core-to-core distance (3.6 Å). The presence of paraffinic chains favours a layer structure, the stacks being localized in the lamellae and TCNQ likely filling the space between stacks. Therefore the organization in this mesophase is intermediate between those of smectic and columnar discotic liquid crystals.

A new class of liquid crystals formed by disc-like molecules, (the discotic), was discovered [1] some years ago. Disc-like molecules in which a flat aromatic core is surrounded by paraffinic chains can display a mesomorphic state with a columnar structure. The aromatic moieties are stacked more or less regularly in the central part of the column. The paraffinic chains are in a fluid state and fill the external part of each column in such a way that the columns are parallel and form a two-dimensional crystal without any positional correlation between columns along a direction parallel to their axis.

Such a columnar organization presents some similarities with the segregated stacking of 1D organic conductors. Therefore it was tempting to synthesize organic conductors in which one (or two) conducting chains have a discogen character. The introduction of long chain substituents induces mesogenic properties in a few precursors of organic conductors : di-substituted tetrathiofulvalene [2, 3] or metal complexes dithiene [4] show smectic or nematic liquid crystalline phases without any columnar organization. A hexagonal columnar mesophase has been identified in a

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metallophthalocyanine substituted by eight aliphatic chains, each rigid part being surrounded by a large paraffinic zone [5]. The synthesis of tetra substituted cores may also be an interesting approach for this problem and we prepared disk-like π donors obtained by introducing long chain substituents R into the phenyl rings of the heterocyclic system [6, 7].

For example, in (1) with $\text{R} = \text{C}_n\text{H}_{2n+1}$, $\text{X} = \text{O}$ the high temperature phase seems to be a 2D crystal in which successive layers are uncorrelated [8]. The existence of columns of (1) in each lamella is not excluded; in such a case we will have stacks of molecules which are not fully surrounded by a paraffinic region. Compounds (1) give stable and isolable complexes with TCNQ. The electrical behaviour of the obtained complexes depends on the nature of the hetero atom X (oxygen or sulphur, [9, 10]).

Namely we obtained a conducting TCNQ complex ($\sigma_{\parallel} = 0.7 (\Omega \text{ cm})^{-1}$) at room temperature in the following case :

The phase transformations of this complex were first studied by DTA experiments. The first heating curve (Fig. 1) for the complex is characteristic of a mesogen compound showing a unique mesophase : the enthalpy of the first transformation at $\approx 123^\circ\text{C}$ (melting) is larger than the enthalpy corresponding to the clearing point at 154°C . On cooling, the peaks appear very diffuse; moreover the DTA curves obtained with a further heating show that the sample has not recovered its previous crystalline state. EPR measurements [10] show a discontinuity of the magnetic susceptibility at the melting point.

Texture observation of the complex in a transmission light polarizing microscope is not conclusive since the compound is opaque even in a thin layer. In order to characterize the mesophase, we have performed X-ray diffraction studies with techniques usually employed for the observation of mesophases.

1. X-ray diffraction experiments.

The sample is put in a Lindeman glass capillary of 1.5 mm diameter. An oven maintains the temperature of the sample constant within 1°C . The X-ray $\text{CuK}\alpha$ monochromatic beam is reflected by a double bent pyrolytic graphite and a cylindrical film at 60 mm from the sample collects the diffracted radiations. The sample and film holders are surrounded by a shield which can be evacuated and which is put between the two conic poles of an electromagnet. The magnetic

Fig. 1. — Variation of the DTA signal *versus* temperature in degrees C during the first thermal cycle. The heating and cooling curves ($2^{\circ}/\text{min.}$ rate) are pointed out by arrows. We must notice that the temperature of the first DTA peak obtained by heating can fluctuate between 120 and 127 $^{\circ}\text{C}$ depending on the sample.

field is perpendicular to the X-ray beam and to the capillary tube. Its maximum value at the sample level is of 1.8 T. Oriented diffraction patterns are obtained when the sample is cooled from the isotropic liquid under a magnetic field of 1.7 T (Fig. 2). Along the field direction one can see equally spaced Bragg spots (3 orders of reflection). In a direction perpendicular to the magnetic field one can find three diffuse maxima. When we suppress the magnetic field and make a $\pi/2$ turn of the sample around the capillary axis the Bragg spot disappears and the diffuse spots become three circular rings.

This picture has similarity both with the diffraction patterns of smectic and discotic mesophases : the two outer diffuse lines are similar to the two outer diffuse lines of the pattern of some

Fig. 2. — X-ray diffraction pattern of an aligned sample of the complex in the mesophase temperature range.

ordered hexagonal columnar mesophases (Fig. 3) but the symmetry of the reciprocal space is the same in this mesophase and in a smectic A phase. Moreover the three orders of reflection correspond to a layered structure with a periodicity of $32.2 \text{ \AA}$. The direction and the degree of alignment in the magnetic field are comparable to those obtained for usual smectic A phases but the number of visible reflections is higher.

Fig. 3. — An example of the diffraction pattern of a hexagonal discotic columnar mesophase obtained at 145°C with truxene hexadecanoate.

As in the discotic phases the ring at $4.6 \text{ \AA}$ is characteristic of a fluid state of the paraffinic chains. In our complex the chains remain more or less perpendicular to the layer plane. The outer line at $3.6 \text{ \AA}$ seems to have only a weak curvature. Therefore this line corresponds to diffuse sheets and the curvature is induced by orientational fluctuations. Then such sheets are characteristic of a linear periodicity in a direction parallel to the layer planes. The period is $3.6 \text{ \AA}$ and probably corresponds to stacks of donors and perhaps of TCNQ cores. The direction of these stacks in the layer plane is random but remains quite parallel to the layer plane. The length of the line is consistent with interferences between cores of sizes of about $10 \text{ \AA}$. The width of the line is rather small and the stacks have a coherence length of at least ten molecules ($\approx 40 \text{ \AA}$). This value of the coherence length implies that the stacks are rigid at least at the same scale. Therefore we have probably locally parallel stacks of molecules inside the layer. The distance between neighbouring stacks is not well defined but the third diffuse spot which lies at $24 \text{ \AA}$ gives an idea of the mean distance between two identical stacks. The large value $24 \text{ \AA}$ is consistent with the idea that the space between heterocyclic stacks is filled up with TCNQ. In such a case the intensity dependence along a direction parallel to the layer and perpendicular to the stack is driven by the interference function and by the form factor of the donor stacks (the TCNQ region being of lower density). For this reason the maximum of intensity occurs in a domain where the form factor is quickly decreasing. Therefore the maximum of the interference function corresponds to a mean distance smaller than $24 \text{ \AA}$.

We have attempted to orient the stacks of donor by applying a magnetic field parallel to the layer planes previously oriented. We only obtained a reorientation of the layers perpendicularly to the magnetic field when it reaches 1.5 T . Therefore we cannot say anything about the possible orientational correlation between stacks lying in successive layers.

At last let us say some words about the stability of the mesophase. Fresh samples of the mesophase studied in sealed capillary tubes are stable for one or two days : the X-ray diffraction pattern remains the same, the position and the width of the different spots are only weakly dependent of the temperature. Moreover there is no evidence of the presence of some amount of isotropic or crystalline material. On cooling down such samples we observed a phase transformation below 100° in which an oriented sample of the mesophase is transformed into a fibre of a crystal-

line form. This crystalline form differs from that which exists before any heating since the observed lattice spacings in the fibre pattern are inconsistent with the lattice constants of the crystalline form of the complex $a = 18.47 \text{ \AA}$, $b = 9.14 \text{ \AA}$, $c = 24.64 \text{ \AA}$, $\beta = 110^\circ$, $z = 2$ [11]. Moreover this difference is consistent with the behaviour of the susceptibility under similar conditions [10].

After a long time of aging around 125° the mesophase can be supercooled until room temperature but the evolution of the diffraction pattern (with the aging time or with temperature) implies that a change of composition occurs in the sample. At this state the sample can be a mixture of amorphous and liquid crystalline phases.

2. Discussion.

We can confirm from our X-ray diffraction patterns that the donor molecules form stacks in the mesophase. The core-to-core distance is $3.6 \text{ \AA}$ in a stack. This distance is equal to the minimum core-to-core distance measured in columnar phases. The organization of TCNQ molecules has not been clearly put in evidence. Due to the large difference between the donor and acceptor masses, the X-ray scattering intensity is mainly provided by interferences between donor molecules. The mesophase has a layered structure, the stacks of donor are parallel to the layer plane, the paraffinic chains lying at the interface between two layers. In each layer the stacks are more or less parallel but the mean in-layer distance between two donor stacks is not as regular as the mean distance between two adjacent layers and the space between two stacks in a layer is probably filled by TCNQ molecules.

Assuming a specific gravity of the mesophase of 1 g/cm^3 the in-layer area per complex is $74 \text{ \AA}^2$. This value implies a column to column distance of $\approx 21 \text{ \AA}$. Since the paraffinic chains

Fig. 4. — A schematic representation of the donor organization in the mesophase of the complex (the TCNQ molecules are not represented).

lie two by two perpendicularly to the interface between two layers the area of each chain is $\simeq 37 \text{ \AA}^2$. This value is typical of a lyotropic liquid crystalline phase [12]. Moreover if we assume that the central zone containing the heterocycles has a thickness of about $13 \text{ \AA}$ (the size of tetraphenyl dithiapyranylidene in its plane is $\simeq 13 \times 13 \text{ \AA}^2$ [13]), the thickness of each paraffinic zone is $\simeq 9 \text{ \AA}$. This value is much smaller than the length of an extended chain in its trans-trans conformation ($16 \text{ \AA}$) but fits with the value of the chain specific area. We can also assume that an alternance of donor and acceptor cores in the layer favours a disordered conformation of the chains.

In conclusion the conducting complex (2) forms a fluid anisotropic phase. In this mesophase donor molecules form *stacks* with a short core-to-core distance $3.6 \text{ \AA}$, the surrounding of each stack is anisotropic. In one direction melted paraffinic chains ensure a regular stack-to-stack distance and are at the origin of the lamellar character of the structure. In the other direction, inside a lamella, TCNQ molecules fill the space between two stacks, the mean distance is not regular and varies from $\simeq 20$ to $23 \text{ \AA}$ (Fig. 4). To our knowledge the organization here described is different from all the usually encountered ones as well in lyotropic as in thermotropic systems. The localization and the molten state of the paraffinic chains allow the fluidity of the mesophase and its orientation with a magnetic field but maintain donor and acceptor close together. Nevertheless further information on the organization of TCNQ must be obtained from « local » observation such as EPR or NMR experiments on oriented samples.

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