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STRUCTURAL INVESTIGATION OF SMECTIC Q PHASE

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Abstract Some mesogenic chiral compounds show a smectic Q phase just below the clearing point. The molecules are in a liquid state but they are organized on a tridimensional lattice. At lower temperatures the only possible mesophase-mesophase transformation is towards an antiferroelectric smectic. Three different tetragonal and one hexagonal lattices have been identified. All these phases, except one, can be considered as crystalline arrays of twist grain boundaries inside an antiferroelectric smectic. The twist grain boundaries perpendicular to the smectic planes divide the smectic structure in narrow sheets (their width compares to the molecular length), the smectic planes are twisted by an angle of $\pi/2$ or of $\pi/3$ on each side of a boundary and the successive sheets correspond to one another by a 4_1 or a 6_2 helical axis. The interface between two molecular layers is described by a triply periodic minimal surface.

INTRODUCTION

More than ten years ago a new type of liquid crystalline phases - S_Q - was discovered which occurred in chiral 1-methylheptylterephthalidene-bis-ammino-cinnamate (here abbreviated to M7TAC)[1]. X-ray investigations established a three-dimensional tetragonal lattice superimposed upon a short range liquid order of the centres of mass. One unit cell contains about 350 molecules whose arrangement could not be determined so far.

During the last years we succeeded in synthesizing more than 20 compounds exhibiting a mesophase which was classified as S_Q by textural observations. In all of these compounds this phase is chirally induced, there is a direct transition between the S_Q and the isotropic phase and the only liquid crystalline phase appearing at lower temperatures is the S_{CA} phase. X-ray investigations revealed that these S_Q phases have different anisotropies of the lattice parameters[2].

We have continued the X-ray investigations on several of the S_Q compounds in order to prove the existence of more than one S_Q-type and to enlighten the defect structure characteristic for these phases in detail.

EXPERIMENTAL

The studied S_Q compounds differ by the nature of the core and the nature of grafted chains. For the terephthalidene bis amino cinnamate (TAC) series two identical chiral chains are grafted on each end of a symmetrical core, while the second core, (BB) is non symmetrical and can be grafted by two different groups at each end, but with at least one chiral group (figure 1). The different studied compounds and their polymorphism are listed in table I. Some of these compounds have only the S_Q mesophase, in some cases the S_{CA} phase appears only on cooling. In two cases there are two different S_Q phases in the same compound; the existence of which depends on the thermal history of the sample.

In general, we were able to obtain single crystals of the S_Q phase, and when we could not obtain big crystals we have analyzed powder patterns recorded in a focusing Guinier camera (CuKα1). Single crystals are examined in a different set-up : they are illuminated by a parallel monochromatic X-ray beam (CuKα). Oscillations or rotations of the sample allow a good exploration of the reciprocal space; the diffraction patterns are registered on photographic films or on "Image plates" analyzed and numerized with a "Molecular Dynamics" set-up. The temperature of the sample is controlled within 0.25K.

TABLE I Polymorphism of the studied compounds; transition temperatures in °C; (): monotropic mesophase

Core	R/R_1	R_2	Abbreviation	Polymorphism
TAC	(S)M7		(SS)M7TAC	Cryst 95 S_{CA} 130.5 S_Q 133 I
TAC	(S)M9		(SS)M9TAC	Cryst 104 (S_{CA} 103) S_Q 128 I
TAC	(S)Li3		(SS)Li3TAC	Cryst 127 S_Q 157 I
TAC	(R)Li4		(RR)Li4TAC	Cryst 113 S_Q 163 I
TAC	(S)L4		(SS)L4TAC	Cryst 96 S_Q 137 I
BB	(S)M7	(S)M7	(SS)M7BBM7	Cryst 56 S_{CA} 60 (S_{Q2} ?) S_{Q1} 86 I
BB	(S)L4	44	(S)L4BB44	Glass - 8.6 S_Q 75.9 I
BB	(S)L4	55	(S)L4BB55	Glass -12.7 S_{Q2} 82.3 (S_{Q1} 73.5) I

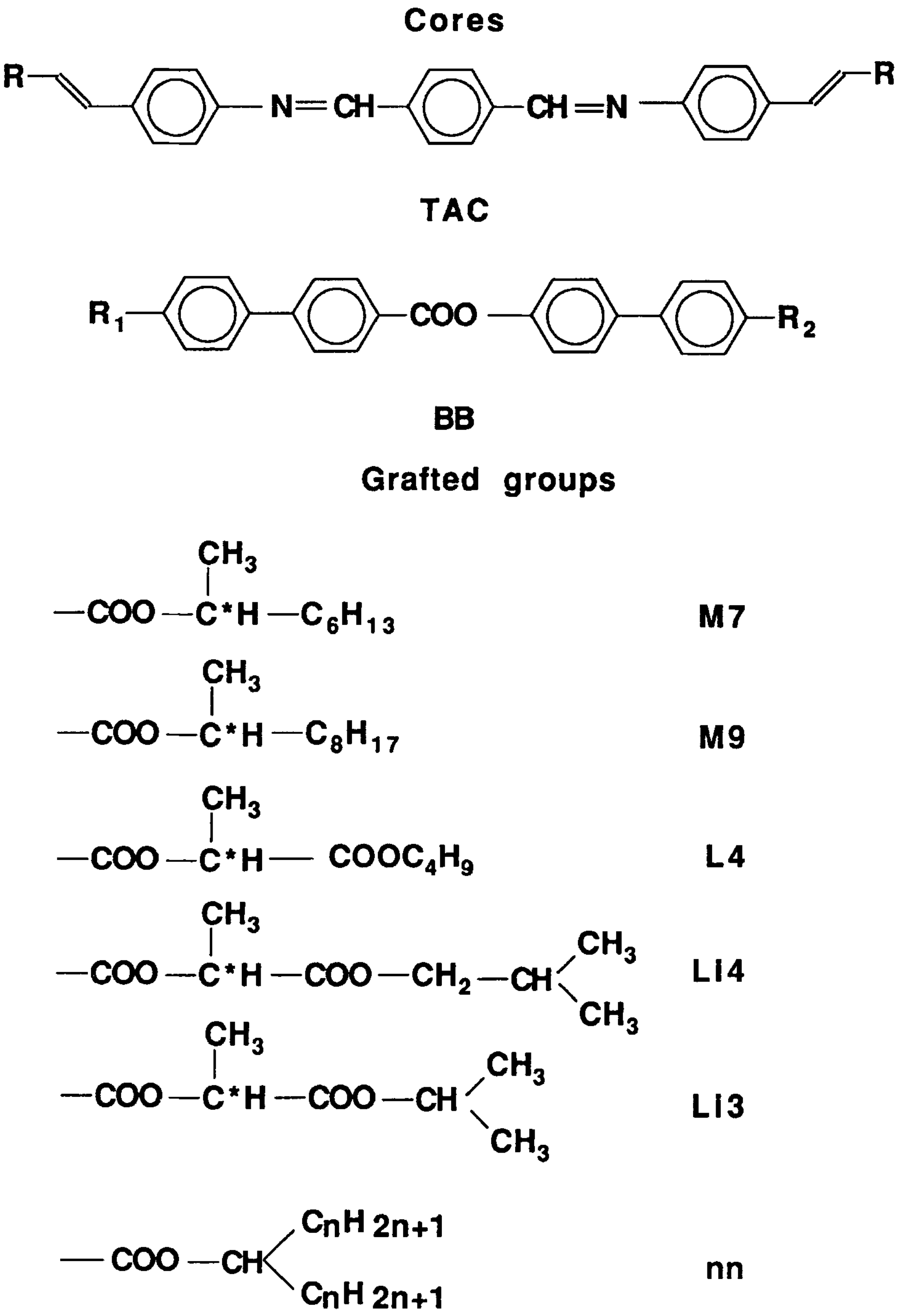

FIGURE 1 Chemical formulae of the studied compounds

RESULTS

In all cases besides the S_{Q2} phases of M7BBM7 and L4BB55 there is a tridimensional organization of body centred tetragonal symmetry superimposed on a liquid-like local order of the molecules. The square basis of the unit cell has edges (**a** = **b**) of about 65-75Å for all the compounds while the third lattice parameter (**c**) varies between 68Å and 140Å (see table II). In fact we can distinguish two kinds of body centred tetragonal lattices: with **c/a** > 1.5 one finds only 00l reflections with l = 4n (characteristic of a four-fold screw axis 4_1) while the 002 reflection is of high intensity if **c/a** < 1.5. The study of binary mixtures of M7TAC with M9TAC confirm that a phase transition takes place around a molar composition of 50 % between a T*I phase (space group I422, **c/a** < 1.5) and a T*II phase ($I4_122$, **c/a** > 1.5)[3].

In general we have not detected any temperature dependence of the lattice parameters but for M7BBM7, we actually observed two tetragonal phases. Indeed, when the isotropic phase is supercooled over more than 5 K, large volume single crystals are growing and then the unit cell is a primitive tetragonal one. Finally, the S_{Q2} phase of L4BB55 has an primitive hexagonal 3d lattice. The diffraction patterns of the S_{Q2} phases of M7BBM7 and L4BB55 show also extinction rules characteristic of a helical axis; the space groups are respectively $P4_122$ (T*III), and $P6_222$ (H*)[3].

TABLE II Crystallographic characteristics of the S_Q phases (**a** perpendicular to the unique axis and **c** parallel to it are in Å)

Space group / designation	Compound	a	c
I422 / T*I	M7TAC	75.45	68.4
	L4TAC	73.9	90.9
	M7BBM7 (S_{Q1})	73.1 - 80	84.2 - 86
	L4BB55 (S_{Q1})	72.5	86.3
$I4_122$ / T*II	M9TAC	75.6	130.7
	Li3TAC	68.95	119.45
	Li4TAC	71.8	120.9
	L4BB44	66.5	115.8
$P4_122$ / T*III	M7BBM7 (S_{Q2})	95.0	125.0
$P6_222$ / H*	L4BB55 (S_{Q2})	67.7	126.2

DISCUSSION

With a tridimensional organization of large size superimposed over a local liquid-like ordering of the molecules, the different S_Q phases belong to the class of "crystals of defects" where the building elements of the crystalline lattice are defect lines which are introduced in a stratified phase (cholesteric, smectic, lyotropic lamellar phase) in order to release the frustration induced by twisting or bending forces[4]. Taking into account the general phase sequence : S_{CA} - S_Q - Isotropic liquid, and the obvious chirality of the S_Q phases it seems natural to compare these phases to the Blue and the TGB phases[5]. We have to distinguish between : on the one hand, the optical definition of the pitch the S_{C*A} phase (c.a.100nm to 1μm), i.e. the period of a helical stack of bilayers each made of two sublalyers with a S_C organization, but with opposite directions of the azimuthal component of the director, and on the other hand, the molecular definition, wich considers the S_{C*A} as a S_{C*} the pitch of which compares to twice a molecular layer thickness. It is noteworthy that this second description is confirmed by the X-ray diffraction since there is no doubling of the smectic periodicity in a S_{C*A} compared to the S_{C*} phase of the same compound. Actually the lattice constants reported in table II compare to this second definition of the pitch of the S_{C*A} phase.

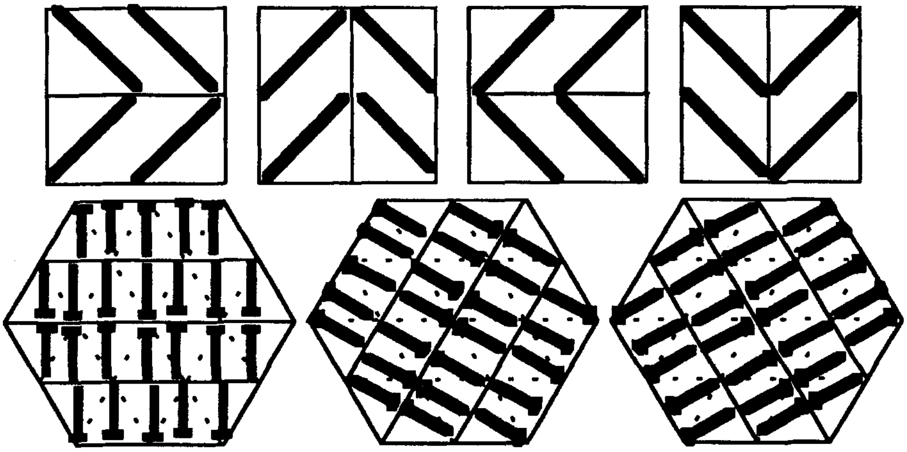

FIGURE 2 Molecular organization in sections perpendicular to the unique axis : top line, T*II lattice (from left to right : z = 0, z = 1/4, z = 1/2, z = 3/4) ; bottom line, H* lattice (from left to right : z = 0, z = 1/3, z = 2/3). Actually two different orientations of the molecules are allowed in each case, but we have shown only one of them for each symmetry : the molecules are in the plane of the section for the T*II lattice and out of this plane (using the usual nail representation) for the H* lattice

The presence of helical axes in three of these phases - T*II, T*III and H* - is a confirmation of the TGB structure. The T*II phase contains four grain boundaries per pitch, the twist angle between the smectic planes on each side of a wall is $\pi/2$, while the H* phase is made of three boundaries with twist angle of $\pi/3$. The underlying lamellar structure is that of the S_{CA} phase, and consequently, the square edge length correspond to the double layer thickness. Taking into account the lattice symmetry and the fact that the square basis edge is equal to three times the layer thickness, we can describe the T*III phase as a TGB phase in a (non helical) triple molecular layer based structure, with four boundaries and a twist angle of $\pi/2$. In all these three cases the distance between walls is of the order of the molecular length and as a consequence the walls have no longer a true existence. The interface between molecular layers is continuous and can be described by a triply periodic minimal surface. In the T*II and the H* phases the molecular orientation on each side of this surface can be defined by the direction of the electric mean dipoles and the surface is the boundary between two media of opposite polarities (figure 2). In the T*III phase the minimal surface is located in the middle of a molecular film, the organization is the same on each side of the film and corresponds to that of the S_{CA} phase. Finally, the presence of fourfold axes in the T*I phase is incompatible with a TGB geometry.

In conclusion, a new class of crystals of defects, in which the lamellar structure and the helical organization of the director coexist and compete one against the other, has been evidenced as a step in the transformation of the antiferroelectric smectic phase in an isotropic fluid. Structural studies performed on less than ten different mesogens allow us to characterize four different phases belonging to this class. Three of them can be considered as periodic arrays of twist grain boundaries, whereas the fourth is likely a crystal of double twist clusters of molecular size.

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3. Both the term smectic which suggest a layered structure and the letter Q, which is used by Luzatti group[4] for labelling the lyotropic cubic mesophases are not appropriate. The best is to refer to the lattice symmetry characterized by the space group. Therefore by analogy with the blue phases sequence we propose to design the different phases by a simple capital letter (i.e. tetragonal phases are labelled TI, TII,...). However contrarywise to the case of the blue phases which have an intrinsic twist character, one can find crystals of defects[4] where the chirality is absent or does not play an important role, while the phases here considered are chirally induced, therefore we will add a "*" as in N* or S_{C*} in order to underline that feature.
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