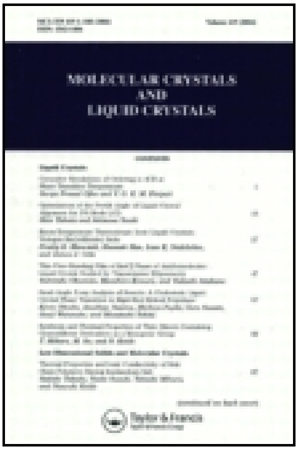

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Molecular Arrangement and Antiferroelectric Behaviour

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Molecular Arrangement and Antiferroelectric Behaviour

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The crystal structures of two chiral molecules giving a antiferroelectric mesophase have been solved. These structures and some other analogs (Hori et al) present the same characteristic features: they adopt a L-shape with their chiral alkyl chains perpendicular to their polyaromatic cores; they present smectic C-like sheets, in which contiguous molecules are antiparallel and associated through transversal dipoles (mode II type); the intersheet interactions between the chiral alkyl chains are quite strong. The crystal structure of another chiral compound giving a S_A mesophase was compared to the preceeding ones. The chiral alkyl chains are in the elongation of the core; contiguous molecules are parallel and associated according to a different mode we named mode III; the interactions between the sheets are quite weak.

Keywords: : liquid crystals; chiral molecules; antiferroelectric compounds; crystal structure; molecular interactions

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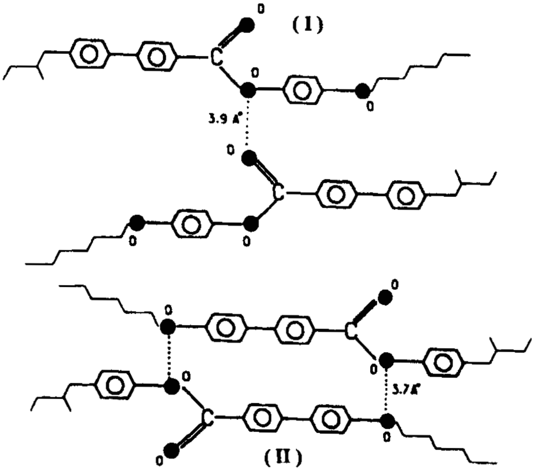
INTRODUCTION

Since the discovery of the ferroelectric smectic C* phase (SmC*) by Meyer et al[1] in 1975 and the discovery of the antiferroelectric smectic C* (SmC*$_A$) phase by Chandani et al[2] in 1989, the search to find new materials has greatly increased, not only for device applications but also for fundamental studies.

Up to now, a good correlation has generally been found between the molecular arrangement in the crystal structures and the mesomorphic behaviour of numerous non-chiral compounds and more recently of a few chiral compounds[3-6]. However it must be kept in mind that these latter do not always present a ferroelectric and/or an antiferroelectric mesophase[7,8].

But, in any case, the molecules are arranged in a parallel or antiparallel fashion according to the interactions between their polar groups (most often ether and ester) so that there is a maximum overlap between contiguous central cores. Hori and Ohashi[6] proposed two possible arrangements in relation with the core fragments inserted between the ether and ester groups (scheme).



Scheme of the association of contiguous molecules
in liquid crystals according to Hori et al.

RESULTS

Crystal Structures

We solved the crystal structures of several chiral mesogenic compounds; a few of them do not present any SmC* or SmC*$_A$ mesophase but a SmA or SmC phase and two others (the C7-Tolan and the C7-Ferro) show the SmC* (ferroelectric) and the SmC*$_A$ (antiferroelectric) mesophases. Their molecular conformations and arrangements are shown in Figs.1 and 2.

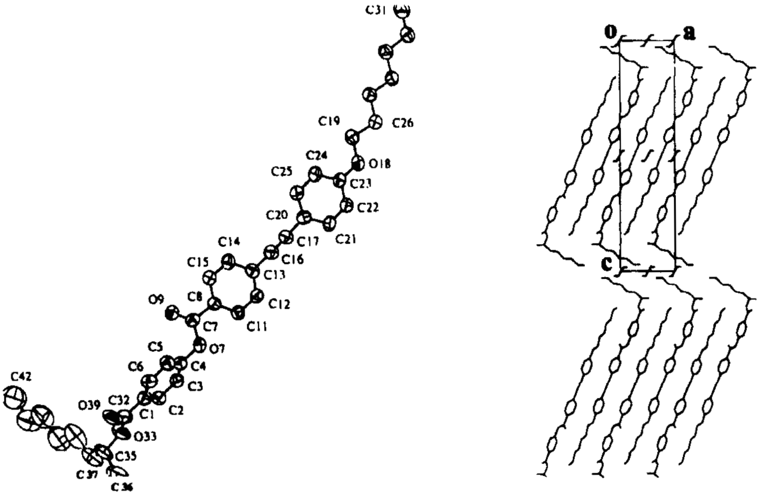


Figure 1 : Molecular conformation and arrangement for the C7-Tolan molecule.

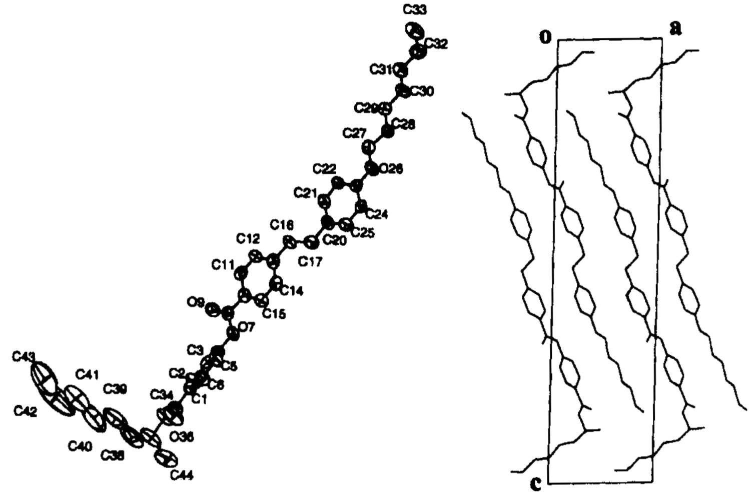


Figure 2 : Molecular conformation and arrangement for the C7-Ferro molecule.

Both structures show the same features :

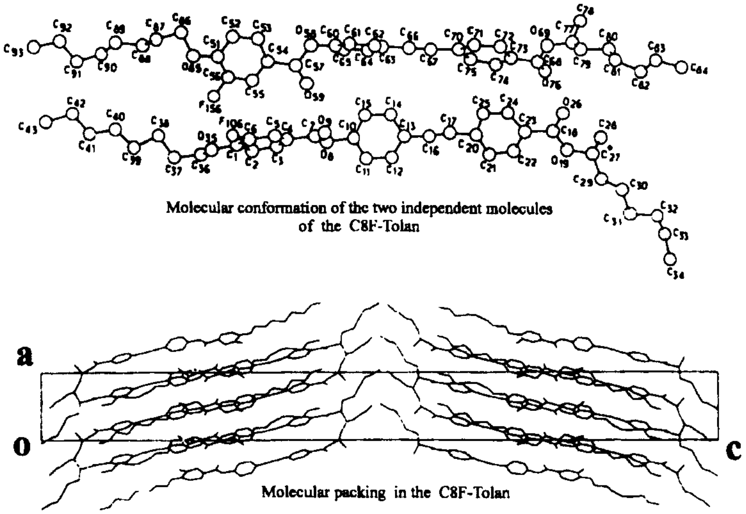
- The molecules present an **L** shape with their linear chiral alkyl chains perpendicular to their cores.

- Contiguous molecules within a sheet are antiparallel with a complete overlap of their cores; they are arranged according to the mode II.

- Contiguous sheets interact through their whole chiral alkyl chains.

Similar structures have recently been solved by Hori et al[3-6] but these authors neither emphasized the presence of L-shaped molecules nor the intersheet interactions between the chiral alkyl chains, which involve an intersheet binding energy much higher than in structures only showing the SmA or SmC mesophase; this is supported by our energy calculations.

In order to emphasize the role of the mode of arrangement on the molecular packing, we solved the crystal structure of a chiral compound only giving the SmA mesophase. There are two contiguous molecules in the asymmetric unit; they are roughly parallel to each other with a characteristic mode of arrangement; this latter is neither the mode I nor the mode II (Fig.3) and we could name it the mode III. Nevertheless it emphasizes the importance of both the position and the length of the core fragments inserted between the ether and ester groups.



Molecular conformation of the two independent molecules of the C8F-Tolan

Molecular packing in the C8F-Tolan

Figure 3 : Molecular conformation and molecular packing for the C8F-Tolan molecule.

The molecules give rise to sheets which are in contact only through their terminal methyl groups so that the intersheet energy is probably much lower than in the C7-Tolan structure. The schematic molecular arrangement taking into account the positions and the lengths of the core fragments for both the C7-Tolan and the C7-Ferro molecules is shown on Fig.4. It appears that in the first two structures the chiral chains should be perpendicular to the cores in order to give sheets.

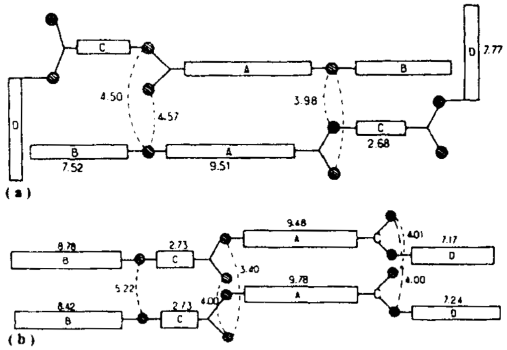


Figure 4 : Schematic representation of C7-Tolan (**a**) and C8F-Tolan (**b**) molecules in the crystal structures.

This has been observed in all the structures of chiral compounds presenting an antiferroelectric mesophase SmC^{*}_{A}. On the contrary, in the second structure, the chiral alkyl chain extends the core.

Binding Energies

The binding energies were calculated using molecular mechanics. Within a sheet the binding energy for one molecule of C7-Tolan to its six neighbours is -142kcal i.e. an average between two contiguous molecules of -26.65 kcal/mole. The binding energy of the "dimer" in C8F-Tolan to its six neighbours is -238 kcal, i.e -39.7 kcal per "dimer". For both structures the contribution of the electrostatic energy is less than 25%. The intersheet energy was evaluated using three sheets with a reasonable number of molecules. The energies of three sheets, then of the medium sheet and finally both the upper and lower sheets, give the intersheet energy, close to -34.8 and -7.1 kcal respectivally for the C7-Tolan and the C8F-Tolan with a very large predominance of van der Waals energy. These values are in agreement with the molecular arrangement in the crystal.

CONCLUSION

As it was already assumed the presence of a chiral alkyl chain is not a sufficient condition to give a ferro or/and an antiferroelectric phase. The crystallographic studies of antiferroelectric mesogens show that :

- the molecules adopt an L-shape with their chiral alkyl chains perpendicular to their polyaromatic core.
- contiguous molecules are antiparallel and are associated according to mode II.
- the interactions between sheets involve the whole chiral alkyl chains with a relatively high binding energy.

More generally in chiral mesogenic structures, contiguous molecules are associated through transverse dipolar interactions, according to a mode which greatly depends on the disposition and on the length of the core fragments inserted between the dipolar groups. To obtain a maximum overlap of the cores it may involve the bending of the chiral alkyl chain, thus giving numerous intersheet interactions and then the formation of an antiferroelectric phase.

This is, of course an hypothesis which, nevertheless matches quite well with the crystal structures and energy calculations.

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