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REENTRANT PHENOMENON IN DISC-LIKE LIQUID CRYSTAL

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Abstract

Several Hexa-*n*-alkanoates of truxene with long alkyl chains exhibit, above and below a N_D nematic phase, an hexagonal columnar phase. It is probably the first example of a reentrant phenomenon for pure disc-like liquid crystals at atmospheric pressure.

Introduction

The existence of the reentrant phenomenon in disc-like liquid crystals has been suggested in the end of 1979¹. This idea originates with the great analogies between rod-like and disc-like liquid crystals: the columnar mesophases are, to a certain extent, the equivalent of smectic ones^{1,2,3} even in optical textures and two dimensional lattice (hexagonal, rectangular, tilted, ordered or disordered arrangement have been found). We have identified the fluid phase present in several hexabenzates of triphenylene^{3,4} and latter in truxene derivatives^{5,6} as a nematic phase build up with disc-like molecules (N_D nematic phase) for which a structure has been proposed³. A good confirmation of the real nematic nature of this phase has been recently given by some X-Ray measurements⁷ and furthermore that the apparition of a chirality in this medium leads to typical cholesteric textures⁸.

The discovery of such a N_D nematic phase, at lower temperature than a viscous columnar one, suggests us at first that it could be a reentrant N_D nematic phase⁵. In fact, we are sure now that it is not a real one. One cannot find, for example, the nematic phase again at higher

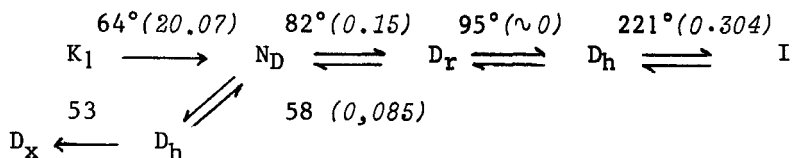
temperature and we call this phenomenon⁵ an inverted nematic-columnar sequence⁶. But the study of highly purified hexa-*n*-alkanoyloxy truxene with very long alkyl chains provide us the required phenomenon : an hexagonal reentrant columnar phase.

Results and discussion

We describe here the hexa-*n*-pentadecanoate of truxene (C₁₄HATX) where the phenomenon is the most evident. The general chemical preparation of these substances has been described elsewhere⁵ and we will give only the thermodynamic and optical data on this derivative.

The purity of the sample was checked by elemental analysis and thin layer chromatography. Transition temperatures were determined using a DSC (Dupont 990) and the textures were observed with a polarizing microscope equipped with a heating and cooling stage (Mettler FP 5).

With the C₁₄HATX derivative the following sequence has been founded :

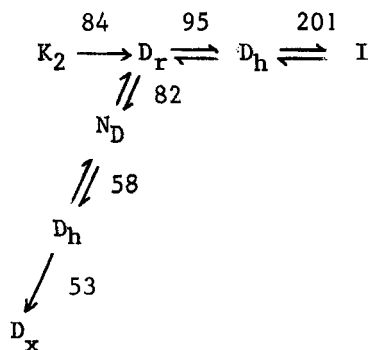


The enthalpies (italic>) are given in Kcal/mole.

The corresponding optical textures are given in figure 1a to 1e. The structure of the highest temperature mesophases has been checked by the well-known contact method with some reference disc-like substances. On the contrary the lowest temperature mesophases which are very metastable cannot be studied by the contact method or by some X-Ray investigations. The striking feature founded in this observation is the perfect superposition of the optical textures of the D_h phase at low temperature (Fig. 1e at 57°C) and high temperature (Fig. 1a at 95°C) even on cooling or heating. We have found the same behaviour⁹ in the classic reentrant tetramorphism NS_A N S_A¹⁰ ; as with these substance we have found here a preorganization of the N_D nematic phase texture near the N_D → D_h transition (Fig. 1d).

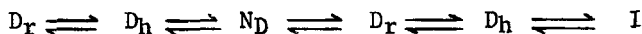
If there is no problem for the identification of the D_h and D_r phases⁶ we have not ascertain for the nature of the lowest temperature columnar phase. Anyway these phases are totally miscible with all other truxene derivatives with shorter alkyl chain length.

We have detected other crystalline phases, and at a very slow heating and cooling (1°C/min) found the following sequence :



As a matter of fact the two N_D and D_h low temperature phases are monotropic for the C_{14} HATX derivative.

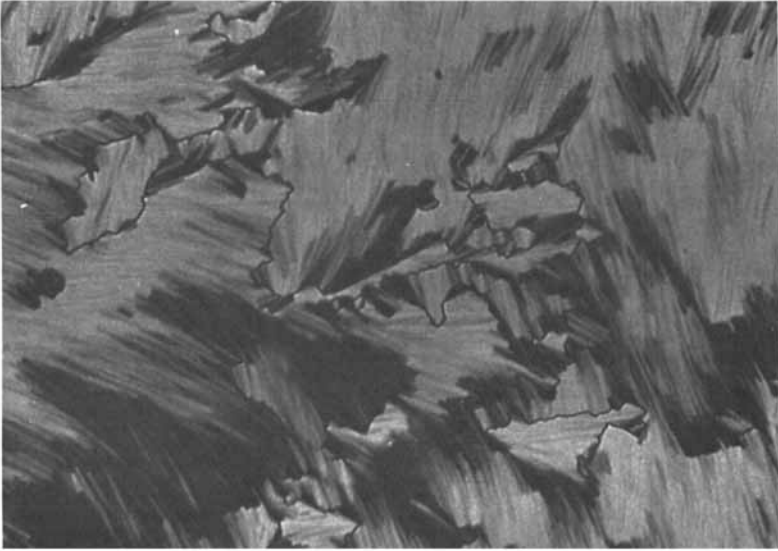
Another phase has been detected near 53°C but its appearance is immediately followed by the crystallization so that we can only say that it is looking like a D_r phase ; if it is true the following reentrant phenomenon should be with respect to temperature :



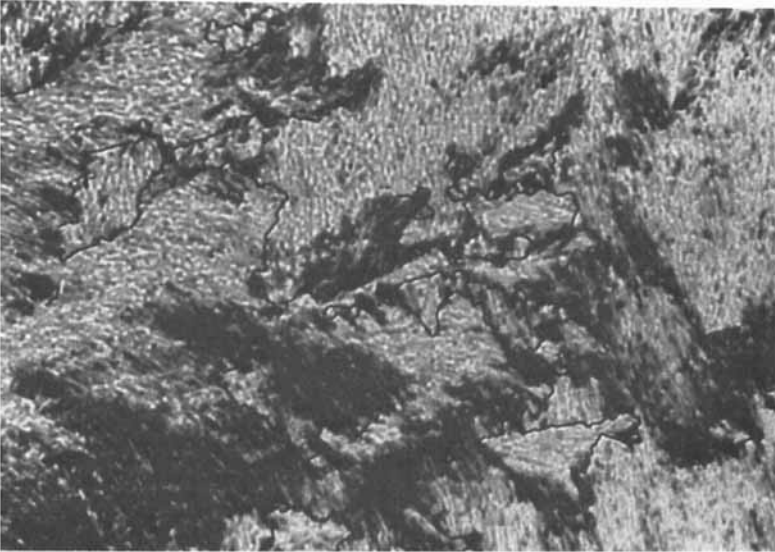
Anyway this new kind of polymorphism set many fundamental problems, one of which is the molecular interpretation of it.

As to the "classic" N, S_A reentrant phases¹¹ the relation between the molecular structure and the influence of the different chemical functions have been largely discussed and the problem is now more clear^{9,12} especially on a dipole moment interactions point of view. In the case of truxene derivatives no permanent dipole moment can be found and another type of explanation has to be found. For example, we can suggest a possibility : a competition between monomolecular and bimolecular arrangement* of molecules in columns as represented in the following figure.

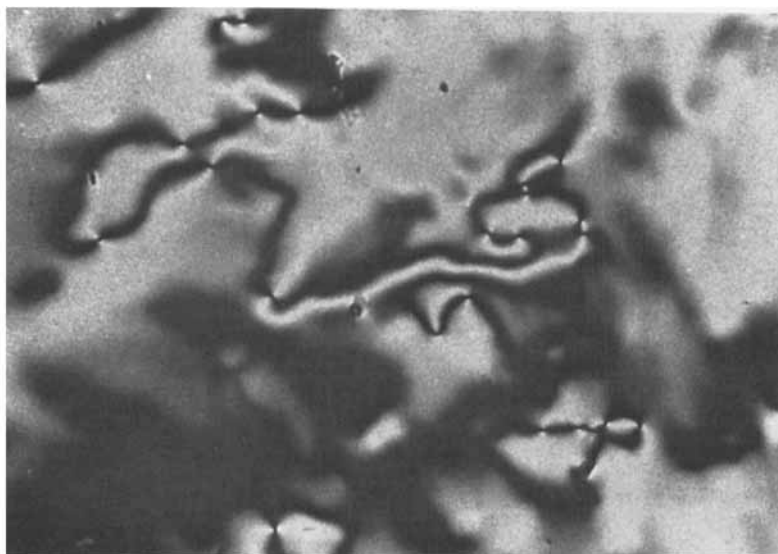
* We must point that the molecular organization proposed in Fig. 2a has been demonstrated in the solid phase of some triphenylene derivatives¹³.



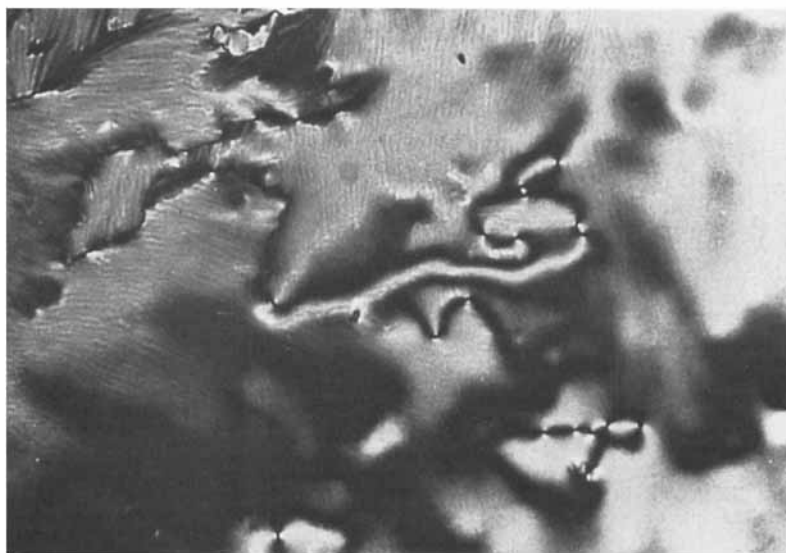
1a



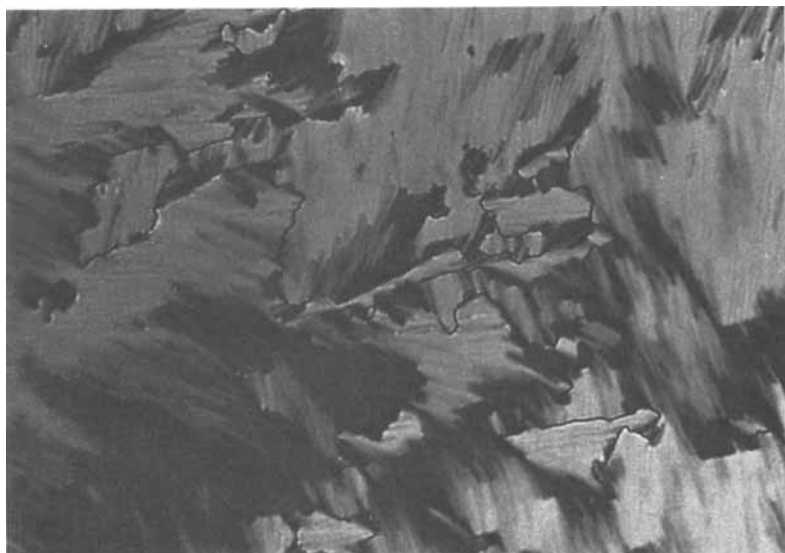
1b



1c



1d



& 1e

Figure 1 : Optical textures observed for the hexapentadecanoate of truxene

- a) D_h columnar phase at 95°C
- b) D_r columnar phase at 84°C
- c) N_D nematic phase at 74°C
- d) N_d nematic phase at 58°C with pretransitional D_h organisation
- e) D_h columnar phase at 57°C

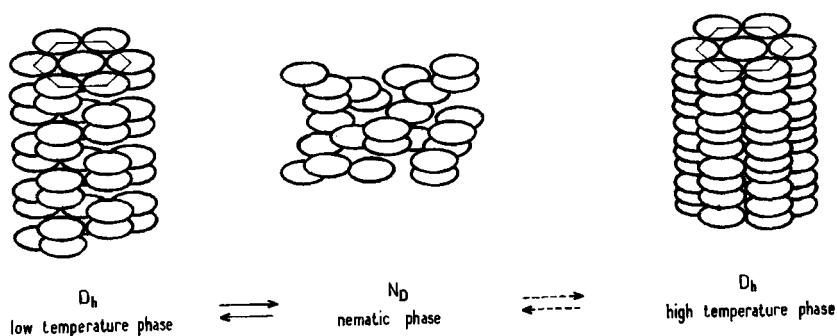


Figure 2 : Molecular arrangement we proposed for the reentrant D_h columnar phase and the intermediate N_D nematic phase.

Conclusion

The first demonstration of the existence of the reentrant phenomenon in disc-like liquid crystals open of course a new field of reflection and research in the field of mesomorphic state of matter. Beyond the fact, now evident, of the great analogies between disc-like and rod-like liquid crystals it suggest that we can foresee a great diversity of new sequences and phases build up with disc-like molecules. Up to now less than 70 substances of this type has been synthesised and the variety of phases and sequences founded is largely bigger than the first results obtained with rod-like liquid crystals.

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