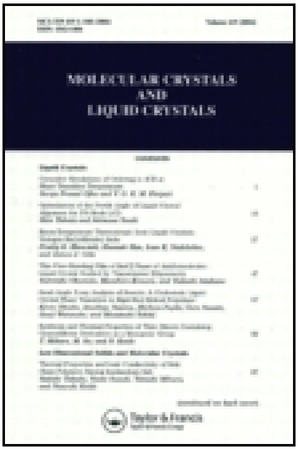

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Truxene Derivatives

C. Destrade [a] , H. Gasparoux [a] , A. Babeau [a] , Nguyen Huu Tinh [a] & J. Malthete [b]

[a] Centre de Recherche Paul Pascal, Domaine Universitaire, 33405, latence, France

[b] Laboratoire de Chimie Organique des Hormones, Collège de France, 75231, Paris, Cédex, France

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Truxene Derivatives: A New Family of Disc-Like Liquid Crystals With an Inverted Nematic-Columnar Sequence

C. DESTRADE, H. GASPAROUX, A. BABEAU and NGUYEN HUU TINH
Centre de Recherche Paul Pascal, Domaine Universitaire 33405, Talence, France

and

J. MALTHETE
**Laboratoire de Chimie Organique des Hormones, Collège de France 75231 Paris, Cédex, France*

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Eight hexa-*n*-alkanoyloxy truxenes are presented. These new disc-like liquid crystals exhibit both columnar and N_D nematic phases. The N_D nematic phase is the first low temperature one. All these compounds show an inverted nematic-columnar sequence: the fluid N_D nematic phase is observed while heating after the crystalline phase below one or two viscous columnar phases and shows a phenomenon quite similar to the reentrant nematic behaviour.

INTRODUCTION

Since the discovery of the existence of thermotropic mesomorphism in some disc-like compounds in 1977, 1978[1,2] several fundamental results have been discovered in this new field of research. The first discovered mesomorphic phases were D columnar ones (phases formed of columns of stacked disc-like molecules).[1,3] Then evidence of a complex polymorphism has been shown.[4–8] The existence of a N_D fluid nematic phase has been demonstrated,[9,10] and the corresponding cholesteric N_D^* phase founded very recently.[10,11] We can

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conclude that disc-like liquid crystals provide a really new condensed state of matter. The analogy with rod-like liquid crystals is very great; in fact the "only" but fundamental difference is that in one case (rod-like L.C.) the director vector is parallel to the molecules while it is perpendicular to them in the case of flat disc-like ones[12] (Figure 1). Another striking similitude has been described in a recent paper:[8] the existence of a fluid N_D nematic phase below a higher viscous columnar one! In fact a kind of reentrant N_D nematic phase.

This behaviour has been discovered in some short alkyl chain hexa-alkanoate of truxene,[8] we present here the complete series and some more informations about the mesomorphic polymorphism and some properties of this inverse (or reentrant ?) N_D nematic phase.

POLYMORPHISM IN DISC-LIKE MESOGENS SERIES

First let us recall something about the different kinds of mesomorphic phases founded with disc-like compounds. In fact two different kinds of mesomorphic phases have been described:[6] D columnar mesophase, N_D nematic phase (and of course the twisted N_D^* nematic phase Figure 1a). Four different D columnar mesophases have been clearly identified by means of optical texture observations, heat measurements and X-ray diffraction. With respect to a regular (o) or irregular (d) (Figure 1) stacking of discs and considering the symmetry of the two dimensional lattice of columns: hexagonal (h) or rectangular (r) (Figure 1) they are called D_{ho}, D_{hd}, D_{rd} or D_t[6,12] (this last one is a tilted phase where the discs appear to be tilted versus the column axis).[6,10] All these D columnar phases are highly viscous and birefringent with optical textures sometime very similar to smectics ones with striated or non striated focal conics, finger prints, broken fan or mosaic textures.[6]

On the contrary the N_D nematic phase is very fluid and presents very typical schlieren textures with classic s $\pm \frac{1}{2}$ and $\pm$ 1 desclination lines and strong thermal fluctuations.[8,9] The structure of this phase is given in Figure 1b by comparison with the nematic phase of rod-like liquid crystals. We think that this phase corresponds to an original molecular organization very similar to the one proposed for the carbonaceous mesophase which occurs at high temperature during the carbonization of graphitizable substances.[13] In fact in both cases the optical sign and the diamagnetic anisotropy are negative.[10,14]

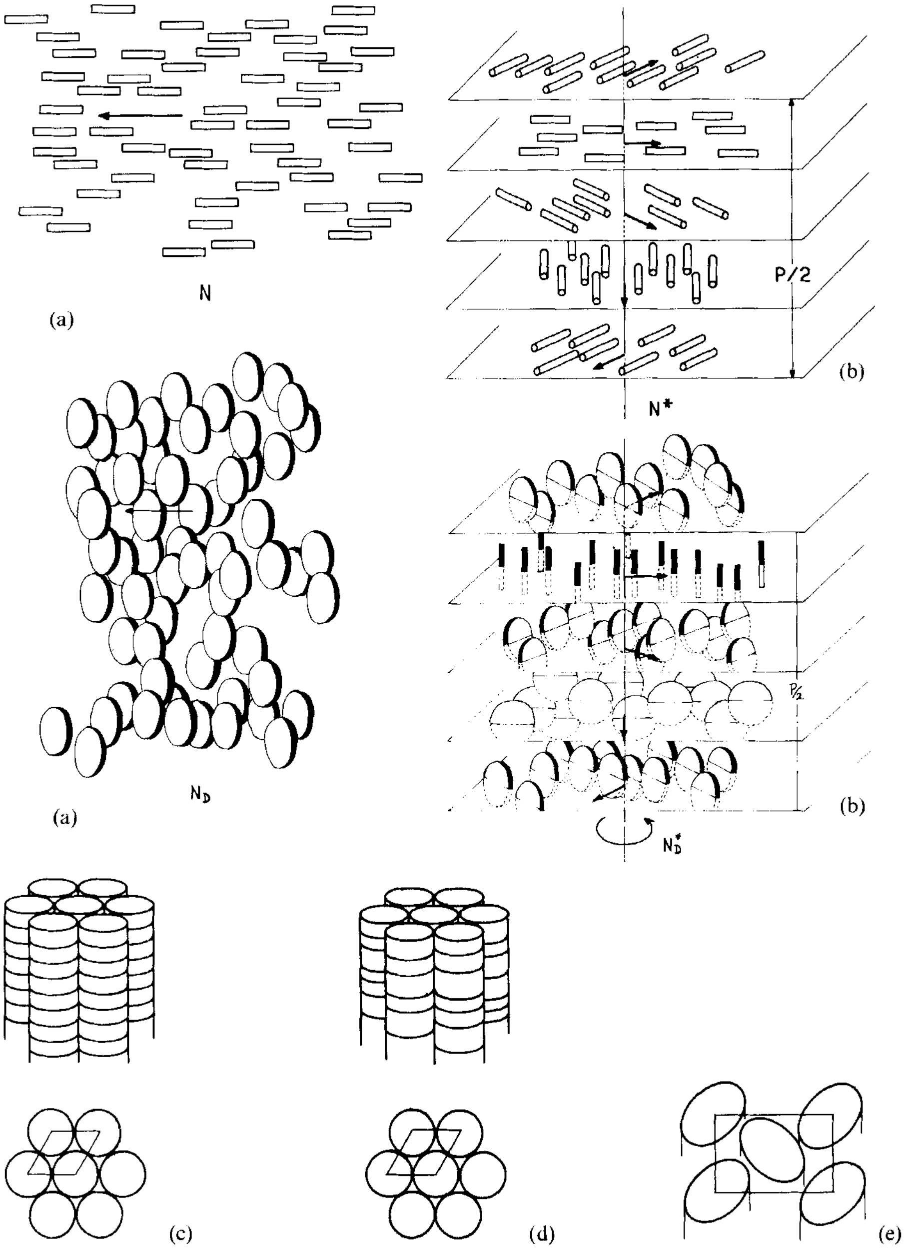


FIGURE 1 1a = Structure of the N and N_D nematic phase; 1b = Structure of the N and N_D cholesteric phase; 1c = Structure of the D_o^h columnar phase; 1d = Structure of the D_{hd} columnar phase; 1e = Two dimensional lattice of the D_r columnar phase.

We have described different "normal" sequences of transition in our triphenylenes series:

$$K - D_{(?)} - D_{\mathrm{rd}} - D_{\mathrm{hd}} - I \quad (5)$$
$$K - N_{\mathrm{D}} - I \quad (7)$$
$$K - D_{\mathrm{t}} - N_{\mathrm{D}} - I \quad (7)$$
$$K - D_{\mathrm{rd}} - N_{\mathrm{D}} - I \quad (7)$$
$$K - D_{\mathrm{rd}} - I \quad (7)$$

K = crystal, D_{rd}, D_{hd}, D_{t} = columnar phases, N_{D} = nematic phase in disc-like mesogens.

Then the inverse columnar–N_{D} nematic phase sequence has been founded in some truxene derivatives:[8]

$$K - N_{\mathrm{D}} - D_{\mathrm{r}} - D_{\mathrm{h}} - I$$

other examples are now presented and also a new sequence:

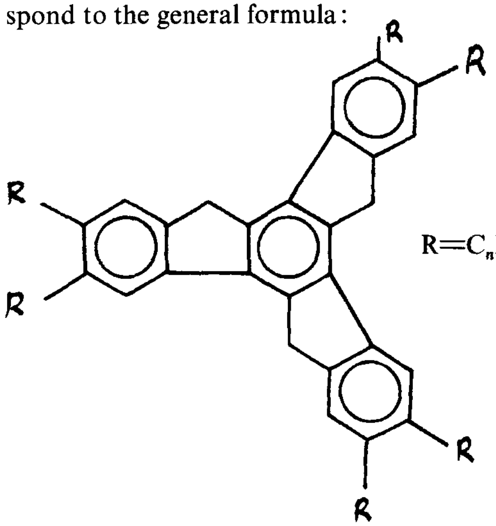
$$K - N_{\mathrm{D}} - D_{\mathrm{h}} - I$$

TRUXENE DERIVATIVES AN HOMOLOGOUS SERIES

The chemical preparation and purification have been reported elsewhere.[8] The purity of the samples has been checked by thin layer chromatography and elemental analysis, for instance:

calculated ($C_{81}H_{114}O_{12}$)	C% 76;	H% 8.92;	O% 15.08
found	C% 75.98;	H% 8.95;	O% 14.86

Eight hexa-*n*-alkanoates of truxene have been prepared and they correspond to the general formula:



R=C_nH_{2n+1}COO— where $13 \geqslant n \geqslant 6$

The transition temperatures are given in Table I and the evolution of the transition temperatures with the alkyl chain length in Figure 2.

The N_D nematic phase is observed in all derivatives but it is very metastable in the two first ones. Optical textures are in any point similar to the ones observed with hexa alkyl or alkoxy benzoates of triphenylene (Figure 3a, b, c) and its fluidity is of the same order of magnitude. Over a drop with free surface schlieren textures with $s \pm \frac{1}{2}$ and $\pm$ 1 desclination lines are observed (Figure 3c). The miscibility of this phase has been checked with the N_D nematic phase of an hexabenzoate of triphenylene; a mixture 50/50 of hexaheptyloxy benzoate of triphenylene ($K \xrightarrow{168} N_D \rightleftharpoons^{253} I$) and of hexadecanoate of truxene exhibits the transitions: $K \xrightarrow{138} N_D \rightleftharpoons^{170} I$.

In most derivatives two viscous and birefringent columnar phases are observed (except for the $C_{13}H_{27}$ COO derivative for which a direct $N_D \rightarrow D_h$ transition is observed). The lower temperature one is probably a D_r rectangular one, in fact optical textures (Figure 4) are very similar to the ones observed with HAB[7] or HAT[4] compounds. The higher temperature one is undoubtedly a D_{ho} columnar phase; as in hexaalkoxy triphenylenes, on cooling from the

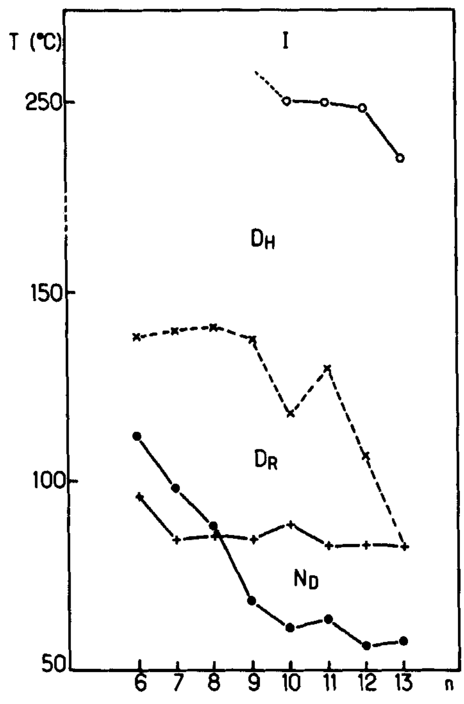


FIGURE 2 Plot of transition temperature against n (number of carbon atom in the alkanoyloxy chain of C_nCOOTRX..

TABLE I

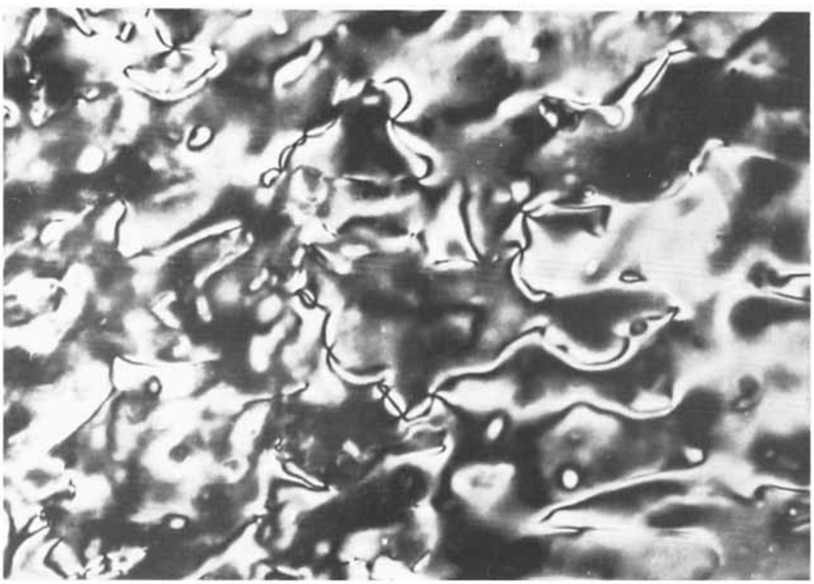
Transition temperature of the different prepared truxene derivatives

R	K	N_D	D_r	D_h	I
C_6H_{13}	112	[96]	138	280	—
C_7H_{15}	98	[85]	140	280	—
C_8H_{17}	88	[87]	141	280	—
C_9H_{19}	68	85	138	280	—
$C_{10}H_{21}$	62	89	118	250	—
$C_{11}H_{23}$	64	83.5	130	250	—
$C_{12}H_{25}$	57	84	107	249	—
$C_{13}H_{27}$	58	83	—	235	—

Transition temperature in Celcius of the different prepared compounds. K = crystal, N_D = nematic "disc-like" phase, D_r and D_h = columnar phases (r = rectangular, h = hexagonal lattice), I = isotropic, [ ] indicate monotropic transition.

isotropic phase, the mesophase appears in domains with digitized contours; on slow cooling areas totally black between crossed polars and rare linear birefringent defects are observed (Figure 5a and 5b).

An interesting modification of the optical texture is observed on cooling with the $C_{11}H_{23}COO$ derivative: needles appear with an angle of 60° (Figure 6a, b) between them, it is possible that this modification corresponds to a change in the column lattice.



(a)

(b)

(c)

FIGURE 3 Schlieren texture of the N_D nematic phase; (a) $C_7COOTRX$ at 90°C, (b) $C_8COOTRX$ at 60°C when the crystalline phase appears, (c) $C_9COOTRX$ at 80°C on a droplet.

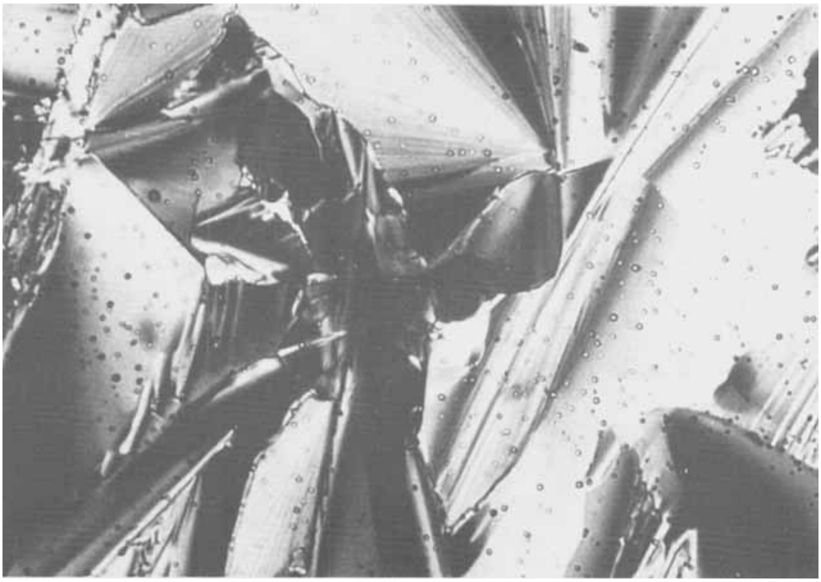


FIGURE 4 Focal conic fan texture of the D_r columnar phase: $C_8COOTRX$ at 100°C

Now about the N_D nematic phase observed in these truxene derivatives is it a reentrant N_D nematic phase?

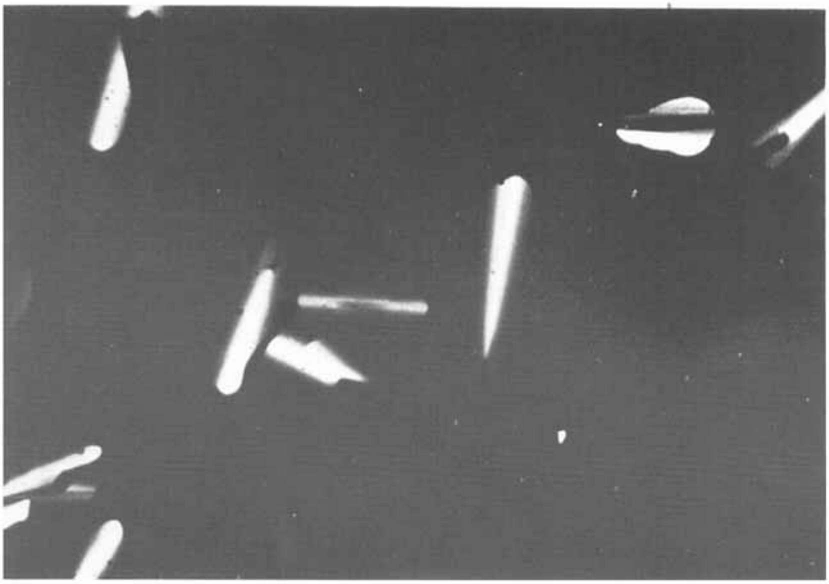
In fact several properties are quite different from the "classic" reentrant one:

— The N_D nematic phase is observed only at low temperature, at high temperature one can only observe a columnar—isotropic-transition.

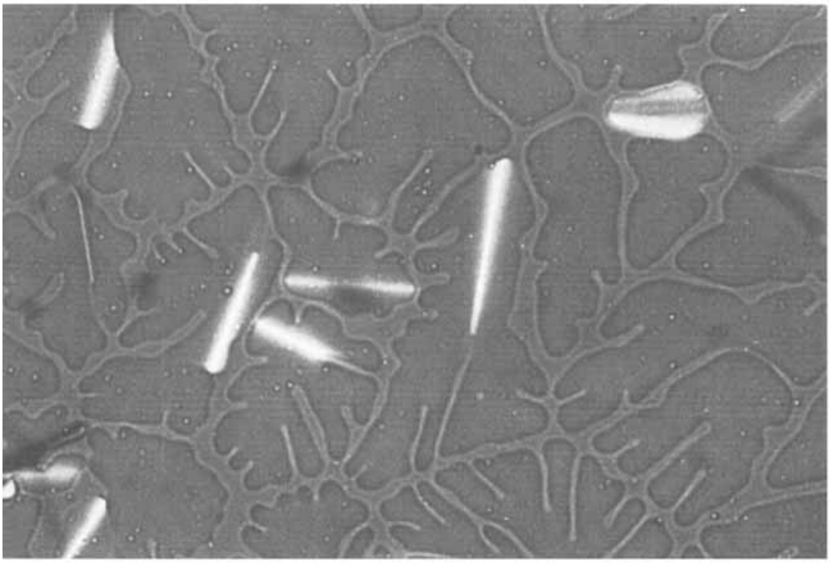
— We have observed a drastic change in the macroscopic viscosity at the N_D–columnar phase transition and the corresponding heat is about 180 cal. mole^{-1}, on opposition with the results obtained in the case of a $K - S_A - N - S_A - N - I$ polymorphism.

So we think that this new phenomena is different from the reentrant one and we propose to call it: "inverse N_D nematic phase" (or inverse sequence). In fact the N_D–columnar transition is always observed (Table I) around 85°C and can correspond to a conformational modification of the truxene core.

Anyway the existence of a fluid N_D nematic phase at lower temperature than a highly viscous D columnar phase provide an exciting observation leading with some new field of research in liquid crystals.

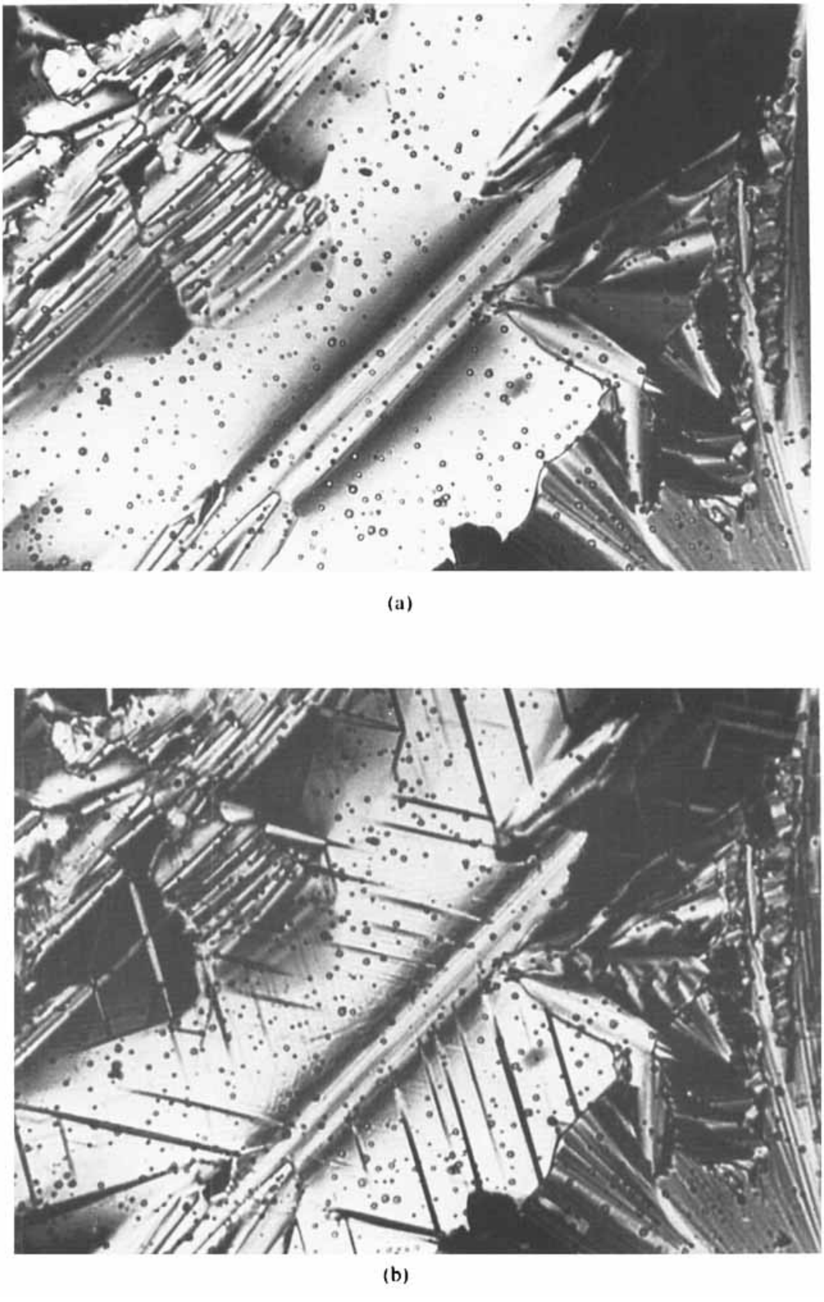


(a)



(b)

FIGURE 5 Homeotropic D_{ho} columnar phase texture: C_{11}COOTRX at 240°C; (a) between crossed polars, (b) between non crossed polars.



(a)

(b)

FIGURE 6 Optical textures observed on cooling with the C_{10}COOTRX derivative; (a) at 120°C, (b) at 101°C.

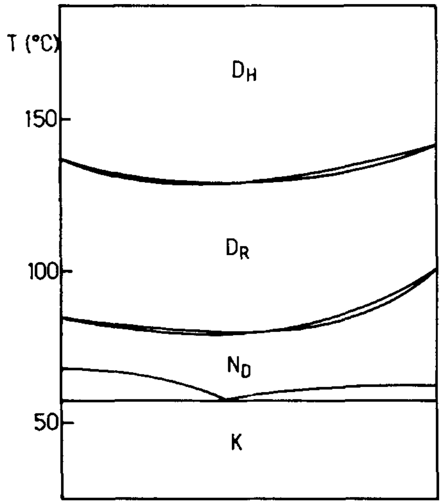


FIGURE 7 Diagram of isobaric state for the mixture of $C_9COOTRX$ (on left) and $C_{10}COOTRX$ (on right).

References

1. S. Chandrasekhar, B. K. Sadashiva, and K. A. Suresh, *Pramana*, **9**, 471 (1977).
2. Nguyen Huu Tinh, J. C. Dubois, J. Malthete, and C. Destrade, *C.R. Acad. Sci. Paris*, **C286**, 463 (1978).
3. A. M. Levelut, *J. Phys. Lett.*, **40**, L81 (1979) and *Proc. Int. Liq. Conf.*, Bangalore 1979 (Heyden and Son, London).
4. C. Destrade, M. C. Mondon, and J. Malthete, *VIIth Int. Liq. Cryst. Conf.*, Bordeaux 1978 and *J. Phys.*, **40**, C3, 17 (1979).
5. C. Destrade, M. C. Mondon-Bernaud, and Nguyen Huu Tinh, *Mol. Cryst. Liq. Cryst. Lett.*, **49**, 169 (1979).
6. C. Destrade, M. C. Mondon, H. Gasparoux, A. M. Levelut, and Nguyen Huu Tinh, *Proc. Int. Liq. Cryst. Conf.*, Bangalore 1979 (Heyden and Son, London).
7. Nguyen Huu Tinh, H. Gasparoux, and C. Destrade, *Proc. 8th Int. Liq. Cryst. Conf.*, Kyoto 1980.
8. C. Destrade, J. Malthete, Nguyen Huu Tinh, and H. Gasparoux, *Phys. Lett. A* under press.
9. Nguyen Huu Tinh, C. Destrade, and H. Gasparoux, *Phys. Lett. A*, **72A**, 251 (1979).
10. A. M. Levelut, F. Hardouin, H. Gasparoux, C. Destrade, and Nguyen Huu Tinh, *J. Phys.* under press.
11. C. Destrade, Nguyen Huu Tinh, J. Malthete, and J. Jaques, *Phys. Lett. A*, under press.
12. C. Destrade, Nguyen Huu Tinh, H. Gasparoux, J. Malthete, and A. M. Levelut, *3rd Liq. Cryst. Conf.*, Budapest 1979 and to be published.
13. H. Gasparoux, G. Fug, and C. Destrade, *Mol. Cryst. Liq. Cryst.*, **59**, 109 (1980).
14. P. Delhaes, J. C. Rouillon, G. Fug, and L. S. Singer, Carbon.