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Reentrant Mesophases in Disc-Like Liquid Crystals†

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The first case of reentrant phenomenon in disc-like mesogens was observed in hexaalkanoyloxytruxenes (Cn HATX). In this series of ten compounds (n = 6 to 15) a few of them, the long chain ones, displayed a reentrant columnar phase. On the other hand, a reentrant N_D nematic series was prepared: truxene p-alkoxybenzoates (Cn HBTX) with n = 6 to 14. Phase transitions between solid, mesomorphic and isotropic phases were studied by hot-stage microscopy and differential scanning calorimetry. Binary phase diagram studies, optical textural observations and X-ray measurements showed a rich polymorphism in these two series: a nematic disc-like phase (N_D), a hexagonal ordered columnar phase (D_{ho}), a hexagonal disordered columnar phase (D_{hd}), a rectangular disordered columnar phase [$D_{rd(P_{21}/a)}$] and a strongly tilted rectangular columnar phase [$D_{rd(C_2/m)}$].

The following mesophase sequences in these two series were found:

K [N_D]	$D_{rd(P_{21}/a)}$		D_{ho}	I
K [D_h]	N_D	$D_{rd(P_{21}/a)}$	D_{ho}	I
K N_D	I			
K D_{rd}	N_D	I		
K $D_{rd(P_{21}/a)}$	N_D	$D_{rd(C_2/m)}$	N_D	I
K $D_{rd(P_{21}/a)}$	N_D	$D_{rd(C_2/m)}$	D_h	I

†Presented at the Ninth International Liquid Crystal Conference, Bangalore, India, December 6–10, 1982.

INTRODUCTION

Since the discovery of a lenticular nematic N_D with disc-like molecules[1,2] in the hexa 4-n-alkoxybenzoates of triphenylene (Cn HBT) and the inverted sequence[3,4] in the hexa-alkanoyloxytruxenes (Cn HATX) **3a** we suggested at end of 1979[5] the possibility of reentrant phenomena in disc-like liquid crystals. This hypothesis originated from the symmetry analogies between the arrangements of rod-like and disc-like liquid crystals: the columnar D and lenticular nematic N_D mesophases are analogous to the smectic S and nematic N phases.

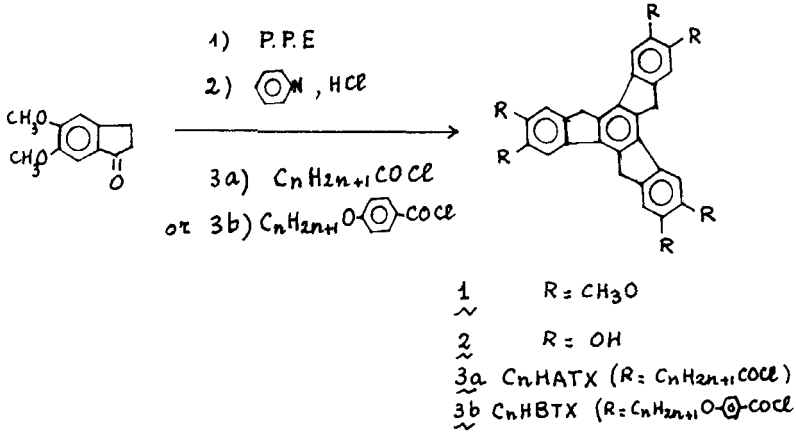
In the Cn HBT series, a *normal* sequence: K, D_{rd}, N_D, I, (N_D at the *higher* temperature) is obtained but in the Cn HATX series an inverted sequence was observed for short chains: K, N_D, D_{rd}, D_{ho}, I(N_D at *low* temperature). Long chain Cn HATX (**3a**) derivatives and hexa *p*-alkoxybenzoates of truxene (Cn HBTX) **3b** were prepared in the hope of obtaining reentrant columnar and nematic N_D phases.

Here we present two homologous series of disc-like mesogens where a reentrant columnar phase is found with long chain on Cn HATX and a reentrant lenticular nematic phase is found in the Cn HBTX series.

RESULTS AND DISCUSSION

1. Synthesis

Compounds on both series were prepared according to the scheme I:



1 R = CH_3O

2 R = OH

3a CnHATX (R = $C_nH_{2n+1}COCl$)

3b CnHBTX (R = $C_nH_{2n+1}O$-C6H4-COCl)

5,6-Dimethoxy-1-indanone (Aldrich) in ethyl polyphosphate (PPE) leads to hexamethoxytruxene **1**. After demethylation with pyridine hydrochloride, **2** was esterified with *n*-acylchloride (HATX, **3a**) or *p*-alkoxybenzoyl chloride (HBTX, **3b**)[6].

Purification of **3a** and **3b** was achieved by repeated chromatography over silica gel using a hexane-ether mixture (80 : 20) for **3a** series and benzene-ether mixture (95 : 5) for **3b** series as the eluent followed by recrystallization from an ethanol-benzene mixture. Purities of samples were checked by thin-layer chromatography and elemental analysis.

2. Optical and thermodynamic studies

The mesophases of these compounds were observed by means of a polarizing microscope equipped with a heating and cooling stage (Mettler FP5). Transition temperatures and enthalpies were determined by means of a differential scanning calorimeter (Dupont 990).

The results are listed in Tables I and II:

**Series 3a (Table I).* When R = $C_nH_{2n+1}COO$— (Figure 1) the short chain derivatives (n = 6 to 11) exhibit the inverted sequence:

$$KN_D D_{rd(P21/a)} D_{ho} I$$

Transition temperatures $D_{ho} - I$ are very high (> 280 °C) and at this temperature the compounds begin to decompose. On slow cooling from the *isotropic* phase, the D_{ho} phase grows from little homeotropic hexagons changing into digitated stars which merge into *developable* domains. This phase is uniaxial (Figure 2). Below this D_{ho} phase, a biaxial D_{rd} columnar phase was observed. On further cooling we can observe a fluid N_D nematic phase with a thread like or marbled texture and with disclination lines ($S = \pm \frac{1}{2}$ and ± 1).

At longer chain lengths (n = 12 to n = 15) another columnar phase was observed below the N_D nematic phase. The following sequence was found[7] for the derivative n = 14.

$$K \xrightarrow{64^\circ} N_D \overset{82^\circ}{\rightleftharpoons} D_{rd(P_{21}/a)} \overset{95^\circ}{\rightleftharpoons} D_{hd} \overset{221^\circ}{\rightleftharpoons} I$$

$$\swarrow 58^\circ$$

$$[D_h]$$

The corresponding optical textures are given in Figures 3a to 3d. The striking feature found in this observation is the perfect superposition of the optical textures of the low temperature (Figure 3d at 57 °C)

TABLE I

Transition Temperatures and Enthalpies of Cn Hatx
I: temperature in °celsius
ΔH: transition enthalpies in Kcal.mol^{-1}

R		K	D_{hd}	N_D	$D_{rd(P_{21/a})}$	D_h	I
C_6HAT_x	T	112°	—	[96]		138° ·(*o*)	> 280°
	ΔH	4.8	—			≃ 0	
C_7HAT_x	T	98°	—	[85]		140° ·(*o*)	> 280°
	ΔH	3.1	—			≃ 0	
C_8HAT_x	T	88°	—	[87]		141° ·(*o*)	> 280°
	ΔH	7.6	—	0.3		≃ 0	
C_9HAT_x	T	68°	—	85°		138° ·(*o*)	> 280°
	ΔH	5.1	—	0.24		≃ 0	
$C_{10}HAT_x$	T	62°	—	89°		118° ·(?)	277°
	ΔH	8.4	—	0.21		≃ 0	
$C_{11}HAT_x$	T	64	—	83.5°		130° ·(?)	253°
	ΔH	15.7	—	0.2		≃ 0	
$C_{12}HAT_x$	T	57	[53]	85°		112° ·(*d*)	246°
	ΔH						
$C_{13}HAT_x$	T	61	[56]	84°		112° ·(*d*)	241°
	ΔH	20.4		0.10		≃ 0	
$C_{14}HAT_x$	T	64	[58]	82		95° ·(*d*)	221°
	ΔH	20.1	0.085	0.15		≃ 0	0.3
$C_{15}HAT_x$	T	69	[62]	84		95° ·(*d*)	210°
	ΔH	30		4		≃ 0	0.44

The meaning of the signs used in this table and in the following are: K: crystalline phases, D_h: hexagonal columnar phase, (*o*): ordered, (*d*): disordered, [ ]: metastable phase, D_{rd}: rectangular columnar phase, N_D: nematic phase, ·: the phase exists, —: the phase does not exist.

TABLE II

Transition Temperatures and Enthalpies of Cn HBTX
T: temperatures in °celsius
ΔH: transition enthalpies in Kcal.mol^{-1}

R		K	$D_{rd(P_{21/a})}$	N_D	$D_{rd(C_{2/m})}$	D_h	N_D	I
C_6HBT_x	T	238°	—		—	—	—	> 290°
	ΔH		—		—	—		
C_7HBT_x	T	190°	—		—	—	—	> 290°
	ΔH	5	—		—	—	—	
C_8HBT_x	T	148°	—		—	—	—	> 290°
	ΔH	6.1	—		—		—	
C_9HBT_x	T	126°	131°		—	—	—	> 290°
	ΔH	3.9	02		—	—	—	
$C_{10}HBT_x$	T	106°	131°		—	—	—	> 290°
	ΔH	4.6	02		—	—	—	
$C_{11}HBT_x$	T	90°	137°	172°	284°			> 290°
	ΔH	5.3	0.15	0.17	≃ 0	—		
$C_{12}HBT_x$	T	90°	[79]	179°	260°	—		> 290°
	ΔH	1.9	0.05	≃ 0	≃ 0	—		
$C_{13}HBT_x$	T	80°.5	[75]	139°	223°	> 290°	—	
	ΔH	3.8	0.05	0.10	≃ 0			
$C_{14}HBT_x$	T	78°	[72]	121°	225°	> 290°	—	
	ΔH						—	

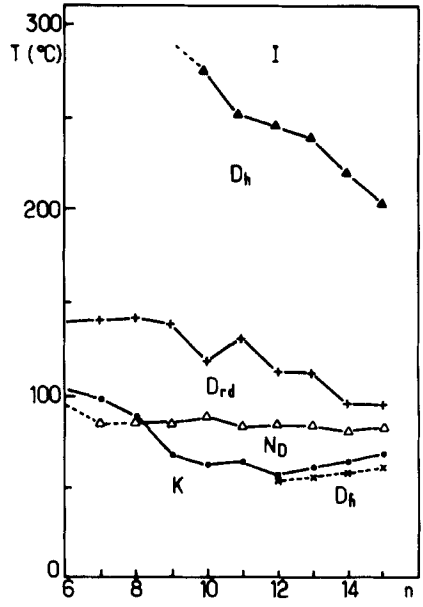


FIGURE 1 Plot of transition temperatures against n, the number of carbon atoms in the chain of Cn HATX.

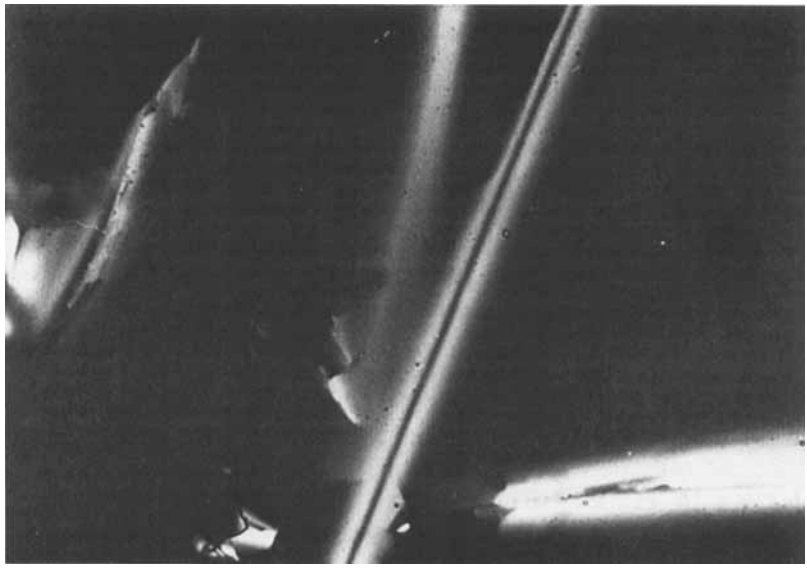


FIGURE 2 Optical texture of the D_{h_D} phase.

and high temperature (Figure 3a at 95 °C) D_h phases even on cooling or heating. In this case the higher temperature columnar phase is D_{hd}. It is an unaxial phase like D_{ho}; but on cooling from the isotropic liquid it grows like a crystal (Figure 4). If there is no problem in the identification of N_D, D_{rd} and D_{hd} phases, it is difficult to ascertain the exact nature of the lowest temperature columnar phase because of its transient nature. Furthermore, it has not been identified by the well known contact method and X-ray measurements.

We must point out that the N_D–D_{rd} transition temperature is almost constant (85 ± 3 °C) for the series. In other words, in this peculiar case the length of the chain does not seem to have an effect upon this mesophase transition temperature. This is probably connected with the diameter of the truxene core relative to the six carboxylate groups.

Transition enthalpies between D_{rd} and D_h columnar phases are very weak and are not detected by DSC. But transition enthalpies between D_{rd} and N_D are about 0.2 Kcal. mol^{-1}.

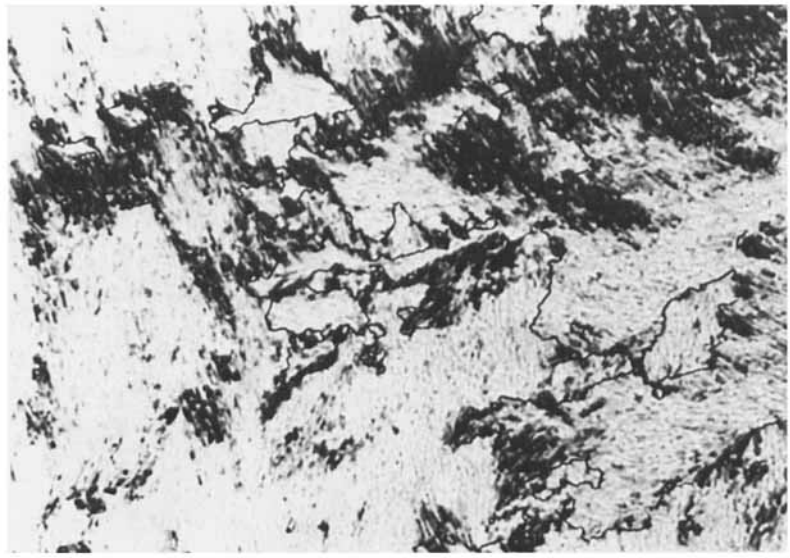
**Series 3b (Table II, Figure 5).* The three first derivatives (n = 6 to 8) only exhibit a N_D nematic phase; n = 9 and 10 derivatives exhibit the *normal* sequence K, D_{rd}, N_D, I like the hexa *p*-alkoxybenzoates of triphenylene (Cn HBT). With n = 11 and 12 we obtained a reentrant N_D nematic phase with the sequence[8]:

$$KD_{rd(P_{2_1/a})}N_D D_{rd(C_{2/m})}N_D I$$

The corresponding optical textures are given in Figures 6a through 6d. At high temperatures (about 290 °C) we observed the N_D nematic phase which showed a schlieren or marbled texture. On cooling, below this N_D phase, the D_{rd} columnar phase appears with a fan shaped texture. On further cooling another schlieren texture is observed followed by a fan shaped phase. In the two compounds with n = 13 and 14 the high temperature N_D nematic phase disappears and this phase is replaced by a hexagonal columnar phase D_h.

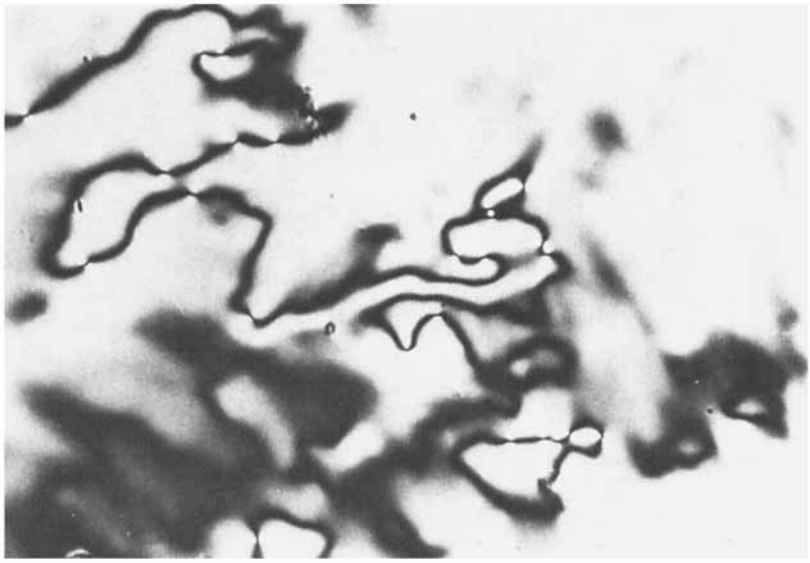
The clearing points N_D–I or D_h–I of all these compounds are very high above 290 °C. The melting points K–N_D or K–D_{rd} quickly decrease with increasing chain length from 238 °C for n = 6 to 78 °C for n = 14. For the HBTX series the transition enthalpies of D_{rd}–D_h are very weak and those of N_D–D_{rd} are also about 0.2 Kcal.mol^{-1} for short chains (n = 6) and 0.1 Kcal.mol^{-1} for longer chains (n = 14).

(a)



(b)

FIGURE 3 Optical textures observed for the C_{14}HATX. (a) D_{hd} columnar phase at 95°C. (b) $D_{rd(P_{21/a})}$ columnar phase at 84°C. (c) N_D nematic phase at 74°C. (d) D_h columnar phase at 57°C.



(c)

(d)

FIGURE 3 (*Continued*)

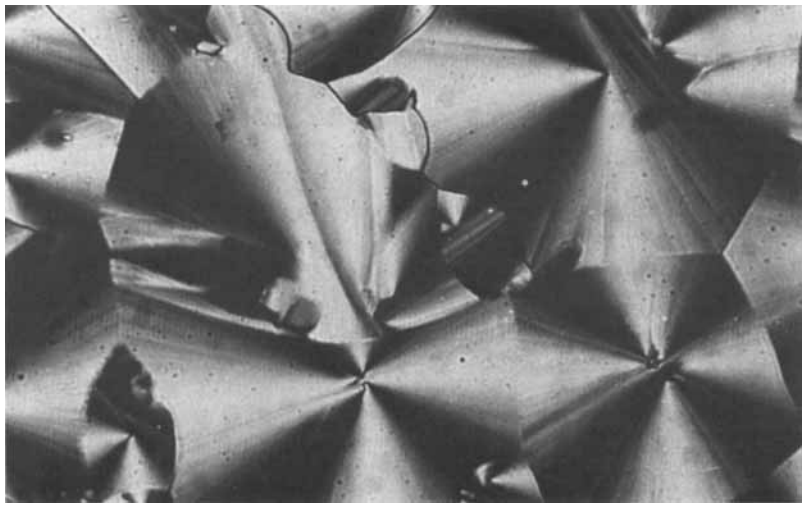


FIGURE 4 Optical texture of the D_{hd} phase.

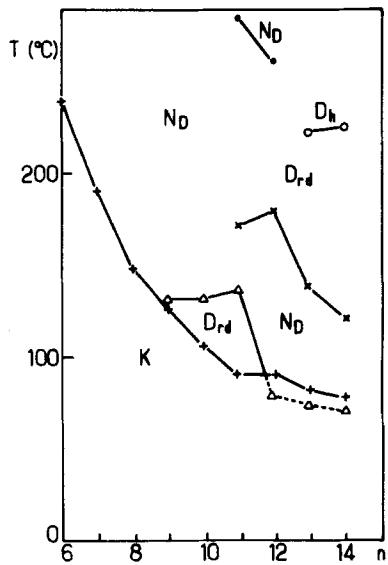
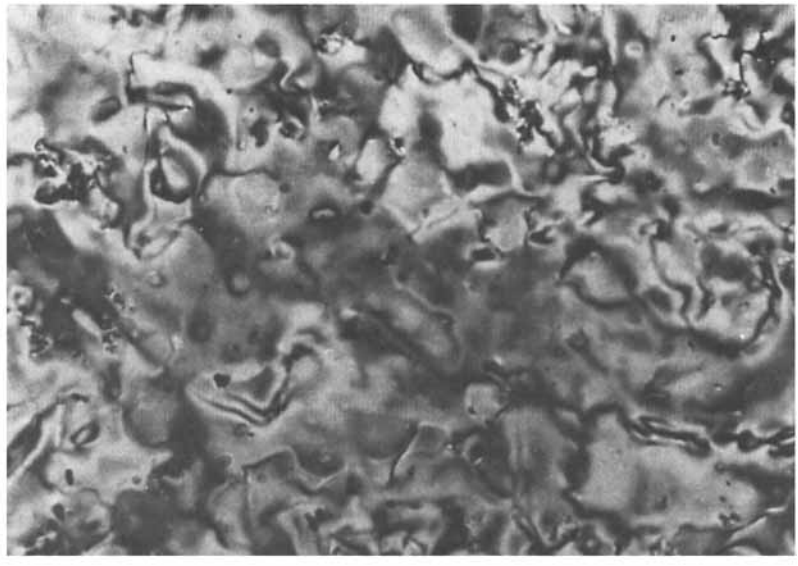
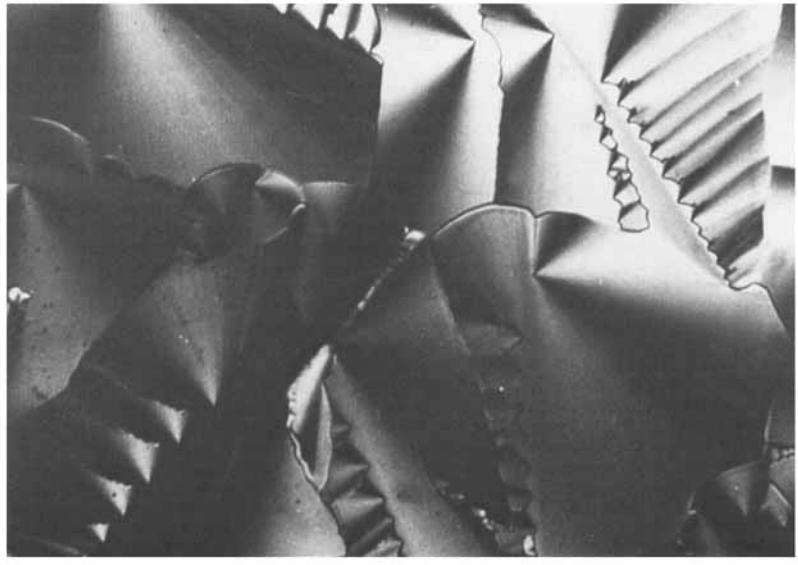


FIGURE 5 Plot of transition temperatures against n, the number of carbon atoms in the chain of Cn HBTX.

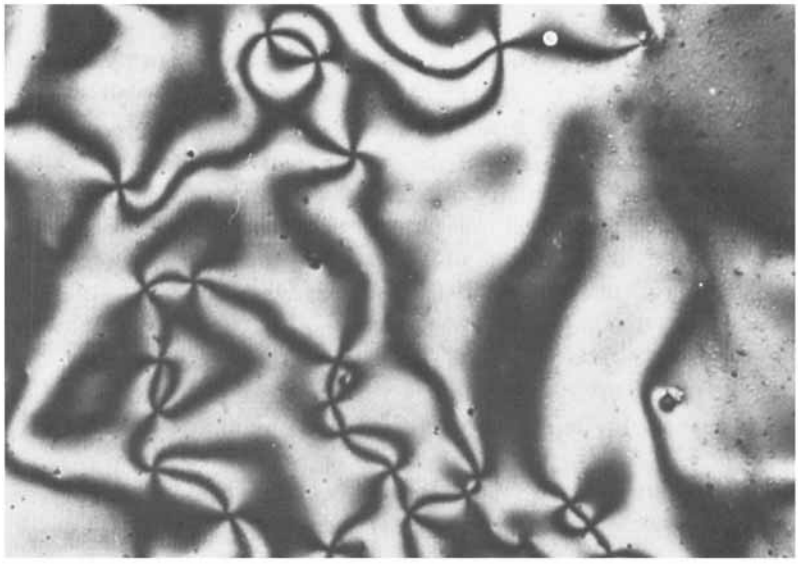


(a)

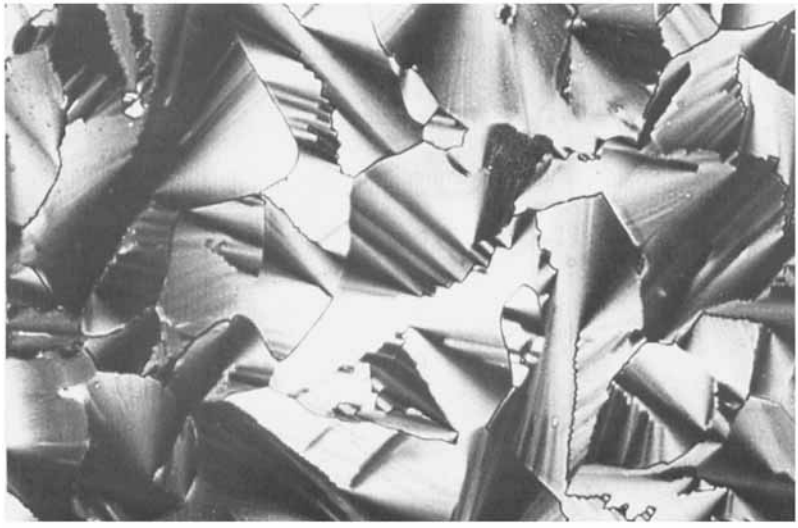


(b)

FIGURE 6 Optical textures of the C_{11}HBTX. (a) N_D nematic phase at 290°C. (b) $D_{rd(C_{2/m})}$ columnar phase at 175°C. (c) N_D reentrant nematic phase at 145°C. (d) $D_{rd(P_{21/a})}$ columnar phase at 130°C.



(c)



(d)

FIGURE 6 (*Continued*)

3. Isomorphism

At first, the low temperature N_D nematic phase of the HATX series is miscible of those of C_7OHBT[2] (*K* 168 N_D 253 *I*). A 50 : 50 mixture of this derivative and C_9HATX exhibits the transition temperatures *K* 138 N_D 170 *I*[3]. It should be noted that in the 15 : 85% of C_7OHBT–C_9HATX binary mixture the two columnar phases of C_9HATX disappear and we only obtain the N_D nematic phase. Similarly the identification of the two N_D nematic phases in the reentrant sequence of the **3b** (R = $C_{11}H_{23}O$) is obtained from the phase diagram with C_{10}OHBT[2] (*K* 142 D_{rd} 191 N_D 212 *I*) (Figure 7). The diagram proves:

—the miscibility between the two N_D nematic phases of **3b** (R = $C_{11}H_{23}O$—) with the N_D phase of C_{10}OHBT; an uninterrupted region exists.

—moreover, the low temperature D_{rd} columnar phase of **3b** (R = $C_{11}H_{23}O$—) is miscible with the $D_{rd(P_{21/a})}$ phase of C_{10}OHBT.

Concerning the other columnar phases of the **3a** and **3b** series, there is miscibility between those inside the same series but we can not show

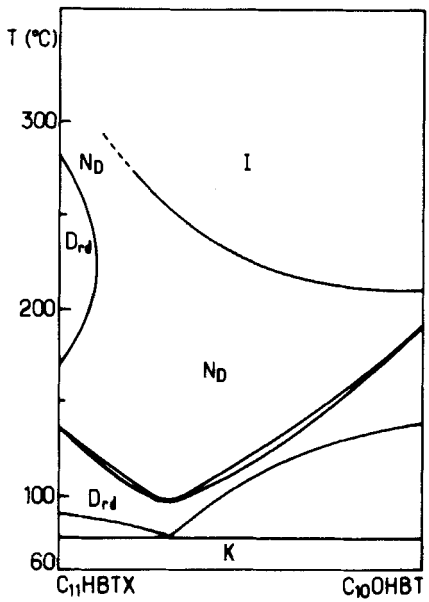


FIGURE 7 Diagram of isobaric state of the mixture of C_{11}HBTX (on left) and C_{10} HBT (on right).

their miscibility with those of the other series which have very different molecular diameters such as triphenylene derivatives. This is one of the two limitations of the contact method in the cases of disc-like mesogens. The other limitation concerns the small number of reference substances available. For these reasons, we have identified the other columnar phases by X-ray measurements.

4. X-ray measurements

Experiments. X-ray diffraction patterns of oriented samples are obtained with a photographic cylindrical camera put in the inlet of an electromagnet. The monochromatic CuK_α X-ray beam is perpendicular to the magnetic field; at the intersection we have an oven the temperature of which is constant within $\pm 0.5°$. The sample is held in a Lindemann glass tube and can be aligned by a 1.7 T magnetic field. It is necessary to rotate the sample about an axis perpendicular to the field in order to obtain a single domain of the nematic phase with the director parallel to the rotation axis. The sample remains oriented during the time of one experiment because of the rather high viscosity of the nematic phase. By heating to or cooling from the nematic phase we are able to partially keep the orientation of the director in the columnar phase.

X-ray powder patterns are performed with a Guinier camera in order to obtain the lattice constants of the columnar phases.

**HATX Series.* Three derivatives where studied: C_9HATX, C_{11}HATX and C_{13}HATX. The nematic phases of the three compounds give an X-ray pattern similar to the pattern of the nematic phase of the C_{11}HBT[9]. We were not able to observe the low temperature hexagonal phase of the C_{13}HATX since crystallization occurs before we can obtain a decernable pattern. By heating from the nematic phase we obtain successively a rectangular phase of $P_{21/a}$ symmetry and a hexagonal phase. There is no evidence of a periodic stacking of the molecular cores along a column in the rectangular phase of the three compounds studied. In the hexagonal columnar phase an external ring corresponding to a lattice constant of 3.6 Å is visible for the X-ray patterns of the derivative with the shortest alkyl chain length. This ring is indicative of a periodic stacking of the molecular cores inside a column. The width of the ring is rather broad, that is to say that the correlation length for this linear order is low. We cannot give a measure the correlation length because of poor orientation of our sample, but it is evident that this length decreases as the

chain length increases. For the hexagonal phase of the C_{13}HATX the columns appear completely disordered.

**HBTX Series.* The C_{11}HBTX and C_{12}HBTX compounds have been studied.

In the low temperature nematic phase the inner ring is split into four spots characteristic of tilted cybotatic groups. Therefore the molecules possibly form clusters of short columns in which the aromatic cores are tilted with respect to the column axis. In the C_{12}HBTX nematic phase the size of the cybotatic groups is nearly independent of the temperature: about 5 × 5 columns of 30 molecules each. The tilt angle of the cores (the angle between the director and the column axis) increases from 49° to 64° between 80 °C and 137 °C. The two columnar phases adjacent to the reentrant nematic phase have a rectangular symmetry with two columns per unit cell. From powder patterns we have determined the lattice constants. The low temperature phase data for the C_{11} derivative are consistent with a rectangular symmetry $P_{21/a}$ while the two high temperature phases correspond to the symmetry $C_{2/m}$. In the low temperature phase of the $C_{12/a}$ derivative the 21 ring characteristic of the symmetry group $P_{21/a}$ is not visible but we have assumed that the symmetry is the same in the corresponding phases of the two compounds. The two kinds of lattices both correspond to pseudo-hexagonal array of tilted columns. In fact the hexagonal formed by the six next neighbours of a column is not regular and the distortion can be measured by the ratio $2(d_{11} - d_{20})/d_{11} + d_{20}$ (Table III). This distortion is large in the two phases. The difference between $C_{2/m}$ and $P_{21/a}$ symmetry is in the director

TABLE III

Lattice Parameters and Reticular Distances in the Different Studied Compounds

Compound	Temperature	Observed reticular distances (Å)	Indexes	Lattice Constant (Å)
C_{11}HBTX	94 °C	26.12	11	a = 44.1
		22.05	20	
		18.64	21	b = 32.7
		16.34	02	
	180 °C	28.09	11	a = 50.6
		25.31	20	b = 33.8
C_{12}HBTX	84 °C	25.95	11	a = 44.6
		22.30	20	
		16.02	02	b = 32.05
	180 °C	27.90	11	a = 45.6
		22.78	20	b = 35.3

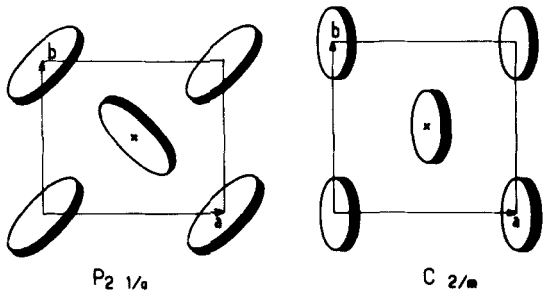


FIGURE 8 Two dimensional lattices of the two rectangular columnar phases.

direction. The directors of the molecules belonging to different columns point in the same direction for $C_{2/m}$ lattice but not for a $P_{21/a}$ symmetry (Figure 8). By X-ray diffraction we are not able to measure either the tilt angle nor the angle between the lattice vectors and the director, but if we refer to the nematic phase the tilt angle appears to be larger than $\pi/4$.

We have not explored the higher temperature nematic phase which lies at too high a temperature for a diffraction pattern to be obtained.

CONCLUSION

We have studied two series of truxene derivatives: Cn HATX and Cn HBTX. The first one displays reentrant hexagonal columnar phase and the second offers the first example of a reentrant nematic N_D phase in disc-like mesogens. The origin of these phenomena is still unknown. However, their origins could be related to those for reentrant nematic phases in rod-like liquid crystals which are different at low and high temperature,[10] due to the presence of dimerized strongly polar molecules. In the case of disc-like liquid crystals, we can also assume the existence of pairs of molecules in the columns in connection with the reentrant phenomenon; the presence of such dimer has been shown by some X-ray diffraction measurements in the crystalline phase of some triphenylene derivatives.[11]

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