Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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Version of record first published: 17 Oct 2011.

To cite this article: Nguyen Huu Tinh , R. Cayuela , C. Destrade & J. Malthete (1985): Trithiatruxenes: A Family of Disc-like Mesogens with a New Polymorphism, Molecular Crystals and Liquid Crystals, 122:1, 141-149

To link to this article: http://dx.doi.org/10.1080/00268948508074748

Mol. Cryst. Liq. Cryst., 1985, Vol. 122, pp. 141–149
0026-8941/85/1224–0141/$15.00/0

Trithiatruxenes: A Family of Disc-like Mesogens with a New Polymorphism†

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(*Received July 19, 1984*)

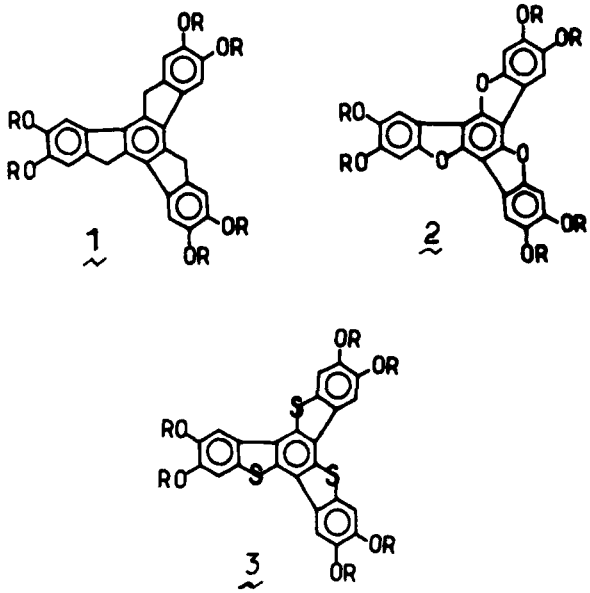
A homologous series of hexa-*n*-alkanoyloxytrithiatruxenes (2, 3, 7, 8, 12, 13-hexa-*n*-alkanoyloxybenzo-[1, 2-*b* : 3, 4-*b'* : 5, 6-*b"*]trisbenzothiophenes) (C_n HATXS) has been prepared with $n = 9$ to $n = 13$ in order to study the influence of the substitution of the three methylenes of the truxene core by three sulphur atoms on the mesomorphic properties. Phase transitions were studied by hot stage microscopy and DSC. This series shows another example of an inverted sequence (crystal–N_D nematic–D columnar–isotropic) and a new polymorphism with a columnar phase between D_h and D_{rd} phases.

INTRODUCTION

Recently, we reported a new family of disc-like mesogens: Trioxatruxenes (**2**)[1,2] in which the three methylene groups of the truxene core (**1**)[3,4] are substituted by oxygen atoms. These substances exhibit the more complex polymorphism found in disc-like liquid crystals with the sequence: K-N_D-D_{obd}-D_{rd}-D_{hd}-I. Following these stimulating results, we have achieved another heteroatomic substitution by using

†Presented at the Tenth International Liquid-Crystal Conference, York, July 15–21, 1984.

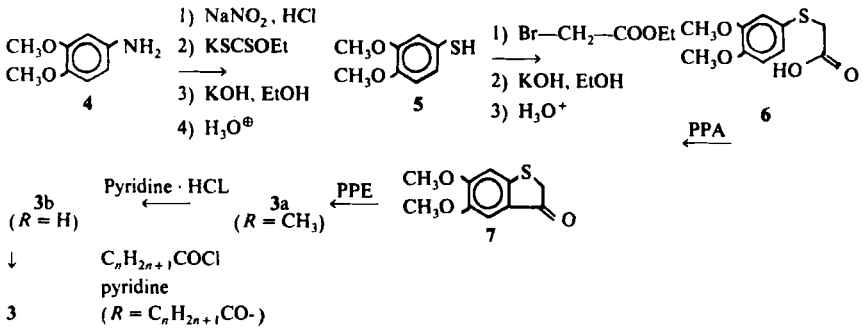
three sulphur atoms instead of the oxygen atoms. Another motivation to build up these compounds, namely the trithiatruxenes (**3**) (C_n HATXS), was their possible potential for use as electron-donors in conducting complexes:



RESULTS AND DISCUSSION

Synthesis

The preparation of the trithiatruxenes (**3**)—the 2, 3, 7, 8, 12, 13-hexa-*n*-alkanoyloxybenzo-[1, 2-*b* : 3, 4-*b'* : 5, 6-*b''*]trisbenzothiophenes—is summarized in the following scheme:



IDENTIFICATION OF THE MESOPHASES

This identification was performed through optical texture observations and using miscibility methods. All the derivatives exhibit, at high temperature, a mesophase the texture of which is very similar to

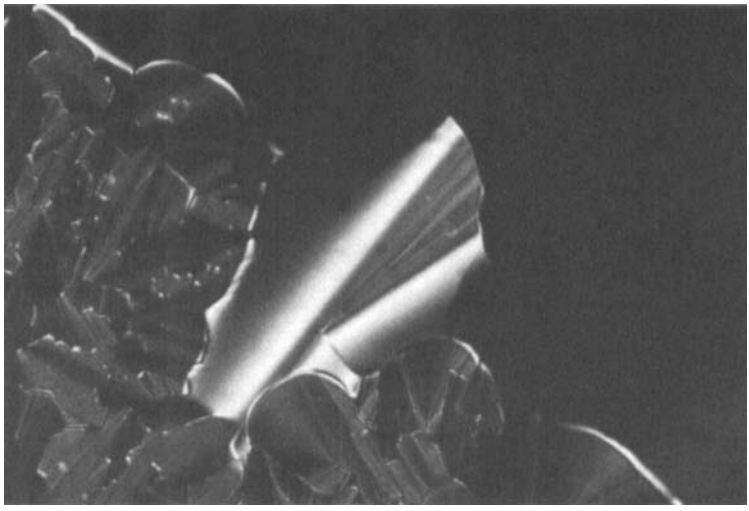


FIGURE 1 Optical textures of the D_h columnar phase of C_{11} HATXS. See Color Plate I, located in the final volume of these Conference Proceedings.

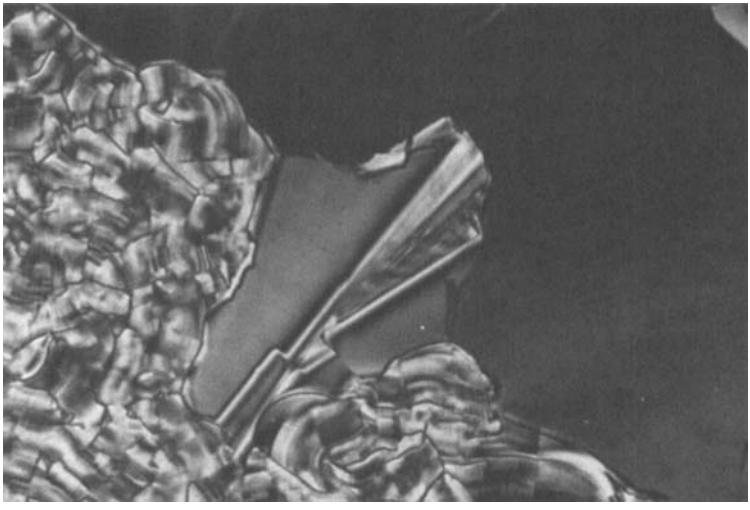


FIGURE 2 Optical textures of the D_{rd} ($P_{2\,1/a}$) columnar phase of C_{11} HATXS. See Color Plate II, located in the final volume of these Conference Proceedings.

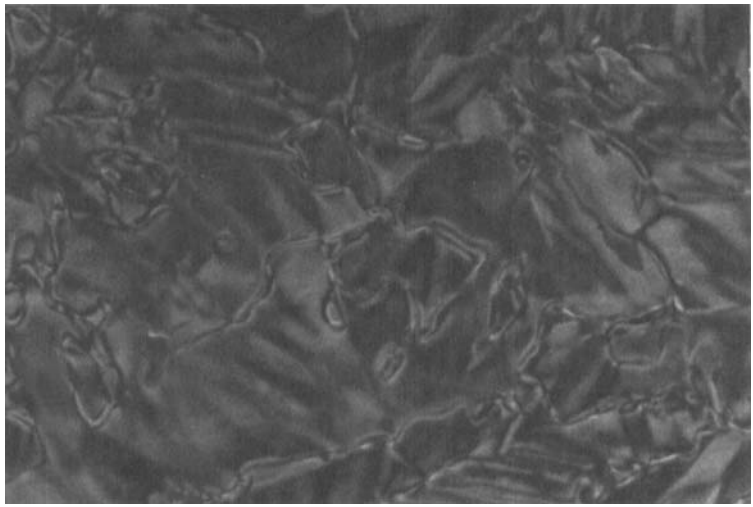


FIGURE 3 Optical textures of the N_D nematic phase of C_{11} HATXS. See Color Plate III, located in the final volume of these Conference Proceedings.

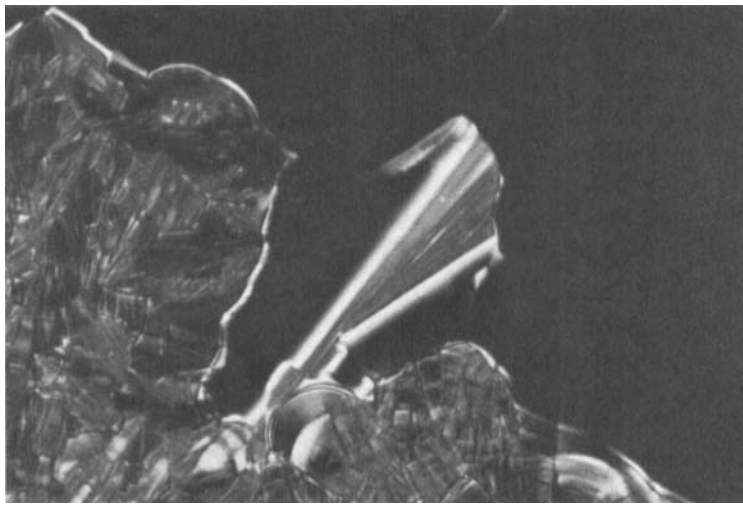


FIGURE 4 Optical textures of the D_7 columnar phase of C_{11} HATXS. See Color Plate IV, located in the final volume of these Conference Proceedings.

a D_h hexagonal columnar phase (Fig. 1) with large homeotropic areas typical of a uniaxial medium and well developed domains of fan-shaped texture. At lower temperatures, another mesophase was also observed with textures in every way similar to those of a D_{rd} ($P_{2\,1/a}$) columnar phase (Fig. 2), with finger print areas or broken fans. On further cooling, a fluid birefringent phase was observed for all deriva-

tives; this had a marbled or threaded texture and exhibited strong thermal fluctuations typical of a N_D nematic phase (Fig. 3). However, with longer chains, another columnar phase is unambiguously detected between the upper and lower columnar phases as a result of a transient textural change (compare Figs. 1, 2, and 4). This texture is much more similar to a rectangular columnar phase than a hexagonal phase, but in order to obtain details of the structural arrangement in this mesophase, X-ray measurements will have to be performed.

This preliminary identification was supported through studies of isomorphism by the contact method. We used the hexa-*n*-undecanoyloxytruxene (C_{10} HATX) as the reference substance which has the following phase sequence:[3,5]

$$K \xrightarrow{64°C} N_D \overset{89°C}{\rightleftharpoons} D_{rd} \overset{118°C}{\rightleftharpoons} D_h \overset{280°C}{\rightleftharpoons} I$$

Figure 5 shows that all the mesophases of C_{10} HATXS are respectively miscible with those of the reference substance and this confirms our optical texture identification. The binary diagram between C_{10} HATX and C_{11} HATXS (Fig. 6) gives evidence of non-miscibility of the second columnar phase of the latter with both the hexagonal and rectangular columnar phases of the former. Finally, we have verified the miscibility of all the various corresponding mesophases in the homologous series of trithiatruxenes (**3**). Full details of the transition temperatures and transition heats are given in Table I. Once more let us emphasise that the *D*–*D* transitions are rather second order in nature.

Interesting points can be made by comparison of the three homologous series of truxenes (**1**), trioxatruxenes (**2**), and trithiatruxenes (**3**):

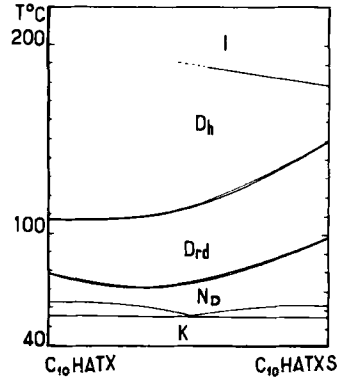


FIGURE 5 Diagram of isobaric state of the mixture of C_{10} HATX (on left) and C_{10} HATXS (on right).

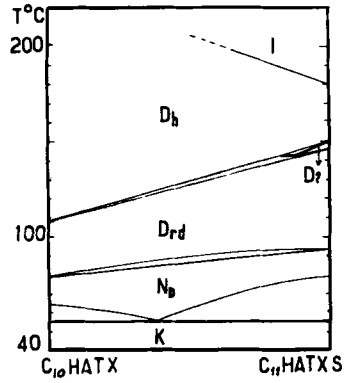


FIGURE 6 Diagram of isobaric state of the mixture of C_{10} HATX (on left) and C_{11} HATXS (on right).

TABLE I

Transition temperatures and enthalpies of (3)
T: temperature in °celsius
ΔH: transition enthalpies in Kcal · mol^{-1}

n		*K*	*N*$_D$	*D*$_{rd}$	*D*	*D*$_h$	*I*
9	T	· 87	· 93	· 185	—	· 210	·
	ΔH	12.13	0.34	0.03		0.31	
10	T	· 63	· 98	· 155	—	· 193	·
	ΔH	13.52	0.22	—			
11	T	· 78	· 93	· 145.5	· 149	· 180	·
	ΔH	13.71	0.25				
13	T	· 82	(· 72)	· 131.5	· 134	· 179	·
	ΔH						

— The inverted sequence $K N_D D I$ is always observed, while the thermal stability of the N_D nematic phase follows the order (1) > (3) > (2), probably as a consequence of the relative steric hindrances of CH_2, S and O.

— However, the O and S heteroatoms are more favourable for complex columnar polymorphism.

CONCLUSION

The synthesis of the homologous series of trithiatruxenes (3)—(C_n HATXS)—provides an interesting new series of disc-like mesogens

with complex polymorphism and especially a middle phase the structure of which has to be proved. As to the question of the possible conducting properties of the materials, several experiments are now in progress.

EXPERIMENTAL

4-Aminoveratrole and ethyl bromacetate were obtained from Fluka Company. Spectral data on products were collected using a Perking-Elmer 225 (ir) and a Bruker 270 (nmr). Elemental analysis results were obtained from Service Central d'Analyse (CNRS).

3,4-Dimethoxyphenylthioacetic acid (6)

The transformation of aniline to thiophenol was achieved following ref. 6. 4-Aminoveratrole (**4**) (38.25 g; 0.25 mol) was slowly added to a cold solution of 250 ml 4M HCl. The suspension was cooled to 0°C and a cold solution of $NaNO_2$ (18.8 g; 0.27 mol) in 60 ml water was added over 1 h. The diazonium salt solution was slowly added (1 h) to a warmed solution (50°C) of potassium ethyl xanthate (47 g; 0.27 mol) in 200 ml water at such a rate that the temperature was maintained 50°C. The oily xanthate was then extracted using two portions of diethyl ether (2 × 300 ml). After usual work up, the diethyl ether was evaporated to give the crude xanthate (oil) which was dissolved in 200 ml EtOH. A solution of KOH was added at a rate sufficient to keep the solution refluxing. After refluxing for an additional 14h, the solution was concentrated to approximatively 50 ml. The resulting slurry was dissolved in 200 ml water and very slowly acidified with 200 ml 15N H_2SO_4 and extracted into diethyl ether (2 × 300 ml). After concentrating the etheral solution to 150 ml, Zn (1 g) was added and the suspension was refluxed for 1 h. The Zn was filtered off the filtrate afforded 31 g of crude, 3,4-dimethoxythiophenol (**5**).

To a solution of the Na thiophenate obtained from the above crude (**5**) and NaOEt (0.17 mol) in 300 ml EtOH were added 20 ml ethyl bromoacetate (0.18 mol). After a 4 h reflux, the mixture was cooled to RT and a solution of ethanolic KOH (100 ml, 10%) was added. After refluxing for 1 h, the solvent was evaporated and the residue was acidified with 250 ml cold solution 3M HCl. After usual work-up, 33.5 g of crude 3,4-dimethoxyphenylthioacetic acid (**6**) were obtained. After purification by chromatography on silica gel, using a benzene

(90%)–diethyl ether (10%) v/v mixture as eluent, recrystallization from ethyl acetate afforded 14–20 g of (**6**), (25–35%) m.p. 102°C.

Anal. calc. ($C_{10}H_{12}O_4S$)	C% 52.63;	H% 5.26;	S% 14.04
Found	C% 52.57;	H% 5.12;	S% 14.6

5, 6-Dimethoxy-2H-benzothiophene-3-one (7)

92 g of P_2O_5 and 63 ml of 85% H_3PO_4 were stirred at 110°C for 90 min. 10 g of acid (**6**) was then added to the clear polyphosphoric acid at 60°C and the mixture stirred at this temperature for 90 min. After usual work-up, chromatography on silica gel with a benzene (95%)–diethyl ether (5%) v/v mixture as eluent afforded 3 g of yellow (**7**), (32%) m.p. 178°C.

Hexamethoxytrithiatruxene (3)

Ketone (**7**) (4 g) was trimerized with PPE following ref. 1 to afford the required hexamethoxy derivative (**3a**), 0.6 g, yield, 15%.

Hexahydroxy trithiatruxene (3b)
(3) and hexa-*n*-alkanoyloxytrithiatruxenes

3a was demethylated by means of pyridine hydrochloride at 240°C for 30 min under dry nitrogen, and the hexaesters (**3**) were obtained following ref. 1 with similar yields. Combustion analysis results are given in Table II.

For C_{13} HATXS:

^{1}H nmr ($CDCl_3$): δ: 1.3 (*t*—18, 6 CH_3 of $-C_{13}H_{27}-$)
1.58 (*m*—120, 60 $-CH_2-$)
2.03 (*p*—12, six $-CH_{2\beta}$)
2.65–2.72 (two *t*—12, six $-CH_{2\alpha}$)
7.8–8.23 (two S—6, six aromatic)

TABLE II

Combustion analysis results for C_n HATXS (3)

	Calculated				Found		
n	C	H	S	Formula	C	H	S
9	71.2	8.5	6.8	$C_{84}H_{120}O_{12}S_3$	70.9	8.5	6.9
10	72.0	8.8	6.4	$C_{90}H_{132}O_{12}S_3$	72.3	8.6	6.8
11	72.7	9.1	6.1	$C_{96}H_{144}O_{12}S_3$	72.3	9.1	6.9
13	73.97	9.59	5.48	$C_{108}H_{168}O_{12}S_3$	73.83	9.76	5.37

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