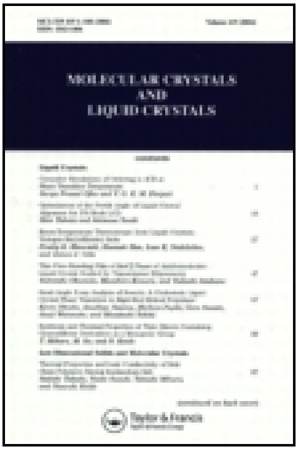

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Two Families of Trithiatruxene Derivatives

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To cite this article: R. Cayuela , H. T. Nguyen , C. Destrade & A. M. Levelut (1989): Two Families of Trithiatruxene Derivatives, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 177:1, 81-91

To link to this article: http://dx.doi.org/10.1080/00268948908047772

Mol. Cryst. Liq. Cryst., 1989, Vol. 177, pp. 81–91
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Printed in the United States of America

Two Families of Trithiatruxene Derivatives

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(Received September 28, 1988; in final form June 9, 1989)

Homologous series of nine mesogenic hexa-*n*-alkanoyloxytrithiatruxenes (C_nHATxS) and hexa-*n*-alkoxybenzoyloxytrithiatruxenes (C_nHBTxS) have been prepared. Optical texture observations, DSC, and X-ray measurements showed that they exhibit a rich polymorphism with a nematic discoid phase occurring in an inverted sequence—a nematic phase and three successive columnar phases. The first example of a $D_{rd}(P2_1/a)$ – $D_{rd}(C2/m)$ transition in the C_nHATxS series was found. In contrast to the rich columnar polymorphism of the hexa-*n*-alkoxybenzoyloxytruxenes, the C_nHBTxS series shows only a N_D nematic discoid phase.

INTRODUCTION

Disk-like mesogens of the truxene ($X = CH_2$) and trioxatruxene ($X = 0$) families exhibit complex discotic polymorphism[1–4]:

For instance: * C_{12} HATx (hexa-*n*-tridecanoyloxytruxene)

$$\begin{tikzcd} K \arrow[r] & N_D \arrow[r, harpoon, shift left] \arrow[dl, shift left] & D_{rd} \arrow[l, harpoon, shift left] \arrow[r, harpoon, shift left] & D_{hd} \arrow[l, harpoon, shift left] \arrow[r, harpoon, shift left] & I \arrow[l, harpoon, shift left] \\ {[D_{hd}]} \arrow[u] \arrow[ur, shift left] & & & & \end{tikzcd}$$

* C_{12} HBTx (hexa-*n*-dodecyloxybenzoyloxytruxene)

$$\begin{tikzcd} K \arrow[r] & N_D \arrow[r, harpoon, shift left] \arrow[dl, shift left] & D_{rd} \arrow[l, harpoon, shift left] \arrow[r, harpoon, shift left] & D_{hd} \arrow[l, harpoon, shift left] \arrow[r, harpoon, shift left] & I \arrow[l, harpoon, shift left] \\ {[D_{rd}]} \arrow[u] \arrow[ur, shift left] & & & & \end{tikzcd}$$

* C_{15} HATxO (hexa-*n*-hexadecanoyloxytrioxatruxene)

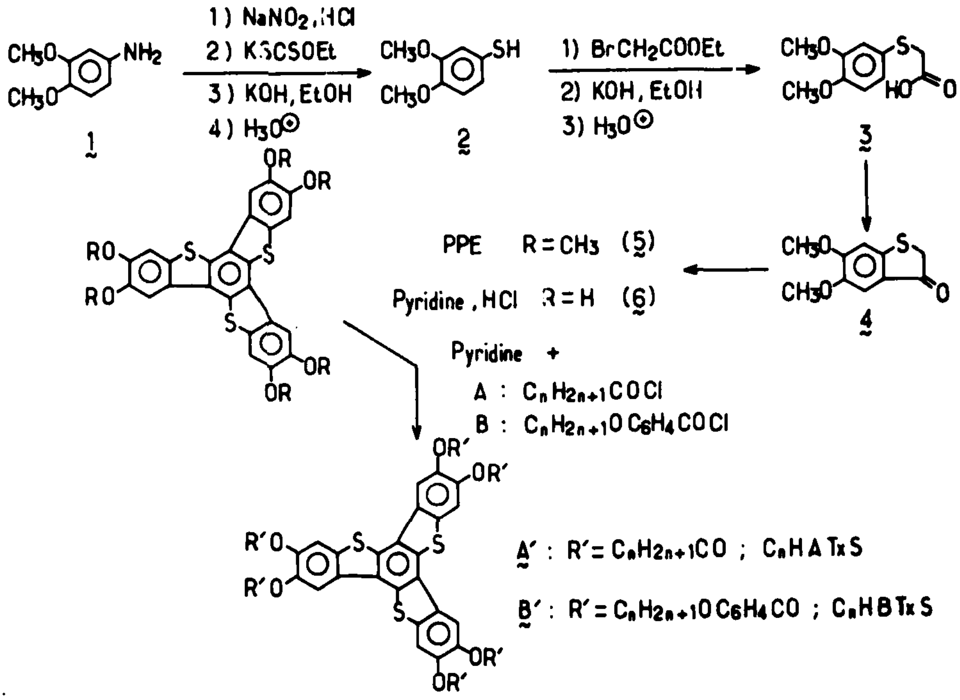
$$\begin{tikzcd} K \arrow[r] & D_{obd} \arrow[r, phantom, "\rightleftharpoons"] \arrow[dl, shift left] & D_{rd} \arrow[r, phantom, "\rightleftharpoons"] & D_{hd} \arrow[r, phantom, "\rightleftharpoons"] & I \\ {[N_D]} \arrow[u] \arrow[ur, shift left] & & & & \end{tikzcd}$$

where D_{rd}, D_{hd}, D_{obd} are respectively rectangular, hexagonal, and oblique disordered columnar phases and where N_D is the nematic discoid phase.

We shall describe here the new mesogens produced by substitution of the three methylene groups of the truxene core by sulfur atoms. The mesogenic properties of these compounds should throw additional light on the intermolecular interactions between the various chemical parts of the truxene core and substituents. Two homologous series of hexa-*n*-alkanoyloxytrithiatruxenes (C_nHATxS) and hexa-*n*-alkoxybenzoyloxytrithiatruxenes (C_nHBTxS) were prepared.

SYNTHESIS

The preparation of the 2,3,7,8,12,13-hexa-*n*-alkanoyloxybenzo-[1,2-b; 3,4-b′; 5,6-b″]trisbenzothiophenes (A′) and the 2,3,7,8,12,13-hexa-*n*-alkoxybenzoyloxybenzo-[1,2-b; 3,4-b′; 5,6-b″]trisbenzothiophenes (B′) is summarized in the following scheme. The experimental details have been described earlier.[5,7]



HEXA-*n*-ALKANOYLOXYTRITHIATRUXENES C_nHATxS

Optical and thermodynamic studies

We have prepared and examined compounds in this series with values of n from 6 to 14. Optical observations were made with a polarizing microscope equipped with a heating and cooling stage (Mettler FP5). The transition temperatures and enthalpies were determined by differential scanning calorimetry (Dupont 990). The results are listed in the Table I.

Only four compounds (n = 8,11,13,14) form the full range of four mesophases.

On cooling the isotropic melt, the first mesophase to occur is clearly a hexagonal columnar phase (cf. Figure 1a). The optical texture contains large homeotropic areas, indicating a uniaxial system, and there are also typical fan shaped areas characteristic of a domain texture. On cooling, the texture fragments (cf. Figure 1b) giving a texture similar to that of a rectangular phase. At lower temperatures, a further mesophase is observed with a texture that is also similar to those of rectangular columnar phases (cf. Figure 1c), with additional finger print areas, and the symmetry of this phase is obviously different from the previous one. Finally, on further cooling, a fluid birefringent phase is observed. This phase has a marbled or threaded texture and shows the pronounced thermal fluctuations typical of a N_D nematic phase (cf. Figure 1d).

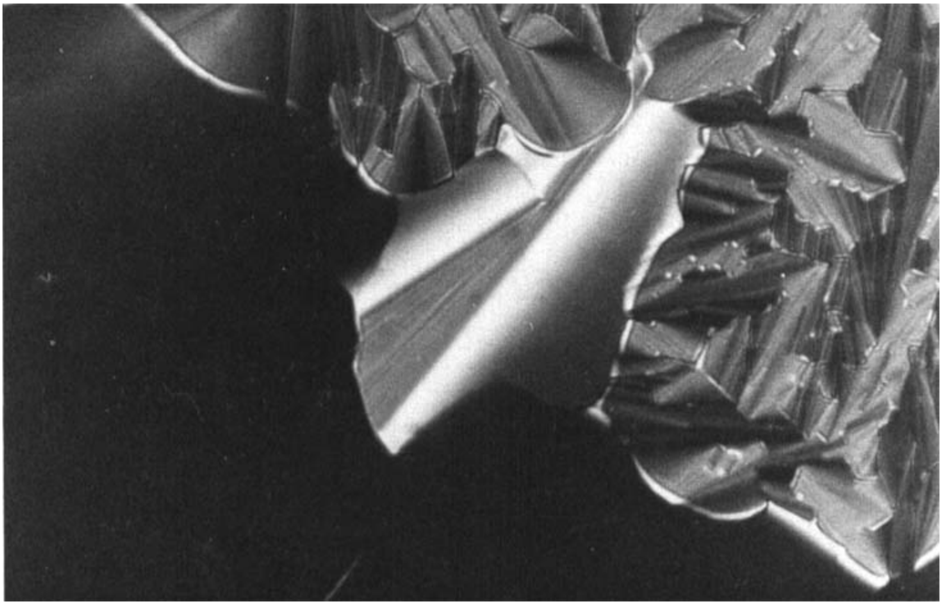
Preliminary identifications were confirmed by studies of isomorphism using contact preparation methods.[5] Binary phase diagrams indicated that the second col-

TABLE I

Thermodynamic data for the compounds C_nHATxS

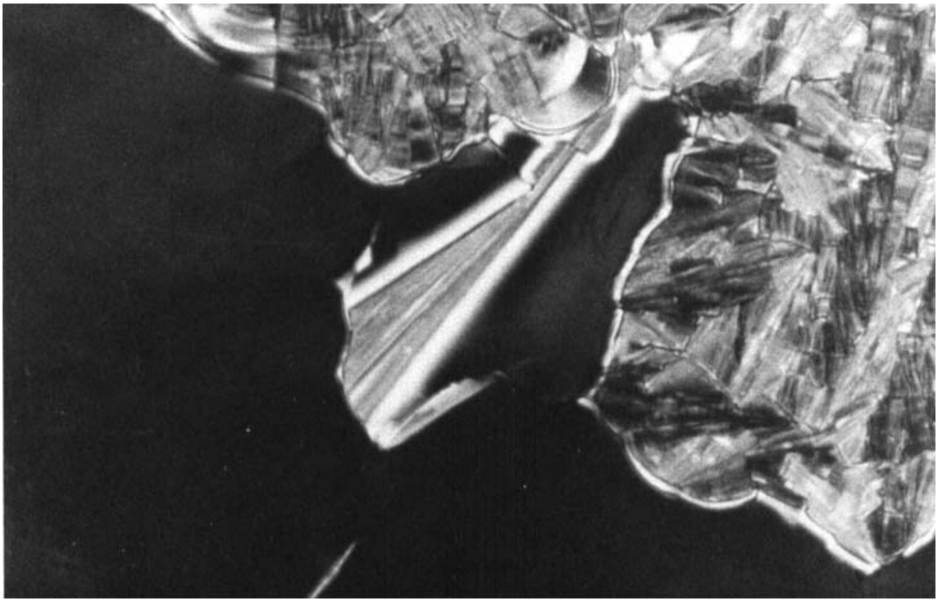
Compound		K	N_D	$D_{rd(P21/a)}$	$D_{rd(C2/m)}$	D_{hd}	I
C_6HATxS	T	• 133	—	• 218	—	• 241	•
	ΔH	5.36		0.06		0.25	
C_7HATxS		• 103	• [92]	• 212	—	• 236	•
		2.6	0.15	0.02		0.2	
C_8HATxS		• 90	• [82]	• 173	• 191	• 229	•
		6.1	0.4	0.008	0.013	0.35	
C_9HATxS		• 87	• 93	• 185	--	• 210	•
		12.1	0.35	0.03		0.3	
$C_{10}HATxS$		• 62	• 98	• 151	—	• 193	•
		13.5	0.2	≃ 0		≃ 0	
$C_{11}HATxS$		• 64	• 93	• 145,5	• 149	• 179	•
		13.7	0.25	≃ 0	≃ 0	≃ 0	
$C_{12}HATxS$		• 79	• 87	• 136	—	• 191	•
		20.5	0.26	≃ 0		≃ 0	
$C_{13}HATxS$		• 82	• [72]	• 131.5	• 134	• 179	•
		16.85	≃ 0	≃ 0	≃ 0	0.1	
$C_{14}HATxS$		• 88	• [81]	• 121	• 125	• 178	•
		29.2	0.3	≃ 0.3	≃ 0	≃ 0.15	

T: transition temperatures (°C)
ΔH: transition enthalpies (kcal mol^{-1})
[•]: monotropic transition



See Color Plate I

(a)



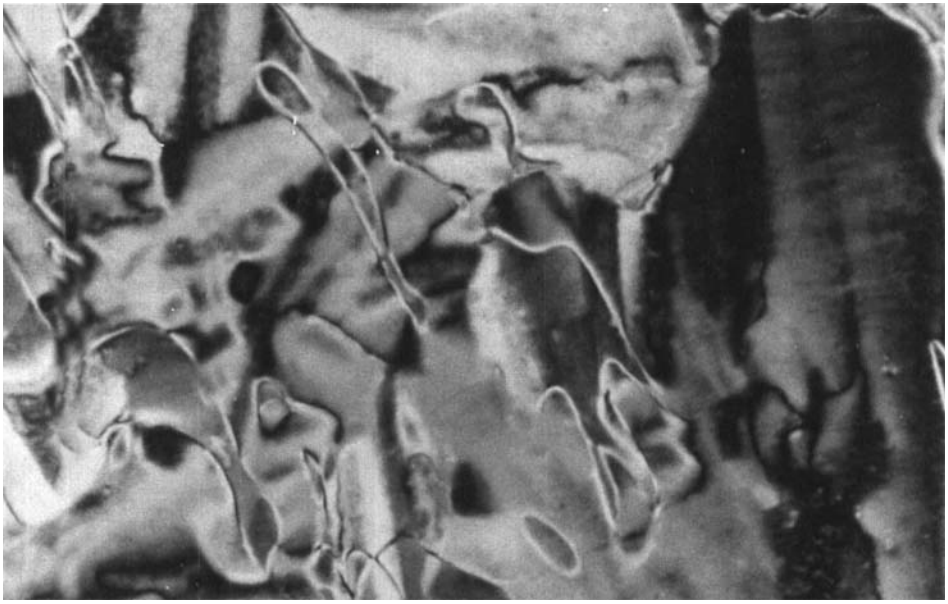
See Color Plate II

(b)

FIGURE 1 Optical textures of C_{11}HATxS between crossed polarizers: (a) 160°C D_{hd} phase, (b) 147°C $D_{rd}(C2/m)$ phase, (c) 140°C $D_{rd}(P2_1/a)$ phase, (d) 60°C N_D phase (same area).

See Color Plate III

(c)



See Color Plate IV

(d)

FIGURE 1 (*continued*)

umnar phase (i.e., that occurring between 173°C and 191°C in C_8HATxS) is immiscible with both the hexagonal and rectangular ($P2_1/a$) columnar phase of the alkanoyloxytruxene compounds. To obtain details about the symmetry of the intermediate columnar phase, X-ray diffraction studies were carried out.

X-Ray Investigation

Two compounds were examined: C_8HATxS and C_{14}HATxS.

Oriented samples can be obtained by the application of a magnetic field to the nematic phase. The diffraction patterns from these samples of trithiatruxene were indistinguishable from those of truxene derivatives.[7] In particular there was no evidence of long range correlation in the stacking of the molecules along the column axes. Therefore more information can be obtained from powder patterns.

X-ray powder patterns were obtained with a Guinier camera to give accurate lattice spacings. The chemical stability of the compounds under prolonged exposure to temperature is poor and the decomposition induced products cause a decrease in the stability of the two low temperature columnar mesophases. Useful information could only obtained for two derivatives—the C_8 and C_{14} compounds: for the C_8HATxS derivative, the temperature range of all the three mesophases is conveniently large and for the C_{14}HATxS compound, we took advantage of the low transition temperature to the hexagonal columnar mesophase.

For these two compounds, the existence of a high temperature hexagonal columnar mesophase was confirmed. For C_{14}HATxS, the two other mesophases appear to have structures where the columns lie in rectangular and centred rectangular lattices (Table II). The two rectangular lattice have nearly the same lattice constants and they can be obtained by a slight distortion of the hexagonal lattice. The transition from the hexagonal to a rectangular phase involves a reduction from six-fold to two-fold symmetry. The intense, sharp ring in the diffraction pattern of the hexagonal phase arises from the superposition of the six symmetry-equivalent reflections of the 1010 type. For the rectangular lattices, this ring splits into a doublet composed of four reflections of the 110 type and two superimposed reflections of the 200 type. A 2D rectangular lattice can belong either to a monoclinic or to an orthorombic 3D symmetry space group (planar group).[6] From optical texture observations and from miscibility studies, we have assigned the monoclinic space group, $P2_1/a$ to the low temperature mesophase (but we cannot in fact distinguish between $P2_1/a$ with unique axis parallel to **b** and $P2_1/b$ with unique axis parallel to **a**). The centred rectangular lattice (indicated by the absence of 210 reflections) is also taken to be monoclinic; since $d_{200} < d_{110}$, the unique axis appears to be in the b direction with the molecular director lying in the (010) plane. Note that the column area projected onto a plane perpendicular to the column axis is virtually the same for the three columnar phases. We conclude therefore that the discs are tilted at the same angle with respect to the column axis in the three phases (In the triphenylene derivatives such an assumption has been confirmed through birefringence measurements[8]). In the hexagonal phase, the molecular director can take at least six orientations, assuming a non polar $P6/mmm$ symmetry, and lies in a site of six-fold symmetry as shown in Figure 2a.

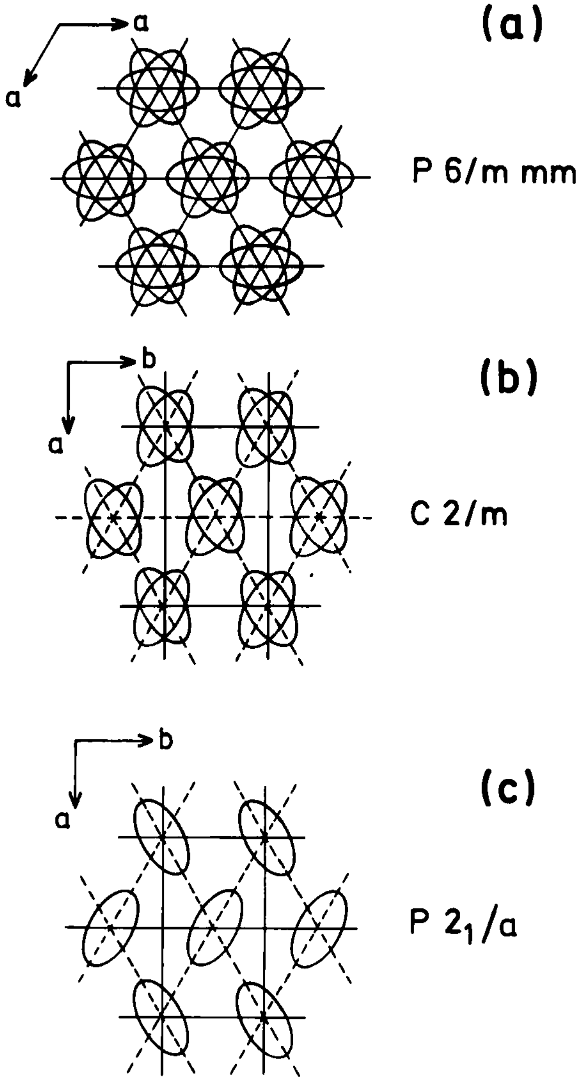


FIGURE 2 The structure of the three columnar mesophases of the truxene derivatives.

The molecules are almost circular but they stack in a tilted fashion giving columns with elliptical cross-sections. The tilt angle is the same in all three mesophases.

The highest temperature, D_{hd} mesophase has *P6/mmm* symmetry. Each column lies is in a site of six-fold symmetry and has six possible orientations (taking into account the tilted stacking). The column axes lie on a perfect hexagonal lattice. The intense sharp ring in the diffraction pattern arises from the three symmetry-equivalent reflections of the 1010 type indicated.

In the D_{rd}(*C2/m*) phase the columns lie in a centred rectangular lattice where each column has two alternative orientations related by a mirror plane (which is vertical in this sketch). The lattice no longer has hexagonal symmetry, but the distortion is small. The pseudo-hexagonal packing is shown by dashed lines.

In the D_{rd}(*P*2_1/*a*) phase the columns lie in a primitive (uncentred) rectangular lattice. Each column has only one possible orientation.

Note: the arrows give the direction of lattice axes.

In the case of the C_8HATxS derivative, the powder patterns of all three mesophases can be indexed in terms of hexagonal lattices where:

a = 50.27 Å at 164°C for the lowest temperature columnar mesophase

a = 25.32 Å at 183°C for the next mesophase

a = 25.70 Å at 210°C for the last columnar mesophase

Although the optical textures and miscibility studies clearly indicate that the two low temperature columnar lattices have monoclinic symmetry, the column axes lie on a hexagonal lattice which is only slightly distorted. This distortion expressed as

$$\frac{d_{110} - d_{200}}{d_{110}}$$

is actually less than 1‰ for the $P2_1/a$ lattice and 3‰ for the $C2/m$ lattice (Table II).

It is rather surprising that twofold symmetry of the monoclinic phases occurs for

TABLE II

Assignment of the observed lattice spacing for the two compounds C_8HATxS and C_{14}HATxS

	C_8HATxS			C_{14}HATxS		
$D_{rd(P21/a)}$	Measured	Calculated	Plane	Measured	Calculated	Plane
	21.81	21.82	110	26.50	26.48	110
	—	—	200	26.06	26.06	200
	16.47	16.49	210	19.88	19.88	210
	12.62	12.60	020	15.37	15.37	020
			310	—	15.12	310
				13.26	13.24	220
	T = 164°C a = 43.64 Å b = 25.19 Å			T = 102°C a = 52.12 Å b = 30.74 Å		
$D_{rd(C2/m)}$	Measured	Calculated	Plane	Measured	Calculated	Plane
	21.87	21.93	110	27.35	27.35	200
	—	—	200	25.76	25.76	110
	12.69	12.66	020	—		
	T = 183°C a = 43.85 Å b = 25.32 Å			T = 118°C a = 54.7 Å b = 29.20 Å		
D_{hd}	Measured	Calculated	Plane	Measured	Calculated	Plane
	22.26	22.26	100	26.50	26.64	$10\bar{1}0$
				15.44	15.39	$11\bar{2}0$
				13.65	13.32	$20\bar{2}0$
	T = 210°C a = 25.70 Å			T = 132°C a = 30.77 Å		

a structure consisting of columns that are nearly circular. Moreover, by increasing the chain length, the ellipticity of the column cross-section is increased. If the tilt angle is constant, the anisotropy of a column is then a function of the libration amplitude of the director around the column axis and this amplitude increases with temperature. The intrinsic anisotropy of the column cross-section is the cause of the quadrupolar (or staggered dipolar) interaction between the columns which leads to the $P2_1/a$ space group, as the lowest energy state (cf. Figure 2c). Since dipolar forces decrease with distance, the interaction is greater for short chain derivatives than for long chains derivatives; consequently the $P2/_1a$ configuration is stable at higher temperatures and with the weaker anisotropy in the columnar section of short chain derivatives.

The occurrence of an intermediate state with a $C2/m$ symmetry is quite surprising. The $P2_1/a$ – $C2/m$ transition would be regarded as an order-disorder transition induced by a critical growth of stacking faults (Figure 2b). This assumption agrees with the poor number of observed reflections for the $C2/m$ phase. Unfortunately however, since we have not been able to obtain single domains of the columnar phase, we cannot test this hypothesis.

Let us remark that this order-disorder transition occurs with modification of the pseudo-hexagonal array at least for the C_{14}HATxS compound. In the diffraction pattern of the $C2/m$ phase, it is the *outer* ring of the 110/200 doublet which is the more intense, but in the diffraction pattern of $P2_1/a$ phase, it is the inner ring which is the stronger. This inversion in the intensities could correspond either to a dramatic difference between the structures of the columns of the two phases or to an inversion of the ordering relation between d_{110} and d_{200} ($d_{110} \lesseqgtr d_{200}$). In this last case, the more intense ring would correspond to the 110 reflections in both phases, in agreement with the fact that there are four 110 reflections and only two 200 reflections. Therefore the two rectangular phases are derived from the hexagonal lattice by distortions in opposite senses—the original hexagonal lattice being elongated along the a axis in one case and compressed in the other. For the C_8HATxS compound, the splitting is so small that we do not know the sense of the distortion in the two rectangular phases.

Different kinds of competitive effects act upon the polymorphism of different members of the series: the strength of the interaction between neighbouring columns, the intensity and the sense of the anisotropy of the pseudo-hexagonal array. Bearing in mind the odd-even effect and the way in which the transition temperatures vary with n, it is possible that the intermediate compounds (where n = 9,10,12) only show the $D_{rd}(P2_1/a)$ phase.

HEXA-n-BENZOYLOXYTRITHIATRUXENES (HBTxS)

We have synthesized four homologues of this series: transition temperatures and enthalpies are given in Table III. They exhibit between the crystal and the isotropic phase only a fluid phase with a threaded texture characteristic of a N_D nematic phase. This result is a little bit surprising, because the hexa-n-alkoxybenzoyloxy-

TABLE III

Thermodynamic data for the compounds HBTxS

Compounds		K_1	N_D	I
$C_{10}HBTxS$	*T*	• 83	• > 300	•
	ΔH	8.7		
$C_{12}HBTxS$		• 81	• 295	•
		2.4		
$C_{13}HBTxS$		• 86	• 280	•
		0.2		
$C_{16}HBTxS$		• 96	• 241	•
		0.2	≃ 0	

T: transition temperatures (°C)
ΔH: transition enthalpies (kcal, mol^{-1})

truxene (C_nHBTx) series leads,[4] as previously reported, to a rich columnar polymorphism. For example:

* $C_{13}HBTx$ (hexa-*n*-tridecanoxybenzoyloxytruxene)

$$K \rightarrow N_D \leftrightarrows D_{rd}(C2/m) \leftrightarrows D_h \leftrightarrows I$$

$$\nwarrow \quad \nearrow\swarrow$$

$$[D_{rd}(P2_1/a)]$$

However, benzoate groups appear to favour the formation of nematic discoid phases, and the first example of N_D re-entrance in a pure compound was observed for a benzoate derivative[4]:

* $C_{11}HBTx$(hexa-*n*-undecanoxybenzoyloxytruxene)

$$K \leftrightarrows D_{rd}(P2_1/a) \leftrightarrows N_D \leftrightarrows D_{rd}(C2/m) \leftrightarrows N_D \leftrightarrows I$$

The N_D nematic phase is stable over an appreciable range of temperature (> 220°C for $C_{10}HBTxS$). We have also observed this behaviour in the C_nHBTx series for aliphatic chains up to $n = 8$, even though higher homologues form columnar phases. For the C_nHBTxS series, the crystal-N_D transition involves surprisingly low enthalpy change. The crystalline solids have a marbled texture similar to that of the N_D phase (although they are rigid) and X-ray diffraction photographs show that the samples are poorly crystalline with the paraffinic chains still in a disordered conformation.

CONCLUSION

The synthesis of two new series of discotic mesogens derived from the truxene core have enabled us to confirm the expected mesomorphic properties that would be promoted by this core.

—The alkanoyloxy series (C_nHATx, C_nHATxO, C_nHATxS) favor a rich polymorphism and in all cases exhibit the inverted sequence N_D phase—columnar phase. The relative thermal stabilities of the N_D phases can be explained in terms of the relative steric hindrances of CH_2, S and O, because the order followed is $C_nHATx > C_nHATxS > C_nHATxO$. It will be interesting to extend this investigation and synthesize new cores where methylene bridges of truxenes are replaced, for example, by N—CH_3, C=O, CH—CH_3. No doubt these new molecules will lead to a rich and diverse polymorphism.

Finally, concerning the C_nHBTx and C_nHBTxS series, bulky chains appear to favour the formation of the N_D phase and are apparently not compatible with columnar polymorphism, especially for the CnHBTxS series.

Acknowledgements

The authors are indebted to Dr. G. DURAND for fruitful discussions and helpful comments.

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