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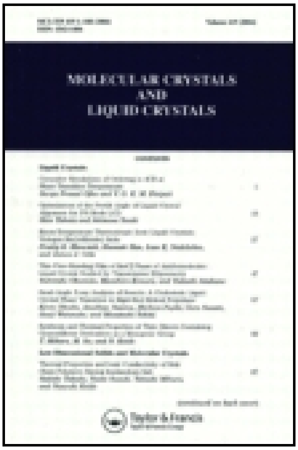

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
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Trioxatruxenes: A New Family of Disc-Like Mesogens with a Complex Polymorphism

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Version of record first published: 20 Apr 2011.

To cite this article: Christian Destwde , Nguyen Huu Tinh , Lonka Mamlok & Jacques Malthete (1984): Trioxatruxenes: A New Family of Disc-Like Mesogens with a Complex Polymorphism, Molecular Crystals and Liquid Crystals, 114:1-3, 139-150

To link to this article: http://dx.doi.org/10.1080/00268948408071705

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Mol. Cryst. Liq. Cryst.,, 1984, Vol. 114, pp. 139-150
0026-8941/84/1143-0139/$20.00/0
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TRIOXATRUXENES : A NEW FAMILY OF DISC-LIKE MESOGENS WITH A COMPLEX POLYMORPHISM

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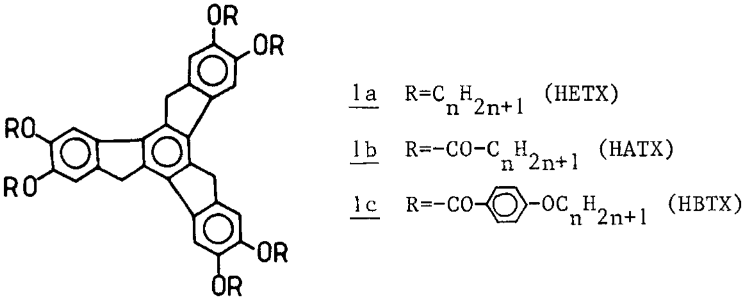
Abstract A homologous series of hexa-n-alkanoyloxytrioxatruxenes has been prepared with n=7 to n=15 in order to check the influence upon the mesomorphic properties exerted by the substitution of the three methylenes of the truxene core by oxygen atoms. Interphase transitions between solid, mesomorphic and isotropic phases were studied by hot stage microscopy and DSC. One of the homologs ($R=C_{13}H_{27}CO-$) was previously identified by X-Ray investigations and used as the reference substance to confirm the structure of the various mesophases by contact method. A new example of the socalled *inverted sequence* (crystal-N_D nematic-D columnar-isotropic) and several examples of the new *oblique* disordered columnar phase (D_{obd}) are reported. Trioxatruxenes can be quoted as able to exhibit the most complex polymorphism found in disc-like liquid crystals with the sequence : $K - N_D - D_{obd} - D_{rd} - D_{hd} - I$.

INTRODUCTION

In the new field of disc-like mesogens[1], the hexasubstituted truxene derivatives 1 had been already indicated worth of interest for their own polymorphism character[2]. The hexa-n-alkoxytruxenes 1a present only one mesophase (hexagonal ordered columnar D (D_{ho}) in a fairly large temperature range[3]), whereas the hexa-n-alkanoyloxytruxenes 1b revealed the existence of



1a R=C_nH_{2n+1} (HETX)

1b R=$-CO-C_nH_{2n+1}$ (HATX)

1c R=$-CO-$◯$-OC_nH_{2n+1}$ (HBTX)

1

the so-called *inverted sequence*[2] (crystal - N_D nematic - D columnar - isotropic). For example with 1b, n=9, the following sequence was observed :

$$K \xrightarrow[5.1]{68°} N_D \underset{.24}{\overset{85°}{\rightleftharpoons}} D_{rd(P2_1/a)} \underset{\sim 0}{\overset{138°}{\rightleftharpoons}} D_{ho} \underset{\textit{decomposition}}{\overset{280°}{\rightleftharpoons}} I$$

(K= crystal; N_D= lenticular nematic phase[1,4]; $D_{rd(P2_1/a)}$= rectangular disordered columnar phase with the $P2_1/a$ plane space group symmetry[1,5]; enthalpy values are given in italics (Kcal.mol^{-1}). Furthermore, it was found within this series that longer homologs provide a first example of a reentrant hexagonal disordered columnar phase (D_{hd})[6]. For example, 1b, n=13 :

$$\begin{tikzcd} K \arrow[r, "61°"] & N_D \arrow[r, shift left, "84°"] \arrow[dl, shift left, "56°"] & D_{rd(P2_1/a)} \arrow[l, shift left] \arrow[r, shift left, "112°"] & D_{hd} \arrow[l, shift left] \arrow[r, shift left, "241°"] & I \arrow[l, shift left] \\ D_{hd} \arrow[ur, shift left] & & & & \end{tikzcd}$$

Finally some hexa-n-alkoxybenzoyloxytruxenes (1c) displayied the reentrant N_D nematic sequence. In the case of 1c, n=11 it has been reported the following thermal profile[7,8] :

$$K \xrightarrow{90°} D_{rd(C2/m)} \overset{137°}{\rightleftharpoons} N_D \overset{171°}{\rightleftharpoons} D_{rd(P2_1/a)} \overset{274°}{\rightleftharpoons} N_D \overset{297°}{\rightleftharpoons} I$$

Up to now, contrary to rod-like systems for which theoretical investigations have been extensively developped[9], no

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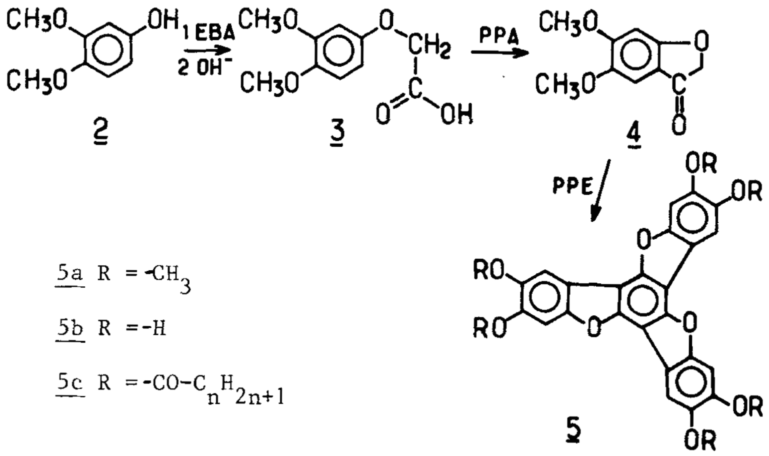
molecular or theoretical interpretation of these inverted or reentrant phenomena have been proposed for disc-like mesogens.

In order to obtain some more information about the intermolecular interactions between the various chemical parts of the truxene core and substituents, we have prepared an homologous series of hexa-n-alkanoyloxytrioxatruxenes 5c (CnHATXO by short) in which the three methylene bridges of truxene have been replaced by oxygen atoms.

SYNTHESIS



5a R = $-CH_3$

5b R = $-H$

5c R = $-CO-C_nH_{2n+1}$

SCHEME 1. Synthesis of hexa-n-alkanoyloxytrioxatruxenes.

Hexa-n-alkanoyloxytrioxatruxenes 5c were prepared starting from commercial 3,4-dimethoxyphenol 2 which was transformed into acid 3 by reacting with ethyl bromoacetate (EBA) followed by saponification. By action of polyphosphoric acid (PPA) 3 was converted to 3,4-dimethoxy-2H-benzofuran-3-one 4 which by reaction with ethyl polyphosphate (PPE) led to hexamethoxytrioxatruxene 5a. 5a was demethylated by means of pyridinium hydrochloride into 5b which was immediately condensed with the required acid chloride to give 5c. The hexaester was then purified by chromatography on silica gel and recrystallization from absolute ethanol. Purity of samples was checked by thin layer chromatography and elemental analysis.

IDENTIFICATION OF THE MESOPHASES

One derivative of the CnHATXO series (5c, n=13) was previously studied by X-Ray diffraction[10] and used in the present work as the reference substance. This compound exhibits the following sequence:

$$K \xrightarrow[\mathit{22.3}]{74°} N_D \xrightleftharpoons[\mathit{0.3}]{58°} D_{obd} \xrightleftharpoons[\mathit{0.1}]{71°} D_{rd(P2_1/a)} \xrightleftharpoons[\mathit{0.03}]{158°} D_{hd} \xrightleftharpoons[\mathit{0.6}]{166°} I$$

(D_{hd} = hexagonal disordered columnar phase; D_{obd} = new columnar phase indexed as an oblique disordered columnar phase[10] in which the columns are arranged in an oblique two-dimensional lattice as represented in figure 1; enthalpy values are given in italics (Kcal.mol^{-1}).

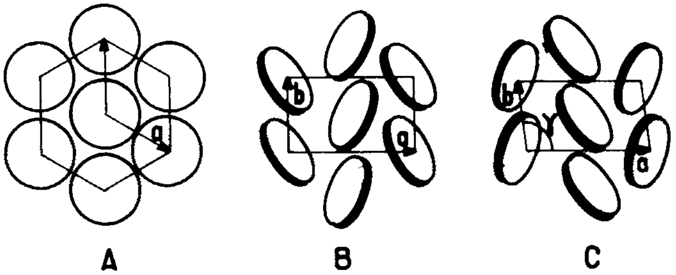


FIGURE 1. Schematic picture of the three columnar lattices. A = hexagonal (a=30Å at θ=160°C); B = rectangular with the $P2_1/a$ plane space group symmetry (a=49.2Å, b=29.3Å at 76°C); C = oblique (a=49.7Å, b=28Å, γ=97.5° at 68°C.

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The various mesophases of the series were identified by studying their miscibilities with those of the reference substance and through the observation of their optical textures performed with a polarizing microscope. The results are listed in table I

TABLE I. Transition temperatures of the hexa-n-alkanoyloxytrioxatruxenes 5c (°C).

$R=C_nH_{2n+1}CO-$	K	N_D	D_{obd}	D_{rd}	D_{hd}	I
n						
7	. 96	[. 89]	-	. 194	-	.
8	. 90	[. 75]	-	. 197	-	.
9	. 82	[. 67.5]	-	. 192	-	.
10	. 76	[. 61.5]	-	. 194	-	.
11	. 78	[. 58]	[. 64]	. 184	-	.
12	. 78	[. 59]	[. 64]	. 172	. 177	.
13	. 74	[. 58]	[. 71]	. 158	. 166	.
15	. 80	[. 60]	. 84	. 138	. 152	.

[ ] = monotropic transition

All the derivatives exhibit the fluid N_D nematic phase, the texture of which (Fig.2a) is in every way similar to that of the common nematic phase but usually with a marbled texture when observed between glass slides.

The $D_{rd(P2_1/a)}$ columnar phase is also present in the whole series but, as previously reported[1,4], it is rather difficult to assign typical textures to this phase. Nevertheless the transition $D_{hd} - D_{rd}$ is somewhat significative for the identification of those last (compare Fig. 2b and 2c) ; usually concentric or a portion of concentric rings occur like in triphenylene hexaalkanoates[1,4]. Anyway, at lower temperature (Fig. 2d), it appears also with a mosaïc texture.

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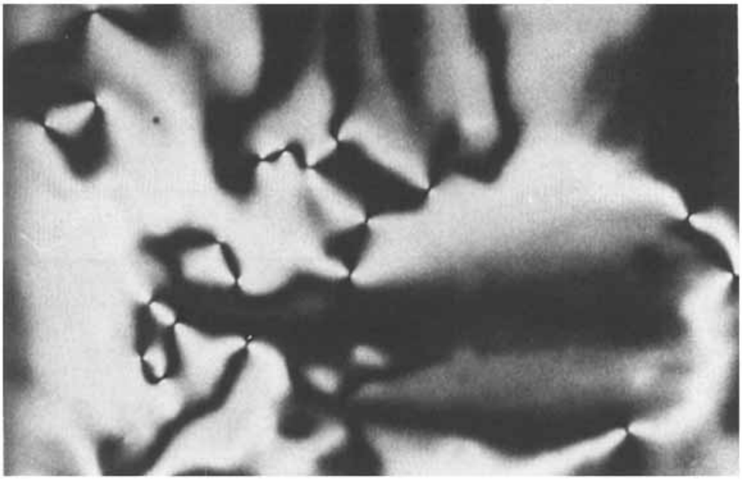
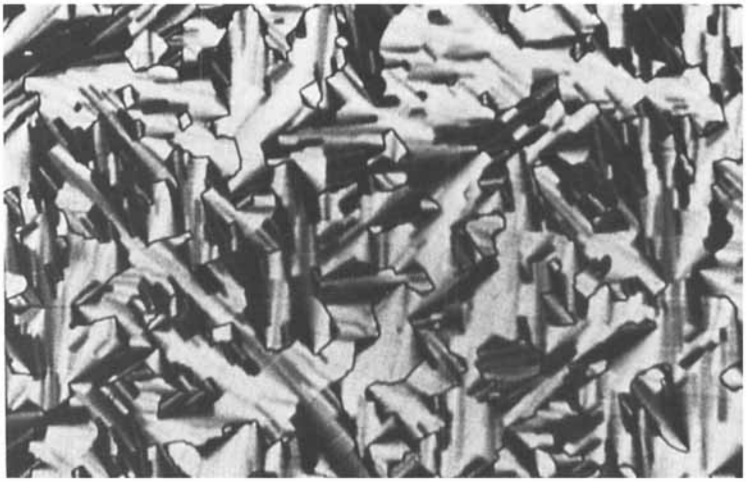


(2a)



(2b)

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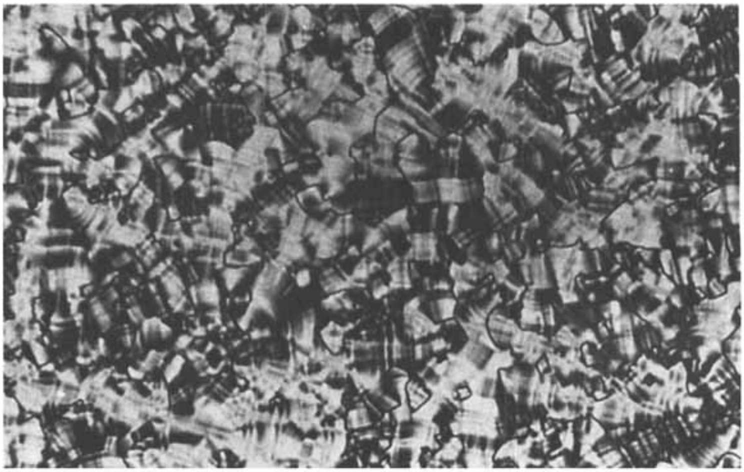

(2c)

(2d)

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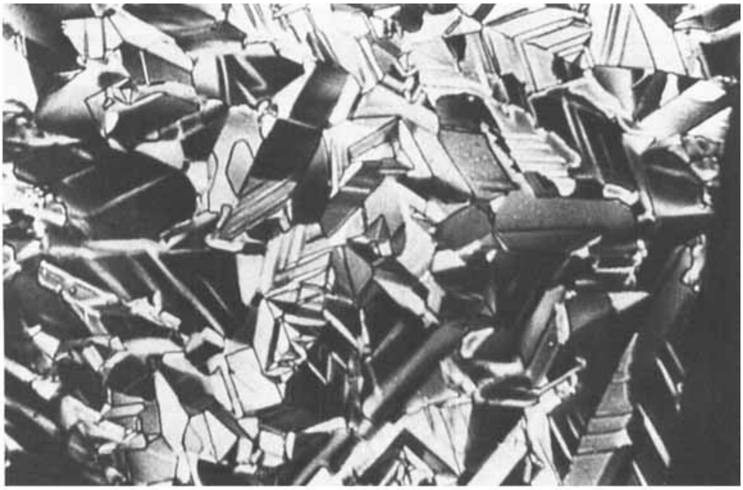

(2e)

FIGURE 2. Optical textures of 5c derivative ($R=C_{13}H_{27}CO-$) : (2a), N_D nematic phase at 55°C; (2b), D_{hd} columnar phase at 163°C; (2c), D_{rd} columnar phase at 144°C; (2d), D_{rd} columnar phase at 75°C; (2e), D_{obd} columnar phase at 63°C.

The transition D_{rd} - D_{obd} is rather obvious under microscope with an evident increase of the birefringence. Otherwise the textures of the two phases are roughly similar but the oblique phase appears much more striated (compare Fig.2d and Fig.2e).

On the contrary the identification of the D_{hd} hexagonal columnar phase is obvious with large homeotropic areas and fan-shaped or focal conic birefringent defects (Fig.2b).

DISCUSSION

The mesomorphic behaviour of the two series : hexa-n-alkanoyloxy truxenes 1b or trioxatruxenes 5c are to some extent

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similar, with in both cases the same inverted sequence : N_D nematic - $D_{rd(P2_1/a)}$ transition on *heating*. This complex polymorphism can be obviously connected with the presence in the two series of six bulky carboxylate substituents leading through their steric hindrance to a rather rich columnar arrangements. On the contrary the hexa-n-alkoxytruxenes lead *only* to a D_{ho} hexagonal ordered arrangement obviously connected with low steric hindrance of the ether linkage. This allows a strong cohesion between the central cores and so enhances the regular packing along the columns (intercore distance = 3.6Å)[3].

The substitution of the three methylenes of the truxene by oxygen atoms leads to interesting modifications of the mesomorphic properties of the corresponding non oxygenated compounds. The appearance of the new oblique columnar phase cannot be however clearly interpreted on a molecular basis. Nevertheless this new series of compounds provid other peculiar behaviours especially for samples with n=11 to n=15. The D_{rd} temperature range is in fact gradually reduced by the appearance at high temperature of the D_{hd} hexagonal phase, and at low temperature by the appearance of the D_{ob} oblique columnar phase (Table I). Moreover the sample with n=15 is of a special interest for some physical investigations because all the columnar phases are enantiotropic on a relatively low temperature range.

CONCLUSION

The results obtained in the thermooptical characterization of a series of hexa-n-alkanoyloxytrioxatruxenes allow to stress conclusions that hopefully will stimulate some further investigation on :

- Theoretical or semi-emperical calculations on the intra and intercolumnar organization in order to shad some light on the origin of the inverted sequence...
- Physical and structural investigations on the oblique columnar phase and new sequence D_{obd} - D_{rd} . Moreover trioxatruxenes are colourless, chemically stable mesomorphic in a relatively low temperature range.

EXPERIMENTAL

3,4-Dimethoxyphenol and ethyl bromoacetate were obtained from Aldrich Chemical Company. Spectral data were collected using a Perkin-Elmer 225 (ir) and a Bruker 270 (nmr) internal TMS standard. The elemental analysis was obtained from Service Central d'Analyse (CNRS).

3,4-Dimethoxyphenoxyacetic acid 3

A well stirred mixture of 3,4-dimethoxyphenol 2 (20g; 0.13 mol), potassium carbonate (68g), ethyl bromoacetate (26ml; 0.23mol) and 520ml acetone was refluxed for 90min. The solvent was then removed and the residue treated with a 2x200ml portion of absolute ethanol to remove most of the ethyl bromoacetate. The crude obtained ester was saponified with 10g KOH in 300ml ethanol (reflux, 150min). The reaction mixture was cooled, treated with crushed ice and 140ml conc. H_2SO_4 and extracted with ether (3x300ml). The organic layer was washed with water, dried over Na_2SO_4 and evaporated off. The crude acid was purified by chromatography on silica gel using a benzene 60%/ether 40% v/v mixture as eluant. Recrystallization from benzene/heptane mixture afforded 10.5g of colourless acid 3 (38%) m.p. 116°C.

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3,4-Dimethoxy-2H-benzofuran-3-one 4

92g of P_2O_5 and 63ml of 85% H_3PO_4 were stirred at 110°C for 90min. 9.5g acid 3 was then added to the clear polyphosphoric acid and stirred around 110°C for 30min. Crushed ice and excess of water was added to the cooled mixture, extracted with 3x300ml ether and the solvent removed. Chromatography on silica gel with a benzene 95%/ether 5% v/v mixture as eluant afforded 4.5g of pure yellow benzofuranone 4 (55%) m.p.170°C.

Hexamethoxytrioxatruxene 5a

A stirred mixture of PPE[11] and 4.5g of 4 (0.025mol) was heated at 140°C for 25min. Excess of water was added to the cooled reaction mixture and the trimerization product extracted with 3x200ml $CHCl_3$. The organic layers were dried on Na_2SO_4 and the solvent removed to give 7g of dark solid. The solid was washed with 100ml of hot ethanol, then with 50ml of cold CH_2Cl_2 and afforded 1.9g of the required hexamethoxytrioxatruxene 5a (46%).

Hexahydroxytrioxatruxene 5b and Hexa-n-alkanoyloxytrioxatruxenes 5c

A stirred mixture of 5a (1g) and 15g of pyridine hydrochloride was heated at 240°C for 30min under dry nitrogen. Water with some ml of conc.HCl was added to the cooled mixture, quickly filtered, dried under vacuo (0.6g, 50%) and condensed as soon as possible with the required acid chloride (2.7g of tetradecanoyl chloride, for instance) in dry pyridine (6ml) for 48h at room temperature. The reaction mixture was hydrolyzed with ice and conc.H_2SO_4, filtered, washed with water and the resulting paste was dissolved into diethyl ether. The organic solution was dried over Na_2SO_4 and the solvent removed. Crude 5c was then purified by chromatography on silica gel (benzene) and recrystallized from absolute ethanol to afford 0.6g of white powdered 5c (40%).

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