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Hexaalkoxytruxenes, A New Series of Disc-Like Mesogens†

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An homologous series of hexa-*n*-alkoxytruxenes has been prepared with values of *n* from 6 to 14. Interphase transitions between solid, mesomorphic and isotropic phases were studied by hot stage microscopy and differential scanning calorimetry. X-ray diffraction measurements showed that all of the mesophases were of the same type; a hexagonal ordered columnar phase (D_{ho}), with an unusually large temperature range. Systematic X-ray studies were performed with respect to temperature and chain length.

I. INTRODUCTION

Two different motivations led us to synthesize a new series of truxene derivatives[1,2]: first, it was interesting to verify that the presence of not very bulky substituents (such as alkoxy chains) leads to the formation of the *h*exagonal *o*rdered columnar phase (D_{ho}).[3] Secondly, we wished

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to check whether the truxene core always gave an inversion in the sequence of mesophases: K N_D D_r D_h I, rather than the usual K D_r N_D I sequence.

II. RESULTS

1. Preparation

The synthesis of 2,3,7,8,12,13 hexa-*n*-alkoxytruxenes **1a** *via* hexahydroxy-truxenes **1b** was ruled out because the corresponding Na or K salt was very unstable. We therefore chose to prepare the compounds **1a** *via* the trimerization of 5,6-di-*n*-alkoxy-1-indanone **2** following the scheme **1**.

The chains were attached in the first step to 3,4-dihydroxyhydrocinnamic acid **4**; then the cyclization of the acid **3** was performed in PPA leading to the indanones **2**, the trimerization of which afforded the corresponding truxenes **1a**.

2. Mesomorphic properties

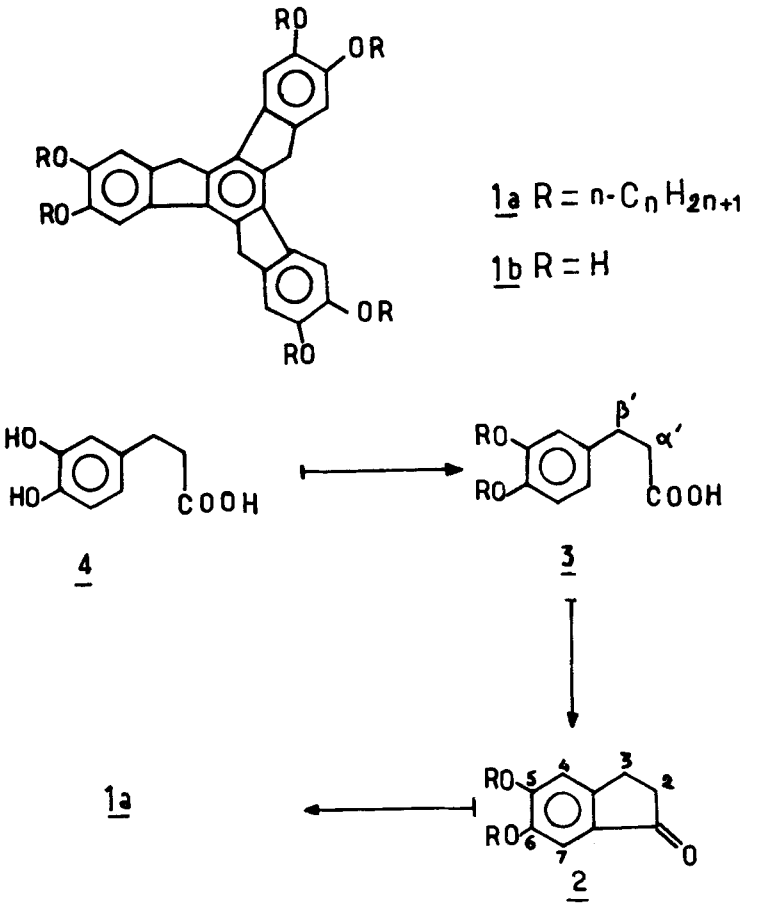
The transition temperatures and enthalpies of compounds **1a**, determined by using a DSC (Dupont 990) are given in Table I. The textures were observed with a polarizing microscope equipped with a heating and cooling stage (Mettler FP5). Only one D columnar phase was observed with all the compounds. The optical textures showed that this phase was uniaxial: on cooling the isotropic liquid, islands of the mesophase grew as small homeotropic hexagons which then developed into digitated stars[5,6,7]: this texture is typical of a hexagonal ordered columnar phase D_{ho}.[8]

Note that there is an unusually large temperature range (230°) for compound **1a** R = C_7H_{15}. A similar wide range was observed with a phthalocyanine derivative[9] (> 250° for compound **5**).

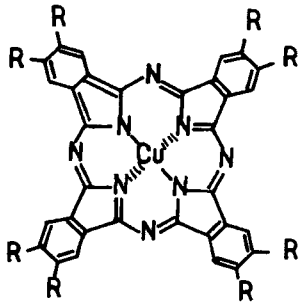
This behaviour seems to be associated with the large diameter of the disk-like molecular core.[8] We also notice a marked fall in the clearing point temperature with chain length which occurs for chains longer than C_9.

3. X-Ray measurements

3.1 Experiment description. In our experiments we compared the patterns of all hexa-*n*-alkoxytruxene derivatives. The X-ray patterns were obtained with partially oriented samples contained in a



SCHEME 1 Synthesis of 2,3,7,8,12,13 hexa-*n*-alkoxytruxenes.



5 : R=$C_{12}H_{25}OCH_2$–

Lindemann glass tube (1.5 mm diameter), aligned with a 1.7 T magnetic field perpendicular to the glass tube axis. Therefore the axis of the columns can be aligned in any direction perpendicular to the magnetic field. The X-ray beam (monochromatic Cu K_α) is perpendicular to the magnetic field and to the tube axis and thus we can detect the ordering inside a column along the vertical axis of the film.[10-12]

3.2 Pattern description of hexagonal ordered columnar phase D_{ho}. In the diffraction patterns we can observe three features related to different aspects of the structure of columnar phases:

—the regularly spaced columns: intercolumnar distance (a) gives rise to some narrow rings at the lower angles. In this case the shape of unit cell corresponds to a hexagonal lattice.

—the diffuse ring corresponding to the disordered paraffinic chains is observed at angles corresponding to an average spacing of 4.5 Å.

TABLE I

Transition Temperatures and Enthalpies of Hexa-*n*-alkoxytruxenes

R		K_1	K_2	D_{ho}	*I*
C_6HETX	*T*	75°	79°	> 300°	
	ΔH	11.3	4.2		
C_7HETX	*T*	70°	—	> 300°	
	ΔH	15.4	—		
C_8HETX	*T*	66°	86°	> 300°	
	ΔH	17.5	10.4		
C_9HETX	*T*	58°	67°	274°	
	ΔH	19.1		2.9	
C_{10}HETX	*T*	61°	67°	260°	
	ΔH	19.5	8.2	1.5	
C_{11}HETX	*T*	56°	64°	*	
	ΔH	15.3	8.6		
C_{12}HETX	*T*	67°	73°	230°	
	ΔH	21.6	11	1.0	
C_{13}HETX	*T*	50°	59°	*	
	ΔH	21	12		
C_{14}HETX	*T*	60°	75°	205°	
	ΔH	29	17.5	1.45	

T temperature (Celcius)
ΔH enthalpy (kcal/mol)
K_1 crystalline phase
K_2 crystalline phase
D_{ho} hexagonal ordered columnar phase
· the phase exists
— the phase does not exist
* decomposition of sample ~ 220°

—the presence of an intense and sharp ring at larger angles depends on the intercore stacking distance within the column. When we can see this reflection the hexagonal columnar phase is ordered (D_{ho}) (lattice parameters Figure 1).

3.3 Inter columnar distances (a). We have studied the variation of intercolumnar distance with respect to the chain length at three different temperatures (80°, 140° and 200°C). Note that this value is inversely proportional to the diameter of the first ring.

As one would expect, the intercolumnar distance increases with both chain length and temperature: on an average 1 Å for one additional CH_2 unit and 0.5 Å for 60°C increase (Figure 2).

3.4 Inter core distances (c). We observe a very slight increase of the intercore distance with temperature and chain length (Figure 3). For example, in the case of the compound **1a** ($R = C_{10}H_{21}$), the distance is: 3.60 Å at 80°C, 3.62 Å at 140°C, 3.64 Å at 200°C, and with compound **1a** ($R = C_{12}H_{25}$): 3.61 Å at 80°C, 3.62 Å at 140°C, 3.65 Å at 200°C.

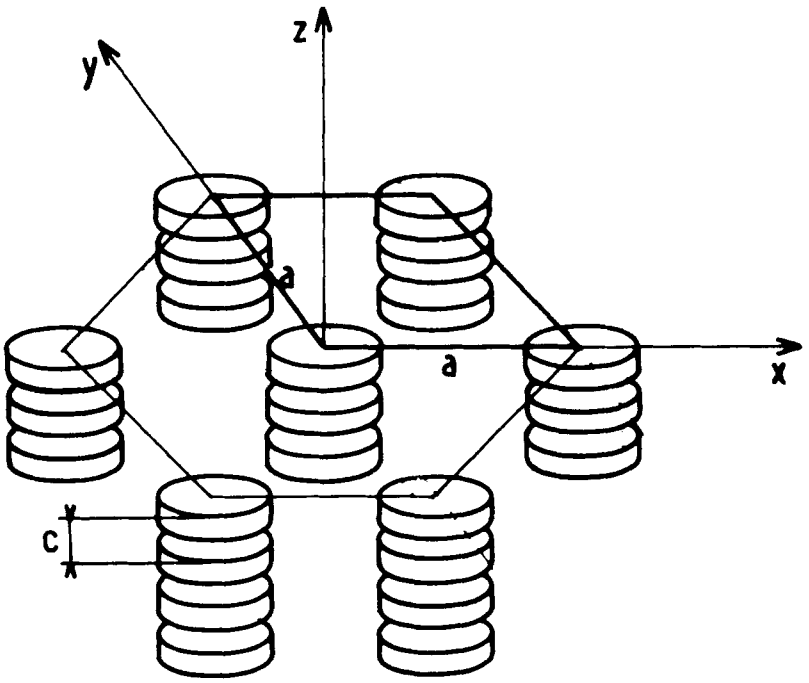


FIGURE 1 Lattice parameters of the D_{ho} hexagonal ordered columnar phase.

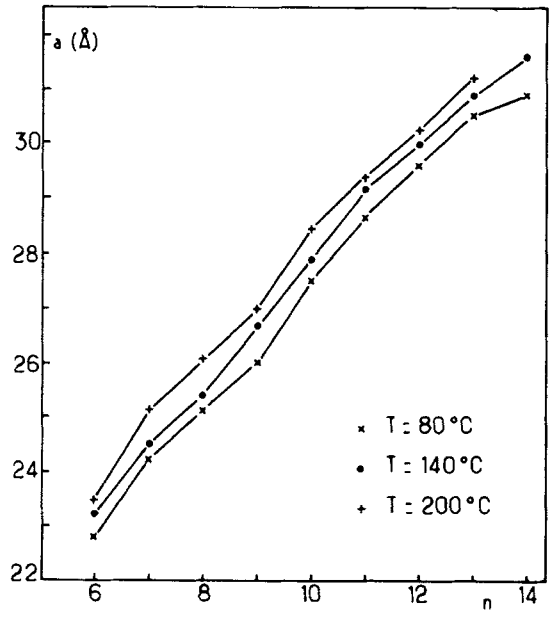


FIGURE 2 Plot of inter-columnar distances (a) against temperatures and n, the number of carbon atoms in the alkoxy chain.

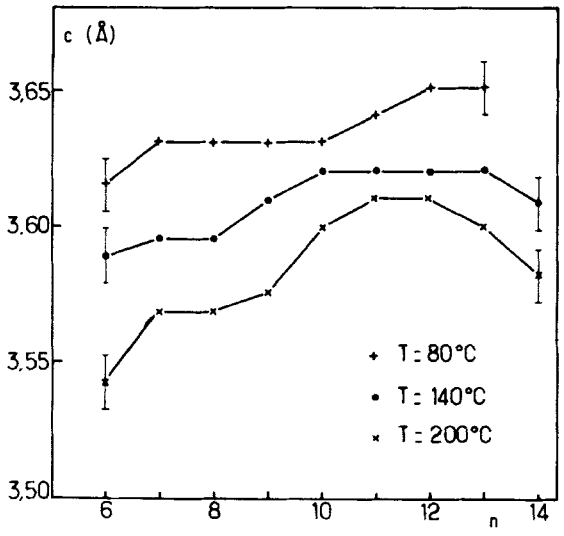


FIGURE 3 Plot of inter-core distances (c) against temperature and n, the number of carbon atoms in the alkoxy chain.

3.5 Volume and density of lattice. We observed a linear increase of the lattice volume with chain length and a slight increase with temperature (Figure 4). In fact the density decreases as the number of carbon atoms increases. From these variations we can obtain information about the core and chain conformations.

The linear increase of the lattice volume implies a constant increment of volume per added methylene group and the decreasing density occurs because the alkyl chains have a lower density than the core (Figure 5)

$$\text{Volume } V\text{: } \frac{\sqrt{3}}{2} a^2 c \text{ Å}^3$$

$$\text{Density: } \rho = \frac{M}{\mathcal{N} V 10^{-24}} \text{ g/cm}^3$$

M: molecular weight

$\mathcal{N}$: Avogadro number

If R_n is the radius of a column for the nth homologue, V the mean volume per CH_2 group, and c the core to core distance inside a column:

$$R_n^2 = R_0^2 + \frac{6nV}{\pi c}$$

where R_0 is the core radius, and the excess volume of the terminal methyl group over that of a methylene unit has been included in the core volume.

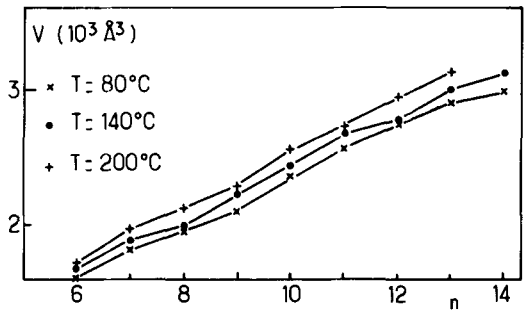


FIGURE 4 Plot of volume of lattice against temperature and n, the number of carbon atoms in the alkoxy chain.

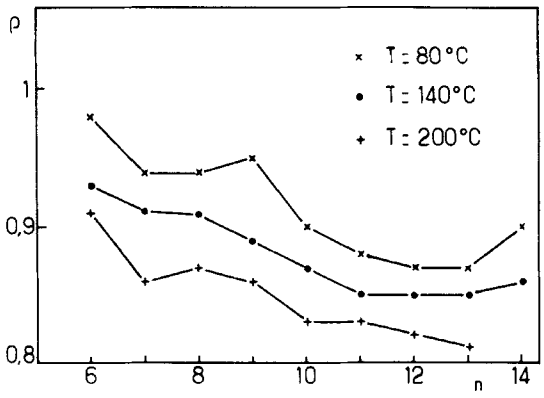


FIGURE 5 Plot of density of lattice against temperature and n, the number of carbon atoms in the alkoxy chain.

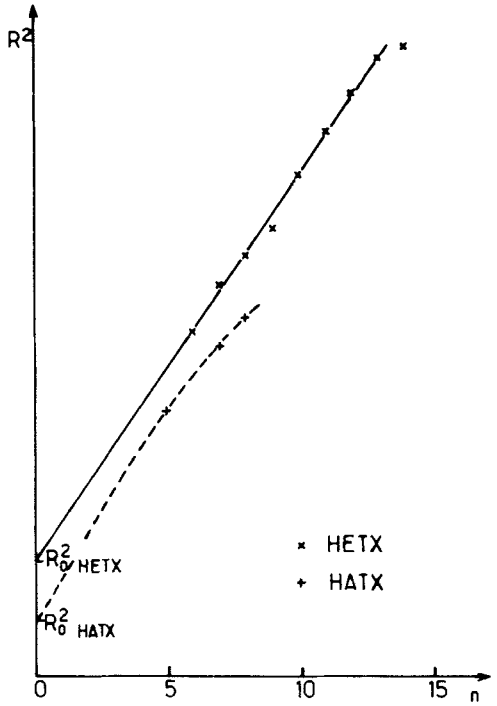


FIGURE 6 Plot of R_n, radius of a column, against n the number of methylene groups of the paraffinic substituent in the HATX and HETX series.

Figure 6 shows that a plot of R_n^2 *versus* n is linear and assuming that the core to core distance c is independent of n and equal to 3.58 Å at 80°C, one has $R_0 = 6.63$ Å and $V = 27.4$ Å^3. This value of R_0 is consistent with the core size and the methylene volume is 11% higher in the mesophase than in a crystalline paraffin (24) Å^3.[14] Therefore the mean paraffinic volume is consistent with the diffraction features showing that the aliphatic moities are in a molten state. Moreover the alkoxy derivatives of the triphenylene do not have the same behaviour[12]: the first methylene groups occupy a higher volume than the subsequent ones (Figure 6). The difference between the behaviour of the two kinds of discs is probably due to their respective core sizes. This distinction appears in the diffraction pattern: the diffuse ring at 4.5 Å is quasi-isotropic in the case of truxene derivatives and indicates appreciable orientational disorder of the aliphatic chains, while in the case of the hexapentyloxytriphenylene the ring is reduced to a pair of spots indicating a more ordered and therefore more rigid configuration of the chains. This point is extensively discussed in ref. 12.

3. Conclusion

The synthesis of an homologous series of hexa-*n*-alkoxytruxenes has provided a new family of disc-like mesogens with a single hexagonal ordered columnar phase D_{ho} with a fairly large temperature range. The existence of such a phase is probably connected with the low steric hindrance of the six ether linkages which allows a strong cohesion between discs, as has been previously observed in the triphenylene series.[3] As a matter of fact, although short chain hexaalkanoyloxytruxenes display a D_{ho} phase,[8] mesophases with disordered molecular columns are invariably obtained with corresponding long chain esters. Furthermore the so-called "inverted" sequence found in the truxene ester series[1] seems to be a consequence of the peculiar shape of the truxene core.[8]

4. Experimental

The infrared spectra were recorded using a Perkin Elmer 225 spectrophotometer and the NMR spectra with a Brucker 270 MHz; the purity of the products was checked by elemental analysis and thin layer chromatography.

4.1 (3,4-di-n-alkoxyphenyl)3'-propionic acids. **3**. All of the alkoxy derivatives were prepared following the same general procedure. We give the preparation of the octyloxy derivative **3** ($R = n - C_8H_{17}$) as an example.

A basic solution was prepared from potassium hydroxide (5 g) in ethanol (25 cm^3). After 3,4-dihydroxyhydrocinnamic acid, 4 (5 g, 0.03 mol) was added to this solution, the 1-bromooctane (17 g, 0.09 mol) was introduced, and the mixture was heated under reflux for 3 h. Then the ethanol was evaporated under reduced pressure. When cool, the reaction mixture was poured onto ice (200 cm^3) and concentrated hydrochloric acid (50 cm^3) and stirred. The organic layer was shaken with ether, and the extract washed with water, dried over sodium sulfate, and evaporated to dryness. (3,4-Dioctyloxyphenyl)3′-propionic acid was purified by chromatography on silica gel, using a benezene/ether solution (15/5) as eluant. (M_p 55 °C (65%)).

IR: large absorption (ν OH, around 3200 cm^{-1})
strong absorption (ν C = O of COOH, 1720 cm^{-1})
(ν C—O—Ar, 1240 cm^{-1})

NMR: ($CDCl_3$) δ: 0.9 ppm (t − 6 CH_3 of RO),
1.2 ppm (m − 20 CH_2 of RO),
1.8 ppm (m − 4 CH_2 β of RO),
2.57 ppm (t − 2 CH_2 β'),
2.88 ppm (t − 2 CH_2 α'),
3.9 ppm (t − 4 CH_2 α of RO),
5.7 ppm (S − 1 OH),
6.7 ppm (m − 3H in aromatic).

4.2 5,6-di-n-alkoxy-1-indanone **2**. A mixture of PPA (150 g) and (3,4-dioctyloxyphenyl)3′-propionic acid (10 g) was heated at 110° for $1\frac{1}{2}$h (the flask was always equipped with condenser and trap). After cooling the solution was poured over ice, the organic product was extracted into ether, and the extract washed and dried (anhydrous sodium sulfate). The solvent was evaporated and the residue purified by chromatography on silica gel. with benzene ether (20/10) as eluant. The yield was nearly 40%.

IR: ν C=O, 1690 cm^{-1}
Alkylation was confirmed through comparison of the IR spectra of **3** and **2**
(no-OH stretching, at 3200 cm^{-1} in spectrum **2**)

NMR: 1.2 ppm (t − 6 CH_3 of RO), 1.4 ppm (n − 20 CH_2 of RO), 1.85 ppm (m − 4 CH_2 β of RO), 2.67 ppm (t − 2 CH_2 (3)), 3.03 ppm (t − 2 CH_2 (2)), 4.06 ppm (t − 2 CH_2 α of RO (6)), 4.00 ppm (t − 2 CH_2 α of RO (5)), 6.86 ppm (S − 1 H (7)), 7.17 ppm (S − 1 H (4)).

4.3 Hexa-n-alkoxytruxenes **1.** A solution of PPE (50 g) and 5,6-dioctyloxy-1-indanone (2.10^{-1} mol) was heated at 140° for 15 minutes.[14] Then the mixture was poured onto ice (100 cm^3), extracted with ether and the extract dried over Na_2SO_4. The product was purified by chromatography on silica gel using benzene hexane (80/20) as eluant and finally recrystallized from ethanol. The yields ranged from 5 to 15%.

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