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Liquid Crystals

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Discotic liquid crystals Physical parameters of some 2,3,7,8,12,13-hexa(alkanoyloxy)truxenes. Observation of a re-entrant isotropic phase in a pure disc-like mesogen

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Discotic liquid crystals

Physical parameters of some 2,3,7,8,12,13-hexa(alkanoyloxy)truxenes. Observation of a re-entrant isotropic phase in a pure disc-like mesogen

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The synthesis of a new discotic mesogen, 2,3,7,8,12,13-hexa(octadecanoyloxy)-truxene is reported. This new compound has been studied using polarization microscopy, differential scanning calorimetry, small angle X-ray scattering and adiabatic calorimetry. The results are compared with those of two other truxene derivatives from the same series: 2,3,7,8,12,13-hexa(decanyloxy)truxene and 2,3,7,8,12,13-hexa(tetradecanoyloxy)truxene. Refractive index measurements have been performed on these three truxene derivatives as a function of temperature. A re-entrant isotropic phase has been observed in 2,3,7,8,12,13-hexa(octadecanoyloxy)truxene. This is the first report of such a phase in a pure mesogen. We also report measurements of the ratio of the Frank constants for splay and bend in the nematic regime of this new mesogen as a function of temperature using the magnetic Frederiks transition technique.

1. Introduction

Since the first discovery of disc-like liquid crystals [1], a great number of discotic mesogens based on a variety of central cores have been reported [2]. However a nematic mesophase with disc-like mesogens is still rather rare. Most of the discotic mesogens reported up till now exhibit one or more columnar phases. Only some derivatives of triphenylene and truxene [3], and possibly some trisubstituted benzenes [4], exhibit a nematic phase. 2,3,6,7,10,11-Hexabenzoyloxytriphenylenes exhibit a normal phase sequence [5] (crystal-columnar-nematic-isotropic); the nematic phase being reached at temperatures around 200°C. 2,3,7,8,12,13-Hexaalkanoyloxy [6] and 2,3,7,8,12,13-hexabenzoyloxytruxenes [7] exhibit a complex polymorphism and the complexity increases with increasing alkyl chain length. The normal sequence, found in the triphenylene derivatives, is reversed in these truxenes leading to a nematic phase at relatively low temperatures followed by one or more columnar phases at higher

temperatures. The existence of a low temperature nematic phase in these truxene derivatives affords an easy access to the study of the physical parameters of a nematic phase composed of disc-like molecules. Despite the existence of an easily accessible low temperature nematic phase no experimental work on the mechanical and thermal properties of the discotic nematic phase of truxene derivatives has been published. A few experimental results in this field have been reported for the nematic phase of some triphenylene derivatives [8, 9].

In search of a convenient synthesis of truxene derivatives we found only a brief description of a synthetic method used by Destrade *et al.* [7, 10]. In the present paper we give a detailed description of the synthesis of the truxene derivatives used in our experiments. We have studied the compounds 2,3,7,8,12,13-hexa(decanoxy)-, 2,3,7,8,12,13-hexa(tetradecanoxy)- and 2,3,7,8,12,13-hexa(octadecanoxy)-truxene [11].

2. Synthesis

The literature indicates [12, 13] that truxene is formed by the self condensation of indan-1-one (**1a**, figure 1). Treatment of indan-1-one with polyphosphate ethyl ester (PPE) at 80°C gives the parent truxene in a quantitative yield [14]. Applying the same procedure to the indanone derivative **1b** which, via **3b** and **3c**, is a precursor of the discotic mesogens **3d-f** (see figure 1), we only obtained the dimeric product **2b** (figure 1) [7, 10, 11]. Changing the reaction conditions revealed that substantial amounts of **3b** are formed only at temperatures exceeding 130°C (see table 1). (A temperature effect on the ratio of dimeric to trimeric product has

Table 1. Synthesis of 2,3,7,8,12,13-hexamethoxytruxene (**3b**) from 5,6-dimethoxy-indane-1-one (**1b**) (a).

Solvent, catalyst	$T/^\circ\text{C}$	Reaction-time/min.	Product per cent	
			2b	3b
(a) Polyphosphate ethyl ester (b)	20	390	3	0
	70	120	50	0
	130	45	56	0
	140	20	–	35–70 (c)
	160	20	–	50–90 (c)
(b) Dowtherm A, 10 mol % <i>p</i> -toluenesulphonic acid	170 (d)	20	0	0
	170 (e)	20	53	0
	260	15	–	27
	260	40	–	47
	260	45	–	49
	260	75	–	< 5 (f)
(c) Pyridine hydrochloride (b)	170–218 (g)	30	48 (h)	32 (h)
	218	30	32 (h)	48 (h)

(a) For reaction conditions see Experimental Section.

(b) This catalyst was also used as solvent.

(c) Yield depends on the quality of polyphosphate ethyl ester.

(d) No catalyst was used.

(e) 10 mol % of H_2SO_4 was used as catalyst.

(f) Compound **3b** decomposes on prolonged heating at 260°C.

(g) Compound **1b** was added at 170°C; reaction was performed at 218°C.

(h) Products are **2c** and **3c**.

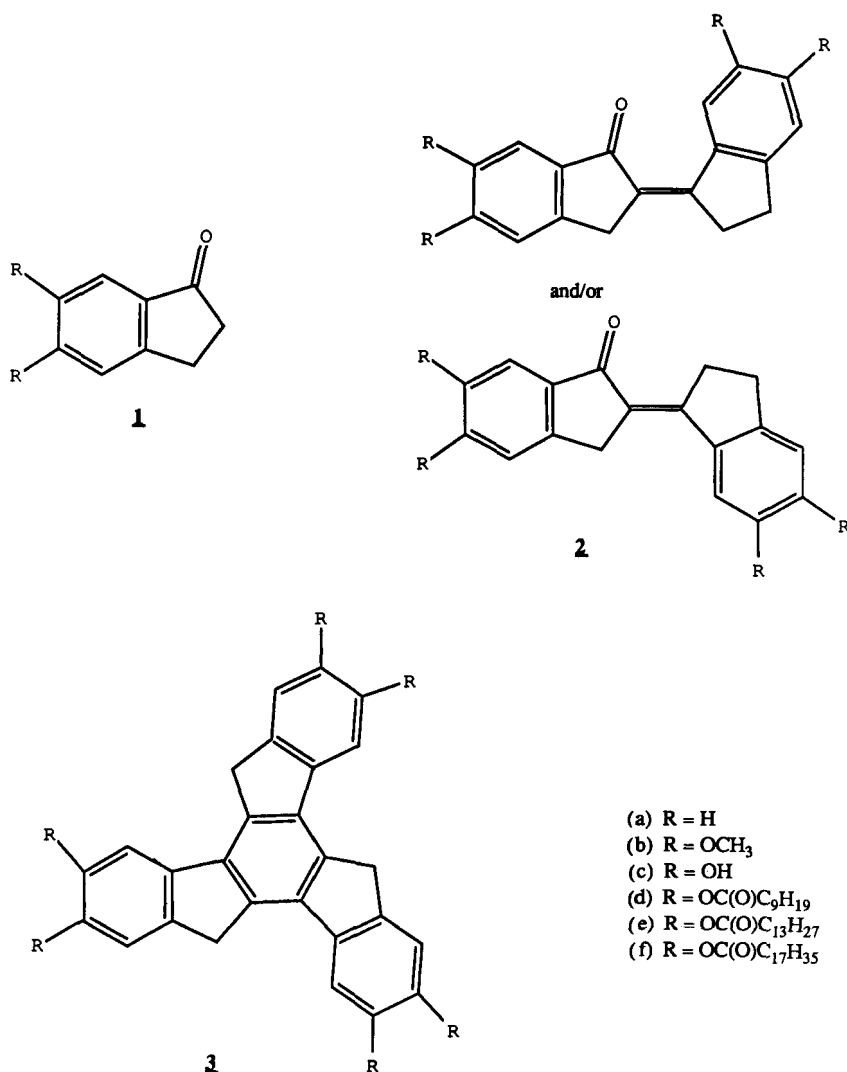


Figure 1. Structure of compounds 1, 2, and 3 [11]. 1: indan-1-one derivatives, 2: 2-(indan-1-ylidene)-indan-1-one derivatives and 3: truxene derivatives.

also been described by Metz [13] and by Chenault and Sainson [14].) Unfortunately PPE decomposes at these elevated temperatures [15]. A compromise was found by using a high temperature (160°C) but a shorter reaction time (20 min.). However, yields are variable due to the decomposition of PPE. The rate of decomposition also depends on the preparation of PPE, as this is a mixture of several components [16].

We have tried to find other ways of inducing the selfcondensation of **1b**. *p*-Toluenesulfonic acid in a solvent mixture of biphenyl and diphenyl ether (Dowtherm A) appeared to be a reasonable substitute of PPE (see table 1), although the yields are somewhat lower. Interestingly, the condensation reaction also proceeds in refluxing pyridine hydrochloride. Since this reagent also effects demethylation [17] the reaction product is a mixture of compounds **2c** and **3c**, the latter compound being obtained in about 50 per cent yield. This mixture was converted into the desired ester derivatives.

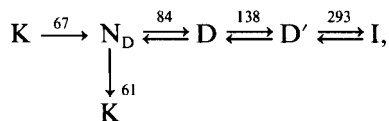
We found that addition of 4-dimethylaminopyridine to the reaction mixture [18] increased the yield of completely esterified products from approximately 10 to 40 per cent. The dimeric (**2d-f**) and trimeric (**3d-f**) products can be separated by column chromatography. This method provides a short two-step route to the hexasubstituted truxenes.

3. Optical and thermodynamic studies

The mesophases of the discotic mesogens **3d-f** were observed using a polarizing microscope equipped with a Mettler FP52 heating and cooling stage. Transition temperatures and enthalpies were determined by differential scanning calorimetry (Setaram DSC 111).

3.1. 2,3,7,8,12,13-Hexa(decanyloxy)truxene (**3d**)

In agreement with literature [7] observation of **3d** with a polarizing microscope showed the transition temperatures:

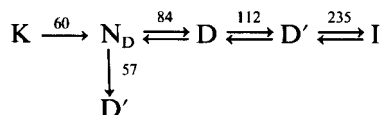


where K indicates a crystalline phase, N_D a discotic nematic phase, D and D' columnar phases and I the isotropic liquid phase. Study of this material by D.S.C. (see figure 2) revealed other crystalline phases not mentioned in the literature [7]. Upon heating a virgin sample (i.e. recrystallized from chloroform-ethanol and not previously melted) a $\text{K}' \rightarrow \text{K}$ transition is detected at 56°C before melting of the material at 67°C to the nematic phase (see figure 2(a)). Upon heating a sample that had been cooled from the melt another transition in the crystalline phase ($\text{K}'' \rightarrow \text{K}$) was observed at 43°C, although we did not detect the reverse transition ($\text{K} \rightarrow \text{K}''$) upon cooling (see figure 2(b)). Probably the K'' -phase grows in very slowly around room temperature.

Heating a sample at 5 K/min from room temperature to the isotropic liquid (300°C), did not reveal any enthalpy changes above 84°C. However, upon heating a fresh sample in the D.S.C. equipment pre-heated at a temperature just below the discotic to isotropic transition temperature, this phase transition was detectable, but at a temperature lower than observed with the polarizing microscope. It disappeared rather quickly upon repeated heating and cooling around the transition temperature, indicating decomposition of the material at these elevated temperatures (see figure 2(c)). The values of ΔH obtained for the $\text{K} \rightarrow \text{N}_D$ and $\text{N}_D \rightarrow \text{D}$ transitions are in agreement with those mentioned in the literature [7].

3.2. 2,3,7,8,12,13-hexa(tetradecanoyloxy)truxene(**3e**)

On heating a virgin sample of **3e**, observation with the polarizing microscope showed a transition to the nematic phase at 78°C. Subsequent heating, after cooling the sample to room temperature, showed transition temperatures in agreement with literature [7]:



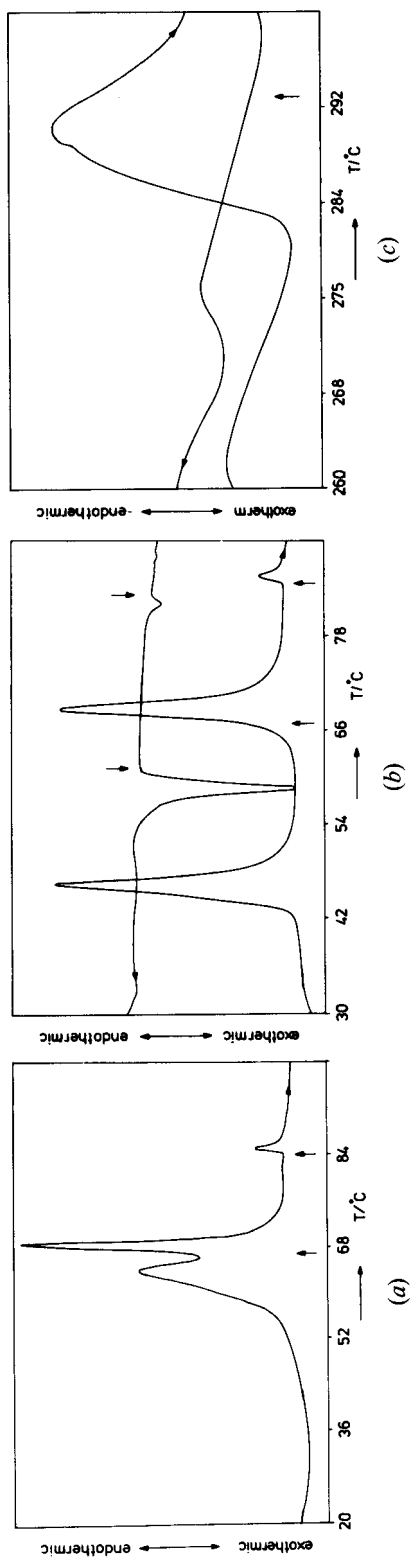


Figure 2. D.S.C. thermograms of 2,3,7,8,12,13-hexa(decanyloxy)truxene (3d). (a) First heating run. (b) Subsequent heating and cooling runs. (c) High temperature discotic to isotropic transition. Arrows indicate the transitions as observed with the polarizing microscope.

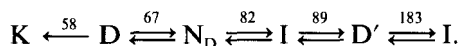
The results of a D.S.C. study are presented in figure 3. Heating a virgin sample (see figure 3(a)) showed an endothermic effect at about 56°C immediately followed by an exothermic effect. A strong endothermic peak at 78°C indicates melting to the nematic phase and at 84°C the transition to the columnar phase is visible. Annealing a virgin sample at 68°C for several hours and subsequent heating after cooling to room temperature only showed transitions at 78°C and 84°C, without any exothermic effects. Subsequent heating of samples that had been cooled from the melt (see figure 3(b)) showed endothermic peaks at 53, 59 and 84°C, respectively. The reverse transitions were detected on cooling, but at lower temperatures: 41.5, 53 and 83°C, respectively (see figure 3(b)). In contrast to literature data [7] and our optical observations the D.S.C. results show that direct melting of the crystalline K phase into the nematic phase does not occur, but that a discotic mesophase D is in between. Evidently the transition K → D is not clearly visible by optical observation.

A possible explanation of the effects observed on heating a virgin sample could be the existence of different crystal structures. If a virgin sample consists of a mixture of the two crystalline phases K and K' the observed effects can be qualitatively accounted for by (partial) melting of the K phase followed by crystallization into the thermodynamically more stable phase K' (viz. K' → N_D: ΔH = 107 kJ/mol and K → N_D: ΔH = 104 kJ/mol).

As we observed with **3d**, while heating at 5 K/min from room temperature to the isotropic phase (260°C) no enthalpy effects were detected above 84°C, but the discotic to isotropic transition could be made visible (see figure 3(c)) in the way described for **3d**. Again we found a transition temperature which was lower than that observed with the polarizing microscope. Again, on repeated heating and cooling around the transition temperature the D.S.C. signal disappears. This behaviour is probably due to decomposition of the sample.

3.3. 2,3,7,8,12,13-Hexa(octadecanoyloxy)truxene(**3f**)

On heating **3f** from the crystalline phase we could not clearly distinguish different mesophases with the polarizing microscope. Changes in the optical texture were visible around 84°C on heating a virgin sample; in subsequent heatings these changes occurred around 70°C and in the region 82–90°C. The material becomes isotropic at approximately 183°C. Upon cooling from the isotropic liquid (> 183°C), however, transition temperatures and optical textures clearly indicated different mesophases, showing the sequence:



A columnar phase D' grows in at 183°C (see figure 4(e)). Below 89°C the texture slowly becomes totally black between crossed polarizers (see figure 4(d)), forming a re-entrant isotropic phase. Figure 4(c) shows the typical schlieren texture of the nematic phase which is obtained below 82°C. At 67°C this nematic phase goes over into a columnar phase (D) (see figure 4(b)). There is a significant resemblance between the optical texture of this phase and the high temperature columnar phase D' (see figure 4(e)), so the former could also be a re-entrant phase. On further cooling, the material crystallizes at 58°C (see figure 4(a)). The occurrence of an isotropic phase between a nematic and a columnar phase is analogous to what is observed for a mixture of 87 per cent of 2,3,7,8,12,13-hexa(tetradecanoyloxy)truxene and 13 per cent of 2,3,7,8,12,13-hexa(4-dodecyloxybenzoyloxy)truxene [19].

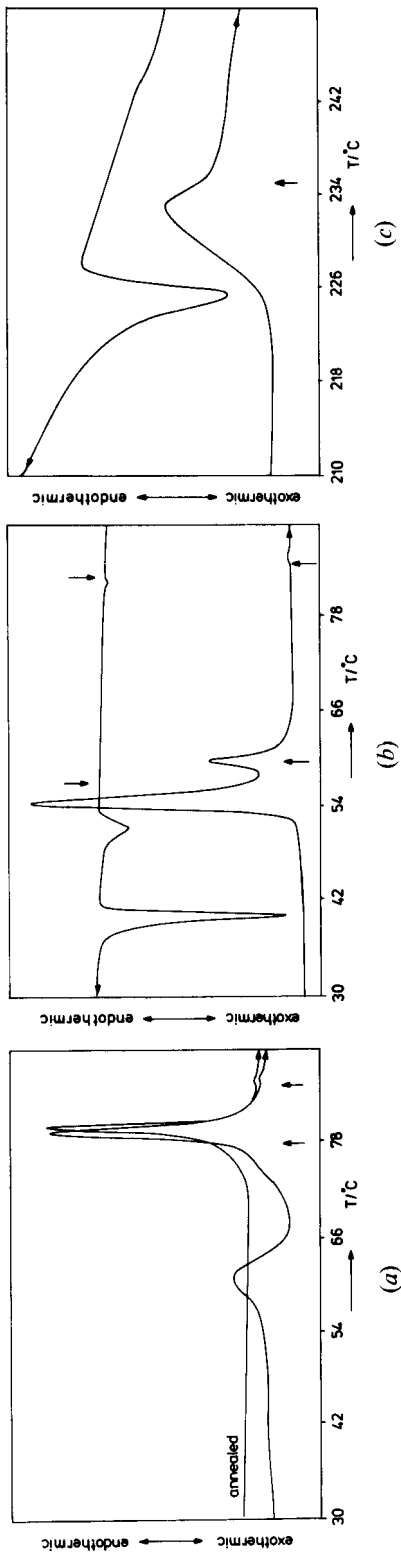


Figure 3. D.S.C. thermograms of 2,3,7,8,12,13-hexa(tetradecanoyloxy)truxene (3e). (a) First heating run. (b) Subsequent heating and cooling runs. (c) High temperature discotic to isotropic transition. Arrows indicate the transitions as observed with the polarizing microscope.

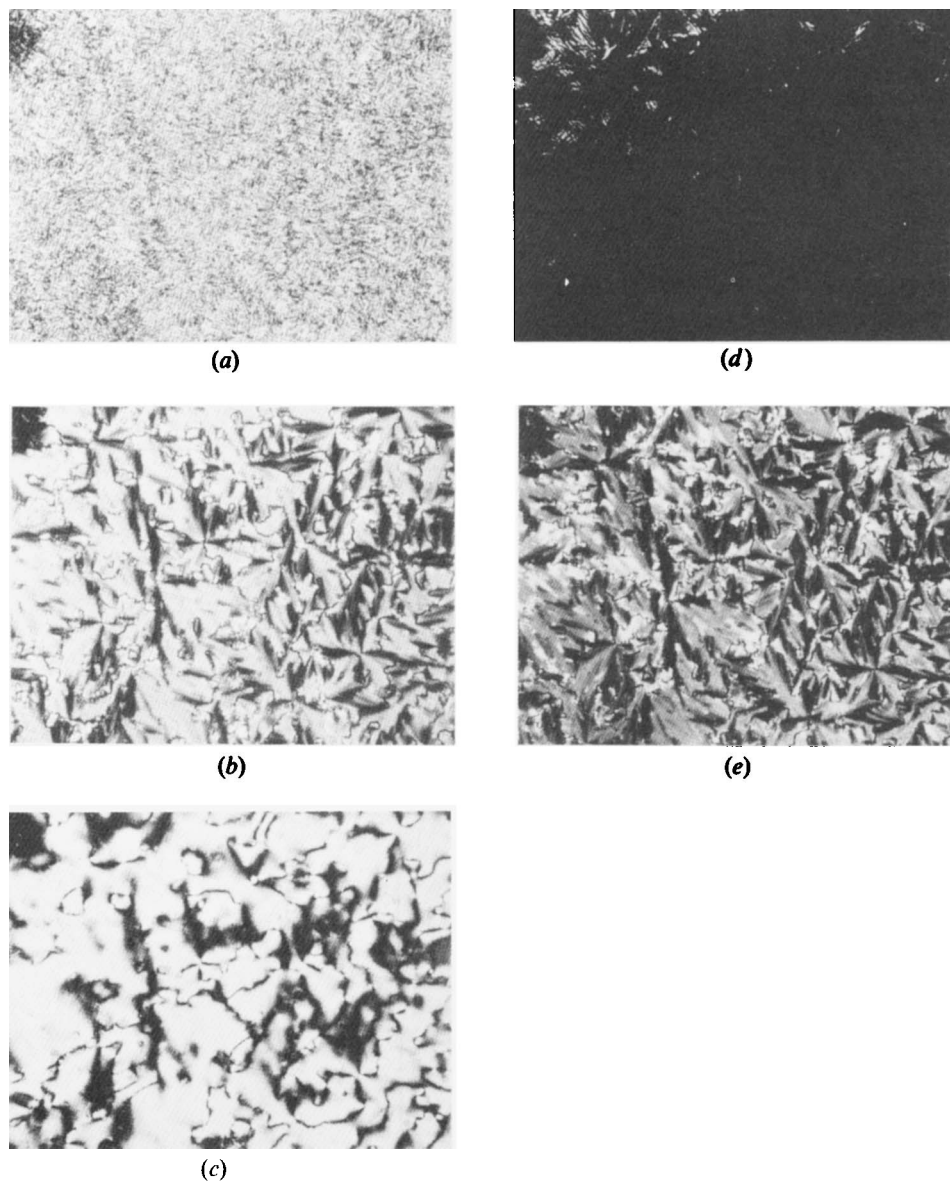


Figure 4. Optical textures observed for 2,3,7,8,12,13-hexa(octadecanoyloxy)truxene (**3f**). (a) Crystalline phase at 47°C. (b) Columnar phase at 61°C. (c) Nematic phase at 77°C. (d) Isotropic phase at 82°C. (e) Columnar phase at 109°C.

It is possible that the optically isotropic phase is not a true re-entrant isotropic liquid phase, but some kind of cubic phase analogous to the 'smectic' D phase in rod-like liquid crystals [20]. However, no birefringence could be detected by rotating the sample or by inducing shear flow by moving the upper glass slide. In addition the fluidity of this optically isotropic phase is much greater than the fluidity of the columnar phases and rather resembles the fluidity of the nematic phase. These observations and also the results of refractive index measurements (*vide infra*) suggest that we are dealing with a normal isotropic liquid phase.

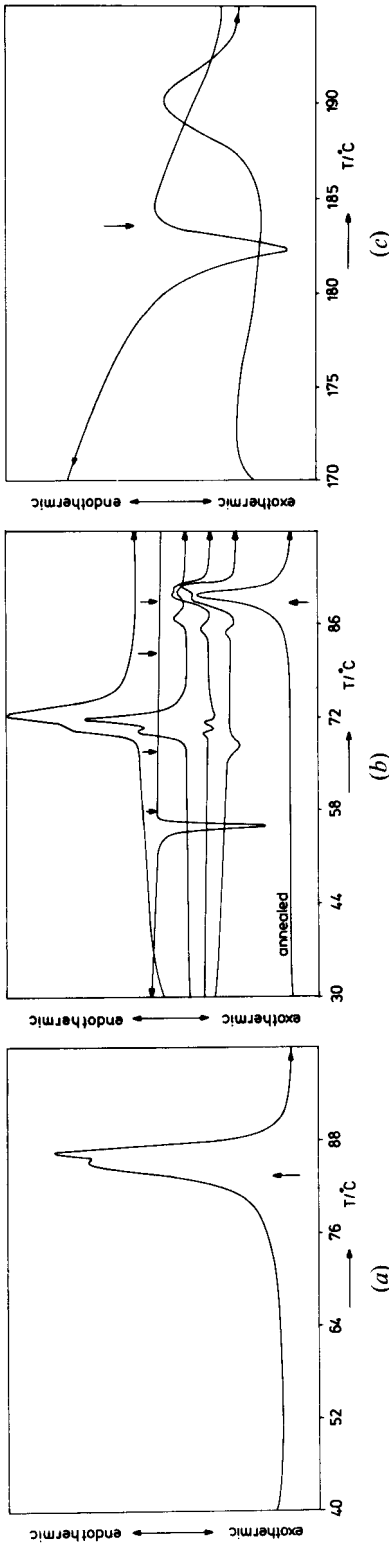


Figure 5. D.S.C. thermograms of 2,3,7,8,12,13-hexa(octadecanoyloxy)truxene (**3f**). (a) First heating run. (b) Subsequent heating and cooling runs. (c) High temperature discotic to isotropic transition. Arrows indicate the transitions as observed with the polarizing microscope.

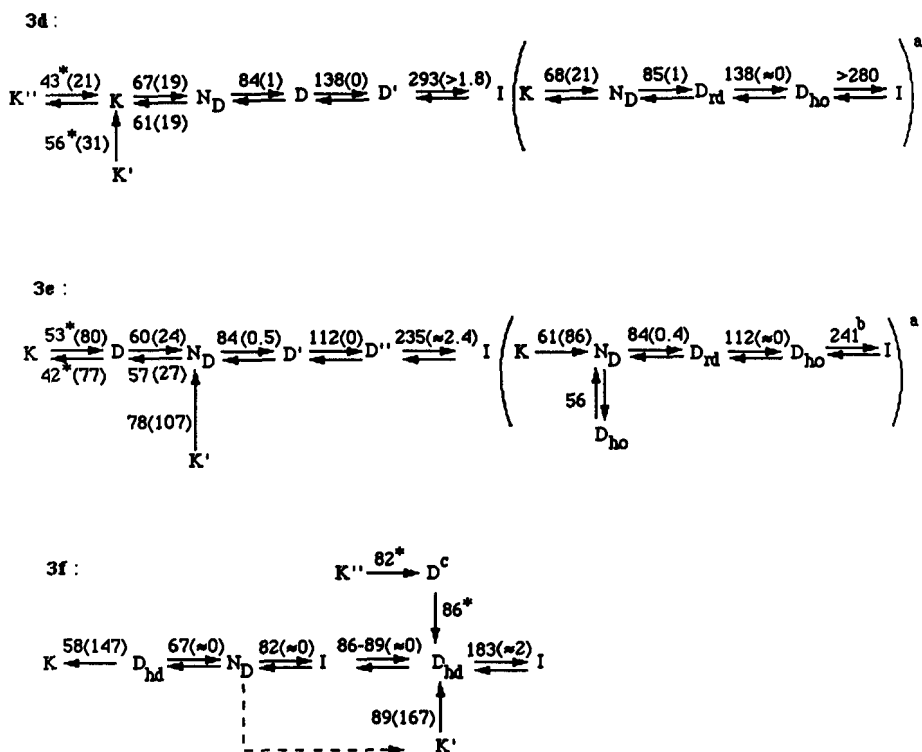


Figure 6. Transition temperatures and enthalpies for truxene derivatives **3d–f** (figure 1). The indicated transition temperatures ($^{\circ}\text{C}$) are those obtained with the polarizing microscope except for those marked with *. The marked temperatures were extracted from the D.S.C. thermograms. Enthalpies (kJ/mol) are indicated between parentheses. K , K' , K'' are crystalline phases, N_D is a nematic phase, D , D' , D'' are columnar phases and I is the isotropic liquid phase. (a) [7]. (b) [2 (*f*)] gives a value of 235°C . (c) Unidentified phase (not isotropic!).

We sometimes observed a very slow crystallization in the nematic region leading to a thermodynamically more stable phase K' , which melts to the columnar phase D' at 89°C .

The study of **3f** by D.S.C. showed a very complex behaviour (see figure 5). Heating a virgin sample shows transitions at 82 and 86°C , respectively (see figure 5(a)). Disregarding this first heating run, that is anomalous for all three compounds, we find thermograms that depend on the heating rate (see figure 5(b)). Increasing the heating rate from 1 to 10 K/min, in the region $60\text{--}75^{\circ}\text{C}$ the transition process changes from exothermic ($\Delta H = -28 \pm 1$ kJ/mol) to strongly endothermic ($\Delta H = +147 \pm 5$ kJ/mol). The total enthalpy change on going from 30 to 100°C remains constant at $+147 \pm 5$ kJ/mol. The exothermic effect is probably caused by a transition into K' and/or K'' (see also figure 6(c)). We tested this hypothesis by annealing a sample of **3f** at 77°C for one night. On cooling to room temperature no transitions were detected for this annealed sample, while on heating only an endothermic peak was detected at 89°C (cf. figure 5(b); see also the adiabatic measurements).

The other endothermic effects which can be seen in figure 5(b) must be related to the transitions observed with the polarizing microscope, as the transition temperatures roughly coincide. However, we did not find any changes in enthalpy

upon cooling except one strongly exothermic crystallization effect at 56°C (see figure 5(b)), while observation with the polarizing microscope clearly showed reversible transitions. Extrapolating the enthalpy changes that occur at the nematic-columnar and columnar-columnar transitions in **3d** and **3e** [7] to **3f** suggests that any enthalpy changes between different mesophases in **3f** are smaller than our detection limit (≈ 0.2 kJ/mol). Assuming that this is indeed the case, we are still left with the question as to how to explain the endothermic effects on heating **3f** from the crystalline phase K. Any observable endothermic effect must then originate from a (partial) melting of a crystalline phase. Since D.S.C. is a fast technique it might be possible that we do not measure at thermodynamic equilibrium and the endothermic effects originate from a complex mechanism of transitions, including transitions between the different crystalline phases and their transitions to the mesophase.

On heating **3f** at 5 K/min to the isotropic phase (200°C) no enthalpy changes were detected above 90°C. Just as we observed with **3d** and **3e** the discotic to isotropic transition could be made visible by heating a fresh sample that was placed in the preheated D.S.C. equipment (see figure 5(c)). Again the transition disappeared on repeated heating and cooling around the transition temperature, due to decomposition of the sample.

Summarizing, upon heating a virgin sample all three derivatives exhibited a phase behaviour different from subsequent heatings. Subsequent heating of the samples gave reproducible results at temperatures below 100°C. Evidently these compounds can occur in different crystal structures depending upon crystallization conditions (e.g. cooling a melt or cooling a solution (recrystallization)). The existence of different crystal structures was also reported for 2,3,7,8,12,13-hexa(pentadecanoyloxy)truxene [6(a)]. At elevated temperatures decomposition took place, making an accurate measurement of the columnar to isotropic transition impossible.

Note that observation with the polarizing microscope indicated a slow decomposition of the samples starting as a change of colour at the edges of the sample. In figure 6 we summarize the transition temperatures as obtained with the polarizing microscope and the enthalpies from the D.S.C. measurements. The transition temperatures as obtained with the polarizing microscope and from the D.S.C. thermograms were generally found to be equal within $\pm 1^\circ\text{C}$, but at low temperatures considerable supercooling is observed in the D.S.C. thermograms. The transition temperatures indicated in figure 6, are those obtained with the polarizing microscope except for transitions that were only visible in the D.S.C. thermograms. Comparing the results for **3d** and **3e** with the literature [7], there is a good agreement in the transition temperatures and enthalpies for **3d**, while there is a slight discrepancy for **3e** at the lower temperatures. In addition we found evidence of other crystalline phases, which makes the phase behaviour of **3d** and **3e** even more complex.

4. Adiabatic calorimetry

In order to reach thermodynamic equilibrium we also studied **3f** by adiabatic calorimetry; we used calorimeter VI, described in [21]. On heating a virgin sample (figure 7(a)) the heat capacity at constant pressure C_p begins to decrease at about 60°C. This indicates the transition to the more stable phase K'. The transition temperature to the discotic phase was found to be $88.6 \pm 0.2^\circ\text{C}$. On slow cooling (approximately 36 hrs.) the material crystallized at 65.5°C. Heating this sample again

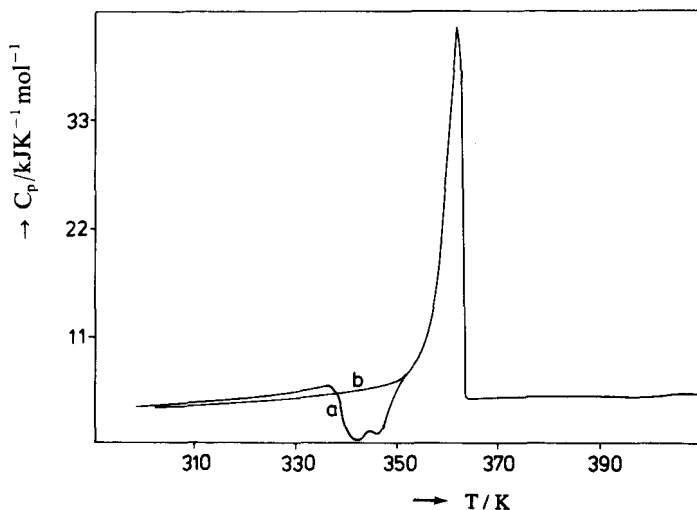


Figure 7. Adiabatic measurements of 2,3,7,8,12,13-hexa(octadecanoyloxy)truxene (**3f**). (a) Virgin sample. (b) Subsequent heating.

(see figure 7 (b)) showed a complete absence of the exothermic effect and only a strong endothermic peak (167 ± 5 kJ/mol) at $88.6 \pm 0.2^\circ\text{C}$. Heating the same sample after rapid cooling to room temperature, again showed a large exothermic effect as was observed for the virgin sample. Heating a sample after cooling to 70°C we could not detect any transitions. These observations are in agreement with our assumption that only transitions which involve a crystalline phase are accompanied by detectable changes in C_p and ΔH . Comparing these adiabatic measurements with the D.S.C. results we also see that the K' phase is the thermodynamically more stable phase (viz. $K' \rightarrow D: \Delta H = 167 \pm 5$ kJ/mol and $K \rightarrow D: \Delta H = 147 \pm 5$ kJ/mol).

5. Small angle X-ray scattering

Preliminary results of small angle X-ray scattering of **3f** showed the existence of a hexagonal columnar phase (D_{hd}) on heating above 90°C , with an intercolumnar spacing of 3.38 nm. Upon cooling we found evidence of a less ordered phase (nematic and/or isotropic) bounded by the D_{hd} phase at both temperature limits. Crystallization of the material occurred at approximately 60°C .

6. Refractive index measurements

The refractive indices of **3d-f** (see figure 1) were studied using a temperature controlled Abbe-refractometer (Zeiss, Abbe-II). The results of these measurements are represented in figure 8 and table 2.

The birefringence in the nematic phase of **3d** and **3e** was clearly detectable. Outside the nematic region we could not clearly detect any refractive indices because the boundary line was not sharp. A sample of **3f** also showed a clear birefringence in the nematic region ($67\text{--}82^\circ\text{C}$) and, in addition, a change in the refractive indices was observed upon cooling below 67°C , indicating the transition to the columnar phase D' . Upon heating, the birefringence disappears above 82°C leaving only one refractive index, which indicates the transition to an isotropic phase. Note that at the

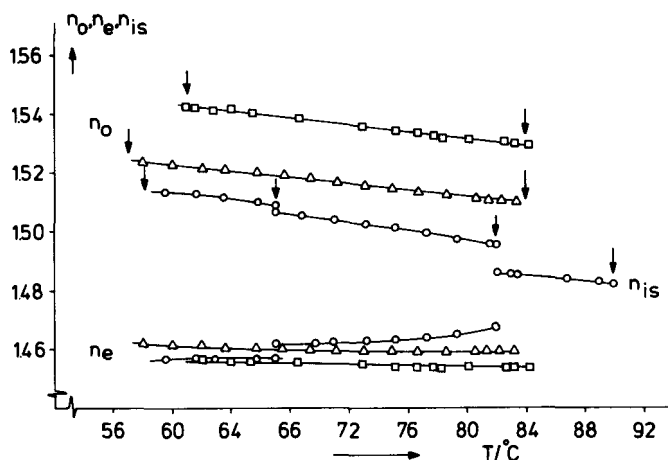


Figure 8. Refractive indices of truxene derivatives **3d-f** (figure 1). **3d** (\square), **3e** (Δ) and **3f** (\circ). The transition temperatures are indicated by the arrows. n_{is} denotes the isotropic refractive index and n_o and n_e denote the ordinary and the extraordinary refractive index, respectively.

Table 2. Refractive indices of truxene derivatives **3d-f** (figure 1).

3d			3e			3f			
$T/^\circ\text{C}$	n_o	n_e	$T/^\circ\text{C}$	n_o	n_e	$T/^\circ\text{C}$	n_o	n_{is}	n_e
84.3	1.5296	1.4534	83.3	1.5102	1.4592	90.0		1.4819	
83.7	1.5289	1.4534	82.3	1.5102	1.4592	89.0		1.4829	
83.3	1.5296	1.4534	81.4	1.5107	1.4593	86.8		1.4839	
82.9	1.5294	1.4534	80.6	1.5110	1.4589	83.4		1.4852	
82.5	1.5307	1.4536	78.6	1.5122	1.4588	83.0		1.4853	
80.1	1.5312	1.4536	76.7	1.5133	1.4589	82.0		1.4859	
78.3	1.5320	1.4534	75.0	1.5146	1.4592	82.0	1.4957		1.4669
77.7	1.5327	1.4537	73.1	1.5157	1.4592	81.6	1.4957		1.4667
76.6	1.5332	1.4534	71.2	1.5169	1.4591	79.3	1.4976		1.4650
75.2	1.5343	1.4538	69.4	1.5182	1.4594	77.3	1.4996		1.4636
72.9	1.5356	1.4546	67.5	1.5194	1.4599	75.2	1.5013		1.4629
68.5	1.5384	1.4552	65.7	1.5202	1.4604	73.2	1.5026		1.4625
65.4	1.5402	1.4556	63.6	1.5214	1.4602	70.9	1.5039		1.4621
64.0	1.5414	1.4556	62.0	1.5217	1.4609	68.7	1.5057		1.4619
62.8	1.5417	1.4559	60.0	1.5226	1.4612	66.9	1.5069		1.4619
62.0	1.5423	1.4562	58.1	1.5239	1.4619	66.9	1.5089		1.4565
61.6	1.5423	1.4562				65.8	1.5100		1.4562
60.9	1.5426	1.4562				63.5	1.5114		1.4564
						61.6	1.5126		1.4564
						59.5	1.5135		1.4564

nematic–isotropic transition the change in the refractive indices is in agreement with $n_{is} = (2n_o + n_e)/3$ [22], where n_{is} is the isotropic refractive index and n_o and n_e indicate the ordinary and the extraordinary refractive index, respectively. Note also that, contrary to what is commonly observed for rod-like liquid crystals, the optical anisotropy $\Delta n = n_e - n_o$ is negative, as is to be expected for planar polyaromatic molecules. Below 58°C and above 90°C we could not measure the refractive index because the boundary line was not sharp.

Figure 8 shows a systematic decrease in the optical anisotropy on raising the temperature and on increasing the alkyl chain length. The decrease in Δn on increasing the temperature originates from the temperature dependence of the nematic order parameter [22], which decreases with increasing temperature. The decrease in Δn on increasing alkyl chain length can be explained by assuming that the anisotropy is mainly caused by the anisotropy of the aromatic core [22]. The volume fraction of the aromatic part as compared with the aliphatic tails will decrease on increasing alkyl chain length and so will the anisotropy per unit volume. In addition there might be a decrease in the nematic order parameter on increasing alkyl chain length.

The transition temperatures observed by the refractive index measurements are in agreement with those obtained from D.S.C. and from observations with the polarizing microscope. The results for **3f** also clearly demonstrate the existence of a re-entrant isotropic phase.

7. Elastic constants

In a previous paper [23] we reported measurements on the ratio of the Frank elastic constants of splay and bend in the nematic regime of **3d** and **3e**, using the magnetic Frederiks transition technique [22]. Here we report measurements for **3f**.

The nematic material was placed between two flat parallel glass plates, coated with a thin polyimide film (Dupont, P12566) [24], which were kept apart by tungsten spacers at a constant distance of some 50 μm . The exact thickness of the sample cells was determined interferometrically. The coated glass surfaces induce a homeotropic alignment, which means that the director (the local axis of uniaxial symmetry) is everywhere perpendicular to the glass surface. As the director in discotic materials is normal to the molecular plane, this implies that the plane of the molecules was, in the average, parallel to the walls. Distortion of the uniform orientational alignment in a nematic liquid crystal increases its free energy. The lowest order expression for this distortion contribution to the free energy density in terms of gradients of the nematic director \mathbf{n} is [25]

$$f_d = 1/2[K_1(\nabla \cdot \mathbf{n})^2 + K_2(\mathbf{n} \cdot \nabla \times \mathbf{n})^2 + K_3(\mathbf{n} \times \nabla \times \mathbf{n})^2],$$

where f_d is the distortion free energy per unit volume, and K_1 , K_2 and K_3 are the elastic constants, usually referred to as Frank constants, associated with splay, twist and bend distortions, respectively. In the presence of a magnetic field \mathbf{B} the expression for the free energy density of a nematic material becomes

$$f_{\text{total}} = f_d - 1/2\mu_0^{-1}\Delta\chi(\mathbf{B} \cdot \mathbf{n})^2,$$

where $\Delta\chi$ is the anisotropic part of the magnetic susceptibility. For the geometry used in our experiments [23] the magnetic field counteracts the force restoring director deformations described by f_d . Above a well defined threshold field the original director pattern becomes unstable and starts to deform. The amplitude of this deformation can be determined optically. For homeotropic samples measurement of this field induced director distortion yields information on $K_3/\Delta\chi$ and K_1/K_3 . The results of these measurements are represented in figure 9. The corresponding numbers have been collected in table 3. We have expressed the temperature in reduced units T/T_{NI} , where T_{NI} is the transition temperature from the nematic to the isotropic phase ($T_{\text{NI}} = 82^\circ\text{C}$).

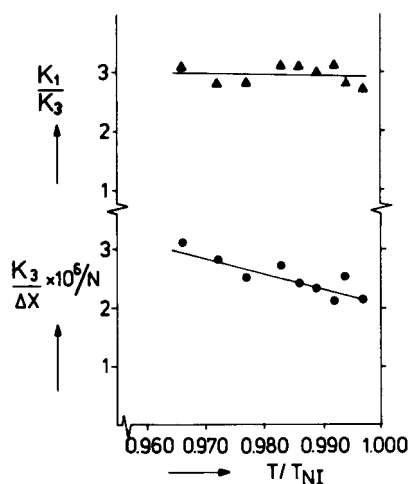


Figure 9. Temperature dependence of the ratio $K_3/\Delta\chi$ (●) and K_1/K_3 (▲) in the nematic region of 2,3,7,8,12,13-hexa(octadecanoyloxy)truxene (**3f**). The temperature is referred to the nematic-isotropic transition temperature, $T_{NI} = 355$ K.

Table 3. Temperature dependence of the ordinary (n_o) and extraordinary (n_e) refractive index, the ratio of the splay and bend elastic constants K_1 and K_3 , and the ratio $K_3/\Delta\chi$ for 2,3,7,8,12,13-hexa(octadecanoyloxy)truxene (**3f**). The reduced temperature is defined as T/T_{NI} , where T_{NI} is the transition temperature from the nematic phase to the (re-entrant) isotropic phase. The estimated error in the K_1/K_3 ratio is 15 and 10 per cent for $K_3/\Delta\chi$.

T/T_{NI}	n_o	n_e	K_1/K_3	$K_3\Delta\chi^{-1} 10^6/N$
0.997	1.466	1.479	2.7	2.1
0.994	1.465	1.498	2.8	2.5
0.992	1.465	1.499	3.1	2.1
0.989	1.464	1.499	3.0	2.3
0.986	1.464	1.500	3.1	2.4
0.983	1.463	1.501	3.1	2.7
0.977	1.463	1.503	2.8	2.5
0.972	1.463	1.504	2.8	2.8
0.966	1.462	1.505	3.1	3.1

We find the ratio $K_3/\Delta\chi$ of the same order of magnitude as in **3d** and **3e** [23] and also $K_1 > K_3$, which is in agreement with the mean field theory of Sokalski and Ruijgrok [26]. The ratio K_1/K_3 , however, is significantly greater than was observed for **3d** and **3e** and, moreover, this ratio hardly changes with temperature, which implies an almost equal temperature dependence of K_1 and K_3 . The ratio $K_3/\Delta\chi$ for **3f** decreases on increasing temperature, whereas for **3d** and **3e** this ratio was found to increase slightly. It is reasonable to assume that the temperature dependences of $\Delta\chi$ and Δn are almost equal, since the variation with temperature of $\Delta\chi$ and Δn is dominated by the same effect, viz. the temperature dependence of the nematic order parameter [22]. Taking into account this temperature dependence of $\Delta\chi$, the value of K_3 is almost temperature independent for **3d** and **3e**, whereas for **3f** K_3 decreases significantly with increasing temperature. This different behaviour of K_3 may be related to the different phase behaviour of these compounds (viz. $N_D \rightarrow D$ for **3d** and **3e**, but $N_D \rightarrow I$ for **3f**). It is commonly found in nematics of rod-like molecules that

the elastic constants decrease on approaching the isotropic liquid [22]. Experiments are in progress to investigate the temperature dependence of the elastic constants in some 2,3,6,7,10,11-hexa(4-alkoxybenzoyloxy)triphenylenes, which exhibit a normal sequence (crystal \rightarrow columnar \rightarrow nematic \rightarrow isotropic).

Finally, just as we observed for **3d** and **3e**, we find for **3f** no evidence of a divergence of the ratio K_1/K_3 on approaching the columnar phase. This is in disagreement with a Landau theory proposed by Swift and Andereck [27] for an (almost) second order transition. Incidentally, we note that our calorimetric data for all three truxene compounds support the hypothesis that the columnar-nematic transition is a continuous, or very weak first order transition.

8. Experimental section

All chemicals were used as purchased. Solvents were dried and distilled before use. Pyridine hydrochloride was prepared according to the method described by Taylor and Grant [28], and stored under a nitrogen atmosphere. Ethyl polyphosphate (PPE) was prepared according to Cava [29] and also stored under dry nitrogen.

2,3,7,8,12,13-Hexamethoxytruxene (3b). Method A. In a nitrogen atmosphere, 3.5 g PPE was placed in a round bottomed flask equipped with a magnetic stirrer and thermometer. The flask was then placed in a preheated oil bath at 160°C. When the PPE had reached a temperature of 140°C, 1.0 g (5.21 mmol) of **1b** was added over a 5 min period. This mixture was subsequently heated for 25 min at 160°C. During this time excessive foaming sometimes occurred. The reaction mixture was hydrolyzed with 50 cm³ of water. After stirring for 30 min, the product was isolated by filtration (G-4 frit) and washed with ethanol and CHCl₃. Yield 0.57 g (62 per cent) of a pink coloured solid **3b**. The product was insoluble in all common solvents, which hampered its characterization. I.R. (KBr) 3000–2800 (CH₂), 2840 (OCH₃), 1610, 1580, 1500 (C=C), 1100 (C–O) cm⁻¹.

When the reaction is carried out at temperatures < 130°C, dimeric product **2b** is obtained (see table 1). This compound is soluble in apolar organic solvents. I.R. (KBr) 2830 (OCH₃), 1665 (CO) cm⁻¹. ¹H N.M.R. (CDCl₃) δ 7.3, 7.25, 6.95, 6.90 (4 \times s, 4H, ArH), 4.0–3.9 (2 \times s, 12H, OCH₃), 3.85 (s, 2H, Ph-CH₂-C=C), 3.6–3.35 (m, 2H, Ph-CH₂-CH₂), 3.1–2.85 (m, 2H, C=C-CH₂-CH₂).

Method B. A mixture of 0.5 g (2.6 mmol) of **1b**, 47 mg (0.27 mmol) of 4-toluene-sulfonic acid and 1.5 cm³ of Dowtherm A was refluxed for 45 min at 260°C. After cooling to room temperature, 10 cm³ of ether was added to the dark red viscous reaction mixture. The product was isolated by filtration (G-4 frit) and washed with CHCl₃. Yield 0.22 g (49 per cent) of **3b**. The product had the same physical properties as described under *Method A*.

Method C. Under a nitrogen atmosphere a mixture of 0.5 g (2.6 mmol) of **1b** and 6 g of pyridine hydrochloride was refluxed for 30 min at 218°C. After cooling to room temperature, 20 cm³ of ice water and 4 cm³ of conc. H₂SO₄ were added. The mixture was stirred vigorously for 30 min. The solid material was isolated by filtration. Yield: 0.3 g of a 2:3 mixture of **2c** and **3c**. This mixture was used directly for the synthesis of **3d–f**. ¹H N.M.R. (DMSO-d₆), **3c**: δ 7.4, 7.2 (2 \times s, 6H, ArH), 7.0–5.5 (br. OH), 4.05 (br, s, 6H, CH₂):

2c: 7.3, 7.05, 7.0, 6.85 (4 \times s, 4H, ArH), 7.0–5.5 (br, OH), 3.8 (s, 2H, Ph-CH₂-C=C), 3.5–3.25 (m, 2H, Ph-CH₂-CH₂), 3.1–2.8 (m, 2H, C=C-CH₂-CH₂).

2,3,7,8,12,13-Hexahydroxytruxene (3c). This compound was prepared by demethylation of 2,3,7,8,12,13-hexamethoxytruxene (**3b**) with pyridine hydrochloride as

described in method C. 0.4 g (0.77 mmol) of **3b** and 8.5 g of pyridine hydrochloride were heated as described; after cooling to room temperature 35 cm³ of ice water and 7 cm³ of conc. H₂SO₄ were added. The yield of **3c** was quantitative.

General procedure for the preparation of 2,3,7,8,12,13-hexa(alkanoyloxy)truxenes (3d-f). To a mixture of 0.44 g (0.1 mmol) of **3c**, 0.15 g (1.2 mmol) of 4-(dimethylamino)pyridine [18], and 4.4 cm³ of pyridine, 6.6 mmol of the appropriate acid chloride was added dropwise at room temperature. The mixture was stirred for 2 days at room temperature and subsequently poured on crushed ice and concentrated hydrochloric acid. The resulting mixture was extracted three times with CHCl₃. The combined extracts were washed with water and 10 per cent aqueous NaHCO₃, dried (MgSO₄), and concentrated in vacuum. The resulting oil was subjected to column chromatography (silica gel, eluent 4 : 1 v/v benzene-hexane) and recrystallized from a chloroform-ethanol mixture to give 40 per cent of the 2,3,7,8,12,13-hexa(alkanoyloxy)-truxene. The latter compound can also be prepared starting from the **2c**, **3c**-mixture obtained by method C (*vide supra*). An amount of 1.1 mmol of acid chloride per mmol OH function was used. Reaction conditions and work up procedures are the same as described previously.

3d (from decanoic acid chloride): I.R. (KBr) 3000–2800 (CH₂), 1765 (C=O), 1620, 1590 (C=C), 1130 (C–O), 720 (CH₂) cm⁻¹; ¹H N.M.R. (CCl₄) δ 7.3, 7.25 (2 × s, 6H, ArH), 3.5–3.2 (br, s, 6H, CH₂ (ring)), 2.8–2.4 (m, 12H, C(O)CH₂), 2.1–1.1 (m, 42H, CH₂), 1.1–0.75 (t, 18H, CH₃). Anal. Calcd. for C₈₇H₁₂₆O₁₂: C, 76.61; H, 9.31; O, 14.08. Found: C, 76.84; H, 9.29; O, 13.87.

3e (from tetradecanoic acid chloride): I.R. (KBr) as given for **3d**; ¹H N.M.R. (CCl₄) as given for **3d** except δ 2.1–1.1 (m, 72 H, CH₂). Anal. Calcd. for C₁₁₁H₁₇₄O₁₂: C, 78.40; H, 10.31; O, 11.29. Found: C, 78.26; H, 10.35; O, 11.39.

3f (from octadecanoic acid chloride): I.R. (KBr) as given for **3d**; ¹H N.M.R. (CCl₄) as given for **3d**, except δ 2.1–1.1 (m, 180 H, CH₂). Anal. Calcd. for C₁₃₅H₂₂₂O₁₂: C, 79.59; H, 10.98; O, 9.43. Found: C, 79.40; H, 11.19; O, 9.41.

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