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Synthesis and thermotropic properties of new discotic 1,3,5-trisubstituted *s*-triazinetriones obtained by cyclotrimerization of isocyanates

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The synthesis of a number of *s*-triazine-2,4,6-triones (isocyanurates) by cyclotrimerization of 4-monoalkoxy-, 3,4-dialkoxy-, or 3,4,5-trialkoxyphenyl-, benzyl-, or styryl-isocyanates is reported. The thermal and phase behaviour of the novel compounds were investigated by optical polarized light microscopy and thermal analysis. No mesophase could be observed for any of the precursors except 4-decyloxybenzoic acid. Mesophases of the isocyanurates were observed only in the series containing 3,4-dialkoxyphenyl moieties. A vinylene group between the inner *s*-triazine ring and the outer phenylene rings gives low melting points and enantiotropic mesophases for C_8 and longer alkyl chains. The phenylisocyanurates may exhibit a monotropic mesophase and normally have the highest melting points of the three types, whereas a methylene spacer suppresses formation of a mesophase. According to the textures observed, the mesophases are hexagonal columnar. This will have to be confirmed by X-ray scattering techniques.

1. Introduction

Discotic mesophase forming compounds have been described as variations of a number of different almost planar cores to which in general six alkyl chains are variously attached [1]. Among the disc-like cores are the benzene ring, cyclohexane ring, condensed aromatic ring systems like triphenylene, anthraquinone, and the porphin ring system [2]. The trisubstituted *s*-triazine ring, which should favour disc-like structures and mesophases, was proposed by LeBarny and coworkers as a central core [3]. Lattermann and Höcker were the first to explore this idea by synthesizing tris(dialkylamino)-*s*-triazines from cyanuric chloride and dialkylamines [4]. The products failed, however, to exhibit mesomorphism. Huang and coworkers reacted a mesogenic 4-methoxybenzylidene-4-iminophenol with cyanuric chloride and reported the product to have a discotic mesophase [5]. We were able to show that cyanurates with similar substituents do not form discotic mesophases as suggested by star-shaped models, but do exhibit normal calamitic nematic and smectic polymorphism [6]. The isomeric ring system of the 2,4,6-trioxo-1,3,5-hexahydrotriazines, to our knowledge, has not been used for the synthesis of disc-like mesogenic structures. Isocyanurates formed from liquid crystalline isocyanates, e.g. 4-butoxyphenyl 4-isocyanatobenzoate did not form any mesophase [6, 7].

Bearing in mind that both ring systems can be built up by cyclotrimerization of cyanate esters or isocyanates, respectively, this approach could become a convenient synthesis for discotic liquid crystals. Since cyclotrimerization of mesogenic di-isocyanates might lead to anisotropic networks, we were interested to explore the structural requirements for isocyanates to yield liquid crystal cyclotrimers.

In a joint project with M. Bauer in Teltow initiated in 1991, we investigated the ability of the two isomeric triazine rings to stabilize a mesophase. In a previous paper we reported the synthesis of diaromatic mono- and di-isocyanates containing the ester group, as well as the corresponding cyanates of the phenyl benzoate type, and explored their mesogenic properties [7]. An investigation of the cyclotrimers obtained from these monomers proved that no mesophases could be obtained from isocyanurates, while certain structural requirements had to be met in the case of cyanurates to obtain calamitic mesophases [6].

The present paper deals with the synthesis and mesogenic properties of discotic isocyanurates obtained by cyclotrimerization of isocyanates containing an alkoxyphenyl group. Results obtained with cyanurates of similar structure will be reported by M. Bauer.

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2. Results and discussion

2.1. *Considerations of structural requirements*

Discotic structures based on the *s*-triazinetrione central ring may vary in the number of flexible chains attached to the central core or by the shape and size of the core itself. Some possible structures are shown in scheme 1.

By analogy with known disc-like mesogens at least six aliphatic chains should be linked to the rigid part of the mesogen [1] (I in scheme 1). Secondary aliphatic isocyanates are required as starting materials for this type of isocyanurate. This route was not pursued since the aminotriazines studied by Lattermann *et al.* [4], which have a similar structure, did not show liquid crystalline behaviour. The number of ring systems grouped around the central heterocyclic ring is another structural parameter one could vary in a systematic investigation, as shown for structure type III in Scheme 1 [6]. A third variation is the distance between the outer ring systems and the central heterocycle. This distance, if varied by a spacer, would in addition allow tailoring of the flexibility and the preferred conformation in the array of different ring systems. This structure type is shown in scheme 1 with the general formula II.

The selection of 'monomers' (II in scheme 1) for the present study was made according to the following criteria:

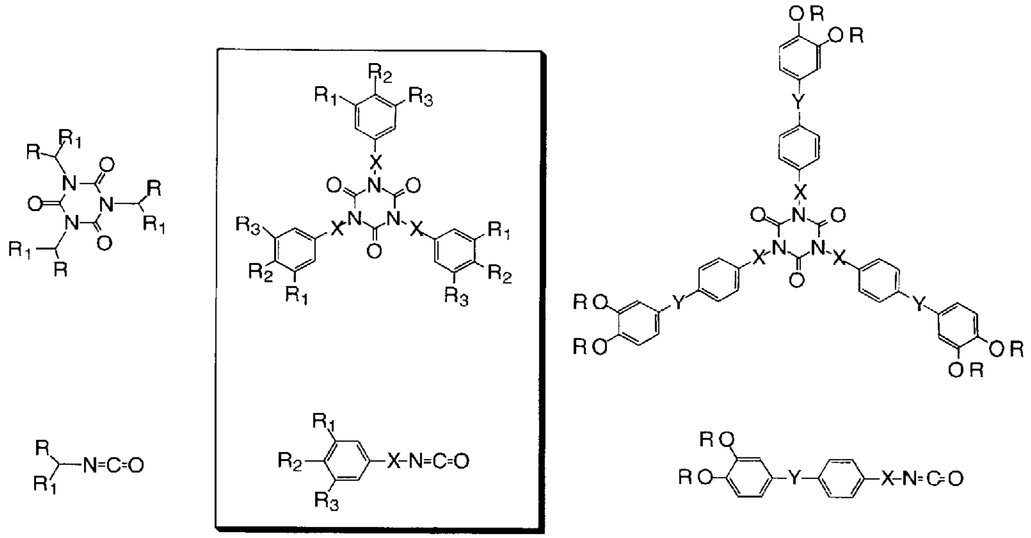
(1) Variation of the number and length of aliphatic chains attached to the outer ring periphery. The number was varied from 1 to 3 per aromatic ring, the length from 4 to 12 carbon atoms.

(2) Variation of the distance and rigidity of attachment of the outer ring system with respect to the central triazine moiety. A nitrogen–benzene single bond between the two regions results from cyclotrimerization of aromatic isocyanates. Due to the two carbonyl groups in the *ortho*-position to each nitrogen, it is highly unlikely that the outer ring is coplanar with the central ring. Isocyanatomethylarenes (benzyl isocyanates) have a methylene group as spacer, which should decrease the influence of the oxo groups. The sp^3-hybridization of the carbon, on the other hand, renders the system more flexible. *Trans-β*-isocyanatostyrenes give the rather rigid and potentially planar vinylene spacer with minor steric requirements and allow the system to adopt a favourable planar and symmetric conformation.

2.2. *Synthesis of isocyanates and isocyanurates*

The synthetic approach chosen in the present paper uses isocyanates as precursors for the cyclotrimers. These are conveniently obtained by the Curtius reaction of carboxylic acid azides in a laboratory scale synthesis. The carboxylic acids with alkyl chains in a suitable position required as intermediates are alkoxy-substituted benzoic acids, phenylacetic acids and cinnamic acids.

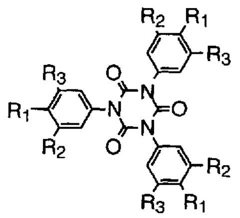
The isocyanurates synthesized and the numbering system used for these isocyanurates and their precursors are shown in table 1. The number stands for a precursor as shown in scheme 2, while the substitution pattern and the length of the alkoxy substitutents are characterized by a letter.

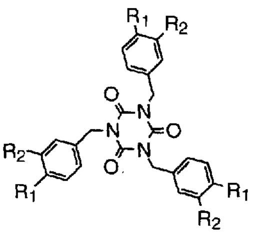


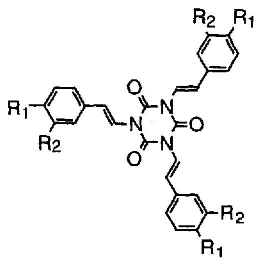
I II III

Scheme 1. Structural types of mesogenic isocyanurates.

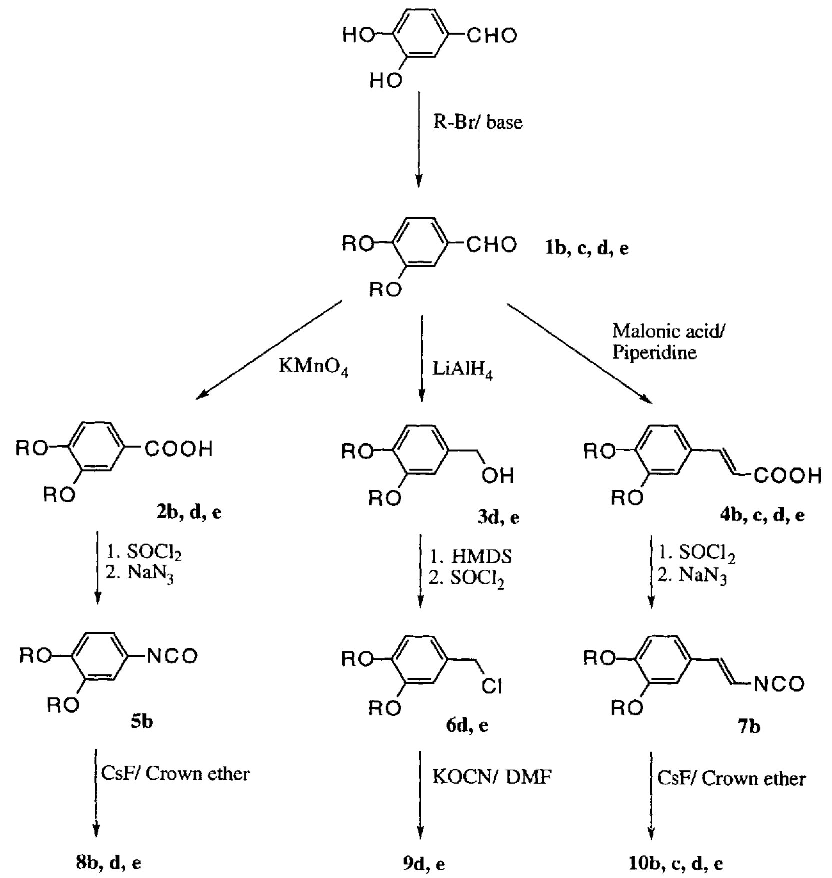
Table 1. Isocyanurates synthesized.







No.	R_1	R_2	R_3	No.	R_1	R_2	No.	R_1	R_2
8	H	H	H	**9**	H	H	**10**	H	H
8a	$OC_{10}H_{21}$	H	H	**9a**	$OC_{10}H_{21}$	H	**10a**	$OC_{10}H_{21}$	H
8b	OC_4H_9	OC_4H_9	H				**10b**	OC_4H_9	OC_4H_9
							10c	OC_8H_{17}	OC_8H_{17}
8d	$OC_{10}H_{21}$	$OC_{10}H_{21}$	H	**9d**	$OC_{10}H_{21}$	$OC_{10}H_{21}$	**10d**	$OC_{10}H_{21}$	$OC_{10}H_{21}$
8e	$OC_{12}H_{25}$	$OC_{12}H_{25}$	H	**9e**	$OC_{12}H_{25}$	$OC_{12}H_{25}$	**10e**	$OC_{12}H_{25}$	$OC_{12}H_{25}$
8f	OC_4H_9	OC_4H_9	OC_4H_9						



Scheme 2. Synthesis of alkoxy substituted phenyl-, benzyl-, and styryl-isocyanurates.

4-Decyloxy-benzoic acid **2a** and -cinnamic acid **4a** were obtained from the corresponding hydroxy acids by reaction with an alkyl bromide in the presence of an acid acceptor as reported by Mertesdorf and Ringsdorf [8]. This route was followed also for 3,4,5-tributoxybenzoic acid **2f** [9].

Starting materials applicable to all three types of isocyanates are the corresponding benzaldehydes. This approach was used for the synthesis of the 3,4-dialkoxyphenyl substituted isocyanurates as shown in scheme 2. Etherification of 3,4-dihydroxybenzaldehyde according to a procedure described by Nguyen *et al.* [10] gave the 3,4-dialkoxybenzaldehydes **1b–e** in good yields. Oxidation with potassium permanganate yielded the dialkoxybenzoic acids **2b**, **2d**, **2e**, and reaction with malonic acid in pyridine as described by Koo *et al.* [11] led to the cinnamic acids **4b–e**. The synthesis of the phenylacetic acids by this route would require reduction of the aldehyde to the benzyl alcohol **3**, conversion to the benzyl chloride **6** with thionyl chloride, and, after reaction with magnesium and subsequently with carbon dioxide, this would yield the acid.

A more convenient synthetic route is that shown in scheme 2. Starting from the benzaldehyde the benzyl alcohols **3d** and **3e** were obtained by reduction with lithium aluminum hydride according to Nystrom [12]. The benzyl alcohols were converted to the silyl ethers with hexamethyldizilazane which upon reaction with thionyl chloride gave the benzyl chlorides **6d** and **6e**. The isocyanate group was introduced now by nucleophilic substitution of chlorine. The isocyanate cannot be isolated in this reaction since potassium cyanate acts as a trimerization catalyst in solvents where it is slightly soluble [13].

Published procedures were adopted whenever possible and slightly modified in order to obtain good yields of precursors at every stage. Direct selective etherification of 3,4-dihydroxybenzyl alcohols gave only about 20% of the desired product [14]; reduction of the corresponding dialkoxybenzaldehydes with lithium aluminium hydride instead gave these compounds in good yields [12].

Benzoic acids and cinnamic acids were treated with thionyl chloride in boiling toluene to give the acid chlorides. In general these were not purified and were used for the reaction with sodium azide (Curtius reaction) after removal of toluene and excess of thionyl chloride. The isocyanates **5** and **7** obtained by the Curtius reaction were either isolated by distillation (**5a**, **5b**, **5f**, **7a**) or converted to the corresponding isocyanurates after removal of the inorganic salts by filtration.

Cyclotrimerization of the isocyanates was achieved in solution in toluene, chlorobenzene or *o*-dichlorobenzene using catalytic amounts of CsF with equivalent amounts of dicyclohexyl-18-crown-6 (2,3,11,12-dicyclohexano- 1,4,7,10,13,16-hexaoxacyclooctadecane). The isocyanurates were purified as indicated in table 3.

The intermediate compounds as well as the isocyanates and isocyanurates were characterized by infrared, NMR spectroscopy and microanalysis. Yields, analytical and spectroscopic data of intermediates not described in the literature so far are summarized in table 2; those of the novel isocyanurates are given in table 3.

2.3. *Thermal and liquid crystal properties of isocyanurates*

All new intermediates and the novel isocyanurates were investigated by polarizing light microscopy and thermal analysis. Except for some of the acids none of the precursors exhibited mesophase behaviour. The thermal data (transition temperatures, transition enthalpies and entropies) of the novel isocyanurates together with those of the three unsubstituted parent compounds are presented in table 4. As most of the substituted isocyanurates had little tendency to crystallize from solution, crystallization was favoured by heating the compounds in boiling *n*-pentane.

The parent compounds are high melting solids (280, 158 and 231°C) for phenyl- **8**, benzyl- **9**, and styrylisocyanurate **10** respectively. The relatively low melting point of **9** as compared to **8** and **10** seems to be due mainly to the gain in entropy of this compound. A 4-decyloxy group causes a big depression of the melting point down to approximately 100°C for all three classes (103, 99 and 128°C) again with a low melting entropy for **8a**, the highest for **9a** and an intermediate value for **10a**. This seems to reflect the rigidity of the different central cores and the possibility of side chain crystallization.

The melting points of the 3,4-dialkoxyarylisocyanurates are in the range 74 to 131°C. No systematic change in terms of a continuous decrease with increasing chain length or with a given central core can be found. The order of melting temperatures phenyl > styryl > benzyl is preserved in those cases where all three isocyanurates have been synthesized. In a given series no monotonic decrease is found. The melting enthalpies, however, show a continous increase with chain length of the alkoxy substituents for each series. In contrast to side chain crystallization observed in comb like polymers [15], no side chain melting is observed and no enthalpy increment for a methylene group can be derived from the melting enthalpies. The single melting endotherms in the DSC traces and the melting entropies confirm the mutual influence of the central core and the hydrocarbon region on the quality of packing of both. X-ray analysis could help to gain further insight here.

Table 2

No.	Yield /%	b.p. /°C	m.p. /°C	^{1}H-NMR (CDCl$_3$)/ppm	^{13}C-NMR (CDCl$_3$)/ppm	Formula	Analysis C	H	N
							calcd./% found/%		
4c	77	—	117	0·89 (t, $^3J=7$ Hz, 6 H); 1·18–1·58 (m, 20 H); 1·75–1·85 (m, 4 H); 4·02 (d, $^3J=6·6$ Hz, 2 H); 4·03 (d, $^3J=6·6$ Hz, 2 H); 6·29 (d, $^3J=16·0$ Hz, 1 H); 6·86 (d, $^3J=8·6$ Hz, 1 H); 7·08–7·12 (m, 2 H); 7·71 (d, $^3J=16·0$ Hz, 1 H); 12–13 (s, 1 H).	14·0; 22·7; 26·0; 29·1; 29·4; 29·6; 29·7; 29·7; 29·8; 32·0; 69·1; 69·4; 112·5; 112·9; 114·6; 123·2; 127·0; 147·2; 149·3; 151·8; 172·3.	$C_{25}H_{40}O_4$ 404·59 g mol^{-1}	74·2 74·4	9·9 9·9	
4d	83	—	131	0·88 (t, $^3J=7$ Hz, 6 H); 1·20–1·55 (m, 28 H); 1·75–1·95 (m, 4 H); 4·02 (t, $^3J=6·6$ Hz, 2 H); 4·03 (t, $^3J=6·6$ Hz, 2 H); 6·29 (d, $^3J=16·0$ Hz, 1 H); 6·86 (d, $^3J=8·8$ Hz, 1 H); 7·08–7·12 (m, 2 H); 7·71 (d, $^3J=16·0$ Hz, 1 H); 12–13 (s, 1 H).	14·1; 22·7; 26·0; 26·1; 29·2; 29·3; 29·4; 29·5; 29·6; 29·7; 32·0; 69·1; 69·4; 112·5; 113·0; 114·5; 123·2; 126·9; 147·2; 149·3; 151·8; 172·3.	$C_{29}H_{48}O_4$ 460·70 g mol^{-1}	75·6 75·2	10·5 10·4	
4e	84	—	130	0·88 (t, $^3J=7$ Hz, 6 H); 1·18–1·58 (m, 36 H); 1·75–1·85 (m, 4 H); 4·02 (d, $^3J=6·6$ Hz, 2 H); 4·03 (d, $^3J=6·6$ Hz, 2 H); 6·29 (d, $^3J=16·0$ Hz, 1 H); 6·86 (d, $^3J=8·6$ Hz, 1 H); 7·08–7·12 (m, 2 H); 7·71 (d, $^3J=16·0$ Hz, 1 H); 12–13 (s, 1 H).	14·1; 22·7; 25·9; 26·0; 29·0; 29·2; 29·3; 29·4; 29·4; 29·6; 29·6; 31·9; 69·1; 69·5; 112·4; 112·9; 114·6; 123·2; 126·9; 147·2; 149·3; 151·7; 172·3.	$C_{33}H_{56}O_4$ 516·81 g mol^{-1}	76·7 76·7	10·9 10·9	
5a	79	88 0·03 mbar	—	0·89 (t, $^3J=7$ Hz, 3 H); 1·25–1·55 (m, 14 H); 1·75–1·90 (m, 2 H); 3·95 (t, $^3J=7$ Hz, 2 H); 6·85 (m, 2 H); 7·00 (m, 2 H).	14·1; 23·0; 26·0; 29·2; 29·3; 29·4; 29·6; 31·9; 68·4; 115·4; 124·2; 125·5; 125·7; 157·0.	$C_{17}H_{25}NO_2$ 275·39 g mol^{-1}	74·2 74·3	9·2 9·1	5·1 5·2
5b	82	190 0·05 mbar	—	1·00 (t, $^3J=7$ Hz, 6 H); 1·40–1·60 (m, 4 H); 1·70–1·90 (m, 4 H); 3·95 (t, $^3J=7$ Hz, 2 H); 4·00 (t, $^3J=7$ Hz, 2 H); 6·55–6·65 (m, 2 H); 6·75 (d, $^3J=9$ Hz, 1 H).	13·9; 19·3; 31·3; 31·4; 69·0; 69·4; 110·6; 114·5; 116·7; 126·3; 147·3; 149·9.	$C_{15}H_{21}NO_3$ 263·34 g mol^{-1}	68·4 68·9	8·0 7·9	5·3 5·3
5f	72	149 0·06 mbar	—	0·96 (t, $^3J=7·2$ Hz, 3 H); 0·98 (t, $^3J=7$ Hz, 6 H); 1·42–1·62 (m, 6 H); 1·64–1·86 (m, 6 H); 3·93 (t, $^3J=6·4$ Hz, 2 H); 3·94 (t, $^3J=6·4$ Hz, 4 H); 6·29 (s, 2 H).	13·8; 13·9; 19·2; 19·2; 31·3; 32·3; 68·9; 73·2; 103·5; 128·4; 136·3; 153·6.	$C_{19}H_{29}NO_4$ 335·44 g mol^{-1}	68·1 68·1	8·7 8·8	4·2 4·1
7a	82	172 0·04 mbar	48	0·89 (t, $^3J=7$ Hz, 3 H); 1·25–1·55 (m, 14 H); 1·75–1·90 (m, 2 H); 3·95 (t, $^3J=7$ Hz, 2 H); 6·35 (d, $^3J=15$ Hz, 1 H); 6·40 (d, $^3J=15$ Hz, 1 H); 6·80 (m, 2 H); 7·20 (m, 2 H).	14·1; 22·7; 26·1; 29·3; 29·4; 29·4; 29·6; 31·9; 68·1; 114·8; 115·4; 124·2; 126·7; 126·9; 127·2; 159·2.	$C_{19}H_{27}NO_2$ 301·43 g mol^{-1}	75·7 75·4	9·0 9·0	4·7 4·5

IR: Cinnamic acids (nujol): 3300–2300 cm^{-1} (O–H), 1660 cm^{-1} (C=O).
Isocyanates (film): 2278 cm^{-1} (N=C=O).

Table 3

No.	Reaction conditions	Purification r (recrystalized) f (flash chrom.) e (extraction)	Yield /%	Thermal behaviour /°C	^{1}H-NMR ($CDCl_3$)/ppm	^{13}C-NMR ($CDCl_3$)/ppm	Analysis		
							C	H calcd./% found./%	N
8a	toluene 7 d room temp.	r: ethanol	73	Cr 103 I	0·90 (t, ^{3}J = 7 Hz, 9 H); 1·20–1·55 (m, 42 H); 1·75–1·90 (m, 6 H); 3·95 (t, ^{3}J = 7 Hz, 6 H); 6·95 (m, 6 H); 7·25 (m, 6 H).	14·1; 22·6; 26·0; 29·2; 29·3; 29·4; 29·5; 31·9; 68·3; 115·1; 126·1; 129·4; 149·2; 159·2	74·1 73·9	9·2 9·2 $C_{51}H_{75}N_3O_6$ 826·17 g mol^{-1}	5·1 5·1
8b	toluene 3 d room temp.	r: ethanol	30	Cr 123 I	0·96 (t, ^{3}J = 6·9 Hz, 18 H); 1·40–1·60 (m, 12 H); 1·70–1·90 (m, 12 H); 3·98 (t, ^{3}J = 6·6 Hz, 6 H); 4·01 (t, ^{3}J = 6·6 Hz, 6 H); 6·87–6·91 (m, 9 H).	13·8; 19·2; 31·2; 69·0; 69·1; 113·3; 113·8; 120·7; 126·3; 149·1; 149·6; 149·7	68·4 68·1	8·0 7·9 $C_{45}H_{63}N_3O_9$ 790·01 g mol^{-1}	5·3 5·2
8d	ODCB 10 d 60°C 20 h 150°C	precipitation toluene/*n*-pentane f: toluene	13	Cr 98 I	0·89 (t, ^{3}J = 6·9 Hz, 18 H); 1·20–1·55 (m, 84 H); 1·75–1·95 (m, 12 H); 3·98 (t, ^{3}J = 6·6 Hz, 6 H); 4·01 (t, ^{3}J = 6·6 Hz, 6 H); 6·87–6·91 (m, 9 H).	14·0; 22·6; 25·9; 29·1; 29·3; 29·3; 29·5; 29·6; 31·8; 69·3; 113·3; 113·7; 120·6; 126·2; 149·0; 149·5; 149·6	75·1 75·1	10·5 10·5 $C_{81}H_{135}N_3O_9$ 1294·97 g mol^{-1}	3·2 3·1
8e	*o*-xylene 3 d room temp. 7 d 50°C 2 d 80°C	r: *iso*-propanol f: toluene	70	Cr 110 1c (85)	0·88 (t, ^{3}J = 6·6 Hz, 18 H); 1·18–1·58 (m, 108 H); 1·75–1·85 (m, 12 H); 3·96 (t, ^{3}J = 6·6 Hz, 6 H); 4·00 (d, ^{3}J = 6·6 Hz, 6 H); 6·86–6·91 (m, 9 H).	12·4; 14·1; 22·7; 26·0; 26·0; 29·2; 29·4; 29·4; 29·7; 29·7; 31·9; 69·3; 113·3; 113·8; 120·7; 126·3; 149·1; 149·6; 149·7	76·3 76·6	11·0 10·9 $C_{93}H_{159}N_3O_9$ 1463·30 g mol^{-1}	2·9 3·0
8f	chlorobenzene 3 d room temp.	e: ethanol	31	Cr 262 I	0·95 (t, ^{3}J = 7·2 Hz, 9 H); 0·97 (t, ^{3}J = 7·2 Hz, 18 H); 1·42–1·62 (m, 18 H); 1·64–1·86 (m, 18 H); 3·93 (t, ^{3}J = 6·4 Hz, 6 H); 3·94 (t, ^{3}J = 6·4 Hz, 12 H); 6·57 (s, 6 H).	13·9; 19·2; 19·3; 31·4; 32·3; 68·9; 73·1; 107·0; 28·4; 148·7; 153·5	68·0 68·0	8·7 8·9 $C_{57}H_{87}N_3O_{12}$ 1006·33 g mol^{-1}	4·2 4·1
9a	6 h 150°C	r: *iso*-propanol f: dichloromethane	61	Cr 99 I	0·88 (t, ^{3}J = 7 Hz, 9 H); 1·26–1·57 (m, 42 H); 1·68–1·79 (m, 6 H); 3·92 (t, ^{3}J = 6·6 Hz, 6 H); 4·94 (s, 6 H); 6·79–7·41 (m, 12 H).	14·1; 22·7; 26·0; 29·2; 29·3; 29·4; 29·6; 31·9; 68·0; 45·8; 114·4; 127·8; 130·7; 149·1; 159·0	74·7 74·9	9·4 9·5 $C_{54}H_{81}N_3O_6$ 868·25 g mol^{-1}	4·8 5·0
9d	12 h 150°C	f: dichloromethane	5	Cr 87 I	0·88 (t, ^{3}J = 7 Hz, 18 H); 1·26–1·57 (m, 84 H); 1·68–1·79 (m, 12 H); 3·95 (d, ^{3}J = 6·6 Hz, 6 H); 3·96 (d, ^{3}J = 6·6 Hz, 6 H); 4·95 (s, 6 H); 6·75–7·05 (m, 9 H).	14·1; 22·7; 25·9; 29·4; 29·7; 31·8; 46·1; 69·5; 113·5; 115·0; 122·0; 135·5; 149·0	75·4 75·3	10·6 10·8 $C_{84}H_{141}N_3O_9$ 1337·06 g mol^{-1}	3·1 2·8
9e	6 h 70°C	f: dichloromethane	20	Cr 81 I	0·88 (t, ^{3}J = 7 Hz, 18 H); 1·26–1·57 (m, 108 H); 1·68–1·79 (m, 12 H); 3·95 (d, ^{3}J = 6·6 Hz, 6 H); 3·96 (d, ^{3}J = 6·6 Hz, 6 H); 4·95 (s, 6 H); 6·75–7·03 (m, 9 H).	14·1; 22·7; 26·0; 26·1; 29·3; 29·4; 29·5; 29·7; 29·7; 29·8; 31·9; 45·9; 69·2; 69·3; 113·5; 115·0; 121·9; 128·5; 149·0; 149·1	76·6 76·8	11·1 11·3 $C_{96}H_{165}N_3O_9$ 1505·38 g mol^{-1}	2·8 2·8
10a	toluene 9 h reflux	r: *iso*-propanol	38	Cr 128 I	0·90 (t, ^{3}J = 7 Hz, 9 H); 1·20–1·55 (m, 42 H); 1·75–1·90 (m, 6 H); 3·95 (t, ^{3}J = 7 Hz, 6 H); 6·85 (m, 6 H); 6·95 (d, ^{3}J = 15 Hz, 3 H); 7·20 (d, ^{3}J = 15 Hz, 3 H); 7·40 (m, 6 H).	14·2; 22·7; 26·1; 29·3; 29·3; 29·4; 29·6; 31·9; 68·1; 114·8; 117·3; 127·0; 128·0; 129·3; 146·8; 159·5	75·7 75·6	9·0 9·1 $C_{57}H_{81}N_3O_6$ 904·28 g mol^{-1}	4·7 4·7

10b	chlorobenzene 3 d 45°C	e: *iso*-propanol	42	Cr 131 I	1·00 (t, $^3J=7·3$ Hz, 18 H); 1·42–1·62 (m, 12 H); 1·74–1·90 (m, 12 H); 4·02 (t, $^3J=6·4$ Hz, 6 H); 4·03 (t, $^3J=6·4$ Hz, 6 H); 6·86 (d, $^3J=8·9$ Hz, 3 H); 6·96–7·00 (m, 6 H); 6·99 (d, $^3J=14·5$ Hz, 3 H); 7·19 (d, $^3J=14·5$ Hz, 3 H).	13·9; 19·3; 31·3; 31·4; 68·9; 69·1; 111·8; 113·6; 117·5; 120·3; 127·5; 129·6; 146·9; 149·3; 149·8	70·5 70·4 $C_{51}H_{69}N_3O_9$ 868·12 g mol^{-1}	8·0 8·0	4·8 4·6
10c	toluene 3 d room temp.	r: *iso*-propanol f: toluene	31	Cr 74 lc[a] 125 I	0·88 (t, $^3J=7$ Hz, 18 H); 1·18–1·58 (m, 60 H); 1·75–1·85 (m, 12 H); 3·99 (d, $^3J=6·6$ Hz, 6 H); 4·00 (d, $^3J=6·6$ Hz, 6 H); 6·81–6·98 (m, 9 H); 6·98 (d, $^3J=14·6$ Hz, 3 H); 7·18 (d, $^3J=14·6$ Hz, 3 H).	14·1; 22·7; 26·0; 29·3; 29·3; 29·4; 31·8; 69·2; 69·3; 111·7; 113·6; 117·5; 120·3; 127·5; 129·6; 146·9; 149·3; 149·8	74·8 75·0 $C_{75}H_{117}N_3O_9$ 1204·76 g mol^{-1}	9·8 9·9	3·4 3·1
10d	chlorobenzene 3 d 45°C	e: *iso*-propanol f: toluene	38	Cr 90 lc[a] 133 I	0·88 (t, $^3J=7$ Hz, 18 H); 1·20–1·55 (m, 84 H); 1·75–1·95 (m, 12 H); 3·99 (t, $^3J=6·6$ Hz, 6 H); 4·00 (t, $^3J=6·6$ Hz, 6 H); 6·86 (d, $^3J=8·9$ Hz, 3 H); 6·96–7·00 (m, 6 H); 6·99 (d, $^3J=14·5$ Hz, 3 H); 7·19 (d, $^3J=14·5$ Hz, 3 H).	14·2; 22·7; 26·1; 29·4; 29·5; 29·6; 29·7; 31·9; 69·2; 69·4; 111·8; 113·3; 117·5; 120·3; 127·5; 146·9; 149·3; 149·8	76·1 76·1 $C_{87}H_{141}N_3O_9$ 1373·09 g mol^{-1}	10·3 10·2	3·1 3·0
10e	*o*-xylene 3 d room temp. 1 d 45°C	r: *iso*-propanol	44	Cr 83 lc[a] 130 I	0·88 (t, $^3J=7$ Hz, 18 H); 1·18–1·58 (m, 108 H); 1·75–1·85 (m, 12 H); 4·00 (d, $^3J=6·6$ Hz, 12 H); 6·81–6·98 (m, 9 H); 6·98 (d, $^3J=14·6$ Hz, 3 H); 7·18 (d, $^3J=14·6$ Hz, 3 H)	14·1; 22·7; 26·0; 26·0; 29·2; 29·3; 29·4; 29·4; 29·6; 29·7; 31·9; 69·2; 69·4; 111·8; 113·6; 117·4; 120·3; 127·5; 129·7; 146·9; 149·3; 149·8	77·3 77·0 $C_{99}H_{165}N_3O_9$ 1541·38 g mol^{-1}	10·6 10·3	2·7 2·4

IR (film): triphenyl- and tristyrylisocyanurates **8**, **9**: 1710 cm^{-1} (C=O); 1420 cm^{-1} (C–N).
Tribenzylisocyanurates **10**: 1690 cm^{-1} (C=O); 1450 cm^{-1} (C–N).

[a] lc refers to a liquid crystal phase considered, on the basis of microscopic texture, to be columnar hexagonal (D_h).

Liquid crystalline properties were found amongst the 3,4-dialkoxy substituted isocyanurates. The texture of **10c** shown in figure 1 is representative of all the liquid crystalline compounds described in this paper. It has all the features of a hexagonal columnar phase. Whether it is ordered or disordered can be decided only on the basis of X-ray analysis. DSC curves are shown for **10c** in figure 2 and for **8e** in figure 3. Figure 2 shows a melting endotherm and a second peak indicative of an enantiotropic phase for **10c**. **8e** has a monotropic mesophase. The transition from the mesophase to the isotropic phase and *vice versa* can be observed in the cooling mode or by heating the supercooled mesophase.

From the data in table 4 it follows that enantiotropic mesophases are obtained only in the series of tris(3,4-dialkoxystyryl)isocyanurates **10c–e** with 8 or more carbon atoms in the chain. With triphenylisocyanurate as the central core, a monotropic mesophase was found for the C_{12} derivative **8e**, while a virtual clearing point could be obtained by extrapolation for **8d** from mixtures with tris(3,4-didodecyloxystyryl)isocyanurate **10e**. In the benzylisocyanurate series, only virtual clearing points were found for **9d** and **9e**, again with **10e** as reference compound. In terms of the ability of the central cores to form discotic mesophases, the order is styrylisocyanurates > phenylisocyanurates > benzylisocyanurates. The results obtained on cyanurates with identical chain lengths indicate that above a chain length of 10 carbon atoms, the clearing points of the phenylisocyanurates and cyanurates are comparable, while the melting points of the former are higher [16].

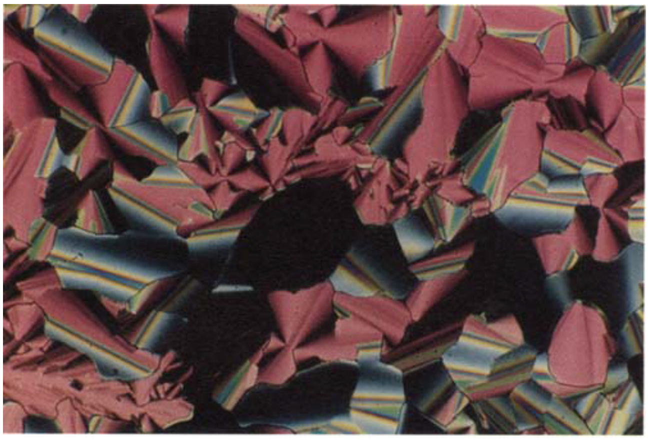


Figure 1. Texture of the mesophase of isocyanurate **10c** (original magnification 300 ×).

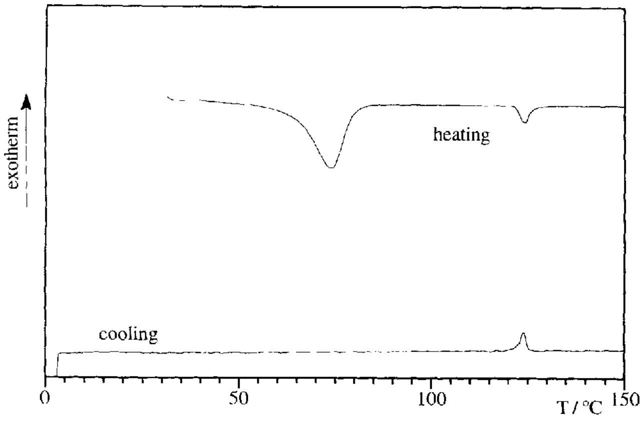


Figure 2. DSC trace of **10c**.

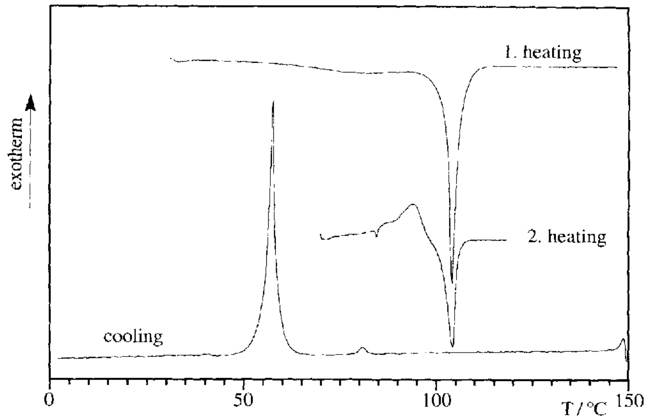


Figure 3. DSC trace of **8e**.

3. Conclusions

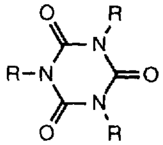
The ability of alkoxysubstituted triphenyl-, tribenzyl-, and tristyryl-isocyanurates, obtained by cyclotrimerization of the corresponding isocyanates, to form discotic mesophases has been investigated. All classes of compound can be obtained in good yields from the corresponding aldehydes in multistep reactions. 3,4-Dioctyloxy, didecyloxy, and didodecyloxy chains gave enantiotropic hexagonal phases for styrylisocyanurates, monotropic mesophases for phenylisocyanurates and no mesophases for benzylisocyanurates. This suggests that apart from the geometry, the electronic properties of the central core are of prime importance, but this will have to be proven with other suitable compounds.

4. Experimental

4.1. *Materials*

Toluene and tetrahydrofuran (THF) were distilled from Na–K alloy, and dimethylformamide (DMF), chlorobenzene and *o*-dichlorobenzene (ODCB) from phosphorous(V) oxide. DMF was collected over molecular sieves 3 Å. Thionyl chloride was distilled prior to use. Chloroform was washed with concentrated sulfuric acid and distilled. Flash chromatography was performed on Merck silica-gel 60/40-63. Air sensitive reactions were

Table 4. Thermal properties of isocyanurates.



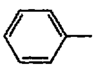
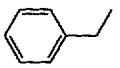
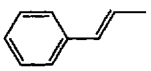
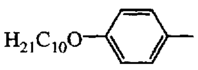
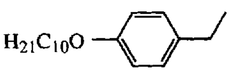
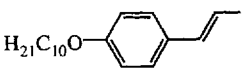
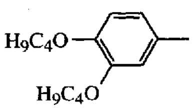
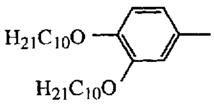
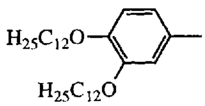
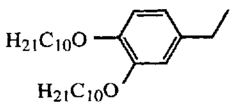
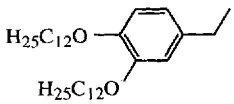
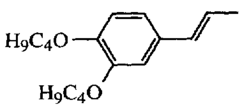
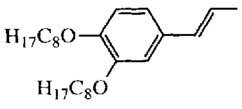
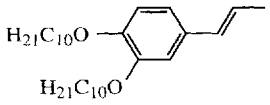
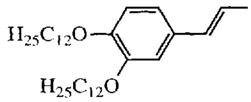
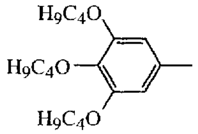
No.	R	T_m /°C	ΔH_m /kJ mol^{-1}	ΔS_m J K^{-1} mol^{-1}	T_i /°C	ΔH_i /kJ mol^{-1}	ΔS_i /J K^{-1} mol^{-1}
8		280	28·8	52·0	—	—	—
9		158	37·0	85·7	—	—	—
10		231	25·5	50·6	—	—	—
8a		103	13·9	40·0	—	—	—
9a		99	57·5	154·7	—	—	—
10a		128	44·1	110·0	—	—	—
8b		123	56·1	141·7	—	—	—
8d		98	58·0	156·3	(40) extrapol.	—	—
8e		110	89·4	233·4	(85)	1·6	4·5
9d		87	56·3	156·1	(25) extrapol.	—	—
9e		81	72·4	204·5	(37) extrapol.	—	—
10b		131	57·8	143·1	(39) extrapol.	—	—

Table 4. (*continued*)

No.	R	T_m /°C	ΔH_m /kJ mol^{-1}	ΔS_m J K^{-1} mol^{-1}	T_i /°C	ΔH_i /kJ mol^{-1}	ΔS_i /J K^{-1} mol^{-1}
10c		74	64·8	171·2	125	4·6	11·5
10d		90	70·5	194·2	133	4·4	10·8
10e		83	83·5	234·5	130	6·6	16·5
8f		262	63·8	119·3	—	—	—

performed using standard Schlenk techniques under dry argon.

4.2. *Methods of characterization*

Infrared spectra were recorded on a Bruker IFS48-FT-IR as films between NaCl plates. Solid samples were either dissolved in an appropriate solvent or prepared as nujol mulls. NMR spectra were obtained with a Bruker AC-200, using chloroform-D with TMS as internal standard. Thermal transitions were investigated with a Nikon Optiphot 2 polarizing microscope equipped with a Mettler FP 82 hot stage and an FP 80 processing unit. Transition enthalpies and temperatures were recorded with a Mettler DSC 30/TC 11 system (heating rate 10 K min^{-1}). Elemental analyses were made by Mikroanalytisches Labor Beller, Göttingen.

4.3. *3,4-Dialkoxybenzaldehydes (***1b–e***)* [17, 10], *4-decyloxy-benzoic acid (***2a***) and -cinnamic acid (***4a***)* [8], *4-decyloxybenzyl alcohol (***3a***)* [14], *3,4,5-tributoxybenzoic acid (***2f***)* [9], *3,4-dibutoxybenzoic acid (***2b***)* [18], *3,4-didecyloxy- and 3,4-didodecyloxy-benzoic acid (***2d, 2e***)* [10]

These compounds were prepared as described in the literature.

4.4. *Dialkoxybenzylalcohols (***3d, 3e***)*

These were prepared according to the literature [12] by reduction of the dialkoxybenzaldehydes. The solids which remained after removal of volatile matter were used without further purification.

4.5. *Chloromethylbenzenes (***6a, 6d, 6e***)*

These compounds were prepared by reaction of trimethylsilyl ethers, derived from the above benzyl alcohols, with thionyl chloride. Details will be presented in a separate paper.

4.6. *3,4-Dialkoxycinnamic acids (***4b–e***)*

These were obtained from 3,4-dialkoxybenzaldehydes **1b–e** according to Koo *et al.* [11]. Purification of the crude products was performed by recrystallisation from glacial acetic acid. Yields and analytical data for **4c–e** are given in Table 2.

4.7. *Acid chlorides*

The acid (**2a, 2b, 2d–f, 4a–e**) was dissolved in a five fold excess of toluene and heated under reflux with a 1·5 fold molar excess of thionyl chloride. After the evolution of gas had finished, the solvent and excess of thionyl chloride were removed and the residue either distilled in vacuum (acids **2a, 2b, 2f, 4a, 4b**) or used for further reaction without purification.

4.8. *Isocyanates*

In a flask equipped with reflux condenser, magnetic stirrer, bubble counter and $CaCl_2$ tube, the acid chloride was dissolved in a three fold excess of toluene, chlorobenzene or ODCB. A 1·3 fold molar excess of sodium azide was added and the mixture heated under reflux. After the carbonyl absorption in the infrared spectrum had disappeared, the inorganic material was filtered off under anhydrous conditions and the filtrate evaporated. The residue was either distilled in vacuum (**5a–c, 7a**) or used for further preparations without purification (**5d–f, 7b–e**). Yields and analytical data for the isolated compounds are shown in table 2.

4.9. *Phenyl- and styryl-isocyanurates (***8a, 8b, 8d–f, 10a–e***)*

To the isocyanate, dissolved in toluene, chlorobenzene or ODCB, 5 mol % each of cesium fluoride and crown ether (dicyclohexyl-[18]-crown-6) were added. With stirring, the mixture was kept under the conditions described in table 3. After the isocyanate absorption in the infrared spectrum had disappeared, the crude product was precipitated by addition of methanol and purified as described in table 3.

4.10. *Tribenzylisocyanurates (***9a, 9d, 9e***)*

The chloromethyl compound was dissolved under anhydrous conditions in a 3 fold excess (v/v) of dry DMF. A 1·2 fold molar excess of potassium cyanate and a catalytic amount of potassium iodide were added and the reaction mixture was stirred and heated as described in table 3. After the isocyanate absorption in the infrared had disappeared, the product was precipitated in methanol and purified as described in table 3.

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References

[1] Chandrasekhar, S., 1993, *Liq. Cryst.*, **14**, 3.

[2] Destrade, C., Nguyen, H. T., Gasparoux, H., Malthête, J., and Levelut, A. M., 1981, *Mol. Cryst. liq. Cryst.*, **71**, 111.

[3] LeBarny, P., Billard, J., and Dubois, J. C., 1984, *Liquid Crystals and Ordered Fluids*, Vol. 4, edited by A.C. Griffin and J.F. Johnson (Plenum Publ. Corp.), p. 57.

[4] Lattermann, G., and Höcker, H., 1986, *Mol. Cryst. liq. Cryst.*, **133**, 245.

[5] Huang, S. J., Feldman, J. A., and Cercena, J. L., 1989, *Polym. Prepr. Am. chem. Soc., Div. polym. Chem.*, **30**, 348.

[6] Mormann, W., and Zimmermann, J. G., 1995, *Liq. Cryst.*, **19**, 481.

[7] Mormann, W., and Zimmermann, J. G., 1995, *Liq. Cryst.*, **19**, 227.

[8] Mertesdorf, C., and Ringsdorf, H., 1989, *Liq. Cryst.*, **5**, 1757.

[9] Rabjohn, N., and Mendel, A., 1957, *J. chem. Soc.*, **22**, 986.

[10] Nguyen, H. T., Destrade, C., and Malthête, J., 1990, *Liq. Cryst.*, **8**, 797.

[11] Koo, J., Fish, M. S., Walker, G. N., and Blake, J., 1963, *Org. Synth. Coll.* Vol. 4, (J. Wiley & Sons), p. 327.

[12] Nystrom, R. F., and Brown, W. G., 1947, *J. Am. chem. Soc.*, **69**, 1197.

[13] Dieterich, D., 1987, *Methoden der organischen Chemie (Houben-Weyl), Makromolekulare Stoffe*, Vol. E 20, edited by H. Bartl and J. Falbe (Georg Thieme Verlag), p. 1741.

[14] Anderson, R. C., Reitter, B. E., and Winslow, C. M., 1986, *Chem. Phys. Lipids*, **39**, 73.

[15] Espenschied, B., and Schulz, R. C., 1983, *Makromol. Chem., Rapid Commun.*, **4**, 633.

[16] Bauer, M., *et al.* (to be published).

[17] Pearl, I. A., and Beyer, D. L., 1953, *J. Am. chem. Soc.*, **75**, 2630.

[18] Moore, M. B., Wright, H. B., Vernsten, M., Freifelder, M., and Richards, R. K., 1954, *J. Am. chem. Soc.*, **76**, 3656.