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Werner Mormann[a]; Jörg G. Zimmermann[a]
[a] Universität-GH Siegen, Siegen, Germany

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Synthesis and mesomorphic properties of cyanurates and isocyanurates. Branched mesogens as model crosslinks for liquid crystalline thermosets†

by WERNER MORMANN* and JÖRG G. ZIMMERMANN
Universität-GH Siegen, Fachbereich 8, Laboratorium für Makromolekulare Chemie,
Adolf-Reichwein-Str. 2, D-57068 Siegen, Germany

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A number of new *s*-triazines (cyanurates and isocyanurates) with diaromatic mesogenic branches have been synthesized and their thermal properties investigated. No liquid crystal phases were found in the series of isocyanurates, while the cyanurates form enantiotropic calamitic mesophases (nematic and in one case smectic). No discotic mesophases could be detected. The mesogenic power of the cyclotrimers is reversed with respect to that of the monomers from which they can be obtained (cyanates and isocyanates). Molecular calculations reveal that the cyanurates can adopt an extended rod-like conformation due to the flexibility introduced by the oxygen bridge between the central ring and the mesogenic branches. The direction of the ester group in the phenyl benzoate mesogenic branches has a tremendous influence on the mesomorphic properties, with the result that mesophases could only be observed if the benzoic acid part was attached to the triazine ring.

1. Introduction

Liquid crystalline compounds based on trisubstituted *s*-triazines were first proposed by LeBarny and co-workers ten years ago [1]. This structure, when used as the central core of mesogens, was thought to favour disc-like structures and discotic mesophases. Tris(dialkylamino)-*s*-triazines, as a first realization of this idea, were reported by Lattermann and Höcker who, however, did not observe discotic mesophases [2]. Huang and co-workers reacted mesogenic 4-(4-methoxybenzylideneamino)-phenol with cyanuric chloride and reported that the resulting 2,4,6-tris[4-(4-methoxybenzylideneamino)phenoxy]-1,3,5-triazine exhibits discotic mesophase behaviour [3]. Ober *et al.*, demonstrated in a recent paper that thermosets with a frozen liquid crystalline organization can be obtained by polymerization of mesogenic triaromatic dicyanates [4]. A cyanurate model compound, which they synthesized by cyclotrimerization of 4-cyanatophenyl 4-butoxybenzoate (compound **2 c** in table 1 and 3) did not show liquid crystalline behaviour.

Isocyanurates (1,3,5-trisubstituted triazine 2,4,6-triones) are isomers of cyanurates which can be obtained by cyclotrimerization of isocyanates. Liquid crystalline isocyanurates have not been reported so far, though a number of mesogenic di-isocyanates have been described in the literature [5, 6]. Two-dimensional formulae of the isomeric triazines (cf. schemes 1 and 2) suggest that disc-like structures are likely to be formed from both isomeric triazines.

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. Difunctional cyanates and isocyanates are both used as monomers for thermosets, in which triazine rings constitute the crosslinks which form during the network built up. Hence, knowledge of the mesogenic power of the two isomeric triazine rings, i.e. the stabilization or destabilization of a mesophase in terms of melting and clearing transitions is also of interest for the systematic study of liquid crystalline thermosets.

In a foregoing paper, we described the synthesis and mesomorphic properties of isocyanates and isostructural cyanates, and we arrived at the conclusion that the isocyanate group has a much higher mesogenic power than the isomeric cyanate group probably because of the more favourable aspect ratio of the former [7].

The present paper deals with the results of the investigation of a series of 2,4,6-aryloxy-1,3,5-triazines (cyanurates) and their isocyanurate counterparts (1,3,5-aryl substituted triazine triones).

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* Author for correspondence.

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2. Experimental

2.1. *Methods of characterization*

Infrared spectra were recorded on a Bruker IFS48-FT-IR spectrometer using films between NaCl plates. Solid samples were either prepared as films from an appropriate solvent or as nujol mulls. NMR spectra were recorded on a Bruker AC-200 spectrometer using deuteriochloroform 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 FP 80 processing unit. Transition enthalpies and temperatures were recorded with a Mettler DSC/30 TC 11 system (heating rate 20 K min^{-1}). The virtual clearing point of **2c** was determined from mixtures with **3c** as reference compound. Elemental analyses were carried out by Mikroanalytisches Labor Beller, Göttingen.

Semi-empirical calculations PM3 [14, 15] were made on an IBM RS6000 workstation using Spartan 3.1.2 (Wavefunction Inc. Irvine, Cal.)

2.2. *Materials*

Cyanuric chloride was purchased from Aldrich. Hexamethyldisilazane was a gift from Bayer AG, Leverkusen. 1,2-Dichlorobenzene and dimethylformamide were distilled over phosphorus (V) oxide. Toluene and hexane were distilled over sodium. Acetone was distilled over calcium chloride.

The synthesis of 4-butoxyphenyl 4-cyanatobenzoate and 4-cyanatophenyl 4-butoxy benzoate has been reported previously [7]. 4-Methoxyphenyl 4-hydroxybenzoate [11], 4-cyano-4′-hydroxyazobenzene [17] and 4-hydroxy-4′-methoxybiphenyl [18] were synthesized as reported in the literature.

2.3. *Silylation of phenols* (**3s**, **5s**, **6s**, **7s**); *general procedure*

4-Cyano-4′-trimethylsiloxyazobenzene (**7s**) and 4-methoxy-4′-trimethylsiloxybiphenyl (**6s**) were synthesized according to reference [19]. 0·1 mol of the phenol and 0·055 mol of hexamethyldisilazane, together with a small amount of saccharine, were stirred at 100°C until the evolution of gas had finished. Volatiles were removed *in vacuo* and the crude products were purified by distillation in a Büchi Kugelrohr apparatus. For yields, analytical and physical properties see table 2.

2.4. *Cyanurates* (**1c**, **2c**, **8c**, **9c**) *by cyclotrimerization; general procedure*

10 mmol of the cyanate and 1 mol% of copper(II) acetylacetonate were dissolved in dry hexane (10% w/w). The mixture was stirred at reflux temperature for 36 h, and the conversion of cyanate groups was monitored by FT-IR. The precipitated cyanurate was filtered off, washed twice with hot hexane, and recrystallized from acetone, 1,2-dichlorobenzene, or toluene. For yields, analytical and physical properties see table 1.

2.5. *Cyanurates* (**3c**, **5c**, **6c**, **7c**); *silyl method-general procedure*

30 mmol of the trimethylsiloxy compound, 9·5 mmol of cyanuric chloride and a crystal of 4-*N*,*N*-dimethylaminopyridine as catalyst were dissolved in dry 1,2-dichlorobenzene. The mixture was stirred at 140–180°C for 2–4 h. After the theoretical amount of trimethylchlorosilane had distilled off, the precipitated cyanurate was filtered off, washed with hot hexane, and recrystallized from acetone, 1,2-dichlorobenzene, or toluene. For yields, analytical and physical properties see table 1.

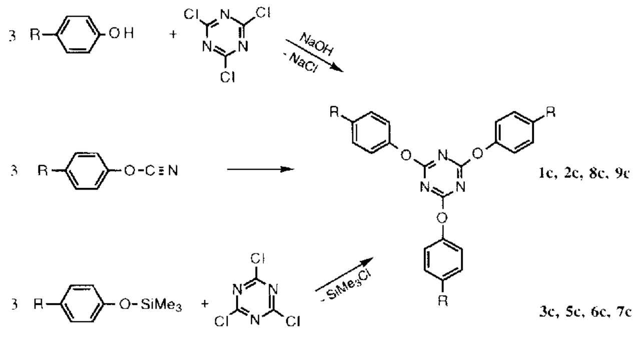
2.6. *Isocyanurates* (**1i**, **2i**, **4i**); *general procedure*

30 mmol of the isocyanate, 5 mg of dicyclohexano-18-crown-6, and a small crystal of cesium fluoride were dissolved in 15 ml of dry toluene. The mixture was stirred at room temperature for 5 h and the isocyanurate was precipitated in methanol and purified by recrystallization from ethanol. For yields, analytical and physical properties see table 1.

3. Results and discussion

3.1. *Synthesis of mesogenic cyanurates and isocyanurates*

The cyanurates and isocyanurates synthesized for the present study were selected partly on the basis of the corresponding cyanates and isocyanates which had been investigated in a previous study [7]. Further compounds were synthesized to vary the structure of the mesogenic branches (biphenylene, azobenzene). The two cyanurates without terminal groups 2,4,6-tris(4-phenoxycarbonylphenoxy)-1,3,5-triazine, and 2,4,6-tris(4-benzoyloxyphenoxy)-1,3,5-triazine, which are different only with respect to the direction of the ester group, were also included in order to learn about the effect caused by this



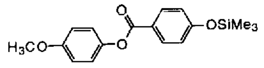
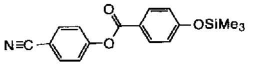
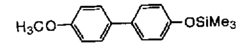
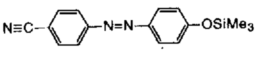
Scheme 1.

Table 1. Yields, purification, analytical data, spectroscopic properties of mesogenic cyanurates and isocyanurates.

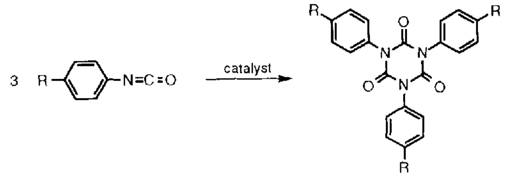
Compound	^{1}H NMR ($CDCl_3$) δ/ppm (number of H per branch)	Molecular formula	Elemental analysis/per cent			T_m/°C	Yield/per cent (Purification)
			C	H	N		
1c	8·28 (d, ^3J = 8·7 Hz, 2 H), 7·30–7·10 (m, 4 H), 6·90 (d, ^3J = 7·3 Hz, 2 H), 3·98 (t, ^3J = 6·7 Hz, 2 H), 1·80 (m, 2 H), 1·45 (m, 2 H), 1·00 (t, ^3J = 6·7 Hz, 3 H)	$C_{54}H_{51}N_3O_{12}$ (934·01)	69·44 (69·13)	5·50 (5·45)	4·50 (4·30)	157	59 (from acetone)
2c	8·10 (d, ^3J = 8·7 Hz, 2 H), 7·20 (m, 4 H), 6·92 (d, ^3J = 7·3 Hz, 2 H), 4·08 (t, ^3J = 6·7 Hz, 2 H), 1·86 (m, 2 H), 1·55 (m, 2 H), 1·00 (t, ^3J = 6·7 Hz, 3 H)	$C_{54}H_{51}N_3O_{12}$ (934·01)	69·44 (68·94)	5·50 (5·37)	4·50 (4·40)	239	48 (from toluene)
3c	8·24–6·87 (m, 8 H, AA'XX'), 3·81 (s, 3 H)	$C_{45}H_{33}N_3O_{12}$ (807·77)	66·91 (66·80)	4·12 (4·20)	5·20 (5·20)	199	94 (washed with hexane)
5c	8·20–7·45 (m, 8 H, AA'XX')	$C_{45}H_{24}N_6O_9$ (792·72)	68·18 (67·40)	3·05 (3·10)	10·60 (11·20)	250	87 (from ODCB)
6c	7·53–7·41 (m, 4 H), 7·27–7·17 (m, 2 H), 6·96–6·91 (m, 2 H), 3·89 (s, 3 H)	$C_{42}H_{33}N_3O_6$ (675·74)	74·65 (74·50)	4·92 (5·00)	6·22 (6·30)	219	73 (from toluene)
7c	8·02–7·34 (m, 8 H, AA'XX')	$C_{42}H_{24}N_{12}O_3$ (744·73)	67·77 (67·50)	3·24 (3·30)	22·54 (22·60)	286	81 (from ODCB)
8c	8·34–7·10 (m, 9 H)	$C_{42}H_{27}N_3O_9$ (717·69)	70·29 (69·90)	3·79 (3·83)	5·85 (5·84)	g	86 (freeze drying)
9c	Insufficient solubility in common deuteriated solvents	$C_{42}H_{27}N_3O_9$ (717·69)	70·29 (70·05)	3·79 (4·04)	5·85 (5·87)	264	78 (from DMF)
1i	8·5–7·5 (m, 4 H, AA'XX'), 7·2–6·8 (m, 4 H, AA'XX') 4·0 (t, 2H), 2·0–1·2 (m, 4H), 1·0 (t, 3H)	$C_{54}H_{51}N_3O_{12}$ (934·01)	69·44 (69·80)	5·50 (5·76)	4·50 —	224	58 crude product
2i	8·2–6·8 (m, 8 H, AA'XX'), 4·1 (t, 2 H), 2·0–1·2 (m, 4 H), 1·0 (t, 3 H)	$C_{54}H_{51}N_3O_{12}$ (934·01)	69·44 (69·40)	5·50 (5·70)	4·50 (4·50)	189	50 (from ethanol)
4i	8·3–6·9 (m, 8 H, AA'XX'), 3·9 (s, 3 H)	$C_{45}H_{33}N_3O_{12}$ (807·77)	66·91 (66·70)	4·12 (4·80)	5·20 (5·10)	330	60 (from ethanol)

IR all compounds: –C=N– 1560–1580, 1360–1380 cm^{-1} (triazine)
g: amorphous.

Table 2. Yields, analytical data, and spectroscopic properties of silylated phenols.

Compound	Structure	^{1}H NMR ($CDCl_3$) δ/ppm	Molecular formula	Elemental analysis /per cent calculated (found)		Bp_{mbar}/°C	Yield/ per cent
				C	H		
3s		0·44 (s, 9 H), 3·76 (s, 3 H), 6·91–8·18 (AA'XX', 8 H)	$C_{17}H_{20}O_4Si$ (316·43)	64·53 (64·75)	6·37 (6·40)	$180_{0\cdot08}$	77
5s		0·30 (s, 9 H), 6·91–8·11 (AA'XX', 8 H)	$C_{17}H_{17}NO_3Si$ (311·41)	65·57 (64·55)	5·50 (5·70)	$200_{0\cdot06}$	87
6s		0·33 (s, 9 H), 3·86 (s, 3 H), 6·92–7·01 (m, 4 H), 7·43–7·53 (m, 4 H)				$210_{0\cdot04}$	87
7s		0·32 (s, 9 H), 6·96–7·97 (AA'XX', 8 H)				$210_{0\cdot06}$	70

IR all compounds –C=C– 1600 cm^{-1} (aromatic), $SiCH_3$ 1267, 846 cm^{-1}.



1i, 2i, 4i

Scheme 2.

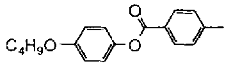
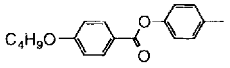
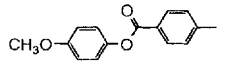
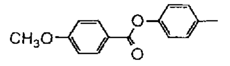
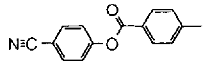
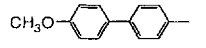
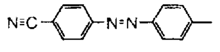
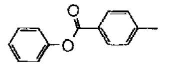
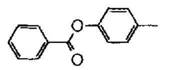
inversion which had shown a pronounced influence on the mesomorphic properties of the corresponding monomers. The nomenclature used in this paper has identical numbers for cyanurates, isocyanurates and silylated phenols with identical mesogenic branches with the addition of a **c** for cyanurate, an **i** for an isocyanurate, and an **s** for a silylated phenol.

There are two major routes to obtain 2,4,6-tris(aryloxy)-1,3,5-triazines as shown in scheme 1. Most frequently used is the cyclotrimerization of aromatic cyanates, which is also the basis of polycyanurate thermosets [8]. This reaction is catalysed by (Lewis) acids and bases. A very clean reaction is observed if the same phenol is used as catalyst as that from which the cyanate to be cyclotrimerized was obtained [9]. The second route to cyanurates is a nucleophilic displacement reaction of the chlorine atoms in cyanuric chloride. This reaction requires molar amounts of an acid acceptor like sodium hydroxide. If trimethylsiloxy arenes (silylated phenols) instead of phenols are reacted with cyanuric chloride, cyanurates are formed in high yields and purity. This type of reaction works well with carboxylic acid chlorides [10] and proved to be applicable also to cyanuric chloride. Only catalytic amounts of an acid or base are required in this reaction, trimethylchlorosilane is formed as by-product, and no reverse reaction is observed. It is convenient, however, to remove trimethylchlorosilane from the reaction mixture in order to monitor the reaction. A further advantage is the higher volatility of the siloxyarenes as compared to the phenols; this allows purification by distillation instead of repeated recrystallization, as required for the phenols. Cyanurates obtained by this method are almost analytically pure without further purification. The silyl method and the cyclotrimerization were used exclusively in this study.

The cyanates used have been described in a previous paper [7]. The trimethylsiloxyarenes were obtained from the corresponding phenols by reaction with hexamethyldisilazane in the presence of saccharine as catalyst. The crude siloxyarenes can be used for the esterification, but if necessary they can be purified by short path distillation in a Büchi Kugelrohr apparatus. The phenols used have also been described in detail previously [7, 11–13]; the analytical and physical properties of the siloxyarenes are summarized in table 2.

Eight different cyanurates were synthesized. They were purified by recrystallization and characterized by infrared

Table 3. Thermal transitions, enthalpies, and phase behaviour of mesogenic cyanurates and isocyanurates.

Cyanurate						Isocyanurate				
Compound	T_m/°C	$T_{N\text{-}I}$/°C	ΔH_m/ kJ mol^{-1}	$\Delta H_{N\text{-}I}$/ kJ mol^{-1}	Mesogenic core	Compound	T_m/°C	$T_{N\text{-}I}$/°C	ΔH_m/ kJ mol^{-1}	$\Delta H_{N\text{-}I}$/ kJ mol^{-1}
1c	157	217/ 224	37·1	0·84/ 1·05		**1i**	224	—	17·0	—
2c	239	virt. (76)	51·1	—		**2i**	189	—	21·3	—
3c	199	238	33·0	0·81		—				
—						**4i**	330		45·7	
5c	250	>300	55·2	—		—				
6c	219	(209)	52·0	—		—				
7c	286	305	36·6	1·20		—				
8c	g	—	—	—		—				
9c	264	—	70·0	—		—				

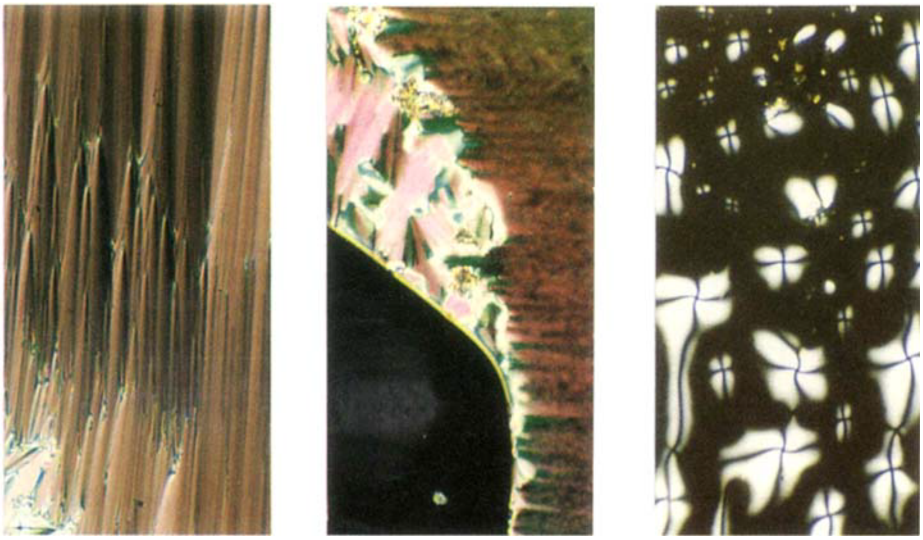

(*a*) (*b*) (*c*)

Figure 1. Textures of **1c** at (*a*) 214°C, (*b*) 217°C, and (*c*) 224°C, 120 × magnification.

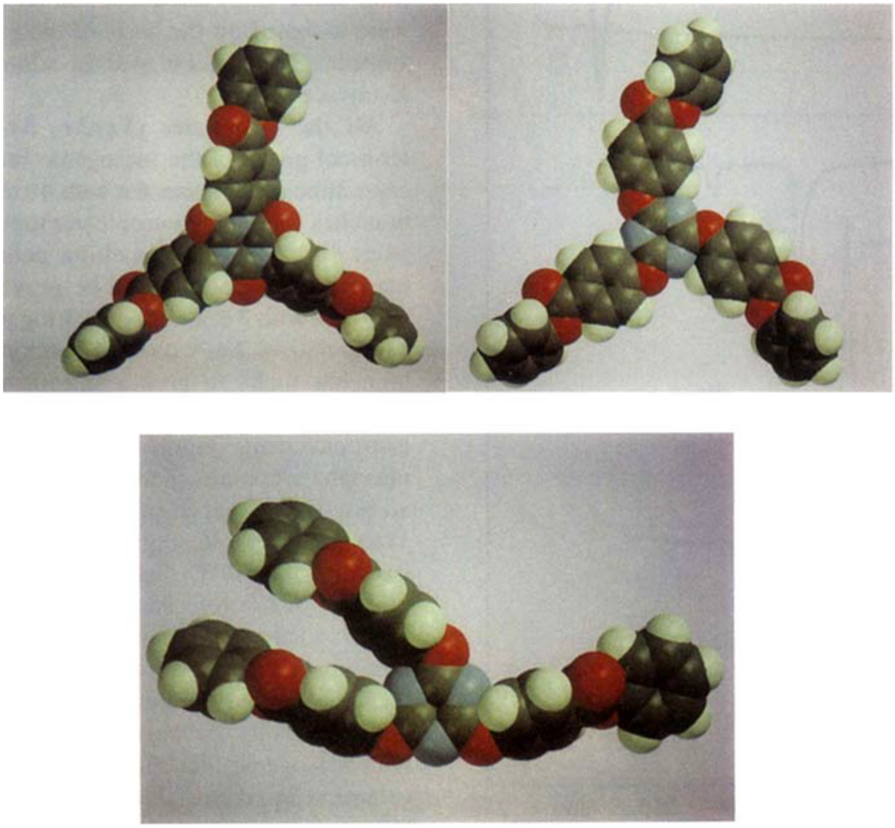


Figure 4. Space filling models of cyanurates and isocyanurates (upper left isocyanurate star-shaped, upper right cyanurate star-shaped, lower cyanurate rod-like).

and NMR spectroscopy and by elemental analyses. Purity was checked by thin layer chromatography. Yields and analytical data for the cyanurates are given in table 1.

The method of choice for the synthesis of mesogenic isocyanurates is the cyclotrimerization of the corresponding isocyanates as shown in scheme 2; the reaction was effected in the presence of CsF/crown ether in toluene as solvent. The isocyanates used were synthesized from an appropriate benzoyl chloride and a siloxybenzene and have been described previously. The isocyanurates precipitated from the solution and were almost analytically pure as crude products. Three isocyanurates with phenyl benzoate mesogenic branches were prepared; their analytical properties are included in table 1.

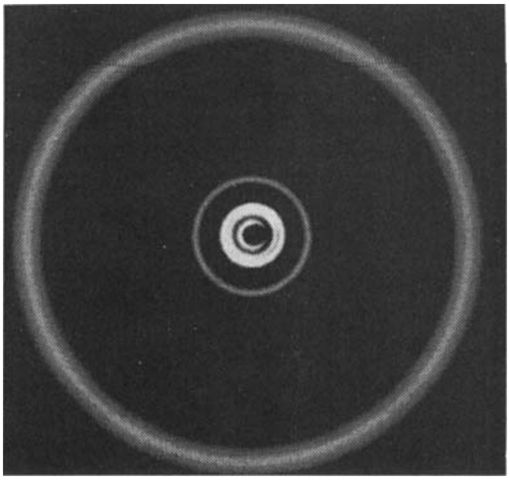


Figure 2. X-ray diffraction pattern of **1c** at 180°C.

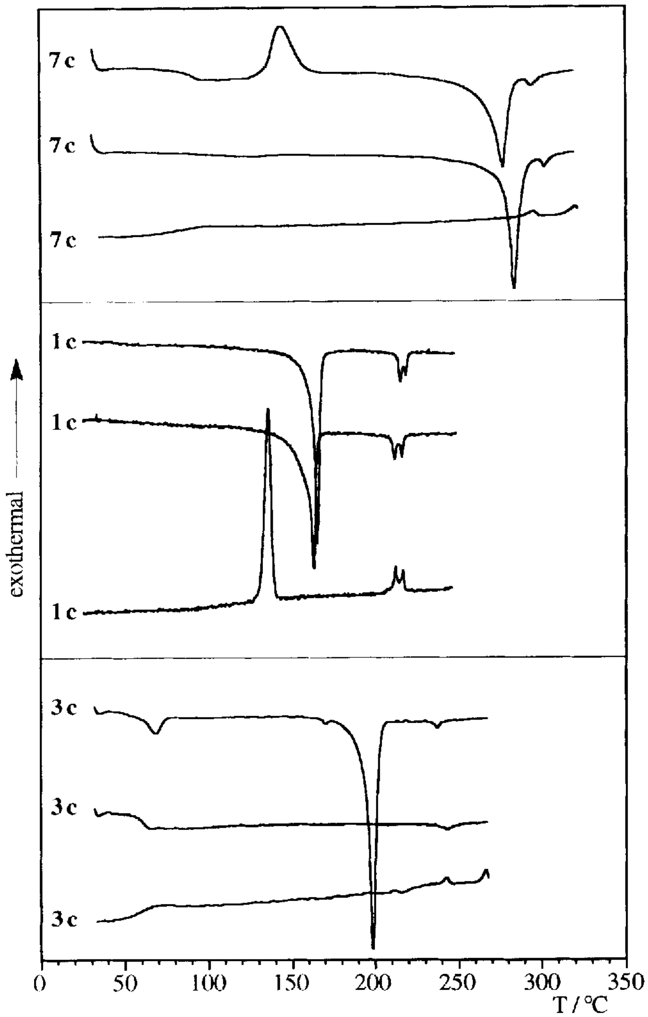


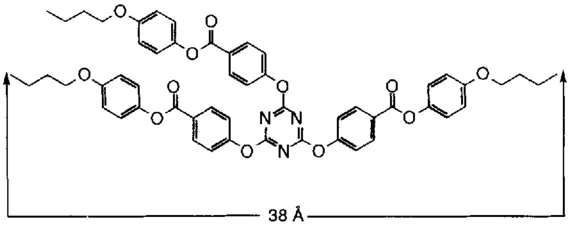
Figure 3. DSC traces of **1c**, **3c**, and **7c**; heating and cooling rate 20 K min^{-1} (1st heating: upper curve; 1st cooling: lower; 2nd heating: middle).

3.2. *Mesomorphic properties*

The mesophase behaviour of the new compounds was investigated by polarized light microscopy and thermal analysis (differential scanning calorimetry). The thermal transitions, together with the corresponding enthalpies, are given in table 3. Each entry contains the properties of cyanurate on the left hand side, while those of the isocyanurates are given on the right hand side. Isostructural compounds are contained on one line. The phases were assigned on the basis of their typical textures. The smectic phase of **1c**, was in addition, investigated by X-ray scattering.

All the cyanurates (**1c**–**3c**, **5c**–**7c**) which have a terminal group in the mesogenic branches form a liquid crystalline mesophase. **6c** with 4′-methoxybiphenyl-4-yl branches has a monotropic mesophase with a clearing point 10°C below the melting point, while for **2c**, the mesogenic character could be proven only by studies of mixtures with **3c**; a virtual clearing point was obtained by extrapolation. **1c**, with 4-(4-butoxybenzoyloxy)phenoxy branches melts to give a smectic mesophase which is transformed into a nematic phase and finally forms an isotropic melt. Figure 1 shows micrographs of the mesophase textures of this compound at different temperatures: the fan shaped smectic texture at 214°C (see figure 1(*a*)), the biphasic region during the smectic–nematic transition at 217°C (see figure 1(*b*)), and the nematic droplets just before isotropization at 224°C (see figure 1(*c*)). All the other compounds formed only a nematic mesophase. No indication or proof of a discotic mesophase could be derived from the textures [12], and in agreement with the results of Ober [4], we conclude that cyanurates with mesogenic branches of the kind typically used for calamitic liquid crystals do not form discotic mesophases. Hence the assignment by Huang *et al.*, very likely is not correct [3].

X-ray investigation of **1c** at 180°C, see figure 2, gave reflections which correspond to 19·3 and 38·5 Å. A molecular model based on an extended rod-like conformation has an end to end distance of 38 Å. Antiparallel arrangement of adjacent cyclotrimers, which is required for space filling reasons, divides the layers in two halves with the cyanurate ring as one boundary and the butoxy terminal group as the second boundary, and hence gives rise to the reflection with the 19·3 Å layer spacing. This seems to be reasonable, as this reflection is less sharp than that corresponding to the length of the whole cyclotrimer. A third sharp reflection at still lower angle is also observed and is equivalent to a 51 Å layer thickness. No molecular interpretation can be given at this point. The results, however confirm a smectic A phase for **1 c**.



1 c

The melting points of the cyanurates vary from approximately 150°C (**1 c**) to almost 300°C (**7 c**), while clearing points were in the range between 210 and 305°C, depending on the structure of the mesogenic branch and the terminal group. The influence of the mesogenic branch (azobenzene > phenyl benzoate > biphenylyl) and of the terminal groups ($-\mathrm{CN} > -\mathrm{OCH_3} > -\mathrm{OC_4H_9}$) is in agreement with the results found for linear mesogens [13].

The thermal transitions of the cyanurates are almost unchanged on second heating cycles as can be seen from the DSC traces shown for **1 c**, **3 c**, and **7 c** in figure 3. The thermal stability is limited by the chemical nature of the mesogenic branches. It is also noteworthy that cyanurates with short terminal groups in the mesogenic branches (**3 c**, **7 c**) have only a weak tendency to recrystallize on cooling. Nematic glasses are obtained, which either recrystallize on second heating (**7 c**) or remain nematic up to the clearing point. The butoxy terminal group obviously acts as an internal solvent which imparts sufficient mobility to the core to enable crystallization when the sample is cooled. This assumption is supported by the thermal properties of 2,4,6-tris(4-phenoxycarbonylphenoxy)-*s*-triazine (**8 c**), which could be obtained in crystalline form neither from the melt nor from a number of different solvents.

The 'direction' of the ester group in the phenyl benzoate branches has a remarkable influence on the thermal transitions. If the triazine ring is attached to the benzoic acid part of the mesogen (**1 c**, **3 c**, **5 c**, **8 c**) the melting point is lower and the clearing transition is higher than in those cases where the hydroquinone part of the mesogen is attached to it (**2 c**, **9 c**). It is not clear whether electronic effects are responsible for this behaviour, as used to explain similar results for the corresponding cyanates and isocyanates [7]. It is very likely, however, that 2,4,6-tris(4-phenoxycarbonylphenoxy)-*s*-triazines (**1 c**, **8 c**) have a higher mobility and a lower degree of order in the solid state than the isomeric 2,4,6-tris(4-benzoyloxyphenoxy)-*s*-triazines (**2 c**, **9 c**). This follows from the lower enthalpy and entropy of melting of the former in comparison with the latter (**1 c**: $\Delta S = 86{\cdot}3\,\mathrm{J\,K^{-1}\,mol^{-1}}$; **2 c**: $\Delta S = 99{\cdot}8\,\mathrm{J\,K^{-1}\,mol^{-1}}$). Why, on the other hand, the liquid crystalline behaviour is strongly suppressed in these isomers cannot be explained at present.

The isocyanurates **1 i** and **2 i** which have mesogenic branches identical with those of the corresponding cyanurates **1 c** and **2 c** did not exhibit mesomorphic behaviour, either discotic or calamitic. We tried to determine the virtual clearing point of **2 i** from mixtures with **3 c**. Homogeneous mixtures could be prepared only with a maximum content of 10 per cent of **2 i**. Extrapolation gave a virtual clearing point of − 199°C. This does not have a real physical meaning, but it does show that isocyanurates with calamitic mesogenic branches directly attached to the central ring do not have any tendency to form a calamitic mesophase.

Why do the isomeric triazines behave in such a different way, and why is the mesogenic power of the cyclotrimers reversed with respect to the monomers from which they can be made?

The molecular structure of isocyanurates in comparison with cyanurates (cf. schemes 2 and 1) reveals that isocyanurates have the mesogenic branch directly attached to the central heterocycle, while the mesogens are separated by an oxygen bridge from the central ring in the cyanurates. The oxo groups in the triazine trione, in addition, interfere with the branches and twist them out of the plane of the central ring. Semi-empirical quantum chemical calculations (PM3) [14, 15] were performed with two isomeric triazines, a cyanurate and an isocyanurate with identical branches: (4-phenoxycarbonylphenoxy). The results are given in figure 4. A propeller-like, star-shaped structure is found as the most stable conformation for both the isocyanurate (see figure 4, upper left) and the cyanurate (see figure 4, upper right) in agreement with the above arguments. The planar structure of the cyanurate is less stable by 45 kJ mol^{-1} than the propeller-like conformer, compared to 65 kJ mol^{-1} for the isocyanurate in which the central ring is no longer planar. Neither the planar nor the propeller-like structure, however, can be responsible for the mesomorphic properties of the cyanurates, since they suggest the formation of discotic mesophases, which is in contrast to the experimental results.

The flexibility of the cyanurates caused by the oxygen bridge is most probably the key to understanding the formation of calamitic mesophases. Rotation of one branch by 180° about the oxygen–(heterocyclic) carbon bond aligns two branches almost parallel and gives the molecule a more extended shape. Rotation of these two branches or of all three about the oxygen–mesogen single bond minimizes repulsion between adjacent branches and maintains the elongated structure (see figure 4 lower row). This was confirmed by the calculations which gave a heat of formation only 0·8 kJ mol^{-1} higher than that of the propeller like conformer of the cyanurate.

A further question of interest is the function of the triazine moiety in the mesogens. In this discussion we treated the cyanurates as a core with mesogenic branches. This core obviously contributes to the stabilization of the mesophase. It probably increases the aspect ratio [16], though it disturbs the geometry of the rod by the *meta*-linkage in connection with an odd number of atoms between the mesogens; this causes a bend and hence should be unfavourable. To what extent the 'paring of mesogens' compensates this drawback cannot be answered at present.

4. Conclusions

Three armed mesogenic cyanurates and isocyanurates with diaromatic mesogenic branches have been investigated. No discotic mesophases were formed from these compounds. Calamitic mesophases, however, result, if the branches can be aligned parallel to give a more rod-like extended shape; this is possible only for the cyanurates. Hence these compounds are bifurcated or branched mesogens rather than star-shaped. As a consequence, the mesogenic power of the cyclotrimers (cyanurates $\gg$ isocyanurates) is reversed with respect to the monomers from which they can be made (isocyanate $\gg$ cyanate). Within the class of cyanurates, the effect of linking groups and terminal groups is the same as for non-branched linear mesogens.

On the basis of these results, mesogenic cyanates seem to be suitable monomers for the synthesis of thermoset networks with a liquid crystalline organization of the monomers which will be the subject of a forthcoming paper.

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