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Liquid Crystals

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Liquid crystalline aromatic esters containing a 1,3,5-triazine moiety

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Liquid crystalline aromatic esters containing a 1,3,5-triazine moiety

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The syntheses of new mesogenic aromatic esters containing a 1,3,5-triazine moiety by esterification of 6-substituted 2,4-bis-(4-carboxyphenoxy)-1,3,5-triazines with the appropriate phenols are described. The mesomorphic properties of these new materials are discussed in relation to their dependence on the terminal substituents of the aromatic nucleus and the substituents at the 6-position of the triazine ring.

1. Introduction

Compounds with a 1,3,5-substituted aromatic nucleus involving an ether linkage usually do not exhibit mesomorphism [1]. But recently, a few examples of triazine containing polymers exhibiting liquid crystalline phases have been described [2, 3]. These polymers of the structure given in scheme 1 belong to a new class of mesomorphic main chain polyesters which contain substituted *sym*-triazine moieties having flexible ether linkages as a structural modification. Their synthesis has been realized from 6-substituted 2,4-bis-(4-carboxyphenoxy)1,3,5-triazines by solution polymerization with diphenols.

To continue our investigations on liquid crystalline 1,3,5-triazines, we tried to find out if *sym*-triazine-modified low molar mass aromatic esters would also show mesomorphic behaviour, even though from the molecular geometry of these compounds they would not be expected to be mesogenic.

The first results on the synthesis and mesomorphic properties of such new 1,3,5-triazines is now presented.

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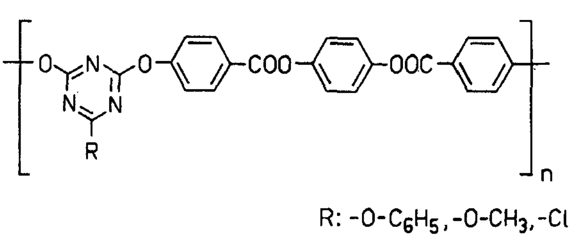
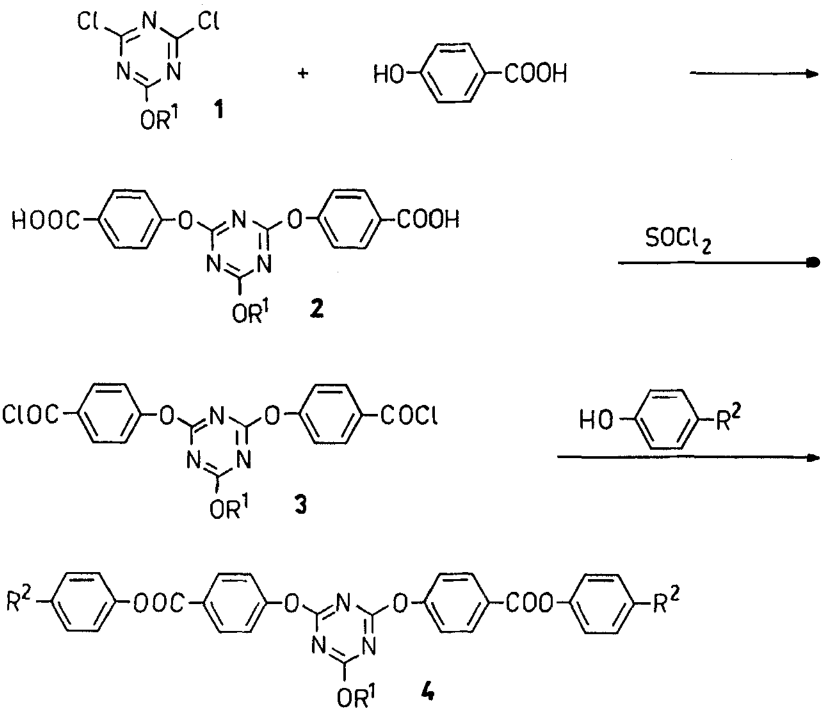


Scheme 1. Structure of the mesomorphic main chain polyesters containing 1,3,5-triazine units.



Scheme 2. Synthesis of the triazine-containing aromatic esters 4.

2. Synthesis

The synthesis of the novel mesomorphic triazines 4 was carried out starting from cyanuric chloride. The 2,4-dichloro-6-phenoxy(alkoxy)-1,3,5-triazines 1 were made by reaction with phenol [4] or aliphatic alcohols [5, 6]. The 2,4-bis-(4-carboxyphenoxy)-1,3,5-triazines 2 were obtained from the dichlorotriazines 1 and 4-hydroxybenzoic acid by a slightly modified procedure described in [7]. Treatment of the dicarboxylic acids 2 with thionyl chloride yielded the acid chlorides 3. The triazinyl-bis-aryl esters 4 were prepared by reaction of the acid chlorides 3 with the corresponding phenols. The synthesis is outlined in scheme 2 and full details are given in the experimental section.

3. Results and discussion

The structures and constitutions of the triazines 4 were confirmed by IR and NMR spectroscopy, as well as by mass spectrometry. The spectroscopic data are summarized in table 2. The investigation of the mesomorphic properties of the compounds 4 was

Table 1. Thermodynamic data for compounds **4a–g**; enthalpies and entropies have an accuracy of ±5%.

Compound	R^1	R^2	T_m/°C	ΔH/kJ mol^{-1}	ΔS/J mol^{-1} K^{-1}	T_i/°C	ΔH/kJ mol^{-1}	ΔS/J mol^{-1} K^{-1}	Phase
4a	C_6H_5	H	115						
4b	CH_3	H	146						
4c	C_6H_5	C_6H_5	143·0	30·3	73	178·2	3·8	8·4	N
4d	C_3H_7	C_6H_5	229·5 [186·7]	58·0	116	(220·1)	0·6	1·2	N
4e	CH_3	C_6H_5	226·8	51·5	103	252·8	0·35	0·82	S
4f	CH_3	CN	230·0 [131·1]	42·7	84	(206·2)	2·8	5·8	N
4g	CH_3	OC_3H_7	151·3	25·6	60	174·6	0·5	1·1	N

Monotropic transitions are in round brackets and recrystallization temperatures for **4d** and **4f** are in square brackets.

Table 2. Spectroscopic data for the 1,3,5-triazines **4**.

Compound	Molecular formula	MS (70 eV) $(m/z)/\%$	IR (KBr) ν/cm^{-1}	^{1}H NMR ($CDCl_3$) δ/ppm	^{13}C NMR ($CDCl_3$) δ/ppm
4a	$C_{35}H_{23}N_3O_7$ (597·6)	597(M^+, 15)	1740, 1560, 1370, 1190	7·10–7·50 (m, 19 H), 8·18–8·28 (m, 4 H)	120·5 (d, 2 C), 121·6(d, 4 C), 121·9(d, 4 C), 122·3 (d, 1 C), 125·9 (d, 2 C), 127·4 (s, 2 C), 129·5 (d, 4 C), 130·2 (d, 2 C), 131·9 (d, 4 C), 150·8 (s, 2 C), 151·5 (s, 1 C), 155·5 (s, 2 C), 164·3 (s, 2 C), 173·1 (s, 2 C), 173·9 (s, 1 C)
4b	$C_{30}H_{21}N_3O_7$ (535·2)	535 (M^+, 2)	1730, 1560, 1360, 1190	3·97 (s, 3 H), 7·18–7·47 (m, 14 H), 8·25–8·30 (m, 4 H)	56·0 (q, 1 C), 121·6 (d, 4 C), 121·8 (d, 4 C), 126·0 (d, 2 C), 127·5 (s, 2 C), 129·5 (d, 4 C) 131·9 (d, 4 C), 150·8 (s, 2 C), 155·5 (s, 2 C), 164·2 (s, 2 C), 173·1 (s, 2 C), 174·1 (s, 1 C)
4c	$C_{47}H_{31}N_3O_7$ (749·8)	580 ($M^+ - 169$ [$C_{12}H_9O$], 4)	1735, 1560, 1370, 1200	7·15–7·50 (m, 19 H), 7·55–7·60 (m, 8 H), 8·20–8·25 (m, 4 H)	120·5 (d, 2 C), 121·0 (d, 2 C), 121·2 (d, 2 C), 122·1 (d, 1 C), 122·6 (d, 2 C), 122·8 (d, 2 C), 126·3 (d, 2 C), 126·6 (s, 2 C), 127·5 (d, 4 C), 128·0 (d, 4 C), 129·0 (d, 2 C), 129·6 (d, 2 C), 130·4 (d, 2 C), 131·1 (d, 2 C), 132·8 (d, 2 C), 139·1 (s, 2 C), 140·3 (s, 2 C), 150·2 (s, 2 C), 151·4 (s, 1 C), 155·5 (s, 2 C), 164·3 (s, 2 C), 173·2 (s, 2 C), 173·9 (s, 1 C)
4d	$C_{44}H_{33}N_3O_7$ (715·8)	715 (M^+, 30)	1735, 1580, 1360, 1190	0·99 (t, 3 H, $J = 7·4$ Hz), 1·79 (qt, 2 H, $J = 7·4$ Hz, 6·6), 4·32 (t, 2 H, $J = 6·6$ Hz) 7·24–7·64 (m, 22 H), 8·25–8·30 (m, 4 H)	10·2 (q, 1 C), 21·8 (t, 1 C), 70·9 (t, 1 C), 121·8 (d, 4 C), 121·9 (d, 4 C), 127·1 (d, 4 C), 127·4 (d, s, 4 C), 128·2 (d, 4 C), 128·8 (d, 4 C), 131·9 (d, 4 C), 139·2 (s, 2 C), 140·3 (s, 2 C), 150·3 (s, 2 C), 155·7 (s, 2 C), 164·3 (s, 2 C), 173·0 (s, 2 C), 173·9 (s, 1 C)

4e	$C_{42}H_{29}N_3O_7$ (687·4)	687 (M^+, 16)	1730, 1550, 1360, 1200	4·00 (s, 3 H), 7·20–7·70 (m, 22 H), 8·22–8·35 (m, 4 H)	55·1 (q, 1 C), 121·0 (d, 4 C), 122·7 (d, 4 C), 126·2 (d, 2 C), 126·6 (s, 2 C), 127·4 (d, 4 C) 127·9 (d, 4 C), 129·0 (d, 2 C), 129·6 (d, 2 C), 131·1 (d, 2 C), 132·7 (d, 2 C), 139·2 (s, 2 C), 140·3 (s, 2 C), 150·2 (s, 2 C), 155·7 (s, 2 C), 164·2 (s, 2 C), 173·1 (s, 2 C), 174·3 (s, 1 C)
4f	$C_{32}H_{19}N_5O_7$ (585·5)	467 (M^+ – 118 [C_7H_4NO], 100)	2220, 1720, 1570, 1360, 1200	3·97 (s, 3 H), 7·25–7·37 (m, 8 H), 7·71–7·76 (m, 4 H), 8·23–8·27 (m, 4 H)	56·0 (q, 1 C), 110·0 (s, 2 C), 118·1 (s, 2 C), 122·0 (d, 4 C), 122·9 (d, 4 C), 126·6 (s, 2 C), 132·1 (d, 4 C), 133·8 (d, 4 C), 154·1 (s, 2 C), 155·9 (s, 2 C), 163·4 (s, 2 C), 173·0 (s, 2 C), 174·1 (s, 1 C)
4g	$C_{36}H_{33}N_3O_9$ (651·7)	651 (M^+, 1)	1735, 1580, 1360, 1220, 1190	1·03 (t, 6 H, J = 7·3 Hz), 1·79 (qt, 4 H, J = 7·3 Hz, 6·5), 3·31 (t, 4 H, J = 6·5 Hz), 3·97 (s, 3 H), 6·88–6·93 (m, 4 H), 7·06–7·11 (m, 4 H), 7·26–7·32 (m, 4 H), 8·22–8·26 (m, 4 H)	10·5 (q, 2 C), 22·6 (t, 2 C), 55·9 (q, 1 C), 69·9 (t, 2 C), 115·1 (d, 4 C), 121·7 (d, 4 C), 122·3 (d, 4 C), 127·7 (s, 2 C), 131·9 (d, 4 C), 144·1 (s, 2 C), 155·5 (s, 2 C), 157·0 (s, 2 C), 164·6 (s, 2 C), 173·1 (s, 2 C), 174·1 (s, 1 C)

†All compounds gave satisfactory elemental analyses.

accomplished by polarizing microscopy and differential scanning calorimetry (DSC). The results are collected in table 1.

The mesophase behaviour strongly depends on the substituents in both the 6-position of the triazine ring and the *p*-position of the terminal aromatic nucleus. Whereas the unsubstituted phenyl esters **4a** and **b** do not form mesophases, the introduction of a phenyl, cyano or propyloxy substituent leads to the liquid crystalline compounds **4c–g**, respectively although the molecular structure of the 1,3,5-triazine moiety disfavours liquid crystal formation.

In the series of the phenyl substituted aromatic esters **4c–e**, compound **4c** containing a phenoxy group at the 6-position of the triazine ring was found to form an enantiotropic nematic mesophase. A monotropic nematic phase was observed for the triazine **4d**, where a propyloxy substituent is present in the triazine ring. In contrast, the 6-methoxy-triazinyl ester **4e** exhibits an enantiotropic smectic phase, the nature of which is subject to further investigations.

The dependence of the liquid crystalline properties on the terminal aromatic substituents of the 6-methoxy-1,3,5-triazines **4f** and **4g** may be compared with the smectic behaviour of **4e**. Thus, the propyloxy substituted compound **4g** exhibits an enantiotropic nematic phase, but only a monotropic nematic phase was observed for **4f** containing cyano groups at the 4-positions of the terminal aromatic rings. The nematic–isotropic transition temperature of the cyano compound **4f** is however higher than that of **4g**, emphasizing the critical importance of the melting point.

The enthalpies and entropies of transition obtained from DSC measurements (see table 1) were typical for liquid crystalline compounds [8], as were the optical textures and droplets which confirmed the nematic mesophases of the triazinyl esters **4c** and **d** and **4f** and **g**, respectively. The occurrence of these mesophases is not easily visualized on the basis of the molecular geometry of compounds **4c–g**, and the investigation is being continued by X-ray analysis and molecular modelling.

Thermogravimetric analysis of **4a–g** showed negligible mass losses up to around 300°C (heating rate 20 K min^{-1}). At temperatures above 300°C, mass loss increased and was dramatic around 500°C.

4. Experimental

The chemicals used in the syntheses were purchased from Merck, Fluka and Aldrich. Elemental analyses were performed using a Carlo Erba CHNS-O EA 1108 Elemental Analyser. IR spectra were obtained with a Perkin–Elmer 457 spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded using Varian Gemini 2000 and Varian Unity 400 instruments, respectively. For mass spectra, a Varian MAT 711 (70 eV) spectrometer was used. Thermograms were measured using a Mettler DSC 30 and a Perkin–Elmer DSC 7. Texture observations were made using a Leitz polarizing microscope in conjunction with a Mettler FP 82 heating stage and Mettler FB 800 control unit. Thermogravimetric analysis was performed using a Mettler TG 50 (Neste Ltd, Kulloo, Finland). GPC analyses were run on PLGel columns at ambient temperature with tetrahydrofuran as eluent (Neste Ltd, Kulloo, Finland). The *2,4-dichloro-6-phenoxy(alkoxy)-1,3,5-triazines* **1** were prepared according to known procedures [4–6].

2,4-Bis-(4-carboxyphenoxy)-1,3,5-triazines 2

0·025 mol of the appropriate dichlorotriazine **1** was dissolved or suspended in 50 ml of acetone. A solution of 6·9 g (0·1 mol) of sodium hydroxide in 50 ml of water was added dropwise to the mixture, keeping the temperature at 5–10°C. After the addition was complete, stirring and cooling were continued for 3 h. The temperature was raised to room temperature, and after standing overnight, the reaction mixture was acidified with hydrochloric acid. The reaction product was filtered off, washed several times with hot water and dried. The dicarboxylic acids **2** were obtained in 74–89 per cent yield and were used without further purification for the next reaction step.

2,4-Bis-(4-chlorocarbonylphenoxy)-1,3,5-triazines **3**

After the addition of a few drops of dry pyridine, a mixture of 2g of the corresponding dicarboxylic acid **2** and 20 ml of thionyl chloride was heated under reflux until gas evolution had ceased. Boiling was continued for 1 h, and the solution was cooled to room temperature, filtered and the excess of thionyl chloride removed under reduced pressure. The residue was purified by recrystallization from hexane or a toluene/hexane mixture to yield 57–89 per cent of the diacid dichlorides **3**.

2,4-Bis-[4-(aryloxycarbonyl)phenoxyl]-1,3,5-triazines **4**

To a stirred solution of 5 mmol of the appropriate phenol in 20 ml of dry pyridine, 2·5 mmol of the diacid dichloride **3** were added. Excluding moisture, the reaction mixture was stirred at ambient temperature for 24 h. The mixture was poured into 150 ml of ice/water, acidified with hydrochloric acid and the precipitate collected by filtration. The solid was washed several times with dilute sodium hydroxide solution (2 per cent) and with water, and dried. After purification by recrystallization from dioxan/water, the triazines **4** were obtained in 49–68 per cent yield.

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