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New disc-shaped triarylamino-1,3,5-triazines with heteroaromatic central cores

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New disc-shaped triarylamino-1,3,5-triazines were prepared by reaction of cyanuric chloride with two-fold alkoxy substituted anilines. Each of the triarylmelamines exhibits an enantiotropic mesophase. X-ray investigations reveal the formation of columnar liquid crystalline structures with either a hexagonal or a rectangular lattice. The lattice parameters, as well as the intracolumnar ordering, depend on the length of the flexible lateral side chains. The new melamines form Langmuir monolayers at the air/water interface due to their amphiphilic nature. The monolayer organization is characterized by a side-on arrangement of the molecules. The polar central molecular parts lie flat on the water, whereas the lateral alkyl chains are oriented perpendicular to the water surface.

1. Introduction

The shape of molecules is known to be a major factor in controlling the formation of liquid crystalline phases: new types of primary chemical structures with different molecular symmetries have frequently resulted in novel types of mesophases [1]. Yet the shape is not the only structure-controlling factor. Examples are known of mesogenic compounds which are not expected to be liquid crystalline when considering just their molecular symmetry. Aromatic esters containing a 1,3,5-triazine moiety form calamitic mesophases [2, 3] although the molecular geometry of the triazine ring, suitable only for modifications at the 2-, 4- and 6-positions, does not fulfil the criteria for conventional rod-like molecules [4].

Furthermore, we have synthesized novel types of oligomer with either discotic penta-alkyne or triphenylene side groups attached to amino substituted 1,3,5-triazine units in the main chain. The mesophase structure of these discotic oligomers is characterized by an unusual lamellar layer arrangement which results from intermolecular interactions between the amino substituted triazine main chains [5]. Although the triazine units of these oligomers are not form-anisotropic, they play an important role in structure formation. Hence, the general question arises whether it might be possible to modify the substitution pattern of the 1,3,5-triazine core in such a way that form-anisotropic molecules result that are able to form discotic mesophases.

Several attempts have already been made to synthesize disc-like mesogens with only threefold substituted central cores. These include, for example, 1,3,5-trisubstituted benzene compounds [6–9], triarylpyrylium salts [10–12], threefold aryl substituted tetrahedral methane derivatives [8, 13], decacyclenes containing three side chains [14] and cone-shaped cyclotribenzylene compounds [8, 15]. However, trialkylamino-1,3,5-triazines investigated so far have been found to exhibit no mesomorphism [16] or to form liquid crystalline phases only by complementary interactions with acids [17].

Our concept for obtaining discotic 1,3,5-triazines able to form mesogenic structures due to the form-anisotropic shape of the single molecules consists in attaching to the heteroaromatic triazine nucleus substituents which will give rise to more rigidity and space filling of the central molecular part. We report here results on the synthesis, the monolayer behaviour at the air/water interface and the mesomorphic properties of new star-like melamines characterized by a central 1,3,5-triazine core which is threefold substituted via amino groups with phenyl rings bearing two alkoxy chains.

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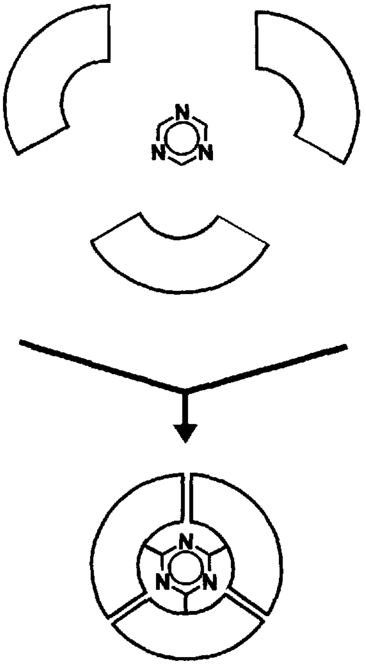

Figure 1. General construction of discotic 1,3,5-triazines.

2. Results and discussion

2.1. *Synthesis*

The synthesis of the new 2,4,6-triarylamino-1,3,5-triazines **2** is presented in figure 2. The triarylmelamines **2** were obtained by the reaction of the alkoxy substituted anilines **1** [18] with cyanuric chloride in the presence of potassium carbonate. Alkoxy chains with different numbers of methylene groups were thus attached to the central molecular part of the melamines **2** in order to modify the total diameter of the molecules. Spectroscopic data and elemental analytical data are consistent with the threefold aminophenyl substituted structure of the triazines **2**. Especially, it is noted that ^{13}C NMR spectra do not give evidence of a chlorine substituted triazine carbon. Full details are given in the experimental section.

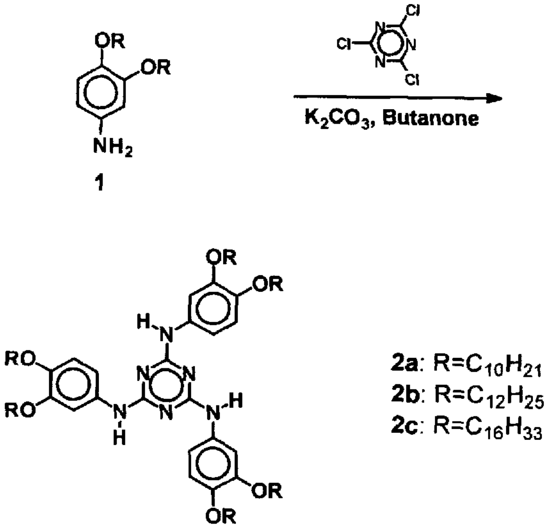

Figure 2. Synthetic route to the triarylmelamines **2**.

2.2. *Thermal behaviour of the triarylamino-1,3,5-triazines* 2

The investigation of the thermal properties of the new melamines **2** was accomplished by polarizing optical microscopy and differential scanning calorimetry. The finding was that each of the triazines **2** investigated here exhibits an enantiotropic mesophase irrespective of the length of the peripheral alkoxy chains. Fan-like optical textures were observed for triazines **2a** and **2b** between crossed polarizers on cooling from the isotropic state (figure 3). In contrast, compound **2c** exhibited a broken, mottled texture (figure 4).

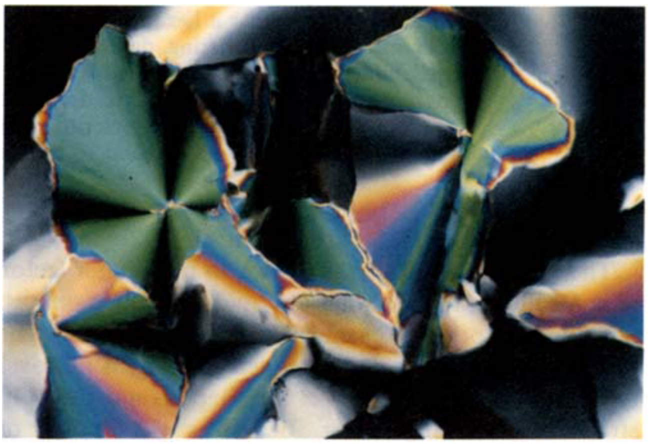

Figure 3. Optical texture of the D_{hd} phase of the triazine **2b** between crossed polarizers; 1st cooling (10 K min^{-1}) at 50°C.

Figure 4. Microphotograph of the rectangular columnar (D_{ro}) mesophase of compound **2c** between crossed polarizers; 1st cooling (1 K min^{-1}) at 66°C.

The phase transition data for the triarylaminotriazines **2** determined by DSC are summarized in the table. The thermal behaviour of the triazines **2a** and **2b** is characterized by a reluctance to recrystallize during cooling. For this reason the second and the following DSC heating cycles do not give accurate values for the melting transitions if they are performed immediately after the first cooling. However, satisfactory data for T_m were obtained when the samples were kept at room temperature for at least two days before measuring the second heating. The data on the phase transition into the isotropic state are reproducible for all the melamines **2a–c**, independent of the time between the first and the following DSC scans. Furthermore, a decrease of the clearing temperatures is observed as a function of increasing length of the peripheral flexible alkoxy chains.

2.3. *X-ray investigations*

Temperature dependent X-ray investigations were performed to determine the structures of the liquid crystalline phases of the triarylaminotriazines **2a–c**. The X-ray studies reveal that both compounds **2a** and **2b** exhibit a hexagonal columnar mesophase with lattice constants $a_{hex} = 30·2$ Å (**2a**; $n = 10$) and $a_{hex} = 32·8$ Å (**2b**; $n = 12$). These lattice parameters correspond well with the different lengths of the alkoxy substituents of melamines **2a** and **2b**. Only a diffuse halo is observed at larger scattering angles for both triazines **2a,b**. Thus, the triarylmelamines **2a** and **2b** display a disordered hexagonal columnar (D_{hd}) mesophase.

A major structural change takes place with a further increase of the peripheral chain length. The X-ray diffractogram of compound **2c** ($n = 16$) displays a set of reflections in the short angle region (figure 5) which can be attributed to a rectangular lattice with lattice dimensions $a = 42$ Å and $b = 33$ Å. The intracolumnar packing is evidently enhanced compared with **2a,b**. A sharp reflection is present in the wide angle region indicating a periodic stacking of the molecules within the columns. The intracolumnar distance is 4·22 Å. The triazine **2c** thus exhibits an ordered rectangular columnar (D_{ro}) phase.

Table. Phase transition data for the triarylamino-1,3,5-triazines **2**. Transition temperatures (°C) were determined by differential scanning calorimetry on heating at 10 k min^{-1}. Transition enthalpies kJ mol^{-1} are given in parentheses.

Compound	Cr		M		I
2a	●	70·4 (14·03)	●^{a}	154·6 (2·44)	●
2b	●	54·4 (30·08)	●^{a}	90·8 (3·24)	●
2c	●	64·8 (95·91)	●^{b}	76·9 (1·05)	●

Cr: crystalline; M: mesophase; I: isotropic.
[a] Disordered hexagonal columnar (D_{hd}).
[b] Ordered rectangular columnar (D_{ro}).

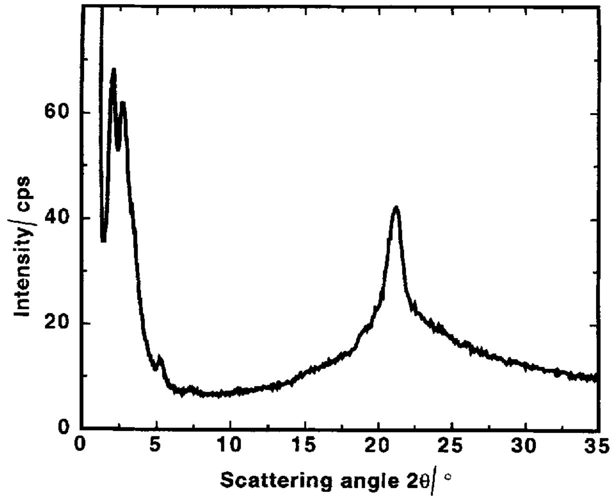

Figure 5. Wide angle X-ray diffractogram of the discotic triarylmelamine **2c** at 66°C.

The different columnar lattices determined by X-ray are in agreement with the different thermal behaviours of **2a,b** and **2c** observed by optical microscopy and DSC.

2.4. *Langmuir monolayers of the triarylamino triazines at the air/water interface*

The triarylmelamines **2** are characterized by a polar, threefold amino substituted 1,3,5-triazine core and long non-polar alkoxy chains. It was expected that amphiphilic properties should arise from the melamines **2** from this combination of different structural elements. To prove this hypothesis we investigated the behaviour of the compounds **2** at an air/water interface. It was found that all triarylmelamines **2** form monolayers on the water surface. The surface pressure–area isotherms are

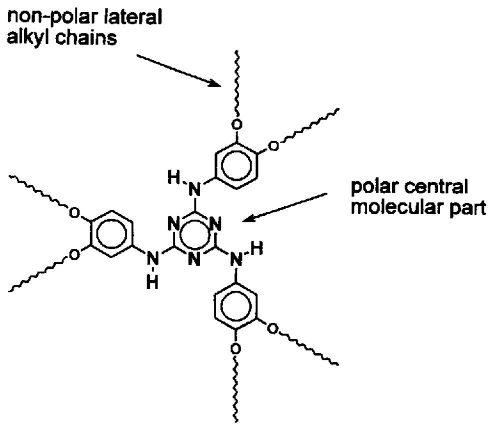

Figure 6. Molecular parameters of the discotic triarylaminotriazines **2**.

given in figure 7. The collapse areas range between 1·15 and 1·25 nm^2 per molecule; the area requirement does not depend on the length of the peripheral alkyl chains. Usually an occupied area of about 0·2 nm^2 is found per aliphatic chain of single molecules in compressed monolayers of fatty acids and phospholipids [19]. Thus, the values of about 1·20 nm^2 observed for the melamines **2** agree quite well with the number of six peripheral hydrocarbon chains, considering that they are oriented in the all-*trans* conformation more or less perpendicular to the water interface. The amino-modified central triazine ring is the most hydrophilic molecular part and lies flat on the water (side-on intermolecular orientation). This type of orientation which has already been shown for the monolayer arrangement of amphiphilic discotic azamacrocycles [20, 21] and azo discs [22] is presented schematically in figure 8.

3. Conclusions

The mesogenic triarylmelamines **2** investigated here represent a novel class of discotic liquid crystals with a heteroaromatic central core. The two-dimensional lattice parameters of the columnar phases and the intracolumnar ordering of the melamines **2** are controlled by the length of the flexible alkoxy substituents. The triazines **2** not only form liquid crystalline structures resulting from the form-anisotropic shape of the molecules, but also side-on oriented monolayers at the air/water interface due to their amphiphilic nature.

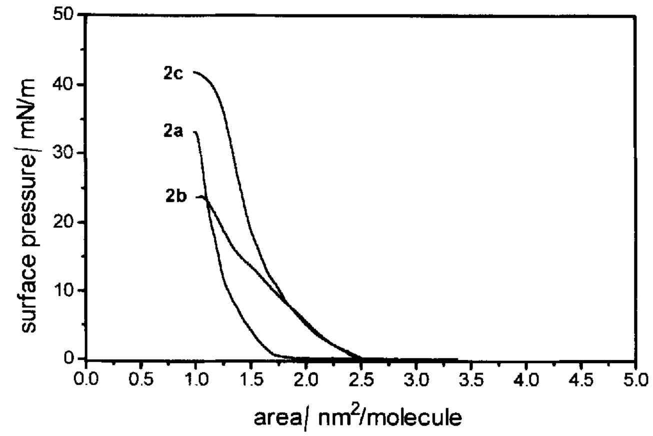

Figure 7. Surface pressure–area isotherms of the melamines **2**.

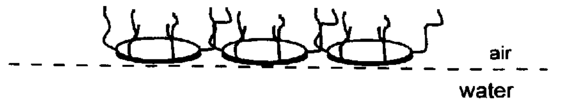

Figure 8. Schematic presentation of the side-on molecular orientation of the amphiphilic discotic triarylaminotriazines **2** at the air/water interface.

4. Experimental

4.1. *Synthesis*

The 3,4-dialkoxyanilines **1** were prepared according to the procedures described in [18] and purified by recrystallization from ethanol before they were used for the subsequent reaction with cyanuric chloride.

4.1.1. *Disc-shaped 2,4,6-triarylamino-1,3,5-triazines* **2**

To a stirred solution of 2·6 mmol of the appropriate 3,4-dialkoxyaniline **1**, dissolved in 50 ml of dry ethyl methyl ketone, 170 mg (0·87 mmol) of cyanuric chloride and 390 mg (2·8 mmol) of potassium carbonate were added. The mixture was stirred and heated at reflux under a nitrogen atmosphere for 4 h. After cooling to room temperature, the solvent was removed under reduced pressure. The residue was poured into 50 ml of water and the resulting precipitate was collected by filtration, dried and recrystallized from acetone. Further purification was performed by flash chromatography (Kieselgel 60, 230–400 mesh) using light petroleum/ethyl acetate (10 : 4) as eluent, followed by a final recrystallization from acetone.

4.1.2. *2,4,6-Tris[3,4-bis(decyloxy)phenyl-1-amino]-1,3,5-triazine* **2a**

Yield: 77·7 per cent. Elemental analysis: $C_{81}H_{138}N_6O_6$ (M_w = 1292·0). Calc: C, 75·30; H, 10·93; N, 6·50. Found: C, 75·78; H, 11·39; N, 5·94 per cent. IR (KBr): ν = 3400, 1570, 1260, 1140, 845 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 7·0 (s, 3H, phenyl), 6·9 (d, 3H, phenyl; J = 8·6 Hz), 6·7 (d, 3H, phenyl; J = 8·6 Hz), 3·8 (t, 12H, CH_2–O–phenyl; J = 6·4 Hz), 3·6 (s, 3H, NH), 1·6–1·7 (m, 12H, CH_2), 1·1–1·3 (m, 84H, CH_2), 0·8 (t, 18H, CH_3; J = 6·8 Hz) ppm. ^{13}C NMR ($CDCl_3$): δ = 164·5 (3C, triazine C–NH), 149·4 (3C, phenyl C–NH), 145·5 (3C, phenyl C–O), 132·1 (3C, phenyl C–O), 114·6 (3C, phenyl CH), 113·4 (3C, phenyl CH), 108·2 (3C, phenyl CH), 69·9 (3C, O–CH_2), 69·1 (3C, O–CH_2), 31·9, 30·9, 29·7, 29·5, 29·4, 29·3, 26·1, 22·7 (48C, CH_2 decyl chains), 14·1 (6C, CH_3) ppm.

4.1.3. *2,4,6-Tris[3,4-bis(dodecyloxy)phenyl-1-amino]-1,3,5-triazine* **2b**

Yield: 81·9 per cent. Elemental analysis: $C_{93}H_{162}N_6O_6$ (M_w = 1460·3). Calc: C, 76·49; H, 11·11; N, 5·61. Found: C, 76·12; H, 11·50; N, 5·93 per cent. IR (KBr): ν = 3400, 1570, 1260, 1140, 845 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 7·0 (s, 3H, phenyl); 6·9 (d, 3H, phenyl; J = 8·7 Hz), 6·7 (d, 3H, phenyl; J = 8·7 Hz), 3·9 (t, 12H, CH_2–O–phenyl; J = 6·6 Hz), 3·7 (s, 3H, NH), 1·6–1·7 (m, 12H, CH_2), 1·1–1·3 (m, 108H, CH_2), 0·8 (t, 18H, CH_3; J = 7·0 Hz) ppm. ^{13}C NMR ($CDCl_3$): δ = 164·4 (3C, triazine C–NH), 149·4 (3C, phenyl C–NH), 145·5 (3C, phenyl C–O), 132·1 (3C, phenyl C–O), 114·6 (3C, phenyl CH), 113·4 (3C, phenyl CH), 108·3 (3C, phenyl CH), 69·9 (3C, OCH_2), 69·1 (3C,

OCH_2), 31·9, 29·7, 29·6, 29·5, 29·4, 29·3, 26·1, 22·8 (60C, CH_2 dodecyl chains), 14·1 (6C, CH_3) ppm.

4.1.4. *2,4,6-Tris[3,4-bis(hexadecyloxy)phenyl-1-amino]-1,3,5-triazine* **2c**

Yield: 42·1 per cent. Elemental analysis: $C_{117}H_{210}N_6O_6$ ($\bar{M}_w = 1797{\cdot}0$). Calc: C, 78·16; H, 11·81; N, 4·97. Found: C, 78·41; H, 11·70; N, 4·97 per cent. IR (KBr): $\nu = 3400$, 1580, 1260, 1140, 850 cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 7{\cdot}0$ (s, 3H, phenyl), 6·9 (d, 3H, phenyl; $J = 8{\cdot}5$ Hz), 6·7 (d, 3H, phenyl; $J = 8{\cdot}5$ Hz), 3·9 (t, 12H, CH_2–O–phenyl; $J = 6{\cdot}4$ Hz), 3·7 (s, 3H, NH), 1·6–1·7 (m, 12H, CH_2), 1·1–1·3 (m, 156H, CH_2), 0·8 (t, 18H, CH_3; $J = 6{\cdot}9$ Hz) ppm. ^{13}C NMR ($CDCl_3$): $\delta = 164{\cdot}4$ (3C, triazine C–NH), 149·4 (3C, phenyl C–NH), 145·6 (3C, phenyl C–O), 132·1 (3C, phenyl C–O), 114·6 (3C, phenyl CH), 113·5 (3C, phenyl CH), 108·1 (3C, phenyl CH), 69·9 (3C, OCH_2), 69·2 (3C, OCH_2), 31·9, 29·7, 29·6, 29·5, 29·4, 29·3, 26·1, 22·7 (84C, CH_2 hexadecyl chains), 14·1 (6C, CH_3) ppm.

4.2. *Instrumental*

^1H NMR and ^{13}C NMR spectra were recorded using a Bruker AMX 300 spectrometer. IR spectra were obtained with an M 80 spectrometer (Carl Zeiss Jena). Elemental analyses were performed using a Carlo Erba CHNS-O EA 1108 Elemental Analyser. Texture observations were made with an Olympus BHS polarizing microscope fitted with a Linkam TMH/S 600 hot stage and a Linkam TP 92 control unit. Microphotographs were obtained with an Olympus OM-4 Ti system camera. Thermograms were measured using a Perkin Elmer DSC7. Wide angle scattering analyses were performed with a goniometer from Siemens (D5000). Investigations on the monolayer behaviour of the melamines **2** on a pure Milli-Q water sub-phase were carried out at 18°C using a KSV-5000 LB trough. The concentrations of the spreading solutions of compounds **2** (chloroform, E. Merck, p.a.) were approximately 0·5 mg ml^{-1}. A barrier speed of 10 mm min^{-1} was used in all experiments.

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