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Liquid crystalline 1,3,5-triazines incorporating rod-like azobenzene sub-units

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New liquid crystalline 1,3,5-triazines are presented that incorporate three mesogenic groups based on rod-like azobenzene moieties. The synthesis was carried out by reaction of cyanuric chloride with 4-alkoxy-4′-aminoazobenzene derivatives. The mesomorphic behaviour was investigated by polarizing microscopy, differential scanning calorimetry and X-ray scattering. Besides a nematic and a SmA phase, the trisazomelamines form a higher ordered mesophase within a broad temperature range below the smectic A phase. With respect to the rod-like azobenzene sub-units, the low temperature phases display a smectic 'bilayer' structure. The molecules are antiparallel aligned within one layer. Furthermore, 1,3,5-triazines incorporating just two azobenzene groups are presented, these were prepared to investigate the influence of the number of rod-like sub-units linked to the triazine core on the mesomorphic properties.

1. Introduction

Low molecular mass thermotropic liquid crystals are usually composed of molecules incorporating just one rigid core, whereas liquid crystalline polymers arise from either attaching mesogenic groups to a polymer backbone or from incorporation of anisometric units into a polymer main chain. However, the number of mesogenic units that can be linked chemically in this way is non-specific and depends, for example, on the molecular mass distribution of the polymers and on the degree of polymerization.

One approach towards oligomeric mesogens with a well defined molecular structure just bridging the gap between monomeric and polymeric mesogens consists in the chemical linkage of a defined number of form-anisotropic sub-units. Beside various dimeric mesogens [1], appropriate trimers and tetramers are available by connecting three or four mesogenic groups with a central linking unit. Examples are tetrameric liquid crystals with biphenyl and phenylcyclohexyl groups linked to a tetrahedral penta-erythritol unit [2], azomethine oligomers derived from benzene-1,3,5-tricarboxylic acid [3] and trimers and tetramers incorporating rod-like thiadiazole mesogenic units [4, 5].

On the other hand, it has been demonstrated that the 1,3,5-triazine ring is a suitable structural element to be incorporated into thermotropic liquid crystals. Thus, aromatic esters involving a 1,3,5-triazine moiety were found to exhibit calamitic mesophases [6, 7]. Furthermore, novel types of oligomers have been realized with either disc-like triphenylene or penta-alkyne side groups attached to amino substituted 1,3,5-triazine units in the main chain. The mesophase structure of these oligomers is characterized by an unusual lamellar arrangement resulting from intermolecular hydrogen bonding between the amino substituted triazine units of the main chains [8]. More recently, we presented new 2,4,6-triarylamino-1,3,5-triazines bearing six long peripheral alkoxy chains which form enantiotropic columnar mesophases, although the molecules are characterized by a lack of inherent molecular planarity [9].

Consequently, the question arises as to how to modify the substitution pattern of the 1,3,5-triazine ring in such a way that liquid crystalline compounds result, probably exhibiting highly ordered smectic phases. Our approach consists in attaching three rod-like molecular sub-units to the 2-, 4- and 6-positions of the triazine nucleus (figure 1).

We report here the new liquid crystalline melamines **4** which are threefold substituted via amino groups with

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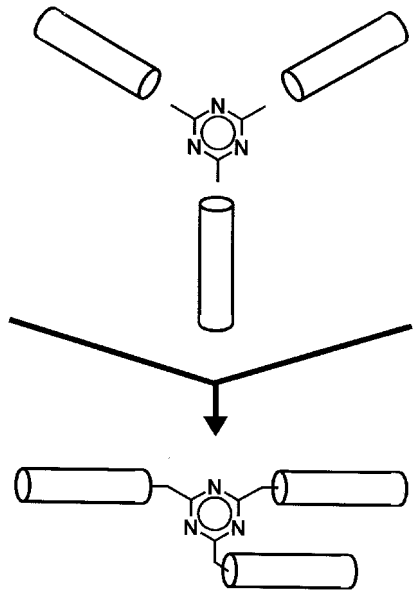


Figure 1. Liquid crystalline 1,3,5-triazines through incorporation of three rod-like molecular sub-units.

rod-like azobenzene sub-units (figure 2). These compounds may be considered as calamitic homotrimers with a 1,3,5-triazine core as the central linking unit. Furthermore, the 1,3,5-triazines **5** are presented that incorporate just two rigid azobenzene groups. These have been prepared so that the influence that the number of rod-like sub-units attached to the triazine ring has on the mesomorphic behaviour may be investigated.

2. Results and discussion

2.1. *Synthesis*

The synthesis of the new 1,3,5-triazines **4** containing three rod-like azobenzene sub-units was carried out starting from 4-hydroxy-4′-nitroazobenzene **1** [10]. Etherification of **1** with alkyl bromides containing a different number of methylene groups in the presence of potassium carbonate resulted in the alkoxy substituted intermediates **2**. Subsequent reduction of the nitro group of the derivatives **2** with an aqueous solution of sodium hydrogen sulphide yielded the 4-alkoxy-4′-aminoazobenzenes **3**. The new trisazomelamines **4** were obtained by the reaction of the anilines **3** with cyanuric chloride in the presence of potassium carbonate. The synthesis of the new melamines **4** incorporating three rod-like azobenzene moieties is presented in figure 2.

Spectroscopic data and elemental analysis confirmed the structures of the threefold azobenzene substituted triazines **4**. Full details are given in the experimental section.

2.2. *Thermal properties of the trisazomelamines* **4**

The thermal properties of the new melamines **4** were investigated by polarizing optical microscopy and differential scanning calorimetry (DSC). Cooling from the isotropic state results in the formation of a nematic phase for all triazines **4**, easily identified by its typical schlieren texture. Upon cooling the nematic phases focal-conic fan textures develop for compounds **4a,b** [figure 3 (*a*)] whereas the texture of the triazine **4c** becomes homeotropic. The pseudo-isotropic areas are separated by oily streaks. These textures are typical for smectic A phases. Optical microscopy, furthermore, clearly confirmed the appearance of a further enantiotropic smectic phase for all melamines **4** at lower temperatures (denoted here as SmX) characterized by marked mosaic textures [figure 3 (*b*)]. However, the transition from the SmX to the SmA phases cannot be detected with accuracy

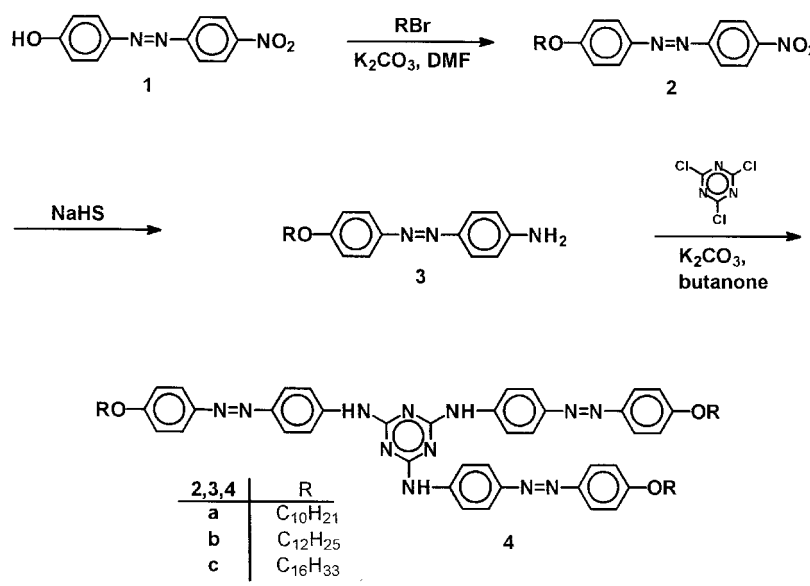
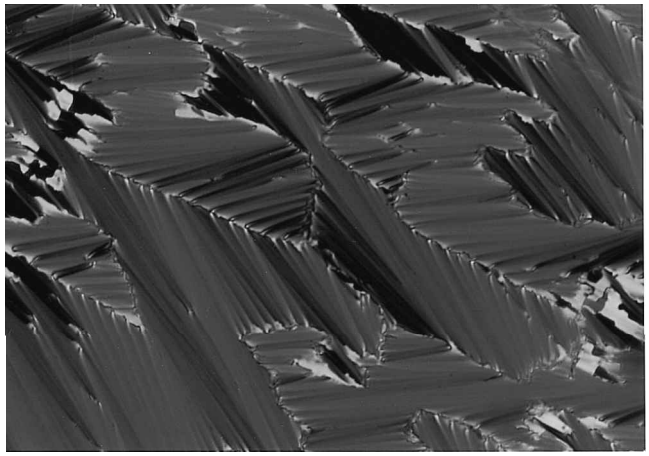
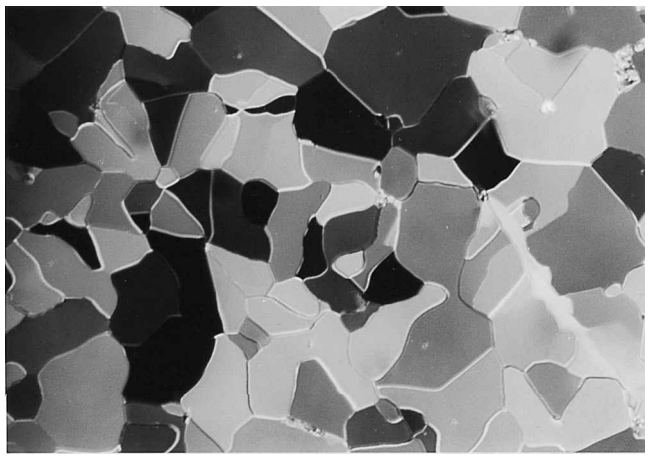


Figure 2. Synthetic route to the trisazomelamines **4**.



(*a*)



(*b*)

Figure 3. Photomicrographs of the mesophase textures of melamine **4b** between crossed polarizers. (*a*) Focal conic fan texture of the Smectic A phase at 184.7°C; 2nd cooling at 5 K min^{-1}. (*b*) Mosaic texture of low temperature SmX phase at 132.5°C; 2nd cooling at 5 K min^{-1}.

by DSC due to the very low transition enthalpies. This implies that the structures of the low temperature SmX and the smectic A phases are very close.

The thermal behaviour of the triazines **4a,b** furthermore, is characterized by a glass transition above room temperature. The occurrence of the glass transition is surprising in so far as the formation of stable glassy states well above room temperature is usually a characteristic feature of liquid crystalline polymers. Thus, in this respect, the melamines **4** bearing three calamitic azo groups combine a well-defined molecular structure with the thermal properties of polymeric mesogens.

The transition temperatures of the trisazomelamines **4** obtained by DSC are summarized in table 1.

The length of the peripheral flexible chains influences the phase transition data for the triazines **4**. The clearing temperatures decrease as a function of increasing length of the alkoxy groups. Elongation of the alkoxy chain length, furthermore, leads to a decrease of the temperature range of the nematic and smectic A phases whereas the low temperature SmX phase is remarkably broad in all cases.

It seems particularly noteworthy that the nitro substituted azobenzene compounds **2** exhibit an enantiotropic smectic A phase (see also [11]), whereas the corresponding anilines **3** are crystalline materials. Thus, replacing the nitro groups of the alkoxy substituted azobenzenes **2** by an amino substituent completely suppresses mesomorphic behaviour. Simply by chemically linking the anilines **3** to the 1,3,5-triazine ring via the amino groups, liquid crystalline structure formation is restored. The transition temperatures of the azobenzene compounds and their melting points are also given in table 1.

The possibility of freezing the smectic phases of the melamines **4** in a glassy state at room temperature along

Table 1. Phase transition data for the melamines **4** incorporating three calamitic azobenzene sub-units and for the 4-alkoxyazobenzene derivatives **2** and **3** determined by differential scanning calorimetry on second heating (10 K min^{-1}); temperatures are in °C and transition enthalpies (kJ mol^{-1}) are given in brackets. Cr = crystalline; T_g = glass temperature; SmX = smectic; SmA = smectic A; N = nematic; I = isotropic.

Compound	Cr		T_g		SmX		SmA		N		I
2a	•	83.0 (46.44)	—		—		•	92.9 (2.82)	—		•
2b	•	75.7 (49.79)	—		—		•	93.8 (3.50)	—		•
2c	•	83.1 (58.27)	—		—		•	90.9 (4.54)	—		•
3a	•	104.8 (44.59)	—		—		—		—		•
3b	•	88.6 (40.66)	—		—		—		—		•
3c	•	94.2 (45.37)	—		—		—		—		•
4a	—		•	85.1	•	167.6[a]	•	210.4 (0.28)	•	240.7 (0.53)	•
4b	—		•	32.3	•	178.5[a]	•	220.6 (0.31)	•	239.2 (0.97)	•
4c	•	95.9 (6.62)	—		•	180.3[a]	•	183.1 (0.87)	•	203.4 (0.29)	•

[a] Determined by polarizing microscopy

with the ability of the incorporated azobenzene moieties to be switched by light make these novel mesomorphic triazines promising materials for optical data storage.

2.3. *X-ray investigations*

The X-ray diagrams of the melamine derivatives **4** in the low temperature SmX mesophase display a set of narrow reflections in the small angle region and a diffuse halo at larger scattering angles (figure 4). It is obvious that a smectic layer structure exists; no mixed reflections were found. The layer structure is characterized by only small longitudinal displacements, since reflections up to the 3rd order were detected. The Bragg spacings are given in table 2. On the other hand, the halo indicates the presence of only a short range order within the layers.

It has been shown previously that a parallel arrangement of at least two rod-like sub-units is most preferable for liquid crystalline oligomers with three or four mesogenic moieties attached to the same central linking unit [2–4, 12]. Figure 5 shows a molecular model of compound **4a** in such a fork-like conformation.

Assuming this conformation, the molecular length in the most extended form amounts to approximately 5.2 nm in the case of compound **4a**, 5.6 nm for the triazine **4b** and 6.4 nm for compound **4c** (Cerius 2; force field Dreiding 2). Thus, with respect to the rod-like azobenzene units, the smectic low temperature phases can be regarded as bilayer structures due to a segregation of the polar central triazine ring from the non-polar

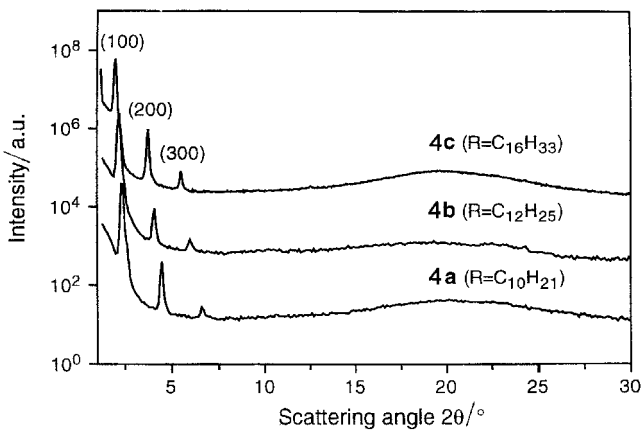


Figure 4. Wide angle X-ray diffractograms obtained for the low temperature SmX phase of the trisazomelamines **4**.

Table 2. Bragg spacing (nm) of the low temperature SmX phase of the compounds **4**.

Compound	d_{100}	d_{200}	d_{300}
4a	3.97	1.96	1.33
4b	4.38	2.19	1.48
4c	4.75	2.36	1.60

Figure 5. Molecular model of compound **4a** in a fork-like conformation (Cerius 2).

aliphatic chains. An optimum of space filling within one 'bilayer' arises from an antiparallel alignment of the molecules [13].

The layer spacings show a linear dependance on the number of carbon atoms of the alkoxy chains. Extrapolation to zero methylene groups yields a value of 2.77 nm which is in excellent agreement with the dimension of the molecular fragment of the compounds **4** arranged like a fork, but without alkoxy substituents, as calculated from molecular modelling (2.7 nm). Thus, it is most likely that the rigid azobenzene moieties of the triazines **4** are not tilted with respect to the layer normal.

The fact that the layer periodicities are about 20% smaller than the maximum molecular dimensions of the melamines **4** may be attributed to a slight interdigitation of the flexible alkyl chains. However, the spacings would also be quite reasonable for a non-interdigitated structure with a disordered packing of the chains [14]. A possible model for the low temperature SmX phase of the trisazomelamines **4**, arising from these considerations, is given in figure 6.

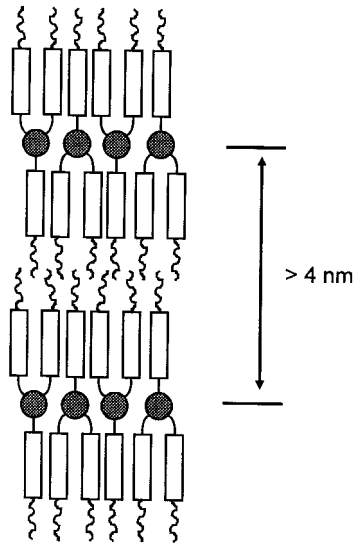
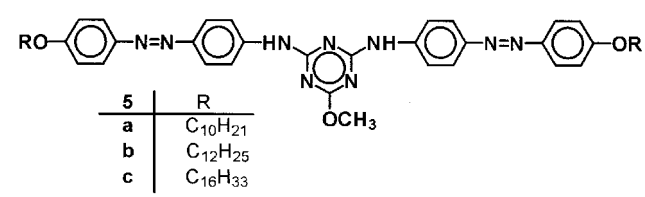


Figure 6. Two-dimensional structure model for the SmX phase of the melamines **4**.

The layer ordering according to figure 6 could also explain the observed mosaic textures because such a well ordered lamellar structure may frustrate the tendency to layer bending that causes the focal-conic fan textures of a common SmA phase (in this respect see also [2]). Furthermore, computer simulations (Cerius 2; force field Dreiding 2) were performed to prove the proposed structural model. The calculated layer dimensions and the values obtained from the X-ray measurements agree well.

2.4. *1,3,5-Triazines* **5** *incorporating two rod-like azobenzene moieties*

The replacement of one aminoazobenzene group of the melamines **4** by a methoxy substituent gives rise to the triazines **5** (figure 7) incorporating just two rod-like azobenzene sub-units. These were prepared in order to elucidate the influence of the number of rod-like sub-units on the mesomorphic behaviour of 1,3,5-triazines containing the azobenzene group. Except for the 6-methoxy substituent all further molecular parameters of the triazines **5** were kept constant compared to the compounds **4**. The synthesis of the bisazotriazines **5** follows



5	R
a	$C_{10}H_{21}$
b	$C_{12}H_{25}$
c	$C_{16}H_{33}$

Figure 7. Chemical structure of the 1,3,5-triazines **5** containing two rod-like azobenzene units.

the reaction sequence outlined in figure 2, but using 2,4-dichloro-6-methoxy-1,3,5-triazine [15, 16] instead of cyanuric chloride.

The finding is that all the triazines **5** exhibit one enantiotropic mesophase. The transition data are given in table 3. The melting as well as the clearing temperatures decrease with increasing chain length of the alkoxy groups at the terminal positions of the azobenzene moieties. The temperature range of the mesophases is about 40°C in all cases. The isotropization temperatures are lower than those of the trisazomelamines **4**.

The X-ray diffraction patterns reveal a smectic layer structure without long range order in the layers for the bisazotriazines **5a** and **5c** (figure 8). The layer dimensions are 4.15 nm for compound **5a** and 4.59 nm for **5c**. The Bragg spacings are summarized in table 4. Although it

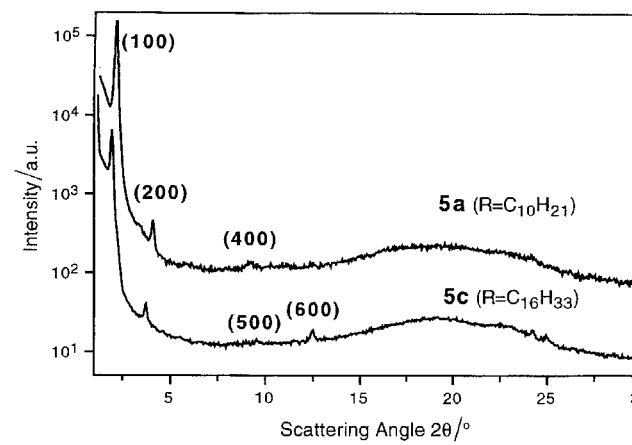


Figure 8. WAXS diagrams of the 1,3,5-triazines **5a** and **5c** incorporating two calamitic azobenzene moieties.

Table 3. Phase transition data for the twofold azobenzene substituted 1,3,5-triazines **5**. Transition temperatures (°C) were determined by differential scanning calorimetry (second heating with 10 K min^{-1}); transition enthalpies (kJ mol^{-1}) are given in brackets. Cr = crystalline; M = mesophase; I = isotropic; SmC = smectic C; Col_h = hexagonal columnar.

Compound	Cr		M		I	Phase type
5a	•	167.9 (38.72)	•	208.3 (4.71)	•	SmC
5b	•	159.6 (43.41)	•	203.8 (7.03)	•	Col_h
5c	•	145.8 (79.49)	•	197.9 (11.30)	•	SmC

Table 4. Bragg spacing (nm) of the 1,3,5-triazines **5**.

Compound	d_{100}	d_{110}	d_{200}	d_{300}	d_{400}	d_{500}	d_{600}
5a	4.15	—	2.10	—	1.01	—	—
5b	4.12	2.43	—	—	—	—	—
5c	4.59	—	2.36	1.60	—	0.92	0.73

was not possible to obtain oriented samples, the X-ray patterns along with the schlieren textures observed between crossed polarizers suggest a smectic C phase for both compounds.

The scattering diagram of the triazine **5b** incorporating two azobenzene groups, each substituted with a lateral dodecyloxy chain, also shows an amorphous halo in the wide angle region indicating a mesophase with only a short range order in one dimension. However, in contrast to compounds **5a** and **5c**, the two sharp reflections visible in the small angle region can be indexed as (1 0 0) and (1 1 0) reflections with a ratio of the lattice spacings $d_{100}:d_{110}=1/3^{1/2}$ (table 4). These scattering characteristics give evidence of a hexagonal columnar (Col_h) mesophase with a lattice constant $a_{hex}=4.76$ nm. The dimension of the hexagonal lattice constant suggests that more than one molecule might be present in one slice of a column, probably similar to the case of the columnar mesophases of polycatenar compounds [17].

The hexagonal columnar phase observed for compound **5b** is rather surprising. A rod-like molecular shape usually causes the formation of smectic liquid crystalline structures and so far only a few examples of rod-like molecules have been described as forming a columnar mesophase [18–20]. This behaviour has been discussed in terms of segregation effects [20]. However, it is not obvious to us why just the two-fold dodecyloxy terminated triazine **5b** exhibits a columnar phase and thus differs from the structure formation of the two homologues **5a** and **5c**.

3. Conclusions

The mesogenic 1,3,5-triazines **4** and **5** are a novel class of calamitic liquid crystals incorporating either two or three rod-like sub-units based on azobenzene and linked via secondary amino groups to the central 1,3,5-triazine ring. The types of mesophases formed predominantly depend on the number of rod-like groups. Whereas the trisazomelamines **4** exhibit a well ordered smectic 'bilayer' mesophase besides a nematic and a SmA phase, the triazines **5** incorporating only two azobenzene groups form either a smectic C or a columnar phase. It thus seems that the concept of attaching different numbers of rod-like anisometric sub-units to a central linking unit based on the 1,3,5-triazine core offers novel modes of controlling liquid crystalline structure formation.

4. Experimental

4.1. *Synthesis*

4.1.1. *4-Hydroxy-4′-nitroazobenzene* **1**

The synthesis of this compound [10] was performed by diazotisation of 4-nitroaniline and azo coupling with phenol according to standard procedures.

4.1.2. *4-Alkoxy-4′-nitroazobenzenes* **2**

These were obtained by the following procedure. A mixture containing 4.5 g (18.4 mmol) of 4-hydroxy-4′-nitroazobenzene **1**, 24.0 mmol of the appropriate alkyl bromide, 3.4 g (24.0 mmol) of potassium carbonate, 0.5 g (3.0 mmol) of potassium iodide and 90 ml of dry dimethylformamide was stirred and heated at reflux under a nitrogen atmosphere for 2 h. After cooling to room temperature the mixture was poured into 200 ml of ice/water and the resulting orange precipitate was collected by filtration and washed carefully with water. After drying the crude products in vacuum, purification was effected by recrystallization from ethanol.

4.1.2.1. *4-Decyloxy-4′-nitroazobenzene* **2a**. Yield: 98.2%, $C_{22}H_{29}N_3O_3$ (383.2). IR (KBr): $\nu=2920$, 2860, 1650, 1600, 1530, 1340, 1250, 1145, 860, 835, 690 cm^{-1}. ^1H NMR ($CDCl_3$): $\delta=8.3$ (d, 2H, phenyl; $J=8.9$ Hz), 7.9 (m, 4H, phenyl), 7.0 (d, 2H, phenyl; $J=8.9$ Hz), 4.0 (t, 2H, O–CH_2; $J=6.5$ Hz), 1.8 (m, 2H, CH_2), 1.3 (m, 14H, CH_2), 0.9 (t, 3H, CH_3; $J=6.9$ Hz) ppm. ^{13}C NMR ($CDCl_3$): $\delta=162.9$ (1C, phenyl C–O), 156.0 (1C, phenyl C–N), 148.1 (1C, phenyl C–NO_2), 146.7 (1C, phenyl C–N), 125.6 (2C, phenyl CH), 124.7 (2C, phenyl CH), 123.1 (2C, phenyl CH), 114.9 (2C, phenyl CH), 68.5 (1C, O–CH_2), 31.9, 29.5, 29.4, 29.3, 29.1, 26.0, 22.7 (8C, CH_2, decyl chain), 14.1 (1C, CH_3) ppm. MS *m/z* (%): 383.2 (M^+).

4.1.2.2. *4-Dodecyloxy-4′-nitroazobenzene* **2b**. Yield: 93.6%, $C_{24}H_{33}N_3O_3$ (411.2). IR (KBr): $\nu=2920$, 2860, 1650, 1600, 1530, 1345, 1250, 1150, 860, 840, 690 cm^{-1}. ^1H NMR ($CDCl_3$): $\delta=8.3$ (d, 2H, phenyl; $J=8.7$ Hz), 8.0 (m, 4H, phenyl), 7.0 (d, 2H, phenyl; $J=8.8$ Hz), 4.1 (t, 2H, O–CH_2; $J=6.5$ Hz), 1.8 (m, 2H, CH_2), 1.3 (m, 18H, CH_2), 0.9 (t, 3H, CH_3; $J=6.8$ Hz) ppm. ^{13}C NMR ($CDCl_3$): $\delta=162.9$ (1C, phenyl C–O), 156.0 (1C, phenyl C–N), 148.2 (1C, phenyl C–NO_2), 146.8 (1C, phenyl C–N), 125.6 (2C, phenyl CH), 124.7 (2C, phenyl CH), 123.1 (2C, phenyl CH), 114.9 (2C, phenyl CH), 68.5 (1C, O–CH_2), 31.9, 29.6, 29.5, 29.4, 29.1, 26.0, 22.7 (10C, CH_2, dodecyl chain), 14.1 (1C, CH_3) ppm. MS *m/z* (%): 411.2 (M^+).

4.1.2.3. *4-Hexadecyloxy-4′-nitroazobenzene* **2c**. Yield: 66.3%, $C_{28}H_{41}N_3O_3$ (467.3). IR (KBr): $\nu=2920$, 2860, 1650, 1600, 1535, 1340, 1250, 1145, 860, 835, 690 cm^{-1}.

^{1}H NMR ($CDCl_3$): $\delta = 8.3$ (d, 2H, phenyl; $J = 8.9$ Hz), 8.0 (m, 4H, phenyl), 7.0 (d, 2H, phenyl; $J = 8.9$ Hz), 4.1 (t, 2H, O–CH_2; $J = 6.5$ Hz), 1.8 (m, 2H, CH_2), 1.3 (m, 26H, CH_2), 0.9 (t, 3H, CH_3; $J = 6.9$ Hz) ppm. ^{13}C NMR ($CDCl_3$): $\delta = 162.9$ (1C, phenyl C–O), 156.0 (1C, phenyl C–N), 148.2 (1C, phenyl C–NO_2), 146.7 (1C, phenyl C–N), 125.6 (2C, phenyl CH), 124.7 (2C, phenyl CH), 123.1 (2C, phenyl CH), 114.9 (2C, phenyl CH), 68.5 (1C, O–CH_2), 31.9, 29.7, 29.6, 29.5, 29.4, 29.3, 29.1 26.1, 26.0, 22.7 (14C, CH_2, hexadecyl chain), 14.1 (1C, CH_3) ppm. MS *m/z* (%): 467.3 (M^+).

4.1.3. *4-Alkoxy-4′-aminoazobenzenes* **3**

The syntheses of these compounds started with the corresponding 4-alkoxy-4′-nitro substituted azobenzenes **2**. 10.4 mmol of the appropriate compound **2** were dissolved in 60 ml of hot ethanol. Aqueous sodium hydrogen sulphide (4.3 ml, 9M) was added dropwise with stirring and heating under reflux, which was continued until a clear solution was obtained. The mixture was cooled to room temperature and 200 ml of water added. The precipitate was collected by filtration, washed with water, dried in vacuum and recrystallized from ethanol. Further purification was effected by subsequent flash chromatography (Kieselgel 60, 230–400 mesh) using dichloromethane as eluent.

4.1.3.1. *4-Amino-4′-decyloxyazobenzene* ***3a***. Yield: 66.0%, $C_{22}H_{31}N_3O$ (353.2). IR (KBr): $\nu = 3410$, 3325, 2920, 2860, 1625, 1600, 1465, 1250, 1145, 850 cm^{-1}. ^{1}H NMR ($CDCl_3$): $\delta = 7.8$ (m, 4H, phenyl), 7.0 (d, 2H, phenyl; $J = 8.9$ Hz), 6.7 (d, 2H, phenyl; $J = 8.6$ Hz), 4.0 (m, 2H, O–CH_2; 2H, NH_2), 1.8 (m, 2H, CH_2), 1.3 (m, 14H, CH_2), 0.9 (t, 3H, CH_3; $J = 6.9$ Hz) ppm. ^{13}C NMR ($CDCl_3$): $\delta = 160.8$ (1C, phenyl C–O), 148.9 (1C, phenyl C–NH_2), 147.0 (1C, phenyl C–N), 145.6 (1C, phenyl C–N), 124.6 (2C, phenyl CH), 124.0 (2C, phenyl CH), 114.7 (2C, phenyl CH), 114.6 (2C, phenyl CH), 68.3 (1C, O–CH_2), 31.9, 29.5, 29.4, 29.3, 29.2, 26.0, 22.6 (8C, CH_2, decyl chain), 14.1 (1C, CH_3) ppm. MS *m/z* (%): 353.2 (M^+).

4.1.3.2. *4-Amino-4′-dodecyloxyazobenzene* ***3b***. Yield: 77.8%, $C_{24}H_{35}N_3O$ (381.2). IR (KBr): $\nu = 3410$, 3325, 2920, 2860, 1630, 1600, 1470, 1250, 1150, 850 cm^{-1}. ^{1}H NMR ($CDCl_3$): $\delta = 7.8$ (m, 4H, phenyl), 7.0 (d, 2H, phenyl; $J = 8.9$ Hz), 6.8 (d, 2H, phenyl; $J = 8.6$ Hz), 4.0 (m, 2H, O–CH_2; 2H, NH_2), 1.8 (m, 2H, CH_2), 1.3 (m, 18H, CH_2), 0.9 (t, 3H, CH_3; $J = 6.9$ Hz) ppm. ^{13}C NMR ($CDCl_3$): $\delta = 160.8$ (1C, phenyl C–O), 148.9 (1C, phenyl C–NH_2), 147.0 (1C, phenyl C–N), 145.6 (1C, phenyl C–N), 124.6 (2C, phenyl CH), 124.0 (2C, phenyl CH), 114.7 (2C, phenyl CH), 114.6 (2C, phenyl CH), 68.3 (1C, O–CH_2), 31.9, 29.6, 29.5, 29.4, 29.3, 29.2, 26.0, 22.7 (10C, CH_2, dodecyl chain), 14.1 (1C, CH_3) ppm. MS *m/z* (%): 381.3 (M^+).

4.1.3.3. *4-Amino-4′-hexadecyloxyazobenzene* ***3c***. Yield: 80.2%, $C_{28}H_{43}N_3O$ (437.9). IR (KBr): $\nu = 3420$, 3325, 2920, 2855, 1635, 1600, 1470, 1250, 1150, 840 cm^{-1}. ^{1}H NMR ($CDCl_3$): $\delta = 7.8$ (m, 4H, phenyl), 7.0 (d, 2H, phenyl; $J = 8.9$ Hz), 6.7 (d, 2H, phenyl; $J = 8.6$ Hz), 4.0 (m, 2H, O–CH_2; 2H, NH_2), 1.8 (m, 2H, CH_2), 1.3 (m, 26H, CH_2), 0.9 (t, 3H, CH_3; $J = 6.9$ Hz) ppm. ^{13}C NMR ($CDCl_3$): $\delta = 160.8$ (1C, phenyl C–O), 148.9 (1C, phenyl C–NH_2), 147.0 (1C, phenyl C–N), 145.6 (1C, phenyl C–N), 124.6 (2C, phenyl CH), 124.0 (2C, phenyl CH), 114.7 (2C, phenyl CH), 114.6 (2C, phenyl CH), 68.3 (1C, O–CH_2), 31.9, 29.7, 29.6, 29.4, 29.3, 29.2, 26.0, 22.7 (14C, CH_2, hexadecyl chain), 14.1 (1C, CH_3) ppm. MS *m/z* (%): 437.4 (M^+).

4.1.4. *Trisazomelamines* **4**

To a stirred solution of 5.7 mmol of the appropriate 4-alkoxy-4′-aminoazobenzene **3**, dissolved in 80 ml of dry ethyl methyl ketone, 0.34 g (1.9 mmol) of cyanuric chloride and 0.78 g (5.7 mmol) of potassium carbonate were added. The mixture was stirred and heated at reflux under a nitrogen atmosphere for 10 h. After cooling to room temperature, the reaction mixture was poured into 200 ml of ice/water and the slowly precipitating solid was collected by filtration, washed with water and dried in vacuum. The pure threefold azobenzene-substituted melamines **4** were obtained by flash chromatography using Kieselgel 60, 230–400 mesh.

4.1.4.1. *2,4,6-Tris[4-decyloxy-4′-aminoazobenzene]-1,3,5-triazine* ***4a***†. Yield: 65.3%. Eluent for chromatographic purification: dichloromethane/ethyl acetate 10 : 0.2. Elemental analysis: $C_{63}H_{90}N_{12}O_3$ ($M_w = 1062.7$); calc C 71.19, H 7.80, N 14.56; found C 70.92, H 7.83, N 14.06%. IR (KBr): $\nu = 3395$, 2920, 2850, 1600, 1580, 1500, 1420, 1250, 840 cm^{-1}. ^{1}H NMR ($CDCl_3$): $\delta = 7.9$ (d, 12H, phenyl; $J = 8.8$ Hz), 7.7 (d, 6H, phenyl; $J = 8.6$ Hz), 7.4 (s, 3H, NH), 7.0 (d, 6H, phenyl; $J = 9.0$ Hz), 4.0 (t, 6H, O–CH_2; $J = 6.5$ Hz), 1.8 (m, 6H, CH_2), 1.3 (m, 42H, CH_2), 0.9 (t, 9H, CH_3; $J = 6.9$ Hz) ppm. ^{13}C NMR ($CDCl_3$): $\delta = 164.1$ (3C, triazine C–N), 161.6 (3C, phenyl C–O), 148.6 (3C, phenyl C–NH), 146.9 (3C, phenyl C–N), 140.3 (3C, phenyl C–N), 124.6 (6C, phenyl CH), 123.5 (6C, phenyl CH), 120.4 (6C, phenyl CH), 114.6 (6C, phenyl CH), 68.3 (3C, O–CH_2), 31.9, 29.6, 29.4, 29.3, 29.2, 26.0, 22.7 (24C, CH_2, decyl chains), 14.1 (3C, CH_3) ppm.

†Although this nomenclature is conveniently simple, a stricter alternative nomenclature for the compounds **4** would be tris[4-(4-alkyloxyphenylazo)phenylamino]-1,3,5-triazines.

4.1.4.2. *2,4,6-Tris[4-dodecyloxy-4′-aminoazobenzene]-1,3,5-triazine* ***4b***. Yield: 66.1%. Eluent for chromatographic purification: dichloromethane/ethyl acetate 10:0.1. Elemental analysis: $C_{75}H_{102}N_{12}O_3$ ($M_w = 1219.6$); calc C 72.64, H 8.29, N 13.55; found C 72.74, H 8.35, N 12.99%. IR (KBr): $\nu = 3400$, 2920, 2860, 1600, 1570, 1500, 1420, 1250, 845 cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 7.9$ (d, 12H, phenyl; $J = 8.8$ Hz), 7.7 (d, 6H, phenyl; $J = 8.6$ Hz), 7.4 (s, 3H, NH), 7.0 (d, 6H, phenyl; $J = 9.0$ Hz), 4.0 (t, 6H, O–CH_2; $J = 6.5$ Hz), 1.8 (m, 6H, CH_2), 1.3 (m, 48H, CH_2), 0.9 (t, 9H, CH_3; $J = 6.9$ Hz) ppm. ^{13}C NMR ($CDCl_3$): $\delta = 164.2$ (3C, triazine C–N), 161.6 (3C, phenyl C–O), 148.6 (3C, phenyl C–NH), 146.9 (3C, phenyl C–N), 140.4 (3C, phenyl C–N), 124.6 (6C, phenyl CH), 123.6 (6C, phenyl CH), 120.4 (6C, phenyl CH), 114.7 (6C, phenyl CH), 68.3 (3C, O–CH_2), 31.9, 29.9, 29.6, 29.4, 29.2, 26.0, 22.7 (30C, CH_2, dodecyl chains), 14.1 (3C, CH_3) ppm.

4.1.4.3. *2,4,6-Tris[4-hexadecyloxy-4′-aminoazobenzene]-1,3,5-triazine* ***4c***. Yield: 54.3%. Eluent for chromatographic purification: dichloromethane/ethyl acetate 10:0.1. Elemental analysis: $C_{87}H_{126}N_{12}O_3$ ($M_w = 1386$); calc C 74.42, H 9.17, N 11.52; found C 74.51, H 8.93, N 11.82%. IR (KBr): $\nu = 3400$, 2920, 2860, 1600, 1570, 1500, 1420, 1250, 840 cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 7.9$ (d, 12H, phenyl; $J = 8.6$ Hz), 7.7 (d, 6H, phenyl; $J = 8.0$ Hz), 7.3 (s, 3H, NH), 7.0 (d, 6H, phenyl; $J = 8.7$ Hz), 3.9 (t, 6H, O–CH_2; $J = 6.4$ Hz), 1.8 (m, 6H, CH_2), 1.3 (m, 78H, CH_2), 0.9 (t, 9H, CH_3; $J = 6.8$ Hz) ppm. ^{13}C NMR ($CDCl_3$): $\delta = 164.1$ (3C, triazine C–N), 161.6 (3C, phenyl C–O), 148.6 (3C, phenyl C–NH), 146.9 (3C, phenyl C–N), 140.4 (3C, phenyl C–N), 124.6 (6C, phenyl CH), 123.6 (6C, phenyl CH), 120.4 (6C, phenyl CH), 114.7 (6C, phenyl CH), 68.3 (3C, O–CH_2), 31.9, 29.7, 29.5, 29.4, 29.2, 26.0, 25.9, 22.7 (42C, CH_2, hexadecyl chains), 14.1 (3C, CH_3) ppm.

4.1.5. *1,3,5-Triazines* ***5****, incorporating two rod-like azobenzene groups*

To prepare the 1,3,5-triazines **5**, 3.7 mmol of the appropriate 4-alkoxy-substituted aminoazobenzene derivative **3**, 0.33 g (1.9 mmol) 2,4-dichloro-6-methoxy-1,3,5-triazine [15, 16] and 0.25 g (1.9 mmol) potassium carbonate in 80 ml of dry ethyl methyl ketone were stirred and heated under reflux under a nitrogen atmosphere for 2 h. After cooling to room temperature the mixture was poured into 400 ml of ice/water and the precipitate was collected by filtration. The solid was washed several times with water and dried in vacuum. The triazine derivatives **5** were purified by flash chromatography using Kieselgel 60, 230–400 mesh.

4.1.5.1. *2,4-Bis[4-decyloxy-4′-aminoazobenzene]-6-methoxy-1,3,5-triazine* ***5a***‡. Yield: 40.9%. Eluent for chromatographic purification: dichloromethane/ethyl acetate 10:0.1. Elemental analysis: $C_{48}H_{63}N_9O_3$ ($M_w = 813.5$); calc C 70.81, H 7.80, N 15.48; found C 69.51, H 7.92, N 15.44%. IR (KBr): $\nu = 3410$, 2940, 2860, 1625, 1610, 1500, 1470, 1420, 1250, 1155, 850, 815 cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 7.9$ (dd, 8H, phenyl; $J = 8.8$ Hz), 7.8 (d, 4H, phenyl; $J = 8.8$ Hz), 7.3 (s, 2H, NH), 7.0 (d, 4H, phenyl; $J = 9.0$ Hz), 4.0 (t, 4H, O–CH_2; $J = 6.8$ Hz), 1.8 (m, 4H, CH_2), 1.6 (s, 3H, OCH_3), 1.3 (m, 28H, CH_2), 0.9 (t, 6H, CH_3; $J = 6.3$ Hz) ppm. ^{13}C NMR ($CDCl_3$): $\delta = 171.3$ (1C, triazine O–C), 165.3 (2C, triazine C–N), 161.5 (2C, phenyl C–O), 148.8 (2C, phenyl C–NH), 146.9 (2C, phenyl C–N), 140.1 (2C, phenyl C–N), 124.6 (4C, phenyl CH), 123.6 (4C, phenyl CH), 120.4 (4C, phenyl CH), 114.7 (4C, phenyl CH), 68.4 (2C, O–CH_2), 54.7 (1C, O–CH_3), 31.9, 29.6, 29.4, 29.3, 29.2, 26.0, 22.7 (16C, CH_2, decyl chains), 14.1 (2C, CH_3) ppm.

4.1.5.2. *2,4-Bis[4-dodecyloxy-4′-aminoazobenzene]-6-methoxy-1,3,5-triazine* ***5b***. Yield: 51.4%. Eluent for chromatographic purification: dichloromethane/ethyl acetate 10:0.1. Elemental analysis: $C_{52}H_{71}N_9O_3$ ($M_w = 870.2$); calc C 71.77, H 8.22, N 14.48; found C 71.30, H 8.34, N 14.46%. IR (KBr): $\nu = 3420$, 2930, 2860, 1625, 1600, 1510, 1470, 1410, 1250, 1160, 845, 815 cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 7.9$ (dd, 8H, phenyl; $J = 8.8$ Hz), 7.8 (d, 4H, phenyl; $J = 8.8$ Hz), 7.4 (s, 2H, NH), 7.0 (d, 4H, phenyl; $J = 8.9$ Hz), 4.0 (t, 4H, O–CH_2; $J = 6.8$ Hz), 1.8 (m, 4H, CH_2), 1.6 (s, 3H, OCH_3), 1.3 (m, 36H, CH_2), 0.9 (t, 6H, CH_3; $J = 6.3$ Hz) ppm. ^{13}C NMR ($CDCl_3$): $\delta = 171.3$ (1C, triazine O–C), 165.4 (2C, triazine C–N), 161.5 (2C, phenyl C–O), 148.8 (2C, phenyl C–NH), 146.9 (2C, phenyl C–N), 140.1 (2C, phenyl C–N), 124.6 (4C, phenyl CH), 123.6 (4C, phenyl CH), 120.4 (4C, phenyl CH), 114.7 (4C, phenyl CH), 68.4 (2C, O–CH_2), 54.7 (1C, O–CH_3), 31.9, 29.6, 29.5, 29.4, 29.3, 29.2, 26.0, 22.7 (20C, CH_2, dodecyl chains), 14.1 (2C, CH_3) ppm.

4.1.5.3. *2,4-Bis[4-hexadecyloxy-4′-aminoazobenzene]-6-methoxy-1,3,5-triazine* ***5c***. Yield: 20.3%. Eluent for chromatographic purification: dichloromethane/ethyl acetate 10:0.3. Elemental analysis: $C_{60}H_{87}N_9O_3$ ($M_w = 982.4$); calc C 73.35, H 8.93, N 12.83; found C 72.91, H 9.05, N 12.81%. IR (KBr): $\nu = 3395$, 2940, 2865, 1605, 1625, 1505, 1470, 1420, 1255, 1160, 845, 820 cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 7.9$ (dd, 8H, phenyl; $J = 8.6$ Hz), 7.8 (d, 4H, phenyl; $J = 8.8$ Hz), 7.4 (s, 2H, NH), 7.0 (d, 4H, phenyl; $J = 8.9$ Hz), 4.0 (t, 4H, O–CH_2; $J = 6.4$ Hz), 1.8 (m, 4H, CH_2), 1.6 (s, 3H, OCH_3), 1.3 (m, 52H, CH_2),

‡ Alternatively, 2,4-bis[4-(4-decyloxyphenylazo)phenylamino]-6-methoxy-1,3,5-triazine.

0.9 (t, 6H, CH_3; $J = 6.1$ Hz) ppm. ^{13}C NMR ($CDCl_3$): $\delta = 171.3$ (1C, triazine O–C), 165.3 (2C, triazine C–N), 161.5 (2C, phenyl C–O), 148.8 (2C, phenyl C–NH), 146.9 (2C, phenyl C–N), 140.1 (2C, phenyl C–N), 124.6 (4C, phenyl CH), 123.6 (4C, phenyl CH), 120.4 (4C, phenyl CH), 114.7 (4C, phenyl CH), 68.4 (2C, O–CH_2), 54.7 (1C, O–CH_3), 31.9, 29.7, 29.6, 29.4, 29.2, 26.0, 22.7 (28C, CH_2, hexadecyl chains), 14.1 (2C, CH_3) ppm.

4.2. *Instrumental*

Elemental analyses were performed using a Carlo Erba CHNS-O EA 1108 Elemental Analyser. IR spectra were obtained with an M 80 spectrometer (Carl Zeiss Jena). ^1H NMR and ^{13}C NMR spectra were recorded using a Bruker AMX 300 spectrometer. For mass spectra, a Finnigan SSQ MAT 710 spectrometer was used. Thermograms were measured using a Netzsch DSC 200. 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. Photomicrographs were obtained with an Olympus OM-4 Ti system camera. Wide angle scattering analyses were performed with a goniometer from Siemens (D 5000).

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