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Liquid Crystals

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Online publication date: 06 August 2010

To cite this Article Goldmann, Daniela , Dietel, Reinhard , Janietz, Dietmar , Schmidt, Claudia and Wendorff, Joachim H.(1998) 'Sheet-shaped mesogens based on 1,3,5-triazines: variation of columnar mesophases through intermolecular hydrogen bonding', Liquid Crystals, 24: 3, 407 — 411

To link to this Article: DOI: 10.1080/026782998207226

URL: http://dx.doi.org/10.1080/026782998207226

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Liquid Crystals, 1998, Vol. 24, No. 3, 407–411

Sheet-shaped mesogens based on 1,3,5-triazines: variation of columnar mesophases through intermolecular hydrogen bonding

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(*Received 9 June 1997; in final form 5 August 1997; accepted 19 September 1997*)

The mesomorphic behaviour of a liquid crystalline sheet-shaped 2,4,6-triarylamino-1,3,5-triazine bearing six peripheral decyloxy chains has been investigated in binary mixtures with two-fold alkoxy substituted non-mesomorphic benzoic acids. Each investigated equimolar mixture exhibits an enantiotropic columnar phase with either a hexagonal or a rectangular lattice. The two-dimensional lattice parameters depend on the length and positions of the flexible alkoxy chains of the aromatic carboxylic acids. The structure formation of the mixed systems giving rise to variations of the mesophase structure of the pure triarylaminotriazine results from intermolecular hydrogen bonding between the complementary melamine and acid components.

1. Introduction

The formation of thermotropic nematic, smectic or columnar mesophases is predominantly caused by the anisometric rod-like or sheet-like shape of the single molecules. However, form anisotropic aggregates giving rise to liquid crystalline structures can also arise through specific intermolecular interactions between identical or different individual molecules. Such attractive interactions may, for example, result from intermolecular hydrogen bonding [1]. However, only a few systems are known which exhibit columnar mesophases due to supramolecular hydrogen bonded associates.

Examples that belong to this special category are monoaryl esters of cyclohexane-1,3,5-triol [2–4], inositol ethers [5, 6], three-fold alkoxy substituted primary benzamides [7], binary mixtures of 2,6-diacylamino-pyridines with uracil derivatives [8], phenanthridinones [9] and 1,3-diacylaminobenzenes [10, 11]. A common characteristic of all these systems is that the single molecules do not fulfil the criteria of a disc-like form anisotropy [12]. The flat mesogenic unit is only formed by the aggregation of two or more molecules via hydrogen bonding.

Recently we presented new 2,4,6-triarylamino-1,3,5-triazines characterized by six long peripheral alkoxy chains. These triazines are the first representatives of a novel class of sheet-shaped mesogens which exhibit thermotropic columnar mesophases. The two-dimensional lattice parameters, hexagonal or rectangular, were found to depend on the length of the incorporated lateral flexible molecular segments [13]. These triarylmelamines are characterized by a heterocyclic 1,3,5-triazine core with three-fold substitution with secondary amino groups.

These structural features (figure 1) are similar to those of 2,6-diacylaminopyridines and of alkylamino substituted 1,3,5-triazine derivatives, which have been described as forming liquid cystalline complexes with aromatic or aliphatic carboxylic acids, respectively [14–16]. We therefore expected that the aminotriazine core of the triarylmelamines should promote attractive interactions with complementary functional molecules via intermolecular hydrogen bonding. By combining the two principles of structure formation, the form anisotropic shape of a single molecule and the intermolecular hydrogen bonding, it should be possible to control the formation of columnar liquid crystalline structures. To prove this hypothesis we have investigated the thermal

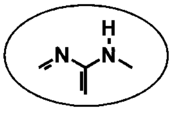

Figure 1. Functional sub-unit of the heterocyclic core region of sheet-shaped triarylmelamines.

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properties of binary mixtures of the triarylmelamine **1** characterized by six lateral decyloxy chains with the alkoxy modified benzoic acids **2** and **3**. Whereas the molecular parameters of the melamine component were kept constant, the benzoic acids **2** and **3** were varied with respect to the lengths and the positions of the alkoxy groups.

2. Experimental

2.1. *Materials and sample preparation*

The chemical structures of the compounds **1–3** investigated are presented in figure 2. The synthesis of the melamine **1** is given in detail elsewhere [13]. The carboxylic acids **2** and **3** were prepared by Claisen etherification of the respective dihydroxybenzoic acid methyl (ethyl) esters with the appropriate alkyl bromides, followed by alkaline ester cleavage (refluxing in KOH/ethanol) according to known procedures [17–19]. Characterization was performed by means of IR, NMR and elemental analysis.

Equimolar mixtures of melamine **1** and the benzoic acids **2** and **3** were prepared by dissolving the components separately in *n*-hexane, mixing the solutions and evaporating the solvent. All further investigations were performed after annealing the residues in the isotropic state at 120°C for 2 h. No significant mass loss was observed by thermogravimetric measurements during this thermal treatment, indicating good thermal stability of the samples. The phase transition temperatures of the pure compounds **1–3** and of the binary mixtures **1/2** and **1/3** obtained by differential scanning calorimetry (DSC) are summarized in table 1. For IR spectroscopy the melamine **1** and the benzoic acids **2** and **3** were prepared as KBr pellets, while the IR measurements of the appropriate binary mixtures were performed on thin films on a germanium substrate. Pure KBr pellets and uncovered Ge plates, respectively, were used as references.

2.2. *Instrumental*

IR spectra were recorded with an FTIR Nicolet Magna 550 spectrometer. ^{1}H NMR and ^{13}C NMR spectra were obtained using a Bruker AMX 300 spectrometer. Elemental analyses were made with a Carlo Erba CHNS-O EA 1108 Elemental Analyser. Optical texture observations were made using an Olympus BHS polarizing microscope in conjunction with a Linkam TMH/S 600 hot state and a Linkam TP 92 control unit. Photomicrographs were obtained with an Olympus OM-4 Ti system camera. Calorimetric investigations were carried out with a Perkin-Elmer DSC 7 and with a Netzsch DSC 200. Wide angle X-ray scattering analyses were performed employing a goniometer from Siemens (D 5000).

3. Results and discussion

3.1. *Thermal behaviour of equimolar mixtures of the melamine **1** wth the benzoic acids **2** and **3***

The pure 2,4,6-tris(3,4-didecyloxyphenyl-1-amino)-1,3,5-triazine **1** exhibits an enantiotropic mesophase within the temperature range given in table 1. The mesophase structure is characterized by a hexagonal columnar arrangement with an irregular intracolumnar stacking of the molecules (Col$_{hd}$) (see table 2). In contrast, the two-fold alkoxy substituted benzoic acids **2** and **3** are non-mesomorphic (see also [17, 20]).

Microscopic investigations (contact preparations, as well as defined mixtures) reveal complete miscibility of the melamine **1** with the acids **2** and **3** at a molar ratio of 1:1. Each of these equimolar mixtures exhibits an enantiotropic mesophase. The growth of a star-like optical texture (on cooling from the isotropic melt) and the simultaneous appearance of homeotropic domains is typical for all equimolar mixtures of the triazine **1** with the benzoic acids **2** and **3**. Further cooling results in the formation of focal-conic textures which are characteristic for smectic structures [21] as well as for columnar mesophases, with an irregular ordering of the molecules within the columns [12].

The phase transition data are summarized in table 1. The transition temperatures of the appropriate mixtures of **1** with the benzoic acids **2** and **3** are lower than those of the pure triazine **1**. Considering a completion of the disc shape of the melamine through association with the complementary acid units (see §3.3) one might expect

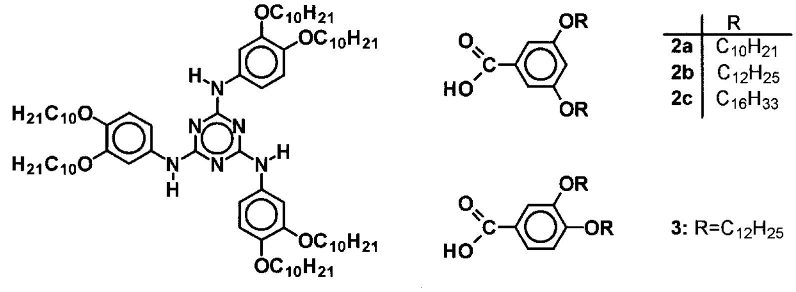

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Figure 2. Chemical structure of the sheet-shaped 2,4,6-triarylamino-1,3,5-triazine **1** and of the two-fold alkoxy substituted benzoic acids **2** and **3**.

Table 1. Phase transition temperatures (°C) of the triazine **1** [13], of the pure compounds **2**, **3** and of equimolar mixtures of the melamine **1** with the benzoic acids **2** and **3** determined by differential scanning calorimetry (DSC) on heating at 10 K min^{-1}; transition enthalpies (kJ mol^{-1}) are given in brackets. Cr = crystalline, M = mesophase, I = isotropic phase.

Sample	Cr		M		I
1	•	70·4 (14·03)	•	154·6 (2·44)	•
2a	•	60·6 (39·19)	—		•
2b	•	66·5 (49·83)	—		•
2c	•	79·5 (72·39)	—		•
3[a]	•	122·6 (51·58)	—		•
1/2a	•	32·4 (33·44)	•	68·4 (3·38)	•
1/2b	•	34·5 (13·42)	•	75·1 (3·90)	•
1/2c	•	18·7 (15·41)	•	73·6 (3·49)	•
1/3	•	62·2 (9·27)	•	88·7 (4·91)	•

[a] For the carboxylic acid **3** polymorphism in the solid state was observed; the transition data are for the highest melting modification.

an increase of the clearing temperatures of the mixtures compared with those of compound **1**. Such an effect has been observed, for example, in calamitic liquid crystalline hydrogen bonded binary mixtures made from stilbazole derivatives [22, 23]. Nevertheless, calamitic complexes formed through intermolecular hydrogen bonds between two different compounds and showing a decrease in isotropization temperatures compared with the (mesogenic) single components have also been reported [24, 25]. On the other hand, except for the binary mixture **1/2c**, the clearing temperatures of the mixed systems of the melamine **1** with the 3,5-dialkoxy substituted benzoic acids **2** are higher than the melting points of the respective pure acids. The opposite effect is observed in case of the 3,4-substitution pattern of the acid component (**1/3**).

3.2. *X-ray investigations*

Solely on the basis of polarizing microscopy and DSC, a satisfactory determination of the types of mesophase structures of the binary mixtures **1/2** and **1/3** is not possible. Therefore, temperature dependent X-ray investigations were performed. The X-ray diffractograms of all investigated mixtures **1/2**, characterized by benzoic acids with two alkoxy chains fixed at the 3,5-positions of the phenyl ring, show sharp (1 0 0) and (1 1 0) reflections in the small angle region with a ratio of the lattice spacings $d_{100} : d_{110} = 1/3^{1/2}$. The reflections (2 0 0), (3 0 0) and (2 3 0) are very weak in all cases (figure 3). The investigations give evidence of a hexagonal columnar ($\mathrm{Col_h}$) structure in the mesophase. The hexagonal lattice constants are increased compared with those for the pure melamine **1**. Furthermore, an increase of the intercolumnar distances is observed as a function of increasing alkoxy chain lengths of the benzoic acids **2**. The lattice constants are summarized in table 2.

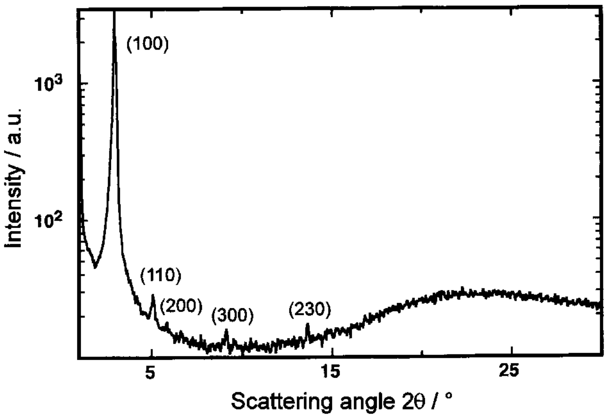

Figure 3. Wide angle X-ray diffractogram of the binary mixture of melamine **1** with 3,5-dihexadecyloxybenzoic acid **2c** at 56°C.

A major structural change takes place on changing the positions of the alkoxy groups of the acid component. The X-ray diffractogram of the equimolar mixture of the triazine **1** with the 3,4-didodecyloxybenzoic acid **3** is shown in figure 4. The appearance of the strong (0 1 0) reflection (corresponding to 30·1 Å) in addition to the (1 0 0), (2 0 0) and (3 0 0) Bragg reflections corresponding to 35·8, 17·9 and 12·1 Å, respectively, reveal that the binary mixture **1/3** displays a rectangular columnar ($\mathrm{Col_r}$) mesophase (see table 2).

A characteristic feature of all X-ray diffractograms of the binary mixtures of melamine **1** with the benzoic acids **2** and **3** is the absence of a sharp reflection in the wide angle region. Only a diffuse halo is visible caused by the liquid-like arrangement of the alkyl side chains. This indicates an irregular (disordered) arrangement

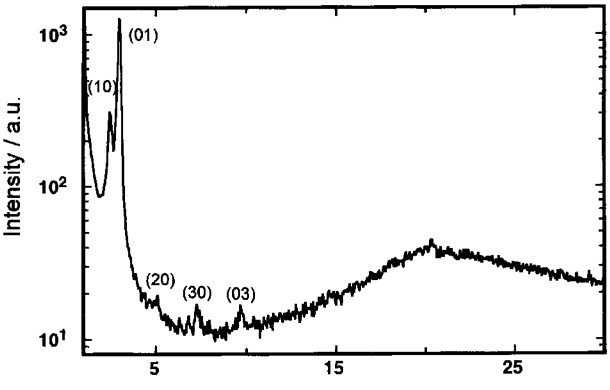

Figure 4. WAXS diagram of the equimolar mixture of triazine **1** with 3,4-didodecyloxybenzoic acid **3** ($T = 69$°C).

Table 2. Lattice parameters (Å) and mesophase structures of the sheet-shaped triarylmelamine **1** [13] and of the equimolar mixtures of the triazine **1** with the carboxylic acids **2** and **3** for comparison. $\mathrm{Col_{hd}}$ = disordered hexagonal columnar; $\mathrm{Col_{rd}}$ = disordered rectangular columnar.

Sample	*a*	*b*	Phase type
1	30·2	—	$\mathrm{Col_{hd}}$
1/2a	32·4	—	$\mathrm{Col_{hd}}$
1/2b	33·2	—	$\mathrm{Col_{hd}}$
1/2c	34·4	—	$\mathrm{Col_{hd}}$
1/3	35·8	30·1	$\mathrm{Col_{rd}}$

of the molecules within the parallel aligned columns, independent of the two-dimensional lattice.

Although it seems so far that the variations in the liquid crystalline structures of columnar phase-forming, functional triarylmelamines is restricted to the intercolumnar lattice parameters in binary mixtures with aromatic carboxylic acids, the number of methylene groups of the 3,5-dialkoxybenzoic acids **2** allows control over the spacings between the hexagonally arranged columns. In contrast, the 3,4-dialkoxy substitution pattern of the aromatic acid **3** gives rise to the induction of a rectangular columnar phase by interaction with the melamine **1**.

3.3. *IR spectroscopic investigations*

IR spectroscopic investigations were performed in order to characterize the nature of the intermolecular interactions between melamine **1** and the benzoic acids **2** and **3**. The FTIR transmission spectrum of the mixture **1/2a**, along with the appropriate spectra of the pure melamine **1** and the 3,5-didecyloxybenzoic acid **2a**, each obtained after thermal treatment of the samples at 120°C, are given in figure 5.

The $\nu(\mathrm{C=O})$ absorption band of the carboxylic group at $1695\,\mathrm{cm^{-1}}$ for the pure benzoic acid **2a** is shifted to $1665\,\mathrm{cm^{-1}}$. The intensity of the broad $\nu(\mathrm{OH})$ band between 3300 and $2400\,\mathrm{cm^{-1}}$ decreases and the two bands at 2640 and $2520\,\mathrm{cm^{-1}}$ assigned to overtones and combinations of the OH-bending and CO-stretching vibrations of the benzoic acid do not appear in the spectrum of the binary mixture **1/2a**. Moreover, the $\gamma(\mathrm{OH})$ absorption [26] of the carboxylic acid **2a** located at $930\,\mathrm{cm^{-1}}$ is not visible in the spectrum of the mixed system. Satisfactory information regarding changes of the NH-deformation band visible at $1580\,\mathrm{cm^{-1}}$ for the pure melamine **1** is not available because of the intense absorption of the benzoic acid **2a** at $1600\,\mathrm{cm^{-1}}$ which is still present in the spectrum of the mixture **1/2a**. However, the two bands at 3390 and $3290\,\mathrm{cm^{-1}}$ in the region of the NH-stretching vibrations [26] of the melamine **1** change their relative intensities after thermal treatment with the acid **2a**.

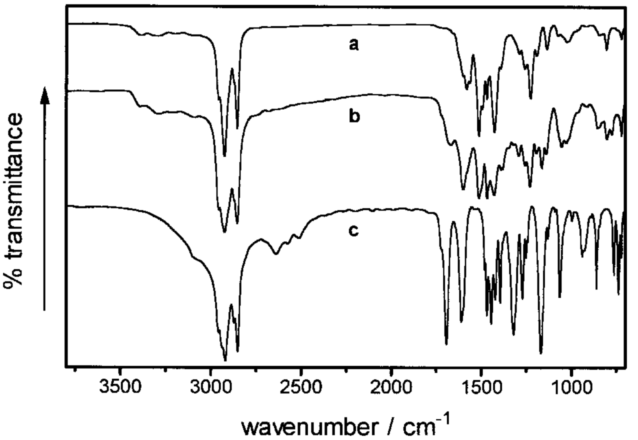

Figure 5. FTIR spectra obtained after thermal treatment of the samples in the isotropic state at 120°C for 2 h: (a) 2,4,6-tris(3,4-didecyloxyphenyl-1-amino)-1,3,5-triazine **1**; (b) equimolar mixture **1/2a**; (c) 3,5-didecyloxybenzoic acid **2a**.

It is obvious that the triarylamino-1,3,5-triazine **1** and the alkoxy substituted benzoic acids **2** and **3** do not behave as individual species after thermal treatment of the binary mixtures **1/2** and **1/3** in the isotropic state. As concluded from the IR investigations, this behaviour originates from the formation of intermolecular hydrogen bonds between the amino substituted triazine core of the melamine **1** and the complementary acid components. Taking into account the three hydrogen bonding sites of the melamine, the interaction with the complementary aromatic acids may lead to non-covalently bonded aggregates consisting of one triazine molecule and up to three molecules of the acid. In the case of the equimolar mixtures investigated here, association of the aminotriazine **1** with more than one equivalent of the acids **2** and **3** would certainly lead to a considerable amount of the melamine remaining uncomplexed. However, it has to be emphasized that the non-associated pure compound **1** is not detectable in the binary mixtures with the benzoic acids **2** and **3**, strongly supporting our conclusion that predominantly dimers are formed as shown schematically in figure 6.

Further work is in progress with variations of the melamine as well as of the acid components regarding the number, positions and chain lengths of incorporated alkoxy groups. The aim is to investigate the influence of lateral flexible segments of both functional molecular species on the liquid crystalline properties of appropriate binary mixtures.

4. Conclusions

The present results show that the liquid crystalline structure of the sheet-shaped melamine **1** which already

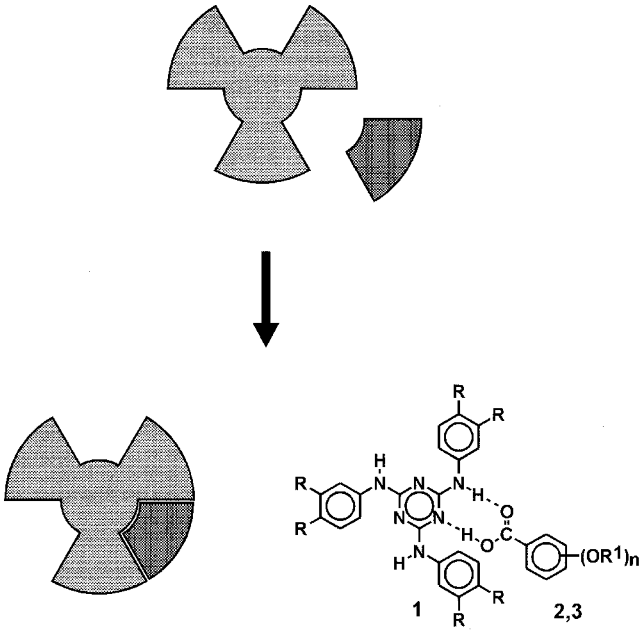

Figure 6. Molecular recognition between the liquid crystalline 2,4,6-triarylamino-1,3,5-triazine **1** and the two-fold alkoxy substituted benzoic acids **2** and **3** due to intermolecular hydrogen bonding which gives rise to the variation of the columnar mesophase structure of the melamine **1**.

exhibits a hexagonal columnar mesophase as a single compound can be varied through molecular recognition based on associations with complementary compounds. The two-dimensional lattice parameters of binary mixtures prepared from the triazine **1** and two-fold alkoxy substituted benzoic acids are controlled via the positions and the number of methylene groups within the flexible chains of the acid component. However, so far it seems that the attractive intermolecular interactions of the melamine **1** with aromatic carboxylic acids are restricted to equimolar mixtures, probably due to steric hindrance. This feature, as well as further variations of molecular parameters of both the complementary amino triazine and acid components, will be an important subject for further studies.

The financial support of the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

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