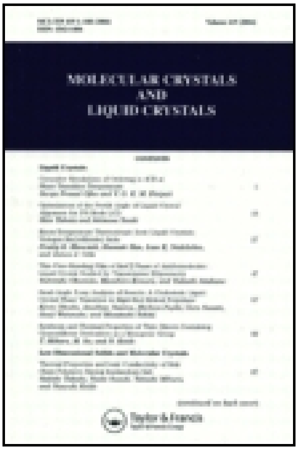

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Control of Mesomorphic Structures of 1,3,5-Triazines Through Molecular Shape and Intramolecular Functionalization

Dietmar Janietz [a], Daniela Goldmann [a], Claudia Schmidt [b] & Joachim H. Wendorff [b]

[a] Universität Potsdam, Fachbereich Chemie und Institut für Dünnschicht-technologie und Mikrosensorik, D-14513, Teltow, Germany

[b] Universität Marburg, Institut für Physikalische Chemie und Wissenschaftliches Zentrum für Materialwissenschaften, D-35032, Marburg, Germany

To cite this article: Dietmar Janietz, Daniela Goldmann, Claudia Schmidt & Joachim H. Wendorff (1999): Control of Mesomorphic Structures of 1,3,5-Triazines Through Molecular Shape and Intramolecular Functionalization, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 332:1, 141-148

To link to this article: http://dx.doi.org/10.1080/10587259908023754

Mol. Cryst. Liq. Cryst., 1999, Vol. 332, pp. 141-148
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under the
Gordon and Breach Science Publishers imprint.
Printed in Malaysia

Control of Mesomorphic Structures of 1,3,5-Triazines Through Molecular Shape and Intramolecular Functionalization

DIETMAR JANIETZ[a], DANIELA GOLDMANN[a],
CLAUDIA SCHMIDT[b] and JOACHIM H. WENDORFF[b]

[a]*Universität Potsdam, Fachbereich Chemie und Institut für Dünnschicht-technologie und Mikrosensorik, D-14513 Teltow, Germany and* [b]*Universität Marburg, Institut für Physikalische Chemie und Wissenschaftliches Zentrum für Materialwissenschaften, D-35032 Marburg, Germany*

The thermal behaviour of a non-mesomorphic 2,4,6-triarylamino-1,3,5-triazine fitted with three peripheral dodecyloxy chains has been investigated in binary mixtures with 4-octyloxy-benzoic acid and with nitrofluorenone based electron acceptors. Attractive interactions between the complementary components, related to intermolecular hydrogen bonding or charge transfer complex formation, give rise to inductions of columnar as well as smectic liquid crystalline structures.

Keywords: 2,4,6-triarylamino-1,3,5-triazine; hydrogen bonding; donor-acceptor interactions; mesophase inductions; columnar and smectic phases

INTRODUCTION

Directed intermolecular forces between complementary molecules may give rise to the induction of thermotropic liquid crystalline structures as well as to manipulations of the phase type.

Thus, it is well known that electron rich flat aromatic compounds such as triphenylenes or radial multialkynylbenzene derivatives form charge-transfer complexes with electron acceptors. The CT interactions may cause the stabilization as well as the induction of columnar mesophases[1-4].

A further approach towards columnar phase forming non-covalently associated aggregates may arise from intermolecular hydrogen bonding[5] between two different individual molecules. For example, associations of 2,6-diacylaminopyridines with complementary uracil derivatives lead to the induction of columnar phases on either a hexagonal[6,7] or a rectangular[8] two-dimensional array. More recently, it was shown that the two-dimensional lattice parameters of a hexagonal columnar phase forming 2,4,6-triarylamino-1,3,5-triazine bearing six peripheral alkoxy substituents[9] can be controlled via molecular recognition in mixtures with two-fold alkoxy substituted benzoic acids[10].

However, individual molecules having the capacity to induce columnar liquid crystalline phases by both, intermolecular hydrogen bonding as well as donor-acceptor interactions, have to our knowledge not been reported so far.

We present here the non-mesomorphic triarylmelamine **1** incorporating three flexible alkoxy side chains. We will, in particular, focus on the thermal behaviour of compound **1** in binary mixtures with 4-octyloxybenzoic acid **2** and with the nitrofluorenone based acceptor derivatives **3** and **4**.

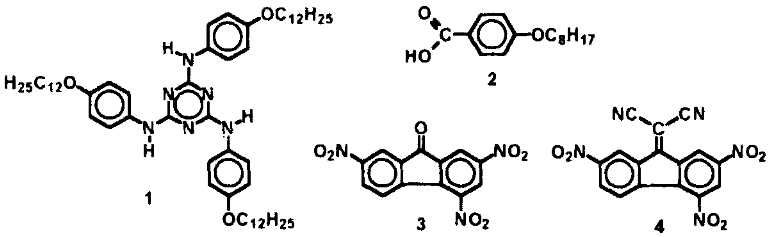

FIGURE 1 Chemical structures of the investigated compounds **1-4**.

MATERIALS AND METHODS

The synthesis of 2,4,6-tris(4-dodecyloxyphenyl-1-amino)-1,3,5-triazine **1** will be presented in detail elsewhere. The 4-octyloxybenzoic acid **2** was obtained according to standard procedures[11]. 2,4,7-Trinitrofluoren-9-one (TNF) **3** and 2,4,7-trinitrofluoren-9-ylidene malodinitrile **4** were commercially available from Ferak and Lancaster, respectively.

Binary mixtures of the melamine **1** and the acid **2** were prepared by dissolving equimolar amounts of the components separately in n-hexane, mixing the solutions and evaporating the solvent. Equimolar mixtures of the triazine **1** with either TNF **3** or the acceptor **4** were obtained according to the same procedure but using dichloromethane as the solvent. All thermal investigations were performed after annealing the samples in the isotropic state and subsequent drying in vacuum.

Optical texture observations were made with an Olympus 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. Calorimetric investigations were carried out with a Netzsch DSC 200. Wide angle X-ray scattering analyses were performed with a Siemens 5000 diffractometer.

RESULTS AND DISCUSSION

The melamine **1** and the alkoxy substituted benzoic acid **2** show complete miscibility at a molar ratio of the components of 1:1. The equimolar mixture **1/2** exhibits an enantiotropic mesophase within the temperature range given in table 1. The X-ray diffractogram of the binary mixture **1/2** shows sharp (100) and (110) reflections in the small angle region (table 2) and a diffuse halo at larger scattering angles which is caused by a liquid-like arrangement of the flexible alkoxy side chains. These scattering characteristics give evidence of a hexagonal columnar disordered (Col_{hd}) mesophase (table 2).

TABLE 1 Phase transition temperatures (°C) of equimolar mixtures of the triazine **1** with the benzoic acid **2** and with the acceptors **3** and **4** determined by DSC on heating at 10 K/min; transition enthalpies (kJ/mol) are given in brackets.

sample	transition temperatures				
1/2	Cr	35.9 (16.26)	Col_{hd}	80.4 (2.68)	I
1/3	Cr	135.1 (20.11)	Col_{rd}	154.9 (3.28)	I
1/4	Cr	98.2 (7.49)	S_A	168.4 (3.25)	I

Cr: crystalline; Col_{hd}: hexagonal columnar disordered; Col_{rd}: rectangular columnar disordered; S_A: smectic A; I: isotropic.

It has to be emphasized that neither the thermal nor the X-ray investigations indicate the appearance of a calamitic phase characteristic for the benzoic acid **2** in its pure state[12], due to a dimerization of the acid. Hence, the association with the aminotriazine **1** completely frustrates the tendency of the aromatic acid to form dimers.

FT-IR spectroscopic investigations confirm that the association of the complementary molecules is related to hydrogen bonding between the amino substituted triazine core and the acid component. Further details will be presented elsewhere.

Taking into account the three hydrogen bonding sites of the melamine **1** it seems rather surprising that the induction of a columnar mesophase is restricted to an equimolar composition of the two components **1** and **2**.

Molecular mechanics simulations (Cerius 2; force field Dreiding 2) reveal that a peripheral attack (side-by-side interaction) of the acid component to the inner functional core region of the aminotriazine **1** gives rise to an anisometric hydrogen bonded aggregate only, if the association process is accomplished by the formation and freezing-in of a non-symmetric conformation of the melamine **1**. It follows that a disc-like central core already originates from the docking of one equivalent of the aromatic acid whereas two molecular recognition sites of the triazine remain uncomplexed due to steric hindrance (figure 2). Thus, the flat shape that arises for dimers of the melamine **1** and the alkoxybenzoic acid **2** may explain the induction of a hexagonal columnar mesophase of the appropriate equimolar mixture **1/2** quite well.

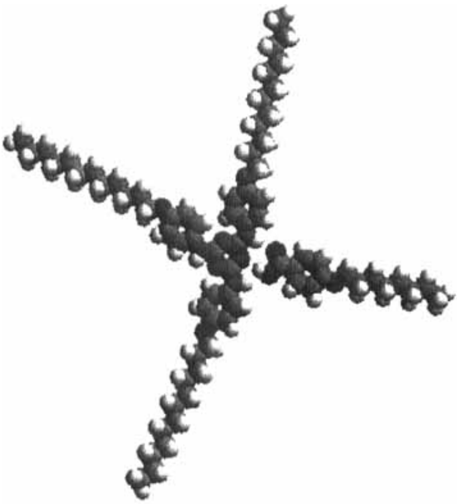

FIGURE 2 Molecular model (Cerius 2; force field Dreiding 2) of the hexagonal columnar phase forming hydrogen bonded complex between the melamine **1** (left) and the carboxylic acid **2** (right).

The intermolecular hydrogen bonding between the melamine **1** and the carboxylic acid **2**, however, does not lead to a columnar mesophase with a periodical intracolumnar ordering. We expected that it might be possible to enhance the intracolumnar order by CT-interactions of compound **1** with the flat but non-mesomorphic electron acceptors **3** and **4**.

Binary mixtures **1/3** and **1/4** exhibit an induced enantiotropic mesophase at an equimolar ratio of the components (Table 1). The X-ray diffraction pattern confirm a columnar structure for the equimolar mixture of the triazine **1** with TNF **3**. The reflections in the small angle region can be indexed as (100), (010) and (200) Bragg reflections on the basis of a two-dimensional rectangular lattice (Table 2). The lattice dimensions amount to a=38.5Å and b=32.7Å. The amorphous halo in the wide angle region indicates an irregular arrangement of the molecules within the parallelly aligned columns. Thus, the binary system **1/3** exhibits a rectangular columnar disordered (Col_{rd}) mesophase.

TABLE 2 Bragg spacings (Å) of the equimolar mixtures of the melamine **1** with the carboxylic acid **2** and the electron acceptors **3** and **4**.

sample	d_{100}	d_{010}	d_{110}	d_{200}	d_{300}	
1b/2	28.3	-	16.4	-	-	a_{hex}=32.7
1b/3	38.5	32.7	-	19.6	-	a=38.5; b=32.7
1b/4	30.9	-	-	16.1	11.0	a=32.2

The induced Col_{rd} phase observed here is not common in so far as, except for a few cases[12,13], the columnar phases formed by binary mixtures of flat electron-rich donor molecules and TNF are of the hexagonal or the nematic columnar type.

The scattering diagram of the equimolar donor-acceptor complex **1/4** displays a set of reflections in the short angle region and a diffuse halo at larger scattering angles as well. It is, however, obvious that a smectic layer structure exists since no mixed reflections were found (Table 2). The layer spacing amounts to a=32.2Å. The halo indicates the presence of only a short range order within the layers. Thus, the X-ray investigations along with the focal-conic fan textures observed by polarizing microscopy reveal that the binary mixture **1/4** exhibits a smectic A mesophase.

The formation of thermotropic smectic mesophases is predominantly caused by a rod-like anisometric shape of the molecules. Taking into account that an intercalated structure with close face-to-face contacts of the donor and the acceptor is strongly preferable we are forced to the conclusion that the induction of a S_A phase originates from a more or less rod-shaped conformation of the aminotriazine **1** which is frozen-in by CT-interactions with the acceptor molecules **4**.

CONCLUSIONS

The central core region of the melamine **1** characterized by a 1,3,5-triazine heterocycle substituted via secondary amino groups with phenyl rings promotes intermolecular hydrogen bonding with the aromatic acid **2** as well as charge-transfer complex formation with the electron acceptors **3** and **4**. The attractive intermolecular interactions between the complementary molecules impose a freezing-in of certain specific anisometric rigid conformations of the melamine **1** giving rise to inductions of columnar as well as smectic liquid crystalline phases.

Acknowledgements

The financial support of the Deutsche Forschungsgemeinschaft and of the Land Brandenburg are kindly acknowledged.

References

[1] H. Bengs, M. Ebert, O. Karthaus, B. Kohne, K. Praefcke, H. Ringsdorf, J.H. Wendorff, and R. Wüstefeld, *Adv. Mater.* **2,** 141 (1990).

[2] M. Ebert, G. Frick, C. Baehr, J.H Wendorff, R. Wüstefeld, and H. Ringsdorf. *Liq. Cryst.* **11,** 293 (1992).

[3] K. Praefcke, and J.D. Holbrey, *J. Incl. Phenom. Mol. Recog. Chem.* **24,** 19 (1996).

[4] D. Janietz, *J. Mater. Chem.* **8,** 265 (1998).
[5] C.M. Paleos, and D. Tsiourvas, *Angew. Chem.* **107,** 1839 (1995).
[6] M.J. Brienne, J. Gabard, J.-M. Lehn, and I. Stibor, *J. Chem. Soc., Chem. Commun.* **1989,** 1868.
[7] C. Fouquey, J.-M. Lehn, and A.-M. Levelut, *Adv. Mater.* **2,** 254 (1990).
[8] J.-M. Lehn, *Makromol. Chem., Macromol. Symp.,* **69,** 1 (1993).
[9] D. Goldmann, D. Janietz, R. Festag, C. Schmidt, and J.H. Wendorff, *Liq. Cryst.* **21,** 619 (1996).
[10] D. Goldmann, R. Dietel, D. Janietz, C. Schmidt, and J.H. Wendorff, *Liq. Cryst.* **24,** 407 (1998).
[11] G.W. Gray, and B. Jones, *J. Chem. Soc.* **1953,** 4179.
[12] D. Demus, and H. Zaschke, *Flüssige Kristalle in Tabellen* (Deutscher Verlag für Grundstoffindustrie, Leipzig, 1973), p. 57.
[13] D. Janietz, R. Festag, C. Schmidt, and J.H. Wendorff, *Lid. Cryst.* **20,** 459 (1996).