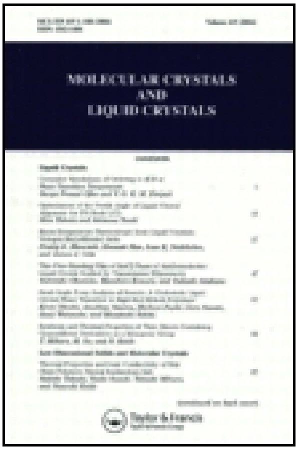

Molecular Crystals and Liquid Crystals

Smectic and Columnar Liquid Crystalline Phases through Charge-Transfer Interactions

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SMECTIC AND COLUMNAR LIQUID CRYSTALLINE PHASES THROUGH CHARGE-TRANSFER INTERACTIONS

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New heterocyclic electron donors based on a 1,3,5-triazine nucleus are presented. Three phenyl rings are grafted to the triazine core either via secondary amino groups or by a direct C,C-linkage and a specific number of decyloxy chains is attached to the molecular periphery. The compounds are non-liquid crystalline in their pure states. Lamellar or columnar mesophases are induced by attractive interactions with electron acceptors.

Keywords: 1,3,5-triazine; mesophase inductions; smectic and columnar phases

INTRODUCTION

It has become apparent that thermotropic mesomorphism is not restricted to form-anisotropic molecules. During the last few years various non-anisometric compounds have been reported to exhibit liquid crystalline

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behaviour. Microphase segregation between incompatible molecular subunits, for example of polar and non-polar regions leads in this case to the formation of lamellar, cylindrical or spheroidal aggregates which organize to smectic, columnar and cubic mesophases [1]. We reported in this context on 2,4,6-triarylamino-1,3,5-triazines substituted with six long peripheral alkoxy chains which exhibit columnar liquid crystalline phases [2] and on hydrogen bonding of the melamines with aromatic carboxylic acids giving rise to the control of the two-dimensional lattice symmetries [3,4].

Mesomorphic structure formation can also arise for non-covalently bonded aggregates formed, for example, by charge transfer (CT) interactions. Thus, doping of electron rich flat aromatic compounds with electron acceptors usually may cause the stabilization as well as the induction of columnar mesophases [5–7]. However, more recently we found six-fold alkoxy substituted triarylmelamines to be the first examples of columnar phase forming electron donors which display an induction of smectic liquid crystalline structures by mixing with nitrofluorenone based acceptors [8].

We report in this contribution the three-fold alkoxy substituted 2,4,6-triarylamino-1,3,5-triazine **4** and the triaryltriazine **8** with six peripheral alkoxy tails but with a direct linkage of the phenyl groups to the triazine nucleus (Scheme 1). We will focus on the synthesis of compounds **4** and **8**, their thermal behaviour in the pure state as well as the structure formation in mixtures with electron deficient counterparts.

EXPERIMENTAL

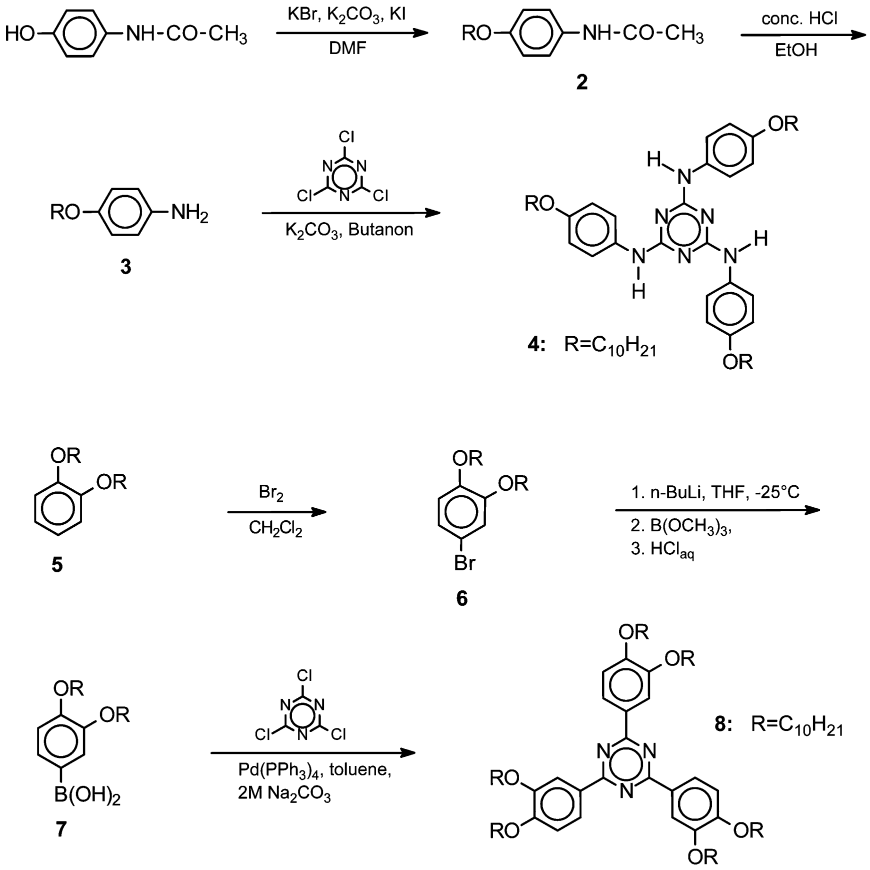
Mixtures of the triarylmelamine **4** and the triaryltriazine **8** with either TNF **9** or the cyano modified acceptor **10** (Scheme 2) were prepared by dissolving the components separately in dichloromethane and combining the solutions. The thermal investigations were performed after evaporating the solvents and drying the residues in vacuum.

Texture observations were made with an Olympus polarizing microscope fitted with a Linkam TMH/S 600 hot stage in conjunction with a Linkam TP 92 control unit. Photo micrographs were obtained with an Olympus OM-4 Ti system camera. Calorimetric investigations were performed with a Netzsch DSC 200. Wide angle X-ray scattering analysis was carried out with a Siemens 5000 diffractometer.

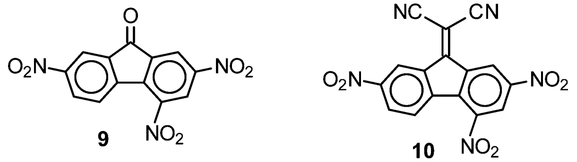
RESULTS AND DISCUSSION

Synthesis

The synthesis of 1,3,5-triazine **4** substituted with three 4-decyloxyphenylamino groups was carried out starting from 4-hydroxyacetanilide.



SCHEME 1 Synthetic routes to the 1,3,5-triazines **4** and **8**.



SCHEME 2 Chemical structure of the nitrofluorenone based electron acceptors **9** and **10**.

Etherification with decylbromide provided the 4-decyloxyacetanilide **2**. N-acetate cleavage of compound **2** with hydrochloric acid and ethanol as the solvent resulted in the aniline **3**. Finally, the alkoxy substituted triarylmelamine **4** was obtained by the reaction of compound **3** with cyanuric chloride in the presence of potassium carbonate.

To prepare the 2,4,6-triaryl-1,3,5-triazine **8**, the 1,2-bis-decyloxybenzene **5** was brominated yielding the dialkoxy substituted bromobenzene compound **6**. Compound **6** was converted into the corresponding boronic acid **7** by reaction of the intermediate lithium organyl with trimethyl borate. By applying conditions we previously reported for the synthesis of 4,6-diphenyl-1,3,5-triazines [9], palladium-catalysed cross-coupling reaction between the phenylboronic acid **7** and cyanuric chloride yielded the triaryltriazine **8**.

Thermal Properties

Each compound **4** and **8** exhibits only a direct transition from the crystalline state to the isotropic liquid (Table 1). It seems that for both triazines **4** and **8** mesomorphic structure formation is suppressed by a disturbed balance of the molecular polar – non-polar relationship.

In case of the melamine **4** the three phenyl substituents are linked to the central heterocyclic triazine ring via secondary amino groups giving rise to a significant polarity of the central molecular region. However, the triphenylmelamine core is substituted with only three non-polar aliphatic chains. Thus, the lipophilic character of the molecular periphery is reduced compared with structurally related columnar phase forming triarylmelamines bearing six lipophilic alkyl chains [2].

TABLE 1 Phase Transition Temperatures (°C) of the Pure 1,3,5-triazines **4** and **8** and of Equimolar Compositions with the Electron Acceptors **9** and **10** (DSC 2nd Heating at 10 K/min); Transition Enthalpies (kJ/mol) in Parenthesis; Monotropic Phase Transitions in Square Brackets

Sample	Transition temperatures				
4	Cr	111.5 (42.12)			I
8	Cr	116.5 (133.2)			I
4/9	Cr	139.1 (20.1)	SmA	154.9 (3.28)	I
8/9	Cr	100.6 (54.2)			I
	Cr	[78.2 (−47.2)]	Col	[86.5 (−3.6)]	I
8/10	Cr	104.6 (24.6)	Col	130.7 (3.3)	I

Cr: crystalline; SmA: smectic A; Col: columnar; I: isotropic.

The reverse situation is valid for the phenyltriazine **8**. Compared with compound **4** the peripheral lipophilicity is enhanced by introducing six long chain alkoxy groups. However, the secondary exocyclic amino groups were omitted and replaced by direct C,C-linkages between the triazine heterocycle and the phenyl substituents. The polarity of the core region is thus reduced.

We expected that the tendency of the triazines **4** and **8** towards liquid crystalline structure formation should be enhanced through interactions with flat electron acceptors such as 2,4,7-trinitrofluoren-9-one (TNF) **9** and 2,4,7-trinitrofluoren-9-ylidene malodinitrile **10** (Scheme 2).

Doping of the triarylamino-1,3,5-triazine **4** with TNF **9** leads to the induction of enantiotropic mesomorphism at an equimolar ratio of the components. Upon cooling from the isotropic state focal-conic fan textures develop (Fig. 1), indicative of the formation of a SmA phase. The X-ray diagram of the equimolar mixture **4**/**9** displays three equidistant reflections in the small angle region ($d_{100} = 28.8$ Å; $d_{200} = 14.7$ Å; $d_{300} = 10.6$ Å) and an amorphous halo at larger scattering angles. The small angle peaks reveal a periodic layer structure along one direction whereas the diffuse scattering in the wide angle region indicates the presence of only a short range order within the layers. The X-ray investigations, thus, confirm the findings from polarizing microscopy that the melamine **4** mixed with the acceptor **9** exhibits a smectic A-type mesophase.

The 1,3,5-triazine **8** forms a monotropic liquid crystalline phase in 1:1 mixtures with TNF **9** on cooling from the isotropic liquid (Table 1).

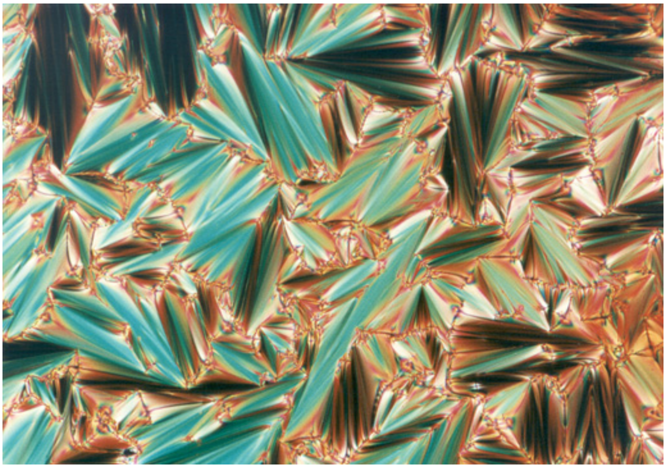


FIGURE 1 Optical texture of the mesophase of the equimolar mixture **4**/**9** between crossed polarizers; 1st cooling ($1\ \mathrm{K\ min^{-1}}$) at 153.8°C. (See COLOR PLATE VIII)

Enantiotropic mesomorphism is found for the equimolar system **8/10**. On cooling from the isotropic phase the growth of domains of digitated stars with hexagonal symmetry is observed by polarizing microscopy for the mixtures **8/9** and **8/10** (Fig. 2). These optical textures are typical for a hexagonal columnar mesophase.

The deep brownish colour that appears by mixing the triazine and the acceptor components clearly indicates a charge-transfer. However, both attractive interactions provided by electron donor-acceptor interactions perpendicular to the planes of the aromatic cores [10,11] and attractive electrostatic quadrupole interactions [12,13] may contribute to the observed mesophase inductions.

In case of the melamine **4** the phenyl rings can rotate around the C-N single bonds and the core region of the compound can adopt different specific conformations. Taking the fact into account that the formation of smectic liquid crystalline phases is predominantly caused by a rod-like anisometric shape of the molecules it seems likely that the smectic mesophase originates from an elongated linear conformation of the triarylmelamine **4** which becomes favoured during interaction with TNF.

One such conformation with an almost flat geometry of the triphenylaminotriazine core is shown in Figure 3a along with a molecular model of TNF **3**, arranged closely face-to-face with the phenyl rings of the heterocyclic donor **4**. Two of the alkoxyphenyl groups of compound **4** are arranged parallel to each other whereas the third one is turned to the opposite direction. Distinct layered polar regions are formed which

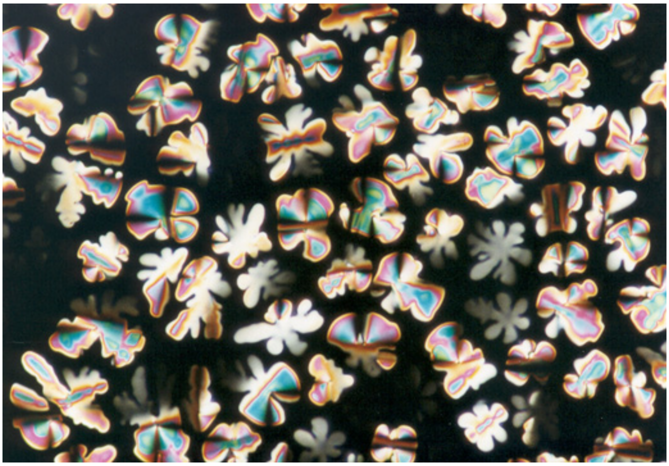


FIGURE 2 Microphotograph of the columnar phase of the mixed system **8/10** between crossed polarizers; 2nd cooling (5 K min^{-1}) at 118.3°C. (See COLOR PLATE IX)

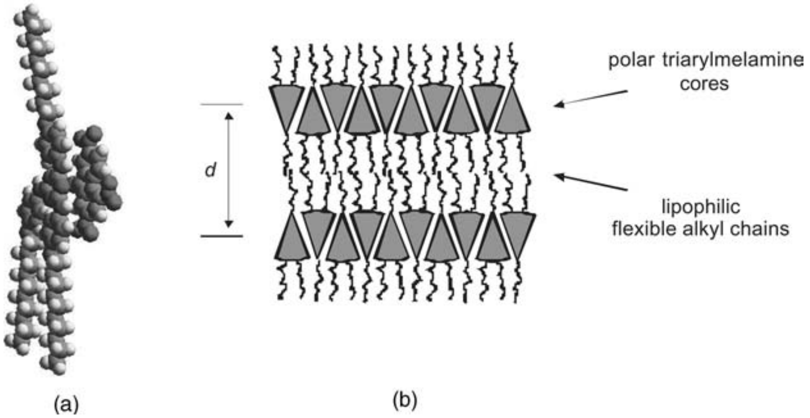


FIGURE 3 a) Fork-like conformation of the melamine **4** (Cerius 2; force field Dreiding 2); b) Structure model for the chemically induced smectic A mesophase of compound **4**.

are separated by the non-polar alkyl chains. The layer spacing determined by X-ray is slightly less than the maximum molecular length for linear conformers of compound **4**. Furthermore, one can imagine, on the average, an antiparallel alignment of the melamine **4**, arranged like a fork, since this gives rise to an optimum of space filling within one layer (Fig. 3b).

Compared with the triarylamino-1,3,5-triazine **4** the conformational mobility of the core region is significantly reduced for the triaryltriazine **8**. In particular, the C,C-linkage between the N-heterocycle and the phenyl moieties prevents conformational changes of the central core region from a discoid shape to a more rod-like molecular geometry. Interactions with the electron acceptors perpendicular to the aromatic rings probably result in a flattening of the central triphenyltriazine part of compound **8**. The association with the polar nitrofluorenone acceptors gives rise to a stiffening of the molecular core and facilitates microphase separation. Thus, microsegregation along with a flat disc-like shape that becomes favoured for the triazine may explain the hexagonal columnar mesophases of the equimolar mixtures **8/9** and **8/10** quite well.

CONCLUSIONS

The 1,3,5-triazines discussed in this contribution combine polar and non-polar segments with the conformational mobility of the central (hetero)aromatic part of the molecules. Depending on the connection of the three phenyl groups with the central 1,3,5-triazine nucleus either rod-like or disc-shaped molecular conformations become favoured by interaction with nitrofluorenone based acceptors. Associations with the electron acceptors, furthermore, improve the gradient of the molecular polarity. This combination of chemically induced anisometry of the phenyl substituted heterocyclic units and the segregation effects to distinct polar and non-polar molecular regions facilitates the induction of lamellar and columnar supermolecular structures.

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