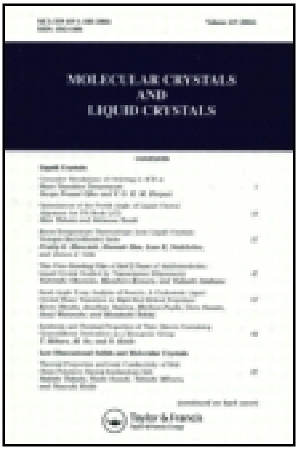

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Trisubstituted s-Triazine Derived from Cyanated Schiff-Base

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To cite this article: Ying-Hung Wang , Yen-Long Hong , Fu-Shan Yen & Jin-Long Hong (1996): Trisubstituted s-Triazine Derived from Cyanated Schiff-Base, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 287:1, 109-113

To link to this article: http://dx.doi.org/10.1080/10587259608038748

Mol. Cryst. Liq. Cryst., 1996, Vol. 287, pp. 109–113
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Trisubstituted *s*-Triazine Derived from Cyanated Schiff-Base

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(Received in final form March 9, 1995)

Liquid crystalline Schiff-base (*M*) with a cyanate terminal group was prepared and characterized. Subsequent cyclotrimerization of compound *M* brings together three cyanate terminals to form a *s*-triazine ring and produces a large molecule, *T*, with three-fold symmetry. The mesophase transition temperatures of *T* are higher than *M*. The *s*-trisine ring serves appropriately as central core of the mesogenic trimer, *T*.

Keywords: Schiff-base, cyanate, cyclotrimerization, liquid crystal.

INTRODUCTION

One of the interesting features of aromatic cyanates is their capability to cyclotrimerize and form *s*-triazine ring, a reaction (so called "cyclotrimerization") widely used in industry.[1,2] This interconnected *s*-triazine ring can be produced by the reaction of phenols with cyanuric chloride under alkaline condition, also. Therefore, Huang et al.[3] used this reaction to produce a triazine-based liquid crystal (LC), 2,4,6-tris[4-alkoxyanilidene)benzylidene]-1,3,5-triazine (AOB in Fig. 1). Nevertheless, a later report from Barclay *et al.*[4] suggested that 2,4,6-tris[4-(4-butoxybenzoyl)oxy] phenyl)-oxy]phenyl-1,3,5-triazine (BOP in Fig. 1), another triazine-based compound synthesized from cyclotrimerization of the corresponding aromatic cyanate, is not a liquid crystalline material.

Interestingly, another later result from Mormann[5] indicated the essential role of the central ester linkages since the isomeric 2,4,6-tris[4-(4-butoxyphenoxy)carbonyl) phenoxy-1,3,5-triazine (BPP in Fig. 1) turned out to be LC. It is therefore essential to clarify the role of *s*-triazine ring as an efficient mesogenic core.

In this communication, a LC Schiff-base with one cyanate terminal group was synthesized and characterized. This monocyanate can be heated to cyclotrimerize and the corresponding product with its central *s*-triazine ring connected by three Schiff-bases also possesses mesomorphic properties. The role of *s*-triazine ring will be briefly discussed.

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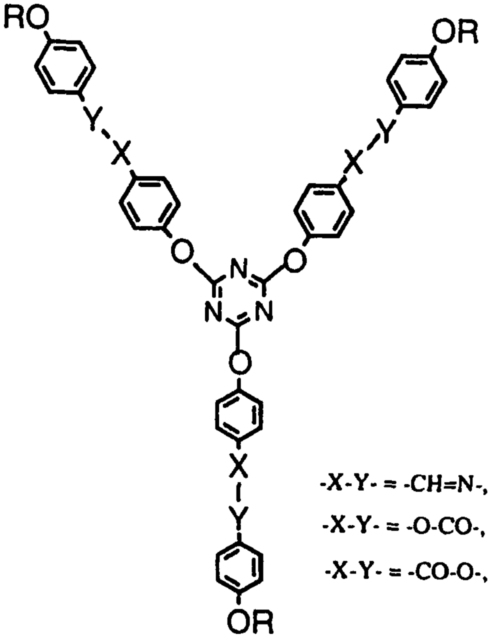


-X-Y- = -CH=N-, R = C_6H_{13} or C_8H_{17}; **AOB**

-X-Y- = -O-CO-, R = C_4H_9; **BOP**

-X-Y- = -CO-O-, R = C_4H_9; **BPP**

FIGURE 1 Chemical structures of different triazine-based compounds.

EXPERIMENTAL

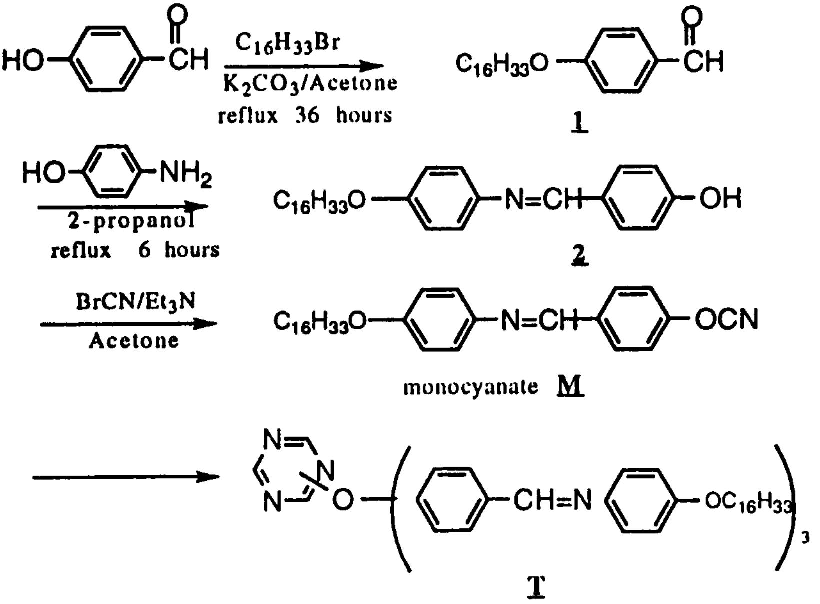
Synthesis

The liquid cyrstalline Schiff-base, *M*, was synthesized acccording to the procedures described in the Scheme 1. Compounds 1 and 2 were synthesized by a similar way described previously.[6]

Cyanation of compound 2 followed Grigat's[1] procedures. Crude product of M was purified by recrystallizations from isopropanol once and acetone twice. ^{1}H NMR of M (300 MHz, THF-d_8): δ8.52 (s, 1H), 8.29 (s, 1H), 7.93–7.90 (d, J=9.3 Hz, 2H), 7.22–7.19 (d, J=7.8 Hz, 2H), 7.08–7.05 (d, J = 8.4 Hz, 2H), 6.86–6.83 (d, J = 7.5 Hz, 2H), 4.16–4.11 (t, J = 6.5 Hz, 2H) (1.93–0.98 (m, 31H).

Cyclotrimerization of M

Monocyanated *M* was heated isothermally at 100 °C for 20 min under nitrogen atmosphere to give the crude product of *T*. The resulting solid was further recrystallized from acetone to give the final product,2,4,6-tris[4-(4-hexadecanoxybenzylidene)anilidene]-1,3,5-triazine (*T*). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.38 (s, 3H), 7.83–7.78 (d, J = 8.8 Hz, 6H), 7.16–7.11 (d, J = 6.9 Hz, 6H), 6.97–6.93 (d, J = 8.5 Hz, 6H), 6.85–6.81 (d, J = 8.8 Hz, 6H), 4,04–3.97 (t, 6H), 1.87–0.81 (m, 93H) MS: m/e 1388 (M^+).



SCHEME 1 Synthesis of monocyanate, *M*, and its cyclotrimerization.

RESULTS AND DISCUSSION

Polarized optical microscopy (POM) was preliminarily used to characterize the mesophase transitions of *M* (see Scheme 1). Under polarizing light, *M* was heated (heating rate = 30 °C/min) to show an anisotropic texture emerged at 70 °C, which immediately transformed into birefrigent droplets and finally to isotropic liquid at 93 °C. Thermogram from differential scanning calorimetry (DSC) study exhibited a low-temperature broad endotherm corresponding to the overlapped melting (T_m) and clearing transitions (T_c), and a high-temperature cyclotrimerization exotherm. Further infrared study indicates melting of *M* actually accompanied by certain degree of cyclotrimerization, which inhibits an unambiguous determination of T_m and T_c. Figure 2 shows FTIR spectra recorded at different temperatures. The gradual disappearance of nitrile (—C≡N) stretching absorptions ranged from 2200–2300 cm^{-1} and the appearance of *s*-triazine stretching absorption at 1370 cm^{-1} suggest cyclotrimerization of *M* actually proceeds easily in its mesomorphic state. The other *s*-triazine stretching absorption at 1570 cm^{-1} is overlapped with the imine (—CH=N—) stretch ing and cannot be resolved well. In reality, sample was further heated at 100 °C for 2 min. The pure trimerized product, 2,4,6-tris[4-(4-hexadecanoxybenzylidene)anilidene]-1,3,5-triazine (*T* in Scheme. 1) was obtained by recrystallization of the crude solid from acetone.

The trimerized *T* showed a Schlieren texture (see Figure 3) in the temperature ranges of 118 to 148 °C as inspected by POM. The rapid crystallization of *T* upon cooling can be prohibited by directly quenching it in liquid N_2 from the mesomorphic state. The corresponding DSC thermogram suggests this quenched sample exhibits a *Tg* at

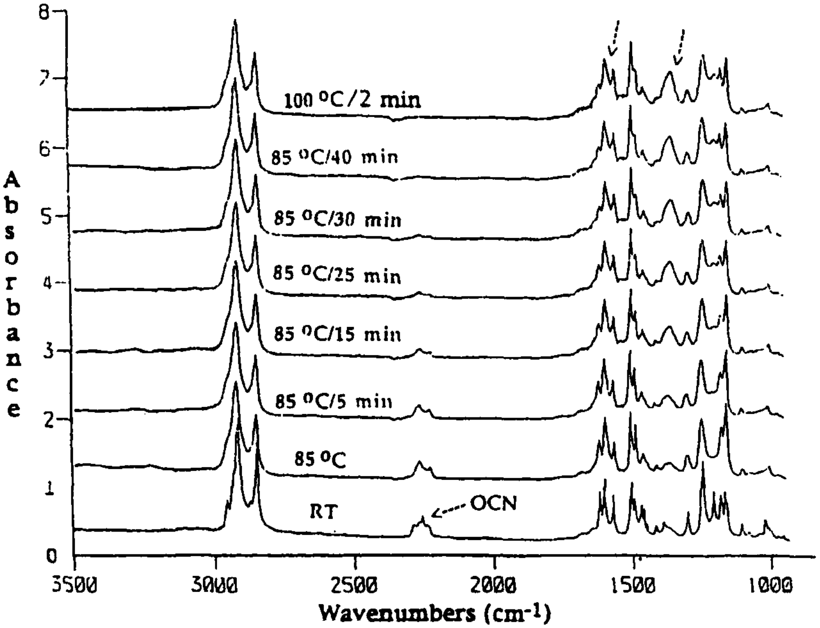


FIGURE 2 Infrared spectra of monocyanate, *M*, at different temperatures.

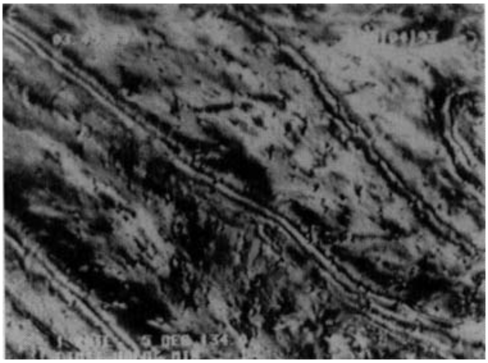


FIGURE 3 Schlieren texture of *T* (magnification = 200).

around 41 °C. In addition to the possible contribution from molecular weight difference, the higher mesophase transition temperatures of *T* than *M* may be due to the steric reason. The terminal C≡N in *M* adapted a non-linear geometry to the neighboring phenylene group,[7] leading to the increase of the molecular width and therefore, an unstable mesophase. This unfavorable factor can be largely alleviated by transforming the non-linear cyanates into the planar *s*-triazine ring during cyclotrimerization. This basically contributes to a stable mesophase in *T*.

Recently, Mahlstedt[8] reported that compounds with central *s*-triazine ring connected by three non-mesogenic 2,4-dialkoxyphenoxyl substituents exhibit mesomorphism at low temperatures. This may suggest that triazine-based materials are discogenes. A reasonable rigidity of the three ether linkages betweeen the three substituents and central *s*-triazine may be expected.

CONCLUSION

Cyclotrimerization of liquid crystalline *M* proceeded in its mesomorphic state and produces trimerized *T*. Compound *T* exhibited a LC texture in the temperature ranges of 118 to 148 °C.

Acknowledgment

We appreciate the financial support of the National Science Council, R.O.C., under contract no. NSC 80-0405-E-110-05.

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