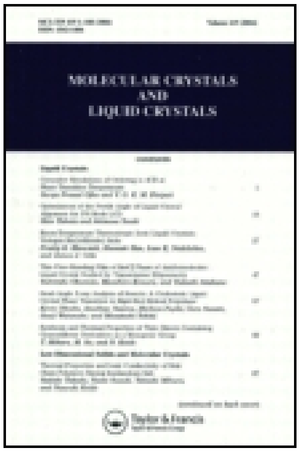


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

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

Tri-substituted s-Triazines as Mesogenic Cores

W.-J. Lo [a], Y.-L. Hong [a], R.-H. Lin [b] & Jin-Long Hong [b]

[a] Department of Chemistry, National Sun Yat-Sen University, Kaohsiung, Taiwan, 80424, R.O.C

[b] Institute of Materials Science and Engineering, National Sun Yat-Sen University, Kaohsiung, Taiwan, 80424, R.O.C

To cite this article: W.-J. Lo, Y.-L. Hong, R.-H. Lin & Jin-Long Hong (1997): Tri-substituted s-Triazines as Mesogenic Cores, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 308:1, 133-146

To link to this article: http://dx.doi.org/10.1080/10587259708045101

Mol. Cryst. Liq. Cryst., 1997, Vol. 308, pp. 133–146
Reprints available directly from the publisher
Photocopying permitted by license only

Tri-substituted *s*-Triazines as Mesogenic Cores

WEN-JIUNN LO[a], YEN-LONG HONG[a], RONG-HSEIH LIN[b]
and JIN-LONG HONG[b,]*

[a]*Department of Chemistry;* [b]*Institute of Materials Science and Engineering,*
National Sun Yat-Sen University, Kaohsiung, Taiwan, 80424 R.O.C

(Received 12 March 1996)

Two series of equivalently- and inequivalently-tri-substituted *s*-triazines (as ESTs and ISTs, respectively) were synthesized and characterized in this study. More than one mesogenic biphenyl substituent were required to display mesomorphic properties, and two or three biphenyl substituents resulted in liquid crystalline textures under polarizing light. The mesophase transition temperatures for both IST and EST series are quite close despite their molecular weight difference. With longer sidechains, *s*-triazine for IST series formed a columnar hexagonal disordered mesophase (D_{hd}); while for the analogous compound in EST series, a perfectly aligned layered structure was found to be co-existed with the D_{hd} phase. With shorter sidechains, the *s*-triazines exhibited nematic mesomorphism.

Keywords: Tri-substituted *s*-triazine; discogen; columnar hexagonal mesophase; perfectly aligned layered sturcture

INTRODUCTION

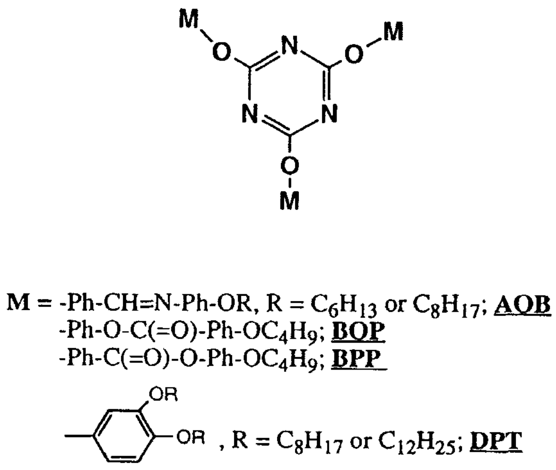
Since the first recognition of benzene hexa-alkanoate (BH) as discotic liquid crystal in 1977 by Chandrasekhar [1], several systems with similar hexa-substituted benzene cores had been prepared and characterized [2, 3]. These systems, all resembling BH, possess a central benzene ring connected to six aliphatic or aromatic substituents through ether or ester linkages and principally behaved as discogens. These systems benefit from synthetic and

---

*To whom correspondence should be addressed.

structural characteristics and offered opportunity to understand discotic mesophases. Tri-substituted systems are of theoretical interest to determine the effect of incomplete filling of the space around the central core of a tri-substituted system. Therefore, tri-substituted central cores [4, 5, 6, 7, 8] had been long sought for to compare with the hexa-substituted cores. There are three simple choices for the central core groups. They are benzene [4–7], cyclohexane [7], and *s*-triazine [8, 9, 10, 11, 12, 13]. More thorough study has been performed on the former two systems, however in certain cases [6, 7], the involved phases have yet to be identified. The last *s*-triazine system is interesting, not only because of its unique structural features but also, the simplicity and versatility of the synthetic approach for the formation of the *s*-triazine ring.

Exploration of *s*-triazine as the central core was previously examined [9]. Studies on mixtures predicted the potential of triphenyl-*s*-triazine to behave as a mesogen; however, Lattermann's study of several tris-(dialkylamine)-*s*-triazines [8] did not yield any mesomorphism. Nevertheless, several recent investigations have proved that *s*-triazine, can indeed serve as central core of a mesogenic unit. The central *s*-triazine can be be produced either by cyclotrimerization of an aromatic cyanate [10] or by condensation of phenols with cyanuric chloride under alkaline conditions [11, 12]. The first example was described by Huang *et al.* [13] where in condensation produced a triazine-based liquid crystal, 2, 4, 6,-tris[4-alkoxyanilidene)benzylidene]-1, 3, 5-triazine (AOB in Fig. 1). A later report from Barclay *et al.* [14] indicated that 2, 4, 6-tris{[4-(4-butoxybenzoyl)oxy]phenoxy}-1, 3, 5-triazine (BOP in Fig. 1), another triazine-based compound derived from cyclotrimerization of a corresponding



M = -Ph-CH=N-Ph-OR, R = C_6H_{13} or C_8H_{17}; AOB
-Ph-O-C(=O)-Ph-OC_4H_9; BOP
-Ph-C(=O)-O-Ph-OC_4H_9; BPP
, R = C_8H_{17} or $C_{12}H_{25}$; DPT

FIGURE 1 Chemical structures of different triazine-based compounds.

aromatic cyanate, did not exhibit mesomorphic properties. More recently, Mormann *et al.* [15] suggested that ester linkages are very important since the isomeric 2,4,6-tris{[4-(4-butoxyphenoxy)carbonyl]phenoxy}-1,3,5-triazine (BPP in Fig. 1) is a liquid crystal. Additively, Mahlstedt [16] reported that compounds with central *s*-triazine connected by three non-mesogenic, 3,4-dialkoxyphenoxyl groups (DPT in Fig. 1) exhibited mesomorphism at low temperatures. The compounds in later series, compared with the other series mentioned above, clearly distinguish themselves as discogens since traditional mesogenic units were not used in this case. In summary, we suggest that *s*-triazine ring can serve as a central core of a liquid crystalline (lc) materials, but its suitability is greatly influenced by the substituents.

In this manuscript, the syntheses of six compounds with a central *s*-triazine structure are described (Scheme 1). Condensation of various phenols and cyanuric chloride produced *s*-triazines with three equivalent (referred to as equivalently-substituted *s*-triazines, ESTs) or inequivalent (inequivalently-substituted *s*-triazins, ISTs) substituents can be successfully prepared. In addition to this basic difference, substituents of either non-mesogenic (i.e. phenoxy) or mesogenic (i.e. biphenylene) units were incorporated with two different aliphatic sidechains were investigated in this study to elucidate the effect of substituents on the mesomorphism.

EXPERIMENTAL

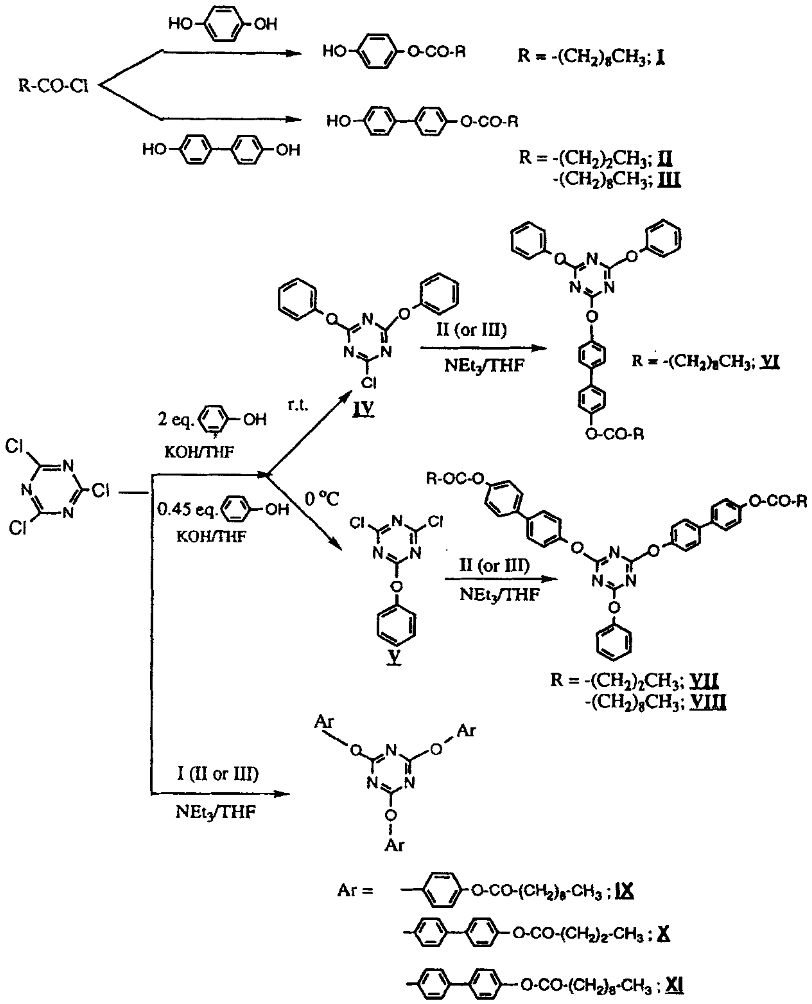
Materials and Instrumentation

All solvent purifications were performed under nitrogen atmosphere. Tetrahydrofuran was distilled from its mixture with sodium and benzophenone. Acetone was distilled after dehydration with phosphorous pentaoxide. Cyanuric chloride was purified by recrystallization from carbon tetrachloride.

^{1}H NMR spectra were recorded with a Varian Gemini-200 MHz model with tetramethylsilane as an internal standard. Low and high resolution mass spectra (LRMS and HRMS) were operated with a Hitachi M-52 and a Jeol JMS-HX 110 models, respectively. Infrared spectra were recorded using a Bio rad FTS-40 Fourier-transform infrared spectrometer. Compound identifications were performed with KBr pellets for solid samples and CaF_2 pellets for liquid samples. Mesophase transition temperatures were determined from a Perkin-Elmer DSC-7 differential scanning calorimeter connected to the thermal analysis data station. Calibration of the calorimeter was conducted for each heating rate using an indium standard. The textures of liquid crystals was observed with a Nikon E-100-microscope. A Siemens diffraktometer D 5000 model was used to obtain the X-ray diffraction patterns. The system was evacuated to a pressure of 10^{-5} torr prior to heat to the various temperatures.

Synthesis

General synthesis steps are briefly illustrated in Scheme 1. Detailed synthesis procedures for representative steps were give below.



SCHEME 1 Syntheses of different trisubstituted *s*-triazines.

General Procedures for Syntheses of 4-alkanoyloxy phenols, I, II and III

Diphenol (hydroquinone or biphenol, 0.072 mol) in 100 ml of acetone was stirred thoroughly with triethylamine (0.024 mol) for 10 min under nitrogen atmosphere (for preparation of I, $Na_2S_2O_4$ (0.04 g) was added as antioxidant). To the above mixture, alkanoyl chlorides (*n*-butyryl or *n*-decanoyl chloride; 0.019 mol) were slowly added dropwise. Reaction was continued for more than 4 hrs at room temperature. The solution was concentrated and 100 ml of chloroform was added to produce a viscous mixture. The solution was further washed with aq. NaCl. The organic layer was separated and dried over magnesium sulfate, filtered and the solvent was removed from the filtrate. The crude products were further purified by column chromatography (compound I and II were eluted with ethyl acetate/hexane 1:2 and 2:5 v/v, respectively; while chloroform was used for III) to give final products in yields ranging from 74 to 82%. Representative analytical data of compound III are given below. ^1H NMR (200 MHz, $CDCl_3$): δ 725(d, $J =$ 8.6 Hz, 2H, aromatic H), 7.40(d, $J = 8.4$ Hz, 2 H, aromatic H), 7.12 (d, $J = 8.2$ Hz, 2H, aromatic H), 6.84 (d, $J = 8.6$ Hz, 2H, aromatic H), 5.25(s, 1 H, -O$\underline{H}$), 2.50(t, $J = 7.4$ Hz, 2 H, -C$\underline{H}_2$-COO-), 1.85 – 1.75 (m, 2 H), 1.50–1.32 (m, 12 H), 0.77(t, $J = 5.3$ Hz, 3 H, C$\underline{H}_3$). IR($CHCl_3$, cm^{-1}): 3391(-OH), 1738(-COOAr). LRMS(EI): m/e 340(M^+). m.p. 130–132°C. Elemental analysis (%): expt. C(77.56), H(8.28); calcd. C(77.60), H(8.29).

General Procedures for Reactions Between Phenol and Cyanuric Chloride to Yield Compounds IV and V

To a nitrogen-blanketed mixture of cyanuric chloride (29.5 mmol), potassium hydroxide (for preparation of V, 0.8 g; while for IV, 3.31 g of KOH was used) in 100 ml of THF, diphenol (13.2 mmol for V, 59 mmol for IV) was slowly added dropwise. For the preparation of V, the reaction mixture was stirred in an ice-bath, instead of room temperature for IV, for 6 hrs. Removal of the THF and the addition of chloroform gave a solution, which was washed with aq. NaCl. The organic layer was dried over magnesium sulfate, filtered, and the solvent was removed from the filtrate. The crude products were purified by column chromatography with chloroform/hexane (1:2 v/v) as eluent to give V in 69% and IV in 80% yield. Representative analytical data of compound V are given below. ^1H NMR (200 MHz, $CDCl_3$): δ 7.53 – 7.10(m, 5 H, aromatic H) IR ($CHCl_3$, cm^{-1}): 1591(—C=N—stretch), 1513(aromatic stretch). HRMS (EI): Expt. m/e 240.9824; calcd. m/e 240.9810. m.p. 112–114°C.

General Procedures for the Syntheses of Tri-Substituted s-Triazines, VI, VII, VIII, IX, X and XI

To a nitrogen-blanketed mixture of 4-alkanoyloxyl phenols (compounds I, II and III, 2.73 mmol) and triethylamine (2.73 mmol) in THF, stoichiometric amounts of cyanuric chloride (or IV or V) was slowly added dropwise. The reaction mixtures were stirred at room temperature for 5 hrs, and the solution was concentrated. To the resulting viscous mixture, 100 ml of chloroform was added and the resulting solution was washed with aq. NaCl. The organic layer was dried over magnesium sulfate, filtered and the solvent was removed from the filtrate. With the exception of X, the other curde products (i.e. VI, VII, VIII, IX and XI) were recrystallized from ethyl acetate to give the final products. The crude product of X was recrystallization from a mixture of ethyl acetate and chloroform. Representative analytical data of compounds XI were given below. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.38(t, $J = 6.7$ Hz, 12 H, aromatic H), 7.03(dd, $J = 8.4$ Hz, 12 H, aromatic H), 2.61(t, $J = 7.6$ Hz, 6 H, —O—CO—C$\underline{H}_2$), 1.75 - 1.55(m, 6 H), 1.42 - 1.12(m, 36 H), 0.92(t, $J = 6.1$ Hz, 9 H, —C$\underline{H}_3$). IR($CHCl_3$, cm^{-1}): 1757(—COOAr), 1573(—C=N—stretch). LRMS (FAB): m/e 1096(MH$^+$); HRMS(FAB): Expt. m/e 1096.5990; calcd. m/e 1095.5952. Elemental analysis (%): expt. C(75.72), H(7.47), N(3.94); calcd. C(75.50), H(7.45), N(3.83).

RESULTS AND DISCUSSION

The syntheses of the tri-substituted *s*-triazine were performed according to the procedures described in Scheme 1. The alkanoyloxy terminals (—O—CO—R, R = —$(CH_2)_2CH_3$ or —$(CH_2)_8CH_3$) were introduced by reaction of phenols (hydroquinone or biphenol) with the corresponding alkanoyl chlorides. To synthesize the inequivalently-substituted *s*-triazines (IST's, such as compounds VI, VII, and VIII), mono- or di-phenoxy substituted *s*-triazines (as compounds V and IV) were first prepared. By lowering the molar ratio of phenol to cyanuric chloride and by conducting the reaction at slightly lower temperatures, mono-substituted *s*-triazine V, instead of di-substituted IV, was obtained as the major product. Lowering reaction temperatures decreased the yield of the di-substituted products, a phenomenon described previously [12]. Due to the *e*-donating characteristics of the phenoxy group, the monophenoxy substituted *s*-triazine (as V) possesses lower reactivity towards the phenolic nucleophile as compared with cyanuric chloride. Hence the addition of the second phenoxy group is slower than the first. Higher temperatures are required for the second addition.

Further preparations of ISTs or equivalently-substituted *s*-triazines (ESTs, such as compounds IX, X and XI) were attempted by similar substitution reactions with different phenols (I, II and III) and cyanuric chlorides. However, special care was needed since the use of KOH can also hydrolyze the esters in compounds I, II and III. Therefore, triethylamine was successfully employed in reactions involving ester groups.

Biphenyl moiety was used in this study as the prinicple mesogenic unit. We concluded that use of a mesogenic biphenyl moiety is essential to introduce liquid crystalline (lc) properties. Compounds VI and IX, which have only one or no biphenyl group about the central *s*-triazine, were found to be non-mesogenic by inspection with a polarized optical microscope (POM). In contrast, compounds with two or three biphenyl substituents (compounds VII, VIII, X and XI) showed typical lc textures by inspection with a polarizing microscope. As shown in Figure 2, compound XI displays a typical mosaic texture, indicative of a smectic mesomorphism. This is different from compound X, which exhibited a nematic schlieren texture under polarizing light. This trend of decreased mesophase order with decreasing sidechain length was also observed in comparison of VIII with VII. The mesophase stability is principally governed by the length of the aliphatic sidechain connected to biphenyl moiety. Selected DSC thermograms of compounds X and XI were shown in Figure 3. Use of butanoyloxy sidechain in compound X resulted in a narrow mesophase range in the two inseparable endotherms shown in Figure 3b. Conversely, the long

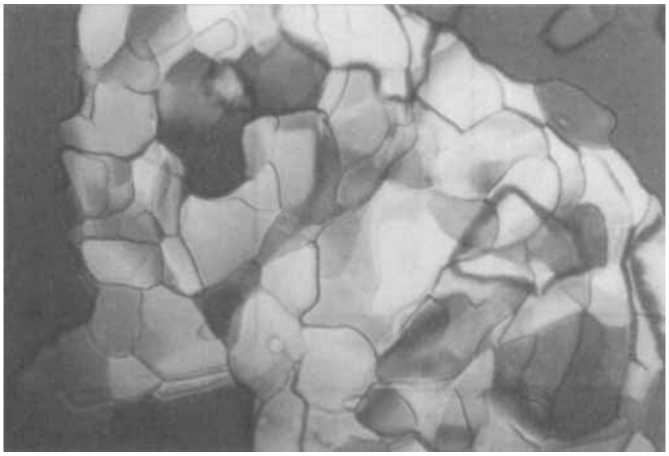


FIGURE 2 Mosaic texture of compound XI at 168°C (× 50, λ plate). (See Color Plate VII).

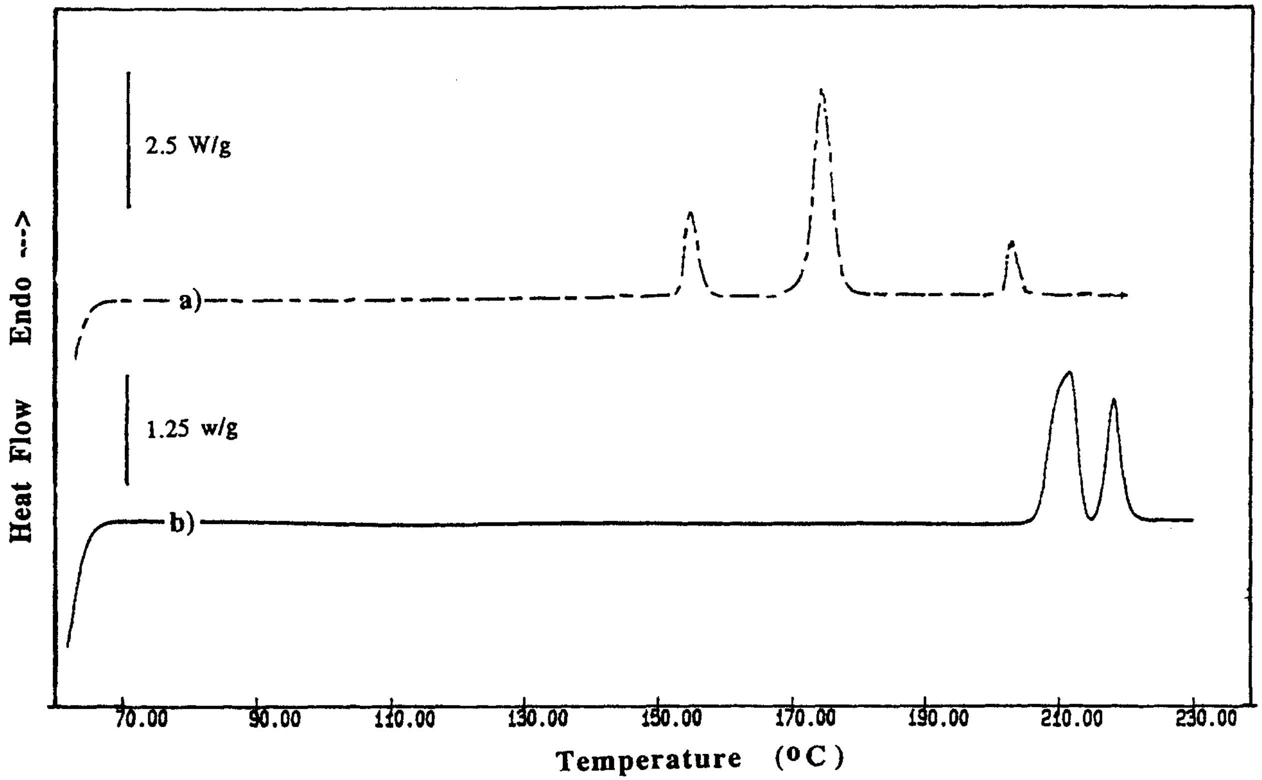


FIGURE 3 DSC thermograms obtained by scanning a) compound XI and b) X at a heating rate of 20°C/min.

decanoyloxy sidechain in compound XI enhanced the mesophase to a range to almost 30°C (Fig. 3a, the first endotherm is attributed to a solid–solid transition). The same trend is observed by comparison of the thermograms for compounds VII and VIII.

A summary of the DSC scans for all the compounds is given in Table I. The relative mesophase stability can be evaluated from the enthalpy (ΔH_i) and entropy (ΔS_i) changes during isotropic melting according to Dewar's and Griffin's [17] study on different esters. Isotropic melting temperatures (T_i's) for compounds XI and VIII are quite close despite their molecular weight difference. Compound XI has higher ΔH_i than VIII; but this high ΔH_i is counterbalanced by its high value of ΔS_i (thermodynamically, T_i is determined by $\Delta H_i/\Delta S_i$), resulting in the comparatively similar values of T_is' for both compounds. In the isotropic state, compounds XI and VIII are situated in the same random state. In the lc phase, compound XI, in considering its more symmetrical chemical structure, is supposed to have a more ordered state than VIII does, resulting in a lower entropy of XI as compared with VIII in their corresponding lc states. Thus, a higher entropy change in passing from the lc to the isotropic liquid state is expected for XI.

The XRD patterns of compound XI at various temperatures is shown in Figure 4. The changes in the pattern between 27 and 120°C may be attributed to the solid–solid transition which was observed in the DSC thermogram (cf Fig. 3a). Further heating resulted in the broadening of

TABLE I Transition temperatures and enthalpies for tri-substituted s-triazines

Compound	T_k[a] (ΔH[d]; ΔS[e])	T_m[b] (ΔH[d]; ΔS[e])	T_i[c] (ΔH[d]; ΔS[e])	*LC phase* *(Texture)*
VII	–	198	208	Nematic
		(4.2; 8.9)	(0.5; 1.0)	(Schlieren)
VIII	152	171	200	Smectic
	(1.3; 3.0)	(5.7; 12.8)	(1.0; 2.1)	(fan-shaped)
VI	–	–	138	Not LC
			(5.6; 13.6)	
IX	–	–	144	Not LC
			(9.2; 22.0)	
X	–	212	218	Nematic
		(4.7; 9.9)	(2.1; 4.4)	(Schlieren)
XI	154	174	202	Smectic
	(2.9; 6.7)	(10.4; 23.2)	(1.6; 3.3)	(Mosaic)

[a] Solid–Solid transition temperature (°C). [b] Melting temperature, temperature (°C) from solid to liquid crystal. [c] Isotropic melting temperature, temperature (°C) from liquid crystal to isotropic liquid. [d] Heat of transition (kcal/mol). [e] Entropy of transition (cal/mol. K).

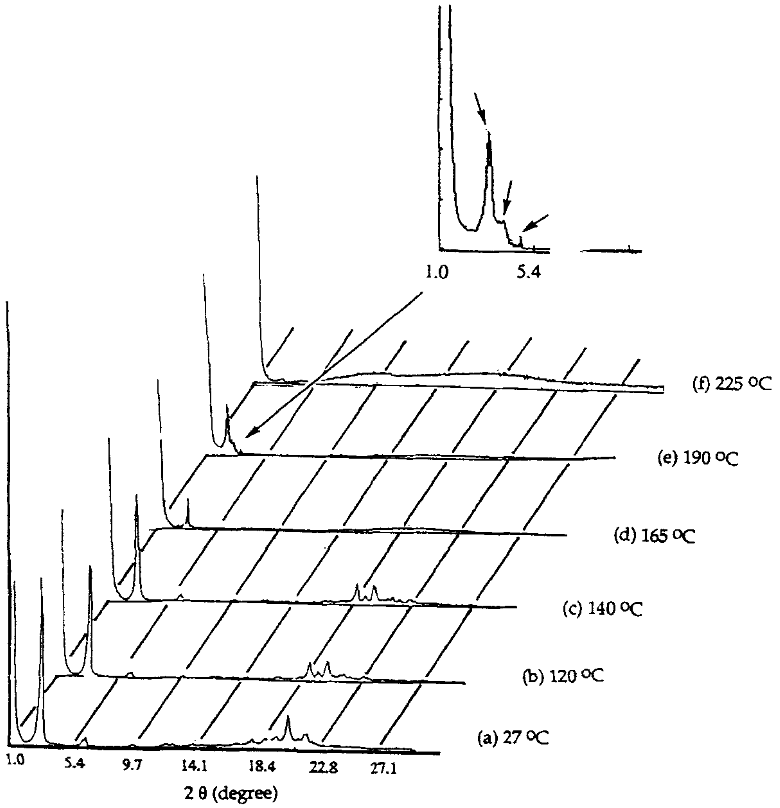


FIGURE 4 X-ray diffraction pattern of compound XI taken at different temperatures. The picture shown on the top is the enlarged portions for the low angle region, in which the arrows, from left to right, indicate diffraction peaks at $2\theta = 2.51, 2.95$ and $3.49°$, respectively.

the peaks in the range of $2\theta = 5$ to $27°$. In addition, the peaks in the low angle region gained intensity as sample was heated from 165 to 190°C. This low angle peak became diffuse as temperature was raised to 225°C, indicating the isotropization of the sample. XRD investigation on compound VIII was also performed and the results for both samples were summarized in Table II. The basic diffraction peaks for both compounds are approximately the same except one extra tiny peak at $2\theta = 3.48°$ is observed for compound XI. From the following discussion, two mesophases are responsible for the diffraction patterns of compound XI.

Except the peak at $2\theta = 3.48°$ for compound XI, all the peaks summarized in Table II can be correlated with a columnar hexagonal disordered (D_{hd}) structure as depicted in Figure 5. The experimental results are compared with the theoretical values (simulated from CSC Chem 3D) in

TABLE II XRD data from compounds VIII and XI at their corresponding mesophases

Compounds	*Temperature* (°C)	2θ (*degree*)	*d-spacing* (Å)
VIII	180	2.59	34.1
		3.03	29.1
		19.13	4.6 (br.)[a]
XI	190	2.51	35.2
		2.95	30.0
		3.49	25.3
		19.39	4.6 (br.)[a]

[a] Broad peak, corresponding to intermolecular spacing between discs.

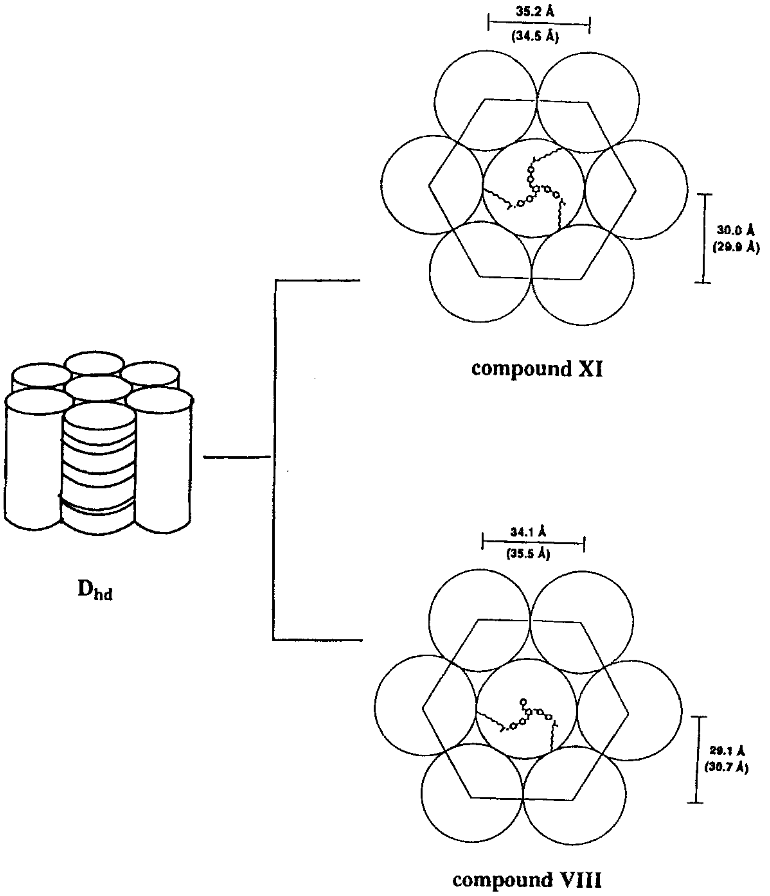


FIGURE 5 The columnar hexagonal structures of compounds a) XI and b) VIII (the numbers in the paranthesess are the results from computer simulation).

parentheses. The related *d*-spacing for $2\theta = 2.51^\circ$ (or 2.59°) is correlated with the disc's diameter ($2r$) while the diffraction around $2\theta = 3^\circ$ corresponds to a spacing of $\sqrt{3}\,r$. The broad peaks centered at $2\theta \sim 19^\circ$ observed in the wide angle region of XRD patterns for both samples indicate the disordered nature of the intermolecular packing within a column. For compound XI, the extra peak at $2\theta = 3.48^\circ$ is related to a parallel, smectic-like layered structure shown in Figure 6. Barclay *et al.* [14] had previously prepared an anisotropic *s*-triazine rigid-rod network by polycyclotrimerization of an aromatic dicyanate

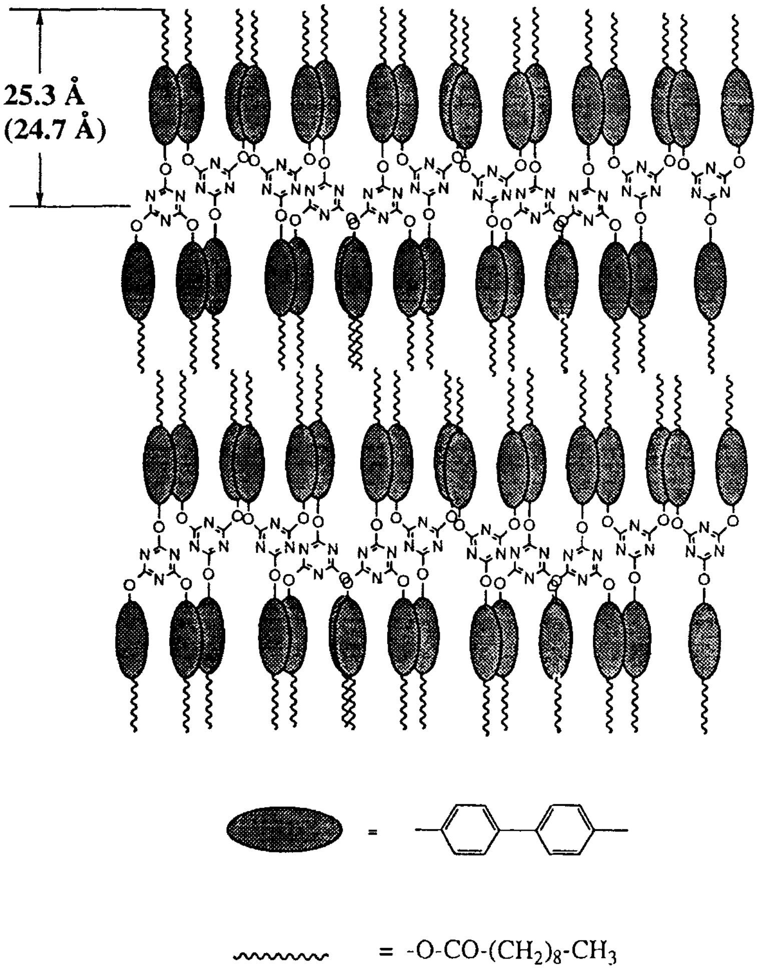


FIGURE 6 The proposed smectic-like layered structure (the number in the paranthesess is the result from computer simulation) co-existed with D_{hd} phase for compound XI.

in the presence of strong magnetic field. A perfectly aligned triazine network with a layered structure was proposed to interpret the X-ray result. Primarily, we may image the transformation between the disc and the smectic-like layered structure through the rotations of the ether linkages between the substituents to the central *s*-triazine ring but, annealing of compound XI at 190°C for 2 hrs made no change on the intensities of the diffraction peaks, which indicates the unlikeness of this transformations. Suggestively, rotations of the ether linkages involve the rotations of the bulky substituents, a process supposed to be more difficult to occur in a weak flow field as compared to the strong magnetic field applied in Barclay's experiment [14].

Since at least two of the three substituents in compounds VIII and XI are mesogenic units, alignments between these mesogens occur readily in the lc state. During mesophase formation, two molecules may approach each other in a manner which have their mesogenic subsituents superimposed intermolecularly. For compound XI, the alignments between intermolecular substituents can be achieved by either the D_{hd} phase or the aligned layered structure. For compound VIII, mesogenic alignments become less probable since one of its three substituents is non-mesogenic. This also explains the fact that the involved mesophase for VIII is less ordered as addressed above. We except that the superimposed (parallel) packing between mesogenic substituents would be more favorable for those with the longer sidechains because of the potential Van der waals interactions between the aliphatic chains. With shorter sidechains, compounds VII and X lost the columnar structures and resulted in the formation of nematic phase (presumably N_D phase).

CONCLUSION

Equivalently- and inequivalently-substituted *s*-triazines (as ESTs and ISTs, respectively) were prepared and characterized. More than one mesogenic biphenyl substituent was required for the triazines to exhibit mesomorphism. Therefore, compounds, VII, VIII, X and XI exhibited mesomorphism under polarizing light.

DSC results suggested that compounds VIII and XI possess similar thermal transition temperatures (T_m and T_i). XRD study revealed a D_{hd} phase for both compounds but for XI, an extra aligned layered structure (cf. Fig. 6) was found to be co-existed with its D_{hd} phase. For compounds with shorter sidechains (as compounds VII and X), a less-ordered nematic phase (presumably N_D phase) was found. The mesophase difference between those with short and long sidechains is due to the contribution from the Van der waals interactions among the aliphatic sidechains.

Acknowledgements

We gratefully acknowledge the financial support of the National Science Council, R.O.C., under contract no. NSC 83-0208-M-110-039.

References

[1] S. Chandrasekhar and B. K. Sadashiva, *Pramana*, **9**, 471 (1977).
[2] C. Destrade and P. Foucher, *Mol. Cryst. Liq. Cryst.*, **106**, 121 (1984).
[3] D. M. Kok and H. Wynberg, *Mol. Cryst. Liq. Cryst.*, **129**, 53 (1985).
[4] K. Nishimura, S. Takenaka and S. Kusabayshi, S., *Mol. Cryst. Liq. Cryst.*, **104**, 347 (1984).
[5] S. Takenaka and K. Nishimura, *Mol. Cryst. Liq. Cryst.*, **111**, 227 (1984).
[6] Y. Matsunga and Y. Nakayasu, *Mol. Cryst. Liq. Cryst.*, **141**, 327 (1986).
[7] G. Lattermann, *Liquid Crystals*, **2**, 723 (1987).
[8] G. Lattermann and H. Hocker, *Mol. Cryst. Liq. Cryst.*, **133**, 245 (1986).
[9] P. L. Barny, J. Billard and J. C. Dubois, *Liquid Crystals and Ordered Fluids*, **4**, edited by A. C. Griiffin and J. F. Johnson (Plenum, New York), p. 57 (1982).
[10] S. Ayano, *Chem. Econ. Eng. Rev.*, **10**, 25 (1978).
[11] J. R. Dudley, J. T. Thurston, F. C. Schaffer, D. Holm-Hansen, C. J. Hull and P. Adams, *J. Amer. Chem. Soc.*, **73**, 2986 (1951).
[12] F. C. Schaffer, J. T. Thurston and J. R. Dudley, *J. Amer. Chem. Soc.*, **73**, 2990 (1951).
[13] S. J. Huang, J. A. Feldmann and J. L. Cercena, *Polym. Prepr.*, **30**(2), 348 (1989).
[14] G. G. Barclay, C. K. Ober, K. I. Papathomas and D. W. Wang, *Macromolecules*, **25**, 2947 (1992).
[15] W. Mormann, C. Irle and J. Zimmmermann, *Polym. Prepr.*, **34**, 704 (1993).
[16] S. Mahlstedt and M. Bauer, *Polym. Mat. Sci. Eng.*, **71**, 801 (1994).
[17] M. J. S. Dewar and A. C. Griffin, *J. Amer. Chem. Soc.*, **97**, 6662 (1995).