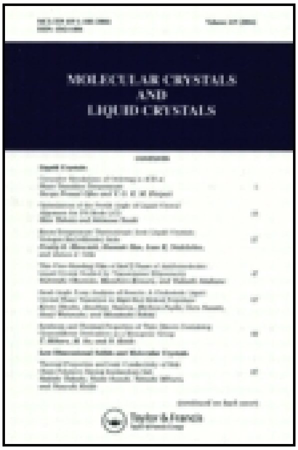

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Synthesis and Characterization of Liquid Crystalline Triaryloxy-s-Triazines

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Synthesis and Characterization of Liquid Crystalline Triaryloxy-*s*-Triazines

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2, 4, 6-Tris [*p*-(*p*′-*n*-alkylphenyliminomethylene)phenoxy]-*s*-triazines (**3**) were found to be calamitic liquid crystals based on X-ray diffraction patterns, optical textures, and molecular modeling results. Replacement of the Schiff's base moieties in the mesogenic "arms" to form 2, 4, 6-tris(*p*-*n*-octyloxycarbonylphenoxy)-*s*-triazine (**7**) did not result in a liquid crystalline compound. The tricarbonate 2, 4, 6-tris(*p*-cholesteryloxycarbonyloxyphenoxy)-*s*-triazine (**11**) was found to be liquid crystalline based on the optical textures observed, although the mesophase type could not be determined due to the high melting transition and thermal instability of this compound. The use of six ester groups around the triazine nucleus, in the form of 2, 4, 6-tris(3, 5-dicarboalkoxyphenoxy)-*s*-triazines (**13**), resulted in compounds which displayed normal melting behavior and no detectable mesomorphism.

Keywords: Triaryloxytriazines; calamitic liquid crystals; triarmed Schiff bases

INTRODUCTION

Over the past ten years, researchers have been probing the use of liquid crystalline networks for the generation of superstructures with enhanced mechanical properties and novel optical and ferroelectric properties [1, 2]. Among the liquid crystalline thermosets studied are epoxies [3, 4], maleimides [5], acetylenes [6], acrylates [7, 8] and vinyl ethers [9]. Cyanate

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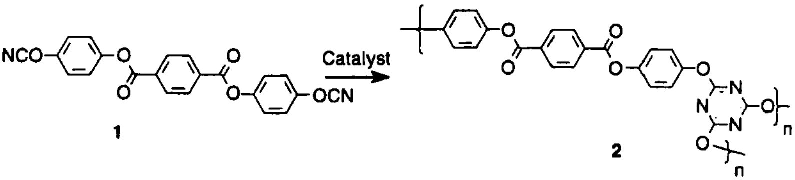
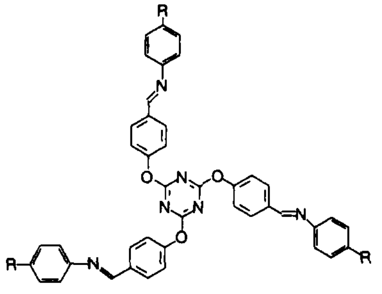
thermosets have been studied extensively because of their remarkable mechanical strength and toughness [1]. These thermosets are generated through the cyclotrimerization (curing) reactions of aromatic dicyanates. The dicyanate **1** of bis(4-hydroxyphenyl) terephthalate is in itself not liquid crystalline, but upon curing by cyclotrimerization produces a thermoset (**2**) with mesomorphic properties. X-ray diffraction profiles and optical microscopy suggested that thermoset **2** was in fact a calamitic smectic mesomorphic system [10] with the triazine "arms" adopting a rod shape.



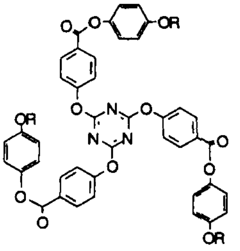
A few researchers have realized the importance of investigating *model* systems to determine the mesomorphic properties of monomeric triaryloxy-*s*-triazines made by trimerization of cyanates. Despite concerted efforts to generalize the liquid crystalline properties of various triaryloxy-*s*-triazines, several contradictions and inconsistencies surfaced. Huang and coworkers [11] reported that compounds **3c** and **3f**, 2,4,6-tris[*p*-(*p*′-alkylphenyliminomethylene) phenoxy]-*s*-triazines, exhibited "discotic liquid crystalline behavior" based on the optical textures obtained in the mesophase; no transition temperature or X-ray diffraction data were given. Some time later, Mormann and Zimmerman [12a] reported that triester **4a** exhibited "discotic mesomorphism". Later, after the present work was nearing completion, Mormann indicated that triesters **4a** and **4b** were calamitic, but again, without mention of X-ray diffraction results or optical textures [12b]. Interestingly, they also claimed that reversal of the outer ester linkage eliminated liquid crystallinity altogether [12b]. Ou and coworkers [13] reported that substitution of the ester groups with stilbene units produced discotic liquid crystalline compound **5** with no mention of confirmatory X-ray diffraction results.

A report by Tahmassebi and Sasaki [14] involving the synthesis of the novel trialdehyde **6** and several of its Schiff's base derivatives originally sparked our interest in the synthesis of the these compounds. It occurred to us that by incorporating *known* mesogenic units around the triazine core, we might be able to engender the shape anisotropy required for mesomorphism. Inspection of the symmetrical nature of trialdehyde **6** gave us the impression that its azomethine, or Schiff's base, derivatives might stack in a columnar



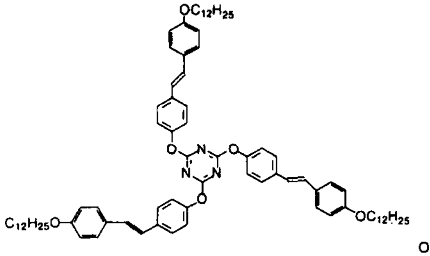
3

a. R = n-C_4H_9
b. R = n-C_5H_{11}
c. R = n-C_6H_{13}
d. R = n-C_7H_{15}
e. R = n-C_8H_{17}
f. R = n-C10H21
g. R = n-$C_{14}H_{29}$
h. R = OC_5H_{11}-n



4

a. R = n-C_4H_9
b. R = CH_3



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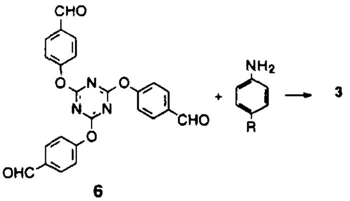

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fashion to produce discotic liquid crystals. Because of this and the confusion we encountered in the literature, in 1994 we began to investigate the synthesis and behavior of triaryloxy-*s*-triazines to develop some basic structure-property information.

RESULTS AND DISCUSSION

A. 2,4,6-Tris[*p*-(*p*′-*n*-alkylphenyliminomethylene)phenoxy]-*s*-triazines (3)

1. Synthesis and Molecular Characterization

The title compounds **3a-e,g,h** were synthesized by reacting trialdehyde **6** with the appropriate substituted anilines; the reactions proceeded in nearly quantitative yields. These compounds were characterized at the molecular level by infrared and NMR spectroscopies, elemental analyses, and high resolution fast atom bombardment (HRFAB) mass spectrometry (MS). For example, the proton NMR spectrum of compound **3a** (Fig. 1) in $CDCl_3$ shows the azomethine protons (a) at 8.43 ppm, doublets at 7.92 and 7.25 ppm which are due to the aryl protons (b, d) of the phenoxy moiety, doublets at 7.31 and 7.16 ppm due to the aryl protons (c, e) of the aniline ring, and the characteristic *n*-butyl resonances (f-i) in the aliphatic region of the spectrum. The NMR spectra of compounds **3a-e,g,h** were virtually identical in the aromatic region and only differed in the aliphatic portion of the spectra. The IR spectra showed a characteristic strong stretch at 1560 cm^{-1} due to the C=N functionality.

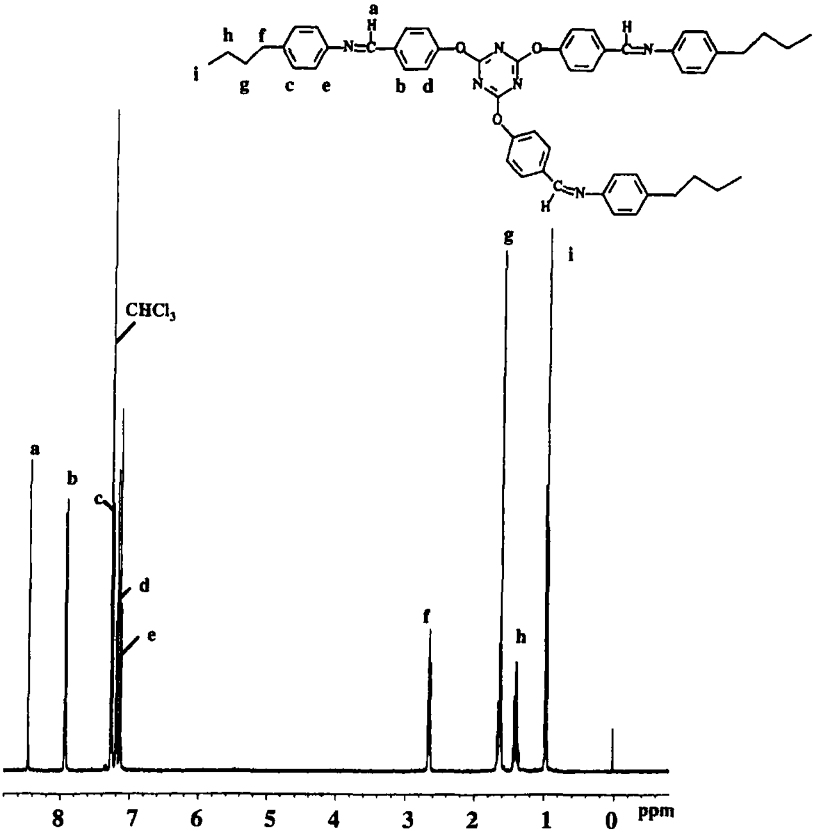

FIGURE 1 The 400 MHz ^1H NMR spectrum of compound **3a** in $CDCl_3$.

2. Phase Transitions

The thermal transitions of compounds **3a-e,g,h** measured by differential scanning calorimetry (DSC) are shown in Table I. Compound **3a**, the *n*-butyl derivative, has an initial melting transition at 180°C followed by isotropization at 191°C. The range of liquid crystallinity increased from 11°C with **3a** to 28.6°C for the *n*-pentyl derivative **3b** on heating, while the initial melting transition decreased due to the longer alkyl chain. The DSC traces (Fig. 2) of compound **3b** reveal two endothermic transitions. The melting endotherm at 172.8°C is due to the reorganization of the molecules into the mesophase, which persists until the liquid crystalline order is lost at

TABLE I Phase behavior* of triazine Schiff's bases 3a–e,g,h

3a	$K \underset{147.0\ (21.9)}{\overset{180.0\ (22.7)}{\rightleftharpoons}} S_A \underset{189.0\ (4.88)}{\overset{191.0\ (4.92)}{\rightleftharpoons}} I$
3b	$K \underset{142.3\ (22.4)}{\overset{172.8\ (23.0)}{\rightleftharpoons}} S_A \underset{197.5\ (5.15)}{\overset{201.4\ (5.19)}{\rightleftharpoons}} I$
3c	$K \underset{141.5\ (26.6)}{\overset{161.0\ (27.9)}{\rightleftharpoons}} S_A \underset{202.2\ (6.18)}{\overset{203.0\ (5.91)}{\rightleftharpoons}} I$
3d	$K \underset{119.0\ (28.9)}{\overset{153.4\ (29.6)}{\rightleftharpoons}} S_A \underset{199.2\ (5.92)}{\overset{203.7\ (5.93)}{\rightleftharpoons}} I$
3e	$K \underset{124.0\ (31.5)}{\overset{152.8\ (33.2)}{\rightleftharpoons}} S_A \underset{186.7\ (6.09)}{\overset{190.0\ (6.16)}{\rightleftharpoons}} I$
3g	$K \underset{?}{\overset{78.6}{\rightleftharpoons}} S_? \underset{63.6\ (48.1)}{\overset{103.4\ (56.1)}{\rightleftharpoons}} S_? \underset{114.4\ (41.1)}{\overset{146.0\ (36.1)}{\rightleftharpoons}} N \underset{165.3\ (7.46)}{\overset{169.8\ (7.91)}{\rightleftharpoons}} I$
3h	$K \underset{171.5\ (34.5)}{\overset{194.9\ (54.5)}{\rightleftharpoons}} S_B \underbrace{\overbrace{\underset{210.0}{\overset{215.0}{\rightleftharpoons}} N \underset{212.7}{\overset{216.8}{\rightleftharpoons}}}^{(3.79)}}_{(3.88)} I$

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* The phase transition temperatures (°C) and enthalpies (in parentheses, kJ/mol) shown above and below the arrows were determined by DSC (10°C/min). K and I represent crystalline and isotropic phases, and S_A, S_B and N represent smectic A, smectic B and nematic mesophases, respectively.

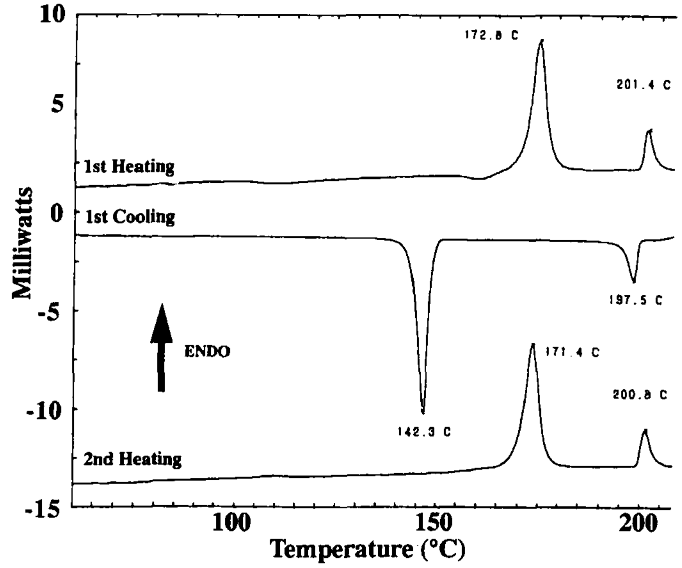


FIGURE 2 DSC traces of compound **3b**: scanning rate 10°C/min.

the isotropization temperature (201.4°C). Upon cooling, the mesophase reforms at 197.5°C, followed by crystallization at 142.3°C. This reversible (enantiotropic) process can be repeated through several heating/cooling cycles without any significant variation in the transition temperatures or sample degradation. The transition enthalpies for **3a**–**3e** are consistent with a columnar disordered phase as evidenced by the relatively small clearing point enthalpies [15], as noted in Table I.

The *n*-tetradecyl derivative **3h** exhibited some interesting thermal behavior. DSC analysis revealed four endothermic transitions upon heating (Fig. 3). The second and enthalpically largest endothermic transition at 103°C could not be due, we believe, to a crystal–crystal transition as the enthalpy is very large. In addition, no change in optical texture could be seen at this transition (see below). This phase then melts at 149°C, allowing organization into the mesophase which persists until the isotropization temperature is reached at 169.5°C. Qualitatively, this mesophase was observed to be of low viscosity and free flowing, suggesting a nematic phase. Interestingly, four transitions are also seen in the second heating cycle, suggesting smectic phases, the lower one probably involving the melting and reorganization of the C_{14} chains.

Compound **3g**, the *n*-pentyloxy derivative, also showed three endotherms on heating and cooling by DSC, suggesting two different types of liquid

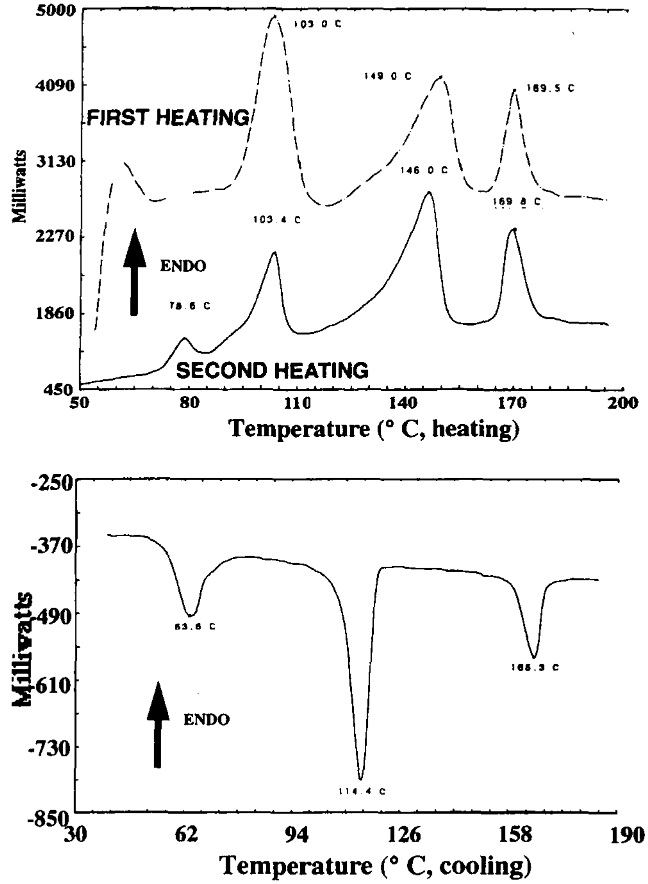


FIGURE 3 DSC traces of compound **3g**: scanning rate 10°C/min.

crystalline phases. This compound's *n*-alkyl equivalent, the *n*-hexyl derivative **3c**, was found to melt at a lower temperature and have a broader range of liquid crystallinity than its *n*-alkoxy counterpart.

3. Optical Textures

While the thermal analyses provided some insight about the energetics involved in the phase transitions of these compounds, only the optical textures under the microscope reveal the true mesophase type (discotic *vs.* calamitic). In the liquid crystalline domains of compounds **3a–e**, on cooling immediately following bâtonnet formation, a classic focal conic fan texture was observed by polarized optical microscopy, suggesting a smectic-A type mesophase and not a discotic mesophase. For example, Figure 4 shows photomicrographs of textures obtained with compounds **3a** and **3b** under crossed polarizers. Qualitatively, the mesophases of **3a**–**3e** were found to be relatively viscous and resistant to shearing. Compound **3g** displayed a free flowing nematic mesophase with transient birefringence above 150°C. Optically, no change in texture could be seen at the 103°C transition (from DSC, above) for this compound. The pentyloxy derivative **3h** showed a

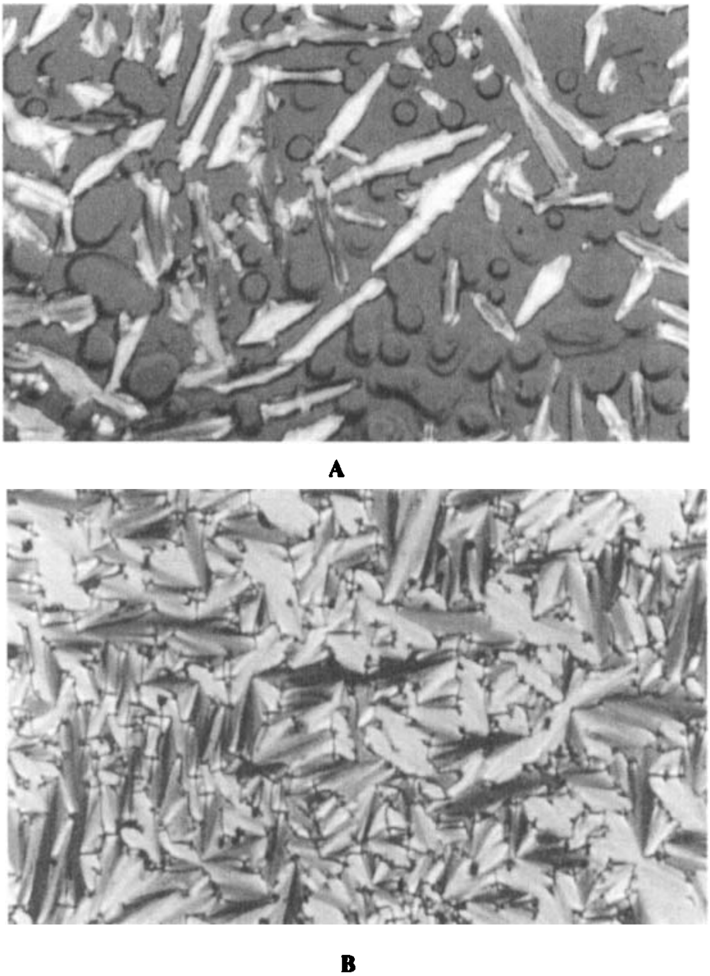


FIGURE 4 Optical textures observed under crossed polarizers. (A) Bâtonnets forming from the isotropic fluid of **3b** at 201°C; (B) Fan texture of **3a** at 172°C upon cooling from the isotropic fluid. (See Color Plate V).

mosaic texture typical of smectic-B mesophases [16] when cooled slowly from the nematic phase, which is transient and short-lived (Fig. 5).

4. Molecular Modeling

The optical textures indicated that these compounds were not discotic mesogens but calamitic mesogens. It remained unclear how these triarmed molecules might adopt an unsymmetrical conformation in which a rod-like shape would result. We failed to realize at first that the triazine core was

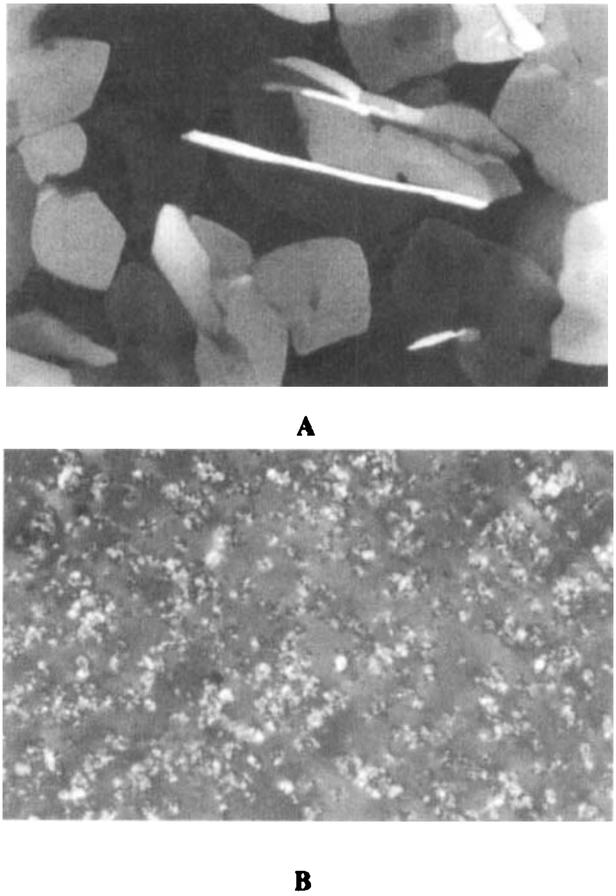


FIGURE 5 Optical textures observed under crossed polarizers with compound **3h**. A: Mosaic texture at 189°C. B: Fluid nematic phase at 194°C. (See Color Plate VI).

rendered flexible by the ether linkages at the 2,4,6-positions of the ring. Molecular modeling was utilized to find the minimum energy conformation. A CPK representation of the *n*-butyl derivative is shown in Figure 6; the alternating folded arrangement of the "arms" of these molecules allows for smectic-A rigid rods in the mesophase. This locally minimized conformation of **3a** had a significantly lower energy (36.7 kcal/mol) than that of the fully extended, symmetrical conformation (47.8 kcal/mol). These "rods" are approximately 7.8 Å in diameter and 34.4 Å in length, reflecting their high aspect ratio. Intuitively, adoption of this conformation seems logical since the flexibility at the ether oxygens attached to the triazine ring and the intramolecular $\pi-\pi$ stacking and van der Waals interactions would be driving forces for this "folded" arrangement. This type of induced "folding" was found in the polycyanurates [10] and also engendered liquid crystallinity in a class of polyether dendrimers as well [17]. In the fully extended symmetrical conformation, stacking in a columnar arrangement would not be favorable due to the large void volumes present along the columns.

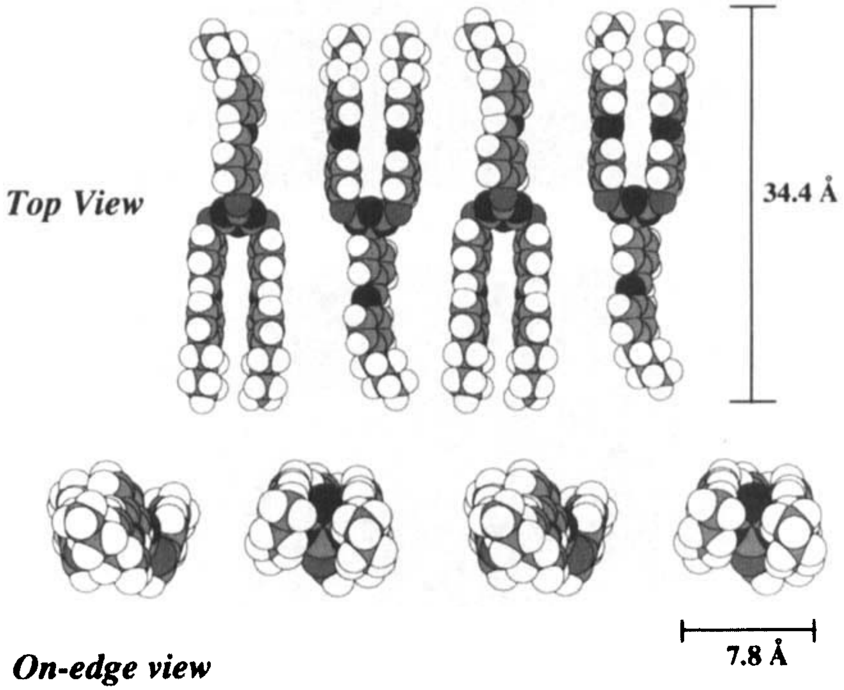


FIGURE 6 CPK representations of compound **3a** in minimized state; steric energy = 36.7 kcal/mol. (See Color Plate VII).

5. Absence of an Odd–Even Effect in the Homologous Series

A plot of the transition temperatures *vs.* carbon number of compounds **3a–e** is shown in Figure 7. As one might expect, the melting points decrease with increasing alkyl chain length, while the isotropic transition temperatures change only modestly. The absence of an odd–even effect in the transition temperatures is consistent with zero net dipole moment of the mesophase due to the antiparallel arrays described schematically in Figure 6.

6. X-ray Diffraction Studies

Figure 8 shows the wide angle X-ray diffraction profile of compound **3a** in the mesophase at 179°C. A *d*-spacing of 32.7 Å in the low angle region represents the molecular length (layer thickness) in the mesophase. This value agrees quite well with the value of 34.4 Å from molecular modeling. In addition, a broad amorphous halo at 4.4 Å is indicative of the correlations between molten *n*-butyl peripheral chains. Additional support for the proposed calamitic architecture is gained by the absence of any peaks in the small angle region indexable to a hexagonal columnar array. X-ray analysis of the *n*-pentyloxy derivative **3h** is also consistent with a smectic-B calamitic

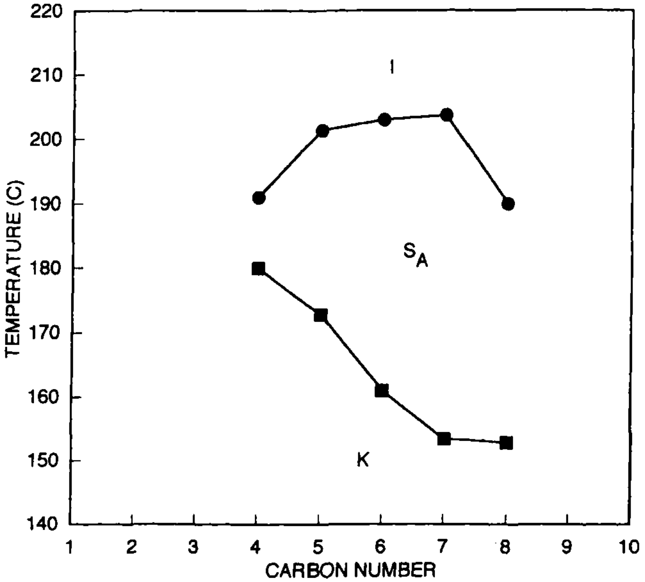


FIGURE 7 Transition temperatures as a function of the number of carbon atoms in the *n*-alkyl groups of compounds **3a–3e**. The square bullets represent the initial melting points and the round bullets denote the isotropization temperatures.

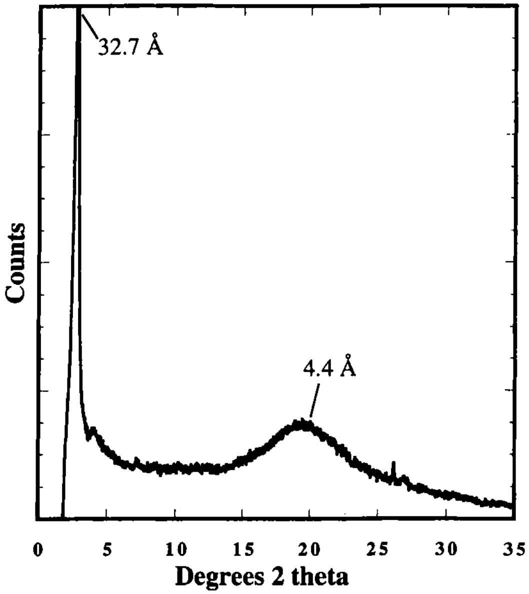


FIGURE 8 Wide angle X-ray diffraction profile of compound **3a** in the mesophase at 179°C. The intense low angle peak (32.7Å) agrees will with the molecular length estimated by molecular modeling (34.4Å). The broad amorphous halo centered at 4.4Å represents the separation between the molten *n*-butyl chains.

phase (Fig. 9), with a strong Bragg reflection at 30.9Å and an amorphous halo centered at 4.7Å due to the molten *n*-pentyloxy peripheral chains. This amorphous halo is much more intense and sharper than with **3a**. In addition, a very sharp peak centered at 2.95Å is most likely due to the intermolecular lateral spacing d_2; note that in smectic-B phases, this distance between molecules is constant, and the sharpness of the peaks reflects the crystalline-like order of this mesophase [18]. Again, no reflections indexable to a discotic phase were found in the small angle region of the diffraction profile.

B. Triaryloxy-*s*-triazines Containing Ester Linkages

While it became apparent that triaryloxy-*s*-triazines with Schiff's base residues in the "arms" produced calamitic liquid crystals and not discotics, we desired to investigate whether this behavior was particular to that class of compounds or general for *any* triaryloxy-*s*-triazine. In addition, the azomethine functionality is highly susceptible to hydrolysis and tends to give high melting points. Therefore, we chose to incorporate ester groups in the "arms" to give a more robust linkage with hopefully lower melting transitions.

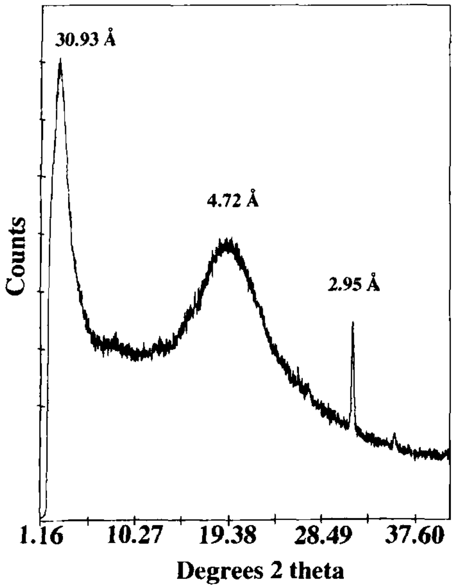
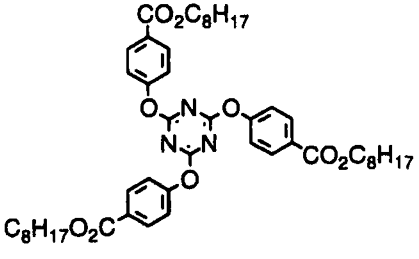


FIGURE 9 Wide angle X-ray diffraction profile of compound **3h** in the mesophase at 215°C. The intense low angle peak (30.9 Å) agrees will with the molecular length estimated by molecular modeling (29.3 Å). The broad amorphous halo centered at 4.7 Å represents the separation between the molten *n*-pentyloxy chains, while the sharp wide angle peak at 2.95 Å is the distance between cylinders in the hexagonal array.

1. Trisubstituted Systems

a. Paraffinic Esters With this in mind, 2,4,6-tris(*p*-*n*-octyloxycarbonylphenoxy)-*s*-triazine (7) was synthesized (96%) by treatment of cyanuric chloride with sodium *n*-octyl *p*-hydroxybenzoate by a method reported for other compounds [19]. Proton and carbon NMR and IR spectroscopic and elemental analyses confirmed the structure of this new compound. The DSC thermogram showed two broad endotherms at 101.3 and 117.2°C on heating and two crystallization exotherms at 92.9°C and 85.4°C on cooling. Identical behavior was seen on the second heating and cooling. Upon slowly cooling from the isotropic state, fibrillar structures were observed at 114°C by optical microscopy and then crystallization at 92.9°C, resulting in a spherulitic fan texture; no change in texture was observed after the final crystallization at 85.4°C. This compound is thus believed to possess two crystalline and no liquid crystalline phases.

b. Cholesteryl-containing Esters It occurred to us that by "bulking up" the outer portion of the triaryloxy-*s*-triazine nucleus, the adoption of the rod-



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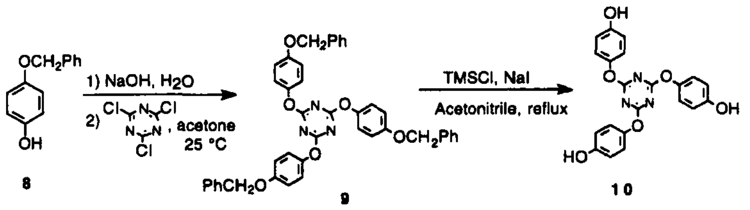
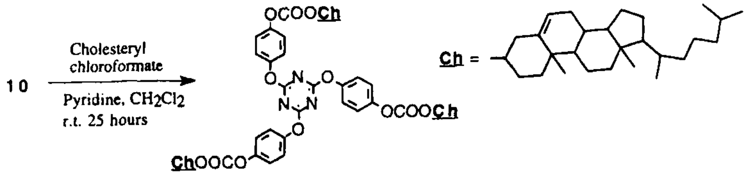
shaped conformation would be less likely and the resulting space-filling ability of the symmetrical conformer might give discotic liquid crystals. The cholesteryl moiety seemed reasonable as it is large, rigid, and imbues liquid crystallinity in a variety of derivatives. As a precursor, the new compound 2,4,6-tris(*p*-benzyloxyphenyl)-*s*-triazine (**9**) was synthesized (81%) by treating cyanuric chloride with an aqueous solution of *p*-benzyloxyphenol (**8**) and sodium hydroxide. The proton NMR and IR spectra and elemental analyses agreed well with the structure. Deprotection of compound **9** involved the use of trimethylsilyl chloride and sodium iodide in acetonitrile [20]. **10** was isolated in 85% yield.



The triphenol **10** was reacted with cholesteryl chloroformate in dichloromethane and pyridine. TLC analysis of the crude product showed two spots, the top spot being UV inactive. Separation of these two compounds was accomplished using preparative thin layer chromatography (PTLC). Isolation of the first band gave a white crystalline solid, mp 174–177°C, identified as dicholesteryl carbonate based on the NMR and IR results and the agreement with the literature melting point [21]. The second band from the PTLC plate (UV active) afforded the desired product **11** (52% yield), mp 256 °C (dec.). The proton NMR spectrum revealed an AB quartet from the hydroquinone moiety, a vinyl resonance at 5.42 ppm and the O-methine signal at 4.59 ppm. The ^{13}C NMR spectrum indicated the incorporation of the triazine nucleus (173.5 ppm), a carbonyl peak

(152.7 ppm) and phenyl carbons. Elemental analyses and the IR spectrum further confirmed the structure of this new compound.



11

It was expected that tricarbonate **11** might be a cholesteric discotic mesogen (D_{N^*}). Optical microscopy was performed to see if it was liquid crystalline. Indeed, at 256°C a free-flowing mesophase, the texture of which is shown in Figure 10, began to form. This nematic-like texture persisted for only a short while, and on further heating the optical birefringence was lost and a blue phase resulted. This phase did not flow, and attempts to crystallize the sample by cooling failed. DSC results supported these observations; no isotropization or crystallization transitions were observed. A crystallization exotherm was seen in the DSC if the sample was cooled immediately after the initial melting temperature was reached. Using microscope slides under shearing conditions, it was found that the pitch of the mesophase die not fall in the visible region of the spectrum as is common with some cholesteric mesophases. X-ray diffraction studies were not particularly informative, as the high temperatures involved and the propensity of this compound to decompose rapidly after melting resulted in a complex and noisy X-ray diffraction profile. In addition, due to the length of the molecule (48 Å by molecular modeling), the layer spacing was beyond the limits of the detector used in the X-ray instrument.

2. Hexasubstituted Systems

Most discotic mesogens contain from 4 to 6 "arms" around a rigid core unit [22]. The above results indicated that perhaps three arms were not sufficient for the space-filling requirements of discotic mesomorphism. The incorporation of six ester groups around the triazine core might prevent "folding" into rods and give the molecules enough breadth to stack in a columnar fashion.

To form the new hexa(alkyl ester)s **13a** and **13b**, the precursor esters **12a** and **12b** were reacted *via* their phenolate salts with cyanuric chloride. The hexamethyl ester **13a** was produced in 90% yield; the proton, ^{13}C NMR and

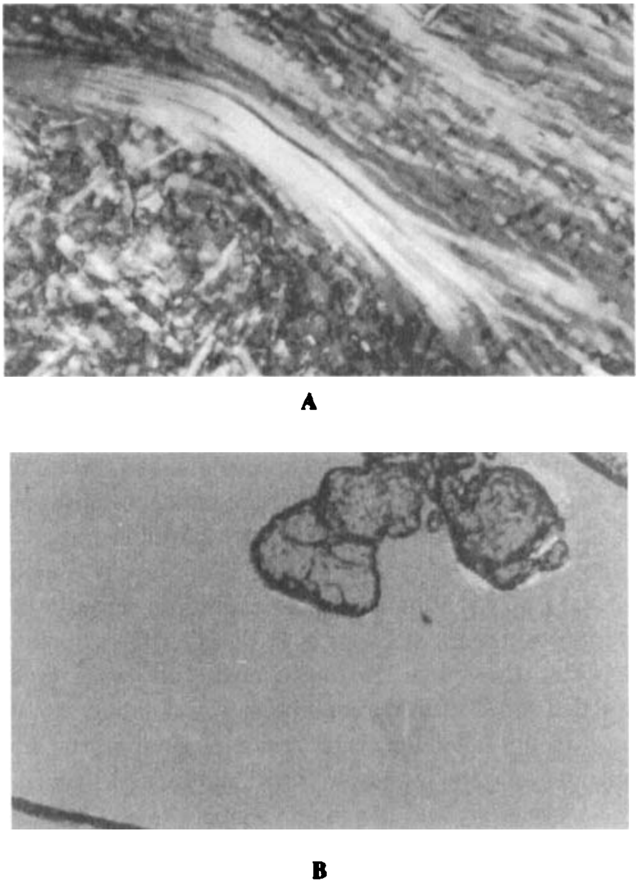
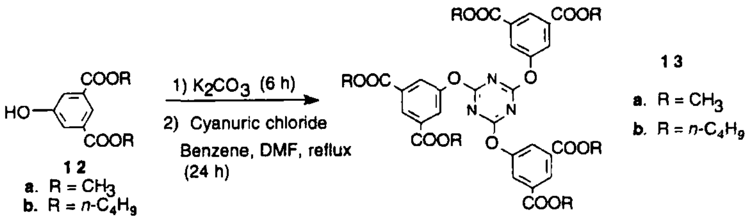


FIGURE 10 Optical micrographs under crossed polarizers for compound **11**. A: Free flowing mesophase at 256°C. B: Blue phase obtained 5 sec. later at 257°C. (See Color Plate VIII).



IR spectra and elemental analyses were consistent with the structure. The melting point was observed to be very broad, and substantial turbidity was seen between 167 and 184°C, indicating that liquid crystallinity might be present. DSC analysis showed overlapping melting transitions on heating and no transitions on cooling. However, a second heating identical to the first revealed no transitions at all, except a T_g. After annealing a fresh sample at 179°C for 30 minutes and cooling, only a T_g was observed in the second heating, indicating that once melting occurs, recrystallization is inhibited and an amorphous glass results. The minimized structure and space filling model of **13a** are shown in Figure 11, revealing the planarity of the molecule. The hexabutyl ester **13b** (mp 136–138°C) was produced by an identical procedure in 99% yield; it displayed no evidence of liquid crystallinity by DSC.

CONCLUSIONS

The 2,4,6-tris[*p*-(*p*′-*n*-alkylphenyliminomethylene)phenoxy]-*s*-triazines (**3**), were found to be calamitic liquid crystals based on X-ray diffraction patterns, optical textures, and molecular modeling results. Replacement of the Schiff's base moieties in the mesogenic "arms" with *p*-*n*-octyloxycarbonylphenoxy groups in **7** did not afford a liquid crystalline phase apparently.

To prevent "folding" in the triaryloxy-*s*-triazines at the ether linkage of the triazine ring, an attempt was made to bulk up the periphery of the molecules to allow proper space filling for discotic mesomorphism.

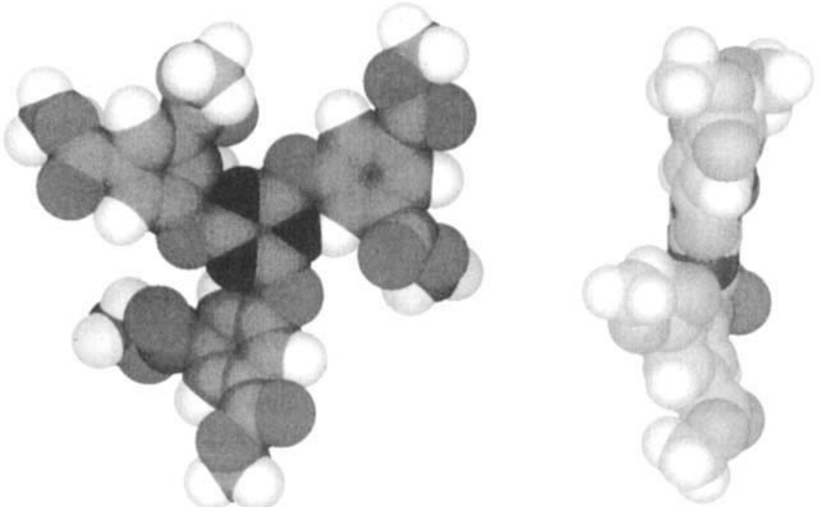


FIGURE 11 Energy minimized CPK representations of compound **13a** reflecting the high aspect ratio inherent in this class of compounds. (See Color Plate IX).

Cholesteryl groups were incorporated in **11** and this compound was found to be liquid crystalline based on the optical textures observed, although the mesophase type could not be determined due to the high melting transition and thermal instability of this compound. The use of six ester groups around the triazine nucleus resulted in compounds **13**, which displayed normal melting behavior and no detectable mesomorphism.'

EXPERIMENTAL

General

Melting points were taken on a Mel-Temp II melting point apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra, recorded in ppm, were obtained using a Varian Unity 400 MHz spectrometer and a Bruker WP-270 MHz spectrometer with tetramethylsilane (TMS) as an internal standard in deuteriochloroform, unless otherwise noted. The following abbreviations are used to denote multiplicities: *s* (singlet), *d* (doublet), *t* (triplet), *p* (pentet), *sx* (sextet), *m* (multiplet). IR spectra, reported in cm.$^{-1}$, were recorded on a Nicolet Impact 400 infrared spectrometer using pulverized potassium bromide as the medium. Optical microscopy was performed on a Zeiss Axioskop (20X objective) using crossed polarizers along with a Linkam Scientific THM600 (PR600 controller) hot stage and a Zeiss M35W camera. Differential scanning calorimetry (DSC) was performed on Seiko SSC-5200 and Perkin-Elmer Series-4 calorimeters (10°C/min unless otherwise noted) under a dry nitrogen purge using indium and tin as the calibration standards. X-ray analyses were obtained both at Virginia Tech and at the University of Pennsylvania in Philadelphia. At Virginia Tech, these analyses were carried out with a nickel-filtered Cu K_α radiation compact using a Philips PW 1720 diffractometer for intermediate to wide angle studies and a Kratky camera for low angle studies. At the University of Pennsylvania, variable temperature X-ray diffraction was measured using Cu K_α radiation on an Inel CPS 120 position-sensitive detector with a XRG 2000 generator, a fine-focus X-ray tube, and a home built heating stage. The temperature was regulated with a Minco CT 137 temperature controller with ±1°C temperature stability. Approximately 2 mg samples were suspended in 0.5 mm Lindermann glass capillaries. The detector was calibrated using mica and silicon standards which were obtained from the National Bureau of Standards (NBS). Elemental analyses and mass spectral data were obtained from Atlantic Microlab, Norcross, GA and the Nebraska Center for Mass Spectrometry, Lincoln, NE, respectively.

Molecular modeling was performed using *Chem 3D Plus*™ by Cambridge Scientific Computing, Inc. Using the MM2 parameters included in the software, each molecule was minimized for structural error until the root mean square error was below 0.01 or the root mean square gradient was below 0.001. In a few instances, the molecular dynamics mode was used and the structures reminimized to ensure that a global minimum was reached.

Starting materials were purchased from Aldrich and were used as received except for 4-*n*-butylaniline, 4-*n*-pentylaniline, and 4-*n*-heptylaniline, which were distilled prior to use.

2,4,6-Tris(*p*-formylphenoxy)-1,3,5-triazine (5)

This trialdehyde was synthesized using a slight modification of the method of Tahmassebi and Sasaki [14]. To a 250 mL three-necked round bottom flask fitted with a mechanical stirrer, Dean-Stark trap and a reflux condenser were added *p*-hydroxybenzaldehyde (8.0 g, 65 mmol) and pulverized Na_2CO_3 (50 g) and the mixture covered with benzene (150 mL) and brought to reflux. After 2 h, H_2O ceased to collect in the Dean-Stark trap. At this time, cyanuric chloride (3.0 g, 16 mmol) in benzene (10 mL) was slowly added from a dropping funnel. The mixture was allowed to stir at reflux for 6 h. After cooling to room temperature (RT), the benzene solution was extracted with 10% aq. Na_2CO_3 (3 × mL) to remove any unreacted *p*-hydroxybenzaldehyde. The benzene solution was dried (Na_2SO_4) and evaporated under vacuum to give crude **5** as a snow white solid (7.19 g, 100%). Recrystallization from EtOAc gave pure **5** as white needles (6.45 g, 91%), mp 173 – 175.2°C (lit [14]. mp 174 – 176°C). IR cm.$^{-1}$: 1695 (s, C=O), 1210 (*vs*, C—O—C). ^{1}H NMR δ: 10.0 (*s*, 3 H, CHO), 7.9 (*d*, J = 8.5 Hz, 6 H), 7.3 (*d*, J = 8.5 Hz, 6 H).

2,4,6-Tris[*p*-(*p*′-*n*-butylphenyliminomethylene)phenoxy]-*s*-triazine (3a)

To a 250 mL Erlenmeyer flask with a stirring bar were added **5** (2.0 g, 4.5 mmol), 4A molecular sieves, and abs. EtOH (150 mL). After this suspension had been slowly heated to reflux, freshly distilled 4-*n*-butylaniline (2.0 g, 13 mmol) was added and the mixture allowed to stir for 4 h at reflux. The off-white solid collected upon filtration was washed several times with cold EtOH and dried to give crude **3a** as a white powder (3.75 g, 100%). Recrystallization from hot EtOAc afforded pure **3a** (3.74 g 99%) as a white fluffy solid, mp 181 – 190°C; IR cm.$^{-1}$: 1560 (*s*, C=N), 1210 (*s*, C—O—C). 1H NMR δ: 8.43 (*s*, 3 H, CH=N), 7.92 (*d*, J = 8.8 Hz, 6 H), 7.31

(*d*, $J = 8.8$ Hz, 6 H), 7.25 (*d*, $J = 6.4$ Hz, 6 H), 7.16 (*d*, $J = 6.4$ Hz, 6 H), 2.63 (*t*, $J = 7.2$ Hz, 6 H), 1.61 (*p*, $J = 7.2$ Hz, 6 H), 1.39 (*sx*, $J = 7.2$ Hz, 6 H), 0.97 (*t*, $J = 7.2$ Hz, 9 H). Elemental anal. calcd. (found) for $C_{54}H_{54}N_6O_3 \cdot 1/2$ EtOAc: C, 76.51 (76.13); H, 6.64 (6.60); N, 9.56 (9.74).

2,4,6-Tris[*p*-(*p*′-*n*-pentylphenyliminomethylene)phenoxy]-*s*-triazine (3b)

Use of the procedure above produced crude **3b** as an off-white powder (3.93 g, 99%). Recrystallization from AcMe gave pure **3b** as a white fluffy powder, mp 172.8–201.4°C (DSC). IR cm.$^{-1}$: 1558 (*s*, C=N), 1210 (*s*, C—O—C). ^{1}H NMR δ: 8.43 (*s*, 3 H, CH=N), 7.91 (*d*, $J =$ 8.8 Hz, 6 H), 7.23 (*d*, $J = 8.8$ Hz, 6 H), 7.16 (*d*, $J = 6.4$ Hz, 6 H), 7.16 (*d*, $J = 6.4$ Hz, 6 H), 2.61 (*t*, $J = 7$ Hz, 6 H), 1.61 (m, 6 H), 1.34 (*m*, 12 H), 0.90 (*t*, $J = 7$ Hz, 9 H). Elemental anal. calcd. (found) for $C_{57}H_{60}N_6O_3 \cdot 1$ AcMe: C, 78.39 (78.09); H, 7.23 (7.27); N, 9.14 (9.15).

2,4,6-Tris[*p*-(*p*′-*n*-hexylphenyliminomethylenephenoxy)-*s*-triazine (3c)

Use of the procedure above produced crude **3c** as an off-white powder (4.1 g, 98%). Recrystallization from AcMe gave a white powder (3.67 g, 89%), mp 161–202.7°C (DSC). IR cm.$^{-1}$: 1560 (*s*, C=N), 1210 (*s*, C—O—C). 1H NMR ($CDCl_3$) δ: 8.43 (*s*, 3 H, CH=N), 7.92 (*d*, $J = 8$ Hz, 6 H), 7.23 (*d*, $J = 8$ Hz, 6 H), 7.18 (*d* $J = 6$ Hz, 6 H), 7.10 (*d*, $J = 6$ Hz, 6 H), 2.60 (*t*, $J = 6.4$ Hz, 6 H), 1.61 (*p*, $J = 6.4$ Hz, 6 H), 1.32 (*sx*, $J = 6.4$ Hz, 6 H), 0.96 (*t*, $J = 6.4$ Hz, 9 H). Elemental anal. calcd. (found) for $C_{60}H_{66}N_6O_3 \cdot 4/3$ AcMe: C, 77.13 (77.15); H, 7.48 (7.30); N, 8.43 (8.64).

2,4,6,-Tris[*p*-(*p*′-*n*-heptylphenyliminomethylene)phenoxy]-*s*-triazine (3d)

Use of the procedure above produced crude **3d** as an off-white powder (4.32 g, 100%). Recrystallization from AcMe gave pure **3d** as a white fluffy powder, mp 153.4–203.7°C (DSC). IR cm.$^{-1}$: 1560 (*s*, C=N), 1210 (*s*, C—O—C). ^{1}H NMR δ: 8.43 (*s*, 3 H, CH=N), 7.91 (*d*, $J = 8.4$ Hz, 6 H), 7.23 (*d*, $J = 8.4$ Hz, 6 H), 7.16 (*d*, $J = 6$ Hz, 6 H), 7.10 (*d*, $J = 6$ Hz, 6 H), 2.62 (*t*, $J = 7.2$ Hz, 6 H), 1.66 (*m*, 6 H), 1.30 (m, 24 H), 0.90 (*t*, $J = 7.2$ Hz, 9 H). Elemental anal. calcd. (found) for $C_{63}H_{72}N_6O_3 \cdot 1/2$ AcMe: C, 78.22 (77.84); H, 7.63 (7.62); N, 8.52 (8.39).

2,4,6-Tris[*p*-(*p*′-*n*-octylphenyliminomethylene)phenoxy]-*s*-triazine (3e)

Use of the procedure above produced crude **3e** as an off-white powder (3.52 g, 78%). Recrystallization from AcMe gave pure **3e** as a white fluffy powder, mp 152.8–190°C (DSC). IR cm.$^{-1}$: 1558 (*s*, C=N), 1210 (*s*, C—O—C). ^{1}H NMR δ: 8.43 (*s*, 3 H, CH=N), 7.91 (*d*, *J* = 8.4 Hz, 6 H), 7.23 (*d*, *J* = 8.4 Hz, 6 H), 7.16 (*d*, *J* = 6 Hz, 6 H), 7.10 (*d*, *J* = 6 Hz, 6 H), 2.62 (*t*, *J* = 7.6 Hz, 6 H), 1.59 (*m*, 6 H), 1.30 (*m*, 30 H), 0.88 (*t*, *J* = 7.6 Hz, 9 H). HRFABMS calcd. (found): 1002.6135 (1002.6213).

2,4,6-Tris[*p*-(*p*′-(*n*-tetradecylphenyliminomethylene)phenoxy]-*s*-triazine (3g)

Use of the procedure above produced crude **3g** as an off-white powder (4.4 g, 98%). Recrystallization from AcMe gave pure **3g** as white needles, mp 103–169.5°C (DSC). IR cm.$^{-1}$: 1558 (*s*, C=N), 1220 (*s*, C—O—C). ^{1}H NMR δ: 8.44 (*s*, 3 H, CH=N), 7.92 (*d*, *J* = 8.4 Hz, 6 H), 7.26 (*d*, *J* = 8.4 Hz, 6 H), 7.18 (*d*, *J* = 6.4 Hz, 6 H), 7.13 (*d*, *J* = 6.4 Hz, 6 H), 2.62 (*t*, *J* = 7.2 Hz, 6 H), 1.63 (br p, 6 H), 1.33–1.22 (*m*, 66 H), 0.88 (*t*, *J* = 7.2 Hz, 9 H). Elemental anal. calcd. (found for $C_{84}H_{114}N_6O_3$: C, 80.33 (80.13); H, 9.15 (9.07); N, 6.69 (6.86).

2,4,6-Tris[*p*-(*p*′-*n*-pentyloxyphenyliminomethylene)phenoxy]-*s*-triazine (3h)

Use of the procedure above produced crude **3h** as an off-white powder (4.4 g, 98%). Recrystallization from AcMe afforded pure **3h** (2.99 g, 72%) as a white crystalline solid, mp 194.9–216.8°C (DSC). IR cm.$^{-1}$: 1550 (*s*, C=N), 1245 (*vs*, C—O—C). ^{1}H NMR ($CDCl_3$) δ: 8.43 (*s*, 3H, CH=N), 7.90 (*d*, *J* = 8 Hz, 6 H), 7.28 (*d*, *J* = 8 Hz, 6 H), 7.19 (*d*, *J* = 7 Hz, 6 H), 6.88 (*d*, *J* = 7 Hz, 6 H), 3.96 (*t*, *J* = 4 Hz, 6 H), 1.79 (*p*, *J* = 4 Hz, 6 H), 1.24 (*m*, 12 H), 0.97 (*t*, *J* = 4 Hz, 9 H). ^{13}C NMR δ: 173.5 (triazine C's), 157.9, 156.5, 153.3, 144.4, 134.6, 129.7, 122.2, 121.8, 114.9, 68.3, 29.01, 28.21, 22.47, 14.01. Elemental anal. calcd. (found) for $C_{57}H_{60}N_6O_6$: C, 74.00 (73.97); H, 6.53 (6.51); N, 9.08 (9.14).

2,4,6-Tris(*p*-*n*-octyloxycarbonylphenoxy)-*s*-triazine (7)

To a 500 mL round bottom flask fitted with a mechanical stirrer and water bath were added cyanuric chloride (9.2 g, 50 mmol) and HPLC grade AcMe

(100 mL) with stirring under N_2. To this solution was added a solution of *n*-octyl 4-hydroxybenzoate (38.0 g, 150 mmol) and NaOH (6.20 g, 155 mmol) in H_2O (100 mL) dropwise over a period of 15 min. A white precipitate appeared immediately and the suspension was stirred vigorously at RT for 3 h. The powdery solid was suction filtered and oven dried to give 39.7 g (96%) of a white solid. Subsequent recrystallization from AcMe and drying under vacuum afforded pure **7** (36.7 g, 89%) as white plates, mp (DSC) 101.3–117.2 °C. ^1H NMR δ: 8.06 (*d*, $J = 7$ Hz, 6 H), 7.24 (*d*, $J = 7$ Hz, 6 H), 4.32 (*t*, $J = 6$ Hz, 6 H), 1.73 (*p*, $J = 6$ Hz, 6 H), 1.4–1.3 (*m*, 10 H), 0.9 (*t*, $J = 6$ Hz, 9 H). ^{13}C NMR δ: 173.4, 165.6, 154.3, 131.6, 129.1, 121.8, 65.6, 32.0, 29.3, 29.0; 26.1, 22.9, 14.1. IR cm.$^{-1}$: 1715 (*vs*, C=O), 1550 (*s*, C=N), 1245 (*vs*, C—O—C stretch). Elemental anal. calcd. (found) for $C_{48}H_{63}N_3O_9$: C, 69.79 (69.89); H, 7.68 (7.72); N, 5.08 (5.11).

2,4,6-Tris(*p*-benzyloxyphenoxy)-*s*-triazine (9)

To a 500 mL round bottom flask with a mechanical stirrer and N_2 bubbler were added cyanuric chloride (18.4 g, 100 mmol) and HPLC grade AcMe (150 mL) under N_2 at RT. To this solution was added a solution of 4-benzyloxyphenol (**8**, 60.3 g, 310 mmol) and NaOH (12.4 g, 310 mmol) in H_2O (150 mL) dropwise over a period of 30 min. A white precipitate appeared immediately, and the mixture was allowed to stir for 3 h. The resulting white solid was suction filtered and dried in a vacuum oven under reduced pressure to give a white powder (54.7 g, 81%). Recrystallization from EtOAc afforded pure **9** as fine white needles, mp 161–163°C (51.9 g, 77%). ^1H NMR (DMSO-d_6) δ: 7.45–7.32 (*m*, 15 H), 7.16 (*d*, $J = 9$ Hz, 6 H), 7.04 (*d*, $J = 9$ Hz, 6 H), 5.09 (*s*, 6 H). IR cm.$^{-1}$: 1550 (*s*, —C=N), 1250 (*vs*, C—O—C). Elemental anal. calcd. (found) for $C_{42}H_{33}N_3O_6$: C, 74.61 (74.51); H, 4.92 (4.93); N, 6.21 (6.19).

2,4,6-Tris(*p*-hydroxyphenoxy)-*s*-triazine (10)

To a 250-mL round bottom flask fitted with a stirring bar and reflux condenser were added **9** (5.0 g, 7.4 mmol) and MeCN (100 mL). Compound **9** was only slightly soluble at room temperature, but fully soluble hot. At this time, trimethylsilyl chloride (4.8 g, 5.7 mL, 44 mmol) was added *via* syringe, followed immediately by NaI (6.7 g, 44 mmol). The mixture was heated at reflux with stirring for 10 h, during which time the mixture became dark red in color. A small aliquot was removed for TLC analysis; no spot due to starting material was present, and an intense spot remained at the baseline (3:1 hexanes/EtOAc). A large spot found at the top of the plate was assumed to be benzyl iodide, the byproduct. A light yellow precipitate (NaCl) was also observed in the reaction mixture. After cooling, the solvent was removed under reduced pressure to afford a red solid which was an extremely potent lachrymator. This solid was triturated with H_2O (150 mL) and the remaining yellow solid filtered. This solid was redissolved in AcMe and precipitated into hexanes to given an off-white powder. This powder was filtered and suspended in H_2O and heated at 100°C for 30 min to hydrolyze any remaining benzyl iodide. Suction filtration and drying (30 Torr @ 110°C) produced compound **10** as an off-white solid (2.56 g, 85%), mp > 350°C (lit.[23] mp 389–392°C). ^{1}H NMR (DMSO-d_6) δ: 9.50 (*s*, 3 H, —OH), 7.01 (*d*, $J = 7$ Hz, 6 H), 6.74 (*d*, $J = 7$ Hz, 6 H). IR cm.$^{-1}$: 3350 (*vs*, —OH stretch), 1540 (*s*, —C=N), 1240 (*vs*, —C—O—C).

2,4,6-Tris(*p*-cholesteryloxycarbonyloxyphenoxy)-*s*-triazine (11)

To a 100 mL 3-necked round bottom flask fitted with a N_2 inlet and stirring bar were added **10** (0.5 g, 1 mmol) and cholesteryl chloroformate (3.3 g, 7.4 mmol) and dry CH_2Cl_2 (50 mL). To this colorless solution was added 6 mL of dry pyridine and the solution immediately turned yellow. The mixture was allowed to stir for 25 h, at which time a white precipitate had formed. A small aliquot was taken for TLC analysis, and the absence of the triphenol spot indicated that the reaction was complete. The reaction mixture was extracted with distilled H_2O (3 x 50 mL) to remove pyridine and its HCl salt. The organic extracts were combined, dried (Na_2SO_4), and the solvent removed under vacuum to afford a white solid, 1.86 g. TLC (silica gel, 70% CH_2Cl_2/hexanes): two spots, $R_f = 0.92$, 0.41. The top spot was UV inactive and could only be seen by staining the plate with an isovanillin solution. PTLC (100 mg, silica gel, 70% CH_2Cl_2/hexanes eluent): two bands, the top band was not UV active. The top band afforded 35 mg of white crystalline solid, dicholesteryl carbonate, mp 174–177°C (lit.[21] mp 174–176°C). ^{1}H NMR δ: 5.41 (*d*, $J = 3$ Hz, 2 H, vinyl), 4.43 (*m*, 2 H, OCH), 2.41–0.64 (*m*, 86 H, other cholesteryl protons). ^{13}C NMR δ: 139.4, 122.8, 77.46, 56.67, 56.10, 49.96, 42.29, 39.69, 39.48, 38.04, 36.85, 36.52, 36.15, 35.76, 31.87, 31.82, 28.20, 27.99, 27.70, 24.25, 23.79, 22.79, 22.54, 21.00, 19.24, 18.68, 11.83. IR cm.$^{-1}$: 1740 (*s*, C=O), 1243 (*vs*, C—O—C). The second band ($R_f = 0.41$, UV active) afforded 46 mg of **11** as a transparent solid, mp 256°C (dec.); the total yield was calcualted to be 52%. ^{1}H NMR δ: 7.19 (*d*, $J = 7$ Hz, 6 H), 7.15 (*d*, $J = 7$ Hz, 6 H), 5.42 (*d*, $J = 2$ Hz, 3 H, vinyl), 4.59 (*m*, 3 H, OCH), 2.44 – 0.64 (*m*, 129 H, other cholesteryl protons). ^{13}C NMR δ: 173.5 (triazine), 152.7 (C=O), 148.8, 148.7, 139.0, 123.2, 122.3, 122.1, 78.97, 56.67, 56.15, 49.95, 42.30, 39.69, 39.49, 37.91, 36.82, 36.53, 36.17, 35.79, 31.88, 31.82, 28.21, 27.98, 27.60, 24.26, 23.84, 22.81, 22.55, 21.05, 19.27, 18.70, 11.85. IR cm.$^{-1}$: 1759 (*s*, C=O), 1570 (*m*, C=N), 1193 (*vs*, C—O—C). Elemental analysis calcd. (found) for $C_{105}H_{147}N_3O_{12}$: C, 76.74 (76.79); H, 9.01 (9.05); N, 2.55 (2.50).

Dimethyl 5-Hydroxyisophthalate (12a)

To a 250 mL, three-necked round bottom flask fitted with a stirring bar, heating mantle, and reflux condenser were added 5-hydroxyisophthalic acid (10.0 g, 54.9 mmol) and MeOH (150 mL). To this solution was added conc. H_2SO_4 (5 mL) carefully with stirring. This solution was heated slowly to reflux and allowed to stir under N_2 overnight. The reaction mixture was cooled to RT and slowly poured into a sat. aq. Na_2CO_3 with stirring. A white flocculent precipitate formed immediately, and this suspension was allowed to stir in a beaker for 30 min. The white solid was collected by vacuum filtration and dried in a vacuum oven at RT (30 Torr) for 3 h to give 10.66 g (96%) of crude **12a**, mp 162 – 168°C. Recrystallization from MeOH gave pure **12a** as white flakes, 9.98 g (90%), mp 166 – 168°C (lit [24] mp 162 – 163.5°C). ^{1}H NMR δ: 8.22 (*t*, 1 H, *J* = 1.6 Hz), 7.69 (*d*, 2 H, *J* = 1.6 Hz), 6.24 (*s*, 1 H, OH), 3.94 (*s*, 6 H, CH_3). IR cm.$^{-1}$: 3360 (*vs*, OH), 1703 (*vs*, C=O), 1250, 1260(*vs*, C—O—C).

Di-*n*-butyl 5-Hydroxyisophthalate (12b)

Application of the above procedure using *n*-BuOH gave 14.42 g (95%) of crude **12b**. Recrystallization from hexanes gave colorless needles, 14.12 g (93%), mp 66 – 68°C (lit.[25] mp 65.3 – 66.6°C). ^{1}H NMR δ: 8.24 (*t*, 1 H, *J* = 2 Hz), 7.78 (*d*, 2 H, *J* = 2 Hz), 6.39 (*s*, 1 H, OH), 4.35 (*t*, 4 H, *J* = 4.8 Hz), 1.78 (*p*, 4 H, *J* = 4.8 Hz), 1.43 (*sextet*, 4 H, *J* = 4.8 Hz), 0.99 (*t*, 6 H, *J* = 4.8 Hz). IR cm.$^{-1}$: 3420 (*vs*., OH), 1710 (*vs*., C=O), 1250, 1310 (*vs*., C—O—C).

2,4,6-Tris[3′,5′-bis(methoxycarbonyl)phenoxy]-*s*-triazine (13a)

To a 500 mL three-necked round bottom flask fitted with a stirring bar, heating mantle, N_2 inlet, dropping funnel, and a Dean-Stark condenser were added **12a** (5.00 g, 23.7 mmol), finely ground anhyd. K_2CO_3 (3.76 g, 35 mmol) and benzene (200 mL), but the diester was insoluble, so *N,N*-dimethylformamide (DMF, 50 mL) was added and the ester dissolved readily. The suspension was heated with stirring to reflux (85°C), and the H_2O of reaction (~1 mL) was collected in the Dean-Stark trap over a period of 6 h. At this time, a solution of cyanuric chloride (1.45 g, 7.9 mmol) in benzene (10 mL) was added from the dropping funnel over a period of 30 min. The refluxing slurry was allowed to stir overnight at 85°C. After cooling, the excess K_2CO_3 was collected by vacuum filtration and washed twice with hot EtOAc (2 × 20 mL). The organic filtrate was then extracted with 10% K_2CO_3 (3 × 75 mL) and then distilled H_2O (50 mL). The organic layer was dried (Na_2SO_4) and concentrated on a rotary evaporator to afford a white solid. This solid was collected and dried in a vacuum oven overnight at RT to give 5.26 g (94%) of crude **13a**, mp 162–179°C. Recrystallization from EtOH/acetone gave pure **13a** as white flakes, 5.01 g (90%), mp 167–184°C. ^{1}H NMR ($CDCl_3$) δ: 8.26 (*t*, 3 H, $J = 2$ Hz), 7.78 (*d*, 6 H, $J = 2$ Hz), 3.92 (*s*, 18 H, CH_3). ^{13}C NMR δ: 193.8, 173.6, 151.4, 132.1, 128.3, 126.6, 52.1. IR cm.$^{-1}$: 1728 (*vs.*, C=O), 1255 (*vs.*, C—O—C). Elemental analysis calcd. (found) for $C_{33}H_{27}N_3O_{15}$: C, 56.17 (56.39); H, 3.85 (4.02); N, 5.95 (6.63).

2,4,6-Tri[3′5′-bis(*n*-butoxycarbonyl)phenoxy]-*s*-triazine (13b)

Application of the above procedure to **12b** gave 7.59 g (100%) of crude **13b**. Recrystallization from hexanes gave pure **13b** as transparent flakes, 7.49 g (99%), mp 136–138°C. ^{1}H NMR δ: 8.53 (*t*, 3 H, $J = 2$ Hz), 7.92 (*d*, 6 H, $J = 2$ Hz), 4.35 (*t*, 12 H, $J = 5$ Hz), 1.74 (*p*, 12 H, $J = 5$ Hz), 1.47 (*sx*, 12 H, $J = 5$ Hz), 0.98 (*t*, 18 H, $J = 5$ Hz). IR cm.$^{-1}$: 1710 (*vs.*, C=O), 1255, 1305 (*vs.*, C—O—C). Elemental analysis calcd. (found) for $C_{51}H_{63}N_3O_{15}$: C, 63.93 (63.69); H, 6.62 (6.60); N, 4.38 (4.28).

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