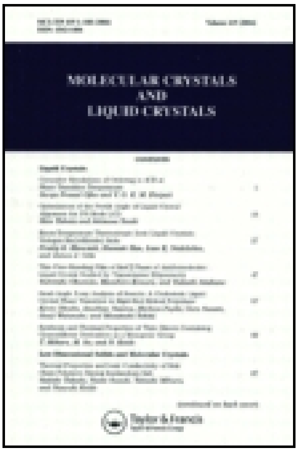

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Synthesis and Mesomorphic Properties of Ferroelectric Liquid Crystals Bearing 6-Phenyl-1,2,4-Triazine Rings

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Synthesis and Mesomorphic Properties of Ferroelectric Liquid Crystals Bearing 6-Phenyl-1,2,4-Triazine Rings

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Seventeen homologs of chiral 6-phenyl-1,2,4-triazines were synthesized and their mesomorphic properties were evaluated with a DSC and a polarizing microscope. It is found that compounds in this series show a strong tendency to generate the chiral smectic C (Sc*) phase which exists in a wide temperature range from about 30°C to 90°C. By comparing the thermal stability of the mesophase (smectic phase) of triazine derivative with that of analogous 5-phenylpyrimidine and 2-phenylpyridazine derivatives, it is clear that the dipole moment perpendicular to the molecule of the core part plays an important role in the thermal stability of the mesophase (smectic phase). Moreover, the electro-optical properties for some compounds were also measured and the results indicate that the switching times (τ's) are relatively fast, though the spontaneous polarizations (Ps's) are very small.

Keywords: ferroelectric liquid crystal, phase transition, triazine

INTRODUCTION

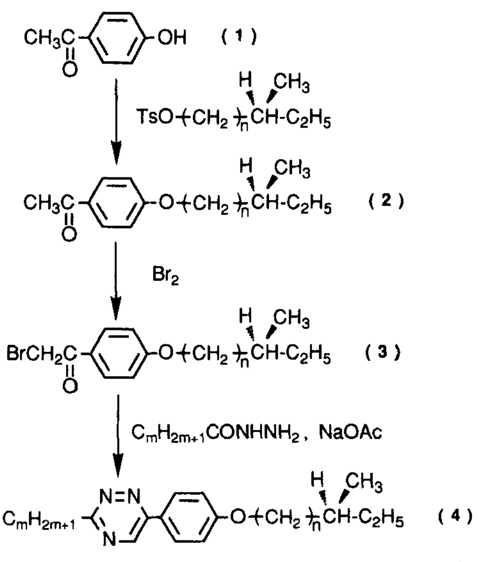
Since the discovery of ferroelectricity in the chiral smectic C (Sc*) phase by R. Meyer in 1975[1] and the proposal of electro-optical devices using ferroelectric liquid crystals by Clark and Lagerwall in 1980,[2] extensive studies have been done on ferroelectric liquid crystal materials and their applications. As pointed out by Goodby, ferroelectric liquid crystals require at least two aromatic rings in the core and two terminal chains at the end of the core, one of which contains at least one chiral group.[3] Various ferroelectric liquid crystals having a heterocycle such as pyrimidine,[4] pyridine,[5] and pyridazine[6] in the core part have been synthesized and their properties were studied. They are of interest because of greater possibilities in the variations of direction and magnitude of their dipole moments and coplanarities and sizes of the core part. About 1,2,4-triazine, however, very little has been reported. There is only one report by H. Zaschke,[7] as far as we know. They synthesized the homologous series of 3,6-diphenyl-1,2,4-triazine derivatives and showed that those compounds have a strong tendency to show a smectic C phase that exists over a wide temperature range from about 80°C to 210°C. We felt that by decreasing the length of the core part and introducing a chiral center into the molecule, we might obtain liquid crystal materials which have a chiral smectic C phase which exists at a lower temperature range, including room temperature, than those of 3,6-diphenyl-1,2,4-triazines. Therefore, we synthesized a series of compounds bearing 6-phenyl-1,2,4-triazine rings as a core and studied their ferroelectric liquid crystal behavior.

SYNTHESIS

The compounds studied were prepared as outlined in Scheme 1. Acetophenone was alkylated with tosylate of corresponding alcohol, followed by bromination with bromine to afford 4′-alkoxy-2-bromo acetophenone (**3**). Construction of the 1,2,4-triazine ring was achieved by treatment with 2 equivalent moles of alkanoic hydrazide in presence with sodium acetate in 15–33% yield.[8] The final products were purified by column chromatography on silica-gel using hexane and ether as the eluent, followed by recrystallization from ethanol.

RESULTS AND DISCUSSION

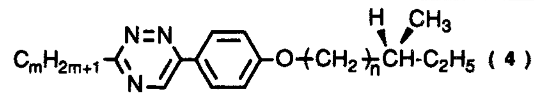
Melting and transition temperatures were measured with a polarizing microscope equipped with a heating stage and a differential scanning calorimeter (DSC). The



SCHEME 1 Synthesis route of 6-phenyl-1,2,4-triazine derivatives.

TABLE I

Phase transition temperatures of triazine derivatives


(4)

Compound	m	n	Cr		Sc*		SA		I
4a	2	5	·	33.0	—		·	85.4	·
4b	3	5	·	34.5	—		·	93.4	·
4c	4	3	·	42.5	·	66.2	·	77.3	·
4d	4	5	·	29.8	·	57.1	·	85.0	·
4e	5	3	·	50.5	·	76.5	·	82.0	·
4f	5	5	·	44.0	·	76.5	·	89.5	·
4g	6	3	·	49.0	·	75.1	·	80.1	·
4h	6	4	·	34.5	·	70.7	·	78.1	·
4i	6	5	·	37.0	·	79.3	·	85.7	·
4j	7	3	·	55.0	·	77.1	·	82.0	·
4k	7	5	·	50.5	·	86.9	·	88.8	·
4l	8	1	·	57.8	—		·	53.8	·
4m	8	3	·	48.0	·	72.1	·	76.9	·
4n	8	4	·	52.5	·	70.0	·	73.0	·
4o	8	5	·	44.5	·	81.2	·	84.6	·
4p	9	5	·	59.5	·	86.0	—		·
4q	10	5	·	51.5	·	81.2	—		·

Phase transition Temperature (℃)[a]

a) Cr: crystalline solid, Sc*: chiral smectic C phase, SA: smectic A phase, I: isotropic liquid phase.

identity of the mesophases was confirmed by examining the texture of a thin sample sandwiched between glass slides.[9] The transition temperatures of homologous series 4 are given in Table I. The phase transition temperatures in relation to the number of carbon atoms in the terminal chain are shown in Figures 1 and 2.

Materials in this series which showed mesomorphic behavior had the mesophology of I-SA-Sc*-Cr (I: Isotropic liquid, SA: Smectic A phase, Sc*: Chiral smectic C phase, Cr: Crystalline solid) and the chiral nematic (N*) phase and high-ordered smectic phases were not observed in any homologs. As shown in Figures 1 and 2, a pronounced odd-even effect,[10] ubiquitous in liquid crystalline homologous series, was observed. In the case of 6-methyloctyloxy derivatives (Figure 1), the thermal stability of mesophases are not affected so much by the length of an alkyl

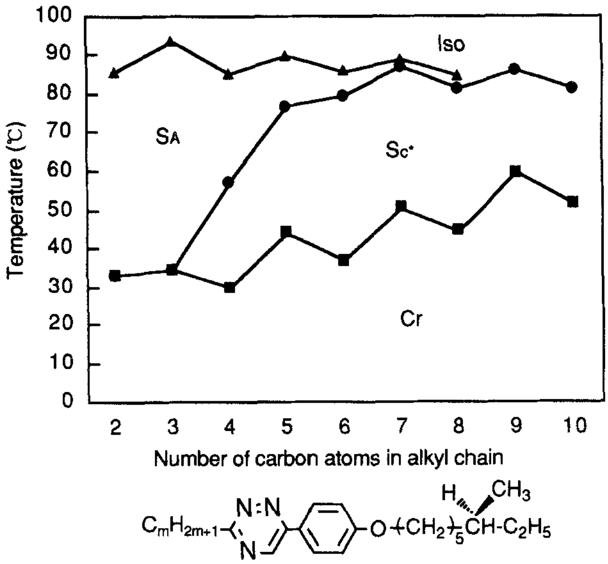


FIGURE 1 The phase transition temperatures in relation to the number of carbon atoms in the terminal chain for (*S*)-3-Alkyl-6-{4-(6-methyloctyloxy)phenyl}-1,2,4-triazine.

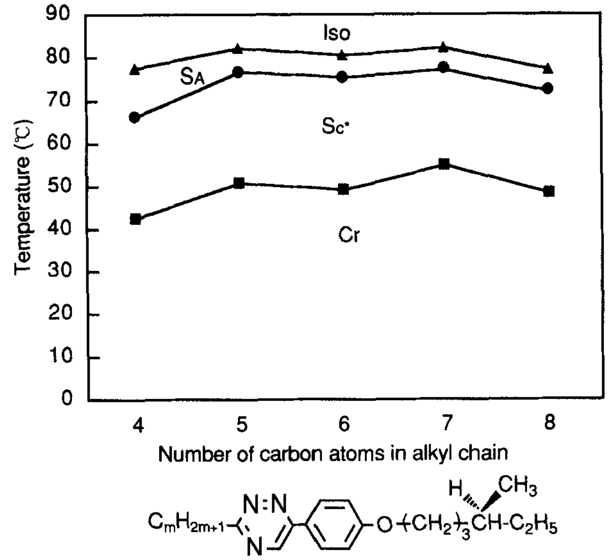
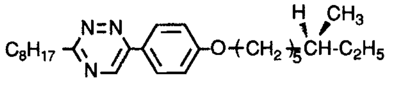


FIGURE 2 The phase transition temperatures in relation to the number of carbon atoms in the terminal chain for (*S*)-3-Alkyl-6-{4-(4-methylhexyloxy)phenyl}-1,2,4-triazine.

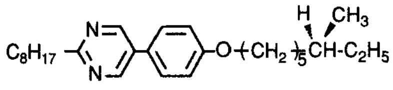
chain attached to the triazine ring. The temperature range of the SA phase narrows with increasing the length of the terminal alkyl chain attached to the triazine ring and the SA phase disappears in the compound having a terminal alkyl chain with nine carbon atoms or more. On the other hand, the stability of the Sc* phase

TABLE II

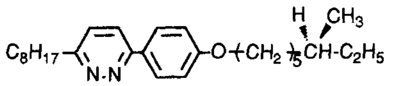
Phase transition temperatures for 6-phenyl-1,2,4-triazine, 5-phenylpyrimidine and 2-phenylpyridazine derivative



Cr 44.5 Sc* 81.2 Sa 84.6 Iso



Cr 40.0 Sc* 48.0 Sa 68.0 Iso



Cr 98.0 (Sx 80.0) Sc* 117.0 Iso

TABLE III

Spontaneous polarizations (Ps), optical response times (τ) and tilt angles (θ) of compounds **4i** and **4o**[a]

Compound	Ps (nC/cm^2)	τ (μsec)	θ (deg.)
4i	<0.1	600	14.0
4o	<0.1	480	17.5

a) Ps , τ and θ were measured on 2 μm thick cells at a temperature 10°C below the upper limit of the Sc* phase.

increases with increasing the length of the terminal alkyl chain from two carbon atoms to six carbon atoms and decreases with increasing the length of the terminal alkyl chain from six carbon atoms to ten carbon atoms. So, the broadest temperature range of the Sc* phase is seen for compound **4i** with six carbon atoms in the terminal alkyl chain. In the case of 4-methylhexyloxy derivatives (Figure 2), both the temperature ranges of the Sa phase and the Sc* phase are not affected by the length of an alkyl chain attached to the triazine ring. It is clear that these 6-phenyl-1,2,4-triazine derivatives have a strong tendency to generate the Sc* phase which exists in a temperature range from about 30°C to 90°C and these temperature ranges are lower than those of 3,6-diphenyl-1,2,4-triazine derivatives by 50–120°C, as we expected. Next, we compared the liquid crystalline behavior of compound **4o** with those of corresponding 5-phenylpyrimidine[4a] and 2-phenylpyridazine[5b] derivatives (Table II). The thermal stability of the mesophase (smectic phase) of triazine (**4o**) is higher than that of the 5-phenyl pyrimidine derivative and is lower than that of the 2-phenylpyridazine derivative. On the other hand, the magnitude of the dipole moment perpendicular to the molecule decreases in the order of 2-phenylpyridazine > 6-phenyl-1,2,4-triazine > 5-phenylpyrimidine. This must imply that the dipole moment perpendicular to the molecule of the core part plays an important role in the stability of the mesophase (smectic phase), that is, the thermal stability of the mesophase (smectic phase) increases with increasing the dipole moment perpendicular to the molecule of the core part.[11]

For the components **4i** and **4o**, the spontaneous polarization (Ps's), optical response times (τ's) and tilt angles (θ) were measured on 2 μm thick cells at a temperature 10°C below the upper limit of the Sc* phase. The results are shown in Table III. Spontaneous polarization was obtained by the triangular wave method (± 10 V, 200 Hz).[12] Optical response times were obtained by applying a rectangular wave (± 10 V, 200 Hz) and were defined as the time difference between voltage reversal and a 90% change in optical transmission. The tile angles (θ) were measured from the scale on the microscope turntable between the two extreme optical states, corresponding to the two polarities of a DC field applied across the sample cell. The Ps values were very small, in agreement with the general rule that if the dipole is remote from the chiral center, the Ps values will be small.[13] Optical response times (τ's), however were relatively fast. As the response time (τ) can be represented by $\tau = \eta/(Ps \times E)$, where η is the rotational viscosity, Ps is the spontaneous polarization and E is an applied electric field, the above result suggests that the rotational viscosities of these compounds are relatively low.

CONCLUSION

Chiral 6-phenyl-1,2,4-triazine derivatives have a strong tendency to generate the Sc* phase which exists at a low temperature range from about 30°C to 90°C. By comparing the thermal stability of the mesophase (smectic phase) of triazine derivatives with those of analogous 5-phenyl pyrimidine and 2-phenyl pyridazine derivatives, it is found that the dipole moment perpendicular to the molecule of the core part plays an important role in the stability of the mesophase (smectic phase). Though the Ps values were very small, optical response times (τ's) were relatively fast because of the low rotational viscosity of the triazine ring.

EXPERIMENTAL

IR, ^{1}H NMR and mass spectra were recorded on a Shimadzu IR-408, Varian EM-360 and Hitachi M-80, respectively, under standard conditions. Final products were purified by column chromatography on silica-gel followed by recrystallization from ethanol. The phase transition temperatures were determined using a Rigaku Denki DSC-8230 apparatus and texture observations were made using a Nikon XTP-II polarizing microscope in conjunction with a Mettler FP-82 hot stage and FP-80 control unit. A typical procedure for the synthesis of triazine derivative is described for **4o**. Other compounds were prepared according to a method similar to **4o**.

(*S*)-4′-(6-methyloctyloxy)acetophenone (**2**: R_1 = (*S*)-6-methyloctyloxy). To an ice cooled suspension of sodium hydride (60% assay in mineral oil 1.51 g, 37.7 mmol) in dry DMF (30 ml) was added dropwise a solution of 4-hydroxyacetophenone (4.66 g, 34.2 mmol)in dry DMF (15 ml). After stirring for half an hour at room temperature, (*S*)-6-methyloctyl-*p*-toluenesulfonate (10.22 g, 34.2 mmol) was added, and then heated at 60°C for 5 h. After being cooled to room temperature, the reaction mixture was poured into cold water and extracted several times with ether. The combined organic layers were washed with water and dried over anhydrous magnesium sulfate. The solvent was evaporated and the residue was purified by column chromatography on silica-gel with hexane-ether as eluent to yield (*S*)-4′-(6-methyloctyloxy)acetophenone (6.78 g, 76.5%) as an oil. IR (film) 1673, 1600, 1570 cm^{-1}; NMR ($CDCl_3$) δ = 0.70–2.00 (17H, m), 2.55 (3H, s), 4.02 (2H, t, J = 7 Hz), 6.93 (2H, d, J = 9 Hz), 7.95 (2H, d, J = 9 Hz); Mass: m/z 262 (m$^+$).

(*S*)-2-bromo-4′-(6-methyloctyloxy)acetophenone (**3**: R_1 = (*S*)-6-methyloctyloxy). To an ice-cooled solution of (*S*)-4′-(6-methyloctyloxy)acetophenone (6.82 g, 26.0 mmol) in ether (30 ml) and dioxane (30 ml) was added dropwise bromine (4.57 g, 28.6 mmol). After stirring for 2 h at the same temperature, stirring was continued for an additional 1 h at room temperature. The reaction mixture was poured into cold water and extracted several times with ether. The combined ethereal extracts were washed successively with aqueous $NaHCO_3$ and water, and dried over anhydrous magnesium sulfate. The solvent was removed and the residue was purified by column chromatography on silica-gel with hexane-ether as eluent to yield (*S*)-2-bromo-4′-(6-methyloctyloxy) acetophenone (6.15 g, 69.3%) as an oil.

IR (Nujol) 1670, 1595, 1570 cm^{-1}; NMR ($CDCl_3$) δ = 0.71–2.00 (17H, m), 4.08 (2H, t, J = 7 Hz), 4.22 (2H, s), 6.96 (2H, d, J = 9 Hz), 8.02 (2H, d, J = 9 Hz); Mass: m/z 340 (m$^+$).

(*S*)-6-(6-methyloctyloxy)phenyl-3-octyl 1,2,4-triazine (**4o**). A solution of (*S*)-2-bromo-4′-(6-methyloctyloxy)acetophenone (1.71 g, 5.0 mmol), octanoic hydrazide (1.84 g, 10.0 mmol) and sodium acetate (0.41 g, 5.0 mmol) in ethanol (15 ml) was heated under reflux for 2 h under nitrogen atmosphere. After cooling to room temperature, the reaction mixture was poured into cold water and extracted with dichloromethane. The combined organic layers were washed with water and dried over anhydrous magnesium sulfate. The solvent was removed and the residue was purified by column chromatography on silica-gel with hexane-ether as eluent followed by recrystallization from ethanol to yield (*S*)-6-(6-methyloctyloxy)phenyl-3-octyl 1,2,4-triazine (0.32 g, 15.5%). IR (Nujol) 1602, 1578, 1510 cm^{-1}; NMR ($CDCl_3$) δ = 0.64–2.06 (32H, m), 3.15 (2H, t, J = 7 Hz), 4.05 (2H, t, J = 7 Hz), 7.06 (2H, d, J = 8 Hz), 8.08 (2H, d, J = 8 Hz), 8.94 (1H, s); Mass: m/z 411 (m$^+$); $[\alpha]_D$ = +4.20° (c = 1.0, $CHCl_3$); Found: C, 76.02; H, 9.95; N, 10.30%. Calcd for $C_{26}N_{41}N_3O$: C, 75.86; H, 10.03; N, 10.20%.

(*S*)-3-ethyl-6-(6-methyloctyloxy)phenyl-1,2,4-triazine (**4a**). IR (Nujol) 1600, 1510 cm^{-1}; NMR (CDC13) δ: 0.69–1.98 (20H, m), 3.19 (2H, t, J = 7 Hz), 4.06 (2H, t, J = 7 Hz), 7.07 (2H, d, J = 8 Hz), 8.05 (2H, d, J = 8 Hz), 8.91 (1H, s); Mass: m/z 327 (m$^+$); $[\alpha]_D$ = +5.67° (c = 1.0, $CHCl_3$); Found: C, 73.47; H, 8.78; N, 12.66%. Calcd for $C_{20}H_{29}N_3O$: C, 73.35; H, 8.93; N, 12.83%.

(*S*)-6-(6-methyloctyloxy)phenyl-3-propyl-1,2,4-triazine (**4b**). IR (Nujol) 1600, 1510 cm^{-1}; NMR (CDCl3) δ = 0.70–2.15 (22H, m), 3.14 (2H, t, *J* = 7 Hz), 4.05 (2H, t, *J* = 7 Hz), 7.06 (2H, d, *J* = 8 Hz), 8.08 (2H, d, *J* = 8 Hz), 8.93 (1H, s); Mass: m/z 341 (m$^+$); $[\alpha]_D$ = +5.10° (*c* = 1.0, $CHCl_3$); Found: C, 74.17; H, 8.87; N, 12.20%. Calcd for $C_{21}H_{31}N_3O$: C, 73.86; H, 9.15; N, 12.31%.

(*S*)-3-butyl-6-(4-methylhexyloxy)phenyl-1,2,4-triazine (**4c**). IR (Nujol) 1602, 1570, 1510 cm^{-1}; NMR ($CDCl_3$) δ = 0.76–2.10 (32H, m), 3.16 (2H, t, *J* = 7 Hz), 4.01 (2H, t, *J* = 7 Hz), 7.05 (2H, d, *J* = 8 Hz), 8.06 (2H, d, *J* = 8 Hz), 8.90 (1H, s); Mass: m/z 327 (m$^+$); $[\alpha]_D$ = +7.03° (*c* = 1.0, $CHCl_3$); Found: C, 73.19; H, 8.98; N, 12.57%. Calcd for $C_{20}H_{29}N_3O$: C, 73.35; H, 8.93; N, 12.83%.

(*S*)-3-butyl-6-(6-methyloctyloxy)phenyl-1,2,4-triazine (**4d**). IR (Nujol) 1603, 1575 cm^{-1}; NMR ($CDCl_3$) δ = 0.75–2.10 (24H, m), 3.18 (2H, t, *J* = 7 Hz), 4.05 (2H, t, *J* = 7 Hz), 7.08 (2H, d, *J* = 8 Hz), 8.10 (2H, d, *J* = 8 Hz), 8.95 (1H, s); Mass: m/z 355 (m$^+$); $[\alpha]_D$ = +5.23° (*c* = 1.0, $CHCl_3$); Found: C, 74.44; H, 9.38; N, 11.73%. Calcd for $C_{22}H_{33}N_3O$: C, 74.32; H, 9.36; N, 11.82%.

(*S*)-6-(4-methylhexyloxy)phenyl-3-pentyl-1,2,4-triazine (**4e**). IR (Nujol) 1600, 1570, 1510 cm^{-1}; NMR ($CDCl_3$) δ = 0.70–2.20 (22H, m), 3.16 (2H, t, *J* = 7 Hz), 4.04 (2H, t, *J* = 7 Hz), 7.06 (2H, d, *J* = 8 Hz), 8.07 (2H, d, *J* = 8 Hz), 8.94 (1H, s); Mass: m/z 341 (m$^+$); $[\alpha]_D$ = +6.23° (*c* = 1.0, $CHCl_3$); Found: C, 73.58; H, 9.17; N, 12.27%. Calcd for $C_{21}H_{31}N_3O$: C, 73.86; H, 9.15; N, 12.31%.

(*S*)-6-(6-methyloctyloxy)phenyl-3-pentyl-1,2,4-triazine (**4f**). IR (Nujol) 1600, 1570, 1508 cm^{-1}; NMR ($CDCl_3$) δ = 0.70–2.10 (26H, m), 3.13 (2H, t, *J* = 7 Hz), 4.03 (2H, t, *J* = 7 Hz), 7.04 (2H, d, *J* = 8 Hz), 8.07 (2H, d, *J* = 8 Hz), 8.92 (1H, s); Mass: m/z 369 (m$^+$); $[\alpha]_D$ = +4.43° (*c* = 1.0, $CHCl_3$); Found: C, 74.58; H, 9.68; N, 11.10%. Calcd for $C_{23}H_{35}N_3O$: C, 74.75; H, 9.55; N, 11.37%.

(*S*)-3-hexyl-6-(4-methylhexyloxy)phenyl-1,2,4-triazine (**4g**). IR (Nujol) 1600, 1575, 1510 cm^{-1}; NMR ($CDCl_3$) δ = 0.70–2.20 (24H, m), 3.16 (2H, t, *J* = 7 Hz), 4.06 (2H, t, *J* = 7 Hz), 7.07 (2H, d, *J* = 8 Hz), 8.08 (2H, d, *J* = 8 Hz), 8.95 (1H, s); Mass: m/z 355 (m$^+$); $[\alpha]_D$ = +5.80° (*c* = 1.0, $CHCl_3$); Found: C, 74.06; H, 9.31; N, 11.85%. Calcd for $C_{22}H_{33}N_3O$: C, 74.32; H, 9.36; N, 11.82%.

(*S*)-3-hexyl-6-(5-methylheptyloxy)phenyl-1,2,4-triazine (**4h**). IR (Nujol) 1600, 1570, 1508 cm^{-1}; NMR ($CDCl_3$) δ = 0.70–2.10 (26H, m), 3.13 (2H, t, *J* = 7 Hz), 4.03 (2H, t, *J* = 7 Hz), 7.04 (2H, d, *J* = 8 Hz), 8.07 (2H, d, *J* = 8 Hz), 8.92 (1H, s); Mass: m/z 369 (m$^+$); $[\alpha]_D$ = +4.80° (*c* = 1.0, $CHCl_3$); Found: C, 74.70; H, 9.37; N, 11.32%. Calcd for $C_{23}H_{35}N_3O$: C, 74.75; H, 9.55; N, 11.37%.

(*S*)-3-hexyl-6-(6-methyloctyloxy)phenyl-1,2,4-triazine (**4i**). IR (Nujol) 1600, 1570, 1510 cm^{-1}; NMR ($CDCl_3$) δ = 0.72–2.12 (2H, m), 3.17 (2H, t, *J* = 7 Hz), 4.07 (2H, t, *J* = 7 Hz), 7.07 (2H, d, *J* = 8 Hz), 8.10 (2H, d, *J* = 8 Hz), 8.92 (1H, s); Mass: m/z 383 (m$^+$); $[\alpha]_D$ = +4.63° (*c* = 1.00, $CHCl_3$); Found: C, 75.19; H, 9.50; N, 10.74%. Calcd for $C_{24}H_{37}N_3O$: C, 75.15; H, 9.72; N, 10.96%.

(*S*)-3-heptyl-6-(4-methylhexyloxy)phenyl-1,2,4-triazine (**4j**). IR (Nujol) 1600, 1570, 1508 cm^{-1}; NMR ($CDCl_3$) δ = 0.70–2.10 (32H, m), 3.13 (2H, t, *J* = 7 Hz), 4.03

(2H, t, $J = 7$ Hz), 7.04 (2H, d, $J = 8$ Hz), 8.07 (2H, d, $J = 8$ Hz), 8.92 (1H, s); Mass: m/z 369 (m^+); $[\alpha]_D = +5.66°$ ($c = 1.0$, $CHCl_3$); Found: C, 74.85; H, 9.63; N, 11.28%. Calcd for $C_{23}H_{35}N_3O$: C, 74.75; H, 9.55; N, 11.37%.

(*S*)-3-heptyl-6-(6-methyloctyloxy)phenyl-1,2,4-triazine (**4k**). IR (Nujol) 1602, 1573, 1510 cm^{-1}; NMR ($CDCl_3$) $\delta = 0.70–2.10$ (30H, m), 3.13 (2H, t, $J = 7$ Hz), 4.04 (2H, t, $J = 7$ Hz), 7.06 (2H, d, $J = 8$ Hz), 8.07 (2H, d, $J = 8$ Hz), 8.90 (1H, s); Mass: m/z 411 (m^+); $[\alpha]_D = +4.27°$ ($c = 1.0$, $CHCl_3$); Found: C, 75.60; H, 9.67; N, 10.64%. Calcd for $C_{25}H_{39}N_3O$: C, 75.52; H, 9.89; N, 10.57%.

(*S*)-6-(2-methylbutyloxy)phenyl-3-octyl-1,2,4-triazine (**4l**). IR (Nujol) 1603, 1572, 1510 cm^{-1}; NMR ($CDCl_3$) $\delta = 0.67–2.10$ (24H, m), 3.15 (2H, t, $J = 7$ Hz), 3.68–4.16 (2H, m), 7.04 (2H, d, $J = 8$ Hz), 8.07 (2H, d, $J = 8$ Hz), 8.92 (1H, s); Mass: m/z 355 (m^+); $[\alpha]_D = +6.80°$ ($c = 1.0$, $CHCl_3$); Found: C, 74.39; H, 9.23; N, 11.98%. Calcd for $C_{22}H_{33}N_3O$: C, 74.32; H, 9.36; N, 11.82%.

(*S*)-6-(4-methylhexyloxy)phenyl-3-octyl-1,2,4-triazine (**4m**). IR (Nujol) 1600, 1570, 1510 cm^{-1}; NMR ($CDCl_3$) $\delta = 0.65–2.10$ (28H, m), 3.14 (2H, t, $J = 7$ Hz), 4.04 (2H, t, $J = 7$ Hz), 7.05 (2H, d, $J = 8$ Hz), 8.07 (2H, d, $J = 8$ Hz), 8.92 (1H, s); Mass: m/z 383 (m^+); $[\alpha]_D = +5.37°$ ($c = 1.0$, $CHCl_3$); Found: C, 74.69; H, 9.77; N, 10.75%. Calcd for $C_{24}H_{37}N_3O$: C, 75.15; H, 9.72; N, 10.75%.

(*S*)-6-(5-methylheptyloxy)phenyl-3-octyl-1,2,4-triazine (**4n**). IR (Nujol) 1600, 1570, 1508 cm^{-1}; NMR ($CDCl_3$) $\delta = 0.70–2.10$ (30H, m), 3.13 (2H, t, $J = 7$ Hz), 4.03 (2H, t, $J = 7$ Hz), 7.04 (2H, d, $J = 9$ Hz), 8.07 (2H, d, $J = 9$ Hz), 8.92 (1H, s); Mass: m/z 397 (m^+); $[\alpha]_D = +4.60°$ ($c = 1.0$, $CHCl_3$); Found: C, 75.22; H, 9.58; N, 10.28%. Calcd for $C_{25}N_{39}N_3O$: C, 75.52; H, 9.89; N, 10.57%.

(*S*)-6-(6-methyloctyloxy)phenyl-3-nonyl-1,2,4-triazine (**4p**). IR (Nujol) 1600, 1505 cm^{-1}; NMR ($CDCl_3$) $\delta = 0.65–2.10$ (34H, m), 3.13 (2H, t, $J = 7$ Hz), 4.04 (2H, t, $J = 7$ Hz), 7.06 (2H, d, $J = 8$ Hz), 8.06 (2H, d, $J = 8$ Hz), 8.94 (1H, s); Mass: m/z 425 (m^+); $[\alpha]_D = + 3.60°$ ($c = 1.0$, $CHCl_3$); Found: C, 75.84; H, 10.18; N, 10.16%. Calcd for $C_{27}H_{43}N_3O$: C, 76.18; H, 10.18; N, 9.87%.

(*S*)-3-decyl-6-(6-methyloctyloxy)phenyl-1,2,4-triazine (**4q**). IR (Nujol) 1600, 1570, 1505 cm^{-1}; NMR ($CDCl_3$) $\delta = 0.70–2.10$ (36H, m), 3.16 (2H, t, $J = 7$ Hz), 4.02 (2H, t, $J = 7$ Hz), 7.04 (2H, d, $J = 8$ Hz), 8.03 (2H, d, $J = 8$ Hz), 9.01 (1H, s); Mass: m/z 439 (m^+); $[\alpha]_D = 4.08°$ ($c = 1.0$, $CHCl_3$); Found: C, 76.11; H, 10.36; N, 9.29%. Calcd for $C_{28}H_{45}N_3O$: C, 76.49; H, 10.32; N, 9.56%.

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