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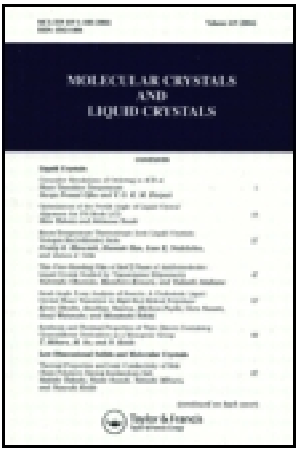

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Liquid Crystalline Symmetrical 3,6-Diaryl-1,2,4,5-Tetrazines

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Liquid Crystalline Symmetrical 3,6-Diaryl-1,2,4,5-Tetrazines

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A new series of symmetrical 3,6-diphenyl-1,2,4,5-tetrazines with four alkoxy tails were synthesized along with new examples with two alkoxy tails. Mesogenic properties were studied by differential scanning calorimetry and polarizing optical microscopy. The influence of the number and length of alkoxy chains attached to the 3,6-diphenyl-1,2,4,5-tetrazine core is discussed. Compared with the two-tailed tetrazines, ***6*** *the four-tailed liquid crystalline tetrazines,* ***5e–g*** *possess lower smectic-C phase transitions, and clearing point temperatures.*

Keywords: Liquid crystals; smectic phase; Tetrazines; π-stacking

1. Introduction

Heterocyclic liquid crystals possess characteristic structural and electronic properties that influence the type of mesophase and the phase transition temperatures [1, 2]. For example, many known heterocyclic liquid crystals are based on 1,4-terphenyl structures in which one or more benzene rings are replaced by heterocycles [1, 3]. Our X-ray crystallographic study of 1,4-bis-(4-dodecyloxyphenyl)-1,2,4,5-tetrazine, ***6k***, revealed a high degree of coplanarity of the central three-ring system. Moreover, the reported computational simulation study of 3,6-bis-(4-butylphenyl)-1,2,4,5-tetrazine showed that the molecule is characterized by adequate conformational rigidity of the central three-ring aromatic fragment [1]. The calculations revealed that the core diphenyltetrazine fragment in the temperature range 0–500 K remains almost unchanged. A 3,6-diphenyltetrazine-ring system can be flat because steric interactions among the rings are relieved (since there are no substituent atoms on the tetrazine ring, unlike the situation in p-terphenyl) and conjugation of the aromatic π-systems favors a coplanar arrangement of the aromatic rings.

Tetrazines have been reported as nematic LC components in guest-host-type optoelectronic displays [4, 5], components in field-induced color switching displays [6], and smectic-C LC in electrooptical display devices [7]. A literature survey of tetrazines revealed

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that they possess nematic and/or smectic liquid crystalline phases, a high inherent color (red or violet), and a marked dichroism in the visible area [4–7]. Studies of a number of 3,6-bis(alkoxyphenyl)tetrazines (***6***, R′ = C-1 to C-10) showed that the type of mesogenic phases depended on the alkoxy chain length. Molecules with C-1 through C-5 alkoxy chains possess nematic phases while molecules with C-6 through C-9 chains, possess both smectic-C and nematic phases. The C-10 derivative has only a smectic-C mesogenic phase [8]. However, their relatively high phase transition temperatures (smectic-C phase transition temperatures range from 163°C to 111°C, Table 3) and poor solubility are undesirable for practical uses. Thus, this work aims to improve the physical and mesogenic properties of 3,6-diaryltetrazines by installing four alkoxy groups at positions 3 and 4 in the terminal aryl groups with variable alkoxy chain lengths.

2. Experimental and Methods

The ^{1}H and ^{13}C NMR spectra were recorded using a Bruker Avance 400 MHz spectrometer with tetramethylsilane as the internal standard. Mass spectra was performed at The Ohio State University, Mass Spectrometry & Proteomics Facility. Differential scanning calorimetry (TA Instruments DSC, scanning rate of 5°C/min) and polarizing microscopy (POM, Mettler FP90 and FP28HP hot stage) were used to study the phase transitions. The texture of mesogenic phases was determined by POM and compared with 3,6-bis(4-dihexyloxyphenyl)-1,2,4,5-tetrazine (**6**, R′ = C-6) for which phase assignments exist in the literature [8]. Reagents and solvents were commercially available and used without further purification.

2.1. General Procedure for the Synthesis of 3,4-Dialkoxybenzonitriles 2a–g

In a 50 mL round-bottom flask with stirbar was charged with 3,4-dihydroxybenzonitrile (2.70 g, 20.0 mmol, 1.0 eq), alkyl bromide (52.0 mmol, 2.6 eq), potassium carbonate (11.06 g, 80.0 mmol, 4.0 eq), potassium iodide (5% of alkyl bromide by weight), and DMF (20 mL). This mixture was stirred at 70°C for 15 hr, cooled to room temperature and transferred to a separatory funnel with 200 mL ethyl acetate and 100 mL water. The organic phase was separated, washed with water (5 × 100 mL), and dried over magnesium sulfate. The solvents were removed under reduced pressure and the crude product was purified by recrystallization from hexanes. The ^{1}H NMR data perfectly fit the proposed structures [9–11].

2.2. General Procedure for the Synthesis of Tetrazoles, 3a–g and 8k–l

An oven dried 50 mL two-neck flask with stirbar was charged with the benzonitrile, ***2a–g*** or ***7k–l*** (10.0 mmol, 1.0 eq), sodium azide (1.30 g, 20.0 mmol, 2.0 eq), lithium chloride (1.27 g, 30.0 mmol, 3.0 eq), NMP (11 mL), and then fitted with a reflux condenser. The mixture was heated at 130°C for 3 days. The mixture was then cooled to room temperature and poured into 50 mL water and acidified to pH 2. The off white precipitate formed was filtered off, washed with water (3 × 50 mL) and recrystallized from 1-propanol. The ^{1}H NMR data perfectly fit the proposed structures [12, 13].

Table 1. Percent yields, melting points, MS, and HRMS data for tetrazines ***5a–g*** and ***6k–l***

Compound	% Yield	m.p.	MS (ESI, m/z) $[M + Na]^+$	HRMS calcd. $[M + Na]^+$/found
5a	27	162°C	601.4	601.3730/601.3718
5b	26	143°C	657.5	657.4356/657.4359
5c	22	144°C	713.5	713.4982/713.4965
5d	17	135°C	769.6	769.5608/769.5596
5e	26	134°C	825.6	825.6234/825.6226
5f	17	131°C	881.7	881.6860/881.6876
5g	12	129°C	993.8	993.8112/993.8109
6k	18	180°C	625.5	625.4457/625.4468
6l	18	116°C	793.6	793.6335/793.6332

2.3. General Procedure for the Synthesis of Trityltetrazoles, 4a–g and 9k–l

The respective tetrazole, ***3a–g*** or ***8k–l*** (4.0 mmol, 1.0 eq), was dissolved in anhydrous DMF (15 mL) and then trityl chloride (1.35 g, 4.83 mmol, 1.2 eq) was added followed by potassium *tert*-butoxide (0.54 g, 4.83 mmol, 1.2 eq). The resulting mixture was stirred under nitrogen at room temperature for 15 hr. The reaction mixture was poured into 100 mL ice-water with stirring, whereupon a white precipitate formed. The precipitate was vacuum filtered, washed with water, and then recrystallized from ethanol. The ^{1}H NMR data perfectly fit the proposed structures.

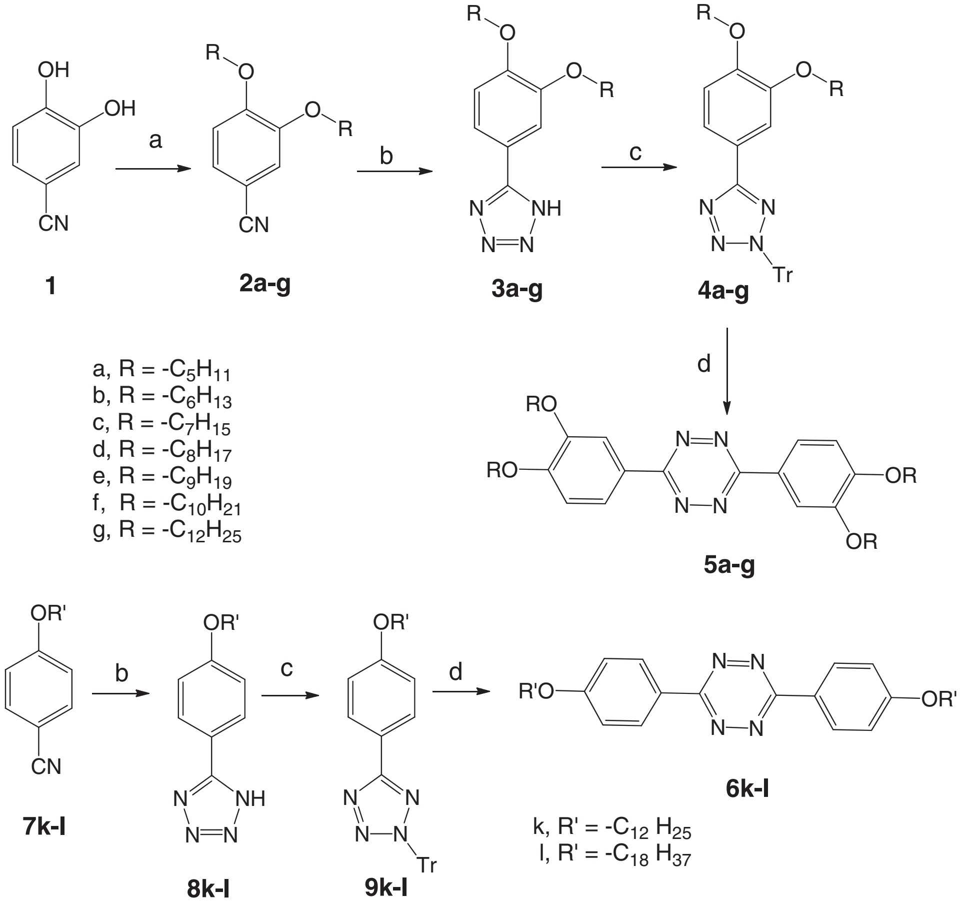
2.4. General Procedure for the Synthesis of Tetrazines, 5a–g and 6k–l

A solution of respective trityltetrazole (2.0 mmol) in benzonitrile (8 mL) was stirred at 150°C under nitrogen for 7 hr. The red precipitate formed upon cooling was isolated by vacuum filtration and recrystallized from hot toluene to yield the final tetrazine product. The ^{1}H and ^{13}C NMR data perfectly fit the proposed structures. Percent yields, melting point (m.p.), MS, and HRMS data are summarized in Table 1.

3. Result and Discussion

3.1. Syntheses

The synthesis of 3,6-bis(3,4-dialkoxyphenyl)-1,2,4,5-tetrazines ***5a–g*** and 3,6-bis(4-alkoxyphenyl)-1,2,4,5-tetrazines ***6k–l*** was carried out as outlined in Scheme 1. Among the available synthetic routes to make *s*-tetrazines [14], the method involving thermolysis of 5-aryl-2-trityl tetrazoles was selected for convenience [15]. Thus, commercially available 3,4-dihydroxybenzonitrile and 4-hydroxybenzonitrile were alkylated and then converted to their corresponding tetrazoles by reaction with lithium chloride and sodium azide in NMP. Tritylation of the tetrazoles with triphenylmethyl chloride and potassium *t*-butoxide in DMF at room temperature was found to be more efficient than the reported method [1] using triphenylmethyl chloride and sodium hydroxide under conditions of phase transfer catalysis. The 2-trityltetrazole products obtained under phase transfer catalysis were always contaminated with unreacted starting materials. Heating the N-trityl tetrazoles in benzonitrile at 150°C leads to a formation of the target tetrazines ***5a–g*** and ***6k–l***. While yields



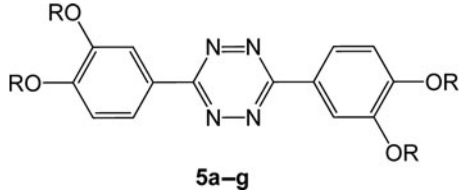
Scheme 1. Synthesis of target tetrazines ***5a–g*** and ***6k–l***. Reagents and conditions: (a) RBr, K_2CO_3, KI, DMF, 70°C, 12 hr; (b) NaN_3, LiCl, NMP, 130°C, 3 days; (c) TrCl, KOtBu, DMF; and (d) benzonitrile, 150°C, 7 hr.

were low in this final step, pure products could be isolated very easily. It is noteworthy that the nitriles and tetrazoles, ***2***, ***3***, ***7***, and ***8*** can be important intermediates for the synthesis of other nitrogen heterocyclic compounds with potential applications in materials and pharmaceutical sciences, e.g., 1,3-oxazoles [16], 2-thiazolines and 2-oxazolines [17], imidazoles [18], isoquinolines [19], and quinazolines [20].

3.2. Mesomorphic Properties

Liquid crystal properties of tetrazines ***5a–g*** and ***6k–l*** were studied using POM as well as using DSC. It turned out that the number and length of alkoxy chains attached to the 3,6-diphenyl-1,2,4,5-tetrazine core influence mesomorphism. For the four-tailed series, no mesophases were observed for compounds ***5a–d*** that have chains of eight or less carbon atoms. A smectic-C phase was observed for compounds ***5e–g*** (chains of 9, 10, and 12 carbon atoms). In contrast, all the two-tailed tetrazines ***6a–l*** examined possess liquid crystal properties [8].

Table 2. Phase transition temperatures of 3,6-bis(3,4-dialkoxyphenyl)-1,2,4,5-tetrazines, ***5a–g*** (the four-tailed tetrazines)



5a–g

		Transition temperature and enthalpy changes	
Compound	R =	Second heating/°C (ΔH, KJ/mol)	First cooling/°C (ΔH, KJ/mol)
5a	$-C_5H_{11}$	Cr 162 (62.39) I	I 143 (72.59) Cr
5b	$-C_6H_{13}$	Cr 143 (7.92) I	I 136 (10.49) Cr
5c	$-C_7H_{15}$	Cr 144 (77.53) I	I 126 (79.23) Cr
5d	$-C_8H_{17}$	Cr 135 (81.66) I	I 128 (84.50) Cr
5e	$-C_9H_{19}$	Cr 109 (12.04) Sc 134 (89.64) I	I 131 (92.21) Sc 108 (10.84) Cr
5f	$-C_{10}H_{21}$	Cr 104 (18.53) Sc 131 (105.78) I	I 121 (109.13) Sc 102 (18.67) Cr
5g	$-C_{12}H_{25}$	Cr_1 36 (5.84) Cr_2 98 (22.33) Sc 129 (125.33) I	I 120 (129.92) Sc 96 (22.14) Cr_2 26 (4.01) Cr_1

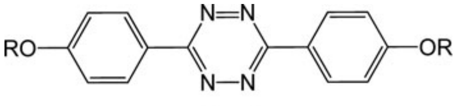
Compared with the two-tailed structures, it is obvious that introducing two more tails (four-tailed tetrazines, ***5e–g***) changes the mesogenic properties of the molecule in several ways, including (1) depression of m.p. and clearing points, (2) loss of the nematic phase prior to melting, (3) depression of the smectic-C phases formation temperatures, and (4) decrease in the mesomorphic range (Tables 2 and 3). The new two-tailed derivatives with C-12 chains—***6k***, and interestingly, the C-18 chains—***6l*** retain the smectic-C phases.

3.3. Crystal Structure of 1,4-bis-(4-Dodecyloxyphenyl)tetrazine, 6k

We have determined the single crystal structure of 1,4-bis-(4-dodecyloxyphenyl)tetrazine, ***6k***. Some relevant structure parameters and X-ray experimental data for compound ***6k*** are briefly summarized in Table 4.

The crystal is built of slip-stacked molecules with coplanar cores (Fig. 1). Adjacent molecules in the stacks are offset by one unit cell length in the â direction. There are no Van der Waals close contacts between molecules within a stack, though there are VdW C–H short contacts between adjacent stacks. The closest intrastack C–C networks of contacts are 3.48 Å (between carbons on neighboring tetrazine rings), with comparable C–C interactions between tetrazine nitrogens and carbons within the phenyl groups of adjacent molecules. We define a natural orthogonal coordinate system based on the tetrazine moiety (with origin at the ring centroid) with x-axis spans the two tetrazine carbons and a z-axis projects perpendicular to the ring (Fig. 2). In this system, the vector between molecular centroids

Table 3. Phase transition temperatures of 3,6-bis(4-alkoxyphenyl)-1,2,4,5-tetrazines, ***6a–l*** (the two-tailed series)*



6a–l

Compound	R =	Transition temperatures °C
6a	$-CH_3$	Cr 247 N 253 I
6b	$-C_2H_5$	Cr 238 N 268 I
6c	$-C_3H_7$	Cr 203 N 224 I
6d	$-C_4H_9$	Cr 190 N 226 I
6e	$-C_5H_{11}$	Cr 181 N 210 I
6f	$-C_6H_{13}$	Cr 163 Sc 181 N 207 I
6g	$-C_7H_{15}$	Cr 146 Sc 183 N 197 I
6h	$-C_8H_{17}$	Cr 131 Sc 187 N 195 I
6i	$-C_9H_{19}$	Cr 120 Sc 188 N 190 I
6j	$-C_{10}H_{21}$	Cr 111 Sc 189 I
6k	$-C_{12}H_{25}$	Cr_2 96 (40.71) Cr_1 112 (29.01) Sc 180 (14.64) I 178 (15.69) Sc 109 (29.61) Cr
6l	$-C_{18}H_{37}$	Cr_2 54 (16.45) Cr_1 107 (35.11) Sc 116 (75.16) I 107 (49.28) Sc (25.23) 44 Cr

*Compounds **6k** and **6l** are new and transitions are reported for heating and cooling. Data for compounds **6a–j** were obtained from reference [8].

(â) in a stack is (3.1 Å, –0.59 Å, 3.40 Å). This is a substantial offset, and implies that the π-orbitals of identical atoms on adjacent cores do not substantially overlap. The overall π-stacking may still be significant, however, as reflected by the relative close C–N and C–C contact networks mentioned above.

Table 4. Structure parameters and experimental data for compound ***6k***

CCDC deposit number	894997
Empirical formula	C38 H58 N4 O2
Formula weight	602.88
Temperature	150 (2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	$a = 4.6394$ (4) Å $\alpha = 83.8450(10)^\circ$
	$b = 8.0165$ (7) Å $\beta = 88.1550(10)^\circ$
	$c = 23.897$ (2) Å $\gamma = 75.9730(10)^\circ$
Volume	857.28 (13) Å^3
Z, Calculated density	1, 1.168 Mg/m^3
Absorption coefficient	0.072 mm^{-1}

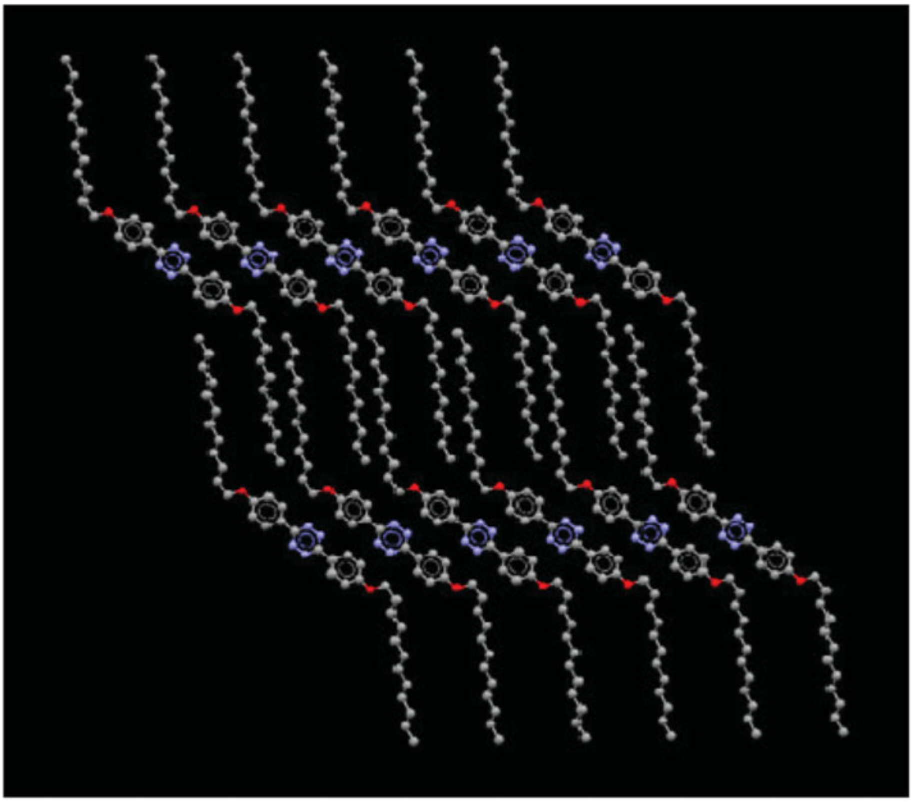


Figure 1. Stacking in compound **6k**. The slip-stacking of the cores (along the horizontal axis of the figure) as well as the interdigitated tails are evident.

In the crystal, the diphenyltetrazine core is highly coplanar with torsion angles less than 1° among the respective atoms (i.e., no atom deviates by more than 0.22 Å from the tetrazine-ring plane). The start of the alkoxy tails (the oxygen and first carbon in the tail) also lies in the ring plane with torsion only about 1°. The tails as a whole, however, project

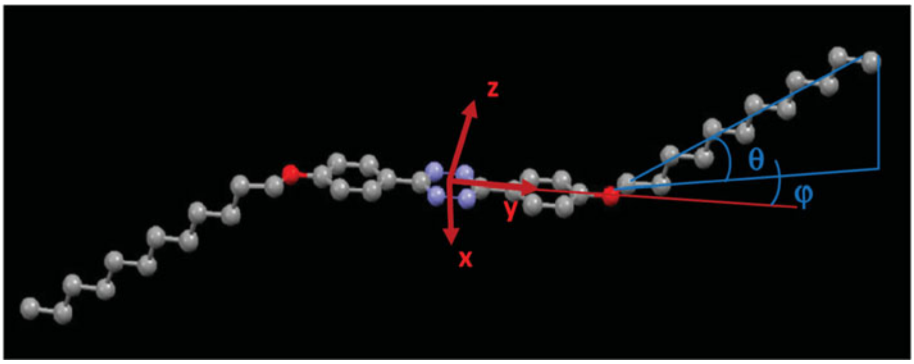


Figure 2. The x-ray structure of a molecule of **6k** showing the orthogonal coordinate system based on the molecular core as well as the angles characterizing the tail geometry.

sharply out of the plane of the molecular core. Indeed, in our orthogonal coordinate system, the tails are rotated by $\theta = 38^\circ$ out of the xy (or ring)-plane and by $\varphi = 36^\circ$ about the z-axis (Fig. 2). Of course, in any phase other than crystalline the spatial relationships of the core units and the conformations of the tails are dynamic and deviate from the "frozen" crystal structure.

Therefore, the overall length of the molecule is substantially smaller than if the tails were lying along the y-axis (the length along $\hat{y}$ is 34.3 Å vs. about 46 Å for the case of the tails lying along y). This will presumably reduce the layer spacing in the smectic phase.

4. Conclusion

We have synthesized a series of symmetrical 3,6-diaryl-1,2,4,5-tetrazines with four or two alkoxy chains with various lengths and investigated their thermotropic liquid crystal properties. Unlike the two-tailed tetrazines, the four-tailed tetrazines with less than 9 carbon chains are not mesogenic. Four-tailed tetrazines with C-9, C-10, and C-12 alkoxy chains possess smectic-C phases. Two-tailed tetrazines with C-12 and C-18 alkoxy chains possess smectic C phases as well. Compared with the two-tailed tetrazines, the four-tailed liquid crystalline tetrazines possess lower smectic-C phase transition temperatures and m.p. and better solubility. A single crystal structure of one of the two-tailed tetrazines was obtained, which is a progenitor to the Sc phase obtained on heating.

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