A New Class of Star-Shaped Discotic Liquid Crystal Containing a 2, 4, 6-Triphenyl-1, 3, 5-triazine Unit as a Core

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A new class of discotic liquid crystals based on 2, 4, 6-triphenyl-1, 3, 5-triazine as a core and [(4-alkoxyphenyl)ethynyl] benzene ester as rigid arms has been synthesized by a Pd(0)/Cu(I)-catalyzed carbon–carbon coupling reaction. The obtained compounds exhibited liquid-crystalline properties.

In recent decades, there has been much interest in the synthesis and characterization of compounds containing a 1, 3, 5-triazine unit,[1] owing to their interesting properties, such as liquid-crystalline and nonlinear optical properties, as well as their applications in other fields.[2–4] Among these materials, disk-like liquid crystals (LCs) are particularly gathering attention.[3] The liquid-crystalline materials are of great interest, especially with respect to their unique optical properties.

We herein report synthesis of a new class of star shaped discotic liquid crystals containing a 2, 4, 6-triphenyl-1, 3, 5-triazine unit as a core with six extended rigid arms.

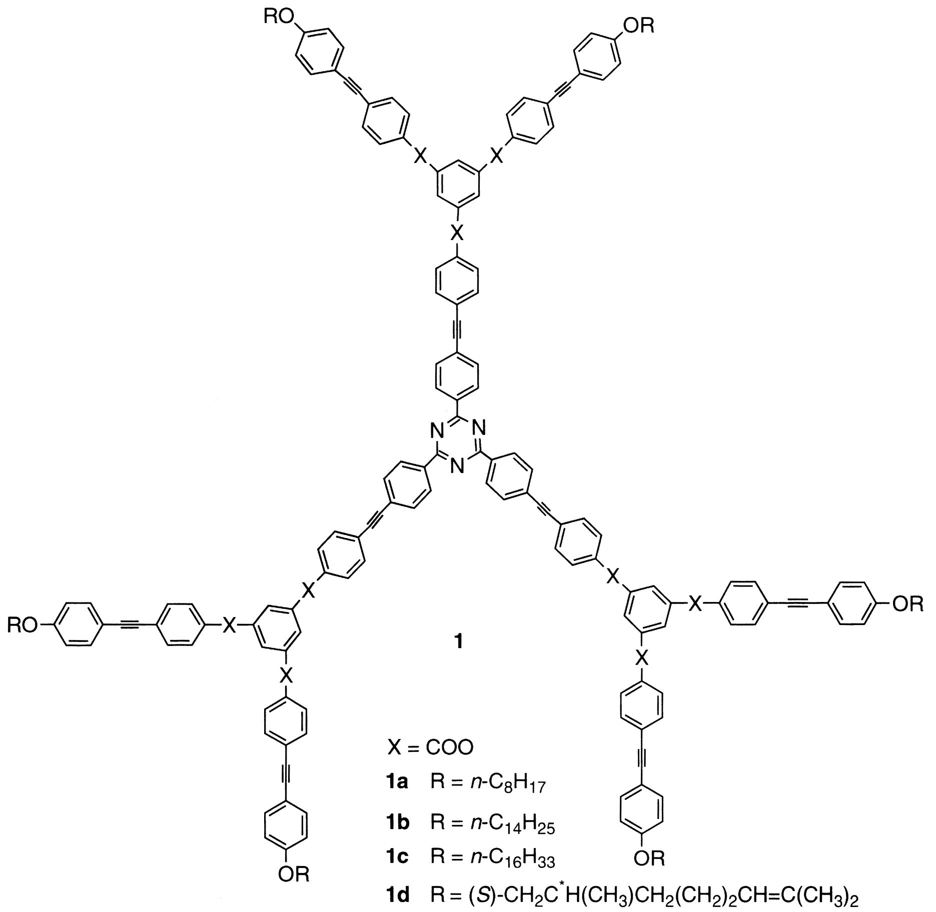
The conjugated diphenylacetylene backbone[4] is a rigid rod that can act as a mesogenic unit, and the synthesized 2, 4, 6-triphenyl-1, 3, 5-triazine derivatives with six extended rigid arms having the long alkoxy groups behave as liquid-crystalline materials. Long alkoxy and alkyl groups play an important role in the generation of large nonlinear optical coefficients[5] and are essential for molecular assembly.[6] It is known that various optical properties (such as electroluminescent and nonlinear optical properties) associated with the delocalized π-electron system are enhanced due to the orientation of molecules induced by liquid-crystalline ordering.[7] 1, 3, 5-Triazine is known to serve as a core of liquid-crystalline materials,[3] and synthesis of the π-conjugated 2, 4, 6-triphenyl-1, 3, 5-triazines with a more rigid and larger π-conjugation system, which shows liquid-crystalline properties, is desired to explore the chemistry of liquid crystals based on 1, 3, 5-triazine. All of the new 2, 4, 6-triphenyl-1, 3, 5-triazine derivatives **1** reported in this paper exhibit liquid-crystalline properties (Scheme 1).

Results and Discussion

Scheme 2 shows the structure and synthesis routes of a discotic LC studied in this works, which are characterized by 2, 4, 6-tri [(4-ethynyl)phenyl]-1, 3, 5-triazine unit linked with [(4-alkoxyphenyl)ethynyl] benzene ester. The synthesis followed the general methodology of ester preparation and a palladium-catalyzed carbon–carbon cross-coupling reaction;[8–10] namely, in the present case, the cross-coupling reaction of 2, 4, 6-tri[(4-ethynyl) phenyl]-1, 3, 5-triazine **5** witth bis [4-(4-alkoxyphenylethynyl)phenyl] 4-iodophenyl 1, 3, 5-benzenetricarboxylate **10** having long alkoxyl groups (Scheme 2). Terminal phenylalkynes **9** having long alkoxy groups were prepared in three steps from p-dihydroxyacetophenone, as previously reported.[11]

2, 4, 6-Tris(*p*-bromophenyl)-1, 3, 5-triazine **3** was prepared from p-bromobenzonitrile according to the reported method[2e] at room temperature in chloroform (Scheme 2). Tris(4-iodophenyl) 1, 3, 5-benzenetricarboxylate (**8**) was prepared by esterification of 4-iodophenol (**7**) with the corresponding acyl chloride **6**. **8** was subsequently reacted with terminal phenylalkynes **9** in a 1:2 molar ratio to give bis [4-(4-alkoxyphenylethynyl) phenyl] 4-iodophenyl 1, 3, 5-benzenetricarboxylate **10** having long alkoxy groups. 2, 4, 6-Tri [(4-ethynyl)phenyl]-1, 3, 5-triazine (**5**) was reacted with the compound **10** through palladium-catalyzed coupling reaction and we could get the desired star-shaped molecule **1** containing 2, 4, 6-triphenyl-1, 3, 5-triazine unit as a core in high yields (89–90%). Final product **1** was isolated using column chromatography on silica gel, and successive reprecipitation (chloroform/methanol) was performed for high purity. All compounds **1** are readily soluble in organic solvents such as tetrahydrofuran, chloroform, and dichloromethane, and can be characterized by NMR spectroscopy. All results of the spectroscopic studies and elemental analysis were consistent with the proposed molecular structures. The key compounds **1** and **10** were carefully identified by ^{1}H NMR, IR, and elemental analyses. Compounds **1a**–**d** are air-stable solids that can be stored at ambient temperature for a period longer than 3 months.

The thermal behavior and phase assignments[12] of compounds **1a**–**d** was checked by polarized optical microscopy (POM) and differencial scanning calorimetry (DSC). As summarized in Table 1, compound **1a** showed crystal to LC phase transition at 172.7 °C and LC to isotropic phase transition at 229.2 °C in the heating trace. In the subsequent cooling cycle, however, only isotropic to LC phase transition with very small enthalpy change (0.1 J g^{-1}) was observed with no further changes down to room temperature. The heating and cooling rates were 10 °C/min. In this LC state, mosaic textures[13] was observed between the crossed polarizers. The DSC thermograms of compounds **1a**–**d** were measured by heating and subsequent cooling. Results of the DSC and POM experiments are summarized in Table 1. Triester **1** exhibited a hexagonal columnar phase. This behavior confirms, as Kok and cowork-



1

X = COO

1a R = n-C_8H_{17}

1b R = n-$C_{14}H_{25}$

1c R = n-$C_{16}H_{33}$

1d R = (S)-$CH_2C^*H(CH_3)CH_2(CH_2)_2CH{=}C(CH_3)_2$

Scheme 1. Structure of star-shaped discotic liquid crystal.

ers have noted,[14] that a benzyloxy group acting as a large and rigid "anchoring point" can efficiently fill the space surrounding the rigid core and that the presence of the three half "super disks" favors columnar mesomorphism.

Compounds **1b**, **1c**, and **1d** showed mesogenic properties. When a crystalline sample of **1b** was heated, it showed two endothermic peaks, at 150.8 °C and 171.8 °C. Compound **1b** exhibited a columnar hexagonal disordered (D_{hd}) mesophase.[3a,c] The transitions were enantiotropic, and LC phase was observed at 170.0 °C in the POM when the sample was cooled. Compounds **1c** and **1d** had mesogenic properties similar to those of compound **1b**, as shown in Table 1. When crystalline samples of **1a–d** were observed by the POM, slow cooling of the sample from the isotropic liquid to the mesophase gave rise to a mosaic texture and hometropic areas.

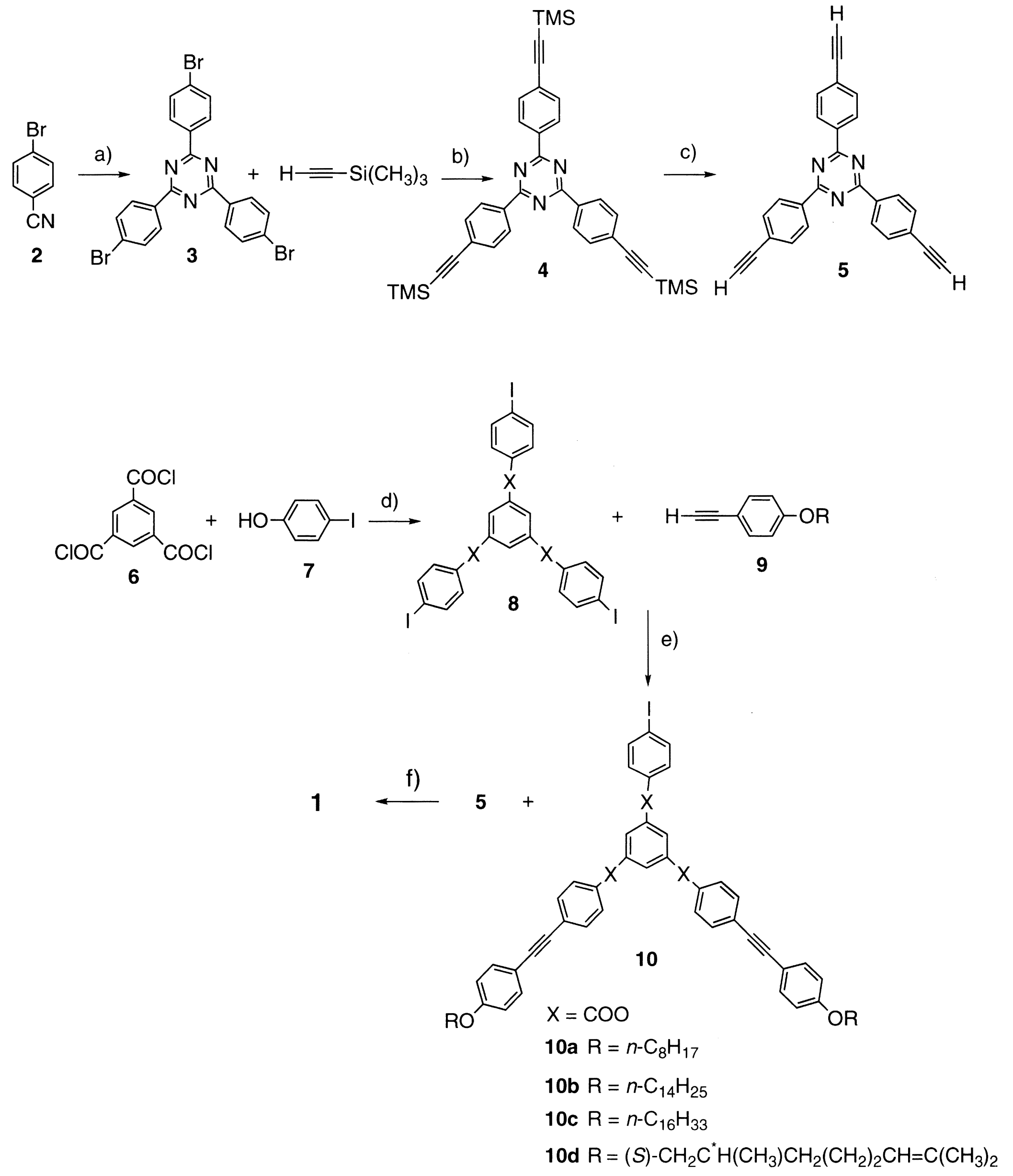
In conclusion, a new class of 2, 4, 6-triphenyl-1, 3, 5-triazine derivatives, **1a–d**, having long alkoxy side chains can be easily synthesized. These compounds behave as liquid crystals. The present findings show that the 2, 4, 6-triphenyl-1, 3, 5-triazine-based core can serve as a new mesogenic unit.

Experimental

General. ^1H NMR spectra were obtained with a JEOL JNM-LA 300 (300 MHz) spectrometer. Elemental analyses were carried out with a Yanagimoto CHN Autocoder Type MT-2. IR spectra were recorded on a JASCO IR-810 spectrometer with KBr pellets. The transition temperatures were determined by a polarizing microscope (OLYMPUS, BHSP) equipped with a hot stage and a controller (JAPAN HYTECH, TH-600RH) and also on the basis of the thermograms recorded on a differential scanning calorimeter (RIGAKU, THERMOFLEX, DSC 8230).

General Procedure. Compound **10c**: A mixture of compound **8** (408.0 mg, 0.5 mmol), $[Pd(PPh_3)_4]$ (58.0 mg, 0.05 mmol), CuI (9.5 mg, 0.05 mmol), 4-(hexadecyloxy)phenyl acetylene (**9c**) (342.6 mg, 1.0 mmol), freshly distilled triethylamine (1.5 mL), and anhydrous THF (20 mL) was degassed and stirred at 55 °C for 10 h under argon. After cooling to room temperature, the mixture was evaporated, washed with saturated aqueous NH_4Cl, and extracted with chloroform. The combined extracts were washed with water and brine, and then dried over anhydrous Na_2SO_4 and evaporated. The product was purifed by column chromatography (SiO_2, eluent, $CHCl_3$) and reprecipitation (chloroform/methanol) to afford a white powder of pure **10c**. Compound **10c** (96%). ^1H NMR (300 MHz, $CDCl_3$) δ 0.88 (t, 6 H, J = 6.6 Hz, CH_3), 1.24 (br, 52 H, CH_2), 1.79 (quint, 12 H, J = 6.6 Hz, CH_2), 3.98 (t, 4H, J = 6.6 Hz, CH_2O), 6.85 (d, 4H, J = 8.8 Hz, arom), 7.03 (d, 2H, J = 8.8 Hz, arom), 7.26 (d, 4 H, J = 8.8 Hz, arom), 7.44 (d, 4 H, J = 8.8 Hz, arom), 7.54 (d, 4 H, J = 8.8 Hz, arom), 7.75 (d, 2 H, J = 7.0 Hz, arom), 9.19 (s, 1 H, arom), 9.21 (s, 2 H, arom). IR (KBr) 1750, 2210) cm^{-1}. Anal. Calcd for $C_{75}H_{89}IO_8$ (1245.43): C 72.33, H 7.20, I 10.19%; found: C 72.41, H 7.18, I 10.04%.

Compound **1c**: A mixture of 2, 4, 6-tris[(4-ethynylphenyl)]-1, 3, 5-triazine **5** (15.3 mg, 0.04 mmol), $[Pd(PPh_3)_4]$ (4.6 mg, 0.004 mmol), CuI (2.3 mg, 0.012 mmol), {1-(4-iodophenyl)-3,5-di[4-(4-hexadecyloxyphenyl) ethynylphenyl]}-1, 3, 5-benzenetricarboxy-



Scheme 2. a) CF_3SO_3H, $CHCl_3$, r. t. b) NEt_3, CuI, $[Pd(PPh_3)_4]$, THF, 55 °C.
c) tetrabutylammonium fluoride, THF, r.t. d) NEt_3, THF, r.t.
e) NEt_3, CuI, $[Pd(PPh_3)_4]$, THF, 55 °C. f) NEt_3, CuI, $[Pd(PPh_3)_4]$, toluene, 60 °C.

Table 1. Phase Transition Temperatures of Star-Shaped Discotic Liquid Crystals Containing 2, 4, 6-Triphenyl-1, 3, 5-triazine Unit[a]

Compound	T/°C(ΔH/J g^{-1})[b]				
	Heating			Cooling[c]	
1a	K 172.7(21.33)	D_{hd} 229.2(0.37)	I	I	229.0 D_{hd}
1b	K 150.8(20.90)	D_{hd} 171.8(0.25)	I	I	170.0 D_{hd}
1c	K 132.0(10.86)	D_{hd} 196.2(0.65)	I	I	191.0 D_{hd}
1d	K 141.3(29.63)	D_{hd} 193.1(1.50)	I	I	187.0 D_{hd}

a) Transition temperatures and enthalpies were determined by DSC (scan rate, 10 °C min^{-1}).

b) K, crystal; D_{hd}, columnar hexagonal disordered; I, isotropic.

c) Transition observed only by POM.

late (**10c**) (150 mg, 0.12 mmol), freshly distilled triethylamine (1 mL) and anhydrous toluene (12 mL) was degassed and stirred at 60 °C for 22 h under argon. After cooling to room temperature, the mixture was evaporated, washed with saturated aqueous NH_4Cl, and extracted with chloroform. The combined extracts were washed with water, and brine, and then dried over anhydrous Na_2SO_4 and evaporated. The product was purified by column chromatography (SiO_2, eluent, hexane/$CHCl_3$ = 1/5) and reprecipitation (chloroform/methanol) to afford a white powder of pure **1c**. Compound **1c** (90%). ^1H NMR (300MHz, $CDCl_3$) δ 0.88 (t, 18 H, J = 6.6 Hz, CH_3), 1.26 (br, 156 H, CH_2), 1.80 (quint, 12 H, J = 6.6 Hz, CH), 3.98 (t, 12 H, J = 6.6 Hz, CH_2O), 6.86–7.70 (m, 72 H, arom), 9.24 (s, 9 H, arom). IR (KBr) 1750, 2210 cm^{-1}. Anal. Calcd for $C_{252}H_{279}N_3O_{24}$ (3733.99): C 81.06, H 7.53, N 1.13%; found: C 80.80, H 7.35, N 1.35%.

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