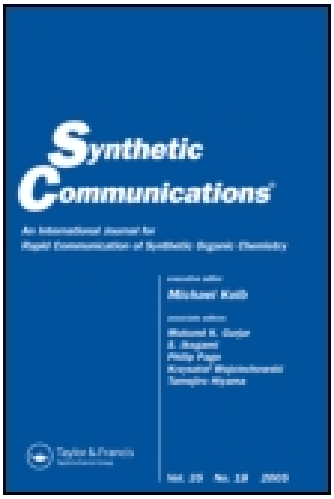

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SYNTHESIS OF CYCLOTRIPHOSPHAZENES CONTAINING CYANOSTILBENES WITH DIFFERENT TERMINAL SUBSTITUENTS

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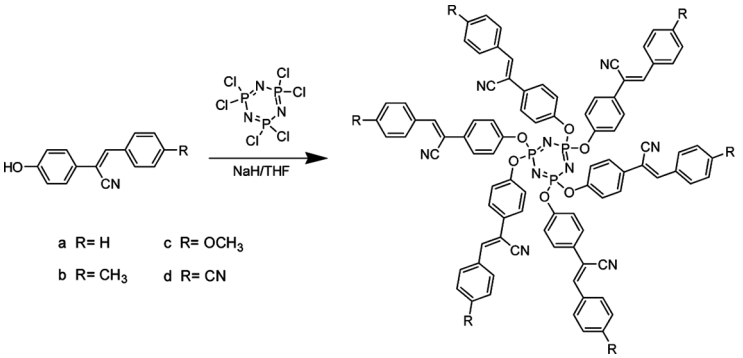
GRAPHICAL ABSTRACT



Abstract *The synthesis and mesomorphic properties of a class of cyclotriphosphazenes containing cyanostilbene groups with different terminal substituents (-H, -CH_3, -OCH_3, -CN) are described. All the resulting compounds are characterized by* ^1H, ^{13}C, *and* ^{31}P *NMR, matrix-assisted laser desorption/ionization time of flight, and elemental analysis. The thermal behaviors of cyclotriphosphazene derivatives are studied by the means of differential scanning calorimetry and polarizing optical microscopy. Nematic phases are observed in cyclotriphosphazenes with terminal substituents (-CH_3, -OCH_3, -CN).*

Keywords Cyanostilbene; cyclotriphosphazene; Knoevenagel condensation; liquid crystal; star-shaped molecule

INTRODUCTION

Cyclotriphosphazene is a broad class of molecules with six arms at the periphery and an alternating nitrogen–phosphorus six-atom ring as the core group.

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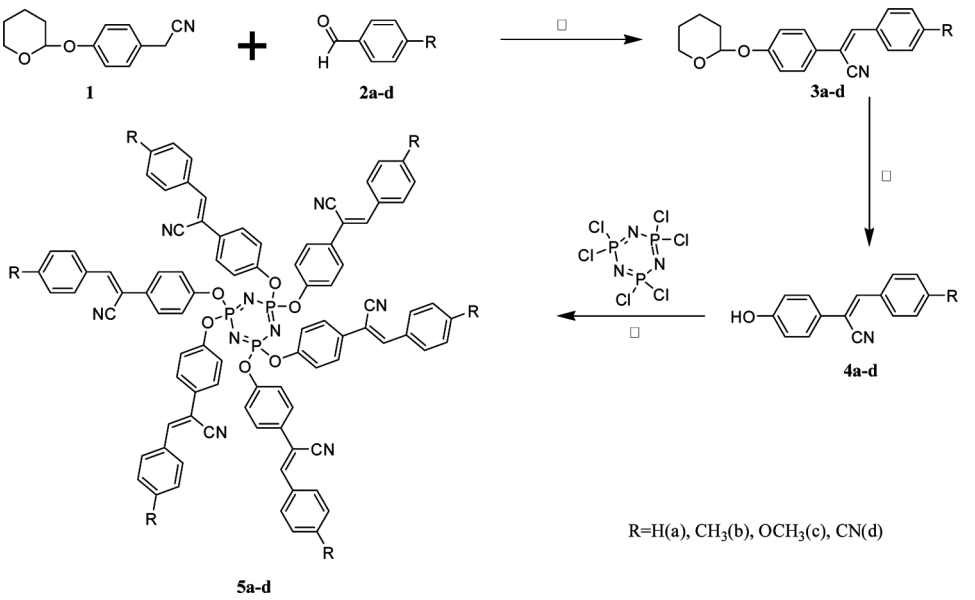

Scheme 1. Synthetic routes leading to compounds **5a–d**. (i) *t*-BuOK, *n*-Bu_4NOH/*t*-BuOH; (ii) TsOH/methanol; and (iii) NaH/THF.

Hexachlorocyclotriphosphazene (HCCP) is usually the starting molecule for the synthesis of cyclotriphosphazene derivatives.[1] Because of the high reactivity of the P-Cl bond, the corresponding substitution method allows the introduction of a wide range of substituents and hence provides cyclotriphosphazene derivatives with different chemical and physical properties.[2] For examples, the cyclotriphosphazenes with different substituents have applications as fire-retardant materials,[3,4] biomedical materials,[5] liquid crystals,[1,6] and optical material.[7]

α-Cyanostilbene is a rigid, conjugated organic group with a strong electron-withdrawing cyano group on the vinyl group. Cyano-poly(*p*-phenylene vinylenes) (CN-PPV) and low-molecular compounds with α-cyanostilbene groups have been extensively synthesized for semiconductor device applications.[8–10] CN-PPV and its derivatives show high photoluminescence (PL) efficiencies and electroluminescence (EL) efficiencies, which are attributed to the electron-withdrawing cyano groups that can facilitate electron injection.[11] The conjugated and rigid structure of α-cyanostilbene also provides it with another important application as the main chain (or side chain) in liquid-crystalline polymers.[12] α-Cyanostilbene derivatives were also found to possess a strong gelation power at room temperature.[13]

In this study, a class of cyclotriphosphazenes bearing six α-cyanostilbene groups with different terminal substituents was synthesized through the nucleophilic reaction. The synthetic routes leading to the compounds **5a–d** are shown in Scheme 1.

RESULTS AND DISCUSSION

Compounds **4a–d** were synthesized by Knoevenagel-type condensation with *t*-BuOH as solvent in the presence of *t*-BuOK and *n*-Bu_4NOH. The terminal substituent

has the effect on the condensation reaction. The terminal electron-withdrawing cyano group facilitated the condensation reaction and reduced the reaction temperature and the reaction time. Comparing to the reaction time for compounds **3a–c**, a shorter reaction time of 15 s was used for the preparation of compound **3d**. Besides the reaction time, the reaction temperature was also reduced from 80 °C to 30 °C. The cyano group also simplified the purification procedure of compound **3d**. Upon the completion of this reaction, a yellow precipitate was formed and readily collected by filtration. In contrast to compound **4a** with no terminal substituent, compound **4d** with electron-withdrawing terminal substituent showed relatively higher melting points of 226–228 °C. Meanwhile, compounds **4b** and **4c** with electron-releasing terminal substituents showed lower melting points than that of compound **4a**.

The nucleophilic reaction was used to prepare compounds **5a–d**. HCCP was reacted with an excess of corresponding compound **4a–d** in the presence of NaH in dry tetrahydrofuran (THF) to yield compounds **5a–d** with isolated yields of 87–92%. The products of compounds **5a–c** were readily purified by reprecipitating the corresponding crude product into methanol to remove the excess compound **4a–c**. All the compounds **5a–d** were characterized by ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectroscopy, mass spectrometry (MALDI-TOF), and elemental analysis. The ^{1}H and ^{13}C NMR spectra of compounds **5a–d** were consistent with the formulas indicated. The ^{31}P spectra of compounds **5a–d** consisted of one sharp peak with signals at positions similar to those observed for other (phenoxy)cyclotriphosphazenes,[1] indicating the completion of the substituted reaction. The MALDI-TOF mass spectra further identified the predicted structures of compounds **5a–d**. Compounds **5a–c** showed good solubilities in common solvents such as $CHCl_3$ and THF. Compound **5d** could not dissolve in low polar solvents even at elevated temperature but exhibited good solubility in high polar solvents at elevated temperature, such as *N*,*N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and pyridine. The melting points of compounds **5b–d** with terminal substituents were higher than those of corresponding compounds **4b–d**; however, the melting point of compound **5a** with no terminal substituent was lower than that of compound **4a**.

The thermal behaviors of compounds **5a–d** were studied by differential scanning calorimetry (DSC). The transition temperatures and associated enthalpy changes of transition are summarized in Table 1. The representative polarized optical micrographs (POM) of compounds **5a–d** are shown in Figure 1.

Table 1. Thermal behavior of compounds **5a–d**

	Phase-transition behavior[a]	
Compounds	Heating	Cooling
5a	Cr 209(73.60) I	I 124(41.00) Cr′ 78(3.55) C*r*
5b	Cr 220(87.24) I	I 1*43*(13.84)N 132(44.02) Cr
5c	Cr 108(−44.79) Cr′ 189(61.28) N 199(3.25) I	I 196(1.85) N 114(2.50) Cr
5d	Cr 154(−17.67) Cr′ 270(47.81) I	I 249(1.16) N 204(1.93) Cr′ 130(5.47) Cr

[a]Transition temperatures (°C) are taken from the second run. Enthalpies (ΔH) of transition (kJ/mol, in parentheses). Cr, crystalline; N, nematic phase; I, isotropic state.

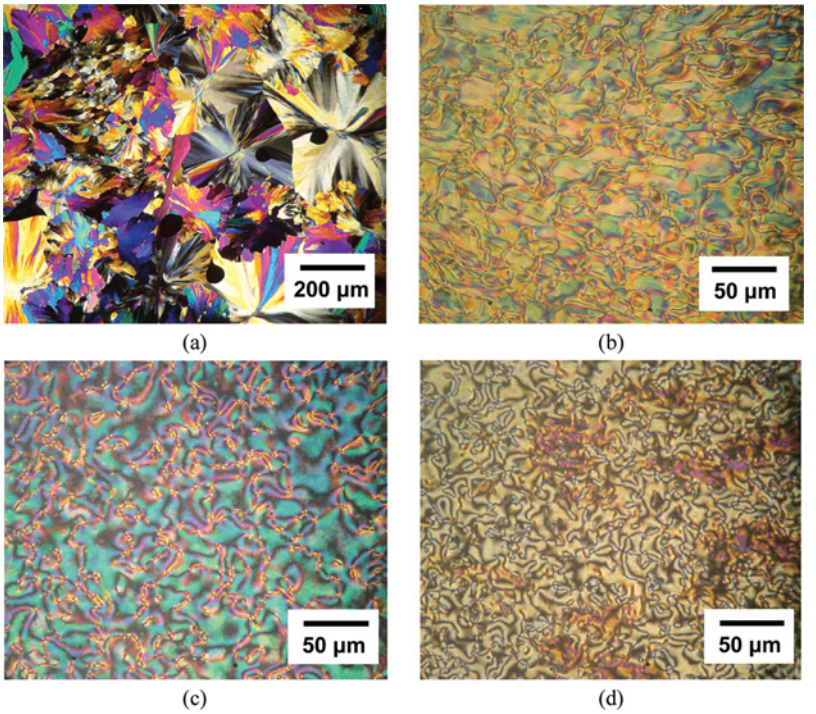

Figure 1. Representative polarized optical micrographs of **5a–d**: (a) **5a** at 110 °C, on cooling; (b) **5b** at 140 °C, on cooling; (c) **5c** at 150 °C, on cooling; and (d) **5d** at 230 °C, on cooling. (Figure is provided in color online.)

The results indicated that compounds **5b–d** exhibited nematic phases while compound **5a** exhibited only crystal phase both on heating and cooling. For **5a**, typical texture of crystal was observed as shown in Figure 1a. For **5b**, threadlike text was observed, which is a typical texture for nematic phase as shown in Figure 1b. For **5c** and **5d**, characteristic schlieren textures, which contribute to nematic phase, were observed as shown in Fig. 1c and 1d.

CONCLUSION

In conclusion, we have synthesized a class of α-cyanostilbene-containing cyclotriphosphazenes with different terminal substituents. All the studied cyclotriphosphazenes with terminal substituents could exhibit nematic phases.

EXPERIMENTAL

HCCP was synthesized according to the literature method.[14] 3,4-Dihydroxypyran, *t*-BuOK, *n*-Bu_4NOH, and 4-cyanobenzaldehyde were purchased from Alfa Aesar. All other chemicals and solvents were purchased from Sinopharm Chemical Reagent Co., Ltd. All solvents were dried by standard techniques before use. ^{1}H, ^{13}C, and ^{31}P NMR spectra were measured on a Bruker AV 400-MHz spectrometer in

deuterated solvent with tetramethylsilane (TMS) as an internal standard (^{1}H and ^{13}C) and with 85% H_3PO_4 as an external reference (^{31}P). High-resolution mass spectra (HRMS) were recorded on the Applied Biosystems API-3000 LC/MS TOF mass spectrometer. MALDI-TOF mass spectrometry was carried out on the Applied Biosystems Voyager-DE-STR MALDI-TOF mass spectrometer. Elemental analyses were performed using a Vario Micro cube analyzer. Thermal behaviors of the trimer derivatives were studied on a Perkin-Elmer Diamond DSC under a heating and cooling rate of 10 °C/min in nitrogen. The peak temperature of the endotherms and exotherms were taken as the phase transition temperatures. Polarized optical microscopy was carried out on Olympus BX51 equipped with a hot stage system.

Synthesis of 4-(Tetrahydro-2-pyranoxy)phenylacetonitrile (1)

Compound **1** was prepared according to the literature method.[15]

General Procedure for the Preparation of Compounds 4a–c

t-BuOK (0.13 g, 1.2 mmol) and *n*-Bu_4NOH (6.91 g, 40% in methanol, 10.6 mmol) were added quickly to a solution of 4-(tetrahydro-2-pyranoxy)phenylacetonitrile (3.85 g, 17.7 mmol) and the corresponding benzaldehyde derivative (16.1 mmol) in *t*-BuOH (40 mL) at 80 °C under nitrogen. After stirring at 80 °C for 30 min, the mixture was poured into water and extracted with ethyl acetate. The organic layer was then washed with water and dried. The solvent was removed under reduced pressure. The crude products of compounds **3a–c** were used in the deprotection reaction without further purification. *p*-Toluenesulfonic acid (TsOH) (0.84 g, 4.9 mmol) was added to the solution of compound **3** in methanol (100 mL), and the mixture was stirred for 1.5 h under reflux. Most of the solvent was removed under reduced pressure. The resulting solid was collected by filtration and then recrystallized from methanol to give compounds **4a–c**.

Synthesis of (Z)-2-(4-Hydroxyphenyl)-3-(4-cyanophenyl) acrylonitrile (4d)

In a procedure similar to the synthetic method of compounds **4a–c** with little modification, *t*-BuOK and *n*-Bu_4NOH were added quickly to the *t*-BuOH solution at 30 °C under nitrogen. The mixture was stirred at 30 °C for 15 s, and then poured quickly into water (200 mL). The resulting solid was collected by filtration and washed with methanol to give compound **3d**. The deprotection reaction was the same as those for compounds **4a–c**.

General Procedure for the Preparation of Compounds 5a–d

A mixture of HCCP (0.30 g, 0.9 mmol), with 20% in excess of compound **4** (6.2 mmol) and NaH [0.25 g, 60% (w/w) dispersed in mineral oil, 6.3 mmol] in dry THF (100 mL), was refluxed for 48 h. Upon completion of the reaction, the mixture was poured into methanol/water (v/v: 1/1, 300 mL) and reprecipitated twice from THF into methanol to give compounds **5a–c** (for compound **5d**, the crude product was recrystallized from DMF).

Data

(Z)-2-(4-Hydroxyphenyl)-3-phenylacrylonitrile (4a). Yield 69%; mp 219–221 °C; white crystal; ^{1}H NMR (DMSO-d_6) δ: 9.92 (s, 1H, OH), 7.88 (d, $J = 7.6$ Hz, 2H, Ar-H), 7.83 [s, 1H, C(CN)=CH], 7.59 (d, $J = 8.4$ Hz, 2H, Ar-H), 7.54–7.44 (m, 3H, Ar-H), 6.89 (d, $J = 8.8$ Hz, 2H, Ar-H). ^{13}C NMR (DMSO-d_6) δ: 159.10, 140.08, 134.58, 130.46, 129.33, 129.26, 127.76, 125.04, 118.56, 116.42, 110.91. HRMS: $C_{15}H_{10}NO^+$ calculated: 220.0762. Found: 220.0786 $[M - H]^+$.

(Z)-2-(4-Hydroxyphenyl)-3-(4-methylphenyl)acrylonitrile (4b). Yield 65%; mp 172–174 °C; yellow crystal; ^{1}H NMR (DMSO-d_6) δ: 9.93 (s, 1H, OH), 7.79 [t, $J = 8.0$ Hz, 3H, Ar-H and C(CN)=CH], 7.58 (d, $J = 8.8$ Hz, 2H, Ar-H), 7.31 (d, $J = 8.0$ Hz, 2H, Ar-H), 6.90 (d, $J = 8.8$ Hz, 2H, Ar-H), 2.36 (s, 3H, CH_3). ^{13}C NMR (DMSO-d_6) δ: 158.94, 140.50, 140.06, 131.82, 129.91, 129.27, 127.61, 125.20, 118.75, 116.40, 109.73, 21.50. HRMS: $C_{16}H_{12}NO^+$ calculated: 234.0919. Found: 234.0944 $[M - H]^+$.

(Z)-2-(4-Hydroxyphenyl)-3-(4-methoxyphenyl)acrylonitrile (4c). Yield 72%; mp 159–161 °C; yellowish crystal; ^{1}H NMR (DMSO-d_6) δ: 9.84 (s, 1H, OH), 7.88 (d, $J = 8.8$ Hz, 2H, Ar-H), 7.74 [s, 1H, C(CN)=CH], 7.54 (d, $J = 6.8$ Hz, 2H, Ar-H), 7.08 (d, $J = 8.8$ Hz, 2H, Ar-H), 6.87 (d, $J = 6.8$ Hz, 2H, Ar-H), 3.83 (s, 3H, OCH_3). ^{13}C NMR (DMSO-d_6) δ: 161.14, 158.69, 139.88, 131.13, 127.42, 127.11, 125.42, 119.05, 116.37, 114.87, 107.84, 55.86. HRMS: $C_{16}H_{12}NO_2^+$ calculated: 250.0868. Found: 250.0893 $[M - H]^+$.

(Z)-2-(4-Hydroxyphenyl)-3-(4-cyanophenyl)acrylonitrile (4d). Yield 74%; mp 226–228 °C; yellow crystal; ^{1}H NMR (DMSO-d_6) δ: 10.05 (s, 1H, OH), 8.01 (q, $J = 8.8$ Hz, 4H, Ar-H), 7.93 [s, 1H, C(CN) = CH], 7.63 (d, $J = 8.8$ Hz, 2H, Ar-H), 6.91 (d, $J = 8.8$ Hz, 2H, Ar-H). ^{13}C NMR (DMSO-d_6) δ: 159.70, 139.06, 137.79, 133.17, 129.84, 128.16, 124.49, 118.99, 117.94, 116.53, 113.95, 112.20. HRMS: $C_{16}H_9N_2O^+$ calculated: 245.0715. Found: 245.0750 $[M - H]^+$.

2,2,4,4,6,6-Hexakis[4-((Z)-1-cyano-2-phenylvinyl)phenoxy]cyclotriphosphazene (5a). Yield 90%; mp 209–211 °C; white powder; ^{1}H NMR ($CDCl_3$) δ: 7.78 (dd, $J = 2.0$, 8.0 Hz, 2H, Ar-H), 7.55 (d, $J = 8.8$ Hz, 2H, Ar-H), 7.48 [s, 1H, C(CN)=CH], 7.39–7.34 (m, 3H, Ar-H), 7.08 [d, $J = 8.4$ Hz, 2H, Ar-H]. ^{13}C NMR ($CDCl_3$) δ: 150.86, 142.57, 133.35, 131.77, 130.66, 129.34, 128.92, 127.28, 121.53, 117.90, 110.18. ^{31}P NMR ($CDCl_3$) δ: 8.53. MS (MALDI-TOF) m/z: 1456.3 $[M + H]^+$, 1478.3 $[M + Na]^+$, 1495.2 $[M + K]^+$. Anal. calcd. for $C_{90}H_{60}N_9O_6P_3$: C, 74.22; H, 4.15; N, 8.66. Found C, 74.21; H, 4.09; N, 8.85.

2,2,4,4,6,6-Hexakis[4-((Z)-1-cyano-2-*p*-tolylvinyl)phenoxy]cyclotriphosphazene (5b). Yield 92%; mp 217–219 °C; white powder; ^{1}H NMR ($CDCl_3$) δ: 7.68 (d, $J = 8.4$ Hz, 2H, Ar-H), 7.53 (d, $J = 8.8$ Hz, 2H, Ar-H), 7.42 [s, 1H, C(CN)=CH], 7.15 (d, $J = 8.4$ Hz, 2H, Ar-H), 7.06 (d, $J = 8.4$ Hz, 2H, Ar-H), 2.38 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$) δ: 150.65, 142.54, 141.15, 131.91, 130.69, 129.57, 129.40, 127.12, 121.48, 118.12, 108.90, 21.56. ^{31}P NMR ($CDCl_3$) δ: 8.59. MS (MALDI-TOF) m/z: 1540.3 $[M + H]^+$, 1562.2 $[M + Na]^+$. Anal. calcd. for $C_{96}H_{72}N_9O_6P_3$: C, 74.84; H, 4.71; N, 8.18. Found C, 74.68; H, 4.61; N, 8.29.

2,2,4,4,6,6-Hexakis{4-[(Z)-1-cyano-2-(4-methoxyphenyl)vinyl] phenoxy} cyclotriphosphazene (5c). Yield 91%; mp 186–193 °C; yellowish crystal; ^{1}H NMR ($CDCl_3$) δ: 7.75 (d, $J = 9.2$ Hz, 2H, Ar-H), 7.49 (d, $J = 8.8$ Hz, 2H, Ar-H), 7.37 [s, 1H, C(CN)=CH], 7.04 (d, $J = 8.4$ Hz, 2H, Ar-H), 6.84 (d, $J = 8.8$ Hz, 2H, Ar-H), 3.84 (s, 3H, OCH_3). ^{13}C NMR ($CDCl_3$) δ: 161.44, 150.51, 142.08, 132.05, 131.32, 126.94, 126.20, 121.51, 118.47, 114.30, 107.11, 55.34. ^{31}P NMR ($CDCl_3$) δ: 8.72. MS (MALDI-TOF) m/z: 1637.2 $[M + H]^+$, 1658.2 $[M + Na]^+$. Anal. calcd. for $C_{96}H_{72}N_9O_{12}P_3$: C, 70.45; H, 4.43; N, 7.70. Found C, 70.68; H, 4.38; N, 7.79.

2,2,4,4,6,6-Hexakis{4-[(Z)-1-cyano-2-(4-cyanophenyl)vinyl] phenoxy} cyclotriphosphazene (5d). Yield 87%; mp 269–279 °C; white crystal; ^{1}H NMR (DMSO-d_6) δ: 7.97 (s, 1H, C(CN)=CH), 7.88 (q, $J = 8.8$ Hz, 4H, Ar-H), 7.67 (d, $J = 8.8$ Hz, 2H, Ar-H), 7.17 (d, $J = 8.8$ Hz, 2H, Ar-H). ^{13}C NMR (DMSO-d_6) δ: 150.98, 141.18, 138.09, 133.02, 130.95, 129.99, 128.12, 121.68, 118.73, 117.48, 112.82, 112.68. ^{31}P NMR (DMSO-d_6) δ: 8.52. MS (MALDI-TOF) m/z: 1607.1 $[M + H]^+$. Anal. calcd. for $C_{96}H_{54}N_{15}O_6P_3$: C, 71.77; H, 3.39; N, 13.08. Found C, 71.29; H, 3.30; N, 13.44.

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