

Synthesis of Twist–Twist π -Conjugated Di-sec-alkylstilbenes and Stilbene Polymers

James E. Gano,* D. J. Osborn, III, Nagendra Kodali, Padmanabhan Sekher, Min Liu, and Eddie D. Luzik, Jr. Department of Chemistry, Bowman-Oddy Laboratories, University of Toledo, Toledo, Ohio 43606

jgano@frii.com

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Abstract: Twist–twist π -conjugated (TTPC) π systems promise unique properties with their 90° twist angles. Disec-alkyl substituted stilbenes, 5, were prepared by lowvalent titanium coupling of phenyl ketones, 4. Long alkyl chains stopped the coupling reaction. Stilbenes 5 were shown to be ~90% TTPC. Inserting TTPC units into poly(pphenylene) polymers created highly fluorescent, soluble, TTPC π systems with weak electronic segmentation for organic light emitting diode (OLED) studies.

Stilbenes have played a central role in many aspects of organic chemistry.¹⁻³ Sufficiently large substituents on the double bond rotate the phenyl groups 90° out of the molecular plane creating twist-twist π conjugation (TTPC).^{4,5} Novel features can result. *tert*-Butyl-substituted TTPC stilbenes have allowed unique mechanistic investigations of bromine addition^{6,7} and phenyl rotation in stilbene photochemistry.8

Electroluminescence in organic compounds was thrust into prominence with the discovery of polymer luminescence in a stilbene relative, poly(p-phenylene vinylene).⁹ Subsequent, rapid advances in organic light-emitting diodes (OLED) led to commercial, flat-panel displays.^{10–28}

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FIGURE 1. HOMO molecular orbital in a TTPC stilbene showing the $\sigma - \pi$ orbital mixing.

On the horizon are flexible displays,²¹ microdisplays,¹⁵ polarized displays,¹¹ organic lasers,²³ and organic sensors.13

New materials fueled OLED advances. Herein is described the first incorporation of the TTPC stilbene unit into soluble polymers. Of fundamental theoretical interest, conjugation in such a polymer is regular but weakly segmented by the TTPC unit. Furthermore, blue light emission, good stability, and minimal interchain quenching are expected in OLED applications.

Sterically congested stilbenes with connected, perpendicular, multiple, π systems, such as **1**, are described herein as twist-twist π conjugated (TTPC). The TTPC HOMO depicted in Figure 1 reveals σ mixing with adjacent π systems.²⁹ Novel electronic properties are expected.³⁰⁻³⁸ Introduction of TTPC features into polymers promises to further expand the varied array of materials that are facilitating rapid advances in OLED technology.^{25,28,39,40}

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^{*} To whom correspondence should be addressed: Voice mail: (970)-493-3328. FAX: (419)530-4033.

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Investigation of the properties of extended TTPC systems **2a**,**b** revealed solubilities rapidly decreased as n increased.⁴¹ Preparation of **2c**-**h** with increased phenylene units only modestly raised the solubilities.⁴²

This Note describes TTPC compounds of high molecular weight, which retain the rigid TTPC geometry, have structural flexibility, and are readily soluble.^{42,43}

Previous attempts to prepare versions of 2a,b with extended alkyl chains to increase solubility failed. Modified TTPC systems with increased solubilities could be prepared, in principle, by attachment of long alkyl groups to 2 either on the benzene rings or on the *tert*-butyl groups. TTPC systems are typically prepared by the lowvalent titanium⁴⁴⁻⁴⁶ coupling of alkyl phenyl ketones, Scheme 1.47 However, 1-(2-methylphenyl)-2,2-dimethyl-1-propanone failed to couple under low-valent titanium conditions, demonstrating an alkyl group cannot be extended from the ortho position of the benzene ring. Although 1-(3-methylphenyl)-2,2-dimethyl-1-propanone readily coupled,⁸ in subsequent steps the presence of the meta substituent prevented low-valent titanium coupling to extend the TTPC system to analogues of 2a,b.41 Finally, adding one methyl or one heptyl to the *tert*-butyl group produced other ketones that failed to couple.

The necessity to simultaneously reduce steric congestion as extended chains are added to increase solubility became evident. A reasonable compromise could be achieved by replacing the *tert*-butyl group with a *sec*-alkyl group. The simplest example of this series is diisopropylstilbene.

(*E*)-Diisopropylstilbene, **5a**, has been prepared by lowvalent titanium coupling.⁴⁸ Evidence indicated it possessed the desired 90° twisted TTPC geometry. Its UV spectrum was blue shifted, compared to stilbene, with maxima at 225 (λ = 7120) and 258 nm (λ = 550).⁴⁹ Its ¹H

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NMR spectrum showed the characteristic upfield shifted methyl resonance at δ 0.77.⁴⁹ However, the smaller isopropyl group may not lock the geometry of **5a** at 90° as effectively as the *tert*-butyl group in **1**. This was suggested by the low-valent titanium coupling results. The preparation of **1** produced no cis isomer, but the similar coupling to produce **5a** produced 12% of cis isomer **6a**. Unlike **1**, additional low-energy conformers must be considered for **5a**. To gain insight into this issue, a computational study of **5a** and **6a** was undertaken.

AM1 provided consistent structures and reasonable relative energies for TTPC systems.^{29,50,51} AM1 calculated heats of formation are shown for the conformers of **5a** and **6a** in Table 1.⁵² The lowest energy conformer is **5a**_{syn,syn}. Its phenyl groups were perpendicular, $\angle_{dihedral} = 90.4^{\circ}$, to the double bond.

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Conformer **5a**_{syn,anti} is 1.84 kcal/mol less stable than **5a**_{syn,syn}. Furthermore, both **5a**_{syn,anti} and **6a**_{syn,anti} can be formed in two ways, syn,anti and anti,syn. Thus, in any equilibrium **5a**_{syn,anti} and **6a**_{syn,anti} enjoy an additional entropy advantage over **5a**_{syn,syn} and **6a**_{syn,syn}. Although one phenyl was still perpendicular to the double bond in **5a**_{syn,anti}, the other, flanked by small hydrogens on both sides, was twisted only 70.6°. Calculated energies for conformers of **6a** showed a similar preference for the syn,syn geometry.

Calculations performed with ZINDO predicted UV absorptions at 217 (ϵ 43 000) and 274 nm (ϵ 1500) for **5a**_{syn,syn} and 221 (ϵ 28 000) and 250 nm (ϵ 17 000) for **5a**_{syn,anti}. The presence of **5a**_{syn,anti} in **5a**_{syn,syn} would be revealed by its strong absorption band between the measured bands for **5a**_{syn,syn} at 225 and 258 nm. The absence of a major feature in this region suggested only a small amount of **5a**_{syn,anti} could be present.

In the 240-nm region, **1**, which has only one conformation, and **5a** showed similar trends. Variable-temperature, UV absorption measurements of **5a** revealed a small absorbance increase at 240 nm from 0.37 to 0.47 as the temperature was raised from 11 to 80 °C. Isosbestic points were evident at 225 and 271 nm. Since the molar absorptivity of **5a**_{syn,anti} was calculated to be 17 000 in the 240-nm region, these results supported the view that **5a** existed primarily as the syn,syn conformer with <10% as the syn,anti conformer. Thus, any polymer containing these TTPC units would have the syn,syn conformation occasionally interspersed with syn,anti sites.

A series of di-*sec*-alkylstilbenes was prepared. Since replacing the methyl groups on **5a** with C_{18} chains would give excellent solubility, **5f** was the initial target. Considering the versatility of the low-valent titanium reaction, the coupling of **4f** to produce **5f** would seem to be straightforward. However, numerous trials failed to produce any **5f**. Therefore, the molecular size was gradually increased by adding longer alkyl chains to ketone **4a** to find suitable conditions. New stilbenes **5b**-**e** were prepared.

Ketones **4b**–**e** were prepared by direct acylation of benzene or alkylation of ketone **3**. Low-valent titanium coupling of these ketones in alumina-dried THF gave stilbenes **5b**–**e** in 12–80% yields. As observed for **5a**, small amounts of **6b**–**e** were evident before purification. The UV and ¹H NMR data supported the TTPC geometries for **5b**–**e**. The melting points for compounds **5a**–**e** were 165–168, 108–110, 110–112, 75–88, and 81–82 °C, respectively, which suggested increased solubilities for derivatives of **5d**,**e**.

Polymers incorporating 5c-e units were prepared according to Scheme 2.

Utilizing iodination in moist methylene chloride,⁵³ iodostilbenes **7c–e** were prepared from stilbenes **5c–e** in 79–82% yields. These were copolymerized with diborane **8** with use of the Suzuki coupling to give polymers **9c–e**.⁵⁴ Optimum polymer yields and highest molecular weights utilized a toluene, DMF, water (2:2:1) mixed solvent system.

The polymeric nature of **9d**,**e** was readily evident by the broadened signals observed in the ¹³C NMR spectrum. This broadening extended to the methylene units nearest the polymer backbone. It only disappeared completely



FIGURE 2. IV absorption (A, B, E) and fluorescence emission (C, D) spectra for **5e** (E), **9e** (B, D), and *p*-quaterphenyl (A, C). The UV absorption data are plotted, for comparison purposes, at identical "chromophor" concentrations.

SCHEME 2. Polymer Synthesis



upon reaching the terminal –CH₂CH₃ units. Polymer **9c** showed low solubility. It was not investigated further.

GPC measurements on **9d**,**e** in THF with polystyrene standards gave $M_n = 8.8 \times 10^4$ and $M_w = 3.1 \times 10^5$ for **9d** and $M_n = 4.5 \times 10^4$ and $M_w = 1.6 \times 10^5$ for **9e**. In contrast, the molecular weight of *tert*-butyl-substituted polymer **2h** was estimated to be 6.7×10^3 from ¹H NMR determination of the number of repeat units, $n = 14.4^2$

Polymers **9d,e** were readily soluble in organic solvents and gave clear films of readily adjustable thickness when coated on glass plates. Since the two different alkyl substituents dictated **9d** to be a \sim 1:1 mixture of two diastereomers, its high solubility was expected.

Thermal stability of stilbenes **5d**,**e** and polymers **9d**,**e** was estimated by simultaneous TG-DTA under a flowing stream of nitrogen. Following melting, **5d** and **5e** evaporated cleanly at 320 and 340 °C, respectively. Polymer **9e** showed no weight change until a 70% weight loss, centered on 460 °C, occurred above 400 °C. Polymer **9d** showed a 5% weight loss at 130–380 °C followed by a weight loss of 73% centered on 460 °C.

The UV absorption spectra of **9e**, **5e**, and *p*-quaterphenyl are compared in Figure 2. Introduction of the *p*-quaterphenyl unit into a TTPC polymer created a 16-

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nm red shift (294 \rightarrow 310 nm) and 8% increase in the absorptivity. When tert-butyl groups replaced the secalkyl groups as in **2h**, a similar, 10-nm shift ($294 \rightarrow 304$ nm) was observed.⁴² Comparison of *p*-quaterphenyl with model compound 2g showed attachment of the C(tertbutyl)C(*tert*-butyl)Ph group to the para and para' positions of *p*-quaterphenyl produced an 8-nm red shift and an increased absorptivity of 75%.

The fluorescence emission spectrum of **9e** is compared to the spectrum of *p*-quaterphenyl in Figure 2. Introduction of the *p*-quaterphenyl unit into a TTPC polymer created an 18-nm red shift ($363 \rightarrow 381$ nm) with some broadening of the vibrational bands. Stilbene 5e (not shown) did not fluoresce significantly. Polymer 9e gave $\phi = 0.55$. This compared to $\phi = 0.89$ for *p*-quaterphenyl.⁵⁵ When *tert*-butyl groups replaced the *sec*-alkyl groups as in **2h**, the fluorescence showed a 15-nm red shift (\sim 362 $\rightarrow \sim 377$ nm). Comparison of *p*-quaterphenyl with model compound 2g showed the attachment of the C(tertbutyl)C(tert-butyl)Ph group to the para and para' positions of *p*-quaterphenyl produced an 8-nm red shift and a negligible decrease in quantum yield.42

In conclusion, the TTPC unit was incorporated into readily soluble polymers with large fluorescence quantum yields. Whereas two 7-tridecyl substituents on the stilbene units maintained good geometric integrity and provided good solubility, two 5-nonyl substituents gave poorly soluble materials. Very long substituents such as octadecyl could not be incorporated by this route.

Experimental Section

Routine mass spectra were obtained by using EI. Melting points were uncorrected. The mode of THF purification was critical to success during McMurry coupling reactions. HPLC (0.005% water) grade was further dried by storing over 4 Å molecular sieves and passing through a basic alumina column directly into the reaction vessel.

Ketones 4c-e are known but not well described. Ketone 4b⁵⁶ was prepared by direct acylation. Ketones $4c,^{\rm 57-59}$ $4d,^{\rm 60} \text{and}$ $4e^{\rm 61}$ were prepared in 65-78% yield by alkylation of ketones 3c-e, respectively. A typical procedure is described for 4e.

2-Hexyl-1-phenyl-1-octanone, 4e. To a solution of 3e (40.8 g, 0.200 mol) and sodium amide (16 g of 50% w/w solution in toluene, 0.21 mol, transferred quickly in open air) in 300 mL of toluene was added 1-bromohexane (38.5 g, 0.232 mol) dropwise under argon over 40 min. This mixture was refluxed for 12 h and quenched with dilute HCl. The organic layer was separated and passed through a basic alumina column (1:1 mixture, CH2-Cl₂ and hexanes). The solvent was removed under vacuum and the crude product was purified by flash column chromatography (silica gel, 230-425 mesh) with use of methylene chloride and hexanes (1:19) followed by fractional distillation under vacuum to obtain 4e (37.3 g, 64.6%): bp^{0.27 mm} 125-135 °C (lit.⁶¹ bp^{8 mm} 192 °C); FTIR (Neat) 1681 (s) cm⁻¹; MS (m/z) 288 (M⁺), 105 (100%); ¹H NMR (400 MHz) δ 7.95 (d, J = 6.80 Hz, 2H), 7.55 (t, J = 7.20 Hz, 1H), 7.46 (t, J = 8.00 Hz, 2H), 3.41 (m, 1H), 1.75

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(m, 2H), 1.50 (m, 2H), 1.24 (m, 16H), 0.84 ppm (t, J = 6.40 Hz, 6H); ¹³C NMR (100 MHz) δ 204.7, 137.8, 132.7, 128.6, 128.1, 46.2, 32.5, 31.7, 29.5, 27.6, 22.6, 14.0 ppm; HRMS (Electrospray) calcd for C₂₀H₃₂0 + Na 311.2351, found 311.2356.

(E)-7,10-Dihexyl-8,9-diphenyl-8-hexadecene, 5e. Zinc powder (21 g, 0.32 mol) was added to a slurry of TiCl₄ (18 mL, 0.16 mol) in dried THF (300 mL) at 0 °C. Under argon, 4e (23.0 g, 0.798 mol) in dry THF (30 mL) was added dropwise. The mixture was refluxed for 48 h. The reaction was quenched with aqueous K₂CO₃. Methylene chloride (200 mL) was added and the organic layer was separated and filtered through a bed of alumina. The solvent was removed under vacuum to obtain a viscous oil. Addition of methanol (\sim 3 mL) led to the crystalline product (8.4 g, 39%); mp 81.0–81.5 °C; FTIR (KBr) 3058 (m), 736 (m), 696 (s) cm⁻¹; \dot{MS} (*m/z*) 544 (M⁺), 91 (100%); ¹H NMR (400 MHz) δ 7.33 (t, J = 7.20 Hz, 4H), 7.26 (t, J = 8.00 Hz, 2H), 7.07 (d, J =6.80 Hz, 4H), 2.16-2.06 (m, 2H), 1.40 (m, 4H), 1.26 (m, 16H), 1.14 (m, 16H), 0.99 (m, 4H), 0.89 ppm (t, J= 6.80 Hz, 12H); ¹³C NMR (100 MHz) δ 142.2, 139.8, 130.2, 127.3, 126.0, 42.8, 33.7, 32.0, 29.6, 28.0, 22.7, 14.1 ppm; HRMS ESI calcd for C₄₀H₆₄ + Na 567.4906, found 567.4903.

(E)-7,10-Dihexyl-8,9-di(4-iodophenyl)-8-hexadecene, 7e. To a solution of 5e (373 mg, 0.685 mmol) in 80 mL of wet methylene chloride, prepareď as described, 53 was added iodine (697 mg, 2.74 mmol), silver sulfate (430 mg, 1.37 mmol), and sodium trifluoromethanesulfonate (8.0 mg, 0.040 mmol). The reaction mixture was stirred at 30-35 °C for 4 h, cooled to room temperature and quenched with 5% aqueous sodium metabisulfite until the violet color disappeared. The mixture was filtered through a silica gel column (60–80 mesh, 9 cm \times 2.5 cm), and the layered filtrate was separated. The aqueous layer was extracted with hexanes. The combined organic layer was washed with water and saturated aqueous sodium chloride and dried over anhydrous sodium sulfate. The solvent was removed under vacuum, and the crude product was purified by flash column chromatography (2.5 cm \times 19 cm, 230–425 mesh silica gel, hexanes) to give (447 mg, 82%) an off-white product: mp 82-83 °C; MS (*m*/*z*) 796 (M⁺, 100%); ¹H NMR (400 MHz,) δ 7.66 (d, J = 8.40 Hz, 4H), 6.79 (d, J = 8.40 Hz, 4H), 2.06 (m, 2H), 1.28 (m, 20H), 1.12 (m, 12H), 1.02 (m, 8H), 0.89 ppm (t, J =6.80 Hz, 12H); ¹³C NMR (100 MHz) δ 141.8, 139.1, 136.6, 132.0, 91.8, 42.9, 33.6, 32.0, 29.6, 28.0, 22.7, 14.1 ppm; HRMS calcd for C40H62I2 796.2945, found 796.2923.

Preparation of Polymer 9e. Recrystallized iodostilbene 7e (398 mg, 0.500 mmol), biphenyl boronate ester 8 (203 mg, 0.500 mmol), Pd(PPh₃)₄ (19.3 mg, 0.0167 mmol), and K₂CO₃ (1.38 g, 10.0 mmol) were placed in a flask under argon and charged with 100 mL of degassed 40:40:20 toluene/DMF/H₂O. After 78 h at 78 °C, the mixture was quenched with water and the organic layer was separated. The polymer was precipitated into methanol and then purified by Soxhlet extraction for 9 days with toluene. The solution was reduced to 25 mL and precipitated in 500 mL of methanol. The precipitation was repeated with acetone, providing 308 mg of a white solid: TGD/DTA mp 300-800 °C dec; ¹H NMR (400 MHz) & 7.79, 7.68, 7.18, 2.27, 1.32, 1.23, 0.93 ppm (all peaks were broad); $^{13}\mathrm{C}$ NMR (100 MHz) δ 142.2, 140.0, 139.4, 139.1, 138.2, 130.7, 127.4, 125.9, 43.2, 33.9, 32.1, 29.7, 28.1, 22.8, 14.2 ppm.

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Supporting Information Available: Characterization of new compounds and ¹H NMR and ¹³C NMR spectra of compounds 4e, 5b-e, and 7c-e. This material is available free of charge via the Internet at http://pubs.acs.org.

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