

Synthesis, Isolation and Crystal Structure Characterization of (*Z*)-4'-(1-Phenyl-2-*p*-tolylvinyl)biphenyl-4-carbaldehyde

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Fluorescent organic materials are used in a range of applications including bio-sensors,¹ optical storage devices,² and organic solar cells.³ They have recently gained particular interest as efficient light emitters and charge transporters in organic light-emitting diodes (OLEDs) due to their significant advantages in energy consumption and flexible applications.⁴ The improved efficiency and stability of blue emitting materials is especially important in the area of OLEDs, because efficient blue emitters are rare due to the intrinsic wide band-gap.⁵ Blue fluorescent materials include oligophenylenes,⁶ diarylanthracenes,⁷ and poly(phenylene vinylene)s.⁸ Recently, organometallic phosphorescent materials including iridium (III) complexes have been studied due to their high efficiency.⁹

Since Hosokawa's pioneering work with 4,4'-bis(2,2-diphenylvinyl)-1,1'-biphenyl (DPVBi) in the 1990s,¹⁰ various distyrylarylenes (DSAs) have been investigated as representative blue fluorescent materials in OLEDs.¹¹ However, their low quantum efficiency, low glass transition temperature and crystallizing tendency have limited their applications in OLEDs.¹² The tendency for crystallization eventually degrades the lifetime of the corresponding devices by destroying the film homogeneity and crystal boundary.¹³ Structural modifications have been investigated to decrease the crystallizing tendency of DSAs, typically by constructing spiro-DSAs¹⁴ and tetrahedral DSAs.¹⁵

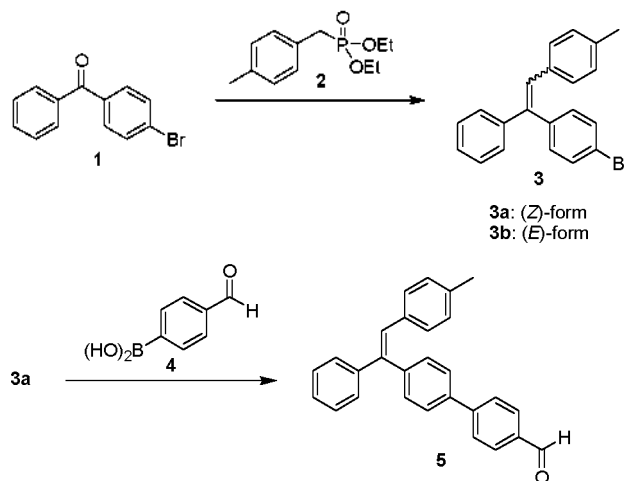
The Horner-Wadsworth-Emmons reaction¹⁶ has been frequently used to prepare π -conjugated hydrocarbons for OLEDs and organic field-effect transistors. While (*E*)-isomers are predominantly produced by reactions of aldehydes with benzyl phosphonates,¹⁷ reactions of ketones generate mixtures of (*E*)- and (*Z*)-geometric isomers that are difficult to be resolved.^{11(b),18} Significant problems in understanding the relationship between chemical structures and physical properties of emitting materials have been encountered because each isomer shows different optical properties.¹⁹ Therefore, an efficient separating process for two geometric isomers has been explored for the systematic development of functional π -conjugated hydrocarbons.

In a program for the development of blue fluorescent materials in our laboratory, 1-(4-bromophenyl)-2-(4-methylphenyl)-1-phenylethylene (**3**), an important intermediate for unsymmetrical DSAs, was prepared by the reaction of 4-bromobenzophenone (**1**) with diethyl (4-methylbenzyl)phosphonate (**2**) (Scheme 1). However, the crude product **3** was obtained as a 60 : 40 mixture of geometric isomers that were not separable

by common chromatographic methods. Fortunately, we observed that a careful recrystallizing process in 2-propanol facilitated the selective isolation of both isomers. Nuclear magnetic resonance (NMR) study showed that the initially recrystallized major product was (*Z*)-isomer, **3a**. (*Z*)-4'-(1-Phenyl-2-*p*-tolylvinyl)biphenyl-4-carbaldehyde (**5**) was prepared by Suzuki-Miyaura reaction of **3a** with 4-formylphenylboronic acid (**4**), and recrystallized in *n*-hexane : Et₂O (8 : 1) to give a single crystal that was characterized by X-ray structure analysis. The results of this study are presented and discussed below.

The reaction of **1** with **2** in the presence of potassium *tert*-butoxide produced a 60 : 40 mixture of geometric isomers of bromotriphenylethylene **3** at the refluxing temperature of THF. While conventional chromatographic methods were not able to resolve those isomers, the recrystallization process in 2-propanol facilitated the selective isolation of each isomer in a crystalline form. The major product **3a** was initially obtained as a clear crystalline solid, which was purified by a double recrystallizing process, in 31% isolated yield with 98% purity. The other isomer **3b** was obtained by the consecutive recrystallization process of the remaining mother liquor.

The crystalline solids of both isomers were not uniform enough for single-crystal X-ray crystallography. Although various spectroscopic analyses were performed to distinguish the configuration of both isomers, their configuration could not be easily identified. Among ¹H-NMR, ¹³C-NMR, correla-



Scheme 1

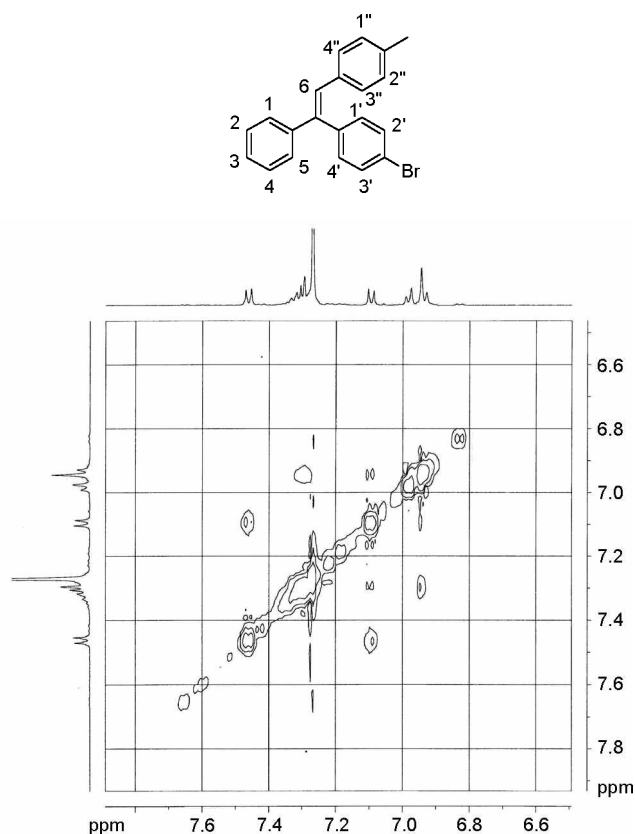


Figure 1. NOESY spectra of **3a**.

tion spectroscopy (COSY), nuclear Overhauser effect spectroscopy (NOESY) and heteronuclear single quantum coherence (HSQC) analyses, the NOESY spectra of **3a** presented a vague clue (Figure 1). The correlations between H-6 at δ 7.05 and H-1 at δ 7.30 and between H-3'' at δ 7.05 and H-1' at δ 6.94 suggested that **3a** may have the *Z*-configuration.

The configuration of **3a** could be clearly determined after the synthesis of **5**. Stilbene **5** was prepared by the palladium-catalyzed cross-coupling reaction of **3a** with **4** in the presence of sodium carbonate. The crude product was purified by column chromatography to give **5** in 85% isolated yield. A single crystal of **5** was obtained by recrystallization of the purified product in *n*-hexane : Et₂O (8 : 1). The single-crystal X-ray crystallography of **5** has not been disclosed before. The structural information of the crystalline **5** is presented in Table 1.

The molecular structure of compound **5** illustrated in Figure 2 clearly shows the configuration and non-planar conformation of **5**. The torsion angles C2-C1-C16-C18, C2-C1-C13-C9, and C1-C2-C6-C10 in **5** were 29.4 (4), 57.8 (4), and 38.4 (4) $^\circ$, respectively. The bond length of C1=C2 was 1.353 (4) Å, which is longer than the reported C=C bond lengths of *trans*-²⁰ and *cis*-stilbenes.²¹

The steric hindrance between rings **a** and **c** created a significant distortion around the ethylene group, and especially broadened the angle C7-C14-C15 to 127.9 (2) $^\circ$. The dihedral angles between rings **a** and **b**, rings **a** and **c** and rings **a** and **d** were 36.6 (2), 57.0 (2), and 76.1 (2) $^\circ$, respectively (Figure 3). Among the six angles in phenyl rings, the angles involving C4, C6, C8, C13, and C16, which are directly connected to

Table 1. Crystal data and structure refinement for **5**.

Empirical formula	C ₂₈ H ₂₂ O
Formula weight	374.46
Temperature	296(2)K
Crystal system, space group	Monoclinic, <i>P2(1)/c</i>
Unit cell dimension	<i>a</i> = 11.684 (2) Å <i>b</i> = 15.626 (2) Å <i>c</i> = 11.325 (2) Å β = 92.66 (1) $^\circ$
Volume	2065.4 (5) Å ³
Z	4
Absorption coefficient	0.07 mm ⁻¹
F(000)	792
Theta range for data collection	2.18 to 28.61 deg.
Index range	-15 $\leq h \leq$ 15 -21 $\leq k \leq$ 20 -13 $\leq l \leq$ 15
Independent reflections	5192 [R (int) = 0.069]
Goodness-of-fit on F ²	1.051
Final R indices [I > 2 σ (I)]	R = 0.1303, R _w = 0.3223
Largest diff. peak and hole	0.33 and -0.42 e/Å ³

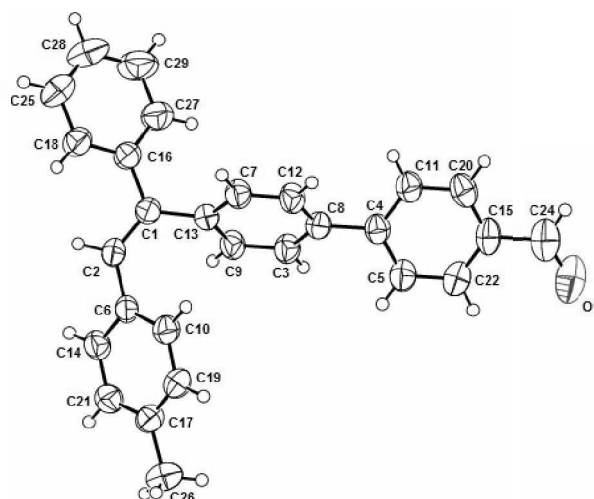


Figure 2. Molecular structure of **5**, showing 50% probability displacement ellipsoids and the atom-numbering scheme.

outside the *sp*² carbon of the ring, were generally smaller than the others.

In summary, bromotriphenylethylene **3** was prepared as a 60 : 40 mixture of geometric isomers and efficiently separated to give both pure (*Z*)- and (*E*)-isomers by a careful recrystallizing process in 2-propanol. NMR study revealed the initially recrystallized major product to be the (*Z*)-isomer, **3a**. The configuration of **3a** was confirmed by the first single crystal X-ray structure analysis of (*Z*)-4'-(1-phenyl-2-*p*-tolylvinyl)biphenyl-4-carbaldehyde (**5**) that was prepared by Suzuki-Miyaura reaction of **3a** with **4** and recrystallized in *n*-hexane : Et₂O (8 : 1). The procedure described in this paper is a promising synthetic route for preparing important intermediates of unsymmetrical DSAs. It is also expected to facilitate the systematic develop-

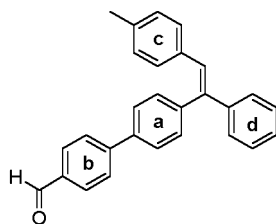


Figure 3. Molecular structure of **5**.

ment of functional π -conjugated hydrocarbons, such as organic fluorescent materials.

Experimental Section

Preparation of 1-(4-bromophenyl)-2-(4-methylphenyl)-1-phenylethylene (3**).** To the mixture of **2** (35.1 mmol, 8.51 g) and potassium *tert*-butoxide (54.0 mmol, 6.06 g) in THF (54 mL) was added a solution of **1** (27.0 mmol, 5.00 g) in THF (200 mL) at room temperature under an Ar atmosphere. The mixture was stirred at refluxing temperature for 3 h. The reaction mixture was cooled to room temperature; diluted with ethyl acetate (300 mL); washed with 1% aqueous HCl (200 mL), water (300 mL) and brine; dried over MgSO_4 ; and concentrated in vacuo. When the crude product was purified by column chromatography, **3** was obtained as a white powder (8.83 g, 94%) that was a 60 : 40 mixture of **3a** and **3b** by GC analysis. When the mixture was recrystallized from 2-propanol, a crystalline product was generated as a 91 : 9 mixture of **3a** and **3b**. This crystalline mixture was purified further by the second recrystallization from 2-propanol to give **3a** as a needle crystal with 98% purity (2.91 g, 31%); TLC R_f 0.73 (*n*-hexane : Et_2O = 1 : 1), mp 119 - 121 °C. ^1H NMR spectrum (500 MHz, CDCl_3) δ 2.28 (s, 3H), 6.93 (d, J = 8.0 Hz, 2H), 6.93 (s, 1H), 6.97 (d, J = 8.0 Hz, 2H), 7.09 (d, J = 8.3 Hz, 2H), 7.27-7.31 (m, 5H), 7.45 (d, J = 8.3 Hz, 2H); ^{13}C NMR spectrum (125 MHz, CDCl_3) δ 21.4, 121.6, 127.8 ($\times 3$), 128.5 ($\times 2$), 128.9, 129.1 ($\times 2$), 129.7 ($\times 2$), 132.1 ($\times 2$), 132.5 ($\times 2$), 134.4, 137.1, 139.8, 140.7, 143.3; HRMS (EI, 70 eV) calcd for $\text{C}_{21}\text{H}_{17}\text{Br}$ (M^+), 348.0514, found 348.0495.

The (*E*)-isomer **3b** was obtained by the consecutive recrystallizing process of the remaining mother liquor. Recrystallization of the white solid that was obtained by concentrating the remaining solution produced a pure crystalline **3b** (0.281 g, 3%); TLC R_f 0.73 (*n*-hexane : Et_2O = 1 : 1), mp 69 - 70 °C. ^1H NMR spectrum (500 MHz, CDCl_3) δ 2.26 (s, 3H), 6.89-6.91 (m, 3H), 6.94 (d, J = 8.1 Hz, 2H), 7.16-7.19 (m, 4H), 7.33-7.34 (m, 3H), 7.41 (d, J = 8.5 Hz, 2H); ^{13}C NMR spectrum (75 MHz, CDCl_3) δ 21.3, 121.6, 127.8, 128.8, 129.0 ($\times 4$), 129.4 ($\times 2$), 129.7 ($\times 2$), 130.6 ($\times 2$), 131.5 ($\times 2$), 134.5, 137.2, 140.3, 140.8, 142.8; HRMS (EI, 70 eV) calcd for $\text{C}_{21}\text{H}_{17}\text{Br}$ (M^+), 348.0514, found 348.0540.

Preparation of 4'-(1-phenyl-2-*p*-tolyl-vinyl)-biphenyl-4-carbaldehyde (5**).** To a solution of **3a** (1.4 mmol, 0.50 g) and $\text{Pd}(\text{PPh}_3)_4$ (0.072 mmol, 0.083 g) in DMF (60 mL) was added 2.0 M aqueous Na_2CO_3 (1.5 mL). To the resulting mixture was added **4** (1.7 mmol, 0.25 g), which was dissolved in MeOH (1 mL). The mixture was stirred at refluxing temperature for 7 h.

The reaction mixture was cooled to room temperature; diluted with ethyl acetate (150 mL); washed with 1% aqueous HCl (100 mL); water (300 mL) and brine; dried over MgSO_4 ; and concentrated in vacuo. The crude compound was purified by column chromatography (*n*-hexane : Et_2O = 4 : 1) to generate **5** (0.445 g, 85%) as a white solid; TLC R_f 0.63 (*n*-hexane : Et_2O = 1 : 1), mp 207 - 208 °C. ^1H NMR spectrum (500 MHz, CDCl_3) δ 2.28 (s, 3H), 6.96-6.99 (m, 5H), 7.32-7.35 (m, 7H), 7.63 (d, J = 8.2 Hz, 2H), 7.82 (d, J = 8.2 Hz, 2H), 7.97 (d, J = 8.2 Hz, 2H), 10.07 (s, 1H); ^{13}C NMR spectrum (75 MHz, CDCl_3) δ 21.2, 127.7 ($\times 4$), 127.9 ($\times 2$), 128.5 ($\times 2$), 129.1, 129.1 ($\times 2$), 129.7 ($\times 2$), 130.6 ($\times 3$), 131.5 ($\times 2$), 134.6, 135.5, 137.1, 138.6, 141.3, 141.3, 143.6, 146.9, 192.3; HRMS (EI, 70 eV) calcd for $\text{C}_{28}\text{H}_{22}\text{O}$ (M^+), 374.1671, found 374.1670. The product was recrystallized from *n*-hexane : Et_2O (8 : 1) to give a single crystal of **5** that was analyzed by X-ray crystallography.

X-ray crystallographic analysis for **5.** A single crystal of **5** was mounted on a glass fiber. The diffraction data for **5** were collected on a Bruker I K SMART CCD-based diffractometer with graphite-monochromated Mo- $K\alpha$ radiation (λ = 0.7107 Å) at 296 K. The reflection data were collected as ϕ and ω scans. Cell parameters were determined and refined by the SMART program.²² Data reduction and empirical absorption correction were performed using SAINT software²³ and the SADABS program,²⁴ respectively.

Supplementary Data. Crystallographic data for the structure **5** reported here have been deposited with the Cambridge Crystallographic Data Centre (Deposition No. CCDC-734302). That data can be obtained free of charge via http://www.ccdc.cam.ac.uk/data_request/cif (or from The CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk).

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