

Preparation and Characterization of (*E*)- and (*Z*)-2-(Biphenyl-4-yl)-1-(4-bromophenyl)-1-phenylethene Isomers

Ho-Jun Son, Dong Woo Lee,[†] Tae-Won Lee, Kang Min Ok,[†] and Kwangyong Park^{*}

School of Chemical Engineering and Materials Science, Chung-Ang University, Seoul 156-756, Korea

^{*}E-mail: kypark@cau.ac.kr

[†]Department of Chemistry, Chung-Ang University, Seoul 156-756, Korea

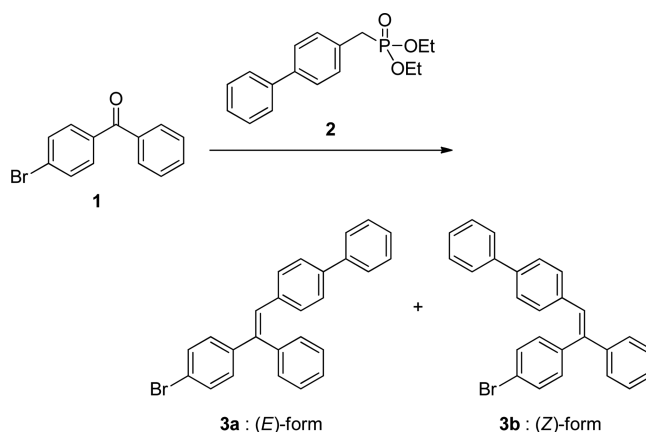
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Various π -conjugated organic compounds have been applied in a wide range of optoelectronic devices such as organic field-effect transistors, organic photovoltaic cells, and organic solid-state lasers.¹ Presently, these materials are attracting great attention because of their application in organic light-emitting diodes (OLEDs), which are typically composed of multiple organic thin layers, including an emissive layer and a hole-transport layer often composed of phenylene and vinylene moieties.² In particular, stilbene compounds, well known for their biological activities,³ have been widely investigated as short subunits of poly(*p*-phenylenevinylene), the first light-emitting polymer,⁴ to understand the emission mechanism and relationship between the molecular structure and emitted light.⁵ Distyrylarylene derivatives are also well known as blue fluorescent materials⁶ and hole-transport materials.⁷

As part of our program directed toward the development of novel blue electroluminescent materials with unsymmetrical stilbene or distyrylarylene skeletons, we have prepared various bromostilbene intermediates by the Horner–Wadsworth–Emmons reaction⁸ of bromobenzophenone derivatives with benzyl phosphonates. However, great difficulties arise when isolating and identifying pure products from these reactions because of the generation of chromatographically inseparable mixtures of (*E*)- and (*Z*)-geometric isomers.⁹ Therefore, an efficient process for separating the two isomers is quite necessary for the systematic development of electroluminescent π -conjugated hydrocarbons.

One of the intermediates, 2-(biphenyl-4-yl)-1-(4-bromophenyl)-1-phenylethene (**3**), was prepared by the reaction of 4-bromobenzophenone (**1**) with diethyl biphenyl-4-ylmethyl phosphonate (**2**) (Scheme 1). Crude product **3** was obtained as a mixture of two geometric isomers that were inseparable by common chromatographic methods. However, it was observed that careful recrystallization in ethyl acetate facilitated the selective crystallization of one isomer. The other form could be also isolated by consecutive recrystallizations of the material remaining in the mother liquor from ethyl acetate. Herein, our efforts toward the synthesis, isolation, and identification of both isomers of **3** by NMR spectroscopic and X-ray crystallographic analyses are presented and dis-



Scheme 1. Reaction scheme.

cussed.

The reaction of **1** and **2** in the presence of potassium *tert*-butoxide at reflux temperature produced a 55:45 mixture of the geometric isomers of bromotriphenylethylene **3** in 89% yield. While conventional chromatographic methods were not able to resolve those isomers, recrystallization of the mixture in ethyl acetate selectively yielded the minor isomer as its crystalline form in about 92% purity. Further recrystallization of the initially obtained crystalline product gave a pure single crystalline solid in 32% isolated yield based on **1**. A similar double recrystallization of the remaining material in the mother liquor provided the major isomer as a very thin needle-like crystalline solid in 14% isolated yield with more than 99% purity.

Among the various spectroscopic analyses, nuclear Overhauser effect spectroscopy (NOESY) presented a reasonable clue for the absolute configuration of both isomers of **3**. ¹H-NMR spectroscopy of the initially crystallized minor isomer showed one singlet at δ 6.97 (H14) and five doublets at δ 7.07 ($J = 8.34$ Hz, H16 and H20), 7.19 ($J = 8.46$ Hz, H3 and H5), 7.37 ($J = 8.34$ Hz, H17 and H19), 7.43 ($J = 8.46$ Hz, H2 and H6), and 7.53 ($J = 7.85$ Hz, H22 and H26) along with other multiplets. Strong NOE interactions of H14 with H16 (or H20) and H3 (or H5) appearing in the NOESY spectrum clearly showed that the minor isomer should be **3a** with (*E*)-

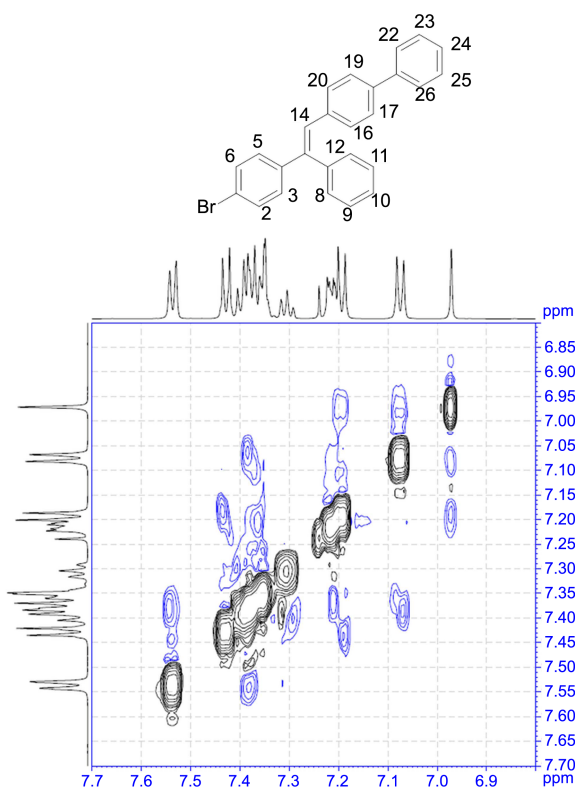


Figure 1. NOESY spectrum of **3a**.

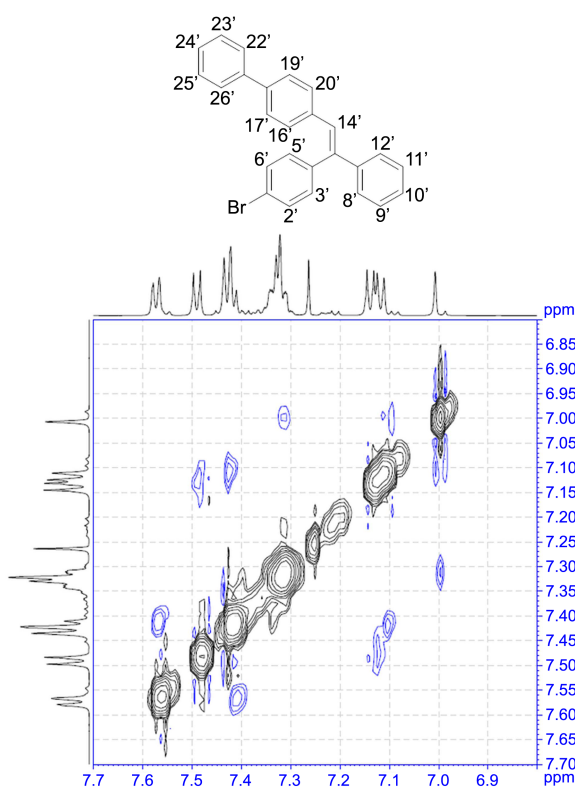


Figure 2. NOESY spectrum of **3b**.

configuration (Figure 1). This was supported by the absence of NOE interaction between H14 and H8 (or H12).

On the other hand, ¹H-NMR spectroscopy of the latter-

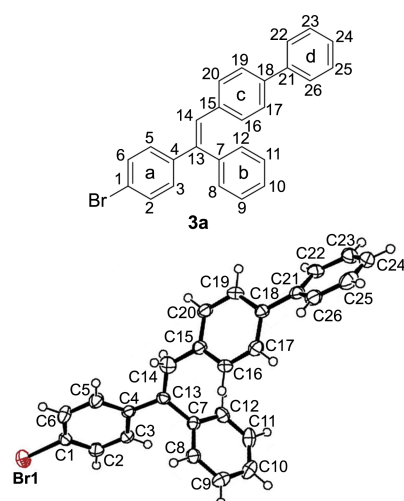


Figure 3. Molecular structure of **3a**.

isolated major product showed one singlet at δ 7.00 (H14') and five doublets at δ 7.12 ($J = 8.24$ Hz, H16' and H20'), 7.14 ($J = 8.32$ Hz, H3' and H5'), 7.43 ($J = 8.24$ Hz, H17' and H19'), 7.49 ($J = 8.32$ Hz, H2' and H6'), and 7.57 ($J = 7.27$ Hz, H22' and H26') along with other multiplets. Strong NOE interactions of H14' with H16' (or H20') and H8' (or H12') that are mixed in a multiplet at δ 7.30–7.36 showed that the major isomer was **3b** with (*Z*)-configuration (Figure 2). This inference was also supported by the absence of NOE interactions between H14' and H3' (or H5').

The molecular structure of minor product **3a** obtained by single-crystal X-ray crystallography, illustrated in Figure 3, was established as having an (*E*)-configuration and possess-

Table 1. Crystallographic data and structure refinement for **3a**

Empirical formula	C ₂₆ H ₁₉ Br
Formula weight	411.32
Temperature	200 K
Crystal system, space group	Triclinic, <i>P</i> -1
Unit cell dimension	$a = 9.3706$ (2) Å $b = 9.9786$ (2) Å $c = 11.8272$ (2) Å $\alpha = 87.880$ (10) ^o $\beta = 76.237$ (10) ^o $\gamma = 63.888$ (10) ^o
Volume	941.41 (10) Å ³
<i>Z</i>	2
Absorption coefficient	2.14 mm ⁻¹
F(000)	420
Theta range for data collection	1.78 ^o –28.36 ^o
Index range	$-12 \leq h \leq 11$ $-13 \leq k \leq 11$ $-15 \leq l \leq 15$
Independent reflections	4684 [R (int) = 0.068]
Goodness-of-fit on F ²	0.898
Final R indices [I > 2σ(I)]	R = 0.041 R _w = 0.076
Largest diff. peak and hole	0.28 and -0.40 e Å ⁻³

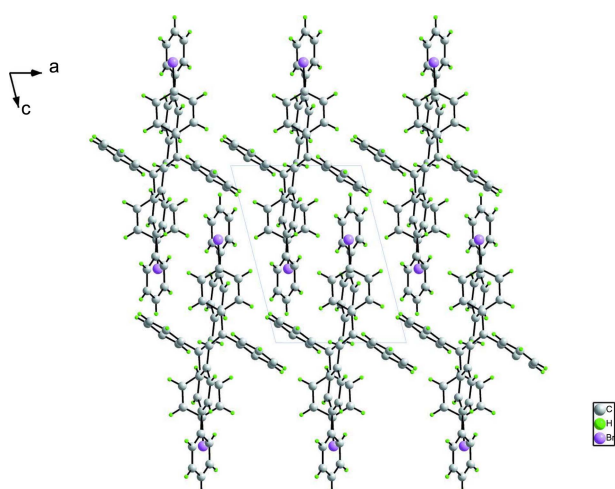


Figure 4. Crystal-packing diagram of **3a**.

ing a nonplanar conformation. The torsion angles of C13-C14-C15-C20, C3-C4-C13-C14, C8-C7-C13-C14, and C19-C18-C21-C22 are 149.6 (2)°, 150.9 (2)°, 123.1 (3)°, and 138.5 (2)°, respectively. The dihedral angles between rings **a** and **c** and between rings **b** and **c** are 66.84 (13)° and 60.14 (13)°, respectively.

Steric hindrance between rings **b** and **c** creates a significant distortion around the ethylene group to widen the angle of C13-C14-C15 to 129.2 (2)°. The bond length of C13=C14 is 1.342 (3) Å, which is at the longer end of such bonds reported in *trans*-stilbenes.¹⁰ Among the six angles in the phenyl rings, those involving C4, C7, C15, C18, and C21, which are directly connected to the outer *sp*² carbon of the ring, are smaller than the others. Detailed structural information of the crystalline structure of **3a** is presented in Table 1. Furthermore, the crystal-packing tendency of **3a**, as disclosed in Figure 4, was identified as adopting that of a head-to-tail pair.

Conclusion

In summary, bromotriphenylethylene **3** was prepared as a 55:45 mixture of geometric isomers, which were separated to yield the pure (*Z*)- and (*E*)-isomers by a careful recrystallization process in ethyl acetate. NOESY and single-crystal X-ray crystallographic studies revealed the initially crystallized minor product (**3a**) to be the (*E*)-isomer and the latter-crystallized major product (**3b**) to be the (*Z*)-isomer. A single molecule of **3a** was disclosed to have a triclinic crystal structure. The synthesis and purification procedures described in this paper are believed to be useful for preparing pure intermediates of unsymmetrical stilbenes and distyrylarylenes. These results should facilitate the systematic development of functional π -conjugated hydrocarbons such as organic fluorescent materials.

Experimental

Preparation of 2-(Biphenyl-4-yl)-1-(4-bromophenyl)-1-

phenylethene (3). To a mixture of diethyl biphenyl-4-ylmethyl phosphonate (**2**, 24.89 mmol, 7.58 g) and potassium *tert*-butoxide (32.36 mmol, 3.63 g) in THF (50 mL) was added a solution of 4-bromobenzophenone (**1**, 19.14 mmol, 5.00 g) in THF (200 mL) at room temperature under an Ar atmosphere. The mixture was stirred at room temperature for 24 h. The mixture was first diluted with diethyl ether (300 mL), then washed with 1% aqueous HCl, water, and brine, and finally dried over MgSO₄ and evaporated. Purification of the crude product by column chromatography yielded **3** as a white powder (7.01 g, 89%) in a 55:45 mixture of (*Z*)- and (*E*)-stereoisomers by GC analysis. The mixture was dissolved in ethyl acetate and heated to 78 °C. The solution was allowed to slowly cool to room temperature. The (*E*)-isomer (**3a**) was initially crystallized with 92% purity. Further recrystallization of the initially crystallized product using the same procedure provided **3a** (2.24 g, 32%) as pure crystals suitable for X-ray diffraction analysis: TLC *R*_f = 0.78 (*n*-hexane:Et₂O = 2:1); mp 171–172 °C (uncorrected); ¹H NMR (600 MHz, CDCl₃) δ 0.00 (TMS), 6.97 (s, 1H), 7.07 (d, *J* = 8.34 Hz, 2H), 7.19 (d, *J* = 8.46 Hz, 2H), 7.20–7.23 (m, 2H), 7.30 (t, *J* = 7.37 Hz, 1H), 7.34–7.41 (m, 5H), 7.37 (d, *J* = 8.34 Hz, 2H), 7.43 (d, *J* = 8.46 Hz, 2H), 7.53 (d, *J* = 7.85 Hz, 2H); ¹³C NMR (150 MHz, CDCl₃) δ 121.5, 126.6 ($\times 2$), 126.8 ($\times 2$), 127.2, 127.7, 128.0, 128.7 ($\times 2$), 128.8 ($\times 2$), 129.1 ($\times 2$), 129.9 ($\times 2$), 130.2 ($\times 2$), 131.3 ($\times 2$), 136.0, 139.5, 139.6, 140.4, 141.5, 142.3; Anal. calcd. for C₂₆H₁₉Br: C, 75.92; H, 4.66. Found: C, 76.02; H, 4.70.

The double recrystallization process (as outlined above) of the material remaining in the mother liquor yielded the (*Z*)-isomer (**3b**) as a very thin needle-like crystalline solid (1.00 g, 14%): TLC *R*_f = 0.78 (*n*-hexane:Et₂O = 2:1); mp 152–153 °C (uncorrected); ¹H NMR (600 MHz, CDCl₃) δ 0.00 (TMS), 7.00 (s, 1H), 7.12 (d, *J* = 8.24 Hz, 2H), 7.14 (d, *J* = 8.34 Hz, 2H), 7.30–7.36 (m, 6H), 7.42 (t, *J* = 7.40 Hz, 2H), 7.43 (d, *J* = 8.24 Hz, 2H), 7.49 (d, *J* = 8.32 Hz, 2H), 7.57 (d, *J* = 7.27 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 121.6, 126.7 ($\times 2$), 126.8 ($\times 2$), 127.3, 127.6 ($\times 2$), 127.7, 128.2, 128.3 ($\times 2$), 128.7 ($\times 2$), 129.9 ($\times 2$), 131.9 ($\times 2$), 132.2 ($\times 2$), 136.0, 139.4, 139.6, 140.4, 141.4, 142.9.

X-ray Crystallographic Analysis of 3a. A single crystal of **3a** was mounted on a glass fiber. The diffraction data were collected on a Bruker SMART BREEZE diffractometer with sealed-tube monochromatized Mo-K α radiation (λ = 0.7107 Å) at 200 K. The reflection data were collected as φ and ω scans. Cell parameters were determined and refined using the *SAINTE* program. Data reduction and empirical absorption corrections were performed using *SAINTE* software and the *SADABS* program, respectively.

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Supplementary Material. CCDC 977781 contains the

supplementary crystallographic data for this paper. This data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK; Telephone: (44) 01223 762910; Facsimile: (44) 01223 336033; E-mail: deposit@ccdc.cam.ac.uk].

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