π-Conjugated Molecules

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Phosphonium- and Borate-Bridged Zwitterionic Ladder Stilbene and Its Extended Analogues**

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Significant efforts have been devoted to the development of new π-conjugated molecules with unique electronic and photophysical properties. The development of such molecules would lead to further advancements in the field of organic electronics. In this regard, ladder π-conjugated molecules having fully ring-fused structures are a promising class of materials.[1] Their flat and rigid π-conjugated skeleton, which lacks any conformational disorder, promises a set of desired properties, such as intense emission and high carrier mobility. Furthermore, their electronic structures can be modulated by the incorporation of appropriate bridging moieties. A number of fascinating ladder systems embedding various elements, such as Group 13 boron,[2] Group 14 silicon,[3] Group 15 nitrogen[4] and phosphorus,[5] and Group 16 sulfur and selenium,[6,7] as the bridging moiety have been reported. We have also synthesized a series of ladder stilbenes and their extended analogues containing main-group elements and have demonstrated that their properties are highly dependent on the nature of the elements.[8–11]

We have now introduced a new entity into this class of ladder compounds: the ladder stilbene **1** having boron[12] and phosphorus[13] bridges, as shown in Figure 1. This design aims at producing a highly polar π skeleton by incorporation of the zwitterionic bridges.[14] Several aspects of this skeleton are of interest. First, the Group 13 boron and Group 15 phosphorus atoms are complementary in terms of their Lewis acidity or basicity. We envisioned that the introduction of the boryl and phosphanyl groups to the diphenylacetylene skeleton would result in a nucleophilic cascade cyclization (Figure 1), thus furnishing the zwitterionic structure. Recently we confirmed that the phosphanyl group has sufficient nucleophilicity to promote the cyclization in the synthesis of the bis(phosphoryl)-bridged stilbenes.[10] Also, a similar activation of the C≡C double bond has recently been reported by Stephan and co-workers.[15] Moreover, according to molecular orbital calculations at the B3LYP/6-31G(d) level, the HOMO and LUMO of **1** are mostly localized on the benzoborole and benzophosphole moieties, respectively, and, as a consequence, **1** has a large dipole moment of 11.9 Debye. Furthermore, compared with other ladder stilbenes with CMe_2 (**3**), PPh (**4**), and P(=O)Ph bridges (**5**), **1** (R^1 = Me, R^2 = Ph) has the smallest HOMO–LUMO gap (Figure 2), thus indicating that the phosphonium and borate bridges can significantly alter the electronic structure of the parent stilbene skeleton. Herein, we report the experimental study of the synthesis of **1** and its extended analogues. Their crystal structures and fundamental properties will be discussed in comparison with the relevant known ladder π systems.

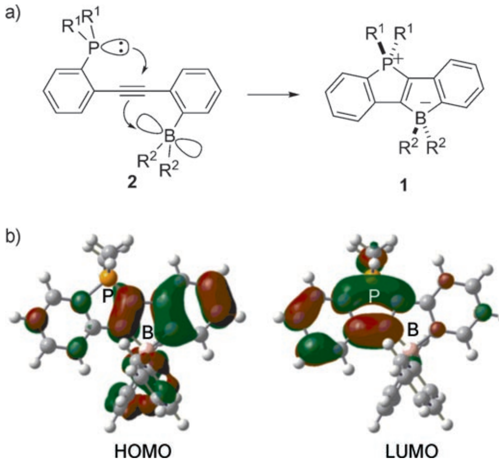

Figure 1. Phosphonium- and borate-bridged stilbene **1**. a) Formation based on a cascade cyclization. b) The Kohn–Sham highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO) of **1** (R^1 = Me, R^2 = Ph) calculated at the B3LYP/6-31G(d) level.

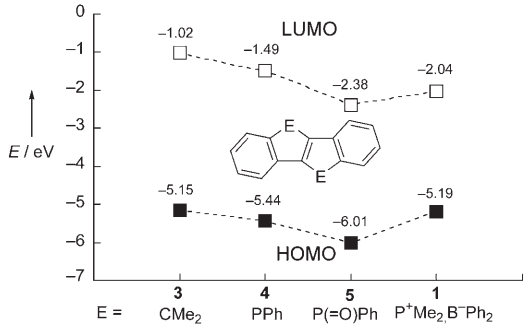

Figure 2. Comparison of the Kohn–Sham HOMO and LUMO energy levels among a series of bridged stilbenes based on calculations at the B3LYP/6-31G(d) level.

Our synthetic strategy is the stepwise introduction of a boryl group and a phosphanyl group onto a diphenylacetylene

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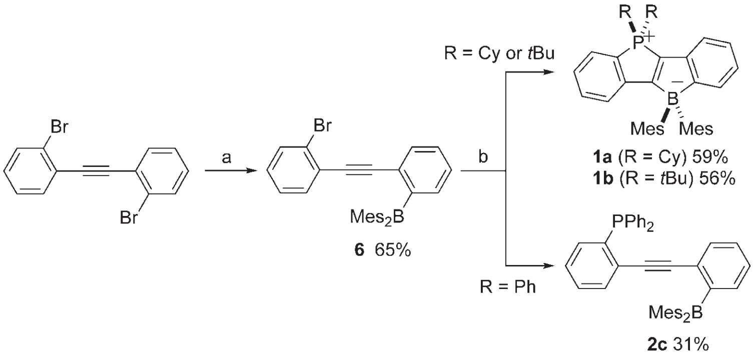
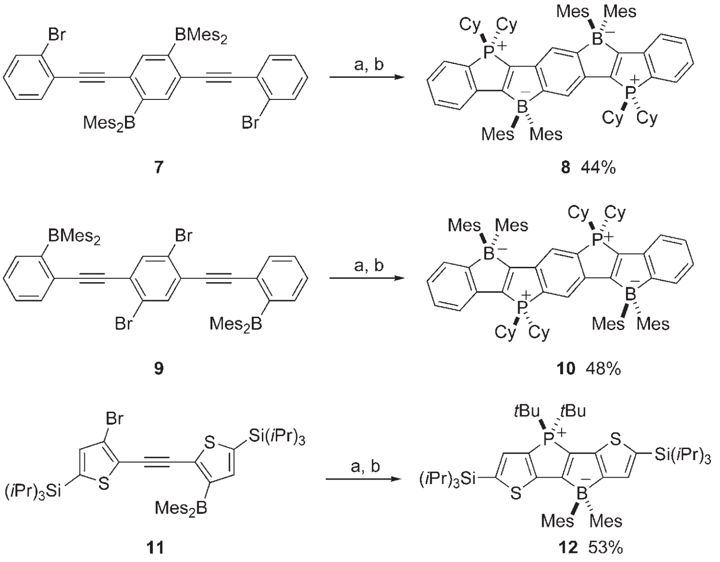
skeleton, as shown in Scheme 1. Thus, the selective monolithiation of bis(2-bromophenyl)acetylene was accomplished using *n*BuLi in THF and subsequent treatment with Mes_2BF to produce the boryl-substituted diphenylacetylene **6** in 63% yield. After the lithiation of **6** with *t*BuLi, R_2PCl was added to the reaction mixture at room temperature. While the reaction using Ph_2PCl afforded (2-borylphenyl)(2-phosphanylphenyl)acetylene **2c** in 31% yield, the use of Cy_2PCl or $(tBu)_2PCl$ resulted in the spontaneous formation of the corresponding cyclized product **1a** or **1b**, which were purified by silica gel column chromatography in 59 and 56% yields, respectively. Compounds **1a** and **1b** are stable towards moisture and air.



Scheme 1. Reagents and conditions: a) *n*BuLi (1 equiv), THF, −78 °C, then Mes_2BF (2.1 equiv); b) *t*BuLi (2 equiv), THF, −78 °C, then R_2PCl (1 equiv). Mes = mesityl, Cy = cyclohexyl.

The phosphonium- and borate-bridged stilbene **1** and the (2-borylphenyl)(2-phosphanylphenyl)acetylene **2** are valence isomers. Based on the calculations of model compounds (R^1 = Ph or Me, R^2 = Ph) at the B3LYP/6-31G(d) level, the cyclized form **1** is approximately 10 kcal mol^{-1} more stable than **2**, regardless of the nature of the R^1 substituents.[16] Therefore, whether or not the cyclization proceeds is likely dependent on the nucleophilicity of the phosphanyl group. The more σ-donating dialkylphosphanyl derivatives favor the production of the cyclized products **1a** and **1b**. In contrast, in the case of the less nucleophilic diphenylphosphanyl derivative **2c**, even heating at reflux in 1,2-dichloroethane only produced a trace amount of the corresponding cyclized product.



Scheme 2. Reagents and conditions: a) *t*BuLi (4 equiv), THF, −78 °C; b) R_2PCl (2.2 equiv Cy_2PCl for **8** and **10**, 1 equiv $(tBu)_2PCl$ for **12**, THF, −78 °C to RT for **8** and **10**, and −78 °C to 60 °C for **12**.

This synthetic methodology is applicable to the preparation of more extended homologues and a heteroaromatic derivative (Scheme 2). Thus, starting from the bis(arylethynyl)diborylbenzene **7**, the dilithiation with *t*BuLi and subsequent treatment with Cy_2PCl at room temperature afforded the $P^+B^-B^-P^+$-bridged distyrylbenzene **8** in 44% yield. Similarly, starting from the bis[(borylphenyl)ethynyl]dibromobenzene **9**, the two-step procedure gave the $B^-P^+P^+B^-$-bridged distyrylbenzene **10** in 48% yield. The thiophene-fused derivative **12** was also obtained in 53% yield from the (borylthienyl)(bromothienyl)acetylene **11**. Notably, this reaction requires a higher temperature (60 °C), while the cyclization of the benzene analogue **6** proceeds even at room temperature. This difference may be due to the severe strain in the fused system containing only five-membered rings as well as to the electronic effect of the thiophene ring on the nucleophilicity of the phosphorus center. The extended homologues **8** and **10** and thiophene derivative **12** are also stable towards moisture and air.

The crystal structures of **1b**, **10**, and **12** have been determined by X-ray crystallography.[17] The ORTEP drawing of **10** is shown in Figure 3. The structure confirms that the entire distyrylbenzene framework has high coplanarity with a dihedral angle between the outer and central benzene rings of 9.63°.

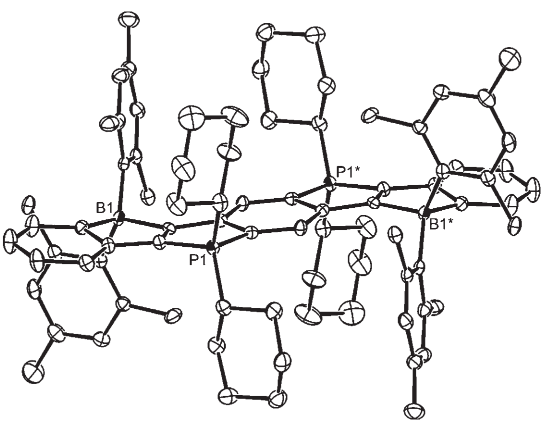


Figure 3. Crystal structure of compound **10**. Thermal ellipsoids are set at the 50% probability level; hydrogen atoms are omitted for clarity.

The photophysical data for phosphonium- and borate-bridged compounds **1a**, **8**, **10**, and **12** are summarized in Table 1, together with those of the valence isomer **2c** and the relevant bridged stilbenes **3**, **4**, and **5** for comparison. In the UV/Vis absorption spectra, the phosphonium- and borate-bridged stilbene **1a** has an absorption band with the maximum (λ_{abs}) at 396 nm and a relatively small molar absorption coefficient $\varepsilon = 5400$. In the fluorescence spectra, **1a** exhibits a yellow fluorescence with a maximum (λ_{em}) at 517 nm, whereas the quantum yield is very low ($\Phi_F = 0.020$). Notably, the emission maximum of **1a** is the longest among the series of bridged stilbenes, and about 160 nm longer than the CMe_2-bridged stilbene **3**. These facts demonstrate that the phosphonium and borate zwitterionic substituents substantially alter the nature of the parent stilbene skeleton.

Table 1: Photophysical data for the bridged stilbenes and related compounds.[a]

Compound	UV/Vis absorption λ_{abs} [nm][b]	UV/Vis absorption $\log\varepsilon$	Fluorescence λ_{em} [nm][c]	Fluorescence Φ_F	Fluorescence τ_s [ns]
1a	396	3.73	517	0.020[d]	2.3
2c	336	4.20	452	0.014[d]	2.1
8	516	4.25	578	0.38[e]	6.4
10	519[f]	4.03	614	0.40[e]	10.1
12	483	4.08	623	0.57[e]	13.0
3[g]	322	4.45	367	0.92[e]	1.6
4[h,i]	351	4.11	415	0.07[e]	1.4, 9.8
5[h,i,j]	395	3.84	480	0.98[e]	15.7

[a] In THF. [b] Only the longest absorption maxima are shown. [c] Emission maxima upon excitation at the absorption maximum wavelengths. [d] Relative fluorescence quantum yields determined with quinine sulfate as a standard. [e] Absolute fluorescence quantum yields determined by a calibrated integrating sphere system within ±3% errors. [f] A shoulder was observed at 550 nm with $\log\varepsilon = 3.93$. [g] Reference [9a]. [h] Reference [10]. [i] In CH_2Cl_2. [j] *trans* isomer.

Both λ_{abs} and λ_{em} of **1a** are considerably longer than those of the valence isomer **2c**, by 60 and 65 nm, respectively. While the lowest-energy transition in **2c** is the intramolecular charge transfer from the triarylphosphane moiety to the triarylborane moiety, that of **1a** is from the benzoborole moiety to the benzophosphole moiety. Thus, the isomerization switches the nature of the intramolecular charge-transfer transition, resulting in the significant differences of λ_{abs} and λ_{em}. Such difference in the nature of electronic transition between **1a** and **2c** would affect the solvent dependency of absorption and emission spectra. In fact, **1a** exhibits hypsochromic shifts both in the absorption and emission spectra ($\lambda_{abs} = 403$ nm in benzene, 396 nm in THF, 390 nm in DMF; $\lambda_{em} = 525$ nm in benzene, 517 nm in THF, 510 nm in DMF), whereas **2c** does not show an obvious solvent effect in the absorption spectra ($\lambda_{abs} = 336$ nm in benzene, 336 nm in THF, 334 nm in DMF). These results indicate that the ground state of **1a** is more polar than the excited state.

As for the extended analogues, the distyrylbenzene derivatives **8** and **10** have $\lambda_{abs} = 516$ and 519 nm and $\lambda_{em} =$ 578 and 614 nm, respectively. These wavelengths are much longer than those of the stilbene **1a**, thus demonstrating the effective extension of the π conjugation. While the stilbene **1a** shows a faint fluorescence, the distyrylbenzene derivatives **8** and **10** show intense orange emissions with Φ_F values of 0.38 and 0.40, respectively. According to the calculations of the radiative and nonradiative decay rate constants k_r and k_{nr} from Φ_F and the fluorescence lifetime τ_s, the enhancement in the fluorescence intensity in **8** and **10** is attributable to both the increase in k_r and the decrease in k_{nr} (**1a** $k_r = 8.7 \times 10^6\,s^{-1}$, $k_{nr} = 4.3 \times 10^8\,s^{-1}$; **8** $k_r = 5.9 \times 10^7\,s^{-1}$, $k_{nr} = 9.7 \times 10^7\,s^{-1}$; **10** $k_r = 4.0 \times 10^7\,s^{-1}$, $k_{nr} = 5.9 \times 10^7\,s^{-1}$). The increase in k_r is mainly due to the enhancement of the oscillator strength by the extension of the π conjugation. Meanwhile, the replacement of the benzene rings of **1a** with thiophene also results in a significant difference in λ_{abs} and λ_{em}. The thiophene derivative **12** shows an intense red emission with a long λ_{em} at 623 nm despite its short π-conjugated length.

The electrochemical properties of the series of phosphonium- and borate-bridged ladder systems were also studied by cyclic voltammetry (Table 2). Compound **1a** shows irreversible oxidation and reduction waves with peak potentials at +0.57 and −2.50 V, respectively (vs. ferrocene/ferrocenium). This is in contrast to the fact that the CMe_2-bridged stilbene **3** only shows reversible oxidation and reduction waves with peak potentials at +0.81 V and −3.27 V, respectively. The incorporation of the zwitterionic bridges significantly affects the electronic structure and provides ambipolar character to the stilbene framework. This observation is consistent with the previously mentioned results of the molecular orbital calculations.

Table 2: Electrochemical data for the bridged stilbenes and related compounds.[a]

Compound	Oxidation potential[b] E_{pa} [V][d]	Reduction potential[c] E_{pc1} [V][d]	Reduction potential[c] E_{pc2} [V][d]
1a	+0.57	−2.55	–[e]
8	+0.13	−2.63	–[e]
10	+0.63	−2.03 (−1.95)[f]	−2.77 (−2.69)[d]
12	+0.21	−2.49	–[e]
3	+0.81 (+0.75)[f]	−3.27[g] (−3.17)[f,g]	–[e,g]
5[g,h]	–[e]	−1.74 (−1.67)[f]	−2.35

[a] Determined by cyclic voltammetry under the following condition: Sample 1 mM; $Bu_4N^+PF_6^-$ 0.1 M in CH_2Cl_2 or THF; scan rate 100 mV s^{-1}. [b] In CH_2Cl_2. [c] In THF. [d] Peak anodic potential (E_{pa}) and peak cathodic potential (E_{pc}) against the ferrocene/ferrocenium couple are given. For reversible processes, the corresponding half redox potentials ($E_{1/2}$) are given in parentheses. [e] Not observed. [f] Reversible process. [g] Reference [10]. [h] *trans* isomer.

Comparison of the redox potentials between **8** and **10** also reveals noticeable features of the zwitterionic modulation of the ladder skeleton. These two derivatives are positional isomers differing only in the arrangement of the bridging moieties, $P^+B^-B^-P^+$ or $B^-P^+P^+B^-$. However, this difference results in a totally opposite electronic modulation. Thus, the $P^+B^-B^-P^+$-bridged **8** has a very low oxidation potential with $E_{pa} = +0.13$ V, while its reduction peak potential (−2.63 V) is comparable to that of the stilbene **1a**. In contrast, the

$B^-P^+P^+B^-$-bridged **10** shows two reversible reduction waves at rather low potentials of −2.03 and −2.77 V, respectively, while the oxidation potential of **10** is comparable to that of **1a**. These results can be rationalized by considering the cumulative electronic effect of the phosphonium and borate bridging moieties. Thus, while the central benzodiborole bis(borate) structure in **8** significantly increases the HOMO level and makes this skeleton electron-donating, the benzodiphosphole bis(phosphonium) structure in **10** effectively decreases the LUMO level and thus endows it highly electron-accepting character.

The thiophene analogue **12** also shows amphoteric redox processes with oxidation and reduction peak potentials at +0.21 and −2.49 V, respectively. Thus, the significant red shifts in the λ_{abs} and λ_{em} from **1a** to **12** are mainly due to the increase in the HOMO level by replacing the benzene rings with the thiophene rings.

In summary, we have demonstrated that the incorporation of the boryl and phosphanyl groups into the appropriate positions of the phenyleneethynylene π-conjugated system furnish the zwitterionic ladder structure. This zwitterionic modulation is a very effective way to alter the nature of the ladder π-conjugated skeleton and provide attractive photophysical and electrochemical properties. The series of molecules may have potential not only for linear but also for nonlinear optical materials.[14b,18,19] Further study in this line as well as the synthesis of a variety of phosphonium- and borate-bridged ladder molecules is now in progress.

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[17] Crystal data for **1b**, **10**, and **12**: see the Supporting Information. CCDC 677303 (**1b**), 677304 (**10**), and 677305 (**12**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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