π-Conjugated Compounds

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Bis(phosphoryl)-Bridged Biphenyls by Radical Phosphanylation: Synthesis and Photophysical and Electrochemical Properties**

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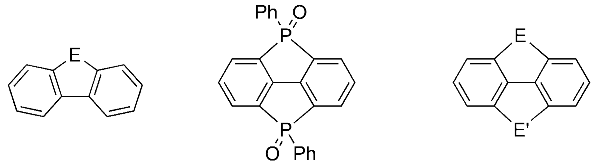
The design of new electron-accepting π-conjugated frameworks is of particular significance for the development of n-type semiconducting materials[1] and narrow-band gap polymers,[2] which show great potential as components in organic electronics, such as thin-film transistors and photovoltaic cells. Biphenyls containing electron-accepting moieties might be simple and viable scaffolds for the design of such π-electron systems. However, by simply introducing electron-withdrawing groups as substituents renders the biphenyl framework to appear in a twist conformation, resulting in a decrease of π-conjugation. This problem can be elegantly solved by incorporating an electron-accepting unit as the bridging moiety. In this regard, main group elements are attractive as the bridging moieties, since they not only fix the biaryl framework in a planar geometry, but also allow the electronic structure to be modified through the choice of element.[3] Accordingly, various electron-accepting dibenzoheteroles **1** featuring Si,[4] P,[5] and S[6] as bridging elements have been reported and used in various applications. In particular, P-containing π-electron systems have so far attracted considerable attention, because of their rich follow-up chemistry, which is attributed to easy transformations to oxides, sulfides, and metal/Lewis acid complexes.[7] Among the various functionalities derived from phosphanes, phosphine oxides or sulfides are of particular interest due to their highly electron-accepting character.[8,9]

As a novel electron-accepting biphenyl, we designed bis(phosphoryl)-bridged biphenyl (BPB) **2**, which displayed the following characteristics: a) compact and planar structure enabling effective orbital overlap and b) high electron-accepting ability owing to two phosphine oxide units. Related biphenyls **3** containing Si,[10,11] S,[12] Se,[13] and C[14] as the bridging moieties have already been reported (Figure 1). Herein, we disclose the synthesis of this novel skeleton and discuss its potential as the electron-accepting unit.



1a: E = SiR_2
1b: E = PR
1c: E = P(O)R
1d: E = SO_2

2

3a: E = E' = $SiMe_2$
3b: E = $SiMe_2$, E' = S
3c: E = E' = S
3d: E = S, E' = Se
3e: E = E' = Se
3f: E = E' = CH_2

Figure 1. Electron-accepting dibenzoheteroles **1** and doubly bridged biphenyls **2** and **3**.

All our initial attempts to access BPB **2** by fourfold lithiation of 2,2,2′,2′-tetrabromobiphenyl (**4**) followed by trapping with dichlorophenylphosphane and P-oxidation failed. The problem was associated with multiple lithiation of **4**.[15]

We have recently shown that radical phosphanylation of reactive aryl radicals is a highly efficient approach for the synthesis of arylphosphanes.[16] The reactions occur under rather mild conditions, and expensive transition-metal catalysts are not necessary. Stannylated and silylated phosphanes have been used as reagents, and reactions occurred in high yields. We envisioned that **2** should be accessible by multiple radical phosphanylation of biphenyl **4** with bis(trimethylstannyl)phenylphosphane and subsequent oxidation.

We first tried radical phosphanylation of **4** with readily prepared $(Me_3Sn)_2PPh$ using α,α'-azobisisobutyronitrile (AIBN) as initiator at 80°C in benzene. Disappointingly, after 24 h little conversion of the starting material had occurred and after H_2O_2 oxidation none of the targeted BPB **2** was identified (Table 1, entry 1). The same result was obtained by performing the reaction at 125°C (Table 1, entry 2). To our delight, switching to 1,1′-azobis(cyclohexane-1-carbonitrile) (V-40) as initiator afforded traces of the desired BPB after 24 h (Table 1, entry 3). Prolonged reaction time led to higher conversion, and after oxidation with H_2O_2 *trans*-**2** and *cis*-**2** were isolated in good yields (Table 1, entry 4). As expected, oxidation did not occur diastereoselectively and both isomers were isolated in similar yields. By running the reaction in benzotrifluoride the reaction time could be shortened to two days without decreasing the yield (Table 1, entry 5). The success of this transformation is an impressive demonstration of the efficiency of the radical phosphanylation: four highly reactive aryl radicals are trapped sequentially and although severe ring strain is generated in the formation of the second five-membered

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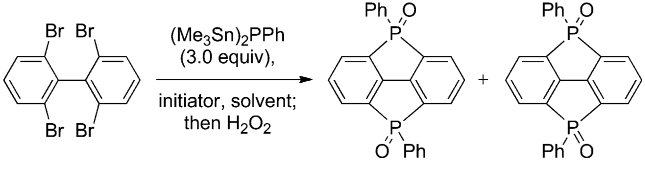
Table 1: Radical phosphanylation of **4** with $(Me_3Sn)_2PPh$.



4 *trans*-**2** *cis*-**2**

Entry	Initiator (equiv)	Solvent	T [°C]	t [h]	Yield [%][a]
1	AIBN (0.2)	PhH	80	24	–
2	AIBN (0.2)	PhH	125	24	–
3	V-40 (0.2)	PhH	125	24	trace
4	V-40 (0.5)	PhH	125	84	30/29
5	V-40 (0.5)	$PhCF_3$	125	50	29/27

[a] Yields of isolated *trans*/*cis* isomers of **2**.

ring (see discussion below) the final intramolecular trapping proceeds in acceptable yield.

Single crystals of both *trans*-**2** and *cis*-**2** were obtained from CH_2Cl_2/*n*-hexane solution and analyzed by X-ray diffraction (Figure 2).[17] As expected bis(phosphoryl)-bridged biphenyl skeletons in *trans*-**2** and *cis*-**2** adopt almost planar geometries, indicating the effective extension of π-conjugation over the framework. Notably, the endocyclic P–C bonds are 1.8369(16)–1.8431(17) Å in *trans*-**2** and 1.828(2)–1.839(2) Å in *cis*-**2**. These are the longest among the already reported triarylphosphine oxides without hydrogen-bonding interactions (1.801–1.833 Å). Moreover, the central C1–C1' bonds (*trans*-**2**: C1–C1* 1.442(3) and 1.443(3) Å; *cis*-**2**: C1–C7 1.442(3) Å) are significantly shortened in comparison to those in biphenyl (C1–C1' 1.494 Å)[18] and dibenzophosphole oxide (C1-C1' 1.480 Å).[19] These results reflect the highly strained structure caused by the annulation with two phosphoryl groups.

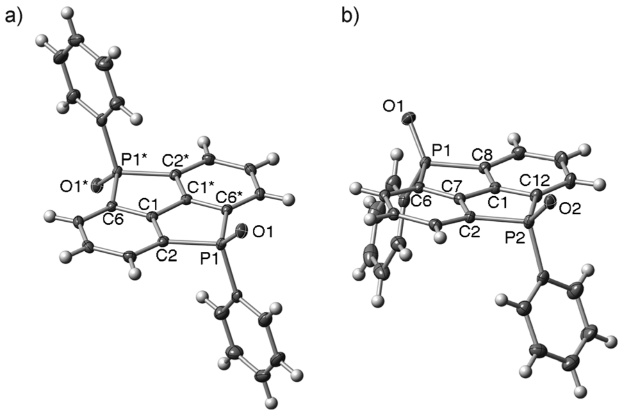
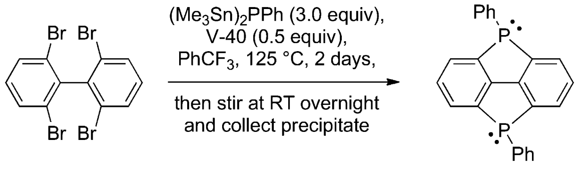


Figure 2. X-ray crystal structures of a) *trans*-**2** and b) *cis*-**2**. Solvent molecules are omitted for clarity for *cis*-**2**. For *trans*-**2**, two crystallographically independent molecules were found in the unit cell, one of which is shown. Thermal ellipsoids are drawn at the 50% probability level.

We found that isomerically pure phosphane *trans*-**5** precipitated in 40% yield by stirring the crude reaction mixture at room temperature overnight (Scheme 1). This result shows that **5** can undergo *trans/cis* isomerization by inversion at phosphorus at room temperature in solution. We measured the isomerization barrier by dissolving *trans*-**5** in $CDCl_3$ and monitoring the *trans*/*cis* isomerization by ^{31}P NMR spectroscopy. The activation energy was determined to be $E_A = (21.0 \pm 1.6)\ \mathrm{kcal\,mol^{-1}}$, which is considerably smaller than those of dibenzophosphole derivatives (25–27 $\mathrm{kcal\,mol^{-1}}$).[20] In general, barriers for the pyramidal inversion at the phosphorus atom in various phosphole derivatives are suggested to be dependent on the extent of aromaticity of the planar phosphole skeleton in the transition state.[20a] To elucidate the relationship between the structure and the aromaticity in the transition state, geometry optimizations for **5** and dibenzophosphole **1b** (R = Ph) were performed at the B3LYP/6-31G(d) level of theory. The activation barriers were estimated to be +25.5 and +27.5 $\mathrm{kcal\,mol^{-1}}$ for **5** and **1b**, respectively, which are semi-quantitatively consistent with the experimental results. However, the nucleus-independent chemical shift (NICS) values in the transition states at the HF/6-311+G(d,p) level of theory using the optimized geometries are comparable to each other (NICS (0): −10.4 for **5**, −9.8 for **1b**; NICS(1): −8.0 for **5**, −8.8 for **1b**). These results indicate that not the aromatic character of the phosphole ring in the P-planar transition state, but the higher ring strain in **5** may be primarily responsible for the decrease in the energy barrier for the inversion at the phosphorus atom at least in this case.

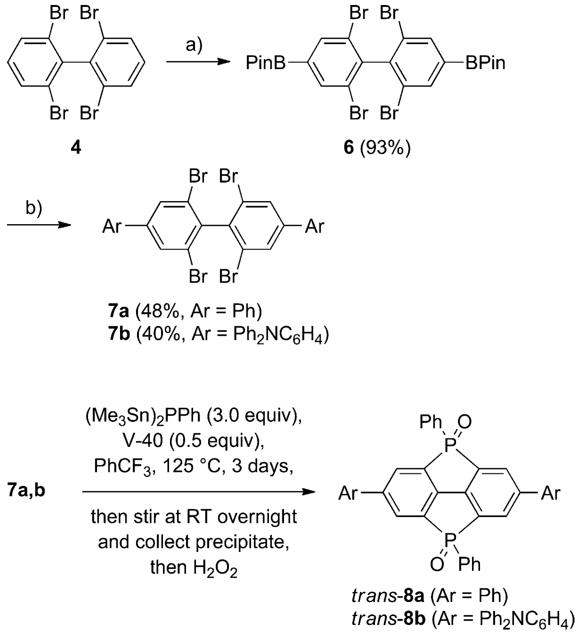


4 *trans*-**5** (40%)

Scheme 1. Synthesis of *trans*-**5**.

Next we focused on the structural modification of the BPB core skeleton. Applying Ir-catalyzed C–H borylation,[21] **4** was converted to bis(pinacolatoboronate) **6**, which was subsequently coupled with different aryl iodides to give diarylated biphenyls **7** (Scheme 2). Radical phosphanylation of biphenyls **7** led to the desired BPBs **8** (*trans*-**8a**: 22%, *trans*-**8b**: 13%).

UV/Vis absorption and fluorescence spectra of the bis(phosphoryl)-bridged biphenyls *cis*-**2**, *trans*-**2**, and the π-extended derivatives *trans*-**8a**,**b** were evaluated. The photophysical data are summarized in Table 2, together with those of mono-phosphoryl-bridged biphenyl (dibenzophosphole oxide) **1c** (R = Ph)[5e] and bis(silicon)-bridged biphenyl **3a**[10] for comparison. In the UV/Vis absorption spectra, the *cis*- and *trans*-bis(phosphoryl)-bridged biphenyls **2** have an absorption band with the maximum wavelength (λ_{abs}) at 347 nm and a relatively small molar absorption coefficient $\varepsilon = 337$ and $\varepsilon = 367$ for *cis*-**2** and *trans*-**2**, respectively. The *cis* and *trans*



Scheme 2. Synthesis of 4,4′-diarylated BPBs. a) [{Ir(OMe)(cod)}$_2$], B$_2$Pin$_2$, TBME, 60 °C. b) ArI, [Pd(PPh$_3$)$_4$], K$_3$PO$_4$, dioxane, water, 100 °C. cod = cyclooctadiene, Pin = pinacol, TBME = *tert*-butylmethyl ether.

Table 2: Photophysical data for the bridged biphenyls.[a]

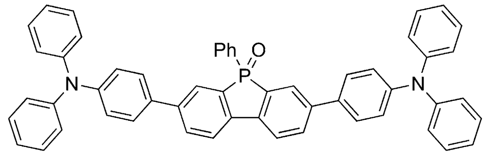
	UV/Vis Absorption		Fluorescence	
Cmpd	λ_{abs} [nm][b]	ε [$\times 10^3$]	λ_{em} [nm][c]	Φ_F[d]
cis-**2**	347	0.337	387	0.03
trans-**2**	347	0.367	387	0.03
trans-**8a**	375 (sh)	3.50	422	0.20
trans-**8b**	399	37.6	547	0.34 (0.30)
1c[e]	332	0.794	366	0.042
3a[f]	285	12.1	361	0.08
9	396	43.5	499	0.89 (0.18)

[a] In CH$_2$Cl$_2$ unless stated otherwise. [b] Only the absorption maxima at the longest wavelengths are shown. [c] Emission maxima upon excitation at the absorption maximum wavelengths. [d] Absolute fluorescence quantum yields determined by a calibrated integrating sphere system within ±3% errors. Fluorescence quantum yields in the solid state are shown in parentheses. [e] Ref. [5e]. [f] Ref. [10]; in cyclohexane.

isomers have essentially identical spectra irrespective of the stereochemistry. In the fluorescence spectra, *cis*- and *trans*-**2** exhibit a violet fluorescence with the maximum wavelength (λ_{em}) at 387 nm, whereas the quantum yield is low ($\Phi_F = 0.03$). Notably, both the absorption and fluorescence of **2** are considerably longer than those of dibenzophosphole oxide **1c** (R = Ph) and bis(silicon)-bridged biphenyl **3a**. These results are attributable to the narrow HOMO–LUMO gap of **2** due to their low-lying LUMO, supported by the quantum chemical calculations using a time-dependent density functional theory (TD-DFT) method (see the Supporting Information).

As for the extended analogues, phenyl- and diphenylaminophenyl-substituted derivatives *trans*-**8a** and *trans*-**8b** have λ_{abs} at 375 nm and 399 nm, and λ_{em} at 422 nm and 547 nm, respectively, which are significantly red-shifted compared to those of the BPBs **2**, demonstrating the effective extension of π conjugation. Whereas the biphenyls **2** only show a faint fluorescence, the π-extended derivatives *trans*-**8a** and *trans*-**8b** show more intense emissions with Φ_F values of 0.20 and 0.34, respectively.

The notable feature of the bis(phosphoryl)-bridged biphenyls is their electron-accepting character due to the electron-withdrawing phosphoryl groups. Remarkably, the λ_{em} of bis(diphenylaminophenyl)-substituted BPB *trans*-**8b** is 122 nm longer than that of bis(diphenylamino)quarterphenylene ($\lambda_{em} = 425$ nm in CHCl$_3$).[22] To compare the electron-accepting properties, we also prepared mono(phosphoryl)-bridged biphenyl **9** starting from 4,4′-dibromo-2,2′-diiodo-1,1′-biphenyl (see the Supporting Information). The photophysical data of the two compounds in various solvents are summarized in Table S7 in the Supporting Information. For both compounds, whereas the absorption maxima show small solvent dependence, the fluorescence spectra show substantial bathochromic shifts as the solvent polarity increases. These facts demonstrate that these molecules have more polar structures in the excited state than in the ground state. To compare the degree of the polarity of the structures in the excited state, we employed the Lippert–Mataga equation [Eq. (1)],[23]



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$$\Delta\nu = \frac{2}{hc}\frac{(\mu_E - \mu_D)^2}{a^3}\Delta f + \text{const.} \tag{1}$$

$$\Delta f = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \tag{2}$$

in which μ_E and μ_G are the dipole moments in the excited state and ground state, respectively, $\Delta\nu$ is the Stokes shift, and Δf is the orientation polarizability. The solvent polarity parameter is given by Equation (2), in which ε is the dielectric constant and n is the refractive index.[24] For the compounds *trans*-**8b** and **9**, linear relationships were observed for the plots of $\Delta\nu$ as a function of Δf (Figure 3). The slopes obtained for *trans*-**8b** and **9** are 16900 and 13400 cm^{-1}, respectively. These results indicate that the extent of the electron-accepting character of bis(phosphoryl)-bridged biphenyl is considerably larger than that of the monophosphoryl-bridged analogue. In addition, little deviation was observed in the Lippert–Mataga plots for both **8a** and **9** in *i*PrOH, indicating that the specific solvent effect due to the hydrogen bonding is likely negligible in *i*PrOH for both **8a** and **9**.

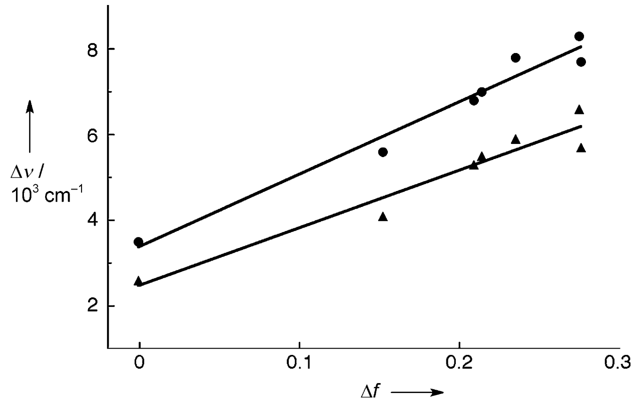

Figure 3. The Lippert–Mataga plots for *trans*-**8b** (●) and **9** (▲).

Importantly, the $Ph_2NC_6H_4$-substituted BPB *trans*-**8b** retains its fluorescence quantum yield even in the solid state ($\Phi_F = 0.30$). This is in contrast to the fact that the Φ_F of dibenzophosphole oxide analogue **9** in the solid state is much smaller than that in CH_2Cl_2 solution ($\Phi_F = 0.18$ in solid, 0.89 in solution). This is likely due to the increased steric demand of the two phosphoryl groups in *trans*-**8b**, which prohibit intermolecular interactions in the solid state, although the reason is still unclear at the moment.

We also evaluated the electrochemical properties of these two π-electron systems. The cyclic voltammograms of *trans*-**8b** and **9** are shown in Figure 4. $Ph_2NC_6H_4$-substituted BPB *trans*-**8b** and dibenzophosphole oxide **9** show the first reversible reduction waves with the reduction potentials of −2.15 and −2.36 V (vs. Fc/Fc$^+$), respectively. These observations also demonstrate that the two phosphoryl bridges in *trans*-**8b** are effective in enhancing the electron-accepting character.

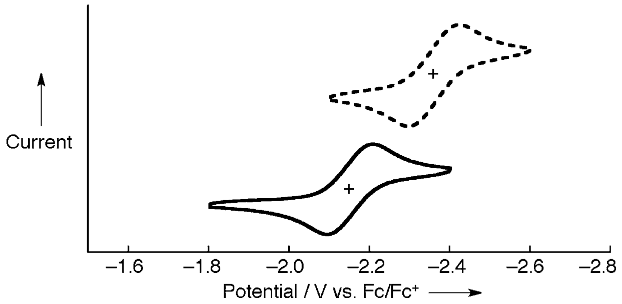

Figure 4. Cyclic voltammograms of *trans*-**8b** (——) and **9** (-----) in THF containing $Bu_4N^+PF_6^-$ (0.1 M) with a scan rate of 100 mV s^{-1}.

In summary, we demonstrated that the radical phosphanylation of tetrabromobiphenyls furnishes highly strained bis(phosphoryl)-bridged biphenyls. The incorporation of two phosphoryl groups as the bridging moieties is an effective way to construct a rigid biphenyl skeleton with a highly electron-accepting character. Recently, several fascinating phosphoryl-bridged π-conjugated skeletons have been developed and applied as useful electron-accepting scaffolds. Among these examples, the bis(phosphoryl)biphenyl disclosed in this study is one of the simplest skeletons and therefore should find many applications as a building block in organic devices and molecular electronics.

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