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Phosphaalkenes in π-Conjugation with Acetylenic Arenes

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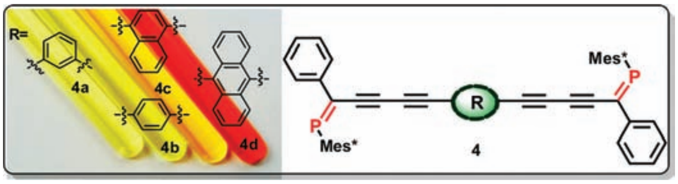
ABSTRACT



Phosphaalkene inclusion at the periphery of acetylenic arenes results in decreased band gaps of the title compounds as verified by spectroscopic and electrochemical techniques. The electronic coupling between two 1-phosphahex-1-ene-3,5-diyne units is mediated by all *para*-substituted arenes and increases from 4b to 4d.

Polyarylvinylenes and -acetylenes are organic semiconductors and as such interesting materials for a broad variety of applications in electronic and photonic devices.[1−4] While the inclusion of heteroatoms in the form of heteroaromatics is a common way to alter electronic properties of the structures, much less research has been conducted on replacing sp and sp^2 hybridized carbon centers of the acetylene and vinylene portion by other main group elements. This is remarkable since such an arrangement would promote the mixing of heteroatom-based orbitals with those of the conjugated π-system, giving rise to new materials with potentially interesting (opto)electronic properties. Only over the last five years, the first polymers that resemble polyvinylphenylenes but contain low-valent phosphorus centers in the form of phosphaalkenes[5] or diphosphenes[6] instead of vinylenes have emerged in the literature. Structurally defined monodisperse segments of these intriguing polymers and detailed studies of the interaction between the phosphorus-containing parts of the molecules are however still scarce. Bis(diphosphenes) that are separated by ferrocene[7] or phenylene[8] linkers have been found to show substantial electronic coupling with a separation of the electrochemically determined reduction potentials of the radical anion and the dianion by 350 and 340 mV, respectively. We have recently determined a coupling of similar magnitude between two phosphaalkenes, mediated by a linear octatetrayne.[9,10] A shorter butadiyne linker in a cross-conjugated, expanded dendralene segment in which the exotopic methylene groups were exchanged by λ^3-σ^2 phosphorus leads to an increased coupling of 530 mV.[11]

Herein, we present a series of P═C terminated acetylenic arenes **4a−d** that were prepared for two purposes: first, to study the extent to which the different bridges would mediate π-conjugation between the P═C units and second, to investigate the effect that π-conjugated phosphorus hetero-

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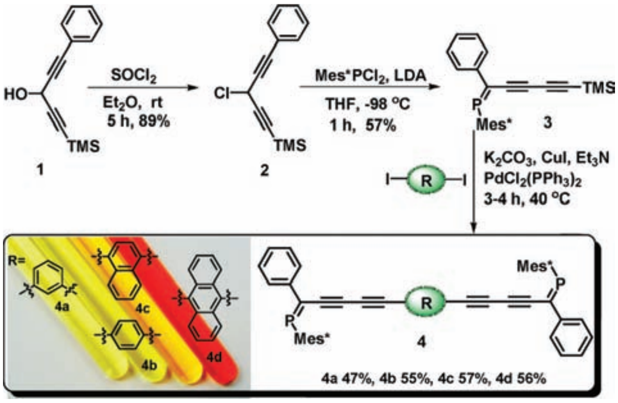
atoms have on the electronic properties of the acetylenic arenes. Considering that the frontier molecular orbitals of phosphaalkenes are closer in energy than those of ethenes,[12,13] we were interested to see whether phosphaalkene incorporation could be used to decrease the HOMO−LUMO gap of the arenes.

TMS-protected, butadiyne-substituted phosphaalkene **3** can be prepared from the diacetylenic chloride **2**, which in turn is accessible from alcohol **1** (Scheme 1).[10] Because of the limited stability of terminally unsubstituted 1-phosphahex-1-ene-3,5-diyne, we employed a one-pot deprotection−Sonogashira coupling protocol[14] to prepare **4a−d**. It is vital for the success of the reaction to use diiodoarenes as coupling partners as the lower reactivity of the corresponding bromides results in decomposition of deprotected **3**. Commercially available 1,4-dibromonaphthalene and 9,10-dibromoanthracene were thus converted to the diiodo derivatives prior to the coupling experiments.[15]

Scheme 1. Synthesis of Bis(1-phosphahex-1-ene-3,5-diyn-6-yl) Arenes **4a−d** (Mes* = 2,4,6-^{t}Bu$_3$Ph)



In a typical experiment, compound **3** was treated with the diiodoarene under customary Sonogashira reaction condition (CuI and PdCl$_2$(PPh$_3$)$_2$) in the presence of excess K$_2$CO$_3$. Whereas **4b** and **4d** could be purified by column chromatography on silica, **4a** and **4c** were isolated by preparative HPLC on a C18 chromatographic column using a mixture of THF and methanol as eluent, and **4a−d** were afforded in acceptable isolated yields. The ^{31}P NMR spectra of **4a−d** show almost identical chemical shifts of $\delta = 313.7$, 313.8, 314.1, and 314.2 ppm, respectively, which are also very similar to that of a monomeric reference compound **5** (Mes*P=C(Ph)-C$_4$-Ph)[9] that is identical to **3** with the exception of a phenyl group at the butadiyne terminus ($\delta = 311$ ppm). It thus seems that the P-centers are largely unaffected by the nature of the arene linker. This behavior is in contrast to previous findings that phenyl groups with electron-withdrawing nitro ($\delta = 319$ ppm) and electron-donating amino substituents ($\delta = 304$ ppm) at the butadiyne terminus have a noticeable effect.

Single crystals of **4d** were grown from a mixture of dichloromethane and methanol, and the structure of **4d** was determined by X-ray diffraction analysis (Figure 1). Reflecting the dimeric character of **4d**, its solid state structure exhibits a crystallographically imposed inversion center of symmetry with a P···P distance of 18.0 Å. The butadiyne is *cis* to the Mes* group and features bond distances in the typical range for $C{\equiv}C$ triple and C$_{sp}$−C$_{sp}$ single bonds. The crystal structure of **4d** gives valuable insights into the degree of communication between the phosphaalkenes and the remaining π-conjugated units of the molecule. As expected, the Mes* group is nearly orthogonal to the plane defined by 1-phosphahex-1-ene-3,5-diyne (PC$_5$) with an angle of 85.9°. The phenyl group at the P=C carbon is twisted out of the PC$_5$ plane by only 18.1°, allowing sizable conjugation between the two units. In contrast, the interplanar angle between PC$_5$ and the anthracene unit is much greater at 52.9°, giving a nonoptimal geometry for π-orbital overlap. It appears that this unfavorable orientation is enforced by steric constraints that would emerge between the anthracene core and the *p-tert*-butyl substituent of the Mes* group if the anthracene were more coplanar with PC$_5$. In other words, since the Mes* group resides under/above the anthracene, π-conjugation between the latter and PC$_5$ is impeded.

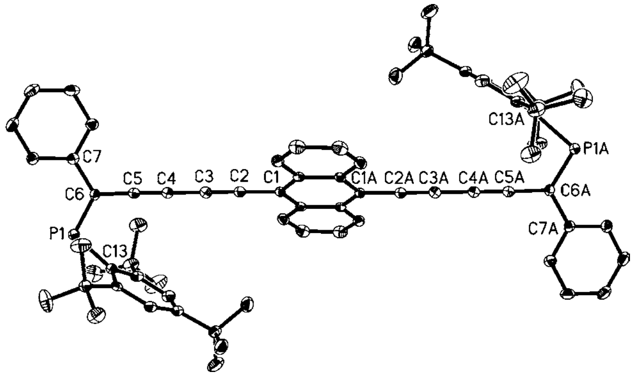


Figure 1. Molecular structure of **4d** (35% probability ellipsoids). All hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [deg]: P1−C6, 1.697; P1−C13, 1.842; C1−C2, 1.427; C2−C3, 1.207; C3−C4, 1.366; C4−C5, 1.206; C5−C6, 1.419; C13−P1−C6, 101.4; P1−C6−C5, 122.0; P1−C6−C7, 121.5; C5−C6−C7, 116.5. Dihedral angle between phenyl and the plane of P1−C6−C5 [deg]: 18.1. Dihedral angle between anthracene and the plane of P1−C6−C5 [deg]: 52.9. Dihedral angle between Mes* and the plane of P1−C6−C5 [deg]: 85.9.

The different bridging units in **4a−d** have a marked effect on the color of the compounds, which progressively changes from light yellow to yellow and red (Scheme 1). Electronic

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absorption spectra of **4a**−**d** in CH_2Cl_2 are shown in Figure 2. Whereas the *m*-phenyl-bridged **4a** exhibits a longest wavelength absorption maximum almost identical to that of monomeric **5** (λ = 379 nm, ε = 17000 $M^{-1}cm^{-1}$),[10] the lowest energy transitions of **4b**−**d** with the *para*-substituted bridges are bathochromically shifted, pointing toward a sizable electronic coupling between the two PC_5 portions. Owing to the most quinoid character of the anthracene bridge, the lowest energy transition of **4d** is red-shifted by 67 and 89 nm compared to that of **4c** and **4b**, respectively.

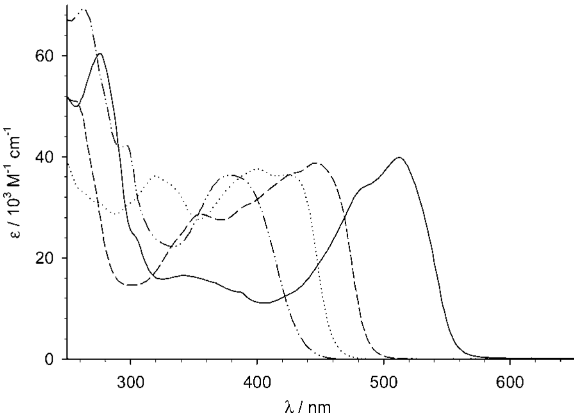

Figure 2. UV−vis Absorption spectra of compounds **4a** (− •• −), **4b** (•••), **4c** (- - -), and **4d** (—) in CH_2Cl_2 at 25 °C.

The influence of the phosphorus centers in **4a**−**d** on the electronic properties of the appended π-systems was evaluated in comparison with structurally related reference compounds that are exclusively based on carbon. The literature compounds that match **4a**−**d** most closely are based on *trans*-1,2-diethynylethenes (DEE), two of which have been interconnected by the same bridging aromatic units as in **4b,d**.[16] *p*-Phenyl-bridged bis-DEE has its lowest energy absorption at 374 nm and thus at higher energy by almost 50 nm compared to **4b** (λ = 423 nm, ε = 36500 M^{-1} cm^{-1}), further supporting the notion that the inclusion of phosphorus heteroatoms leads to decreased HOMO−LUMO gaps. A less dramatic effect is observed for **4d** where the phosphorus centers only lead to a shift of the longest wavelength absorption maximum by 17 nm compared to that of the anthracene-bridged bis-DEE. The partial failure of the P-centers in **4d** to impose a larger impact is presumably due to the poor π-conjugation between P═C and anthracene that is caused by steric repulsions between the latter and the Mes* group (see above). As a further consequence, the lowest energy absorptions of **4b** and **4d** differ by only 89 nm, compared to 121 nm in the DEE series. Compounds **4a**−**d** are not emissive at ambient temperature presumably because of rapid quenching processes that involve the phosphorus centers.[6,17−19]

Further insights into the communication between the two PC_5 units in **4a**−**d** was sought from cyclic voltammetry. All compounds feature an irreversible oxidation at $E_{p,a}$ = 1.03−1.08 V, which is thus largely invariant to the nature of the bridging unit and similar to that of monomeric **5** (Table 1). The presence of only one oxidation wave shows that these processes are isolated to each monomeric subunit, which is in accordance with a recent study of related PC_5-based compounds.[9] A completely different picture emerges from the cathodic scans (Figure 3). Consistent with the optical absorption data, anthracene containing **4d** features the lowest HOMO−LUMO gap and is reversibly reduced at mildest potential of $E_{1/2} = -1.58$ V. This first electron uptake seems to involve the entire π-conjugated system and renders the second reduction less facile by 190 mV. The extent of electronic coupling is often described by the comproportionation constant K_c for the radical anion that can be calculated from $K_c = \exp(F\Delta E_{1/2}/RT)$ with $\Delta E_{1/2} = E_{1/2}{}^{-/0} - E_{1/2}{}^{2-/-}$.[20] In case of **4d**, K_c for the radical anion is 1630. Less

Table 1. Electrochemical Data for 1 mM Solutions in CH_2Cl_2 (0.1 M NBu_4PF_6), Glassy C-Electrode, ν = 100 mV/s[a]

compound	reduction $E_{1/2}$ [V]	oxidation $E_{p,a}$ [V]
5[b]	−1.98	1.05
4a	−2.03	1.08
4b	−1.87, −1.97	1.03
4c	−1.80, −1.92	1.06
4d	−1.58, −1.77	0.92[c,d] 1.04[d]

[a] All potentials are given versus $Fc^{+/0}$. $E_{1/2} = (E_{pa} + E_{pc})/2$. [b] **5** = Mes*P = C(Ph)-C_4-Ph.[9] [c] Anthracene-based oxidation. [d] Resolved by differential pulse voltammetry.

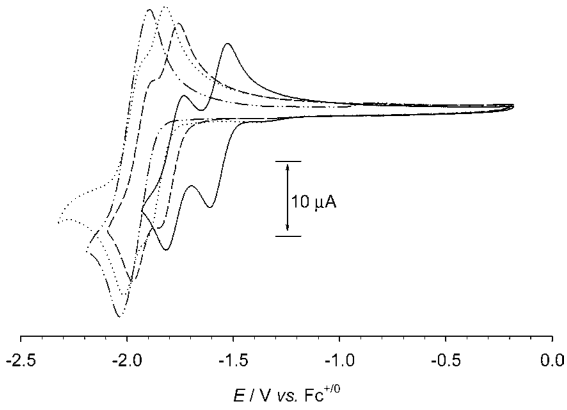

Figure 3. Cyclic voltammograms of **4a** (− •• −), **4b** (•••), **4c** (- - -), and **4d** (—) (1 mM solutions of compounds in CH_2Cl_2, 0.1 M NBu_4PF_6, ν = 100 mV/s).

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delocalization of the radical anion in **4c** is expressed by a smaller difference between the two reduction waves of only 120 mV ($K_c \approx 100$). This trend continues via the *p*-phenyl-linked system (100 mV, $K_c \approx 60$) to the *m*-phenyl-linked **4a** for which only one reduction can be resolved by cyclic voltammetry. Another effect of the decreased coupling between the monomeric units when going from **4d** to **4a** is that the potential required for the first reduction becomes increasingly negative until it is similar to that of monomeric **5**.

Comparing the electrochemical data for **4a−d** with those of the DEE analogues,[16] some striking differences become obvious. The latter are generally more difficult to reduce *and* to oxidize than the former. For example in the phenyl-bridged bis-DEE, the two processes are separated ($E_{pa} - E_{pc}$) by more than 3.5 V ($E_{pc} = -2.44$, $E_{pa} = 1.22$ V), which is considerably more than the difference found in **4b** (~ 2.9 V). A similar effect can be observed when comparing the data of **4d** with those of the anthracene-bridged bis-DEE ($E_{1/2,\mathrm{red}} = -1.72$ V, $E_{\mathrm{p,a\ anthracene}} = 1.22$ V).

In summary, it could be shown that mixing of phosphaalkene-based fragment orbitals with those of acetylenic arene frameworks leads to decreased HOMO−LUMO gaps of the entire π-conjugates in comparison with all-carbon-based reference compounds. Considering the importance of higher acenes with acetylene substituents in organic electronics,[21] additional inclusion of phosphaalkene groups as in **4a−d** may become a new strategy for further band gap reduction. Some of this capacity is however lost when steric constraints force the P═C unit out of conjugation with the arene. These factors need to be considered when designing future low band gap oligomers and polymers that contain low valent λ^3-σ^2 phosphorus.

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Supporting Information Available: Detailed experimental procedures and characterization of all new compounds; cif file for **4d**. This material is available free of charge via the Internet at http://pubs.acs.org.

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