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# Organic Electron Acceptors Comprising a Dicyanomethylene-Bridged Acridophosphine Scaffold: The Impact of the Heteroatom

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**Abstract:** Stable two-electron acceptors comprising a dicyanomethylene-bridged acridophosphine scaffold were synthesized and their reversible reduction potentials were efficiently tuned through derivatization of the phosphorus center. X-ray crystallographic analysis combined with NMR, UV/vis, IR spectroscopic, and electrochemical studies, supported by theoretical calculations, revealed the crucial role of the phosphorus atom for the unique redox, structural, and photophysical properties of these compounds. The results identify the potential of these electron deficient scaffolds for the development of functional n-type materials and redox active chromophores upon further functionalization.

In spite of recent advancements in the area of organic n-type semiconductors, compounds with characteristics comparable to their p-type counterparts still remain rather scarce, mainly due to their often limited stability and poor solubility.<sup>[1]</sup> As a promising strategy to achieve novel n-type materials, *i.e.*, electron acceptors, the functionalization of intrinsically p-type  $\pi$ -conjugated scaffolds with suitable electron-withdrawing groups has been established.<sup>[2]</sup>

Owing to the highly tunable electronic nature of pyramidal phosphorus, organophosphorus compounds have recently entered the stage as auspicious candidates to create novel electron acceptors.<sup>[3]</sup> While trivalent phosphorus with its Lewis basic lone pair is an electron donor, its oxidation affords the electron-withdrawing pentavalent phosphoryl moiety, in which  $\pi$  back-donation from the filled p-orbital at oxygen into the antibonding  $\sigma^*$ -orbital at phosphorus occurs, *i.e.*, negative hyperconjugation.<sup>[4]</sup>

The electron-accepting properties can be further boosted by the attachment of additional strongly electron-withdrawing cyano functions.<sup>[5]</sup> Particularly attractive is the dicyanomethylene (=C(CN)<sub>2</sub>) unit displaying reversible redox chemistry and chemical robustness. Hence, the dicyanomethylene moiety is found, for example, in the paradigmatic electron acceptors 7,7,8,8-tetracyanoquinodimethane (TCNQ) or 11,11,12,12-tetracyano-9,10-anthraquinodimethane (TCAQ),<sup>[6]</sup> functional push-pull chromophores with intense low-energy intramolecular charge-transfer (ICT) bands and innovative materials for organic solar cells.<sup>[7]</sup>

The potential of this combinatorial strategy has been impressively demonstrated by several polycyclic  $\pi$ -conjugated scaffolds

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incorporating heteroatoms such as nitrogen,<sup>[8]</sup> oxygen,<sup>[9]</sup> and sulfur<sup>[10]</sup> in conjunction with the dicyanomethylene acceptor. Phosphorus as the heteroatom would be particularly appealing in such systems as it provides for additional chemistry to adjust the structural, photophysical, and redox properties.<sup>[11]</sup> It is thus all the more surprising that there is hardly anything known about the combination of  $\pi$ -conjugated polycyclic scaffolds incorporating phosphorus with the dicyanomethylene acceptors.<sup>[12]</sup>

Herein, we introduce a new family of stable electron acceptors comprising an acridophosphine scaffold with a bridging dicyanomethylene moiety that are prone to reversible two-electron reduction under electrochemical conditions. Through experimental and computational studies, we elucidate the peculiar impact of the phosphorus atom on the structural, photophysical, and redox properties of these compounds.



Scheme 1. Synthesis of the acridophosphine acceptors 2-5.

The parent acridophosphine scaffold **1** was synthesized according to Snieckus and co-workers through carbanion-mediated cyclization of a carbamoyl-substituted triphenylphosphine oxide precursor followed by selective reduction of the phosphoryl unit (see the Supporting Information).<sup>[13]</sup> Compound **1** was subjected to a microwave-assisted Knoevenagel condensation with malononitrile to afford **2** as a yellow microcrystalline solid (Scheme 1). To tune the electronic properties, further derivatization of trivalent phosphorus in **2** was carried out.<sup>[14]</sup> Treatment of **2** with elemental sulfur provided phosphine sulfide **3** (97% yield), oxidation with H<sub>2</sub>O<sub>2</sub> gave phosphine oxide **4** (98% yield), and methylation with methyl triflate furnished cation **5** (98% yield). All dicyanomethylene-bridged compounds **2–5** were obtained as air-stable, colorless solids which were soluble in common organic solvents. To allow for comparison of the electron-donating/-accepting

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properties of the phosphorus center, the nitrogen-containing benchmark compound **S1** was prepared from 10*H*-acridin-9-one in two steps (65% overall yield).<sup>[8a]</sup>



**Figure 1.** a) Schematic representation of the underlying conformational equilibrium and b) selected VT <sup>31</sup>P NMR spectra of phosphine **2** in toluene- $d_8$ .

In accordance with their increased electron-accepting character (vide infra), the <sup>31</sup>P NMR resonances of the compounds 3-5 (3: 24.3 ppm, 4: 9.0 ppm, 5: 5.5 ppm) in 1,1,2,2-tetrachloroethane $d_2$  appear low-field shifted as compared to the parent phosphine 2 (-19.5 ppm). In the <sup>1</sup>H NMR spectrum of amine S1 at room temperature (rt) sharp signals are observed. In contrast, phosphine 2 shows broadened signals under the same conditions indicating a 'wing-flip' motion of the butterfly-shaped heteroanthracenyl fragment between conformer A and B as already hypothesized for related acridophosphine systems (Figure 1).<sup>[15]</sup> From the variabletemperature (VT) <sup>31</sup>P NMR line-shape analysis a Gibbs free activation energy  $\Delta G^{\ddagger}$  of 14.3 kcal mol<sup>-1</sup> was obtained for this process involving **2**, with  $\Delta H^{\ddagger} = 13.6$  kcal mol<sup>-1</sup> and  $\Delta S^{\ddagger} = -2.2$  cal K<sup>-1</sup> mol<sup>-1</sup> <sup>1</sup>, which is considerably higher than that reported for related dicyanomethylene-bridged nitrogen-containing systems with a calculated  $\Delta G^{\ddagger}$  of ~6.0 kcal mol<sup>-1</sup>.<sup>[8b]</sup> Similar experiments suggest the coalescence temperature for the oxidized organophosphorus compounds 3-5 to be somewhat lower than for 2 (for details, see the Supporting Information). These results indicate a pronounced effect of the geometric situation at the heteroatom on the thermodynamic parameters of the conformational processes.

Single crystals of S1 and 2-5 suitable for X-ray crystallographic analysis were obtained by slow gas phase diffusion of *n*-hexane into a solution of the compound in CH<sub>2</sub>Cl<sub>2</sub> at rt. All compounds exhibit distorted molecular structures which are invoked by the spatial requirements of the heteroatom together with the steric repulsion between the cyano units and the adjacent aryl hydrogens (Figure 2), as previously observed for TCAQ and related compounds.<sup>[16]</sup> Thus, amine **S1** is virtually planar around the nitrogen center with the C-N-C angles adding to 359.2(6)°. In contrast, the organophosphorus compounds show increased pyramidalization around the phosphorus atom ranging from

Table 1. Selected resonance structures and summary of most relevant structural and spectroscopic data of compounds 2–5 and amine S1.



<sup>[a]</sup> The mean value of the two independent molecules in unit cell was calculated for the sake of simplicity; <sup>[b]</sup> Scan rate 0.5 cm<sup>-1</sup> s<sup>-1</sup> (Figure S47); <sup>[c]</sup> Determined from X-ray crystal structure as mean of the two  $d_{C=N}$ .

 $\sum(\angle C-P-C)$  325.0(6)° for phosphonium salt **5** to 301.5(4)° for phosphine **2**. As a consequence of these structural features, an overall butterfly-shaped molecular geometry is observed for all compounds. In the crystal packing dipolar CN···CN<sup>[17]</sup> interactions of the dicyanomethylene moieties together with hydrogen bonds involving the Lewis basic P=O, P=S, and C≡N units are observed

The impact of the heteroatom on the structural and electronic parameters arising from its conjugation with the dicyanomethylene acceptor was subjected to closer scrutiny (Table 1). In the solid state, efficient electron donation from the heteroatom to the dicyanomethylene group, particularly for amine S1, is indicated by the weakening of the cyano bond ( $d_{C=N}$  1.156(4) Å) as compared to compounds **2–5** ( $d_{C=N}$  1.143(4)–1.147(8) Å). To further assess the CN bond strengths, high-resolution IR spectra were recorded for the compounds in the solid state. The C≡N stretching frequency is successively shifted to lower wavenumbers when going from 5 to 2 and S1, denoting an increasing contribution of the resonance structure B and thus a stronger push-pull character (for details, see the Supporting Information).<sup>[18]</sup> Density functional theory (DFT; ωB97XD/def2-TZVP)<sup>[19]</sup> calculations showed that the dual IR absorption mode of the C=N stretching band of compounds S1 and 2-5 can be assigned to a high-energy synchronous ( $\tilde{v}^{s}$ ), and a low-energy asynchronous stretching mode ( $\tilde{v}^{a}$ ), i.e., vibrational coupling of the two terminal cyano units (Table S3).<sup>[20]</sup>

The electronic properties of the title compounds were investigated by UV/vis absorption spectroscopy in  $CH_2Cl_2$  at rt (Figure 3a and Table 2). Solutions of compounds **3–5** are colorless and accordingly show absorptions exclusively in the UV region with



Figure 2. X-ray crystal structures of S1 and 2-5 (50% probability level, solvent molecules and hydrogens are omitted for clarity).

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the maxima around 315 nm. For amine S1 and phosphine 2 an additional bathochromically shifted intramolecular charge-transfer (ICT) band is observed with  $\lambda_{max}$  at 477 nm and 395 nm, respectively, indicating a more efficient electron-donation of the nitrogen to the dicyanomethylene acceptor as compared to the phosphorus.

Protonation of the phosphorus center in 2 with trifluoroacetic acid (TFA) in acetonitrile resulted in disappearance of the longestwavelength absorption band. Subsequent neutralization of the solution with triethylamine completely restored the original absorption features, thus confirming the ICT character of this band (Figure S46). In accordance with the push-pull nature of S1 and 2, positive solvatochromism is detected both in the absorption and emission features upon successive increase of solvent polarity (hexanes  $\rightarrow$  CH<sub>2</sub>Cl<sub>2</sub>) with comparable  $\lambda_{abs}$  shifts for **S1** (17 nm) and **2** (14 nm) and a more pronounced solvatochromic  $\lambda_{em}$  shift for 2 (56 nm) compared to S1 (35 nm) (Figure S44 and S45).

In contrast to compounds S1, 2, 4, and 5, which are all weakly emissive in solution ( $\phi < 0.005$ ), phosphine sulfide 3 does not feature any emission, which is a result of the heavy atom effect of the sulfur promoting spin-orbit coupling in the excited state.<sup>[21]</sup> Interestingly, the Stokes shift observed for phosphine 2 (8950 cm<sup>-1</sup>) is significantly larger than for the amine analogue S1 (1880 cm<sup>-1</sup>) pointing towards a more pronounced structural deformation in the excited state of the phosphine as corroborated by DFT calculations (see the Supporting Information).<sup>[19]</sup> Remarkably, phosphine 2 exhibits significantly enhanced emission with ~90 times enhanced quantum yield when the solvent is changed from neat THF to a mixture containing 99vol% water (Figure 3b). This phenomenon can be ascribed to aggregation induced emission<sup>[22]</sup> resulting from i) the restricted rotation of the phenyl at the phosphorus atom akin to sterically congested phosphole derivatives<sup>[23]</sup> and ii) the suppression of the 'wing-flip' motion in the aggregated state due to the tight molecular packing as observed for TCAQ derivatives.[24]

Further information about the electronic structure of the compounds was obtained by DFT calculations.<sup>[19]</sup> In line with the efficient electronic communication between the nitrogen donor and the dicyanomethylene acceptor, molecular orbital (HOMO) of amine S1 is delocalized over the entire fused ring system (Figure 4). In contrast, the HOMOs of phosphine 2 and phosphine sulfide 3 are mostly localized on the phosphorus atom and the P=S unit, respectively. While phosphine oxide 4 has three essentially de-

Table 2. Photophysica	and electrochemical data	a of the title compounds
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	$\lambda_{ m abs} [ m nm]^{[a]}$ ( $arepsilon$ [M <sup>-1</sup> cm <sup>-1</sup> ])	$E_{ m gap}$ $[eV]^{[b]}$	λ <sub>em</sub> <sup>[a]</sup> [nm]	Stokes shift [cm <sup>-1</sup> ]	E <sub>red,1</sub> [V] <sup>[c]</sup>	E <sub>red,2</sub> [V] <sup>[c]</sup>
S1	296 (29290) 477 (33000)	2.60	524	1880	-1.60	-2.13
2	314 (16710) 395 (3510)	3.14	611	8950	-1.49	-1.74
3	315 (19010)	3.94	-	-	-1.30	-1.53
4	313 (16670)	3.96	423	8308	-1.26	-1.44
5	315 (33740)	3.94	403	6930	-0.96	-1.18

<sup>[a]</sup> In CH<sub>2</sub>Cl<sub>2</sub>. <sup>[b]</sup> Optical band gap calculated from max absorption wavelength  $\lambda_{abs}$ . <sup>[c]</sup> Half-wave potentials recorded by cyclic voltammetry in CH<sub>2</sub>Cl<sub>2</sub> with 0.1 M nBu<sub>4</sub>NPF<sub>6</sub> (scan rate 200 mV s<sup>-1</sup>, referenced vs. Fc/Fc<sup>+</sup>).

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90.0 85.0 10.0 82.5 80.0 0.0 8.0 60.0 0 50 100 Water fraction [Vol% 40.0 20.0 6.0 40 60 80 82.5 85 90 95 9 4.0 2.0 0.0 500 600 700 Wavelength [nm] 800 Figure 3. a) UV/vis absorption (solid lines) and scaled emission spectra (dashed lines; S1  $\lambda_{exc}$  = 390 nm, 2  $\lambda_{exc}$  = 440 nm, 3 and 4  $\lambda_{exc}$  = 280 nm, 5  $\lambda_{exc}$ = 300 nm) in CH<sub>2</sub>Cl<sub>2</sub> at rt; b) Emission spectra of 2 in THF/water mixtures with different water fractions ( $\lambda_{exc}$  = 400 nm) at rt and plot of the emission peak in-

degenerate HOMOs (within 0.06 eV) delocalized over the peripheral aryl and the phosphoryl moiety, cationic 5 possesses a dicyanomethylene-centered HOMO (for details, see the Supporting Information). The lowest unoccupied molecular orbitals (LUMOs) of all species are predominantly localized on the dicyanomethvlene acceptor. Furthermore, the results suggest a gradual decrease of the HOMO level in the order S1, 2, 3, and 4, whereas the HOMO of 5 is slightly increased. As corroborated by time-dependent DFT calculations, the lowest energy excitations of amine S1, phosphine 2, and methylphosphonium cation 5<sup>+</sup> without counterion have significant oscillator strengths and correspond to the HOMO  $\rightarrow$  LUMO transitions (Table S5), synonymous with the ICT to the dicyanomethylene acceptor (Figure 4). In contrast, for compounds 3 and 4 the lowest lying transitions are likely not to be observed experimentally owing to their very low oscillator strengths.

The redox properties of 2-5 and S1 were investigated by cyclic voltammetry in CH<sub>2</sub>Cl<sub>2</sub> (Table 2 and Figure 5). All compounds show two one-electron reductions, the first of which corresponds to a reversible dicyanomethylene-centered reduction event in accordance with the LUMO localization. This electron transfer at E<sub>red.1</sub> (vs. Fc/Fc<sup>+</sup>) is successively shifted towards less negative reduction potentials as the electron-donating capability of the heteroatom decreases in the order S1 (-1.60 V), 2 (-1.49 V), 3 (-1.30 V), 4 (-1.26 V), and 5 (-0.96 V). While the second reduction of amine S1 occurring at E<sub>red,2</sub> -2.13 V is irreversible, introduction of phosphorus in 2 (-1.74 V) results in a pronounced anodic shift of 390 mV and a substantially increased reversibility of the second electron transfer.





5.0

4.0

່ຮ

2.0

tensity vs. the water fraction (inset).

a)

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**Figure 4.** Kohn-Sham frontier molecular orbitals (FMOs;  $\omega$ B97XD/def2-TZVP); **5** was calculated in the presence of the counterion.

The second reduction event becomes further facilitated upon functionalization of the phosphorus center, reaching –1.18 V for the phosphonium salt **5**. Moreover, the potential difference between the two reductions is considerably narrowed when replacing the nitrogen in **S1** (530 mV) with the phosphorus in **2** (250 mV). These observations clearly support the strong electronic and structural impacts of the phosphorus moiety on the dicyanomethylene-bridged  $\pi$ -system, resulting in significantly stabilized LUMO energy levels and decreased electrostatic repulsion in the negatively charged states.<sup>[25]</sup> The calculated adiabatic electron affinities (EAs) nicely reflect the experimentally observed increase of the electron-acceptor strengths when going from amine **S1** to phosphonium cation **5** (Table S6).<sup>[19]</sup>



Figure 5. Cyclic voltammograms of compounds S1, 2–5 (scan rate 100 mV·s<sup>-1</sup>) and 5 (different scan rates 50-1600 mV·s<sup>-1</sup>) in  $CH_2CI_2$  with 0.1 M  $nBu_4NPF_6$ , vs. Fc/Fc<sup>+</sup>).

In summary, through a concise synthetic strategy we realized a series of novel organic electron acceptors based on a dicyanomethylene-bridged acridophosphine scaffold. In contrast to the nitrogen-containing analogue, the organophosphorus compounds readily underwent remarkably facilitated reversible twoelectron electrochemical reductions with the reduction potentials that were efficiently modulated through the derivatization of the phosphorus center. In particular the methylphosphonium salt **5** is a strong reversible two-electron acceptor comparable with, for instance, *p*-benzoquinone or methylviologen which are reduced at approximately –1.00 V under similar conditions.<sup>[26]</sup> Based on thorough X-ray crystallographic analysis in conjunction with spectroscopic, electrochemical, and theoretical studies, we were not only able to assess the capability of phosphorus to participate in  $\pi$ -conjugation with the dicyanomethylene acceptor but also to enlighten its crucial role for the unique redox properties of these compounds. Our findings suggest considerable potential of these stable electron-deficient scaffolds towards the development of functional n-type materials and redox active chromophores upon further functionalization, both aspects that are currently being pursued in our laboratories.

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**Keywords:** phosphorus heterocycles – electron acceptors – reduction – push-pull – cyano

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# COMMUNICATION

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## COMMUNICATION

#### Phosphorus in charge

A series of potent two-electron acceptors comprising dicyanomethylenebridged acridophosphine scaffold have been synthesized and the impact of the heteroatom on the structural, photophysical, and redox features unveiled.



Tobias A. Schaub, Steffen M. Brülls, Dr. Pavlo O. Dral, Dr. Frank Hampel, Dr. Harald Maid, and Dr. Milan Kivala

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Organic Electron Acceptors Comprising a Dicyanomethylene-Bridged Acridophosphine Scaffold: The Impact of the Heteroatom