ORGANIC
LETTERS

2002
Vol. 4, No. 13
2213−2216

Electron-Donating Properties of *p*-Phenylene Phosphine Imides: An Electrochemical and Spectroscopic Investigation

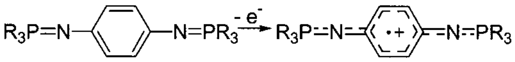
Marcela Escobar, Zhou Jin, and Brett L. Lucht*

Department of Chemistry, University of Rhode Island, Kingston, Rhode Island 02881

blucht@chm.uri.edu

Received April 22, 2002

ABSTRACT



Electronic properties of phosphine imide based organic electron donors have been investigated. *N*,*N*′-*p*-Phenylenebis(triphenyl)phosphine imide ($Ph_3P{=}NC_6H_4N{=}PPh_3$, 1) has two reversible single-electron oxidations (0.04 and 0.53 V vs SCE). Spectroscopic investigations of poly(*p*-phenylene phosphine imide)s (2) are similar to those of polymer model compounds, suggesting formation of localized radical cations on the polymer chains and electronically insulating phosphorus atoms.

The properties of organic conducting materials have been investigated for several years. The primary materials of interest can be separated into two related areas: conjugated polymers and organic donor−acceptor complexes. Conjugated polymers have a wide variety of optoelectric applications including sensors, light emitting diodes (LEDs) and nonlinear optical materials.[1] Conjugated polymers of interest include poly(*p*-phenylene vinylene), polyaniline, and polythiophene. Since the observation of superconductivity in charge-transfers salts of organic electron donors and acceptors, interest in these materials has intensified. Organic conducting materials typically include electron donors related to tetrathiafulvalenes (TTF) and electron acceptors related to tetracyanoquinodimethane (TCNQ).[2] There have been significant recent efforts to couple the two related areas via the preparation of conjugated polymers that incorporate π-donors or acceptors and conjugated oligimers capped with electron-withdrawing or electron-donating groups.[3] Whereas many of the conjugated polymers and related organic donor acceptor complexes have utilized both sulfur and nitrogen, the investigation of the electronic properties of phosphorus containing organic materials has been limited.[4−6]

In this article, we describe the synthesis and investigation of phosphine imide containing organic materials. These materials are related to the widely investigated poly- and cyclophosphazenes, which have four covalent bonds to phosphorus and thus no available p-orbital for involvement in electronic delocalization.[7] While the nature of the phosphorus−nitrogen double bond is debatable, there is strong support for a π-bond resulting from the overlap of a 2p orbital on nitrogen with a 3d orbital on phosphorus.[8] The bond

---

(1) (a) *Conjugated Polymers: The Novel Science and Technology of Highly Conducting and Nonlinear Optically Active Materials*; Bredas, J. L., Silbey, R., Eds.; Kluwer Academic Publishers: Dordecht, 1991. (b) *Handbook of Conducting Polymers*; Skotheim, T. A., Ed.; Marcel Dekker: New York, 1986.

(2) *Introduction to Synthetic Electrical Conductors*; Ferraro, J. R., Williams, J. M.; Academic Press: Orlando, 1987.

(3) Roncali, J. *J. Mater. Chem.* **1997**, *12*, 2307.

(4) (a) Bevierre, M.-O.; Mercier, F.; Ricard, L.; Mathey, F. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 655. (b) Deschamps, E.; Ricard, L.; Mathey, F. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1158.

(5) (a) Withers, H. P., Jr.; Seyferth, D.; Fellmann, J. D.; Garrou, P. E.; Martin, S. *Organometallics* **1982**, *1*, 1283. (b) Honeyman, C. H.; Foucher, D. A.; Dahmen, F. Y.; Rulkens, R.; Lough, A. J.; Manners, I. *Organometallics* **1995**, 14, 5503.

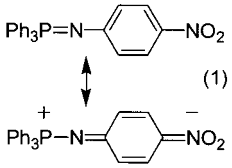
(6) (a) Lucht, B. L., St. Onge, N. O. *Chem. Commun.* **2000**, 2097. (b) Jin, Z.; Lucht, B. L. *J. Organomet. Chem.* **2002**, in press.

(7) (a) Blonsky, P. M.; Shriver, D. F.; Austin, P.; Allcock, H. R. *J. Am. Chem. Soc.* **1984**, *106*, 6854. (b) Allcock, H. R.; Olmeijer, D. L.; O'Connor, S. J. M. *Macromolecules* **1998**, *31*, 753. (c) Gray, F. M. *Solid Polymer Electrolytes: Fundamentals and Technological Applications*; VCH: New York, 1991.

(8) Wisian-Neilson, P. Polyphosphazines. In *Encyclopedia of Inorganic Chemistry*; King, B. R., Ed.; John Wiley & Sons: New York, 1994; Vol. 6, pp 3371−3389.

10.1021/ol026065j CCC: $22.00 © 2002 American Chemical Society
Published on Web 05/23/2002

angles and lengths support electronic delocalization.[9] However, the delocalization is limited to P−N−P units as a result of nodes in the molecular orbitals. The phosphorus atom is considered an insulator atom between islands of electronic delocalization. Infrared spectroscopic investigations of the P═N bond stretch of *p*-substituted phenylphosphine imides supports an expansion of conjugation due to the electron-withdrawing effect of the phosphine imide, via increasing quinoidal character of the aromatic ring (eq 1).[10] The P═N stretching frequency is highly dependent upon the electron-accepting or -donating ability of the *para* substituent. The preparation and investigation of phosphine imide containing π-conjugated materials will provide a better understanding of the P═N bond and the degree of overlap with adjacent π-systems. In addition, the electron-donating nature of the phosphine imide will provide unique and interesting properties of these novel organic materials.



(1)

N,N′-p-Phenylenebis(triphenyl)phosphine imide ($Ph_3P═NC_6H_4N═PPh_3$, **1**) was prepared via the reaction of triphenylphosphine with 1,4-diazidobenzene in high yields (94%) as a yellow powder.[11] Cyclic voltammetry of **1** in a 0.1 M solution of tetrabutylammonium tetrafluoroborate in CH_2Cl_2 affords two single-electron quasi-reversible oxidations at 0.04 and 0.53 V vs SCE (Figure 1). The low oxidation potential indicates that **1** is a better electron donor than TTF (0.30 and 0.66 V SCE).[12] Chemical oxidation of **1** with 0.5 equiv of [bis(trifluoroacetoxy)iodo]benzene results in a shift of the optical absorption bands of **1** (λ_{max} = 261, 269, 277, and 365 nm). The new absorptions (λ_{max} = 393, 497, 540, and 580 nm) are attributed to $\mathbf{1}^{+\bullet}$. Addition of a full equivalent of (bis(trifluoroacetoxy)iodo)benzene results in the loss of the bands consistent with the formation of $\mathbf{1}^{2+}$. Both $\mathbf{1}^{+\bullet}$ and $\mathbf{1}^{2+}$ are stable upon exposure to atmospheric conditions for several hours. Since the oxidation potential of **1** is comparable to that of many electron donors used in conductive organic solids, we investigated the reaction of **1** with TCNQ. The addition of TCNQ to chloroform solutions of **1** results in the formation of a deeply green-colored solution. UV−visible spectroscopy reveals absorptions characteristic of the radical anion of TCNQ (650−900 nm) and $\mathbf{1}^{+\bullet}$ (450−620 nm). Ball milling of TCNQ with **1** in the solid state results in the formations of a reflective black power. These results provide support for the good electron-donating properties of aromatic phosphine imides and the formation of stable radical cationic and dicationic complexes. Compound **1** possesses many characteristics of electron donors in organic conductive solids including high symmetry, high polarizability, low ionization potential, a small separation between the first and second oxidation state, and electron-withdrawing substituents at diametrically different points on the molecule.[2]

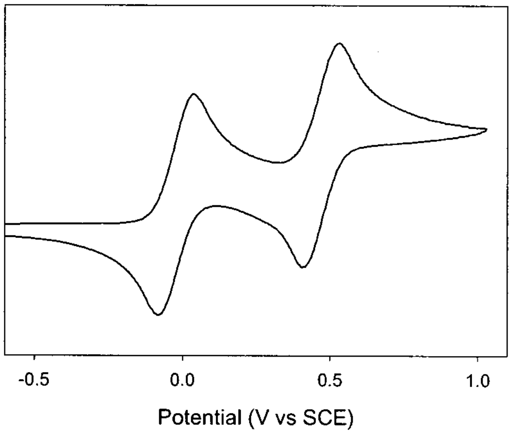
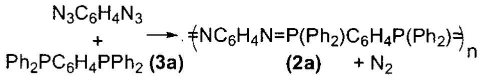


Figure 1. Cyclic voltammogram for **1**.

We extended our investigation of the electronic properties of phosphine imides and the electronic nature of the P═N bond via incorporation into potentially conjugated polymers. Poly(*p*-phenylene phosphine imide)s were first prepared in 1961 as red-orange solids (**2a**, Scheme 1).[11,13] The synthesis and investigation of the poly(*p*-phenylene phosphine imide) **2a** was limited by low yields of the monomer bis(diphenylphosphino)benzene (**3a**, 19%) and poor solubility of the polymer. Newly developed palladium-catalyzed carbon−phosphorus bond forming reactions provide a high yield synthesis of 1,4-bis(diphenylphosphino)benzenes. Addition of 2.2 equiv of diphenylphosphine to 1.0 equiv of 1,4-diiodobenzenes, 1.1 equiv of DABCO, and 0.05 equiv of $Pd(PPh_3)_4$ in toluene followed by heating to 80 °C for 72 h results in slight darkening of the solution along with the formation of a white precipitate characteristic of HI-DABCO. Removal of solvent followed by recrystallization of the crude products in 1:4 degassed Et_2O/MeOH affords **3a,b** (76−88% yield) as white crystalline solids.[14] Incorporation of flexible alkoxy substituents frequently results in a substantial increase in the solubility of conjugated polymers. The addition of 1,4-

Scheme 1



$$\begin{array}{c} N_3C_6H_4N_3 \\ + \\ Ph_2PC_6H_4PPh_2\ \mathbf{(3a)} \end{array} \longrightarrow \underset{\mathbf{(2a)}}{[NC_6H_4N{=}P(Ph_2)C_6H_4P(Ph_2)]_n} + N_2$$

---

(9) Dewar, M. J. S.; Lucken, E. A. C.; Whitehead, M. A. *J. Chem. Soc.* **1960**, 2423.

(10) Wiegrabe, W.; Bock, H. *Chem. Ber.* **1968**, *101*, 1414.

(11) Herring, D. L. *J. Org. Chem.* **1961**, *26*, 3998.

(12) Wheland, R. C.; Gillson, J. L. *J. Am. Chem. Soc.* **1976**, *98*, 3916.

(13) Pomerantz, M.; Victor, M. W. *Macromolecules* **1989**, *22*, 3512.

(14) (a) Hillhouse, J. H. Preparation of Arylalkyl Phosphines, Phosphine Oxides or Phosphine Sulfides. U.S. Patent 5,550,295, 1996. (b) Herd, O.; Hessler, A.; Hingst, M.; Tepper, M.; Stelzer, O. *J. Organomet. Chem.* **1996**, 522, 69.

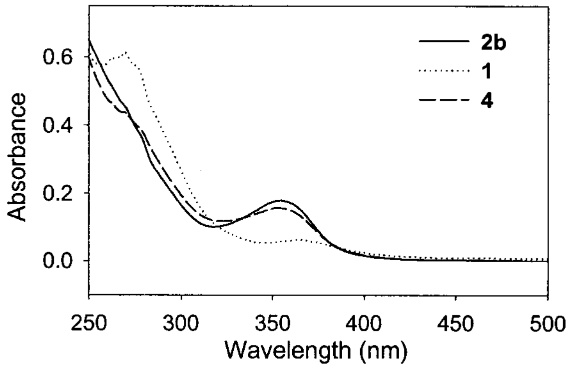
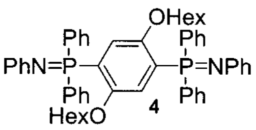


Figure 2. UV-visible spectra of **1**, **2b**, and **4**.

bis(diphenylphosphino)-2,5-dihexyloxybenzene (**3b**) to *p*-diazidobenzene in benzene solution results in the evolution of N_2 and a color change of the solution to light orange. The reaction mixture was stirred for 7 days, and during this time a significant portion of orange solid precipitated from the solution. The benzene solution was filtered to remove the orange precipitate (**2b**, 57%), which was only partially soluble in THF. The THF soluble fraction contains low molecular weight oligomers (**2b**, $M_n = 2000-4000$ GPC vs polystyrene standards, 3−7 repeat units). ^{31}P and ^{1}H NMR spectroscopy and IR spectroscopy support the proposed structure of **2b**. We observe several ^{31}P NMR resonances around 21 ppm consistent with different phosphine imides in the oligomer backbone and resonances around −2.0 ppm consistent with phosphine-terminated oligomers. We also observe two strong infrared absorptions at 1352 and 1312 cm^{-1} consistent with P═N stretches and medium absorptions at 2106 and 2197 cm^{-1} characteristic of residual azido groups terminating the oligomers. IR spectra of the insoluble orange precipitate are similar to the spectra of soluble oligomers except that the absorptions characteristic of the azido groups are much weaker. Thus the insoluble material is considered to be higher molecular weight polymeric material. Thermal gravimetric analysis (TGA) under N_2 reveal decomposition temperatures around 440 °C for **1**, **2b**, and **4**. UV−visible spectra of oligomers **2b** ($\lambda_{max} = 276, 285, 355$ nm) and the polymer model compounds **1** and **4** ($\lambda_{max} = 353$ nm) suggest the presence of primarily isolated chromophores with weak electronic communication in the ground state of the polymer and a break in the conjugation at phosphorus (Figure 2). The results are consistent with electronic delocalization in **2** being limited to P−Ar−P and P−N−Ar−N−P units, as expected from investigations of phosphazines.[7]



We investigated the electrochemical and spectroscopic properties of **2b** to provide further insight into the nature of electronic delocalization of the P═N bond in aromatic phosphine imides. Incorporation of phosphine imides into conjugated polymers followed by chemical or electrochemical oxidation can result in the formation of localized radical cations related to $\mathbf{1}^{+\bullet}$ or delocalized radical cations related to those observed in polyaniline. It is well-known that poly- and oligoanilines are readily oxidized to form quinoidal structures along the polymer backbone.[15] The uncharged oxidized polyanilines can be doped by protonation to high conductivities via the formation of delocalized radical cations. Chemical and electrochemical oxidation of **2b** supports a stepwise conversion to $\mathbf{2b}^{+\bullet}$ and $\mathbf{2b}^{2+}$ via two single-electron transfers. Titration of solutions of **2b** with (bis(trifluoroacetoxy)iodo)benzene (a two-electron oxidant) affords spectroscopic changes similar to those observed for **1**. The λ_{max} is shifted from 355 to 340 nm upon the addition of 0.5 equiv of oxidant and is accompanied by the appearance of new absorption bands at 497, 540, and 580 nm (Figure 3). The spectral changes are consistent with the generation of radical cations along the polymer backbone. As the concentration of oxidant is raised to 1.0 equiv the new bands at 540 and 580 disappear while the absorption at 350 nm is retained, consistent with the conversion of radical cations to dications. Cyclic voltammetry of **2b** provides results similar to those observed for **1**. We observe two quasi-reversible oxidations at 0.07 and 0.38 V vs SCE consistent with the two single-electron transfers (Scheme 2). The oxidation peaks are significantly broader in **2b** than in **1** as would be expected for a mixture of oligomers. While the first oxidation is shifted to slightly higher oxidation potential, the second oxidation potential is significantly lowered. Oxidation of **4** was observed at potentials greater than 1.0 V vs SCE supporting the oxidations depicted in Scheme 2. We do not have a thorough understanding of the source of this shift but suspect

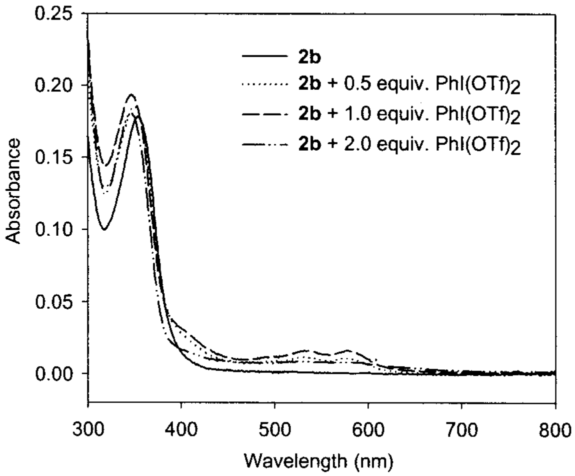
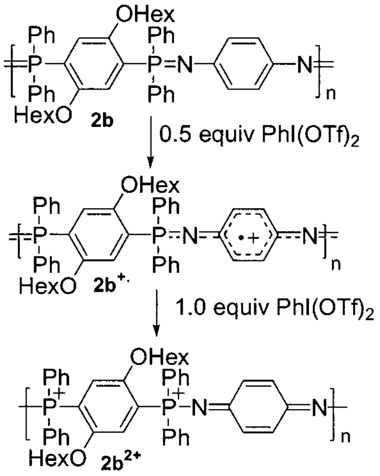


Figure 3. Oxidation of **2b** with $PhI(OTf)_2$ in $CHCl_3$.

---

[15] MacDiarmid, A. G.; Epstein, A. J. *Faraday Discuss. Chem. Soc.* **1989**, 317.

Scheme 2



that it may be the result of the incorporation of the electron-donating alkoxy substituents in **2b**. The similarities of the electrochemical and optical properties of **1** and **2b** suggest that there is little electronic communication through phosphorus in the neutral, radical cationic, or dicationic forms of **2b**. The lack of electronic communication through phosphorus despite the contraction of the d-orbitals upon formation of radical cationic and dicationic phosphonium complexes supports the presumption that the nodal properties of the phosphorus d-orbitals do not allow delocalization through phosphorus along the polymer chain.[9]

We will continue our investigation of the spectroscopic and electronic properties of the incorporation of phosphine imides into π-conjugated materials. The electron-donating properties, ease of synthetic modification, and structural dependence of the oxidation potentials make this new class of organic materials particularly interesting.

Acknowledgment. The authors of this paper would like to thank the University of Rhode Island and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support of this research, and Professor William Euler for helpful discussions.

Supporting Information Available: Experimental procedures and characterization data of **2b**, **3b**, and **4**, CV of **2b**, and UV−visible spectra of **1** and TCNQ. This material is available free of charge via the Internet at http://pubs.acs.org.

OL026065J