# First Examples of Azaphosphanes as Efficient Electron Donors in the Chemical Architecture of Thermally Stable New Nonlinear Optical Materials

Kattesh V. Katti,*[,†,‡,§] Kannan Raghuraman,[‡,§] Nagavarakishore Pillarsetty,[§] Srinivasa R. Karra,[‡,§] Robert J. Gulotty,[||] Mark A. Chartier,[||] and Charles A. Langhoff[||,⊥]

*Departments of Physics, Radiology, and Chemistry, University of Missouri−Columbia, Columbia, Missouri 65211, and Central Research Development Laboratories, Dow Chemical Company, Midland, Michigan 48674*

*Received March 29, 2002*

Chemical vectors that combine electron donors (D) and acceptors (A) across conjugated bonds provide the basis for the chemical architecture of "push−pull" nonlinear optical (NLO) and electro-optical (EO) effects.[1−7] Organic and hybrid organic−inorganic push−pull materials displaying large second-order optical nonlinearities (NLO effects) have found applications in optical data storage, optical information processing, and electro-optic or all optic switching devices.[1−7] Several different classes of electron donor−acceptor functionalized compounds with NLO properties have been designed.[8−17] In push−pull NLO materials design, the donor and acceptor substituents provide the requisite ground-state charge asymmetry, while the $\pi$-conjugation framework provides a pathway for the transfer and redistribution of electric charges under the influence of electric fields.[1−18] Several theoretical and experimental investigations relating to structure−optical property interrelationships have provided important insights into the dependency of hyperpolarizability ($\beta$), into the strengths of donor and acceptor groups, and also into the nature and extent of $\pi$-conjugated paths.[1−18] To gain further understanding of the molecular hyperpolarizability and its relationships between the nature of donor−acceptor groups and the structure of the $\pi$-conjugating spacers, several new and novel combinations of electron donor and acceptor combinations have been investigated.[8−29] Although the active materials used in EO devices involve a host polymeric backbone, functionalized with second-order nonlinear (NLO) chromophores either as guest molecules or via covalent bonding onto the high $T_g$ polymer chains, chemical and thermal stability of the incorporated NLO chromophores play a significant role in the overall design of NLO devices.[1−7] Therefore, development of thermally robust new NLO chromophores is of paramount importance.

In this context, the application of azaphosphanes as a new class of electron donors in the design and development of NLO optical materials has never been explored. Azaphosphanes are a novel class of uninegative anions (Figure 1) that can donate up to three electrons to electron acceptors. In fact, we and others have utilized the powerful electron-donating ability of azaphosphanes to stabilize transition metals in their high oxidation states.[30−33] A wide combination of organic functionalities that can be attached to the

* To whom correspondence should be addressed: Rm. 106, Alton Bldgs Labs, 301, Business Loop 70W, University of Missouri−Columbia, Columbia, MO 65211. Phone: 573-882-5656. Fax: 573-884-5679. E-mail: kattik@health.missouri.edu.

† Department of Physics, University of Missouri−Columbia.

‡ Department of Radiology, University of Missouri−Columbia.

§ Department of Chemistry, University of Missouri−Columbia.

|| Dow Chemical Company.

⊥ Deceased.

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10.1021/cm025564b CCC: $22.00 
Published on Web 05/09/2002

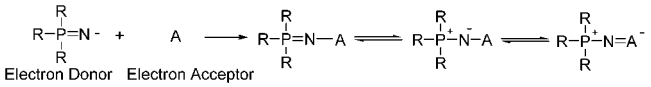


**Figure 1.** Representation of azaphosphane(D)−acceptor(A) conjugate.

phosphorus(V) center will provide unprecedented opportunities for fine-tuning solubility, thermal, and optical properties of this new generation of chromophores (Figure 1). We report, herein, the first example of the application of azaphosphanes as electron donors in the chemical architecture of a new generation of dipolar push−pull donor−acceptor compounds with efficient NLO properties. This communication presents (a) SHG measurements using the electric field second-harmonic (EFISH) technique and (b) the thermal properties of novel azaphosphane-functionalized NLO materials.

Second-order molecular hyperpolarizabilty coefficients for **1** and **2** were measured in solutions at 1579 nm by the EFISH technique.[16,34−38] The 1579-nm fundamental light was generated by Raman shifting 532-nm light from a frequency-doubled $Nd^{3+}$ YAG laser (Quanta-Ray-DCR-2a) to the third Stokes line at 1579 nm. The 1579-nm light was separated spatially from the more intense first and second Stokes lines at 683 and 953 nm using a Pellin-Broca prism and an aperture. In addition, Schott RG-780 and RG-840 red glass long-pass filters were used to block room lights from the sample chamber and a 1500-nm long-pass filter is used to reduce diffusively to scattered first and second Stokes light. A 10-nm band-pass filter at 790 nm is used to collect the second-harmonic light while rejecting the 1579-nm light. We have utilized the commercially available triphenylphosphane as the building block in the development of new donor(D)−acceptor(A) substituted compounds. The interaction of triphenylphosphane with azido-functionalized nitrobenzene or nitroazobenzene via the Staudinger reaction produced the corresponding azaphosphane-based donor−acceptor compounds in >95% yields as outlined in Scheme 1.[39] The azaphosphanes were characterized by $^1H$ and $^{31}P$ NMR spectroscopy and mass spectrometry.[39] Azaphoshane chromophores **1** and **2** are crystalline, air-stable and highly soluble in all common organic solvents. The NLO activity was measured as a $\mu\beta$ product, which is a product of the NLO activity per molecule or molecular hyperpolarizability $\beta$ and the molecular dipole moment $\mu$.

**Scheme I**

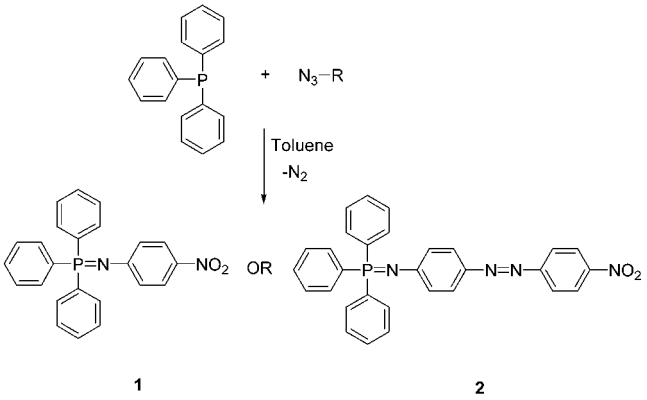


Table 1 summarizes the $\mu\beta$ product values. The $\mu\beta$ value of the simple azaphosphane analogue **1** is 310 × $10^{-48}$ esu whereas for the azobenzene-functionalized analogue **2**, it shifts to 1100 × $10^{-48}$ esu. The $\mu\beta$ value of compound **1** can be rationalized as a combination of electron-donating strength of the triphenylphosphane and the extended conjugation of the P═N bond. The shift in absorption maximum may be attributed to both increased conjugation length and also donor and/or acceptor strengths.[12,16,37,38] In compound **2**, the conjugation is extended by the azaphosphane donor linked via extended conjugation with the electron acceptor. This type of efficient donor (D), acceptor (A), and conjugation should enhance electronic interaction and presumably generate a highly polarizable charge transfer with an asymmetric electron distribution.[12,14,16,37,38] There may also be a contribution of the alignment of the P═N and N═N bonds in the structure to the observed performance. The $\mu\beta$ value as observed for the azaphosphane **2**, although modest as compared to recently reported thiophene-based $\pi$-conjugated chromophores,[40,41] is among the highest within the cyclic and polymeric NLO-active phosphazane compounds.[42] It is also important to recognize that chromophores with very high dipole moments may suffer from decreased solubility in the organic host. In this context, the high solubility of **1** and **2** in organic media may be advantageously used in incorporating them on a polymer matrix.

In addition to achieving high $\mu\beta$ values, the quest in the design of new push−pull NLO materials has always centered around the development of thermally stable chromophores.[1−7,43−45] The inherent high thermal stability associated with phosphorus−nitrogen compounds offer considerable scope for the development of thermally stable NLO active monomers.[46] A key limitation

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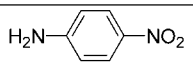
**Table 1. $\mu\beta$ Product Values by EFISH with 1579-nm Fundamental Excitation and Thermal Properties of 1 and 2**

| Compound | Absorption | | NLO Properties | $T_{Decomposition}$ ($^0$C) by TGA | $T_{Decomposition}$ ($^0$C) by DSC |
|---|---|---|---|---|---|
| | $\varepsilon_{790}$ ($M\ cm^{-1}$) | $\lambda_{max}$ (nm), Solvent | $\mu\beta_{1579}$ ($\times 10^{-48}$ esu) | | |
|  | 0.01 | 354[a] | 118 | | |
| **1** | 0.07 | 392[b] | 310 | 282 | 327 |
| **2** | 0.60 | 490[c] | 1100 | 355 | 335 |

[a] In dioxane. [b] In tetrahydrofuran. [c] In dimethylformamide.

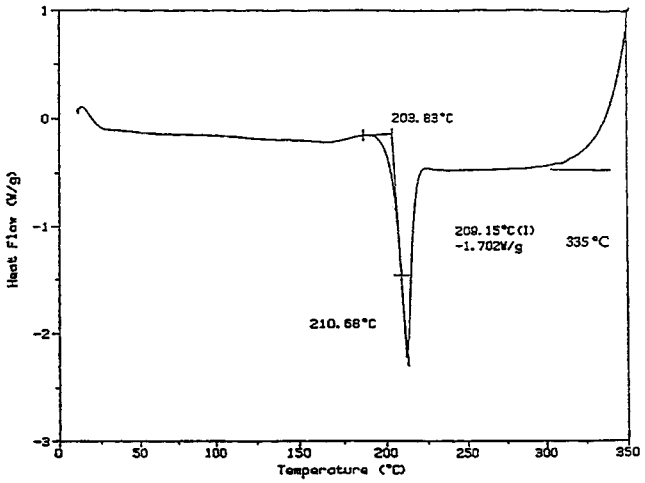



**Figure 2.** DSC of azaphosphane chromophore **2** in air.

to the implementation of polymer-based electro-optic modulators for computing/optical interconnect applications has been the lack of thermally stable nonlinear optical monomers.[1−9,25−42] For these applications, it is imperative to be able to co-process the fabricated EOM with the electrical components. In this case, the device may experience temperatures of 250−350 °C during wave soldering for 5−10 min. In addition, for some applications long-term stabilities at 125−150 °C are necessary. In fact, Twieg and co-workers have developed novel (dicyanomethylene) pyran chromophores with thermal stabilities exceeding 300 °C.[16] Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were used to assess the thermal stabilities of **1** and **2**. As shown in Table 1 and Figure 2, the azaphosphane-based chromophores, compounds **1** and **2**, have thermal stabilities above 280 °C. In fact, the high thermal stability (335° C) as observed for the azaphosphane compound **2** (Figure 2) is among the highest reported for organic nitro acceptor NLO compounds[1−9,11,42] and is also superior compared to those recently reported for push−pull chromophores based on thiophene $\pi$-conjugating spacers.[41]

The role of azaphosphanes as new electron donors offers scope for the development of thermally stable NLO materials. Chemical flexibility of substituents bound to the phosphorus center in **1** and **2** should allow incorporation of such "push−pull" chromophores on high $T_g$ polymers. Studies along those lines are underway.

**Acknowledgment.** This work was supported by funds from the Cooperative Research-Dow/University Partnership in the Discovery program administered by the Dow Chemical Company and the Departments of Radiology, Physics, and the Research Reactor of the University of Missouri−Columbia.

**Supporting Information Available:** Synthesis and characterization details of compounds **1** and **2**; general experimental procedures followed to study thermal and optical properties for compounds **1** and **2**; a schematic of the EFISH apparatus (PDF/DOC). This material is available free of charge via the Internet at http://pubs.acs.org.

CM025564B