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New NLO Stilbene Derivatives Bearing Phosphonate Ester Electron-Withdrawing Groups

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Abstract: The synthesis and characterization of a new class of electron donor-acceptor substituted stilbenes bearing a phosphonate ester as the electron-withdrawing functionality is described. Phosphorylation of aromatic rings was accomplished using Ni-catalyzed Arbuzov reactions, while Pd-catalyzed Heck-type coupling reactions were employed to construct the stilbene derivatives. Through determination of an electro-optic coefficient (r_{33}), it was demonstrated that the phosphonate ester group is effective as an electron-withdrawing group for stilbene-based second-order NLO materials.

INTRODUCTION

The photorefractive effect, found in materials that are both photoconductive and have nonlinear optical properties, is avidly being pursued for optical processing applications. When a photorefractive material is illuminated with light of nonuniform intensity, in the presence of an applied electric field, charges are photogenerated and subsequently transported and trapped at defects. This results in a nonuniform space-charge distribution, affording a refractive index distribution which can be modulated through the electro-optic effect. A phase grating is then created which can diffract light, affording a hologram.[1] Photorefractivity, thus, holds great potential in holographic optical data storage and processing, as well as frequency doubling of laser light.

In order to manifest the photorefractive effect, it is thought that these polymers must contain photocharge generating (CG) and transporting (CT) functionality, charge trapping sites, and nonlinear optical (NLO) chromophores. A number of systems have been reported in which a polymer possessing one of the requisite functionalities, e.g., covalently attached NLO chromophores, is doped with the others, e.g., CG and CT dopants (see, e.g., references 1-5). With the pressing technological demand for more efficient photorefractive and electro-optic materials, it is clear that new types of materials and new synthetic approaches are needed.

The phosphonate ester group is a strong electron-withdrawing functionality.[6] An aniline derivative bearing a phosphonate ester was recently reported to exhibit second-order nonlinear optical properties comparable to the 4-nitroaniline NLO reference.[6] Several stilbene derivatives displaying NLO properties are known but there have been no reports utilizing a phosphonate ester as an electron-withdrawing group for this purpose. Herein, we report the straightforward synthesis and characterization of a new class of electron donor-acceptor substituted stilbene derivatives bearing phosphonate groups (**5** and **6**). A multifunctional carbazole derivative (**5**), bearing two NLO moieties, was prepared, the carbazole core is intended to serve as the charge transporter.

EXPERIMENTAL

Materials. CH_2Cl_2, hexanes, Et_2O, EtOAc, triethylphosphite, ethylene carbonate, Et_3N, DMF, THF, and toluene were distilled before use. EtOH was dried over 4 Å molecular sieves. 4-Bromo-N,N-dimethylaniline was recrystallized before use. 4-Bromoacetophenone, $NaBH_4$, NaH, 3,6-dibromocarbazole, tri-*o*-tolylphosphine, $Pd(OAc)_2$, $NiCl_2$, and fused $KHSO_4$ were used as received from commercial suppliers.

Measurements. ^1H NMR spectra were recorded on a Bruker AM-300 spectrometer. UV-visible measurements were secured using a Hewlett-Packard model 8452A diode array spectrophotometer. High and low resolution mass spectra were obtained using JEOL model SX102A and AX505H mass spectrometers, respectively. 3-Nitrobenzyl alcohol doped with NaI was used as the matrix for fast atom bombardment (FAB) measurements. NH_3 was employed as reagent gas for chemical ionization (CI) measurements.

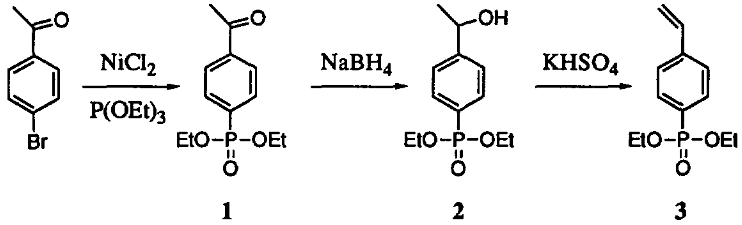
Synthesis of 3,6-bis(diethyl 4-phosphonatestyryl)carbazole (5). To a solution of N-(2-hydroxyethyl)-3,6-dibromocarbazole (4, 0.2 g, 0.54 mmol) in DMF was added $Pd(OAc)_2$ (0.008 g, 0.036 mmol), tri-*o*-tolylphosphine (0.021 g, 0.07 mmol), Et_3N (0.253 g, 2.5 mmol), 4-vinylbenzenephosphonic acid diethyl ester (3, 0.36 g, 1.4 mmol). The yellow reaction mixture was stirred at 60 °C for 12 h. The solvent was removed, and the mixture was poured into water and extracted in CH_2Cl_2. The crude product was purified on a silica gel column (1:20 hexanes/EtOAc), resulting in a bright yellow solid (44% yield). ^1H NMR (300 MHz, $CDCl_3$): δ 1.36 (t, 12H, $-OCR_2CH_3$), 1.98 (s, 1H, -OH), 4.00-4.20 (m, 10H, $-OCH_2CR_3$ and $N-CH_2$), 4.50 (t, 2H, $O-CH_2$), 7.12, 7.17, 7.40, 7.45 (dd, 4H, *trans*-stilbene -CH=CH-), 7.48 (d, 2H, C1, C8 carbazole ArH), 7.64 (m, 6H, ArH *ortho* to C=C and C2, C7 carbazole ArH), 7.78 (dd, 4H, *ortho* to $P(O)(OEt)_2$), 8.27 (s, 2H, C4, C5 carbazole ArH). High resolution MS (FAB, [M+Na]): calc 710.2410; actual: 710.2436. UV-vis: λ_{max} = 340 nm.

Synthesis of 4-diethyl 4'-N,N-dimethylaminostilbenephosphonate (6). 4-Bromo-N,N-dimethylaniline (0.64 g, 3.2 mmol), 3 (0.6 g, 2.64 mmol), $Pd(OAc)_2$ (5.9 mg, 2.64×10^{-2} mmol), tri-*o*-tolylphosphine (16 mg, 5.28×10^{-2} mmol) and Et_3N (0.735 g, 5.28 mmol) were combined in a screw cap vial and heated to 100 °C for 12 h. The reaction mixture was cooled to room temperature, dissolved in acetonitrile, passed through a silica gel plug, washed with sat. NaCl, dried over $MgSO_4$, concentrated, and washed with hexane, resulting in a fluorescent yellow solid (70% yield). ^1H NMR (300 MHz, $CDCl_3$): δ 1.36 (t, 6H, $-OCR_2CH_3$), 3.09 (s, 6H, $-NCH_3$), 4.15 (m, 4H, $-OCH_2CR_3$), 6.78 (m, 2H, ArH *ortho* to N), 6.92 and 7.16 (dd, 2H, *trans* stilbene -CH=CH-), 7.45 (d, 2H, ArH *meta* to N), 7.60 (m, 2H, ArH *meta* to $P(O)(OEt)_2$), 7.75 (dd, 2H, ArH *ortho* to $P(O)(OEt)_2$). High resolution MS (EI, 70 EV): calc 359.1650; actual 359.1644. UV-vis: λ_{max} = 320 nm.

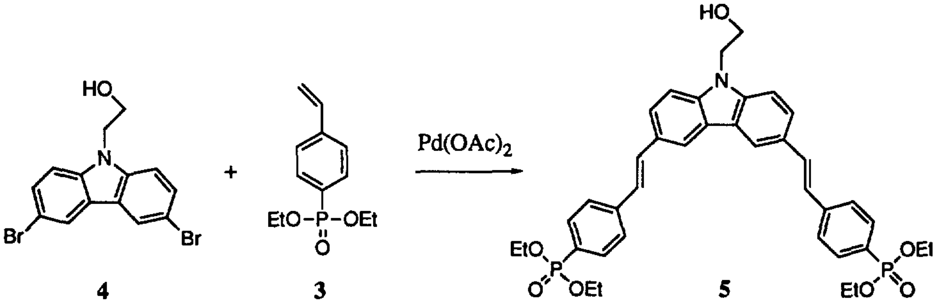
RESULTS AND DISCUSSION

4-Vinylbenzenephosphonic acid diethyl ester (3) was prepared in three steps according to a previously reported procedure illustrated in Scheme 1, in 31% overall yield.[7,8] This sequence involved a $NiCl_2$-mediated Arbuzov-type reaction, reduction with $NaBH_4$, and elimination over $KHSO_4$. Hydroxyethylation of 3,6-dibromocarbazole was conducted with ethylene carbonate, by first forming the amine anion with NaH, affording N-(2-hydroxyethyl)-3,6-dibromocarbazole (4) in 80% yield.[9]

Pd-catalyzed Heck-type cross-coupling reactions[10] were conducted on N-(2-hydroxyethyl)-3,6-dibromocarbazole (4) and 4-bromo-N,N-dimethylaniline, as shown in Schemes 2 and 3, respectively. The Heck reaction between 3 and 4 was carried out with $Pd(OAc)_2$, tri-*o*-tolylphosphine, and Et_3N in DMF at 60 °C. 3,6-Bis(diethyl 4-phosphonatestyryl)carbazole (5) was isolated, and characterized by ^1H NMR and high resolution MS (FAB), confirming formation of the desired compound. FAB MS analysis showed $[M+H]^+$ = 688 and $[M+Na]^+$ = 710, high resolution FAB MS indicated $[M+Na]^+$ = 710.2436 (calc. 710.2410). NMR analysis indicated exclusive formation of the *trans*-stilbenoid olefin geometry, the characteristic doublet of doublets was observed at 7.15 and 7.43 ppm. UV-visible analysis revealed a λ_{max} of 340 nm.



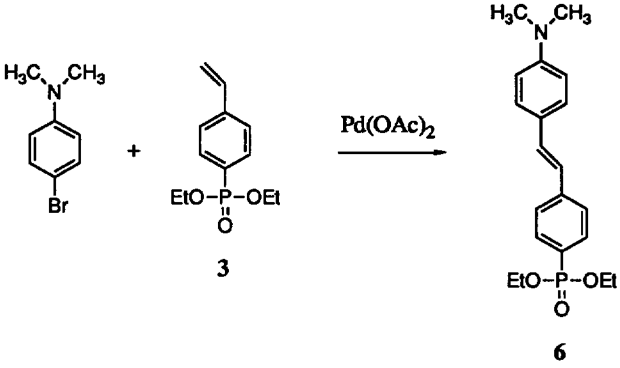
Scheme 1



Scheme 2

Pd-catalyzed cross coupling of 4-bromo-N,N-dimethylaniline and **3** was likewise carried out with $Pd(OAc)_2$ and tri-*o*-tolylphosphine in Et_3N (Scheme 3). Fluorescent yellow 4-diethyl 4'-N,N-dimethylaminostilbenephosphonate (**6**) was obtained, and characterized by ^1H NMR and high resolution MS (EI), confirming formation of the desired compound. CI MS analysis showed $[M+H]^+ = 360$ and $[M+NH_4]^+ = 377$ and EI MS revealed $[M^+] = 359$. High resolution MS afforded $[M^+] = 359.1644$ (calc. 359.1650). NMR analysis also indicated exclusive formation of the *trans*-stilbenoid olefin geometry, with a doublet of doublets at 6.92 and 7.16 ppm. UV-visible spectrophotometric analysis revealed a λ_{max} of 320 nm. Preliminary electro-optic characterization (χ^2) of **6** in poly(methyl methacrylate) indicated that it is a second-order NLO chromophore with $r_{33} = 0.90$ pm/V.[11] The corresponding r_{33} value for 4'-N,N-diethylamino-4-nitrostilbene (DANS) was determined to 2.2 pm/V under similar conditions.[12]

The aforementioned syntheses of novel electron donor-acceptor substituted stilbenes (**5** and **6**) represent an efficient strategy to create potentially important new NLO materials with phosphonate ester groups as the electron-withdrawing functionality. In addition, the carbazole derivative **5** represents a building block for the generation of new photorefractive materials, compounds in which a charge transporter and two NLO chromophores are efficiently incorporated into one multifunctional unit. Furthermore, it was demonstrated that the phosphonate ester group is effective as an electron-withdrawing group for second-order NLO organic materials.



Scheme 3

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11. Poling temperature = 95 °C, $dc_{applied} = 77$ V/μm, $\lambda_{measured} = 676$ nm.
12. Poling temperature = 95 °C, $dc_{applied} = 106$ V/μm, $\lambda_{measured} = 780$ nm.

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