ORGANIC
LETTERS

2000
Vol. 2, No. 16
2419−2422

A Straightforward Modular Approach to NLO-Active β-Amino Vinyl Nitrothiophenes[§]

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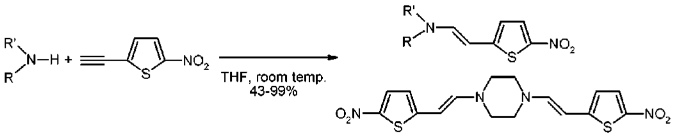
Received May 11, 2000

ABSTRACT



Secondary amines add very efficiently to 2-ethynyl-5-nitrothiophene to give β-amino vinyl nitrothiophenes, a novel class of push–pull chromophores. According to first HRS measurements these highly solvochromic compounds with relatively short dipole axes display remarkably high static first hyperpolarizabilities $\beta^0_{333} = 29–31 \times 10^{-30}$ esu.

A remarkable number of organic chromophores have been investigated with respect to their nonlinear optical (NLO) properties, and still the practical synthesis of novel structural motifs is an ongoing quest, especially since the continuing demand for tailor-made chromophores for photonic applications is rapidly increasing.[1] Structurally and theoretically,[1d] the prerequisite push−pull substitution of organic chromophores is well established; however, the design of relatively short chromophores with high β values overcoming the disadvantages of long and extended π-systems (i.e., bathochromic absorption) is still a challenge. Thienyl-based NLO chromophores display remarkably higher hyperpolarizabilities than the related benzoid systems[1a,2] and also a red-shifted absorption. Even oligothienylenes[3] have been synthesized and shown to be excellent NLO compounds. Thus, the high polarizability of thiophenes can be exploited for both synthesis and electronic properties of NLO target molecules. In particular, the nitro group exerts its strong electron-withdrawing power through the thiophene core and concomitantly activates olefins toward Michael-type additions.[4] Although the amination of alkynes is a well-established industrial process for the preparation of amino vinyl compounds, most alkynes and even *p*-nitrophenyl acetylene[5] react only at elevated temperatures or high pressures.[6] Here we wish to communicate a quite general

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[§] Dedicated to Prof. Dr. Franz Effenberger on the occasion of his 70th birthday.

[†] Organic Chemistry (Haus F).

[‡] Physical Chemistry (Haus E).

(1) For recent reviews on NLO materials, see: (a) Long, N. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 6. (b) Marder, S. R.; Perry, J. W. *Adv. Mater.* **1993**, *5*, 804. (c) Nie, W. *Adv. Mater.* **1993**, *5*, 520. (d) Kanis, D. R.; Ratner, M. A.; Marks, T. J. *Chem. Rev.* **1994**, *94*, 195. (e) Marks, T. J.; Ratner, M. A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 155. (f) Wolff, J. J.; Wortmann, R. *Adv. Phys. Org. Chem.* **1999**, *32*, 121.

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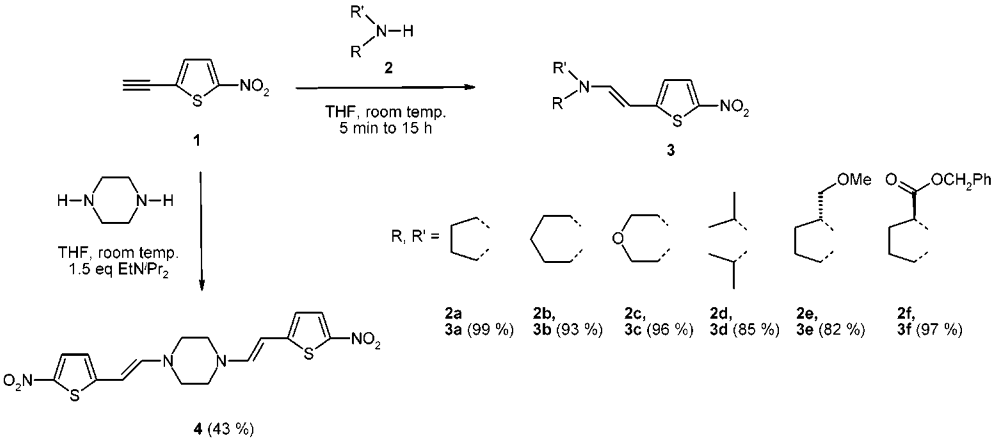
Scheme 1



modular approach to β-amino vinyl nitrothiophenes, a class of compounds with interesting nonlinear optical properties.

2-Ethynyl-5-nitrothiophene[7] (**1**) reacts with secondary amines **2** in THF or dichloromethane at room temperature in the sense of a "thienylogous" Michael addition[8] to furnish in reaction times between 5 min (**3a**) and 16 h (**4**) the β-amino vinyl nitrothiophenes **3** or **4** as violet microcrystals, oils, or resins (**3d**–**f**) in good to excellent yields (Scheme 1).[9,10] This reaction largely depends on steric effects, in analogy to Michael additions to enynals[11] and ynoates[12] which also proceed under mild reaction conditions to give amino vinylated compounds. Hence, the conversion of pyrrolidine (**2a**) to **3a** is complete within 5 min, whereas the bulky diisopropylamine (**2d**) needs 15 h to give the desired product **3d**. Even chiral amines such as (*R*)-(+) 2-(methoxymethyl) pyrrolidine (**2e**) and (*S*) proline benzyl ester (**2f**) can be successfully applied in this modular approach to β-amino vinyl nitrothiophenes.

Since the coupling constants of the vinyl protons ($^3J_{(H,H)}$ = 13.2–13.4 Hz) fall into the transition regime between typical *Z*- and *E*-coupling constants, an unambiguous assignment of the double bond configuration was only possible after performing 2D-NOESY experiments. No cross-peaks of the vinyl proton resonances were detected in any case, and thus, an *E*-configuration can be undoubtedly deduced.

As previously observed for donor-substituted nitrothiophenes,[3a,16] the high polarizability of the delocalized π-electrons along the donor acceptor axis of the molecules results in intense solvochromic absorption maxima (Table 1).

Table 1. Absorption Maxima [nm] (Experimental and Calculated[13]), Dipole Moments [D] (Calculated[13]), and Hyperpolarizabilities[a] of the β-amino Vinyl Nitrothiophenes **3a** and **3b**

	λ_{max}						β^{d}_{333} [c]	
	n-C$_5$H$_{12}$	CHCl$_3$	calcd	μ_g[b]	μ_e[b]	$\Delta\mu$[b]	1500	0
3a	450	520	400	9.73	17.72	7.99	68	31
3b	443	513	398	10.11	18.15	8.04	62	29

[a] Measured by the hyper Rayleigh scattering (HRS) technique at a fundamental wavelength of 1500 nm in a chloroform solution; reference chromophore is *p*-dimethylamino cinnamic aldehyde (DACA).[14] [b] All calculated dipole moments (g, ground state; e, first excited state) are given in D (1 D ≡ 3.336 × 10^{-30} Cm); $\Delta\mu$ is the change of dipole moments between g and e. [c] All β values are given in 10^{-30} esu (10^{-30} esu ≡ 0.37 × 10^{-50} cm^3 V^{-2}); the β^{0}_{333} values were calculated by applying the two-level model[15] on the longest wavelength absorption band.

The examination of the solvochromicity of **3b** (Figure 1) reveals a linear correlation between Reichardt's solvent polarity $E_T(30)$ values[17] and the absorption maxima in various solvents. According to the observed positive solvochromicity, i.e., a bathochromic shift of the charge-transfer band upon

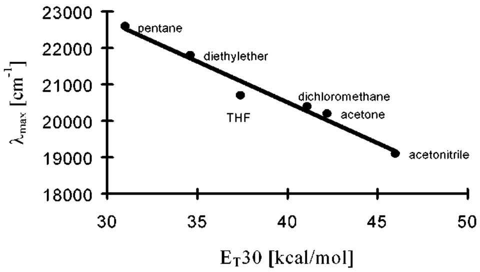


Figure 1. Correlation of Reichardt's solvent polarity $E_T(30)$ values and the absorption maxima of **3b** (r = 0.985).

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(7) Prepared by Sonogashira coupling of 2-bromo-5-nitrothiophene and (trimethylsilyl)acetylene in a refluxing mixture of THF and triethylamine in 85% yield and subsequent desilylation with 2 N aqueous NaOH in methanol in 92% yield.

(8) The same reaction was reported late last year independent from our group: Wu, I.-Y.; Lin, J. T.; Li, C.-S.; Wang, W.-C.; Huang, T. H.; Wen, Y. S.; Chow, T.; Tsai, C. *Tetrahedron* **1999**, *55*, 13973.

(9) **Typical procedure** (**3a**): To a magnetically stirred solution of 200 mg (1.30 mmol) of 2-ethynyl-5-nitrothiophene (**1**) in 5 mL of THF under nitrogen was added 1.7 g (24 mmol) of pyrrolidine (**2a**) dropwise at room temperature. After 5 min of stirring, the reaction mixture was filtered through a short pad of Celite, the solvents were evaporated in vacuo, and the residue was dried under high vacuum to give 290 mg (99%) of analytically pure **3a** as violet microcrystals.

(10) All compounds have been characterized spectroscopically and have the correct elemental analysis or HRMS.

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increasing the solvent polarity, a significant charge-transfer character of the first excited state can be expected.

According to PPP-π-SCF-CI calculations,[13] the intense longest wavelength absorption bands at 530 nm (acetonitrile) with a large dipole moment in the first excited state stems from the HOMO−LUMO transition (Table 1). For these push−pull chromophores, that means a change in the transition dipole moment $\Delta\mu$ of about 8 D, i.e., a charge transfer from the HOMO localized in the amino vinyl fragment (ground state) to the LUMO with a strong density distribution in the nitro group (first exited state) (Figure 2).

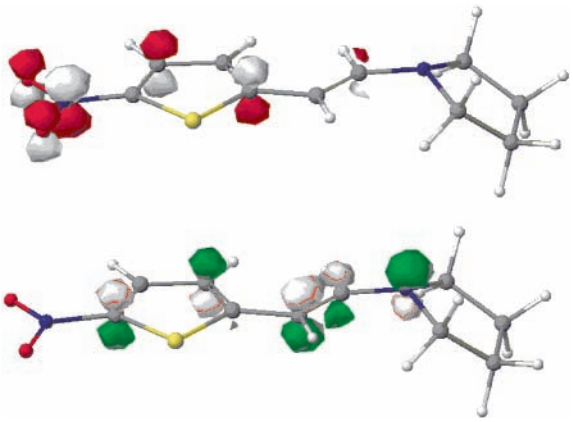
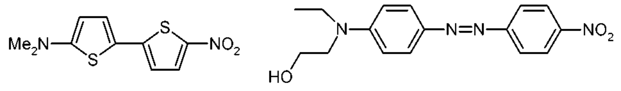


Figure 2. HOMO (bottom) and LUMO (top) of **3a** (calculated from a PM3-optimized gas-phase structure at the ZINDO/CI level of theory).[21]

The first hyperpolarizabilities β of the β-amino vinyl nitrothiophenes **3a** and **3b** were measured by hyper Rayleigh scattering (HRS)[18,19] at a fundamental wavelength of 1500 nm in chloroform solutions (Table 1). Since neither compound displays fluorescence around 750 nm, fluorescence enhancement at the second-harmonic frequency can be excluded.

The extrapolation of the dynamic hyperpolarizabilities $\beta_{333}^{1500\mathrm{nm}}$ to their static counterparts β_{333}^{0} is accomplished by using the two-level model.[15] Both chromophores **3a** and **3b** display similar β values that are surprisingly large for such short dipoles and can be compared to the slightly red shifted bisthiophene compound **5** (Figure 3) ($\beta_{333}^{0} = 54 \times 10^{-30}$ esu, λ_{max} (hexane) = 466 nm, λ_{max} ($CHCl_3$) = 530 nm).[3a,16a] In comparison to the commercially available NLO chromophore Disperse Red 1 (**6**) ($\beta_{333}^{0} = 43 \times 10^{-30}$ esu, λ_{max} ($CHCl_3$) = 487 nm),[20] the β-amino vinyl nitrothiophenes **3**, although the absorption maxima are slightly red shifted (λ_{max} ($CHCl_3$) = 520 nm), display a rather favorable molecular figure of merit, $\beta^0\mu/M_w$ where M_w is the molar mass[1f] (**3a**, $\beta^0\mu/M_w = 1.34$; **3b**, $\beta^0\mu/M_w = 1.23$; **5**, $\beta^0\mu/M_w = 1.69$; **6**, $\beta^0\mu/M_w = 1.03$). This also classifies β-amino vinyl nitrothiophenes as suitable NLO materials with a low molecular mass.



5 **6**

Figure 3.

Interestingly, some of the β-amino vinyl nitrothiophenes **3** are oils (**3d**,**e**) or amorphous glasses (**3f**) at room temperature. This peculiar property is highly promising for incorporation of these compounds at high concentration into phototrefractive (PR) composites for holographic recording.[22] Some may even be used in bulk form as trifunctional chromophores for sensitization, charge transport, and nonlinearity,[23] which are the properties required for photorefractivity.[22] Note that in low-T_g PR materials due to "orientational enhancement" [24] the birefringence contribution $\Delta\alpha\mu_g^2$ ($\Delta\alpha$ is the anisotropy of the linear polarizability, μ_g is the dipole moment) overwhelms the nonlinear electrooptic contribution $\beta\mu_g$ to the index modulation induced in the hologram. The compounds were investigated by differential scanning calorimetry (DSC),[25] revealing glass transitions for the piperidyl compound **3b** ($T_g = -10$ °C), the morpholine derivative **3c** ($T_g = 6$ °C), and the (R)-(+)-2-(methoxymethyl)pyrrolidyl structure **3e** ($T_g = -13$ °C). The use of these novel compounds in PR composites will be the subject of future investigations. Because of the glass-forming properties of these chromophores, good long-term stability is expected. Additionally, by using the racemic mixture of **3e**, the tendency to crystallize can be further reduced.

This amination of alkynylated nitrothiophenes can also be conducted in the sense of a three-component reaction.[26] As exemplified for the reaction of phenylacetylene, diethyl-

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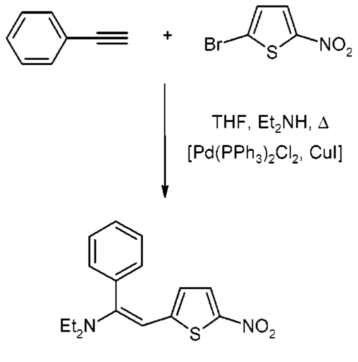
Scheme 2



7 (45 %)

amine, and 2-bromo-5-nitrothiophene under Sonogashira coupling conditions,[27] the consecutive sequence of coupling and amine addition gives rise to the styryl derivative **7** (Scheme 2). Therefore, this amino vinylation can be readily extended to three-component reactions.

In conclusion, we have show that the amination of 2-ethynyl-5-nitrothiophene efficiently gives rise to a number of β-amino vinyl nitrothiophenes with significant first hyperpolarizabilities, β, and interesting morphological stability. This straightforward approach to novel push–pull chromophores concomitantly sets the stage for new combinatorial strategies in optimizing the NLO properties of β-amino vinyl nitrothiophenes and their application as photorefractive materials.[22] Thus, further studies directed toward expanding the scope of this facile amination to related multicomponent reactions based upon coupling–nucleophile–addition sequences with other suitable acceptor components as well as the design of coupled oligomeric NLO chromophores with low T_g for photorefractive composites are currently underway.

Acknowledgment. The financial support of the Fonds der Chemischen Industrie, Deutsche Forschungsgemeinschaft, FORMAT, and the Dr.-Otto-Röhm Gedächtnisstiftung is gratefully acknowledged. We wish to express our appreciation to Prof. H. Mayr for his generous support. We heartily thank Francisco Gallego-Gómez for recording the DSC of compounds **3a**–**c** and **3e** and Ms. Brigitte Janker for recording the fluorescence spectra.

Supporting Information Available: Experimental procedures, characterization data, solvochromicity data of **3a**, **3b**, and **4**, and selected 2D NMR spectra for the β-amino vinyl nitrothiophenes **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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