Functionalized Thiophenes: Second-order Nonlinear Optical Materials

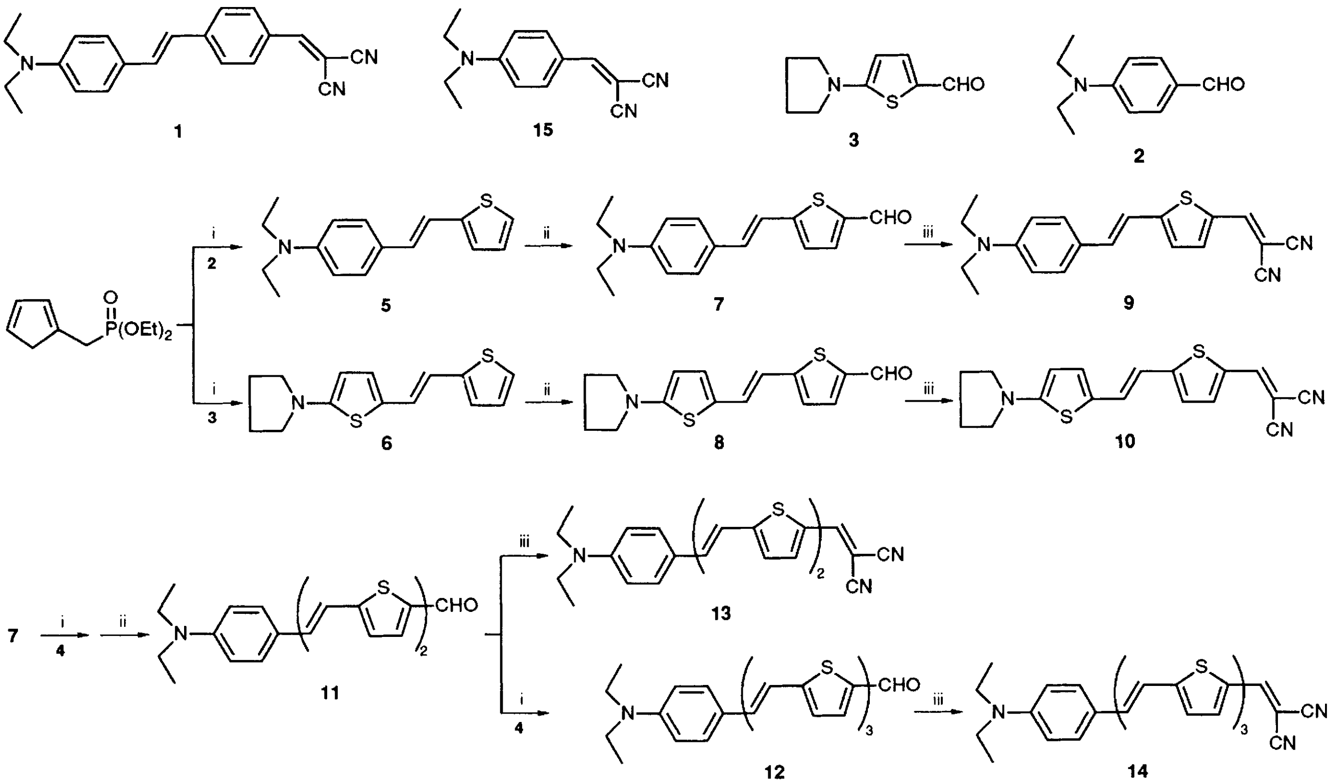
Alex K-Y. Jen,* V. Pushkara Rao,* K. Y. Wong and Kevin J. Drost

EniChem America Inc., Research and Development Center, 2000 Cornwall Road, Monmouth Junction, New Jersey 08852, USA

It is shown experimentally that the complete replacement of benzene rings with thiophene rings in a donor–acceptor substituted stilbene significantly enhances its second-order nonlinear optical hyperpolarizability (β); results obtained with a series of thiophene-substituted donor–acceptor compounds with different conjugation lengths reveal a power law dependence of βμ on the molecular conjugation length.

Organic materials with second-order nonlinear optical (NLO) properties have been the subject of intense investigations owing to their exceptionally large nonlinearity and ultrafast response times.[1] These materials have potential applications in areas such as telecommunications, optical information processing and data storage.[2] Major research efforts have focused on developing NLO chromophores possessing large molecular nonlinearity and good thermal stability as well as improved solubility and processability.

It is well-known that the second-order molecular nonlinear optical hyperpolarizability (β) increases with increasing donor and acceptor strengths and with increasing length of conjugation.[3] Many donor–acceptor conjugated organic molecules reported in the literature fall into the following categories: substituted benzenes, biphenyls, stilbenes, azobenzenes and Schiff bases.[4–7] In all these classes, benzene ring(s) with or without the π-bridges have been employed as the conjugating moieties to connect donor and acceptor functional groups. However, optical studies on compounds containing more than two benzenoid rings have been limited. This could be attributed, in part, to the difficulty in the synthesis of extended conjugated compounds possessing more than two benzenoid rings as they are practically insoluble in most common organic solvents.

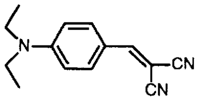
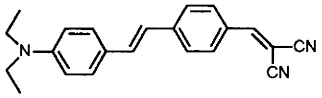
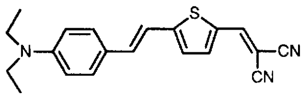
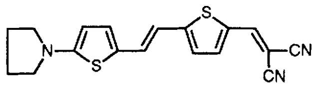
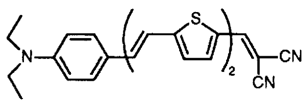
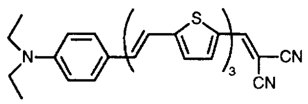


Scheme 1 *Reagents and conditions*: i, Bu^{t}OK–tetrahydrofuran (THF), 0 °C, 2 h; ii, Bu^{n}Li–THF, 0 °C, 2 h, followed by DMF, 25 °C; iii, CH_2CN_2, $CHCl_3$, pyridine

In designing novel push–pull structures that would manifest superior properties to the existing structures, we employed five-membered heteroaromatics such as thiophene as the conjugating units. Since thiophene has a lower delocalization energy than that of benzene,[8] it can offer better effective conjugation than that of benzene in donor–acceptor compounds. The use of thiophene in compounds for nonlinear optics has previously been addressed.[5,9] These studies were concerned with the replacement of one of the two benzene rings with a thiophene ring in donor–acceptor compounds. Results obtained with such systems reveal no significant enhancement of molecular nonlinearity ($\beta\mu$) upon thiophene substitution. Here, we report the first successful demonstration of significant $\beta\mu$ enhancement by replacing both of the benzene rings in a stilbene type molecule with thiophene.

We have chosen 4-diethylamino-4′-dicyanovinylstilbene (DADVS, **1**) as our standard for comparison[10–12] because it has been extensively studied and has been used as a prototype compound for poled polymer applications.[13] Table 1 lists the donor–acceptor stilbenes **1**, **9**, **10**, **13**, **14** and **15** that we have investigated. The general methodology for the synthesis of these compounds is shown in Scheme 1. Compounds **5** and **6** (Scheme 1) were derived from a Wittig–Horner condensation reaction of phosphonate **4**[†] with 4-diethylaminobenzaldehyde **2** and 5-pyrrolidino-2-thiophenecarboxaldehyde **3**, respectively. Lithiation of compounds **5** and **6** with Bu^{n}Li and subsequent quenching with dimethylformamide (DMF) results in aldehydes **7** and **8**. Treatment of these aldehydes with malononitrile gave the corresponding dicyanovinyl compounds **9** and **10** in 80–90% yields. Conjugation length has been extended further to synthesize compounds **13** and **14** by repeating the above procedures. All the double-bond linkages in these compounds were confirmed to be all-*trans* by careful NMR analysis.

Table 1

Compound	λ_{max}/nm in dioxane	$\beta\mu/10^{-48}$ esu at λ = 1.907 μm
15 	419	300
1 	468	1100
9 	513	1300
10 	584	2600
13 	547	2300
14 	556	3800

Comparison of the electronic absorption spectra of compound **1** with **9** and **10** reveals that the replacement of a benzene ring with a thiophene ring causes a dramatic red shift (45 nm shift for compound **9** and 116 nm for **10**) of the charge-transfer absorption band. This observation clearly indicates that the thiophene moiety introduces effective conjugation in donor–acceptor compounds compared with benzenoid moieties.

[†] Phosphonate **4** was prepared in quantitative yield by reacting 1 equiv. of 2-(chloromethyl)thiophene with 1.05 equiv. of triethylphosphite at 140 °C for 3 h.

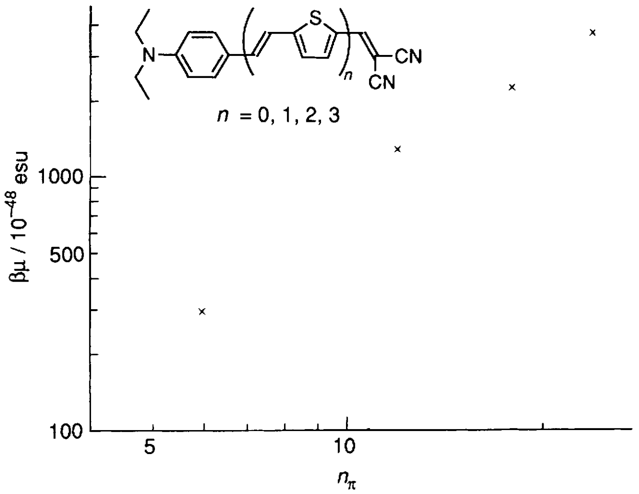


Fig. 1

The second-order nonlinear hyperpolarizability of these compounds (Table 1) were determined by direct current electric-field-induced second-harmonic generation (EFISH) method. All the measurements were performed by using a non-polar solvent (dioxane) and at a fundamental wavelength of 1.907 μm. The second-harmonic measurement is expected to be mostly free of resonance enhancement because it was generated at a wavelength (0.954 μm) that was far removed from the lowest energy electronic transitions of all the molecules studied here. The results from our EFISH experiments are listed in Table 1. While the replacement of one benzene ring in DADVS has marginal effect on its nonlinearity, replacement of both benzene rings in DADVS results in dramatic enhancement in its nonlinearity (βμ for **1** is 1100 × 10^{-48} esu, βμ for **10** is 2600 × 10^{-48} esu). Also, to study the dependence of nonlinearity on molecular length, we have synthesized a series of thiophene-substituted molecules **9**, **13** and **14** with various conjugation lengths. The βμ values measured increase from 1300 × 10^{-48}, 2300 × 10^{-48} and 3800 × 10^{-48} for two-ring, three-ring and four-ring systems, respectively. These results are plotted on a log–log scale in Fig. 1. The significant increase in βμ with length observed for molecules containing more than two rings is a major departure from that observed for benzenoid type molecules. In benzene-type molecules, a pronounced saturation of βμ with length was reported.[14] The nearly straight-line behaviour of βμ against length in the log–log plot of Fig. 1 shows that for thiophene-substituted systems, there is no signficiant saturation at the length scale considered. This result corresponds to a power-law dependence of βμ values on the number of conjugated π-electrons. The best linear fit of the data corresponds to a power law exponent of 1.8.

In conclusion, we have synthesized a series of compounds containing thiophene as a conjugating moiety. Results obtained with these molecules clearly indicate that thiophene substitution has several advantages with respect to benzene, which include enhanced molecular nonlinearity, improved solubility and ease of synthesis.

We gratefully acknowledge Dr Wha Chen and Mr Terry Moran for their contribution to the synthesis of some of the compounds presented in this communication. We are thankful to Dr Robert Mininni for his continuing support and encouragement.

Received, 25th September 1992; Com. 2/05137K

References

1 *Nonlinear Optical Properties of Organic and Polymeric Materials*, ed. D. J. Williams, ACS Symposium series 233, ACS, Washington, DC, 1983.
2 *Materials for Nonlinear Optics: Chemical Perspectives*, ed. S. R. Marder, J. E. Sohn and G. D. Stucky, ACS Symposium series 455, ACS, Washington, DC, 1991.
3 D. J. Williams, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 690.
4 K. D. Singer, J. E. Sohn, L. A. King, H. M. Gordon, H. E. Katz and C. W. Dirk, *J. Opt. Soc. Am. B.*, 1989, **6**, 1339.
5 L. T. Cheng, W. Tam, S. R. Marder, A. E. Stiegman, G. Rikken and C. W. Spangler, *J. Phys. Chem.*, 1991, **95**, 10643.
6 L. T. Cheng, W. Tam, S. H. Stevenson, G. R. Meredith, G. Rikken and S. R. Marder, *J. Phys. Chem.*, 1991, **95**, 10631.
7 A. E. Stiegman, E. Graham, K. J. Perry, L. R. Khundkar, L. T. Chang and J. W. Perry, *J. Am. Chem. Soc.*, 1991, **113**, 7568.
8 G. W. Wheland, *Resonance in Organic Chemistry*, Wiley, New York, 1955, p. 99.
9 G. Mignani, F. Leising, R. Meyrceeix and H. Samson, *Tetrahedron Lett.*, 1990, 4743.
10 A. K. Jen, V. P. Rao, K. Y. Wong, K. Drost and R. M. Mininni, *Mater. Res. Symp. Proc.*, 1992, **247**, 59.
11 V. P. Rao, A. K. Jen, K. Y. Wong, K. Drost and R. M. Mininni, *SPIE Symp. Proc.*, 1992, 1775.
12 K. Y. Wong, A. K. Jen, V. P. Rao, K. Drost and R. M. Mininni, *SPIE Symp. Proc.*, 1992, 1775.
13 L. Y. Chiang, A. F. Garito and D. J. Sandman, *Electrical, Optical and Magnetic Properties of Organic Solid State Materials, Mater. Res. Soc. Symp. Proc.*, 1992, 247.
14 L. T. Cheng, W. Tam, G. R. Meredith, G. Rikken and E. W. Meijer, *SPIE Symp. Proc.*, 1989, **1147**, 61.