Chem. Mater. **1994,** *6,* 2210−2212

Functionalized Fused Thiophenes: A New Class of Thermally Stable and Efficient Second-Order Nonlinear Optical Chromophores

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

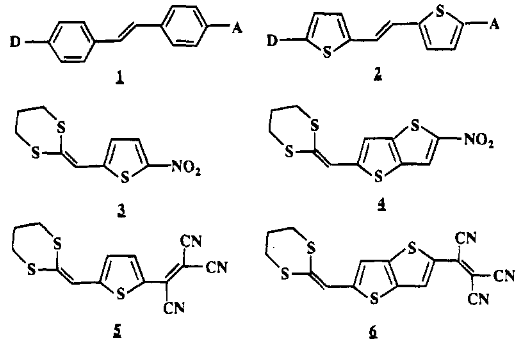
EniChem America Inc.
Research and Development Center
2000 Cornwall Road
Monmouth Junction, New Jersey 08852

Received September 8, 1994

The design and synthesis of new donor−acceptor (D−A) substituted conjugated compounds possessing large molecular second-order nonlinear optical (NLO) coefficients are of current interest, primarily because of their potential use in integrated photonic devices.[2] To realize such applications, these chromophores must possess large nonresonant second-order molecular nonlinearity ($\beta_0\mu$) as well as high thermal stability. While large molecular optical nonlinearities coupled with effective and stable noncentrosymmetric orientation in the macroscopic phase are highly desirable for the performance of such devices, chromophoric stability at high temperatures is absolutely essential to survive the device fabrication steps.[3] With very few exceptions,[4] most of the studies on D−A substituted compounds reported to date have been primarily designed on optimizing the molecular nonlinearity. The real challenge for organic chemists in this field lies in the design and synthesis of NLO compounds which possess multiple properties. In this communication, we address the role of fused-thiophenes (e.g., thieno[3,2-*b*]thiophene) as π-conjugating bridges in the design and synthesis of thermally stable and highly efficient NLO chromophores.

Structure−property relationships that have been established indicate that $\beta_0\mu$ increases with increasing donor and acceptor strengths and with increasing π-conjugation length.[2] Polyenes are often used as π-conjugating units because they provide the most effective pathway for the efficient charge transfer between the donor and acceptor groups.[5] Incorporation of benzene rings into the polyene-based donor−acceptor systems is observed to limit or saturate molecular nonlinearity but enhance thermal stability.[6] The delocalization energy barrier arising from the aromaticity of the benzene ring is believed to be responsible for the reduced or saturated $\beta\mu$ values. To overcome this problem of saturation of molecular nonlinearity, easily delocalizable five-membered heteroaromatic rings are employed in place of benzene rings.[7,8] Our earlier studies clearly demonstrated that the thiophene moiety significantly increases (by a factor of 2) the molecular nonlinear optical properties of donor−acceptor substituted stilbenes (e.g., **1** and **2**, Scheme 1).[8] Although compounds such as **2** offer excellent molecular nonlinearity (e.g., (dialkylamino)tricyanovinyl-substituted **2** possesses a $\beta\mu$ value of 6900×10^{-48} esu at 1.907 μm),[8c] their stability at higher temperatures is somewhat limited by the thermally driven cis−trans isomerization of the olefinic linkage. Furthermore, the cis−trans isomerization of the olefinic linkages results in a local concentration of π-electron density which in turn favors the reaction with electrophiles such as singlet oxygen. To eliminate the thermal instability associated with the olefinic π-bonds, we have designed conjugated systems lacking olefinic bonds (e.g., fused heteroaromatic systems). The longer conjugation length and the lower aromatization energy of fused-heteroaromatics[9] are predicted to enhance the molecular nonlinearity relative to simple aromatic or heteroaromatic conjugating bridges. In this communication, we present the synthesis, linear and nonlinear optical properties, and the thermal behavior of a new class of donor−acceptor compounds employing a fused-thiophene, namely, thieno[3,2-*b*]thiophene, as a conjugating bridge.

Scheme 1



Donor−acceptor-substituted thiophene and fused-thiophene derivatives studied in this work are shown in Scheme 1 (**3**−**6**). The ketene dithioacetal is used as an electron−donor because (a) it can be easily introduced into conjugated systems[10] and (b) it is a more efficient donor compared with the commonly employed dialkylamino group. Conventional, but effective, functional groups such as nitro and tricyanovinyl groups are

---

(1) Dalton, L. R., Lee, C. Y.-C., Jen, A.-K.-Y., Garito, A. F., Eds. Electrical, Optical and Magnetic Properties of Organic Solid State Materials. *Mater. Res. Soc. Symp. Proc.* **1994**, *328*.

(2) Prasad, P. N.; Williams, D. J. *Introduction to Nonlinear Optical Effects in Molecules and Polymers*; John Wiley & Sons: New York, 1991.

(3) Lytel, R.; Lipscomb, G. F. *Mater. Res. Soc. Symp. Proc.* **1992**, *247*, 17.

(4) (a) Moylan, C. R.; Tweig, R. J.; Lee, V. Y.; Swanson, S. A.; Betterton, K. M.; Miller, R. D. *J. Am. Chem. Soc.* **1993**, *115*, 12599. (b) Shi, R. F.; Wu, M. H.; Yamada, S.; Cai, Y. M.; Garito, A. F. *Appl. Phys. Lett.* **1993**, *63*, 1173. (c) Ermer, S.; Leung, D.; Lovejoy, S.; Valley, J.; Stiller, M. In *Org. Thin Films Photonic Applicat. Tech. Digest* **1993**, *17*, 50.

(5) (a) Blanchard-Desce, M.; Ledoux, I.; Lehn, J. M.; Malthete, J.; Zyss, J. *J. Chem. Commun.* **1988**, 736. (b) Meyers, F.; Bredas, J. L.; Zyss, J. *J. Am. Chem. Soc.* **1992**, *114*, 2914. (c) Marder, S. R.; Perry, J. W.; Bourhill, G.; Gorman, C.; Thiemann, B.; Mansour, K. *Science* **1993**, *261*, 186. (d) Huijts, R. A.; Hesselink, G. L. *Chem. Phys. Lett.* **1989**, *156*, 209. (e) Barzoukas, M.; Blanchard-desce, M.; Josse, D.; Lehn, J. M.; Zyss, J. *Chem. Phys.* **1989**, *133*, 323.

(6) (a) Cheng, L. T.; Tam, W.; Marder, S. R.; Stiegman, A. E.; Rikken, G.; Sprangler, C. W. *J. Phys. Chem.* **1991**, *95*, 10631, 10643. (b) Singer, K. D.; Sohn, J. E.; King, L. A.; Gordon, H. M.; Katz, H. E.; Dirk, C. W. *J. Opt. Soc. Am. B.* **1989**, *6*, 1339.

(7) Dirk, C. W.; Katz, H. E.; Schilling, M. L.; King, L. A. *Chem. Mater* **1990**, *2*, 700.

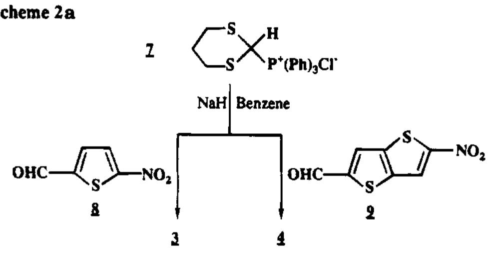
(8) (a) Rao, V. P.; Jen, A. K.-Y.; Wong, K. Y.; Drost, K. J. *Tetrahedron Lett* **1993**, *34*, 1747. (b) Jen, A. K.-Y.; Rao, V. P.; Wong, K. Y.; Drost, K. J. *J. Chem. Soc., Chem. Commun.* **1993**, 90. (c) Rao, V. P.; Jen, A. K.-Y.; Wong, K. Y.; Dorst, K. J. *J. Chem. Soc., Chem. Commun.* **1993**, 1118.

(9) Hess, B. A.; Schaad, L. J. *J. Am. Chem. Soc.* **1973**, *95*, 3907.

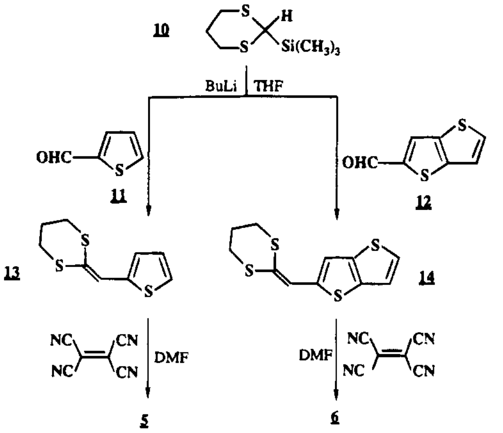
(10) For general synthetic approaches to incorporate ketene dithioacetal group: (a) Carey, F. A.; Court, A. S. *J. Org. Chem.* **1972**, *37*, 1926. (b) Cruse, C. G.; Broekhof, N. L. J. M.; Wijsman, A.; Van der Gen, A. *Tetrahedron Lett.* **1977**, 885.

0897-4756/94/2806-2210$04.50/0

Scheme 2a



Scheme 2b



used as electron acceptors. Different synthetic methodologies were adopted to synthesize the nitro derivatives **3** and **4** (Scheme 2a) and the tricyanovinyl derivatives **5** and **6** (Scheme 2b). Compounds **3** and **4** were prepared by reacting 5-nitrothiophene-2-carboxaldehyde (**8**) and 5-nitrothieno[3,2-*b*]thiophene-2-carboxaldehyde (**9**) with the ylide generated from 1,3-dithian-2-yltriphenylphosphonium chloride (**7**). The tricyanovinyl derivatives **5** and **6**, were prepared by a two-step reaction scheme. The first step involves the synthesis of **13** and **14** by the lithiation of 2-trimethylsilyl-1,3-dithiane (**10**) with BuLi and subsequent reaction with the corresponding aldehydes **11** or **12**. The resulting donor-substituted thiophene and thieno[3,2-*b*]thiophenes **13** and **14** were reacted with tetracyanoethylene (TCNE) to yield the tricyanovinyl derivatives **5** and **6** respectively.

Electronic absorption spectra of both the thiophene and thieno[3,2-*b*]thiophene derivatives are shown in Figure 1. It is clear from Figure 1 that the lowest absorption (ICT, intramolecular charge transfer) band of this class of compounds is very sensitive to the nature of both the π-conjugation and acceptor substitution. The compounds containing the tricyanovinyl group (**5** and **6**) exhibit a substantially red shifted ICT band (~120 nm, frequency: $(14.0-14.5) \times 10^{13}$ s^{-1}) relative to those containing the nitro group (**3** and **4**), indicating the stronger electron-accepting nature of the tricyanovinyl group. The replacement of thiophene conjugating bridge between donor and acceptor substituents with thieno[3,2-*b*]thiophene is observed to result in a red shift of ~15 nm (frequency $(1.3-1.8) \times 10^{13}$ s^{-1}). This red shift in the absorption could be attributed to the extended conjugation present in thieno[3,2-*b*]thiophene.

Experimental molecular nonlinear optical properties of compounds **3**–**6** are presented in Table 1. The $\beta\mu$ values presented in Table 1 were obtained from EFISH studies carried out at the fundamental wavelength of 1.907 μm in dioxane using an experimental setup described earlier.[11] For comparison purposes, these $\beta\mu$ values were reduced to zero-frequency extrapolated values, $\beta_0\mu$. As these molecules are likely to be used as guests in poled polymer films, the $\beta\mu$ values reported here are a relevant figure of merit combining both the nonlinearity of the molecule and the ability of the molecule to couple with a macroscopic poling field. Comparison of the $\beta\mu$ values of compounds **3** and **5** (or **4** and **6**) reveals that the replacement of the nitro group with the tricyanovinyl group causes a significant enhancement (a factor of 4) in the molecular nonlinearity. This observation supports our earlier studies on tricyanovinyl-substituted benzenoid systems and heteroaromatic stilbenes.[8c],[12] Comparison of the $\beta\mu$ values of **3** and **4** (or **5** and **6**) shows that the use of thienothiophene results in a factor of ~2 increase in molecular nonlinearity compared to simple thiophene. This significant enhancement in $\beta\mu$ with a small bathochromic shift (~15 nm) in the absorption observed for substituted thieno[3,2-*b*]thiophenes over simple thiophenes suggests that an excellent tradeoff between $\lambda_{\max}$ and $\beta\mu$ can be achieved with the use of thieno[3,2-*b*]thiophene as a π-conjugating bridge in NLO chromophores. The extended π-conjugation and the lower resonance energy-per-electron of thienothiophene[9]

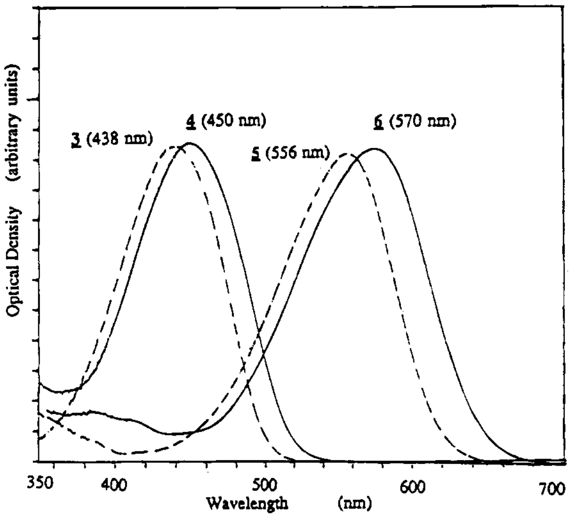


Figure 1. Electronic absorption spectra of donor–acceptor substituted thiophene (**3** and **5**, dashed lines) and thieno[3,2-*b*]thiophene (**4** and **6**, solid lines) derivatives in 1,4-dioxane.

Table 1. First Molecular Electronic Hyperpolarizability and Thermal Stability Data Obtained for Nonlinear Optical Compounds 3–6

compound[a]	$\beta\mu \times 10^{48}$ (esu)[b]	$\beta_0\mu \times 10^{48}$ (esu)[c]	T_d (°C)[d]
3	200	150	252
4	380	280	265
5	940	565	300
6	2200	1287	310

[a] Dioxane was used as solvent for all the measurements. [b] EFISH experiments were done at a fundamental wavelength 1.907 μm. [c] Zero-requency values were extrapolated using the two-level model. [d] Decomposition temperatures were estimated from DSC measurements. Experiments were done in sealed DSC pans to eliminate any problems associated with the evaporation or sublimation of materials.

---

(11) (a) Wong, K. Y.; Jen, A. K.-Y., Rao, V. P. *Phys. Rev. A* **1994**, *49*, 3077. (b) Wong, K. Y.; Jen, A. K.-Y.; Rao, V. P.; Drost, K. J. *J. Chem. Phys.* **1994**, *100*, 6818.

(12) Katz, H. E.; Singer, K. D.; Sohn, J. E.; Dirk, C. W.; King, L. A.; Gordon, H. M. *J. Am. Chem. Soc.* **1987**, *109*, 6561.

compared to that of thiophene may be responsible for the enhanced molecular nonlinearities observed in these systems.

Inherent thermal stability data of these compounds were obtained by differential scanning calorimetry (DSC). All the samples were heated in a sealed DSC pan at the rate of 20 °C/min, and the decomposition temperatures (T_d) were estimated from the intercept of the leading edge of the decomposition exotherm with the base line. The results are shown in Table 1. All four compounds studied here possess high thermal stability (>250 °C). The tricyanovinyl compounds seem to possess more thermal stability than the nitro compounds. The thieno[3,2-*b*]thiophene derivatives seem to be more stable than the thiophene derivatives. As these T_d's vary with the rate at which the sample is heated (for example, heating rate of 10 °C/min resulted in 5--15 °C lower T_d's in all these cases), care must be taken in interpreting the results obtained from this study. For this reason, we have also evaluated their stabilities with isothermal heating process at two different temperatures, 250 and 275 °C, for 30 min. While at 250 °C all four compounds studied here seem to be stable, only compound **6** survived this test at 275 °C. As these compounds will be used as guests in poled polymer films, the survival of these compounds in polymer processing conditions is highly desirable. To understand the thermal stability behavior of this class of compounds in polymeric thin films, compound **6** was dissolved in a poly(amic acid), PIQ-2200 (Hitachi), and cured at 220 °C. Electronic absorption spectra were compared before curing at 100 °C, after curing at 220 and at 275 °C. No change in the intensity of absorption due to the dye was observed at the above temperatures, indicating the high thermal stability of the thienothiophene derivative **6**.

Our studies conclude that an *excellent tradeoff between the optical(linear and nonlinear) and thermal properties can be achieved in donor–acceptor compounds by using thienothiophene as the conjugating bridge*. By having more heteroaromatic rings in the fused-ring systems much higher nonlinearities may be observed, but it is essential to watch the solubility behavior because larger fused-ring aromatic or heteroaromatic systems have poor solubility. Thermal stabilities of these compounds may be increased further by incorporating more thermally stable donor and acceptor substituents.

Acknowledgment. We are grateful to Dr. Robert M. Mininni for his continuing support and encouragement.

Supplementary Material Available: Spectral and analytical data and synthetic procedure for compounds **3–6** (2 pages). Ordering information is given on any current masthead page.