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First Order Hyperpolarizabilities of 2-[2-(*p*-Diethylaminophenyl)vinyl]-furan Derivatives

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Abstract: The first evaluation of the β for 2-[2-(*p*-diethylaminophenyl)vinyl]furan derivatives is reported in comparison with the corresponding thiophene derivative. © 1998 Elsevier Science Ltd. All rights reserved.

Donor-acceptor substituted organic molecules with large second order nonlinear optical (NLO) property have been the subject of considerable research efforts due to their potential applications in the areas such as telecommunications, optical information processing and storage.[2] A large number of such compounds have been examined by experiments and theoretical calculations to establish the structure-property relationships.[2-4] Results of these studies reveal that the molecular hyperpolarizability of the NLO chromophores vary strongly, depending upon the donor-acceptor abilities as well as the nature of the conjugated double bonds.

Recently, thiophene has been used as a conjugating moiety in compounds for nonlinear optics.[3] Since thiophene has lower resonance stabilization energy than benzene, it can provide more effective conjugation between the donor and acceptor and thus enhance the molecular hyperpolarizability. However, most of the data report βμ values rather than β, which makes it difficult to compare their hyperpolarizabilities. In addition, theoretical calculations predict that the thiophene derivatives should have larger β values than the furan analogues despite that the latter has lower aromatic resonance energy and thus might exhibit larger β.[4,5] However, little experimental work has been reported for the furan derivatives. Here, we report the first result of experimentally measured β values of a series of 2-[2-(*p*-diethylaminophenyl)vinyl]furan derivatives with

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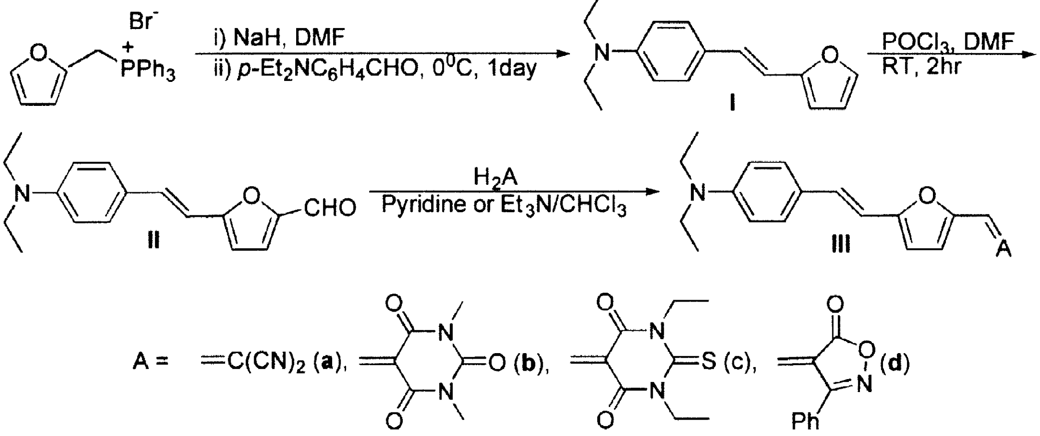
systematic variation of the acceptors.

Table 1 lists the furan derivatives that we have synthesized. Also included is the thiophene analog as standard for comparison. The general methodology for the synthesis of these compounds is shown in Scheme 1.[3] Compound **I** was synthesized in reasonable yield by the Wittig reaction between 2-furyl-triphenylphosphonium ylid and *p*-diethylaminobenzaldehyde.[6] Formylation of **I** with $POCl_3$ and DMF

Scheme 1

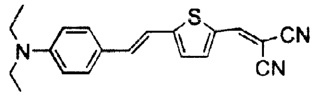
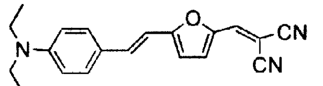
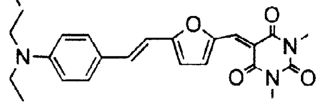
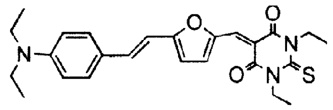
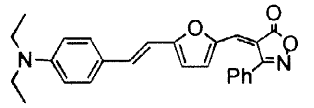


afforded **II** in 77 % yield. The furan derivatives with various acceptors **IIIa-d** were prepared in high yields by reacting **II** with malononitrile, 1,3-dimethylbarbituric acid, 1,3-diethyl-2-thiobarbituric acid, and 3-phenyl-5-isoxazolone, respectively, at room temperature for 1 hr either in pyridine or in $CHCl_3$ in the presence of Et_3N. The spectral data and the results of elemental analysis for all of the products were consistent with the proposed structures.[6] The second-order nonlinear hyperpolarizability of these compounds were determined in DMSO by hyper-Rayleigh scattering as reported previously.[7] The fundamental wavelength was shifted to 1560 nm by using a Raman shifter containing deuterium in order to avoid the absorption of the HRS signal by the chromophores.

The linear and nonlinear optical properties of various chromophores are summarized in Table 1. For a given acceptor, the β value is larger for the furan than that for the thiophene derivative. The result is in contrast to the prediction by the theoretical calculation and earlier result measured by the EFISH method.[4,8] For furan derivatives, the $\beta(0)$ value increases systematically as the acceptor strength is increased. Considering that these compounds have a limited conjugation length, the $\beta(0)$ values ranging from 34 to101 x 10^{-30} esu observed for **IIIa-d** are remarkable. It has been well established that the β value increases until it reaches a maximum and then decreases as the bond length alternation (BLA) decreases from a large positive value toward a negative one.[9] Since the BLA should decrease as the strength of the acceptor increases in the order **a** < **b** < **c** < **d**,[10] the present result can most reasonably be attributed to the gradual decrease in the BLA from a large positive value toward the optimum with the same variation of the acceptor.[2]

In conclusion, we have synthesized a series of compounds containing furan as a conjugating moiety.

Table 1. Optical Properties of 2-[2-(*p*-Diethylaminophenyl)vinyl]furan Derivatives

compound	λ_{max}/nm (ε) in DMSO	$\lambda_{cut\ off}$/nm	$\beta/10^{-30}$ esu at λ=1560 nm	$\beta(0)/10^{-30}$ esu
	554 (31,000)	686	61.9	26.8
 (IIIa)	552 (25,100)	686	76.6	34.0
 (IIIb)	568 (62,900)	692	86.8	34.7
 (IIIc)	630 (42,000)	776	254	75.0
 (IIId)	604 (42,300)	732	300	101

The result of HRS measurements indicates that the β value increases as the conjugating moiety is made less aromatic and as the acceptor strength is increased.

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6. The yield (%), melting point (℃), NMR (500 MHz), IR(KBr, C=O, cm^{-1}), and combustion analysis data for these compounds are as follows. (*E*)-5-[2-(*p*-Diethylaminophenyl)vinyl]-2-(2,2-dicyanovinyl)furan (**IIIa**): yield 78.0; mp 206-208; IR 2213; NMR ($CDCl_3$) δ 7.43 (d, *J* = 9.0, 2H), 7.41 (s, 1H), 7.25 (d, *J* = 16.0, 1H), 6.74 (d, *J* = 16.0, 1H), 6.67 (d, *J* =3.6, 1H), 6.65 (d, *J* = 9.0, 2H), 6.51 (d, *J* = 3.6, 1H), 3.43 (q, *J* = 7.1, 4H), 1.23 (t, *J* = 7.1, 6H). Anal. Calcd for $C_{20}H_{19}N_3O$: C, 75.69; H, 6.03; N,13.24.

Found: C, 75.39; H, 6.31; N, 13.43. (*E*)-5-{5-[2-(*p*-Diethylaminophenyl)vinyl]furan-2-ylidene}-1,3-dimethylhexahydropyrimidine-2,4,6-trione (**IIIb**): yield 59; mp 234-235; IR 1719, 1657, 1596; NMR ($CDCl_3$) δ8.79 (d, *J* = 4.1, 1H), 8.41 (s, 1H), 7.44 (d, *J* = 9.0, 2H), 7.39 (d, *J* = 16, 1H), 6.74 (d, *J* = 16, 2H), 6.68 (d, *J* = 9.0, 2H), 6.65 (d, *J* = 4.1, 1H), 3.43 (q, *J* = 7.1, 4H), 3.43 (s, 3H), 3.42 (s, 3H), 1.23 (t, *J* = 7.1, 6H). Anal. Calcd for $C_{23}H_{25}N_3O_4$: C, 67.78; H, 6.19; N, 10.32. Found: C, 67.65; H, 6.21; N, 10.28. (*E*)-5-{5-[2-(*p*-Diethylaminophenyl)vinyl]furan-2-ylidene}-1,3-diethyl-2-thioxohexahydro-pyrimidine-4,6-dione (**IIIc**): yield 83; mp 180-181; IR 1656, 1593; NMR ($CDCl_3$) δ8.88 (d, *J* = 3.6, 1H), 8.39 (s, 1H), 7.44 (d, *J* = 9.0, 2H), 7.42 (d, *J* = 16, 1H), 6.73 (d, *J* = 16, 1H), 6.69 (d, *J* = 9.0, 1H), 6.68 (d, *J* = 3.6, 1H), 4.62 (q, *J* = 6.9, 4H), 3.44 (q, *J* = 7.1, 4H), 1.32 (t, *J* = 6.9, 6H), 1.22 (t, *J* = 7.1, 6H). Anal. Calcd for $C_{25}H_{29}N_3O_3S$: C, 66.46; H, 6.47; N, 9.31; S, 7.10. Found: C, 66.55; H, 6.81; N, 9.57; S, 7.04. (*E*)-4-{5-[2-(*p*-Diethylaminophenyl)vinyl]furan-2-ylidene}-3-phenyl-5-isoxazolone (**IIId**): yield 79; mp 140-142; IR(KBr)1733, 1576; NMR ($CDCl_3$) δ7.65 (dd, *J* = 6.0, 3.6, 2H), 7.60-7.57 (m, 3H), 7.48 (s, 1H), 7.41 (d, *J* = 8.9, 2H), 7.33 (d, *J* = 16, 1H), 6.71 (d, *J* = 16, 1H), 6.67 (d, *J* = 8.9, 2H), 6.68-6.65 (m, 2H), 3.43 (q, *J* = 7.1, 4H), δ1.23(t, *J* = 7.1, 6H). Anal. Calcd for $C_{26}H_{24}N_2O_3$: C, 75.71; H, 5.86; , 6.79. Found: C, 75.64; H, 5.91; N, 6.73.

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