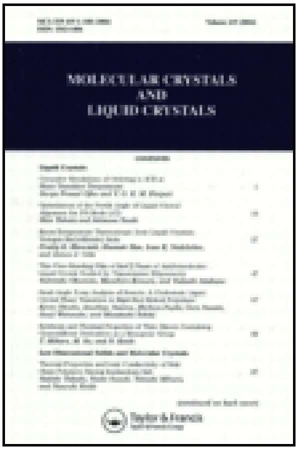

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First Hyperpolarizabilities of Stilbenes Derivatives

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Stilbene and heteroaromatic stilbene derivatives have been synthesized and their β values were determined. The result of HRS measurements indicates that the β(0) values are larger for the heteroaromatic stilbenes than the stilbenes. For stilbene derivatives, the β(0) increased as the acceptor strength was increased.

Key words: Stilbene, Nonlinear optics, Hyperpolarizability, Dipole

INTRODUCTION

Organic nonlinear optical (NLO) materials have been the subject of considerable research because of their potential applications in the areas such as telecommunications, optical information processing and storage.[1] One of the most well known dipolar NLO molecule is donor-acceptor substituted stilbene. Various stilbenes and heteroaromatic stilbene derivatives have been examined by experiments and theoretical calculations to establish the structure-property relationships.[1-4] Very recently, we reported that the donor- acceptor substituted styrylfuran derivatives also exhibit large molecular hyperpolarizabilities, which increase as the acceptor strength is increased.[5] However, no attempt has been made to assess the effect of the substituent on the first-order hyperpolarizability of the stilbene by expanding the range of the acceptor strength beyond the *p*-nitro group. Here, we report the first result of experimentally measured β values of a series of stilbene derivatives with a wide variety of donors and acceptors.

EXPERIMENTAL

The stilbene and heteroaromatic stilbene derivatives were synthesized by the literature procedure.[4] The yield (%), melting point (°C), IR (KBr, cm^{-1}), NMR (300 MHz, $CDCl_3$), and combustion analysis data for these compounds are as follows.

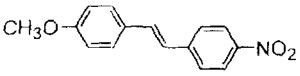
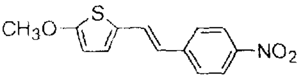
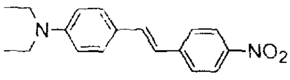
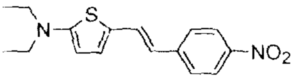
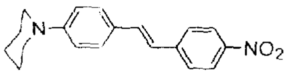
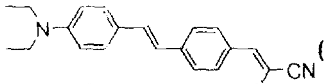
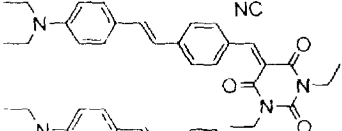
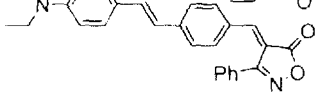
4-[(*E*)-*p*-diethylaminostyryl]benylidenemalonitrile (Id): Yield, 53; mp 158; IR: 2222 (CN); NMR δ 7.86 (d, *J* = 8.7, 2H), 7.65 (s, 1H), 7.56 (d, *J* = 8.7, 2H), 7.42 (d, *J* = 8.7, 2H), 7.24 (d, *J* = 15.5, 1H), 6.88 (d, *J* = 15.5, 1H), 6.67 (d, *J* = 8.7, 2H), 3.41 (q, *J* = 7.2, 4H), 1.20 (t, *J* = 7.2, 6H). Anal Calcd for $C_{22}H_{21}N_3$: C, 80.70; H, 6.47; N, 12.83. Found: C, 80.56; H, 6.31; N, 12.82. **5-{4-[(*E*)-*p*-diethylaminostyryl]benylidene}-1,3-diethylhexahydropyrimidine-2,4,6-trione (Ie)**: Yield, 21; mp 214; IR: 1723, 1661 (C=O); NMR: δ 7.64 (d, *J* = 8.4, 2H), 7.49 (d, *J* = 8.4, 2H), 7.45 (s, 1H), 7.43 (d, *J* = 9.0, 2H), 7.17 (d, *J* = 16.2, 1H), 6.88 (d, *J* = 16.2, 1H), 6.67 (d, *J* = 9.0, 2H), 3.39 (q, *J* = 7.2, 8H), 1.20 (t, *J* = 7.2, 12H). Anal Calcd for $C_{27}H_{31}N_3O_3$: C, 72.78; H, 7.01; N, 9.43. Found: C, 72.65; H, 6.83; N, 9.41. **4-{4-[(*E*)-*p*-diethylaminostyryl]benylidene}-3-phenyl-4*H*-isoxazol-5-one (If)**: Yield, 31; mp 155-158; IR: 1739 (C=O); NMR: δ8.35 (d, *J* = 8.7, 2H), 7.57 (q, 8H), 7.43 (d, J = 8.7, 2H), 7.26 (d, J = 16.2, 1H), 6.91 (d, *J* = 16.2, 1H), 6.67 (d, *J* = 8.7, 2H), 3.41 (q, *J* = 14.1, 4H), 1.20 (t, *J* = 14.1, 6H). Anal Calcd for $C_{28}H_{26}N_2O_2$: C, 79.59; H, 6.20; N, 6.63. Found: C, 79.40; H, 6.35; N, 6.52. **5-[(*E*)-*p*-nitrostyryl]-2-methoxythiophene (IIa)**: Yield, 24; mp168; IR: 1542, 1335 (NO_2); NMR: δ 8.05 (d, *J* = 8.7, 2H), 7.37 (d, *J* = 8.7, 2H), 7.10 (d, *J* = 14.1, 1H), 6.68 (d, *J* = 3.9, 2H), 6.50 (d, *J* = 14.1, 1H), 6.00 (d, *J* = 3.9, 2H), 3.80 (s, 3H). Anal Calcd for $C_{13}H_{11}NO_3S$: C, 59.77; H, 4.25; N, 5.36; S, 12.25. Found: C, 60.06; H, 4.55; N: 5.05; S, 12.00. **5-[(*E*)-*p*-nitrostyryl]-2-diethylaminothiophene (IIb)**: Yield, 46; mp 126; IR: 1499, 1320 (NO_2); NMR: δ 8.13 (d, *J* = 8.9, 2H), 7.43 (d, *J* = 8.9, 1H), 7.27 (d, *J* = 16, 1H), 6.87 (d, *J* = 4.2, 2H), 6.43 (d, *J* = 16, 1H), 5.75 (d, *J* = 4.2, 1H), 3.37 (q, *J* = 6.9, 4H), 1.24 (t, *J* = 6.9, 6H). Anal Calcd for $C_{16}H_{18}N_2O_2S$: C, 63.55; H, 6.00; N, 9.26; S, 10.60. Found: C, 63.48; H, 6.33; N, 9.06; S, 10.75.

RESULTS AND DISCUSSION

Table 1 lists the stilbene derivatives that we have synthesized. Also included are the thiophene analogs for comparison. Compounds **1a-1c** were synthesized by the literature method.[4] Compounds **1d-f** and **IIa-b** were prepared by the same methodology for the synthesis of styrylfuran derivatives.[5] The molecular hyperpolarizabilities of these compounds were determined in $CHCl_3$ by hyper-Rayleigh scattering method as reported previously.[6] The fundamental wavelength was shifted to 1360 nm by using an OPO laser in order to avoid the absorption of the HRS signal by the chromophores. The β(0) values were calculated by the use of two-level model.[7]

The linear and nonlinear optical properties of the various stilbene derivatives are summarized in Table 1. For a given donor- acceptor pair, the β(0) value is larger for the styrylthiophene (**II**) than that for the

Table 1. Optical Properties of Donor-Acceptor Substituted Stilbene Derivatives in $CHCl_3$

compound		$\lambda_{max}{}^{a}$	$\beta^{b,c}$	$\beta(0)^{b}$
	**(Ia)**	378	65.9	42.0
	**(IIa)**	498	164	66.4
	**(Ib)**	430	74.5	40.2
	**(IIb)**	476	173	77.4
	**(Ic)**	424	96.6	53.3
	**(Id)**	512	111	41.3
	**(Ie)**	538	547	177
	**(If)**	532	478	157

[a] nm, [b] 10^{-30}esu, [c] meausred at 1360 nm.

stilbene derivatives (**I**). The result is consistent with the prediction by the theoretical calculation and earlier result measured by the EFISH method.[3,4] For both **Ia-c** and **IIa-b**, theβ(0) value increases as the donor strength is increased. Comparison of the β(0) values for **Ib** and **Id-f** reveals that the value increases systematically in the order **Ib** < **Id** < **Ie** until it reaches a maximum value of 177×10^{-30} esu and then decreases slightly for **If**. Noteworthy is the 4-fold enhancement of the β(0) value by the variation of the acceptor.

The slightly larger β(0) value for **Id** than that for **Ib** appears to be due to the increased conjugation length. On the other hand, the change in the β(0) values for **Id-f** can be attributed to the increased acceptor strength. It is well established that the β(0) value increases until it reaches a maximum value and then decreases as the bond length alternation (BLA) decreases from a large positive value toward a negative one.[8] Since the BLA should decrease as the acceptor strength is increased in the order **d** < **e** < **f**, the β(0) value should increase until the BLA reaches at the optimum value. A further increase in the acceptor strength would decrease the BLA smaller than the optimum value, which would in turn decrease the β(0) value. The present result is consistent with this prediction.

In conclusion, we have synthesized a series of stilbene derivatives with various donor-acceptor pairs. The result of HRS measurements indicates that the β(0) value increases as the conjugating moiety is made less aromatic and as the acceptor strength is increased. This result demonstrates that changing the substituent can significantly increase the first-order hyperpolarizabilities of the stilbene derivatives.

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