First Hyperpolarizabilities of Heteroaromatic Stilbene Derivatives

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2-(p-Diethylaminostyryl)pyrrole (**I**) and 2-[5-diethylaminothienyl]vinyl]pyrrole (**II**) derivatives with systematic variation of the acceptors have been synthesized and their first hyperpolarizabilities were measured. The β values increased systematically as the aromatic resonance energy decreased. Moreover, the value of β for the former increased gradually as the acceptor strength increased. The opposite trend observed in the latter series of compounds has been attributed to the distorted structure caused by the steric hindrance between the N-methyl group and the acceptor moiety.

Key words: hyperpolarizability, stilbene derivatives

INTRODUCTION

There is on-going research interest in the development of new types of nonlinear optical (NLO) chromophores due to their potential applications in new photonic technologies such as optical data processing [1]. Much efforts have been focused to establish the structure-property relationship of the donor-acceptor substituted π-conjugated molecules [2-7]. The results of these studies reveal that the molecular hyperpolarizabilities of the NLO chromophores vary strongly, depending upon the donor-acceptor abilities as well as the nature of the conjugated double bonds. It is well established that the use of the thiophene or furan as the conjugating moiety in the stilbene derivatives increases the β value significantly [3-5]. The larger β values for the heteroaromatic stilbene derivatives have been attributed to the more easily delocalizable π-orbitals in the five-membered heteroaromatic rings than that in benzene. In view of the fact that the aromatic resonance energy of pyrrole is in between those for the thiophene and furan, it seems interesting to compare the β values for the pyrrole derivatives with other heteroaromatic stilbene derivatives [8]. A theoretical study indicates that β values of the latter increases as the five-membered heteroaromatic rings is changed in the order thiophene < furan < pyrrole [4]. Recently we reported that the $\beta(0)$ values of styrylfuran derivatives are slightly larger than that of the thiophene analogue and increase as the acceptor strength was increased [5]. However, no experimental result has been reported for the pyrrole derivatives. Here, we report the first result of experimentally measured β values of a series of 2-(p-diethylaminostyryl) pyrrole and 2-[5-diethylaminothienyl] vinyl]pyrrole derivatives with systematic variation of the acceptors (Chart 1).
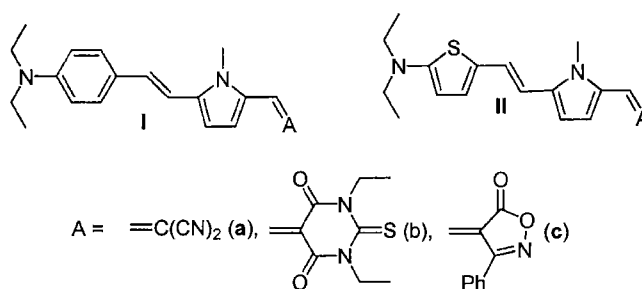

Chart 1.

EXPERIMENTAL

Synthesis. N,N-(p-Diethylaminostyryl)-N-methylpyrrole was synthesized by refluxing the solution of N,N-diethylaminobenzyltriphenylphosphonium ylid with N-methylpyrrole -2-carboxaldehyde in DMF for 1hr as reported previously [5]. The pyrrole derivatives with various acceptors **Ia-c** were prepared by formylation of with POCl₃ in DMF, followed by the condensation of the N,N-(p-diethylaminostyryl)-N-methylpyrrole-2-carboxaldehyde with malononitrile, 1,3-diethyl-2-thiobarbituric acid, and 3-phenyl-5-isoxazolone, respectively, in EtOH in the presence of piperidine. The thiophene derivatives **IIb-c** were prepared by similar procedure. The spectral data and the results of elemental analysis for all of the products were consistent with the proposed structures. The yield (%), melting point (°C), NMR (CDCl₃ , 200 MHz), IR (KBr, cm⁻¹), and combustion analysis data for these compounds are as follows.

5-[2-(E)-p-Diethylaminostyryl]-N-methylpyrrol-2-ylmethylidenemalononitrile (Ia). yield 96.0; mp 244-245; IR 2208 (CN); NMR δ 7.74 (d, J = 5.1, 1 H), 7.38 (d, J = 9.0, 2 H), 7.33 (s, 1 H), 7.14 (d, J = 15.4, 1 H), 6.70 (m, 4 H), 3.67 (s, 3H), 3.40 (q, J = 7.2, 4 H), 1.18 (t, J = 7.2, 6 H). Anal. Calcd for $C_{21}H_{22}N_4$: C, 76.33; H, 6.71; N, 16.96. Found: C, 75.69; H, 6.48; N, 16.70.

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5-{5-[(E)-p-Diethylaminostyryl]-N-methylpyrrol-2-ylmeth-ylidene}-1,3-diethyl-2-thioxodihydropyrimidine-4,6-dione (Ib). yield 71; mp 240-242; IR 1637,1593 (C = O); NMR δ 8.84 (d, J = 5.0, 1 H), 8.27 (s, 1 H), 7.42 (d, J = 9.0, 2 H), 7.25 (d, J = 15.7, 1 H), 6.84 (d, J = 5.0, 1 H), 6.80 (d, J = 15.7, 1 H), 6.64 (d, J = 8.7, 2 H), 4.60 (m, 4 H), 3.85 (s, 3 H), 3.41 (q, J = 7.2, 4 H), 1.35 (m, 6 H), 1.22 (t, J = 7.2, 6 H). Anal. Calcd for $C_{26}H_{32}N_4O_2S$: C, 67.21; H, 6.94; N, 12.06, S, 6.90. Found: C, 67.06; H, 7.23; N, 12.11; S, 7.15.

4-{5-[(E)-p-Diethylaminostyryl]-N-methylpyrrol-2-ylmeth-ylidene}-3-phenyl-5-isoxazolone (Ic). yield 20; mp 239-240; IR 1577 (C = O); NMR δ 8.88 (d, J = 4.0, 1 H), 7.60 (m, 5 H), 7.41 (d, J = 8.9, 2 H), 7.28 (s, 1 H), 7.24 (d, J = 15.9, 1 H), 6.82 (d, J = 4.8, 1 H), 6.73 (d, J = 15.9, 1 H), 6.60 (d, J = 8.9, 2 H), 3.62 (s, 3 H), 3.41 (q, J = 7.2, 4 H), 1.20 (t, J = 7.2, 6 H). Anal. Calcd for $C_{27}H_{27}N_3O_2$: C, 76.21; H, 6.40; N, 9.87. Found: C, 76.12; H, 6.38; N, 9.85.

5-{2-[(E)-5-Diethylaminothiophene-2-yl]vinyl}-N-methylpyrrol-2-ylmethylidene}-1,3-diethyl-2-thioxodihydropyrimidine-4,6-dione (IIb). yield 69; mp 279-281; IR 1634, 1575 (C = O); NMR δ 8.81 (d, J = 5.0, 1 H), 8.22 (s, 1 H), 7.28 (d, J = 14.8, 1 H), 6.97 (d, J = 5.0, 1 H), 6.75 (d, J = 5.3, 1 H), 6.25 (d, J = 14.8, 1 H), 5.80 (d, J = 5.3, 1 H), 4.62 (q, J = 7.1, 4 H), 3.76 (s, 3 H), 3.40 (q, J = 7.1, 4 H), 1.30 (m, 12 H). Anal. Calcd for $C_{26}H_{32}N_4O_2S$: C, 67.21; H, 6.94; N, 12.06, S, 6.90. Found: C, 67.06; H, 7.23; N, 12.11; S, 7.15.
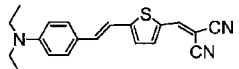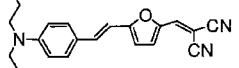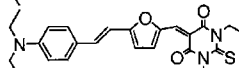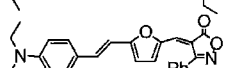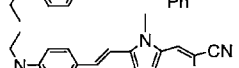
5-{2-[(E)-5-Diethylaminothiophene-2-yl]vinyl}-N-methylpyrrol-2-ylmethylidene} -3-phenyl-5-isoxazolone (IIc). yield 20; mp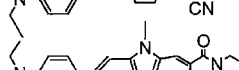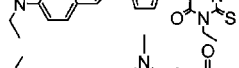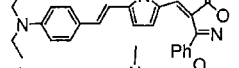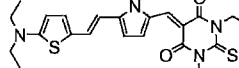 239-240; IR 1577 (C = O); NMR δ 8.82 (d, J = 5.3, 1 H), 7.58 (m, 5 H), 7.23 (d, J = 14.9, 1 H), 7.20 (s, 1 H), 6.93 (d, J = 5.3, 1 H), 6.72 (d, J = 5.4, 1 H), 6.18 (d, J = 14.9, 1 H), 5.79 (d, J = 5.4, 1 H), 3.52 (s, 3 H), 3.38 (q, J = 7.2, 4 H), 1.20 (t, J = 7.2, 6 H). Anal. Calcd for $C_{27}H_{27}N_3O_2$: C, 76.21; H, 6.40; N, 9.87. Found: C, 76.12; H, 6.38; N, 9.85.

Measurement of β. The β values of the heteroaromatic stilbene derivatives were measured at 1560 nm by Hyper-Rayleigh Scattering (HRS) method [9]. To avoid complications due to the multi-photon excitation, the excitation wavelength was shifted to 1560 nm with the OPO laser (Continuum Surelite OPO, 5 ns pulses), which was pumped by 355 nm third harmonic of the Nd:YAG laser (Continuum SL-II-10, Q-switched, 10 Hz).

RESULTS AND DISCUSSION

Table 1 lists the optical properties of the pyrrole derivatives (**Ia-c** and **IIb,c**) that we have synthesized. Also included are the thiophene and furan analogs for comparison. The general methodology for the synthesis of these compounds is shown in Scheme 1 [3]. *N,N-(p*-Diethylaminostyryl)-*N*-methylpyrrole was obtained in 74% yield by refluxing the solution of

Table 1. Optical Properties of Heteroaromatic stilbene Derivatives[a].

Entry	Compound	λ_{max}/ nm(ε)	$\lambda_{cut\,off}$/ nm	β / 10^{-30} esu at λ = 1560 nm	$\beta(0)$ / 10^{-30} esu
1		554 (31,000)	686	61.9	26.8[b]
2		552 (25,100)	686	76.6	34.0[b]
3		630 (42,000)	776	254	75.0[b]
4		604 (42,300)	732	300	101[b]
5	(Ia)	520 (13,200)	657	98.0	48.4
6	(Ib)	588 (10,000)	675	122	45.2
7	(Ic)	570 (42,300)	673	72.0	29.1
8	(IIb)	647(105,000)	720	176	45.8
9	(IIc)	628 (80,000)	714	216	66.1

[a]Determined in DMSO.   [b]Reference [5].
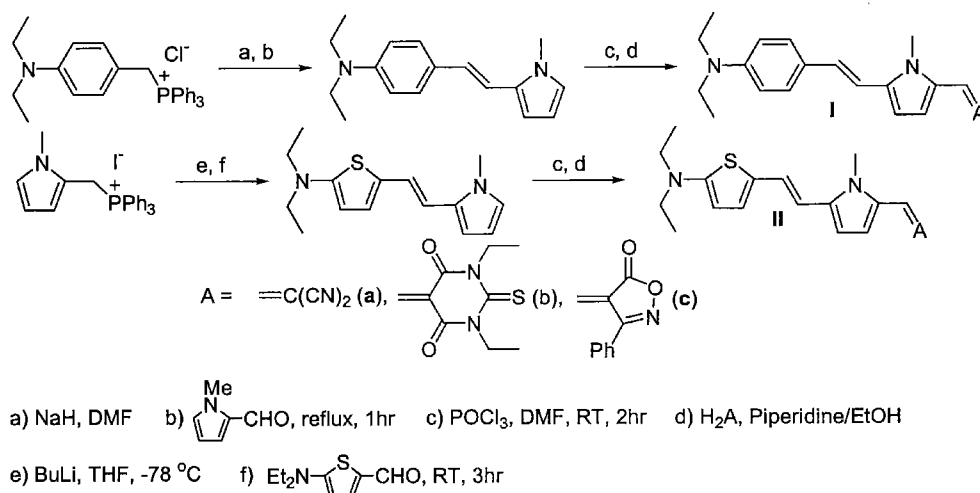
Scheme 1.

N,N-diethylaminobenzyltriphenylphosphinium ylid with *N*-methylpyrrole-2-carboxaldehyde in DMF for 1hr. The pyrrole derivatives with various acceptors **Ia-c** were prepared in modest to excellent yields by the formylation of the latter, followed by the condensation of the *N,N*-(*p*-diethylaminostyryl) -*N*-methylpyrrole-2-carboxaldehyde with appropriate acceptors. The thiophene derivatives **IIb-c** were obtained in nearly the same yields by similar procedure. For both syntheses the yields were always lower when 3-phenyl-5-isoxazolone was used as the acceptor.

The second-order nonlinear hyperpolarizability of these compounds were determined in DMSO by hyper-Rayleigh scattering at 1560 nm as reported previously [9]. All of the chromophores showed $\lambda_{cut\ off} < 780$ nm and emitted no fluorescence at 780 nm when excited at λ_{max}. This result indicates the reliability of the HRS measurement as it is neither underestimated by the absorption bands nor over-estimated by the two-photon induced fluorescence.

The linear and nonlinear optical properties of various chromophores are summarized in Table 1. When the acceptor is dicyanovinyl, the $\beta(0)$ value increases as the five-membered heteroaromatic ring is changed in the order thiophene < furan < pyrrole (entries 1, 2, 5). Similar increase in $\beta(0)$ is observed for the same change in the aromatic moiety from phenyl (**Ib** and **Ic**) to thiophene (**IIb** and **IIc**) (entries 6 & 8, 7 & 9). The results are consistent with the theoretical calculation [7]. Moreover, the $\beta(0)$ value increases with the acceptor strength from **IIb** to **IIc** (entries 8 & 9). Similar results were observed for stilbene derivatives as well as for the furan and thiophene analogues [5]. These results can readily be explained with the gradual decrease in the bond length alternation (BLA). It is well established that the β value increases until it reaches a maximum and then decreases as the BLA decreases from a large positive value toward a negative one [6]. Since the BLA should decrease as the strength of the acceptor increases in

the order **a** < **b** < **c** [10] and as the aromatic resonance energy decreases, the observed increase in $\beta(0)$ value with a decreased aromatic resonance energy and a stronger acceptor 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 chromophore structure. In contrast, when thiobabituric acid is used as the acceptor the $\beta(0)$ of the *N*-methylpyrrole derivative is smaller than the furan derivative (entries 3 & 6). Similarly, the $\beta(0)$ of 2-(*N,N*-diethylaminostyryl) pyrrole derivatives **Ia-c** decreases gradually as the acceptor strength is increased (entries 5-7). The results are exactly opposite to what we have just discussed. The dichotomy in the $\beta(0)$ value may be attributed to the distorted structure of the chromophores due to the steric effect. When the acceptor moiety is rather small, the structures of the chromophores are expected to be nearly planar. However, the pyrrole derivatives (**Ia-c**) with bigger acceptor could be significantly distorted from planarity due to the steric hindrance between the *N*-methyl group and the acceptor groups. Furthermore, the distortion would become more important as the steric bulkiness of the acceptor increases. This would interrupt the conjugation between the donor and acceptor to decrease the first hyperpolarizability, as observed.

In conclusion, we have synthesized a series of compounds containing pyrrole as a conjugating moiety. The result of HRS measurements indicates that the $\beta(0)$ values increases as the conjugating moiety is made less aromatic and as the acceptor strength is increased. Opposite trend is observed in the pyrrole derivatives with bulky acceptors probably because of the steric effect.

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