First Hyperpolarizabilities of Nonlinear Optical Compounds: Susceptibility in Donor-Acceptor Stilbene Analogs

Gyoosoon Park, Woo Sik Jung,[†] and Choon Sup Ra[‡,*]

Department of Chemistry, Kookmin University, Seoul 136-702, Korea
[†]School of Chemical Engineering and Technology, Yeungnam University, Gyongsan 712-749, Korea
[‡]Department of Chemistry and Institute of Natural Science, Yeungnam University, Gyongsan 712-749, Korea

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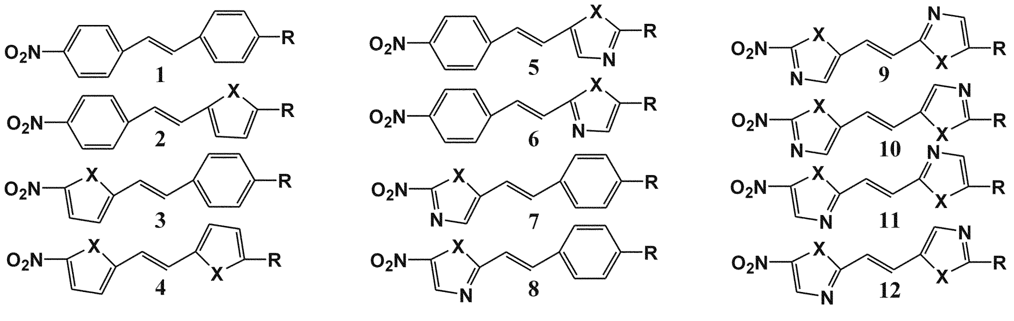
The nonlinear optical (NLO) responses induced in various materials are of great interest in recent years because of the potential applications in photonic technologies such as optical communications, computing and data storage, and image processing.[1-5] The design and synthesis of optimized molecules is the key step in this area of research. Recent efforts have been focused to develop organic molecules with large molecular nonlinear optical (NLO) response (β, first hyperpolarizability), improved optical transparency, and good thermal stability. Most investigated chromophores for NLO applications are conjugated bridges such as substituted polyenes and polyynes endcapped with strong donor and acceptor groups. Incorporation of aromatic rings into the push-pull polyenes like substituted stilbenes enhances thermal stability, but decrease molecular hyperpolarizability.[6] Recent studies have shown that replacement of the aromatic rings with more easily delocalizable 5-membered heteroaromatics such as thiophene, furan and pyrrole results in an enhanced molecular hyperpolarizability.[7] Theoretical studies of several 5-membered heteroaromatic donor-acceptor stilbene analogs have shown that heteroaromatics enhance values by several factors: i) the electron density of the ring systems,[8] ii) the electron poor and rich nature of the ring systems,[8,9] iii) the relative orientation of the heteroaromatic ring.[10] Though these results may explain several aspects of the molecular enhancement in those NLO chromophores, the comprehensive account on the quantitative structure-property relationships that can be readily served as a guideline in designing optimal NLO chromophores is still lacking. In this work, we studied the first hyperpolarizabilities of various heteroaromatic as well as aromatic ring analogs of donor-acceptor stilbenes **1-12** (as shown in Figure 1) by the *ab initio* method. The effects by modifying the conjugated bridges and tuning the donor/acceptor groups of the conjugated bridges on the first hyperpolalizabilties were investigated.

Computation method. All molecules fully optimized at Hartree-Fock level using the 6-31G basis set in the *Gaussian* 98 program[11] show almost planar structures. The tensor components of the static first hyperpolarizabilities (β) were analytically calculated by using the coupled perturbed Hartree-Fock (CPHF) method. The intrinsic hyperpolarizability $\|\beta\|$ is given by magnitude of the vector component of the hyperpolarizability (β); $\|\beta\| = ({}_x{}^2+{}_y{}^2+{}_z{}^2)^{1/2}$, where ${}_x$, ${}_y$ and ${}_z$ are the vector components of the hyperpolarizability tensor in the direction of the x, y and z molecular axis, respectively. The calculated values were converted into electrostatic units (1 a.u. = 8.6398 × 10^{-33} esu). The values of the first hyperpolarizabilities (β) and susceptibility (ρ) are summarized in Table 1.

Results and Discussion

Calculations are made on various structures shown in Figure 1, where one end of the conjugated bridge has a nitro group and the other end is substituted with a variety of



(R = H, Me, Oh, OMe, NH_2, NMe_2; X = O, S)

Figure 1. Aromatic and heteroaromatic stilbene analogs.

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[*] Corresponding Author. e-mail: csra@yu.ac.kr

Table 1. The calculated values[a]

nX (X=O,S)	R=H (0.00)[c]	R=Me (-0.33)[c]	R=OH (-0.55)[c]	R=OMe (-0.80)[c]	R=NH_2 (-1.19)[c]	R=NMe_2 (-1.73)[c]	ρ^b
1	21.8	27.7	31.4	35.5	51.6	63.1	-24.93
2O	29.1	37.0	40.6	47.0	63.5	78.3	-29.28
3O	25.1	31.5	34.8	39.4	55.4	68.0	-25.72
4O	29.9	38.3	42.5	49.4	65.0	81.9	-30.62
2S	21.0	26.6	28.9	35.3	50.9	66.7	-27.41
3S	27.8	35.4	38.8	43.6	65.0	80.6	-31.77
4S	27.3	34.8	38.7	46.8	66.8	90.2	-37.35
5O	19.5	24.3	24.8	28.7	38.6	50.8	-18.26
6O	16.2	20.9	22.6	26.0	38.3	47.0	-18.57
5S	16.8	21.5	24.0	27.9	39.1	52.7	-21.09
6S	13.9	18.6	21.5	25.1	39.6	52.7	-23.24
7O	24.3	30.7	34.0	38.6	54.2	67.1	-25.58
8O	24.8	31.7	35.2	40.0	56.0	70.2	-26.99
7S	24.4	31.6	34.9	39.9	58.4	72.8	-29.02
8S	33.0	42.1	46.0	52.5	73.4	92.2	-35.16
9O	17.0	22.6	24.7	28.5	42.3	54.8	-22.44
10O	19.1	24.6	25.9	30.2	40.9	56.3	-21.49
11O	17.7	23.8	26.0	30.3	45.2	60.0	-25.00
12O	19.6	25.4	26.6	31.2	42.2	58.6	-22.48
9S	16.7	21.9	24.6	28.4	44.2	60.4	-25.93
10S	15.2	19.5	21.2	24.8	35.8	51.3	-21.02
11S	21.7	28.7	31.9	37.1	57.8	80.2	-34.59
12S	23.6	28.6	31.5	39.4	54.6	76.7	-31.50

[a]Unit of β is 10^{-30} esu. [b]Avarage slope of β against σ^+. [c]See ref. 13.

substituents (*i.e.*, R=H, Me, OH, OMe, NH_2, NMe_2). There are 138 chromophores, which are categorized into three classes (A, B, and C). Class A stands for stilbene series (**1**). Class B is for stilbene analogs with furan or thiophene (**2-4**). Class C is for oxazole or thiazole analogs of stilbene (**5-12**). Here the stilbene series **1** was chosen as the representative system for comparing β values with other classes.

Dependence of on the substituents. The nature of the π-conjugation in NLO molecules is altered by the electron-donating/accepting ability of the substituents located at the ends of π-conjugated bridges and thereby the charge transfer within the π-conjugating pathway and the molecular nonlinearity would be affected. In all chromophores investigated, values increase with the electron-donating ability by the order of $NMe_2 > NH_2 >$ OMe > OH > Me > H without an exception.[12] It shows a good linear correlation between β and substituent constants (σ_{gas}^+) as reported in literature before.[12,14]

Heteroaromatic effect (Class B). Within the same substituted pattern at the ends of the aromatic/heteroaromatic rings, the magnitude of the value increase depends strongly on both the nature of conjugated bridges and its

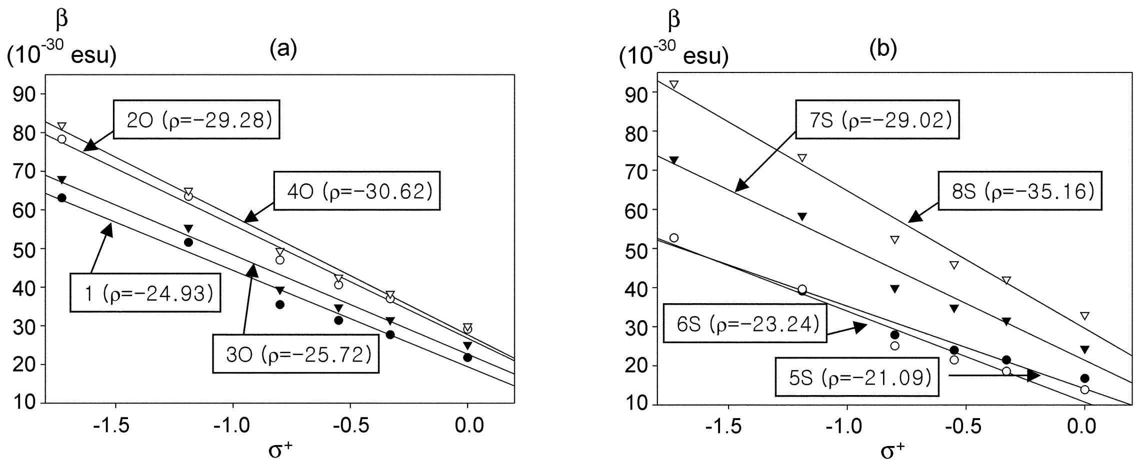
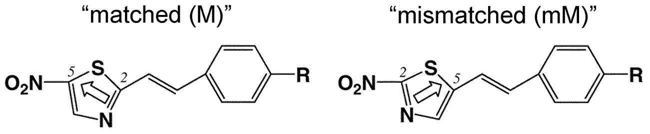


Figure 2. Plot of β against substituent constants (σ^+).



8S ρ = 35.16 **7S** ρ = 29.02

Figure 3. Matched and mismatched pattern in **7S**/**8S**.

position. While the replacement of the benzene ring on the donor end with 5-membered heteroaromatic rings with one heteroatom results in higher values (**2~4** > **1**), the substitution on the acceptor end with heteroaromatics lowers the activity (**2** > **3**). The calculated reaches the maximum when the systems have two heteroaromatic rings with one heteroatom at both the donor and acceptor end (**4** > **2** > **3**), and this tendency is clearly manifested in the r values as shown in Table 1 and Figure 2a (the r value: for **4O**; 30.62, **2O**; 29.28, **3O**; 25.72).

Effect of the substituting pattern (Class C). The tendency of favoring a 1,3-heteroaromatics in the acceptor end to obtain a higher value is observed (**7**, **8** > **5**, **6**). The substitution pattern is also an another important factor to control the activity. For **7S** *vs*. **8S**, the positioning of nitro group at 5-position of 1,3-thiazole ring rather than 2-position shows higher value for both of β and ρ (ρ value: **8S**(35.16) > **7S**(29.02), see Figure 2b). Similar trend is also shown in oxazole system (ρ value: **8O**(26.99) > **7O**(25.58)). These results can be explained in terms of 'matched' and 'mismatched' property from our previous analysis.[15] The values reaches a maximum when the direction of the dipole moment of the 1,3-heteroaromatic unit is matched with the direction from donor to acceptor in chromophores (see Figure 3). For chromophores having two heteroaromatic rings (**9-12**), the substituting pattern notably affects β values. In series of molecules with the same donating pattern, compounds with the nitrothiazole ring at the 5-position has a higher value than those at the 2-position (**11** > **9**; **12** > **10**). Also these trends are clearly notable in their r values (**11O** (25.00) > **9O** (22.44); **11S** (34.59) > **9S** (25.93); **12O** (22.48) > **10O** (21.49); **12S** (31.50) > **10S** (21.02)).

In summary, we have investigated the first hyperpolarizabilities of 138 chromophores (**1-12**)---stilbene and heteroaromatic analogs---by *ab initio* method. The results reveal a good linear relationship exists between the first hyperpolarizability (β) and gas-phase substituent constants (σ^{+}_{gas}) as known before. The susceptibility (ρ) of the β to the donor strength is found to be quite characteristic of the conjugated bridges. Our results provides a systematic account of the nature of the heteroaromatics and the substitution pattern at the conjugated bridges on molecular hyperpolarizability of donor-acceptor stilbene chromophores and suggests a practical guideline for developing heteroaromatic NLO materials.

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