

First Hyperpolarizabilities of Nonlinear Optical Organic Compounds: The Orientation Effects of Heteroaromatic Rings

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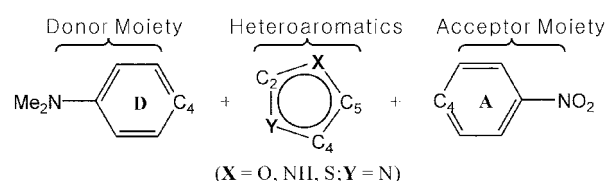
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Organic nonlinear optical materials¹⁻³ has attracted a keen interest in recent years owing to their potential applications in various photonic technologies. Significant efforts have focused on studying the electronic and structural properties of donor-acceptor substituted π -conjugated organic molecules with large molecular nonlinear optical (NLO) response (β , first-order hyperpolarizability).⁴ Two factors are attributed to NLO properties of such molecules in an electric field: the altered ground state charge distribution by the donor and acceptor moieties and the enhanced π -electronic charge redistribution through the π -conjugation.¹ Introduction of aromatic units into polyenes and polyyenes systems enhance thermal stability but severely reduce the hyperpolarizability.⁵ For example, the stilbene analogs are much more thermally stable than donor-acceptor substituted polyenes of equal length, however, their molecular hyperpolarizability decreases dramatically. Synthetic studies have shown that replacement of the aromatic π -bridge with more easily delocalizable 5-membered heteroaromatics such as thiophene, furan and pyrrole results in an enhanced molecular hyperpolarizability in general.^{6,7} Recent theoretical calculations made interesting suggestions as to the role of heteroaromatics in enhancing values *via* modifying: i) the electron density of the ring systems,⁸ ii) the electron-poor and -rich nature of the ring systems.^{8,9} McMahon *et al.* demonstrated in a theoretical study of several thiazole analogs of donor-acceptor stilbenes that hyperpolarizabilities strongly depend on the relative orientation of a thiazole subunit.¹⁰ Despite the growing interest in NLO heteroaromatic chromophores, relevant information regarding the structure-property relationships for NLO heteroaromatic systems is still scarce. Particularly, the structure-property study of NLO systems having a 5-membered heteroaromatic π -bridging core has never been reported. We have considered theoretically the structure-property relationship for the donor-acceptor systems (D-A) containing a heteroaromatic (oxazole, imidazole, and thiazole) π -bridging unit. Herein we present a distinct relationship between the molecular hyperpolarizability (β) and the relative orientation of heteroaromatic rings (HA) in terms of the dipole moment orientation of heteroaromatics and the substitution pattern in D-HA-A.

All molecules fully optimized at HartreeFock level using the 6-31G basis set in the *Gaussian 98* program¹¹ show almost planar structures. The tensor components of the static



first hyperpolarizabilities (β)¹² were analytically calculated by using the coupled perturbed HartreeFock (CPHF) method (Table 1).

The general findings revealed in Table 1 are: i) the magnitude of hyperpolarizability in "donor-(C₂/C₅)-acceptor" and "donor-(C₅/C₂)-acceptor" system is substantially larger than in the "donor-(C₂/C₄)-acceptor" and "donor-(C₄/C₂)-acceptor" system (1/2 > 3/4 and 5/6 > 7/8); ii) a system with a donor substituted at the electron-deficient position of heteroaromatic unit and an acceptor at the electron-rich position (*i.e.*, "donor-(C₂/C₅)-acceptor") affords larger hyperpolarizability than that with opposite substitution patterns (*i.e.*, "donor-(C₅/C₂)-acceptor") (1 > 2, 5 > 6 and 9 > 10). The same trend works for C₂/C₄ systems (3 > 4, 7 > 8 and 11 > 12).

Incorporation of a heteroaromatic ring between donor and acceptor moieties makes an efficient charge transfer from donors to acceptors possible by providing " \oplus/\ominus -paired"

Table 1. Calculated hyperpolarizability (β) using CPHF/6-31G method

compound	heterocycle system ^a	bonding system ^b	β (10 ⁻³⁰)
1	X=O, Y=N	D-(C ₂ /C ₅)-A	50.1
2	X=O, Y=N	D-(C ₅ /C ₂)-A	46.8
3	X=O, Y=N	D-(C ₂ /C ₄)-A	29.9
4	X=O, Y=N	D-(C ₄ /C ₂)-A	27.0
5	X=NH, Y=N	D-(C ₂ /C ₅)-A	51.0
6	X=NH, Y=N	D-(C ₅ /C ₂)-A	46.8
7	X=NH, Y=N	D-(C ₂ /C ₄)-A	33.8
8	X=NH, Y=N	D-(C ₄ /C ₂)-A	26.4
9	X=S, Y=N	D-(C ₂ /C ₅)-A	58.4
10	X=S, Y=N	D-(C ₅ /C ₂)-A	49.4
11	X=S, Y=N	D-(C ₂ /C ₄)-A	35.0
12	X=S, Y=N	D-(C ₄ /C ₂)-A	23.6

^aNumbering system follows on text. ^bD-(atom in hetero-ring bonded to donor)-atom in hetero-ring bonded to acceptor)-A.

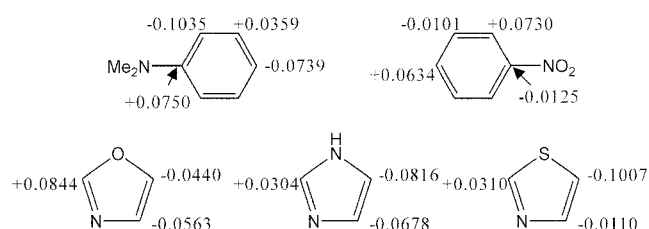


Figure 1. NBO population analysis (HF/6-31G) of π -electron density.

resonance structures at C₂ and C₅. However, the “ \oplus/\ominus -paired” resonance may not be allowed for C₂ and C₄ systems. Therefore a C₂/C₅ (or C₅/C₂) substitution is favored over a C₃/C₄ (or C₄/C₃) substitution. We also calculated π -electron densities of heteroaromatics and donor-acceptor moieties using NBO population analysis.¹³ The C₂ position of heteroaromatics is π -electron poor and C₅ is electron-rich (for example, +0.0310 at C₂ of thiazole and -0.1007 at C₅) (see Figure 1). Densities of π -electron at C₄ in both donor and acceptor are -0.0739 and +0.0634, respectively.

Orientation of the dipole moment (“matched” vs. “mismatched”) and substitution pattern (“favored” vs. “unfavored”). Molecular structures of three heteroaromatic units (thiazole, oxazole and imidazole) examined are shown in Figure 2, where the calculated overall dipole moment of those rings are depicted as thick arrows. In **1**, **5** and **9**, the overall dipole moment in heteroaromatic subunits is keeping with the direction from donor to acceptor. Here we refer to this cases as “matched”, “M”. However, the overall dipole moment in **2**, **6** and **10** is opposing to the direction from donor to acceptor (referred to as “mismatched”, “mM”).

Also the hyperpolarizability strongly depends on the position of the substituted donor/acceptor moieties in the heteroaromatic core. While ‘matching’ property between the direction of dipole moment of the heteroaromatic unit and that of D-A charge transfer should prevail in the C₂/C₅ (or C₅/C₂) substituted cases, that property in the C₃/C₄ (or C₄/C₃)

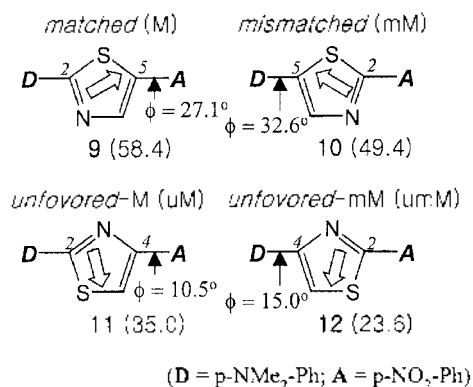


Figure 2. Four types of thiazole chromophore system. (*Arrow indicates the direction of dipole moment. **Values in parentheses are β in unit of 10^{-30} . *** ϕ indicates torsion angle, N3-C2-C4(Ph)-C3(Ph), otherwise zero.)

substituted cases should diminish because the direction of D-A charge transfer is away from the inherent dipole moment of the hetero unit. We refer to the former situation as “favored” and the latter as “unfavored” (prefixed with “u”). This expected tendency of molecular hyperpolarizability: “M” > “mM” > “uM” > “umM” is obviously manifested in all three heteroaromatic chromophore systems. Four types of thiazole chromophore system are shown in Figure 2.

Our results provides a systematic account of electronic and conformational factors on molecular hyperpolarizability of NLO chromophores containing heteroaromatic core units and suggests a practical guide for a rational design in developing heteroaromatic NLO materials.

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