The Important Role of Heteroaromatics in the Design of Efficient Second-Order Nonlinear Optical Molecules: Theoretical Investigation on Push−Pull Heteroaromatic Stilbenes

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Abstract: First hyperpolarizabilities of a large number of push−pull substituted conjugated systems with heteroaromatic spacers have been calculated. The static, nonresonant components were computed at the ab initio level (4-31G basis) using the coupled perturbed Hartree−Fock approach and at the AM1 level employing the finite field method. Sum-over-states procedure has also been used with the AM1/CI method to compute β_0 and β at an excitation energy of 1.17 eV. The computed β values at the various levels are reasonably similar and exhibit the same trends. The largest values are obtained with a donor on pyrrole and an acceptor on thiophene or thiazole. The variations do not always inversely follow the order of delocalization energies of the heterocyclic rings. The trends in the dipole moment changes and transition energies between the ground and first excited charge-transfer state primarily determine the variations in the computed β values.

Introduction

There is a growing need for organic polymeric electro-optic materials owing to their potential applications in new photonic technologies such as optical data processing.[1] The development of such materials primarily depends on the optimization of molecular as well as material second-order nonlinear optical responses. During the past decade, considerable progress has been made in understanding the factors that affect the molecular and material properties.[2−4] Molecular nonlinear optical response (β, first-order hyperpolarizability) is generally observed in donor−acceptor-substituted π-conjugated molecules containing built-in dipole moment. In such molecules, the π-conjugation provides a pathway for the redistribution of electronic charge under the influence of an electric field, whereas the donor and acceptor substituents provide the required ground state charge asymmetry. Structure−property relationships that have been established indicate that β increases with increasing donor and acceptor strengths and with increasing π-conjugation length.[5,6] Polyenes are often used as π-conjugating units as they provide the most effective pathway for the efficient charge transfer between the donor and acceptor groups.[7] Incorporation of benzene rings into the push−pull polyenes is observed to limit or saturate molecular nonlinearity but to enhance thermal stability.[8] The barrier due to the aromatic delocalization energy of the benzene ring is believed to be responsible for the reduced or saturated β values. To overcome the problem of saturation of molecular nonlinearity, recently several groups have developed systems that contain easily delocalizable five-membered heteroaromatic rings.[9−11]

Using thiophene (in place of benzene) as a conjugating segment, we studied several classes of donor−acceptor compounds.[9] Experimental EFISH data indicate that in many molecular systems, the thiophene substitution causes a signifi-

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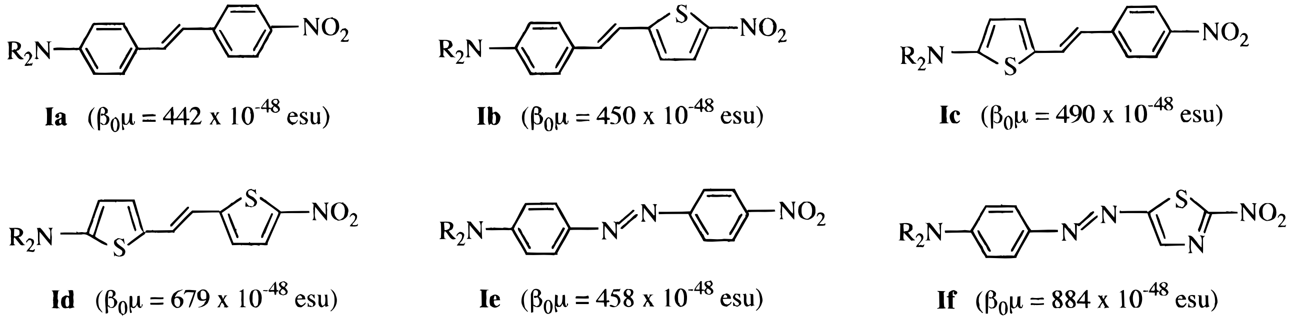
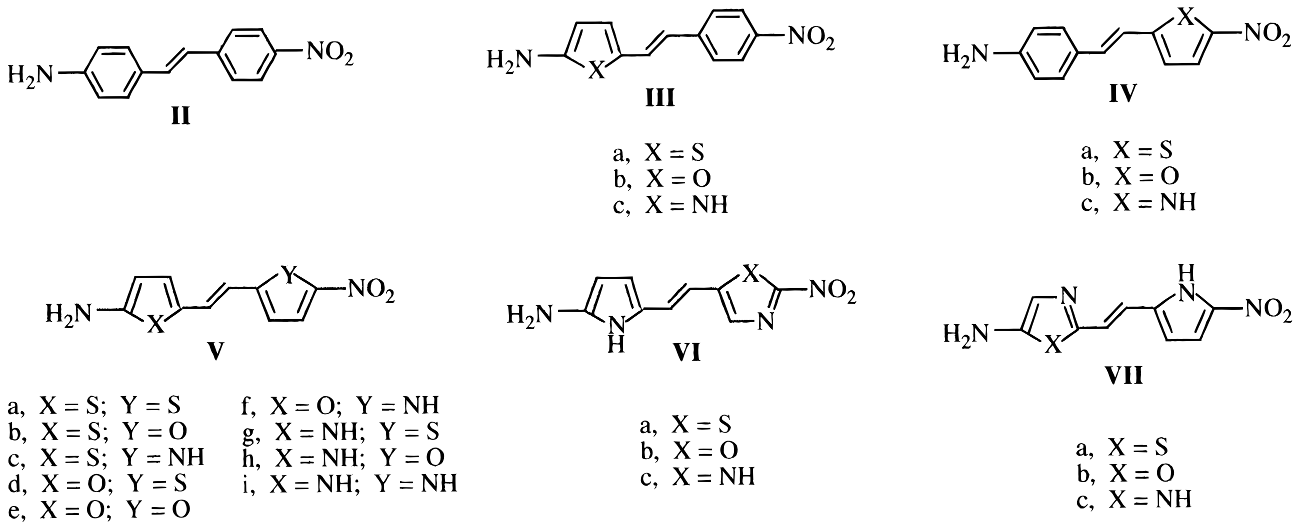
Chart 1. Experimentally Studied Representative Thiophene- and Thiazole-Incorporated Donor−Acceptor Compounds



Ia ($\beta_0\mu = 442 \times 10^{-48}$ esu)
Ib ($\beta_0\mu = 450 \times 10^{-48}$ esu)
Ic ($\beta_0\mu = 490 \times 10^{-48}$ esu)
Id ($\beta_0\mu = 679 \times 10^{-48}$ esu)
Ie ($\beta_0\mu = 458 \times 10^{-48}$ esu)
If ($\beta_0\mu = 884 \times 10^{-48}$ esu)

Chart 2. Donor−Acceptor Structures Examined in the Present Study



II

III

a, X = S
b, X = O
c, X = NH

IV

a, X = S
b, X = O
c, X = NH

V

a, X = S; Y = S
b, X = S; Y = O
c, X = S; Y = NH
d, X = O; Y = S
e, X = O; Y = O
f, X = O; Y = NH
g, X = NH; Y = S
h, X = NH; Y = O
i, X = NH; Y = NH

VI

a, X = S
b, X = O
c, X = NH

VII

a, X = S
b, X = O
c, X = NH

cant enhancement of β. For example, the experimental $\beta\mu$ values obtained for dialkylamino, nitro-substituted stilbene **Ia** and its thiophene analogs **Ib**−**d** (Chart 1) suggest that significantly higher molecular nonlinear optical activity can be achieved by replacing both the benzene rings of **I** with thiophene.[9a] We rationalized these results on the basis of the lower aromatic delocalization energy of thiophene (29 kcal/mol) relative to benzene (36 kcal/mol).[12] Prior to our studies, Dirk et al.[10] reported EFISH studies on thiazole-containing donor−acceptor-substituted azobenzenes (e.g., **If**, Chart 1). Their studies revealed that the replacement of the benzene ring on the acceptor end with thiazole resulted in enhanced β values. They also attributed the observed enhancement to the lower aromatic delocalization of thiazole (25 kcal/mol). Although both thiophene and thiazole possess lower delocalization energy relative to benzene, the presence of thiophene on the acceptor end (as in **Ib**) does not result in any noticeable change in β, unlike the results seen with the thiazole derivative **If**. These two observations together suggest that the lower delocalization energy of heteroaromatic rings is not the only major factor determining the first hyperpolarizability. To understand the role of heteroaromatic conjugating units in the optimization of β, we have carried out hyperpolarizability calculations on a number of donor−acceptor stilbenes using a wide variety of heteroaromatic conjugating units.[13] Our initial theoretical studies which were aimed at rationalizing our own experimental results on thiophene systems were reported elsewhere.[9e] In this account, we provide a comprehensive picture of the effect of heteroaromatics on the second-order nonlinear optical properties using ab initio and semiempirical quantum mechanical calculations.

Molecular Structures

Molecular structures examined in this study are shown in Chart 2. Although many experimentally studied molecules contain a dialkylamino electron-releasing group, the simple amino group was chosen for the purpose of calculations, primarily to minimize computational time. The nitro group serves as a conventional electron acceptor in all the structures examined. Stilbene **II** was chosen as the representative benzenoid system, while its heteroaromatic derivatives **III**−**VII** were designed to understand the role of the heteroaromatic ring(s) in influencing the nonlinear optical response. Series **III**−**V** represent structures derived from the substitution of rings containing one heteroatom (such as thiophene, furan, and pyrrole), whereas series **VI**−**VII** are made up of rings containing two heteroatoms (such as thiazole, oxazole, and imidazole).

All the molecular structures were first optimized at the MNDO level assuming planar geometries.[14,15] Complete geometry optimizations (including dihedral angles) without any symmetry constraints were then carried out using the AM1 method.[14,15] Hyperpolarizability calculations were carried out on both planar and fully optimized geometries.

Methodology

We carried out both ab initio and semiempirical quantum chemical calculations of the molecular hyperpolarizabilities. In one approach,

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the ground state electronic energy or the dipole moment in the presence of a static external field is expanded as a Taylor series (eq 1). The

$$W(E) = W_0 - \sum_i \mu_0 E_i - {}^1/_{2!} \sum_{ij} \alpha_{ij} E_i E_j - {}^1/_3 \sum_{ijk} \beta_{ijk} E_i E_j E_k \quad (1)$$

tensor components of the molecular polarizability and hyperpolarizability can be calculated by taking the appropriate derivatives with respect to the field. These can be obtained numerically as in the finite field (FF) method or analytically using the coupled perturbed Hartree−Fock (CPHF) procedure.[16]

The SOS method is based on the perturbation expansion of the Stark energy. Different order Stark energy terms are related to optical nonlinearities based on their order in the field strength. In this approach, therefore, the optical, nonlinearities are introduced as a result of Stark mixing of the various excited states. The mixing terms are summed over various excited states to obtain α, β, and γ. The SOS expression for the first hyperpolarizability, shown in eq 2a,is adequate as a basis

$$\beta_{ijk}(-\omega_\sigma; \omega_1,\omega_2) = \left(\frac{-e^3}{4H^2}\right) \sum_p \sum_{e,e'} \frac{\langle g|\mu_i|e\rangle\langle e|\mu_j|e'\rangle\langle e'|\mu_k|g\rangle}{(\omega_{eg} - \omega_\sigma)(\omega_{e'g} - \omega_1)} \quad (2)$$

for the discussion of certain qualitative features. The most explicit versions of this expression can be found in references.[5,6,16,17]

In the above equation, ω_1 and ω_2 are the frequencies of the applied field and ω_σ is the output frequency (which is the sum of the input frequencies). The indices: g denotes the molecular ground state, and e and e' refer to excited electronic states of the system having transition frequencies given by ω_{eg} and $\omega_{e'g}$, respectively. The summation over p generates terms by permutation of the pairs $\{(-\omega_\sigma,i); (\omega_1,j); (\omega_2,k)\}$. The accuracy of these types of calculations are strongly dependent on the formalism employed in deriving the ground and excited state properties.

At the ab initio level, the CPHF procedure was employed as implemented in the Gaussian 92 series of programs.[18] The split-valence 4-31G basis set was used. A recent comparative study of different basis sets for predicting the hyperpolarizability of a representative push−pull system, 2-methyl-4-nitroaniline, has shown that the 4-31G basis is adequate.[19] Planar-constrained optimized geometries obtained from MNDO calculations as well as fully optimized nonplanar AM1 geometries were used. Hyperpolarizabilities derived from these calculations are the static nonresonant response functions. Equivalent data were also computed using the AM1 procedure in conjunction with the FF method.[16b]

The fully optimized AM1 geometries were also used in another set of AM1/CI calculations to obtain β values with the SOS method.[19] The results were found to converge with singles and pair excitation configuration interaction (PECI) involving 18 MO's spanning the frontier orbitals. Contributions from about 150 lowest singlet states were included. Using this approach, β values were computed with excitation energies of 0 and 1.17 eV. As experimentally measured β values are often resonance enhanced because of the overlap between the second harmonic of fundamental operating frequencies and the charge-transfer absorption of the molecular system, the values obtained at 1.17 eV provide a measure of this effect.

The β values are often defined using different conventions, which differ by constant multiplicative factors.[20] To enable a uniform comparison, the data were converted to convention B in the notation of Willetts et al. From these values, the average β_{vec} data, as defined in eqs 3 and 4, were computed (Tables 1−3):

$$\beta_{\text{vec}} = (\sum_i \beta_i^2)^{1/2} \quad (3)$$

$$\beta_i = \beta_{iii} + {}^1/_3 \sum_{j \neq i} (\beta_{ijj} + 2\beta_{jji}) \quad (4)$$

Along with β values, some of the parameters relevant to the first excited state such as transition wavelength, change in dipole moment between ground and first excited states ($\Delta\mu$), and transition dipole length (r) were also computed on fully optimized molecules in order to understand the dependence of β on the electronic properties of the first excited state.

Results

We have computed first hyperpolarizabilities of all the molecules considered in this study using the CPHF, FF, and SOS methods in conjunction with ab initio or semiempirical procedures. Geometric effects have been considered in a set of calculations by using planar and fully optimized structures. In the SOS procedure, resonance enhancement of β has been evaluated. Thus several sets of data have been obtained. However, representative values are provided in Tables 1−3. Ab initio data using planar and nonplanar geometries are given first. This is followed by AM1 values using the FF method and two sets of β values employing the SOS method. To interpret the trends in these values, properties associated with the lowest excitation process determined at the AM1/CI level are included.

The computed β values of all the structures show some common trends. The 4-31G values using the planar geometry are uniformly higher than the corresponding values obtained for the more realistic nonplanar optimized geometries. Obviously, the donor−acceptor interactions are more effective in the planar-constrained geometries. However, the variations due to geometry change are relatively modest.

The computed β_0 values at different theoretical levels, but using the same geometries, are quite similar. This is remarkable considering the differences in the procedures employed. The trends in the computed hyperpolarizabilities are virtually identical. There are occasional differences in the relative β values, but the discrepancies are minor.

The SOS calculations enable the evaluation of resonance enhancement of β. In all the systems considered, β using an excitation energy of 1.17 eV is higher than the static value. The magnitude of enhancement varies over a wide range. Nevertheless, the major trends in the computed β at excitation energies of 0 and 1.17 eV remain the same. Therefore, any one set of data provided in Tables 1−3 should be good enough to derive generalizations on the hyperpolarizabilities of the heteroaromatic push−pull systems.

The computed β values indicate that the replacement of benzene rings in stilbene **II** (Chart 2) with heteroaromatic rings significantly alters the first hyperpolarizability. The magnitude of increase or decrease of β with respect to that of the model stilbene **II** depends on both the nature of the heteroaromatic ring and its position in the molecular framework.

The replacement of the benzene ring on the donor end of **II** with rings containing one heteroatom such as thiophene, furan, or pyrrole results in higher β values: Substitution by pyrrole results in a larger effect than by furan which in turn has a larger effect than thiophene (Table 1: **IIIc** > **IIIb** > **IIIa**). On the other hand, in molecular systems where the same heteroaromatic rings are present on the acceptor end of **II**, the opposite trends are noted (Table 1: **IVa** > **IVb** > **IVc**). These results indicate that pyrrole when placed on the donor end causes significant

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Table 1. Calculated Hyperpolarizabilities (10^{-30} esu cm^{-5}), Transition Wavelength (nm), Change in Dipole Moment (D), and Transition Dipole Length (Å) for the Molecular Structures **II**−**IV**

	4-31G, β_0 (CPHF)		AM1/fully optimized geometries						
structure	planar	opt	β_0 (FF)	β_0 (SOS)	$\beta_{1.17}$ (SOS)	β (two-state)	λ	$\Delta\mu$	*r*
II	26.0	23.3	29.9	23.8	48.6	30.3	341.9	4.5	1.8
IIIa	31.3	27.7	31.7	22.8	52.8	29.4	363.1	3.8	1.8
IIIb	34.7	29.7	36.1	29.0	77.8	43.5	379.5	5.0	1.8
IIIc	45.2	39.6	46.1	38.8	106.6	57.6	384.2	6.5	1.9
IVa	29.4	27.7	34.6	27.8	71.0	42.4	371.6	4.9	1.9
IVb	25.8	24.7	31.5	25.0	61.0	30.9	373.4	3.5	1.9
IVc	21.6	19.7	22.1	17.8	40.0	18.2	365.0	2.2	1.9

Table 2. Calculated Hyperpolarizabilities (10^{-30} esu cm^{-5}), Transition Wavelength (nm), Change in Dipole Moment (D), and Transition Dipole Length (Å) for the Molecular Structure **V**

	4-31G, β_0 (CPHF)		AM1/fully optimized geometries						
structure	planar	opt	β_0 (FF)	β_0 (SOS)	$\beta_{1.17}$ (SOS)	β (two-state)	λ	$\Delta\mu$	*r*
Va	32.9	31.5	35.5	28.4	84.0	46.5	389.9	4.5	2.0
Vb	29.0	28.0	32.2	21.2	61.8	27.6	394.7	2.8	1.9
Vc	23.0	22.2	22.5	15.0	37.6	14.5	385.5	1.5	1.9
Vd	36.9	34.0	40.9	32.0	108.4	55.1	403.2	5.5	1.9
Ve	32.1	30.4	37.4	29.8	101.6	42.2	411.4	3.9	1.9
Vf	27.5	24.4	26.7	21.2	63.4	26.9	399.5	2.7	1.9
Vg	47.1	44.0	51.6	44.1	158.2	74.4	412.2	7.0	1.9
Vh	40.8	38.8	46.4	38.0	137.8	54.2	418.4	4.9	1.9
Vi	35.0	31.6	33.7	28.6	88.2	37.6	402.6	3.7	1.9

Table 3. Calculated Hyperpolarizabilities (10^{-30} esu cm^{-5}), Transition Wavelength (nm), Change in Dipole Moment (D), and Transition Dipole Length (Å) for the Molecular Structures **VI** and **VII**

	4-31G, β_0 (CPHF)		AM1/fully optimized geometries						
structure	planar	opt	β_0 (FF)	β_0 (SOS)	$\beta_{1.17}$ (SOS)	β (two-state)	λ	$\Delta\mu$	*r*
VIa	50.8	49.9	62.4	55.8	246.2	94.7	431.3	7.7	1.9
VIb	45.3	42.7	52.6	44.8	167.8	66.4	420.5	5.7	1.9
VIc	37.3	34.5	38.2	32.4	102.6	45.0	403.4	4.3	1.9
VIIa	18.0	16.4	15.6	11.6	29.0	10.6	380.6	1.1	2.0
VIIb	20.2	17.6	17.9	18.4	47.0	23.5	378.7	2.6	1.9
VIIc	26.3	23.7	23.6	23.8	61.8	32.5	378.4	3.7	1.9

enhancement in the molecular nonlinearity but lowers the activity when it is on the acceptor end. Furan substitution at the donor end is also effective but leads only to a small enhancement at the acceptor end. The presence of thiophene causes a marginal increase in the β_0 value, irrespective of its position in the molecular system (**IIIa** and **IVa**).

Similar trends can be seen from the calculated data (Table 2) obtained for fully heteroaromatic stilbenes (series **V**, Chart 2). Thus, the increase or decrease of molecular nonlinear activity in these systems depends on the nature as well as the location of the heteroaromatic ring. Of all the nine combinations studied in this series, the system **Vg** with pyrrole and thiophene on the donor and acceptor ends, respectively, is predicted to be the most active one. When both the rings contain the same heteroatoms as in structures **Va**,**e**,**i**, the computed values show differing trends. However, the variations in β in these molecules are relatively small. The same type of ring present on either side of the molecule evidently induces conflicting responses. The ring which enhances nonlinearity at the donor end is comparatively ineffective at the acceptor end and *vice versa*. Nevertheless, within the series of molecules **Va**, **IVa**, and **IIIa**, the presence of two thiophene rings leads to enhanced activity compared to just one, which in turn has a larger β value than the derivative with two benzene rings. Our previous experimental hyperpolarizability values obtained for the thiophene compounds support the conclusions drawn from the present calculated data.

The data shown in Table 3 suggest that more pronounced effects can be observed by using rings containing two heteroatoms. In structures **VI** and **VII**, one of the rings is pyrrole (on the donor side in **VI** and acceptor side in **VII**), while the other ring has two heteroatoms (e.g., thiazole, oxazole, and imidazole). Substantially higher β values are noted for systems **VI** in which the diheteroatom ring is present on the acceptor end. These systems also show the largest resonance enhancements in all the systems considered here. Thiazole is found to be more effective than oxazole which in turn is more effective than imidazole. In contrast, the compounds **VII**, where the same two-heteroatom rings are present on the donor end, show reduced β values, the least active one being the thiazole-derived system **VIIa**.

Thus, calculated β values predict that the molecular nonlinear optical activity of amino, nitro-substituted stilbenes can be fine-tuned by replacing both the benzene rings of the stilbene framework with heteroaromatic rings. The magnitude of enhancement or reduction is more prominent with rings containing two heteroatoms than those with one heteroatom. In addition to the nature of the ring system, the β values are also dependent on their position in the molecular framework.

Discussion

The trends in β values suggest that heteroaromatics play a subtle role in influencing the molecular nonlinear response. In the following, we have attempted to rationalize the computed variations on the basis of a number of molecular properties.

Dependence of β on the Delocalization Energy of the Ring System(s). One of the parameters affecting the coupling between the donor and acceptor substituents is the energy barrier imposed by the conjugating bridge. This factor becomes relevant and important especially if the conjugating pathway is made up of aromatic rings. The lower the aromatic delocalization energy barrier, the higher the first hyperpolarizability should be. Simple five-membered heteroaromatics such as thiophene (29 kcal/mol), pyrrole (21 kcal/mol), and furan (16 kcal/mol) possess lower delocalization energy[12] relative to benzene (36 kcal/mol) and, therefore, are expected to be more effective than benzene in promoting charge transfer, thus increasing the β value. This description is oversimplified. As pointed out earlier the magnitude of β is determined not only by the nature of the heterocyclic ring but also by its location. Thiophene leads to larger β values at the acceptor end, while pyrrole is more effective at the donor end. These trends are clearly contrary to expectations based on delocalization energies alone. Hence, the role of other electronic factors needs to be considered.

Dependence of β on the Electron-Rich or Electron-Deficient Nature of the Ring System(s). In donor−acceptor-substituted NLO molecules, π-configuration commonly provides a pathway for the redistribution of electrons under the influence of an electric field. In some cases, the nature of the π-conjugation can alter the electron-donating and -accepting ability of the substituents. For example, if any of the segments within the π-conjugating pathway possesses electron-releasing or -withdrawing characteristics, the overall electron-donating or -accepting ability of the substituents, and thereby the effective charge transfer and molecular nonlinearity, will be affected. These effects not only depend on the nature of the conjugating segments but also on their location in the molecular framework. With heteroaromatic rings being electron-rich or -poor depending on the nature of the heteroatom and its hybridization, the dependence of β on these factors must be addressed.

First, consider the varying dependence of the β values on the nature of the heterocyclic ring in the series **III** and **IV**. The differences in the computed data for **IIIc** and **IVc** are particularly striking (e.g., 4-31G, β_0: 39.6 and 19.7). These values indicate that the location of the pyrrole ring alone can either dramatically enhance or decrease the overall molecular nonlinearity of the system. These results can only be rationalized by viewing pyrrole not only as a conjugating segment but also as a structural unit which affects the overall electron-donating and -accepting properties of the system. Pyrrole, being the most electron-rich five-membered heteroaromatic ring studied here, assists the amino group in **IIIc** resulting in a more pronounced electron-donating effect, whereas in **IVc** it counteracts the electron-withdrawing effect of the nitro group resulting in a decrease in β. Similar, but less prominent, trends observed for furan-containing compounds **IIIb** and **IVb** can be attributed to the lower electron-rich character of furan with respect to pyrrole. Thiophene, being the least electron-rich heteroaromatic ring studied here, and the observed trends in **IIIa** and **IVa** may be attributed mainly to its lower delocalization energy with respect to benzene.

Now, let us turn our attention to the series **VI** and **VII** in which one of the two heteroaromatic rings has two heteroatoms. The trends in β values (Table 3) clearly point out that the position of the thiazole, oxazole, or imidazole ring produces a significant effect. The presence of thiazole/oxazole/imidazole on the acceptor end of the molecular system in **VI** causes a dramatic enhancement in β, whereas their presence on the donor end of the molecular system in **VII** substantially decreases the activity, i.e., β for **VIa**,**b**,**c** > **VIIa**,**b**,**c**. In contrast to rings containing one heteroatom (such as pyrrole, furan, and thiophene), rings with two heteroatoms (such as thiazole, oxazole, and imidazole) are electron-deficient in nature, due to the $-\mathrm{C}{=}\mathrm{N}-$ linkage. Thiazole being the most electron-deficient ring (electron deficiency decreases in the order: thiazole > oxazole > imidazole)[12] assists the nitro group resulting in a more pronounced electron-accepting effect in **VIa** and counteracts the electron-donating effect of the amino group in **VIIa**. Comparatively less electron-deficient ring systems such as oxazole and imidazole produce similar but much less pronounced effects.

Dependence of β on the Properties of the First Charge-Transfer Excited State. In many experimentally studied organic molecules, a simple two-state model is frequently used to rationalize the trends in β.[8,11a] The basic assumption is that polarization results primarily from the mixing of the lowest energy charge-transfer state and the ground state under the influence of the applied electric field. Using the SOS perturbation procedure, the value for β (according to convention *B*) reduces to a simple expression:[20]

$$\beta = 3\langle g|\mu|e\rangle^2(\mu_e - \mu_g)/(E_e - E_g)^2 \tag{5}$$

The value of β is strongly dependent on the transition dipole connecting the ground and first excited singlet states and corresponding difference in dipole moments and inversely related to the energy separation between the states. This simplified approach is particularly useful while examining a series of related molecules, as in the present study.

The AM1/CI procedure we have employed can be used to obtain the key parameters which determine β within this model. In Tables 1−3, the transition wavelength, change in dipole moments, and transition dipole length computed for all the molecules are provided. These data can be used for a qualitative assessment of the variations in computed β values.

The calculated transition dipole lengths are fairly constant in the various systems examined. The nature of the electronic transition remains the same in all the molecules. Hence, this factor cannot be crucial in determining the β values.

The transition wavelengths are fairly large and also show a fair degree of variation in the molecules, ranging from 363 to 431 nm. The systems with longer wavelength transition invariably are computed to have a higher β. This is especially true for the resonance-enhanced $\beta(1.17)$ data computed at the AM1 level using the SOS procedure. More extended conjugation generally leads to a smaller energy difference between the ground and charge-transfer excited states.

The importance of dipole moment change following excitation is also evident from the tables. The efficiency of charge polarization leading to a large β is clearly reflected in the data obtained for various groups of molecules. Thus, at the donor end, a pyrrole ring leads to a large dipole moment change. In contrast, the ring is ineffective at the acceptor end (Table 3). The importance of the $\Delta\mu$ values is revealed by the data for the series **V**. While the transition wavelengths for **Vd**,**g**−**i** are comparable, the higher dipole moment change in **Vg** makes it a better candidate for nonlinear response. Compound **VIa**, calculated to have the highest β in the present study, is also characterized by a low-energy charge-transfer excited state with a large associated dipole moment change.

Conclusions

A large class of donor−acceptor-substituted molecules with heterocyclic rings have been examined for their molecular nonlinear response. First hyperpolarizabilities have been computed using FF and sum-over-states procedures. Ab initio and semiempirical methods have been employed. All the calculations reveal the same general trends in the computed β values.

Molecules in which the same heterocyclic ring is present on the donor as well as the acceptor ends are calculated to have a larger β than the corresponding stilbene derivative with two benzene rings. However, the effects of the heterocyclic ring on the magnitude of β vary in a more subtle manner. The nonlinear response depends strongly not only on the nature but also on the location of the heterocyclic ring. For example, a pyrrole ring at the donor end is very effective in enhancing β. At the acceptor end, this ring leads to a lower β than the corresponding benzene derivative. A furan ring causes smaller changes. Thiophene leads to a larger β values more effectively at the acceptor end. Molecules with the largest β have to be designed appropriately. Among the systems considered, the highest β values have been computed for systems in which pyrrole is at the donor end and thiophene or thiazole is at the acceptor end of the molecule.

The computed β values do not follow a simple increasing pattern along the series benzene, thiophene, and furan, expected from the decreasing order of aromaticity of the rings. Donor and acceptor type substituents do not lead to equivalent loss in delocalization energies in the rings. The electron-rich or -deficient nature of the ring controls its response to the presence of additional substituents.

The computed β values can be correlated within the two-state model. While the transition dipoles are roughly constant for the lowest energy transition in all the systems, the transition wavelength and associated dipole moment change show a fair degree of variation. In general, molecules with a longer wavelength transition have a higher computed β. The effect is enhanced in all the systems in which the dipole moment change is also significant.

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