

# Enhanced Nonlinear Optical Response in Zwitterionic Molecules: A Computational Study on the Role of Orbital Interactions through $\sigma$ Bonds<sup>1</sup>

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Ab initio coupled perturbed Hartree–Fock calculations, using 6-31G\*\* basis sets, on a heterocyclic zwitterionic molecule with a  $\sigma$ -spacer between the donor and the acceptor ring shows a static first hyperpolarizability ( $\beta_0$ ) of around  $240 \times 10^{-30}$  esu. Substitution of electron withdrawing functional groups, such as  $\text{NO}_2$ , on the acceptor ring of this molecule enhances the  $\beta_0$  value to around  $3960 \times 10^{-30}$  esu. Studies on various such zwitterionic molecules demonstrate the importance of  $\pi$ – $\sigma$  orbital mixing (through bond interaction) between the  $\pi$ -aromatic rings and the  $\sigma$ -spacers in enhancing the nonlinear optical (NLO) response. Analysis of the transitions reveals low oscillator strengths, large changes in the dipole moments, and very low energy charge transfers that take place in the excited states of the molecule, while in the ground state they are stabilized in a charge separated resonance form. This is mainly responsible for the large NLO response. MP2 calculations on small molecules with dominant through bond interactions show that the inclusion of electron correlation further enhances the  $\beta_0$  value. The molecules, which have a strong IR absorption, have potential applications in filters, polarizers, optical recording, etc.

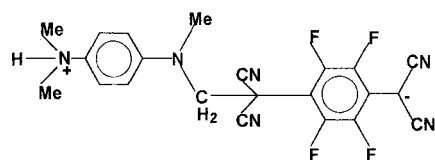
## 1. Introduction

The design of nonlinear optical (NLO) molecules has become a focus of current research in view of their potential applications in various photonic technologies.<sup>2–11</sup> Materials with NLO activity find use as electrooptic switching elements for telecommunication and optical information processing. The NLO process requires materials that manipulate the amplitude, phase, polarization, and frequency of optical beams. While a variety of materials including inorganic, organometallic, organic and polymeric have been studied for their NLO activity, it is the organic materials that have been receiving the maximum attention. In addition to the advantage in synthesis, organic materials have ultrafast response time, photostability, and large hyperpolarizability ( $\beta$ ) values. In particular,  $\pi$ -conjugated systems linking a donor (D) and an acceptor (A) show a large NLO response and hence have been well studied. The drawbacks with these systems are that they are not transparent in the visible region, and as the conjugation increases their thermal stability and photostability decreases. Another major problem is the retention of the NLO activity when incorporated into devices. To retain the hyperpolarizability in bulk state, they either have to crystallize into a noncentrosymmetric crystal, or in a poled polymer the noncentrosymmetric alignment should be retained on removal of the applied electric field. Polar molecules usually tend to crystallize into a centrosymmetric crystal, restricting their usage as a NLO device in the crystal form, but these find applications in poled polymers where large dipole moments ( $\mu$ ) play an important role. Currently, there is a need to develop molecules with large dipoles and hyperpolarizabilities for poled polymers, as they seem to be closest to technological applications.<sup>10</sup>

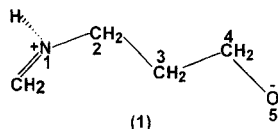
Aromatic rings with powerful donor and acceptor substitutions have been shown to possess large hyperpolarizability values.<sup>11</sup> In particular, stilbene derivatives have  $\beta$  values of very large magnitude that is further enhanced 2–3 times by replacing the

donor–acceptor functional groups with zwitterionic groups.<sup>12–14</sup> This has been predicted in terms of bond length variation by Marder and co-workers who have demonstrated for  $\pi$ -conjugated systems that large positive  $\beta$  values are obtained for the polyene limit on one end, and the large negative  $\beta$  is obtained for the polymethine type at the other end.<sup>15–16</sup> An alternative approach to designing molecular chromophores has been suggested by Albert et. al.<sup>17–18</sup> In this approach, molecules with a break in the conjugation which enforces zwitterionic behavior in the ground state and provides low oscillator strength and low energy charge transfer have shown to have large NLO activity. Thus, two heterocyclic aromatic rings in a zwitterionic molecule linked directly to each other would show large  $\beta$  values when the dihedral angle between them is twisted to nearly 90 degrees. This is because the  $\sigma$ – $\pi$  mixing still takes place at this angle and allows a low energy charge transfer (CT) between the charge localized and separated rings.

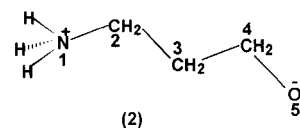
**This Work.** Most of the studies on hyperpolarizabilities reported in the literature have been on  $\pi$ -electron conjugated systems, and there are only a few reports on  $\sigma$ -bonded donor–acceptor systems.<sup>19–21</sup> In the case of charge separated systems, to the best of our knowledge, experimental studies on the static  $\beta$  of zwitterionic  $\sigma$ -bonded molecules have not been carried out. One zwitterionic crystal structure (structure **1**) in which the D and A are linked by a  $\sigma$ -bond has been reported for NLO applications, but the  $\beta$  value for this system has not been estimated either theoretically or experimentally.<sup>22</sup> In an earlier work on computational design of zwitterionic molecules to achieve charge separation, we inserted a  $\sigma$ -spacer between the aromatic donor and acceptor ring.<sup>20</sup> The  $\sigma$ -bond breaks the conjugation and enforces zwitterionic behavior while the  $\pi$ – $\sigma$ – $\pi$  through bond interaction (TBI) leads to a low energy CT. This gives rise to a large NLO response. We have also observed, by theoretical calculations, with aromatic D and A that if NLO activity has to be enhanced in a D– $\sigma$ –A system,



Structure 1



(1)



(2)

Figure 1. The molecules considered for electron correlation studies.

then the conformation of the molecule should be in such a way that the TBI is maximized.<sup>20–21</sup>

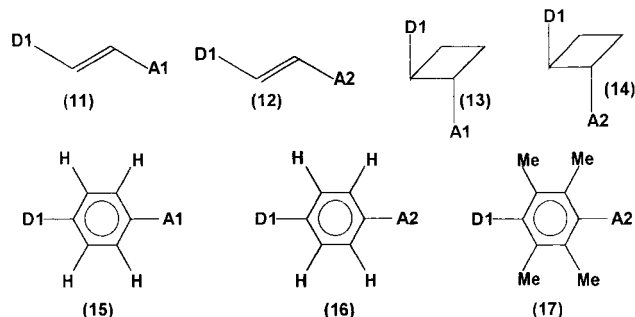
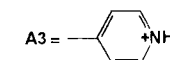
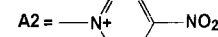
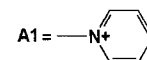
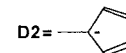
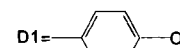
In this work, we show that by attaching an electron withdrawing functional group at the acceptor end of a  $\sigma$ -bonded heterocyclic zwitterion, there is a larger charge separation and more intense CT. This leads to  $\beta_0$  values enhanced at least by 10–15 times than that of the molecules without the electron withdrawing functional groups. These are one of the highest reported  $\beta_0$  values at HF ab initio level using the coupled perturbed Hartree–Fock (CPHF) formalism. Further through ab initio CIS calculations, we see that to a large extent these are transparent in the visible region, having absorption bands one at low energy and the other at a higher energy with a large “window” in between. It has been suggested that chromophores of this kind, which exhibit two distinct types of excitation, have potential applications in optical limiting.<sup>18,23</sup> We also report at the MP2 level the  $\beta_0$  values of two small molecules, shown in Figure 1, one having a large TBI, to estimate the effect of electron correlation on the NLO response of  $\pi$ - $\sigma$ - $\pi$  conjugated molecules.

## 2. Computational Methods

Earlier studies have shown that the HF/6-31G level of calculations is adequate to reproduce the molecular structures, dipole moments, and hyperpolarizabilities of zwitterionic organic molecules, but in view of the TBI involved in this study we have used a much larger basis set, 6-31G\*\*, at the HF level.<sup>12–14</sup> The molecular structures studied are shown in Figure 2. The molecules have been so chosen that they have an aromatic donor and an aromatic acceptor linked by a  $\sigma$ -bond, and they are zwitterionic and in each case the electron donor molecular orbitals would interact with the empty low lying electron acceptor orbital due to TBI. Where possible, the molecules have been studied only in the all *trans* conformation (*anti*); since in this conformation the effects of TBI are maximum and these would then have a dominant  $\pi$ - $\sigma$ - $\pi$  interaction.<sup>24–26</sup> The ab initio calculations were carried out using Gaussian 98 suit of programs to predict the structures (bond lengths and angles) of these molecules.<sup>27</sup> The HF/6-31G\*\* optimized geometries have then been used to calculate the static  $\beta_0$ , using the CPHF method implemented in the package.

D(#)-(CH<sub>2</sub>)<sub>n</sub>-A(#)

n	Donor (D)	Acceptor (A)	Molecule
0	D1	A1	3
0	D1	A2	4
2	D1	A1	5
2	D1	A2	6
3	D1	A1	7
3	D1	A2	8
3	D1	A3	9
3	D2	A2	10

Figure 2. The molecules considered for static  $\beta_0$  calculation at HF/6-31G\*\* level.

Hyperpolarizability ( $\beta_0$ ) reported here is defined as

$$\beta_0 = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2}$$

where

$$\beta_i = (1/3) \sum_{k=x,y,z} (\beta_{ikk} + \beta_{kik} + \beta_{kki}); i=x,y,z$$

For the two small molecules **1** and **2**, shown in Figure 1, HF, MP2 (frozen core), MP2 (full) using the 6-31G\*\* basis sets along with the semiempirical methods were used to calculate the  $\beta_0$  values. For the MP2 finite field (FF) calculations, we used the GAMESS-US package.<sup>28–29</sup> Here for reliable NLO properties a tight SCF convergence is required, and hence the options, ICUT = 24 (integrals less than  $10^{-24}$  are ignored), ITOL = 30 (products of parameters whose preexponential factor is less than  $10^{-30}$  are skipped), INTTYP = HONDO (HONDO integrals are more accurate), and NCONV = 10 for convergence in the SCF cycle have been used in the GAMESS calculations.<sup>30</sup> For the semiempirical coupled HF methods, the AM1 Hamiltonian implemented in GAMESS package was used.<sup>31</sup> Here again the  $\beta$  value is calculated using TDHF method at zero frequency albeit the semiempirical methods.

Singly excited CI studies using ab initio CIS have proven to be reliable in analyzing the transitions in molecules, and hence the HF/6-31G\*\* optimized geometries were used to calculate the oscillator strength ( $f$ ) and  $\lambda_{\max}$  implemented in the Gaussian 98 program.<sup>32</sup> We also carried out 250 states CI studies using ZINDO semiempirical program.<sup>33</sup> The absolute values of  $f$  and  $\lambda_{\max}$  obtained are much larger than those calculated using ab initio CIS method, but the trend is nearly the same. We report only the ab initio CIS values here since the larger values obtained by ZINDO could be because INDO/S is not parameterized for these type of molecules. Differences in the  $f$  values and  $\lambda$  between the two methods was also observed by Abe et al. in their study on zwitterionic molecules.<sup>13–14</sup>

Finally, we have calculated the static  $\beta_0$  for an additional set of molecules with various donors, acceptors, and chain length variation. These molecules were calculated at the HF/6-31G level to save computer time. It is shown later based on test calculations that the variation of the response property with these modifications would be only around 10–15%.

### 3. Results and Discussion

**3.1 Electron Correlation.** TBI between functional groups linked by  $\sigma$ -framework is strongly dependent on conformation, and  $\sigma$ - $\pi$  ( $p$ ) mixing occurs accordingly.<sup>25–26,34</sup> Since the delocalization takes place through the  $\sigma$ -bond, the possibility of electron correlation playing an important role is not ruled out. The electron correlation studies at the MP2 level of the large molecules (**3–17**) shown in Figure 2, is beyond scope of this work. To study the effect of electron correlation on the hyperpolarizabilities of molecules having TBI, we have selected two small zwitterionic molecules **1** and **2** (Figure 1) to carry out MP2 studies. Both the molecules have been so chosen such that the D and A are linked by a  $\sigma$ -bond and they are in the all *trans* (*anti*) conformation. The donor, in both the molecules, is the functional group  $O^-$ , while the acceptor in the first molecule is the  $sp^2 N^+$  and in the second molecule  $sp^3 N^+$ . To understand the molecular orbitals generated, we use the orbital interaction through bond (OITB) model.<sup>26</sup> This model has been used with success to explain long-range electron transfer through saturated ( $\sigma$ ) bonds; it is also referred to as superexchange mechanism. In both molecules, the orbitals of oxygen mix with the  $\sigma$ -orbitals of the framework. While only in molecule **1** does the other functional group ( $N^+$ ), i.e., the acceptor, mix with the  $\sigma$ -orbitals. The molecular orbitals in molecule **1** have a smaller energy gap between the HOMO and the LUMO. The  $\sigma$ - $\pi$  mixing creates a pathway in the molecule between the donor and the acceptor for the charge transfer in the excited state. Molecule **1** is a model molecule of the larger molecules shown in Figure 2.

We optimized the molecules **1** and **2** using a 6-31G\*\* basis set in the frozen core and the full MP2 methods. The MP2/6-31G\*\* optimized geometry is then used in finite field (FF) method implemented in the GAMESS package to calculate the dominant component of  $\beta_0$  by MP2 methods.<sup>35</sup> The  $X$ -axis has been chosen to coincide with the main axis of the molecule. The calculation of the main component of  $\beta_0$ , i.e.,  $\beta_{xxx}$  follows straightforwardly from the Taylor expansion of energy of the molecule in a weak electric field through the third order. The built-in FF algorithm in GAMESS carries out calculations at two different field strengths,  $F$  and  $2F$ . The equation for  $\beta_{xxx}$  is

$$\beta_{xxx} = \frac{[E(F_x) - E(-F_x)] - (1/2)[E(2F_x) - E(-2F_x)]}{F_x^3}$$

where  $E(F_x)$  denotes the energy of the molecule in the homogeneous electric field in the  $X$  direction with the strength  $F_x$ . Here we adopt a numerically stable  $\beta_{xxx}$ , which is obtained by using small field strengths,  $7.0 \times 10^{-4}$  au for these systems. The bond lengths along with  $\mu$  and  $\beta_0$  are shown in Table 1. The AM1 optimized values  $\mu$  and  $\beta_0$  calculated by ZINDO at the ab initio geometry are also shown for comparison. Molecule **2** where the TBI between the D and A is almost absent is shown in Table 2.

The results shown in Table 1 predict at the HF level the bond R34 to be around 1.584 Å. This is in line with the OITB model to account for the lengthening due to bond interactions through  $\sigma$  bonds. The  $\sigma$  MOs of this bond play the dominant role, and

**TABLE 1: Bond Lengths (Å), Dipole Moments,  $\mu$  (in Debye), and Static Hyperpolarizability,  $\beta_0$  ( $\times 10^{-30}$  esu), Values of Molecule 1 Computed using Various Methods**

method	R12	R23	R34	R45	$\mu_x$	$\beta_0$
HF/6-31G**	1.490	1.519	1.584	1.292	18.6	28.6
MP2//6-31G** <sup>b</sup>	1.460	1.512	1.643	1.291	14.4	245.9 <sup>a</sup>
MP2/6-31G**	1.457	1.511	1.641	1.289	14.4	244.8 <sup>a</sup>
AM1 (TDHF)	1.479	1.494	1.635	1.289	15.7	156.6
ZINDO (SOS) <sup>c</sup>					18.9	318.6

<sup>a</sup>  $\beta_{xxx}$  calculated using Finite Field method. <sup>b</sup> Frozen core approximation. <sup>c</sup> Calculated at the MP2/6-31G\*\* minimized geometry.

**TABLE 2: Bond Lengths (Å), Dipole Moments,  $\mu$  (in Debye), and Static Hyperpolarizability,  $\beta_0$  ( $\times 10^{-30}$  esu), Values of Molecule 2 Computed Using Various Methods**

method	R12	R23	R34	R45	$\mu_x$	$\beta_0$
HF/6-31G**	1.537	1.507	1.587	1.292	17.7	4.7
MP2//6-31G** <sup>b</sup>	1.545	1.489	1.628	1.296	16.7	14.9 <sup>a</sup>
MP2/6-31G**	1.542	1.487	1.625	1.296	16.7	14.8 <sup>a</sup>
AM1 (TDHF)	1.528	1.477	1.656	1.284	16.2	45.1
ZINDO (SOS) <sup>c</sup>					20.8	3.6

<sup>a</sup>  $\beta_{xxx}$  calculated using Finite Field method. <sup>b</sup> Frozen core approximation. <sup>c</sup> Calculated at the MP2/6-31G\*\* minimized geometry.

thus they interact with the orbitals of the oxygen functional groups in an antisymmetric fashion and this weakens the bond and elongates it as observed in the table.<sup>26</sup> As it is well-known, the electron correlation amplifies the TBI, and thus the MP2 predicts an even slightly longer bond length for this bond.<sup>34</sup> The R12 is predicted to be 0.03 Å shorter by MP2. The C–O bond length is predicted to be the same by both the methods and thus unaffected by electron correlation. The dipole is reduced to  $\sim 14$  D in the MP2 calculation, while in the HF it was about 18 D. Reduction of dipole in the MP2 calculations is because the RHF theory overestimates bond polarities for dipolar species, and inclusion of the electron correlation reduces it.<sup>36</sup> In Table 2, which gives the values for molecule **2**, the geometry again is predicted to be in the same lines as molecule **1**. The bond R34 is lengthened by a similar amount. The dipole reduces only a little, when calculations are carried out at the MP2 level. The R12 bond lengths are longer for molecule **2** because of less covalent interactions.

The calculated hyperpolarizability components,  $\beta_{xxx}$ , of the molecules show an interesting trend. Molecule **1**, at HF/6-31G\*\* shows a  $\beta_{xxx}$  value of  $28 \times 10^{-30}$  esu, which is only 50% smaller than the  $\beta$  of dimethylamino-nitro stilbene (DANS) obtained using similar basis set.<sup>5</sup> The dipole is very large here, nearly double of DANS, which means that the  $\mu \cdot \beta$  values are approximately same. The MP2 value is nearly 9 times larger than the value calculated at HF level. Hyper Rayleigh scattering (HRS) results for nonzwitterionic but  $\pi$ - $\sigma$ - $\pi$ -conjugated DA molecules show very large  $\beta$  indicating that the electron correlation included calculations may be closer to the experimental values.<sup>37</sup> Recent electron correlation computations on *p*-nitroaniline show that the hyperpolarizability value by MP2 methods is nearly double that of the value obtained at the HF level.<sup>5</sup>

Molecule **2** has a large dipole moment but at the HF level has a  $\beta_0$  value of only  $4 \times 10^{-30}$  esu. This drastic reduction is explained by the OITB model that in molecule **2**, there is no  $\pi$ -orbital on the acceptor for interaction with the  $\sigma$ -orbital (*vide supra*). The MP2 calculated value, though enhanced, is only  $14 \times 10^{-30}$  esu. Semiempirical AM1 Hamiltonian (TDHF) results for molecule **1** seem to be in agreement with the ab initio values, but in molecule **2** they are slightly overestimated. For comparison, MP2 minimized geometry was used to calculate



**TABLE 3: Excited States Contributions To  $\beta_0$  in Molecule 1 Calculated Using ab Initio CIS at 6-31G\*\* Level**

transition	$\Delta E$ (eV)	$\lambda$ (nm)	$f$	major component	$C_i$
1 $\rightarrow$ 2	3.57	347	0.134	HOMO-1 $\rightarrow$ LUMO	0.69
1 $\rightarrow$ 3	3.64	340	0.025	HOMO $\rightarrow$ LUMO	0.70
1 $\rightarrow$ 4	6.50	191	0.015	HOMO-1 $\rightarrow$ LUMO+1	0.66
1 $\rightarrow$ 5	6.82	182	0.001	HOMO $\rightarrow$ LUMO+1	0.66

**TABLE 4: Excited States Contributions to  $\beta_0$  in Molecule 2 Calculated Using ab Initio CIS at 6-31G\*\* Level**

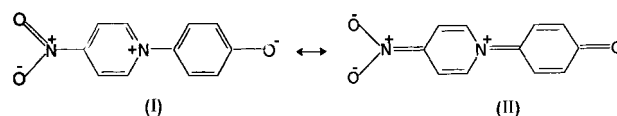
transition	$\Delta E$ (eV)	$\lambda$ (nm)	$f$	major component	$C_i$
1 $\rightarrow$ 2	5.64	220	0.068	HOMO-1 $\rightarrow$ LUMO	0.69
1 $\rightarrow$ 3	5.77	215	0.000	HOMO $\rightarrow$ LUMO	0.69
1 $\rightarrow$ 4	7.30	170	0.023	HOMO-1 $\rightarrow$ LUMO+3	0.51
1 $\rightarrow$ 5	7.41	167	0.026	HOMO $\rightarrow$ LUMO+3	0.58

the static  $\beta$  value by SOS method implemented in ZINDO program. The  $\beta_0$  value of molecule **1** calculated by the SOS method is in the same order of magnitude as predicted by MP2. In molecule **2**, it drops to a very small value. The trend is very much in the line with the HF/MP2 – FF calculations.

To analyze the  $\beta$  in terms of the energy of transition, oscillator strength, and the major coefficients of the vectors, transitions have been computed using ab initio CIS which are shown in Tables 3 and 4 for molecules **1** and **2**, respectively. The major transition for molecule **1** occurs at 347 nm and has a large change in dipole moment. The oscillator strength is also quite large indicating that the majority of the  $\beta_{xxx}$  contribution is from this transition. At the MO level, this corresponds to a HOMO-1 to LUMO charge transfer. The HOMO is localized more on the donor and the LUMO on the acceptor and the HOMO–LUMO is the second transition. In the case of molecule **2**, the absence of  $\pi$ – $\sigma$ – $\pi$  conjugation is reflected in the forbidden transition between the HOMO and the LUMO and a weak transition from HOMO-1 to LUMO, and hence smaller  $\beta_0$  values are obtained (Table 4). While both the model molecules chosen for electron correlation study can only be an approximation for the other molecules, **3–17** (Figure 2), it serves the purpose of showing that the absence of  $\pi$ – $\sigma$ – $\pi$  conjugation decreases the hyperpolarizability. The molecules with a double bond in the middle, i.e.,  $\text{NH}_3^+ - \text{CH}=\text{CH} - \text{O}^-$  and  $\text{CH}_2=\text{NH}^+ - \text{CH}=\text{CH} - \text{O}^-$  shows very small  $\beta_0$  values (not indicated in the Tables). This is to be expected as the ground-state resonance decreases the charges on both the D and A.

**3.2 Molecular Hyperpolarizability.** Donor–acceptor substituted biphenyls show diminishing  $\beta_0$  when the phenyl rings are rotated with respect to each other. This is because of a decrease in conjugation when the phenyl rings are at an angle greater than  $0^\circ$ .<sup>38</sup> In contrast, in merocyanines and quinopyrans when the aromatic rings are rotated with respect to each other,  $\beta_0$  increases and the value, when the aromatic rings are nearly perpendicular to each other, is as large as  $353 \times 10^{-30}$  esu.<sup>17–18</sup> This has been attributed to the aromatic stabilization of the resultant pyridinium(pyrylium) and phenolate ions where the charge separation has taken place. A similar behavior is expected in a heterocyclic betaine, molecule **3** (Figure 2).

Two major resonance forms of a *p*-substituted betaine, molecule **4**, are shown in Figure 3 as an example. In the twisted conformation, the type **I** form dominates. Generally, betaines with or without *p*-substitution prefer the twisted form, and the bond length of the linking C–N<sup>+</sup> bond is 1.424 Å, which is a single bond. Because of a charge separation in the ground state even in an unsubstituted betaine large static  $\beta$  values are obtained, like the value of  $89.4 \times 10^{-30}$  esu for molecule **3** as shown in Table 5. The value is further enhanced with the

**Figure 3.** Resonance forms of molecule **4**.**TABLE 5: Dipole Moments  $\mu$  (Debye) and  $\beta_0$  ( $\times 10^{-30}$  esu) Values of Molecules (**3–17**) Calculated at HF/6-31G\*\* Level**

molecule	$\mu$	$\beta_0$	molecule	$\mu$	$\beta_0$
<b>3</b>	15.3	89.4	<b>11</b>	16.1	156.7
<b>4</b>	4.2	140.0	<b>12</b>	0.8	14.2
<b>5</b>	27.8	143.8	<b>13</b>	20.4	47.3
<b>6</b>	21.4	1604.0	<b>14</b>	17.8	278.7
<b>7</b>	31.9	241.6	<b>15</b>	22.9	558.7
<b>8</b>	26.3	3960.0	<b>16</b>	4.3	262.0
<b>9</b>	33.8	818.7	<b>17</b>	27.7	337.2
<b>10</b>	18.8	2842.9			

*p*-substitution, molecule **4** (Table 5), because of the greater charge separation in the dominant resonance form **I** in this molecule. In general, molecules (such as the ones shown in Figure 2) with the resonance form **I** as the dominant one would show large hyperpolarizabilities. It should be noted that unlike the betaines the planar quinopyrans or merocyanines have a ground-state resonance form where there is no charge separation at all (quinonidal), and hence these unsubstituted heterocycles show very small static  $\beta$  values.<sup>17–18</sup> Insertion of spacer, which breaks the conjugation in quinopyran (merocyanine) or gives a greater charge separation in the betaine, should show a large NLO response. Thus, molecule **5** in Figure 2 shows an enhanced  $\beta_0$  value of  $\sim 143 \times 10^{-30}$  esu. Molecule **9** which has pyridinium and phenolate rings linked by a  $\sigma$ -spacer shows a larger enhancement of the  $\beta_0$ , i.e.,  $818 \times 10^{-30}$  esu. This can be explained by noting that in molecule **9** there is a greater charge separation and a larger change in dipole moment. In molecule **6**, where in the *p*-position a  $\text{NO}_2$  functional group is attached, the intensity of the transition increases and the computed static  $\beta$  value of this molecule is around  $1604 \times 10^{-30}$  esu, which is around 10 times the value of the unsubstituted molecule **5**.

Introducing a double bond between the directly linked betaine, molecule **11**, shows an increase in the static  $\beta$  value because the dominant resonance form would be zwitterionic with charges localized on both the aromatic rings. Substitution of the  $\text{NO}_2$  group in the *p*-position of the acceptor, as in molecule **12**, brings down the NLO response drastically to  $14 \times 10^{-30}$  esu due to the domination of the resonance form, type **II** in the ground state.

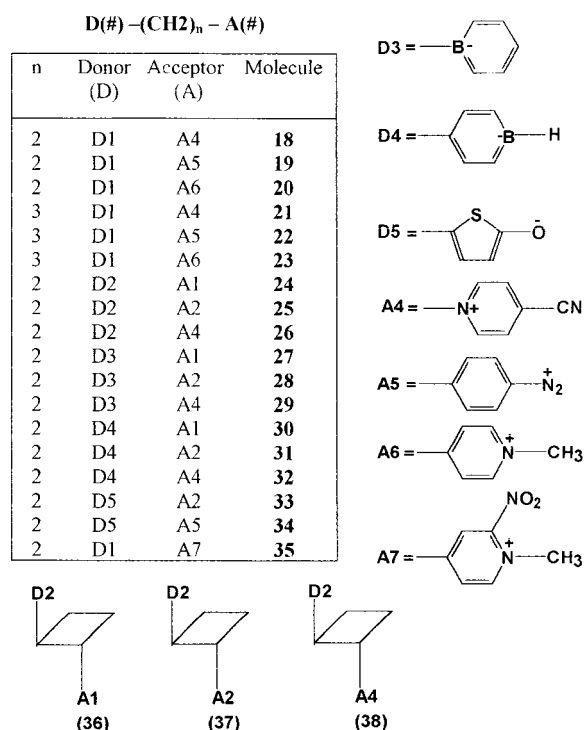
To understand the effect of reduced TBI on hyperpolarizability, we calculated the NLO response of molecules **13** and **14** where the  $\sigma$ -spacer is a cyclobutane. The  $\pi$ -orbitals of the functional groups have less interaction with the  $\sigma$ -orbitals. The results are as expected, i.e., a general reduction of the  $\beta_0$  value in both molecules, nevertheless in the order of magnitude of DANS in one case, and in the *p*-substituted molecule it is around 4 times of DANS. The chain length of the spacer is varied to study its effect on  $\beta_0$  by changing the number of  $\text{CH}_2$  moieties. When the value of *n* is 1, with an acceptor A2 the bond elongates and breaks; hence, this case is not indicated in the tables. Increasing the  $\sigma$ -chain length to three bonds enhances both the  $\beta_0$  and the  $\mu$ . This is reflected for example in the results of molecules **5** and **7** and **6** and **8**. The value of  $\beta_0$  of molecule **8** is close to  $3900 \times 10^{-30}$  esu, more than double of molecule **6**. Increasing the chain length beyond *n* = 3 for donor D1 and acceptor A2, a general decrease of  $\beta_0$  is observed, and hence studies for *n* > 3 are not carried out. Replacing the D group by

a different donor, cyclopentadienyl anion (donor D2), the  $\beta_0$  value is only slightly decreased, as seen in the table for molecule **10**.

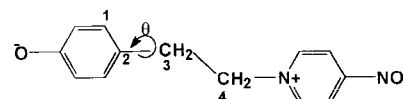
We have also considered a phenyl ring itself as a spacer linking the acceptors A1/A2 and donor D1. Recent experimental studies using one or more thiophene based spacers between *N*-alkylpyridinium acceptor and a negatively charged dicyanomethanide donor enhanced the hyperpolarizability, and a value of  $27000 \times 10^{-48}$  esu was obtained for  $\mu\beta$ , while another study combining similar fragments and different substitutions yielded a value of  $13450 \times 10^{-48}$  esu.<sup>39</sup> Theoretical calculations of the full planar case, molecule **15**, yields a very high  $\beta_0$  value of  $\sim 558 \times 10^{-30}$  esu, but adding an NO<sub>2</sub> group to *p*-position of the acceptor, the value comes down to around  $262 \times 10^{-30}$  esu. This is because the resonance form of molecule **15** is dominated by the charge separated form type **I**, but in the case of molecule **16**, the type **II** form is more dominant. Slightly twisting the molecule, using steric repulsions, by placing methyl groups on the spacer enhances the response as shown in the table for molecule **17**. Thus, a break in conjugation in the molecule increases the contribution of type **I** resonance form. Another interesting result is that substituting NO<sub>2</sub> in molecule **15**, to get molecule **16**, the dipole drops from 22.9 D to 4.3 D. Thus designing molecules with large-to-small dipole moments along with the tunability of hyperpolarizabilities is an attractive feature in these type of chromophores.

The transitions in molecule **5** and **6** have been analyzed using ab initio CIS (Tables 6 and 7). The first transition in molecule **5** has an *f* value of 0.124 when compared to the value of 0.307 in molecule **6**. Roughly, this has scaled by three times when an electron-withdrawing group is attached to the acceptor. The wavelength of the first transition shows a red-shift upon substitution. It is clear that the higher oscillator strength and the lower energy of the dominant transition in molecule **6** is responsible for the enhancement in NLO response. At the MO level, the primary transitions correspond to the HOMO-LUMO CT in both molecules. A very interesting aspect is that molecule **6** shows first transitions in the IR, and then the next allowed ones only at 433 nm, around 500 nm lower, i.e., there is a large gap between the transitions. This leaves a fairly large transparent window in the visible region, and with the large  $\beta_0$  values they possess these molecules could be ideal candidates for SHG. If these molecules are considered as two subfragments, the donor ring and the acceptor ring, then the lower energy transition between the two rings upon forming a single molecule is the primary transition. This is followed by the high-energy transitions in the fragments (intraring).<sup>17-18</sup> Unlike the transitions in molecule **6**, molecule **5** has a smaller window between the interring transition and intraring transitions.

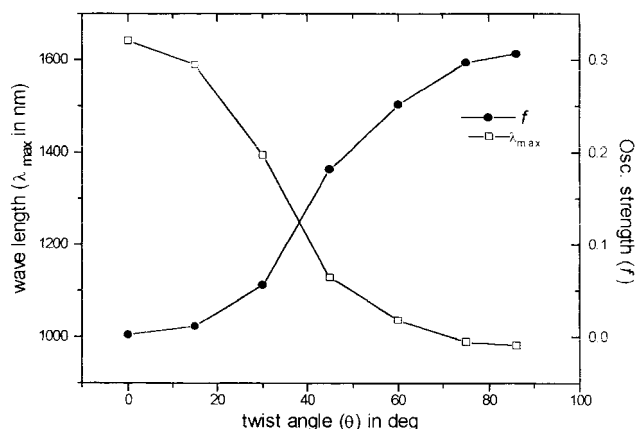
To understand the effect of  $\sigma-\pi$  mixing on the oscillator strength and  $\lambda_{\max}$ , we rotated the D group in molecule **6** at equal intervals from its HF/6-31G\*\* minimized geometry as shown in Figure 5. Further minimization was not carried out and at each angle the unoptimized geometry was used to estimate the *f* and CT using ab initio CIS. The variation of *f* and  $\lambda$  with the twist angle is shown in Figure 6. As the  $\sigma-\pi$  mixing decreases, the  $\lambda_{\max}$  shifts to a longer wavelength and the *f* weakens. In other words, the oscillator strength and the  $\lambda_{\max}$  bear an inverse relationship. In terms of tunability, it means that increasing TBI in the molecule would shift the  $\lambda_{\max}$  to a shorter wavelength and the *f* to higher intensities and this would enhance the  $\beta_0$  value. It should be noted here at  $\sim 90.0^\circ$ , the TBI is maximum. The *f* values, along with  $\lambda_{\max}$  calculated using ab initio CIS at the HF/6-31G\*\* optimized geometry for molecules **3-17**, are



**Figure 4.** The molecules considered for static  $\beta_0$  calculation at HF/6-31G level.



**Figure 5.** Rotation of the donor ring in molecule **6**.



**Figure 6.** Variation of *f* and  $\lambda_{\max}$  as a function of the twist angle  $\theta$ , in molecule **6**.

**TABLE 6: Excited States Contributions to  $\beta_0$  in Molecule 5 Calculated Using ab Initio CIS at 6-31G\*\* Level**

transition	$\Delta E$ (eV)	$\lambda$ (nm)	<i>f</i>	major component	$C_i$
1 → 2	2.18	569	0.124	HOMO → LUMO	0.70
1 → 3	3.28	378	0.000	HOMO → LUMO+1	0.70
1 → 4	5.00	248	0.006	HOMO-1 → LUMO	0.68
1 → 5	5.23	237	0.120	HOMO → LUMO+6	0.65
1 → 6	5.52	225	0.000	HOMO-2 → LUMO	0.66

shown in Table 8. As observed earlier in molecules **5** and **6**, here also stronger resonance due to the withdrawing group enhances the *f* and increases the  $\lambda_{\max}$ . Molecule **16** shows a very high *f* and a low energy CT, but the  $\beta_0$  value is not in the order of magnitude of molecule **15**. This is because the resonance form **II** dominates in this planar molecule and the

**TABLE 7: Excited States Contributions to  $\beta_0$  in Molecule 6 Calculated Using ab Initio CIS at 6-31G\*\* Level**

transition	$\Delta E$ (eV)	$\lambda$ (nm)	$f$	major component	$C_i$
1 $\rightarrow$ 2	1.26	983	0.307	HOMO $\rightarrow$ LUMO	0.70
1 $\rightarrow$ 3	2.87	433	0.000	HOMO $\rightarrow$ LUMO+1	0.70
1 $\rightarrow$ 4	3.96	313	0.001	HOMO-1 $\rightarrow$ LUMO	0.70
1 $\rightarrow$ 5	4.39	282	0.000	HOMO-2 $\rightarrow$ LUMO	0.68
1 $\rightarrow$ 6	4.92	252	0.021	HOMO $\rightarrow$ LUMO+2	0.68

**TABLE 8: Oscillator Strengths,  $f$ , and  $\lambda_{\max}$  (in nm) of Molecules (3–17) Calculated Using ab Initio CIS at the HF/6-31G\*\* Minimized Geometry**

molecule	$\lambda_{\max}$	$f$
3	395	0.629 <sup>a</sup>
4	426	1.406 <sup>a</sup>
5	569	0.124
6	983	0.307
7	720	0.085
8	1391	0.342
9	780	0.279
10	1247	0.403
11	417	1.642 <sup>a</sup>
12	420	2.228 <sup>a</sup>
13	479	0.095
14	751	0.154
15	483	1.987 <sup>a</sup>
16	506	2.978 <sup>a</sup>
17	1014	0.034 <sup>a</sup>

<sup>a</sup> These values are for non- $\sigma$ -bonded DA molecules.

**TABLE 9: Dipole Moments  $\mu$  (Debye) and  $\beta_0$  ( $\times 10^{-30}$  esu) Values of Molecules (18–38) Calculated at the HF/6-31G Level**

molecule	$\mu$	$\beta_0$	molecule	$\mu$	$\beta_0$
18	23.9	1063.6	28	14.2	187.5
19	30.9	2490.8	29	15.3	6.0
20	34.4	515.7	30	24.5	121.7
21	28.0	2629.9	31	16.2	2218.2
22	32.4	2853.9	32	19.6	812.8
23	36.2	821.7	33	19.3	1663.9
24	20.7	111.1	34	30.3	2365.0
25	12.2	1624.7	35	25.6	1833.8
26	15.7	686.6	36	13.7	40.6
27	19.8	15.1	37	9.6	175.3
			38	10.7	101.3

primary transition is due to the spacer phenyl ring donating electron to the  $N^+$  of the acceptor. This short-range transfer does not proceed with a large change in dipole moment,  $\Delta\mu$ , is only 5 D.

Calculations of the static  $\beta$  using the HF/6-31G basis set for molecule 5 yields a value of  $158.7 \times 10^{-30}$  esu as compared to the value  $143.8 \times 10^{-30}$  esu with basis set 6-31g\*\*, a change of hardly around 10%. The basis set effect in the *p*-substituted molecules could be slightly larger, but nevertheless a general trend can be obtained with the lower basis. Keeping in view the computer time saving, for the molecules shown in Figure 4, we used the lower basis set, and the results are tabulated in Table 9. The variation of  $\beta_0$  and  $\mu$  with respect to the change in D and A, along with the change in spacers can be inferred from this table. Replacing the electron withdrawal function group with -CN we see a general decrease in the static  $\beta_0$  value, while the dipole moments are slightly larger. This is attributed to the electron withdrawing capacity of the -CN group which is less than in the functional group -NO<sub>2</sub>. To analyze the effect of a heteroatom in the ring, we have used a boron atom. This would retain the aromaticity of the ring and yet have excess electrons (donors D3 and D4). In fact, boro stilbenes have been suggested as NLO materials recently since they show fairly large

NLO response.<sup>40</sup> Thus, when the heteroatom in the donor ring is a boron directly linked to the  $\sigma$ -bond, then the  $\beta_0$  decreases drastically for molecules 27 and 29, while in molecule 28 the enhancement is only one-tenth of that seen in molecule 6. In the case of the boron atom not linked directly to the  $\sigma$ -framework like molecules 30, 31, and 32, there is a general increase in the NLO response. The dipole moments do not vary appreciably except for molecule 30, which has a slightly large value. Purely for the purpose of estimating  $\beta_0$  when the electron deficient acceptor is attached *para* to the aromatic ring the reactive group  $N_2^+$  was used (A5 in Figure 4). The effect of this change in  $\beta$  is very large as seen in molecules 19, 22, and 34. The dipole moments are also large here. This would mean that if the length of the zwitterionic molecule were increased a larger  $\beta_0$  would be obtained. The rest of the molecules follow a general variation with the strength of the D and A along with their overlap with the central bond playing the pivotal role. One other interesting result is seen for the molecule 35, which shows an increase in the NLO response in *m*-substitution.

#### 4. Conclusions

Strong IR absorbers with high oscillator strength find applications in filters, polarizers, optical recording, etc. Designing chromophores with enhanced NLO response in this region of electromagnetic radiation is of current interest in view of the potential applications. Previous studies on zwitterions such as heterocyclic betaines or quinopyrans show that with a break in the conjugation pathway between the aromatic rings large hyperpolarizability is obtained due to low energy charge transfer. It was also demonstrated that by insertion of a  $\sigma$ -pathway between the rings enhanced NLO response is achieved.

In this work we have studied, using ab initio CPHF methods, zwitterionic molecules with electron withdrawing functional groups on the acceptor ring of the above-mentioned heterocyclic molecules. The NLO response is enhanced 10–15 times when compared to response in the molecules without the functional groups. In addition, they also show large dipole moments which can be manipulated by substitution. The static  $\beta_0$  values so obtained, to the best of our knowledge, are the highest reported in the literature, in these types of molecules, using the ab initio CPHF formalism. These chromophores also offer an attractive feature like tunability of the NLO response, the dipole moments, and the range of absorption.

Analysis of the hyperpolarizability reveals that the charge separation stabilized by the benzenoid character in the ground state is responsible for this large NLO response, while the through bond interaction arising due to the  $\sigma$ - $\pi$  mixing between the functional groups and the  $\sigma$ -spacers plays the role of a pathway in the excited state. MP2 studies on small molecules show that the effect of electron correlation enhances the NLO response when the through bond interaction is involved.

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