Heterocycle-Based Isomeric Chromophores with Substantially Varying NLO Properties: A New Structure−Property Correlation Study

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A number of heterocycle-based aromatic and quinonoid molecular systems have been considered for the theoretical study of their electric response properties. The nonlinear optical (NLO) parameters have been calculated by using the ab initio MO and DFT methods. An approximate scheme for calculating the first hyperpolarizability (β) and second hyperpolarizability (γ) in the framework of the sum-over-state (SOS) method have been proposed by exploiting the generalized Thomas−Kuhn sum rule (TK-SR). The NLO properties in the present scheme can be evaluated solely from the ground-state dipole moment (μ) and linear polarizability (α) and have been found to correlate fairly with the ab initio calculated values. The approximate scheme can be reasonably used to explain the wider range of variation of higher-order polarizabilities in terms of the above quantities. The position of the N atom in the thiazole ring at the ortho position (versus meta position) to the acceptor increases β and decreases γ for aromatic compounds, while the reverse trend is found with quinonoid compounds. In the case of the pyridine ring, the shifting of the N atom toward the acceptor enhances γ, with insignificant variation of β predicted for both the aromatic and quinonoid molecules. The negative contribution of the cubic polarizability of the quinonoid species increases linearly with α^2/mean transition energy (ΔE).

1. Introduction

Compounds[1–15] having heterocycle rings as a structural motif received overwhelming attention in the field of nonlinear optics (NLO) due to their relative ease of synthesis and varying degree of polarity. Moreover, different heterocycle rings can modulate the NLO responses differently when placed at identical structural sites. The variation of electric response properties coming out of different heterocycle-based chromophores had accounted for the reduced ring aromaticity,[1] the different ring charge density[2,6] due to the varying position of heteroatoms in the ring, the orientation of the ring dipole moment,[14] and the variable longitudinal charge-transfer interaction due to the auxiliary[2,6,12] electron donor/acceptor nature of the ring while attached to a donor/acceptor group. On the basis of such an analysis, heterocycle rings can be properly chosen while designing potential NLO-phores. Moreover, the theoretically calculated value of NLO properties depends largely on the methods employed. However, for a structurally related series of molecules, the general trend and structure−property correlations in the gas phase can be achieved satisfactorily with a given method. The absolute value of the hyperpolarizabilities, however, depends largely on the extent of inclusion of electron correlation treatment and also the solvent effect, which are essential while comparing with the experimental results.

Since its inception, the SOS scheme[16,17] has grown increasingly popular because of chemical interest as it can directly relate NLO responses to the spectroscopic property of an individual molecule. However, calculation of the hyperpolarizabilities using this scheme needs huge computational resources, especially for larger molecular systems. In this respect, the two-state model (TSM)[18,19] of β (the simplest SOS expression) has frequently been used to interpret the variation of the first hyperpolarizability of push−pull molecular systems[20–24] rather qualitatively. Likewise, the second hyperpolarizability approximated[24] as the two-state term and the two-photon term has been used to explain the variation of γ, especially the origin of its negative value. The acceptability of the TSM was amply illustrated in the linear correlation between the log β versus log η plots obtained for many push−pull molecular systems, where 2η refers to the HOMO−LUMO energy gap. Recently, we obtained simplified SOS expressions[25] for calculating the higher-order NLO properties, which showed a fair degree of correlation with the MP2-calculated values. In that work, the higher-order terms in the SOS expression of NLO coefficients were approximated as the one-electron multipole moments. In the present investigation, we have attempted to transform the higher-order terms (many-photon terms) of the commonly used SOS expressions into the lower-order terms (one-photon terms) and intended to find a useful structure−property correlation for the chosen molecular systems solely in terms of simple ground-state properties.

The generalized Thomas−Kuhn sum rules (TK-SR)[26–28] in conjunction with the closure approximation of the mean excitation energy will be used to reduce the octopolar part of the second-order polarizability (β) and the hexadecapolar and octopolar parts of the third-order polarizability (γ) into the corresponding lower-order terms. To test the applicability of the present model expressions of the NLO properties, we have considered four structurally different series of model chromophores, set 1 [**I** (a−f) and **II** (b,c,e,f)], set 2 [**III** (a−f) and **IV** (b,c,e,f)], set 3 [**V** (a−f) and **VI** (b,c,e,f)], and set 4 [**VII** (a−f) and **VIII** (b,c,e,f)] (Scheme 1), which are isomers to each other and have an identical length of conjugation. So far, to

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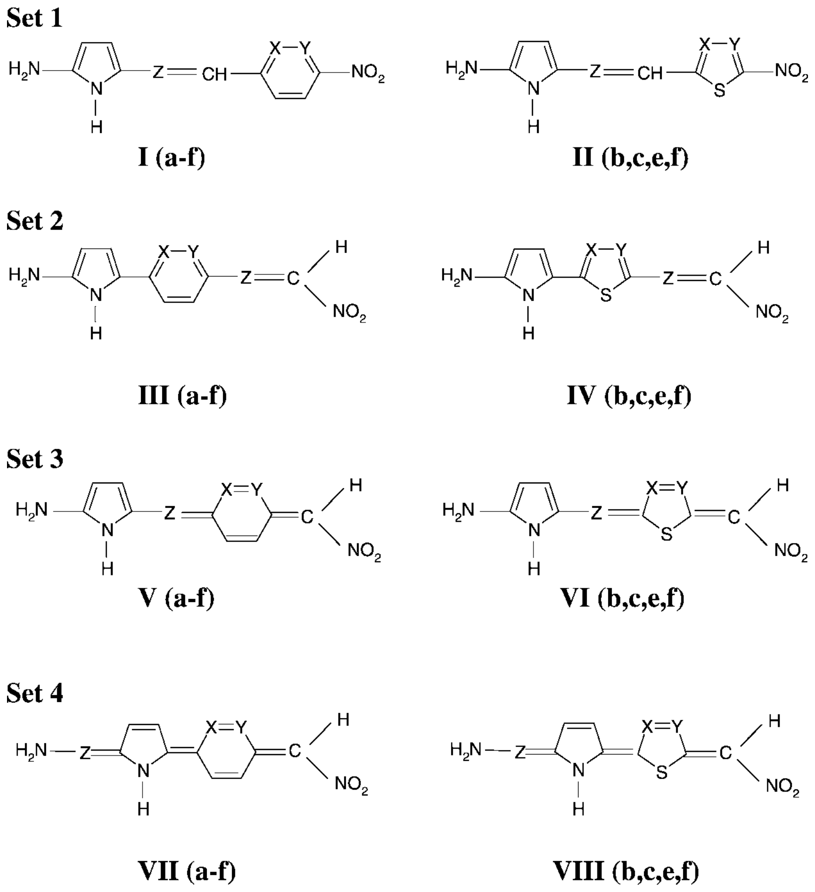
SCHEME 1



(a) X=CH Y=CH Z=CH (d) X=CH Y=CH Z=N

(b) X=N Y=CH Z=CH (e) X=N Y=CH Z=N

(c) X=CH Y=N Z=CH (f) X=CH Y=N Z=N

our knowledge, no experimental investigations of the chosen molecules had been carried out, while only a very few theoretical calculations of β were done for molecules **I**a[1,2] and **II**c.[1] These theoretical studies considered quite a large number of stilbene-like model chromophores constructed with various heterocycle rings to illustrate the nature of the influence of different rings on β. In the present investigation, we have considered benzene, pyrrole, pyridine, and thiazole rings along with the N atom with varying positions in the last two rings. The molecules of the first two sets (I–IV) contain aromatic rings, the third set (V and VI) consists of both aromatic and quinonoid rings, while the fourth set (VII and VIII) has both rings in the quinonoid form. The NLO properties of these species have been calculated at the ab initio HF level analytically and at the B3LYP level numerically using the finite-field (FF) scheme.[29,30] The present DFT method accounts for the exchange and correlation effects by using the hybrid exchange-correlation functional (Becke + Slater + HF exchange and LYP + VWN5 correlations).[31–33] It will be interesting to examine the large structural variations on the response properties of the molecules (Scheme 1) designed for theoretical interest.

2. Theoretical and Computational Details

2.1. Electronic Structure and Properties. The ground-state equilibrium structure of the selected molecules (Scheme 1) were optimized at the HF level with the 6-31G** basis set and at the B3LYP level with the 6-31G** basis set. The fully optimized structure (quasi-planar) having the NH$_2$ group slightly out of plane (N atom making a dihedral angle of ~175 °) has an energy lower than that of the planar structure by about 1.5–2.0 kcal/mol (for aromatic molecules in sets 1 and 2) and 0.2–1.0 kcal/mol (for quinonoid molecules in sets 3 and 4). Each molecule (Scheme 1) was obtained as an energy minimum on the potential energy hypersurface, as confirmed by real frequencies of all normal modes of vibration. Since, in the present study, we are not primarily interested in the effect of conformational changes on the NLO properties of molecules, the planar structure has been taken for comparison at equal footing. However, as a supplement to this problem, additional hyperpolarizability calculations at the B3LYP level were also performed for a fewer number of molecules from each set at the quasi-planar structure.

The static linear and nonlinear polarizabilities of each molecule were computed analytically at the CPHF/6-31G**//HF/6-31G** level and using the finite-field (FF) scheme at the B3LYP/6-31+G*//B3LYP/6-31G** level. The DFT-calculated components of the NLO parameters showed fair agreement between the values obtained from the field-perturbed energy and dipole moment of the molecules. All calculations were done

TABLE 1: The HF/6-31G//HF/6-31G** and B3LYP/6-31+G*//B3LYP/6-31G** Calculated Mean Excitation Energy (ΔE, eV), Ground-State Dipole Moment (μ, D), and Static Linear and Nonlinear Optical Parameters[a] for Molecules in Scheme 1**

	SCF					B3LYP				
	ΔE	μ_x	α_{xx}	β_{xxx}	γ_{xxxx}	ΔE	μ_x	α_{xx}	β_{xxx}	γ_{xxxx}
Ia	19.07	8.86	4.87	70.34	583.1	15.4	11.89	8.12	228.99	1221.1
Ib	19.13	8.89	4.93	80.57	623.6	15.46	12.16	8.18	218.5	889.8
Ic	19.35	10.35	4.73	67.79	558.7	15.67	13.41	7.84	215.53	1215.7
Id	19.56	7.3	4.53	67.08	582.2	15.48	10.87	8.07	229.78	1181.1
Ie	19.67	7.26	4.57	77.92	645.8	15.54	11.22	8.12	219.44	853
If	19.86	8.86	4.4	65.08	557.5	15.78	12.51	7.76	211.75	1169
IIb	18.83	9.24	4.77	74.02	518.7	15.37	12.51	7.74	147.83	416.2
IIc	19.05	9.34	4.59	68.94	552.1	15.21	13.18	7.93	173.9	320.1
IIe	19.29	7.66	4.44	73.09	545.8	15.56	11.53	7.47	129.94	378.5
IIf	19.54	7.99	4.27	65.26	535.2	15.37	12.3	7.79	166.64	270.9
IIIa	19.18	9.28	4.8	68.41	559.8	15.56	12.08	7.89	226.27	1201.8
IIIb	19.24	9.18	4.81	72.12	543.9	15.7	11.86	7.82	213.09	1038.1
IIIc	19.59	10.24	4.49	60.24	511.1	15.86	13.05	7.52	216.51	1320.1
IIId	19.54	8.7	4.57	68.62	565.9	15.54	12.06	8	252.22	977.8
IIIe	19.62	8.62	4.58	71.92	550.1	15.7	11.86	7.89	238.39	873.2
IIIf	20.03	9.91	4.25	58.57	492.2	15.95	13.1	7.52	243.52	1237.6
IVb	19.05	9.02	4.66	58.48	414.2	15.65	11.77	7.42	148.35	643.9
IVc	19.29	8.69	4.47	65.12	538.2	15.35	12.65	7.83	178.43	423.4
IVe	19.35	8.01	4.5	63.93	456.2	15.56	11.67	7.61	161.55	405.1
IVf	19.7	7.92	4.22	66.52	557.5	15.29	12.78	7.99	182.26	106.9
Va	16.71	13.25	7.38	83.63	318.8	14.5	16.99	9.75	66.2	−256.6
Vb	16.87	10.4	7.15	90.12	336	14.67	15.38	9.48	57.96	−269.9
Vc	16.93	15.05	7.18	66.08	210	14.72	18.09	9.45	56.66	−218.5
Vd	16.93	9.71	7.23	135.31	719	14.34	15.37	10.16	73.99	−358.6
Ve	16.49	9.13	7.77	173.6	679.5	14.48	15.55	9.99	56.14	−363.3
Vf	16.85	11.87	7.38	123.58	486.5	14.48	16.73	9.92	60.61	−312
VIb	17.58	9.09	6.05	89.2	543.7	14.86	14.17	8.71	66.96	−148.1
VIc	17.82	12.86	5.89	52.74	288.9	15.1	16.09	8.35	44.34	−65.7
VIe	18.15	6.23	5.63	106.19	775.6	14.78	12.83	8.97	72.04	−237.4
VIf	18.12	10.1	5.69	78.76	481	14.94	14.8	8.7	54.15	−194.5
VIIa	15.92	17.71	8.47	−37.66	−126.4	14.07	19.31	10.59	−40.49	−365.4
VIIb	15.84	16.95	8.66	−36.32	−251.4	14.23	18.97	10.4	−39.28	−421.5
VIIc	16.6	19.31	7.65	−38.48	−0.9	14.45	20.28	9.97	−33.02	−254.4
VIId	16.46	12.22	7.88	−2.55	−25.3	14.18	14.67	10.51	−13.37	−303.9
VIIe	16.46	10.98	7.94	9.04	−80.1	14.34	14.31	10.31	−11.24	−323.9
VIIf	17.06	14.2	7.22	−12.45	25.2	14.56	15.83	9.9	−10.39	−203.9
VIIIb	16.54	13.14	7.17	33.18	102.6	14.42	17.27	9.4	−0.89	−170.5
VIIIc	17.17	17.69	6.4	−9.27	62	14.75	19.25	8.73	−16.7	−76.6
VIIIe	17.33	8.72	6.46	34.42	155.6	14.56	13.08	9.29	16.09	−121.3
VIIIf	17.71	13.37	6.01	2.41	84.1	14.83	15.36	8.73	−1.32	−64.7

[a] Parameter: 1 au of μ = 2.5417 D, 1 au of $\alpha = 1.4817 \times 10^{-25}$ cm^3, 1 au of $\beta = 8.6392 \times 10^{-33}$ cm^4 stratvolt^{-1}, and 1 au of $\gamma = 5.0367 \times 10^{-40}$ cm^5 stratvolt^{-2}.

by using the GAMESS program.[34] The options ICUT = 20, ITOL = 30, and CONV = 1.0d − 7 were used in all of our calculations.

The first hyperpolarizability has generally been represented[21] as

$$\beta_{\text{vec}} = \sqrt{(\beta_x^2 + \beta_y^2 + \beta_z^2)} \qquad (1)$$

which is also known as β_{tot}. The axial component β_i has been calculated using the following expression

$$\beta_i = \beta_{iii} + \frac{1}{3}\sum_{j \neq i} (\beta_{ijj} + \beta_{jij} + \beta_{jji}) \qquad i,j \in (x,y,z) \qquad (2)$$

By using the Kleinman symmetry, β_i can also be expressed as

$$\beta_i = \sum_j \beta_{ijj}$$

It should be noted that the vector part of β (β_{vec}) as defined above may differ, in general, from the quantity $(\beta \cdot \mu)/|\mu|$ measured by EFISH experiments. The latter quantity should be identical to β_{vec} when the longitudinal charge transfer (CT) takes place parallel to the molecular dipole moment. However, β_{vec} is always positive, although the axial components (β_i) may be positive or negative. Since for the chosen molecules the dipole moment vector lies along the molecular x axis (see Table 1 in the text and also the Supporting Information), which is the direction of longitudinal CT, the major x component of linear and higher-order polarizabilities are reported only.

2.2. The Reduction of Orr−Ward−Bishop (OWB) SOS Scheme of Static NLO Coefficients. The following generalized Thomas−Kuhn sum rule (TK-SR),[26–28] which relates between the energy eigen values and the transition moments, has been used to simplify the standard SOS expressions

$$\sum_{n=g}^{\infty} \left(E_n - \frac{1}{2}(E_m + E_p)\right)\mu_{mn}\mu_{np} = \frac{\hbar^2 N_e}{2m_e}\delta_{mp} \qquad (3)$$

In eq 3, m_e is the mass of electron and N_e is the number of electrons of a molecule. The subscripts g refers to the ground state while m and p refer to the excited electronic states of the system. The above equation can also be written in au as

$$\sum_{n=g}^{\infty}(\Delta E_{nm}+\Delta E_{np})\mu_{mn}\mu_{np}=N_{\mathrm{e}}\delta_{mp} \tag{4}$$

where ΔE_{ij} stands for the energy difference, $(E_{\mathrm{i}}-E_j)$ between the states i and j. For $p = m$, eq 4 becomes

$$\sum_{n=g}^{\infty}\Delta E_{nm}|\mu_{mn}|^2=\frac{N_{\mathrm{e}}}{2}$$

which, upon separating the ground-state term from the summation and using $m = g$, takes the following form

$$\sum_{n\neq g}^{\infty}\Delta E_{ng}|\mu_{ng}|^2=\frac{N_{\mathrm{e}}}{2} \tag{5}$$

Now, using the SOS expression of linear polarizability (α) under the closure approximation of the transition energy (ΔE)

$$\alpha_{xx}=\frac{2}{\Delta E}\sum_{m\neq g}\mu_{gm}\mu_{mg} \tag{6}$$

eq 5 can be written as

$$\alpha_{xx}=\frac{N_{\mathrm{e}}}{\Delta E^2} \tag{7}$$

In the present work, we have calculated ΔE from the valence electrons (N_{v}) of molecules and the mean polarizability $\bar{\alpha}$ (=1/3($\alpha_{xx}+\alpha_{yy}+\alpha_{zz}$)) as follows.

$$\Delta E=\sqrt{\frac{N_{\mathrm{v}}}{\bar{\alpha}}} \tag{8}$$

It can be seen (Figure 1) that our B3LYP-calculated ΔE and the molecular hardness parameter ($\eta = 1/2(\varepsilon_{\mathrm{LUMO}}-\varepsilon_{\mathrm{HOMO}})$)[35] show good correlation. The stronger longitudinal charge-transfer (CT) interaction, in general, should be associated with smaller η and ΔE. The static axial component of SOS β under the closure approximation of the transition energy can be written as

$$\beta_{xxx}=\frac{6}{\Delta E^2}\left[\sum_{m\neq g}\mu_{gm}(\mu_{mm}-\mu_{gg})\mu_{mg}+\sum_{m\neq g}\sum_{n\neq m,g}\mu_{gm}\,\mu_{mn}\,\mu_{ng}\right]$$

which, upon rearrangement, takes the following form, where the μ_{ij} terms stand for the x component of the transition moment integrals between the states i and j and μ_{gg} (=μ_x) is the x component of the ground-state dipole moment

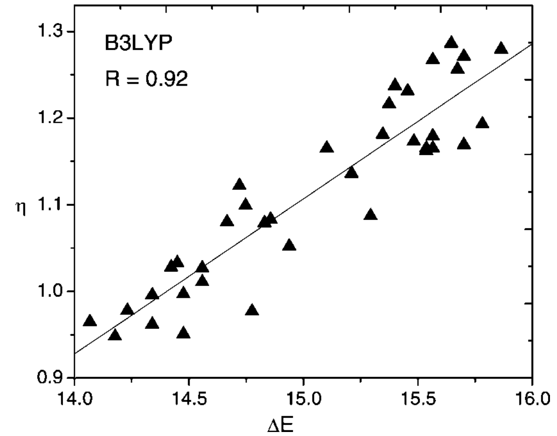


Figure 1. The plot of the B3LYP-calculated molecular hardness parameter (η, eV) against the mean transition energy (ΔE, eV) for the selected species.

$$\beta_{xxx}=\frac{6}{\Delta E^2}\left[\sum_{m\neq g}\sum_{n\neq g}\mu_{gm}\mu_{mn}\mu_{ng}-\mu_x\sum_{m\neq g}\mu_{gm}\mu_{mg}\right] \tag{9}$$

Now our task is to simplify the octopolar part (first term) of β_{xxx}. We start with eq 4 for $m \neq p$

$$\sum_{n=g}^{\infty}(\Delta E_{nm}+\Delta E_{np})\mu_{mn}\mu_{np}=0$$

$$\sum_{n\neq g}^{\infty}(\Delta E_{nm}+\Delta E_{np})\mu_{mn}\mu_{np}=-(\Delta E_{gm}+\Delta E_{gp})\mu_{mg}\mu_{gp}$$

$$\sum_{n\neq g}^{\infty}(\Delta E_{nm}+\Delta E_{np})\mu_{mn}\mu_{np}=(\Delta E_{mg}+\Delta E_{pg})\mu_{mg}\mu_{gp} \tag{10}$$

Assuming the energy difference between the states n and g, $(E_n - E_g) = \Delta E$, as the mean transition energy and expressing the other energy differences in terms of $\sigma\cdot\Delta E$ (where σ is a dimensionless parameter to be estimated using the TK sum rule) $(E_m + E_p) - 2E_n = \sigma\Delta E$ and $(\Delta E_{mg} + \Delta E_{pg}) = [(E_m - E_n) + (E_p - E_n) + 2(E_n - E_g)] = \{(E_m + E_p) - 2E_n\} + 2\,(E_n - E_g) = (\sigma + 2)\Delta E$, eq 10 can be written as

$$-\sum_{n\neq g}^{\infty}(\Delta E_{mn}-\Delta E_{np})\mu_{mn}\mu_{np}=(\sigma+2)\Delta E\mu_{mg}\mu_{gp}$$

$$-\sum_{n\neq g}^{\infty}\sigma\cdot\Delta E\mu_{mn}\mu_{np}=(\sigma+2)\Delta E\mu_{mg}\mu_{gp}$$

$$\sum_{n\neq g}^{\infty}\mu_{mn}\mu_{np}=-\frac{(\sigma+2)}{\sigma}\mu_{mg}\mu_{gp} \tag{11}$$

Multiplying by μ_{gm} and taking the summation over m on both sides of eq 11, one gets

$$\sum_{m\neq g}\sum_{n\neq g}\mu_{gm}\mu_{mn}\mu_{np}=-\left(1+\frac{2}{\sigma}\right)\sum_{m\neq g}\mu_{gm}\mu_{mg}\mu_{gp} \tag{12}$$

which, for $p = g$ becomes

$$\sum_{m\neq g}\sum_{n\neq g}\mu_{gm}\mu_{mn}\mu_{ng}=-\left(1+\frac{2}{\sigma}\right)\mu_x\sum_{m\neq g}|\mu_{mg}|^2 \tag{13}$$

Now substituting this expression of the octopolar term and using the eq 6 in eq 9 followed by simplification leads to

$$\begin{aligned}\beta_{xxx}&=\frac{6}{\Delta E^2}\left[-\left(1+\frac{2}{\sigma}\right)\mu_x\sum_{m\neq g}|\mu_{mg}|^2-\mu_x\sum_{m\neq g}|\mu_{mg}|^2\right]\\&=-\frac{6\mu_x}{\Delta E^2}\left[2\left(1+\frac{1}{\sigma}\right)\sum_{m\neq g}|\mu_{mg}|^2\right]\\&=-\frac{6\mu_x}{\Delta E^2}\left[2\left(1+\frac{1}{\sigma}\right)\frac{\Delta E\alpha_{xx}}{2}\right]\\&=-\frac{6\mu_x\alpha_{xx}}{\Delta E}\left(1+\frac{1}{\sigma}\right)\qquad\text{(in au)}\qquad(14)\\&=-\frac{37.5\mu_x\alpha_{xx}}{\Delta E}\left(1+\frac{1}{\sigma}\right)\times10^{-30}\qquad\text{(in esu)}\qquad(15)\end{aligned}$$

In eq 15, μ_x is in D, ΔE is in eV, and α_{xx} is in 10^{-23} esu. In order to get the simplified expression of static second hyperpolarizability, we consider the following SOS expression for the axial component

$$\gamma_{xxxx} = \frac{24}{\Delta E^3}\Big[\sum_{m\neq g}\sum_{n\neq g}\sum_{p\neq g}\mu_{gm}\mu_{mn}\mu_{np}\mu_{pg} + \sum_{m\neq g}\mu_{gm}\mu_{mg}\mu_{gg}^2 - \sum_{m\neq g}\sum_{n\neq g}(2\mu_{gm}\mu_{mn}\mu_{ng}\mu_{gg} + \mu_{gm}\mu_{mg}\mu_{gn}\mu_{ng})\Big] \quad (16)$$

such that like β (eq 9), it does not explicitly include the dipole moment difference terms. Here, we use the TK sum rule to simplify the first summation term in eq 16. Multiplying by μ_{pg} on both sides and summing over the index p of eq 12, one gets

$$\sum_{m\neq g}\sum_{n\neq g}\sum_{p\neq g}\mu_{gm}\mu_{mn}\mu_{np}\mu_{pg} = -\Big(1+\frac{2}{\sigma}\Big)\sum_{m\neq g}|\mu_{mg}|^2\sum_{p\neq g}|\mu_{pg}|^2$$

Using this relation and that of eq 12, eq 16 can be reduced to

$$\gamma_{xxxx} = \frac{24}{\Delta E^3}\Big[-2\Big(1+\frac{1}{\sigma}\Big)\sum_{m\neq g}|\mu_{mg}|^2\sum_{p\neq g}|\mu_{pg}|^2 + \mu_x^2\sum_{m\neq g}|\mu_{mg}|^2 + 2\Big(1+\frac{2}{\sigma}\Big)\mu_x^2\sum_{m\neq g}|\mu_{mg}|^2\Big] \quad (17)$$

Now, using eq 6 with further simplification, we get the following expression of γ

$$\gamma_{xxxx} = \frac{24}{\Delta E^3}\Big[-2\Big(1+\frac{1}{\sigma}\Big)\Big(\frac{\Delta E\alpha_{xx}}{2}\Big)^2 + \mu_x^2\frac{\Delta E\alpha_{xx}}{2} + 2\Big(1+\frac{2}{\sigma}\Big)\mu_x^2\frac{\Delta E\alpha_{xx}}{2}\Big]$$

$$\gamma_{xxxx} = \Big[\frac{36}{\Delta E^2}(\mu_x^2\alpha_{xx}) - \frac{12}{\Delta E}(\alpha_{xx}^2)\Big] + \frac{1}{\sigma}\Big[\frac{48}{\Delta E^2}(\mu_x^2\alpha_{xx}) - \frac{12}{\Delta E}(\alpha_{xx}^2)\Big] \quad \text{(au)} \quad (18)$$

$$\gamma_{xxxx} = \Big[\frac{140.3}{\Delta E^2}(\mu_x^2\alpha_{xx}) - \frac{747.2}{\Delta E}(\alpha_{xx}^2)\Big] + \frac{1}{\sigma}\Big[\frac{187.02}{\Delta E^2}(\mu_x^2\alpha_{xx}) - \frac{747.2}{\Delta E}(\alpha_{xx}^2)\Big]\times 10^{-36} \quad \text{(esu)} \quad (19)$$

where μ_x is in D, ΔE is in eV, and α_{xx} is in 10^{-23} esu. It should be noted that the signs and magnitudes of both β and γ depend on the sign of σ. Since the negative terms in eq 19 are substantially larger than the first terms within each parentheses, the second part will be positive for the negative value of σ. The following approximate scheme can be used to estimate the σ parameter following eq 11

$$\sum_{n\neq g}^{\infty}\mu_{mn}\mu_{np} = -\frac{(\sigma+2)}{\sigma}\mu_{mg}\mu_{gp}$$

Assuming $\mu_{np}/\mu_{nm} \approx \mu_{gp}/\mu_{gm} = k$ (a constant), one can write

$$k\sum_{n\neq g}^{\infty}\mu_{mn}\mu_{nm} = -k\Big(1+\frac{2}{\sigma}\Big)\mu_{mg}\mu_{gm}$$

$$\sum_{n\neq g}^{\infty}|\mu_{mn}|^2 = -\Big(1+\frac{2}{\sigma}\Big)|\mu_{mg}|^2$$

$$\sum_{n\neq g}^{\infty}|\mu_{ng}|^2 = -\Big(1+\frac{2}{\sigma}\Big)\mu_x^2 \qquad \text{(for } m = g\text{)} \qquad (20)$$

$$\frac{\Delta E\alpha_{xx}}{2} = -\Big(1+\frac{2}{\sigma}\Big)\mu_x^2 \qquad \text{(from eq 6)}$$

$$\sigma = -2\Big(1+\frac{\Delta E\alpha_{xx}}{2\mu_x^2}\Big)^{-1} \qquad (21)$$

This is an alternative expression of σ (eq 21), which can be estimated from the mean transition energy (eq 8), ground-state linear polarizability, and dipole moment of molecules. With this σ value, the evaluation of NLO parameters using the present SOS expressions (eqs 15 and 19) needs effectively two quantities, α and μ. Here, it should be mentioned that the σ values obtained from eq 21 is nearly half of that obtained from eq 15 at both the HF and B3LYP levels. This difference arises from the approximation $\mu_{np}/\mu_{nm} \approx \mu_{gp}/\mu_{gm}$, which is used while deriving eq 21. In general, letting the two ratios differ by a factor f leads subsequently to the following expression

$$\sigma = -\Big(\frac{1}{2} + \frac{1}{f}\Big\{\frac{\Delta E\alpha_{xx}}{4\mu_x^2}\Big\}\Big)^{-1} \qquad (22)$$

Using the value of σ from eq 15 (obtained with no such approximation), the value of f has been found to be ∼2 for the chosen series of molecules. The parameter σ in eq 22 becomes almost twice the σ of eq 21. Thus, to have consistency in the calculation of the third-order polarizability (eq 19) from two sets of σ values obtained from eqs 15 and 21, the latter has been multiplied by a factor of 2. The value of "2σ" from eq 21 will also be used in eq 15 for the calculation of β.

It should be noted (eq 21) that the value of σ should be always negative and depends only on α and μ of a molecule. The negative value of σ [$=\{(E_m + E_p) - 2E_n\}/\Delta E$ or $\{(E_m - E_n) - (E_n - E_p)\}/\Delta E$] indicates that the relatively much lower lying electronic states compared to the higher-energy states around the mean state (E_n) should account for the positive contribution (the part of β (eq 15) and γ (eq 19) with the factor ($1/\sigma$)) of the NLO properties. The greater the polarity (higher μ) and the stronger the longitudinal CT interaction (smaller ΔE) of the molecule, the larger should be the value of $|\sigma|$. The source of the greater negative contribution of NLO parameters of quinonoid species is expected to arise from the relatively larger negative σ values obtained for them. Alternatively, the negative β of a molecule may also arise from the relatively much smaller dipole moment of the excited states compared to that of the ground-state, which makes the dipole moment difference term in the general SOS expression dominant.

3. Results and Discussion

Since the chosen molecules cover a wider range of polarity and charge-transfer characteristics, the present model's expressions of the NLO properties, which depend on the ground-state dipole moment and first-order polarizability (from which the mean transition energy is calculated), are expected to provide the correct qualitative trend of NLO responses. We have, therefore, presented the HF- and B3LYP-calculated ground-state dipole moment (μ) and mean excitation energy (ΔE) along with the static polarizability (α) and hyperpolarizabilities (β and γ) in Table 1. In order to explain the variation of the first and second hyperpolarizabilities in terms of other ground-state properties, it would be appropriate to use the following alternative expressions of NLO properties. β_{xxx} (in esu) can be obtained by substituting 2σ (eq 21) into eq 15, followed by some rearrangement

$$\beta_{xxx} = \Big[75.0\frac{\alpha_{xx}^2}{\mu_x} - 28.1\frac{\mu_x\alpha_{xx}}{\Delta E}\Big]\times 10^{-30} \qquad (23)$$

Likewise, substituting 2σ from eq 21 into eq 19 and σ from eq 15 into eq 19, one gets $\gamma_{xxxx}^{2\sigma}$ and γ_{xxxx}^{σ}, respectively, as follows

$$\gamma^{2\sigma}_{xxxx} = \left[93.5\frac{\mu_x^2\alpha_{xx}}{\Delta E^2} + 1501.0\frac{\alpha_{xx}^3}{\mu_x^2} - 936.7\frac{\alpha_{xx}^2}{\Delta E}\right] \times 10^{-36}(\text{esu}) \tag{24}$$

$$\gamma^{\sigma}_{xxxx} = \left[5.0\beta_{xxx}\left\{4.0\frac{\alpha_{xx}}{\mu_x} - \frac{\mu_x}{\Delta E}\right\} - 46.8\frac{\mu_x^2\alpha_{xx}}{\Delta E^2}\right] \times 10^{-36}(\text{esu}) \tag{25}$$

In the above equations, μ_x is in D, ΔE is in eV, α_{xx} is in 10^{-23} esu, and β_{xxx} is in 10^{-30} esu. From these equations, it can be anticipated that the smaller dipole moment along with the larger polarizability should lead to the greater positive contribution of both β and γ.

In order to find the effect of diffuse functions on the response properties at the HF level, we have calculated NLO properties of one representative molecule from each kind (Ia, Vd, and VIIIc) at the HF/6-31+G**//HF/6-31+G** level. The calculated values of μ_x (D), α_{xx} (10^{-23} esu), β_{xxx}(10^{-30} esu), and γ_{xxxx} (10^{-36} esu) are 9.00, 5.11, 77.56, and 692.3 (Ia); 9.62, 7.59, 150.96, and 901.0 (Vd); and 18.03, 6.83, −11.65, and 101.0 (VIIIc). Upon comparing these set of values with the corresponding HF/6-31G**//HF/6-31G** calculated ones (Table 1), it can be seen that for molecules Ia and Vd, upon inclusion of diffuse basis functions, the dipole moment remains almost unchanged, linear polarizability increases marginally, quadratic polarizability increases by 10.2 and 11.6%, and the cubic polarizability enhances by about 18.7 and 25.3%, respectively. However, for molecule VIIIc, the corresponding dipole moment and the first- and second-order polarizability do not change noticeably, while the third-order property increases rather appreciably (by about 63%). The relative order of these quantities for molecules Ia, Vd, and VIIIc, however, is predicted to be the same with either of the basis sets.

Since the magnitude of NLO parameters calculated in the DFT scheme[36,37] depends largely on the composition of exchange and correlation functionals, it would be appropriate to examine the reliability of the present B3LYP method for the chosen molecular systems, which have identical lengths of conjugation. For this purpose, we have invoked the BHHLYP (including 50% HF + 50% B88 exchange and LYP correlation) method to find the influence of the HF exchange part (versus B3LYP with 20% HF exchange) on the response properties. Additionally, we also employed the MP2 method to find the relative performances between the post-HF and DFT methods since no experimental data are available to compare. The BHHLYP and MP2 calculations were carried out using the 6-31+G* basis set and the B3LYP/6-31G** geometry of some representative molecules from each set. The calculated electric properties obtained at these levels are presented in Table 2 in the Supporting Information section. Here, we mention the general trend noted. For aromatic molecules (Ia−IVb), the order of variation for μ is HF ≈ MP2 < BHHLYP < B3LYP; that for α is HF < MP2 < BHHLYP < B3LYP; for β, it is HF < BHHLYP < B3LYP ≤ MP2; and for γ, the order is HF < B3LYP < BHHLYP < MP2. The pattern of variation of γ at each correlated level was found to be identical. These trends indicate that, compared to MP2, the DFT schemes overestimate the polarity of molecules, which, as a consequence of the functional dependence of hyperpolarizabilities (eqs 23 and 24), should lead to the above trend of β and γ.

For quinonoid molecules (Va−VIIIb), the relative order of variations for μ is HF < MP2 < B3LYP ≤ BHHLYP; for α, it is HF < B3LYP ≈ BHHLYP < MP2; that for $|\beta|$ is B3LYP < HF < BHHLYP < MP2; but the γ values, however, do not follow any definite trend in this respect. The calculated α and β of quinonoids at each correlated level were found to follow an identical pattern. Again, the difference between the MP2- and B3LYP-calculated β values arises from the appreciably overestimation of μ but underestimation of α at B3LYP. Thus, it can be seen that the relative order of variation of all response properties obtained at these levels does not vary uniformly. However, for the purpose of the present work, the relative trend at a given level rather than the absolute value of the NLO properties is more important. A fairly good linear correlation is noted between the B3LYP- and BHHLYP-calculated α, β, and γ values. Again, the B3LYP- and MP2-calculated hyperpolarizabilities (except those for molecules of set 3) can also exhibit satisfactory correlations.

It is important to note that, although the energy of the planar and quasi-planar structures of the chosen molecules differs only marginally, the NLO properties differ significantly. The calculated quantities μ_x, α_{xx}, and β_{xxx} for the quasi-planar structure decrease (with respect to the planar structure) on average by about 12.5, 6.0, and 6.7% for aromatic compounds and 5.1, 0.1, and 11.0% for quinonoid compounds, while γ_{xxxx} increases by 27.8% in the former but decreases by 7.2% for the latter. The lowering of β[12] in the quasi-planar geometry arises from the slight twisting of the NH_2 group so that the longitudinal CT interaction is reduced, which is significant in the case of quinonoid molecules. The opposing variation of γ in aromatics and quinonoids may be attributed to the difference in the variation of μ and β (eq 25). However, the polarizability and hyperpolarizability values obtained at the two geometries were found to bear very good linear correlations ($R = 0.99$). In the following and subsequent sections, discussions have been made on the results obtained for planar structures only.

3.1. NLO Properties of Aromatic Chromophores. We first consider the first set of molecules I (a−f) and II (b, c, e, and f), which are stilbene analogues. The previously calculated values of β (in 10^{-30} esu) of molecules Ia and IIc (39.6 and 49.9 (CPHF/4-31G), 46.1 and 62.4 (AM1(FF)), 38.8 and 55.8 (AM1-CI (SOS)))[1] and Ia (55.7 (correction vector method using the INDO/1 Hamiltonian)[2] (each obtained with the AM1-optimized structure) differ largely from the corresponding values presented in Table 1 because the earlier values were obtained at a relatively lower level of theory. The rather small HF values of Ia and IIc may be due to the smaller size of the basis set. The longitudinal component of β (β_{xxx}) in Table 1 for molecules of sets 1−3 can be seen to be almost equal to β_{vec} (see the Supporting Information). The dipole moment of these molecules varies significantly at the two levels (7−11 D (HF) versus 11−14 D (B3LYP)). It is interesting to note that the replacement of one CH moiety of the ethylene bridge adjacent to the pyrrole ring with the N atom slightly lowers the dipole moment (by ≈ 2 D/1 D at the HF/B3LYP level) and α (by 0.1−0.3 × 10^{-23} esu at both level) of the corresponding stilbene analogues (Ia vs Id, (I−II)b vs (I−II)e, and (I−II)c vs (I−II)f). These small changes in μ and α have an insignificant effect on the NLO parameters. Unless mentioned, we shall use the B3LYP-calculated NLO parameters for the sake of comparison. The relatively larger value of β associated with molecules I (a−e) compared to that of molecules II (b, c, e and f) arises from the relatively larger values of α of the former as the variation of the dipole moment is insignificant. This is consistent with eq 23, where the first term is dominant.

The linear polarizability shows a rather strong enhancement (nearly double) upon inclusion of electron correlation. This makes the first term of β (eq 23) much larger compared to the second term, which results in a rather large increase of β upon going from HF to B3LYP. However, the increase of β in the case of molecules having a thiazole ring is less compared to those with six-membered rings. The relatively smaller value of β in addition to the relatively smaller value of α associated with the thiazole ring causes appreciable lowering of the γ (eq 25) of molecules II (b, c, e, and f) (vs I (a−f)).

Let us now find the variation of the NLO properties of molecules of the second set (III (a−f) and IV (b, c, e, and f)) where the ethylene bridge is placed at the acceptor site. For molecules III (a−f), both β and γ increase appreciably upon going from HF to B3LYP, while for molecules IV (b, c, e, and f), β increases but γ decreases (except for molecule IVb). The enhancement of β occurs due to the larger increase of α relative to μ (eq 23). The appreciable augment of γ for molecules III (a−f) also arises from the larger contributions of first two terms in eq 24. The rather appreciable increase/decrease of γ (B3LYP versus HF) associated with molecule IVb/IVf may be due to the smaller/larger increase of μ so that the negative contribution becomes smaller/larger (eq 25). It is to be noted that, unlike the first set of molecules, the replacement of one CH of the ethylene bridge by N in set 2 (Scheme 1) causes a significant increase of β in some cases. This may partly be accounted for by the increase of α and decrease of μ (eq 23). This variation of α also results in the greater negative contribution of γ (eq 24), which is reflected in the lowering of γ (B3LYP). It is important to note that NLO properties reduce substantially upon decreasing the ring aromaticity at the acceptor end.

3.2. NLO Properties of Quinonoid Chromophores. The third kind of molecular systems V (a−f) and VI (b, c, e, and f) consist of the pyrrole ring at the donor site and the quinonoid ring at the acceptor site. This structural feature enables much stronger CT interactions in these species. The larger dipole moment and smaller mean transition energy (Table 1) account for their enhanced charge transfer compared to that of the fully aromatic chromophores (molecules of subsets I−IV). The inclusion of electron correlation enhances the dipole moment of aromatic−quinonoid molecular systems by 3−5 D and the linear polarizability by $\approx 2.5 \times 10^{-23}$ esu. However, this lowers the transition energy significantly. As a result, the second term of eq 23 becomes increasingly significant, which in turn should reduce the value of β, as reflected in the B3LYP-calculated values of β (versus the HF β). However, the rather appreciable lowering occurs for molecules V (d−f) (Table 1). This pattern of variation of μ, α, and ΔE should lead to the greater negative contribution of γ (eqs 24 and 25). This has been reflected by the negative values of the third-order polarizability (at the B3LYP level), as shown in Table 1.

As before, molecules having the CH (=Z) group in the inter-ring site upon replacement with the N atom generally leads to higher β, which can be ascribed to the smaller increase of α and significant decrease of μ. The notable increase (by about 1 order of magnitude) of β at the HF level may be attributed to the appreciable lowering of μ. The similar trend of β and μ can reasonably account for the larger value of the HF γ (eqs 24 and 25). However, the negative value of γ is predicted at the B3LYP level. The increasingly negative γ is also obtained upon nitrogen substitution at the inter-ring site. This can be rationalized from the negative term of γ (eq 24), which is found to be larger for molecules having relatively higher values of α and smaller values of ΔE.

Let us now consider the full quinonoid system of molecules VII (a−f) and VIII (b, c, e, and f) (set 4). For molecules VII (d−f) and VIII (b,c,f) (Scheme 1), the calculated β_{xxx} differs from β_{vec} (as documented in the Supporting Information); even their dipole moment points along the x axis. At the B3LYP level (compared to HF), both the dipole moment and linear polarizability become larger, while the transition energy is decreased. Therefore, according to eq 23, the negative contribution of β should increase appreciably. This has been indicated by the substantial negative value of β in general at the B3LYP level (vs HF). In this respect, γ becomes rather largely negative, which may be accounted for by the rather larger contribution of the negative term relative to the positive term (eqs 24 and 25). Upon replacement of the CH (=Z) at the donor site with nitrogen, the dipole moment decreases (by about 4−5 D), while the linear polarizability and mean transition energy do not show significant variation. This should appreciably augment the first term and diminish the second term of eq 23, leading to an overall increase of β. This sort of variation of μ, α, and ΔE should also enhance the positive contribution relative to the negative contribution of γ (eqs 24 and 25), thereby leading to an overall increase of the third-order polarizability. It is interesting to note that the half quinonoid (molecules of subsets V and VI) and the full quinonoid systems (molecules of subsets VII and VIII) both possess negative γ values. However, the relative trend of γ of molecules of sets 3 and 4 with regard to the nitrogen substitution shows a rather opposing trend. This difference arises from the relatively higher α, smaller $\Delta\mu$ (change in μ), and smaller ΔE/smaller α, higher $\Delta\mu$, and higher ΔE associated with the aromatic−quinonoid/full quinonoid systems. In fact, a good linear correlation ($R = 0.9$) was noted between the B3LYP γ and the third term ($\alpha^2/\Delta E$) of γ (eq 24) for these molecules. It can be seen from Table 1 that the γ of molecules of sets 3 and 4, in general, increases with the rings of reduced aromatic character, especially when the N atom in the ring remains at the ortho position of the acceptor substituent.

Here, it is worthwhile to mention that the MP2-calculated values of β are found to be much larger (see Supporting Information) than the HF values. The appreciable difference between the B3LYP and MP2 results occurs due to the overestimation of μ and underestimation of α by the former. In order to find the extent of correlation between the ab initio and SOS (eqs 23–25) calculated values of NLO properties of the chosen molecules, we have plotted the first hyperpolarizability in Figure 2a,b and the second hyperpolarizability in Figures 3a,b and 4a,b, respectively. The fair correlation between the ab initio and the SOS results indicates that the present simplified SOS model is appropriate to explain the variation of NLO responses among the chosen compounds.

3.3. The Difference of NLO Responses Between the Aromatic and Quinonoid Chromophores. The notable difference of the hyperpolarizabilities of the aromatic and quinonoidal chromophores arises from the change of position of the ring N atom (thiazole and pyridine) meta (labeled as b and e) to ortho (labeled as c and f) with respect to the acceptor moiety. As can be seen from Table 1, both β and γ (HF) decrease for fully aromatic molecules with the pyridine ring, c (vs b) and f (vs e). However, at the B3LYP level, the change in position of the N in pyridine has an insignificant effect on β but enhances γ (Ib,e vs Ic,f and IIIb,e vs IIIc,f) by an order of magnitude. The variation of the NLO responses with thiazole in this respect may be different due to the lower aromaticity of the ring. At the higher level, β increases, while γ decreases (IIb,e vs IIc,f and IVb,e vs IVc,f) appreciably. The relatively larger B3LYP β obtained for the thiazole ring with its nitrogen atom ortho to the acceptor was also noted earlier by McMahon et al.[6]

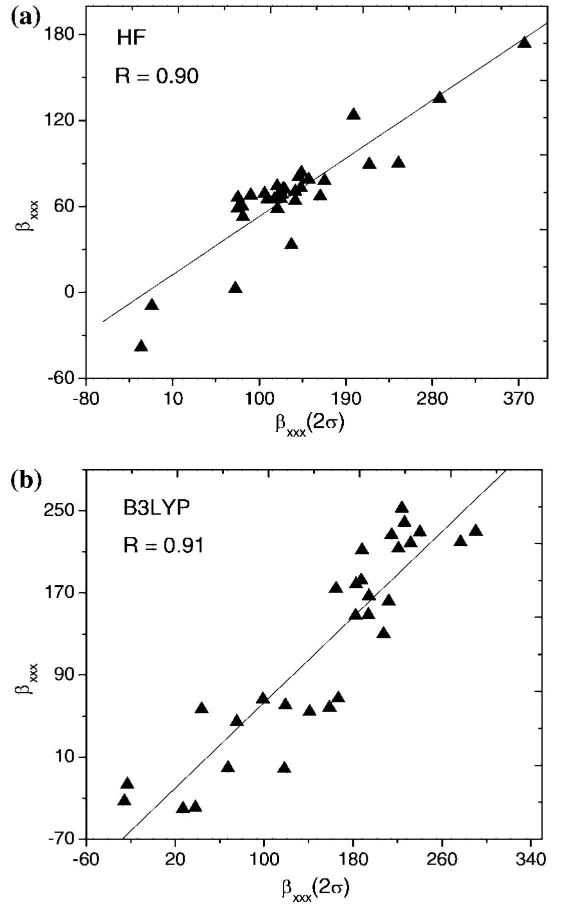


Figure 2. The plot of ab initio calculated β versus SOS β (in 10^{-30} esu) (eq 15) estimated from 2σ (eq 21) at the (a) HF and (b) B3LYP levels, respectively.

Let us now examine this effect in quinonoid systems. Molecules having a quinoidal pyridine ring show an insignificant variation of β but exhibit rather significant enhancement of γ (Vb,e vs Vc,f and VIIb,e vs VIIc,f) (at the B3LYP level) due to a change in the position of N. On the other hand, for molecules having quinoidal thiazole, β decreases, but γ increases (VIb,e vs VIc,f and VIIIb,e vs VIIIc,f) upon shifting the N atom. At the HF level, β decreases with both quinonoidal pyridine and thiazole rings with their nitrogen atom ortho to the acceptor moiety, while no such regular trend can be found for γ.

It is interesting to note that the change in the position of the N atom of the thiazole ring can strongly modulate the NLO responses, the pattern of variation of which, however, depends largely on whether the ring is in the aromatic or quinoidal form. In the case of aromatic systems, the increase of β and decrease of γ may be explained by the increase of α for a rather small increase of μ (eqs 23 and 24), while for the quinonoid species, the reverse trend of β and γ arises from the significant increase of μ and decrease of α.

The difference of NLO properties between the fully aromatic and quinonoidal molecules, in general, arises from the rather significant polarity of the latter, as indicated by the larger dipole moment and polarizability and smaller mean transition energy. The increasingly negative contribution of both the second- and third-order polarizability primarily arises from the decreasing mean transition energy (eqs 23–25). The relatively larger variation of β between the aromatic and quinonoid systems may be attributed to the rather larger difference of their nearly constant value of ($\mu\cdot\alpha$) (see Table 1 and also eq 23).

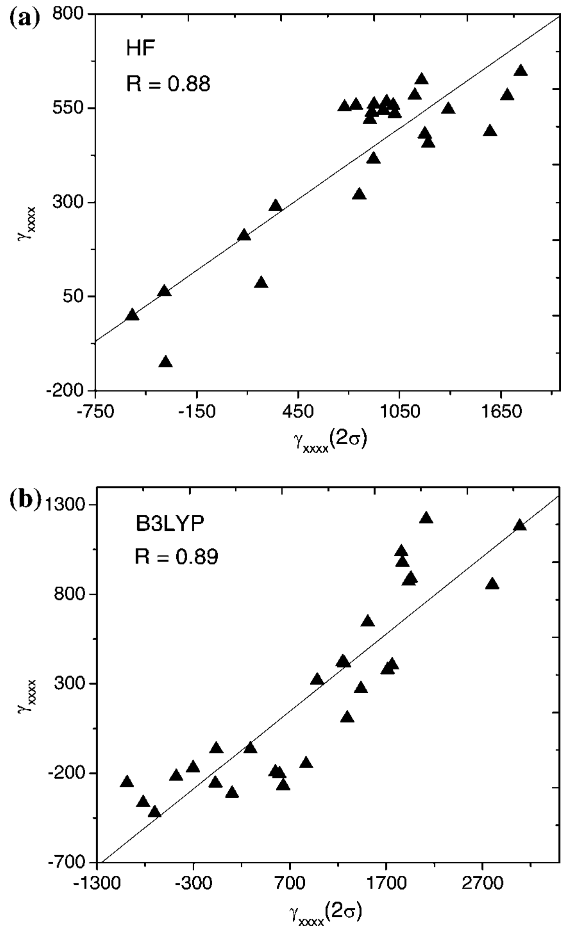


Figure 3. The plot of ab initio calculated γ versus SOS γ (in 10^{-36} esu) (eq 19) estimated from 2σ (eq 21) at the (a) HF and (b) B3LYP levels, respectively.

4. Conclusions

In the present work, a number of heterocycle-based isomeric chromophores with appreciably varying structure and polarity have been considered for the study of their NLO properties. Although the chosen molecules have identical lengths of the conjugative path, the extent of the longitudinal CT interaction differs greatly. The present simplified SOS expressions can be reasonably used to interpret the variation of response properties for such a wider range of molecular systems in terms of the calculated ground-state dipole moment, the polarizability, and the mean excitation energy. The SOS and ab initio calculated NLO properties obtained at each level showed fair agreement with each other. The origin of the sign of both β and γ in the present model can be explained in terms of a single parameter σ, which can be calculated from the ground-state properties of a molecule. The larger value of $|\sigma|$ corresponds to the greater negative contribution of NLO responses, which has been reflected by the increasingly negative β and γ upon going from aromatic to quinonoid molecular systems. The present analysis showed that the enhanced nonlinearity of the donor−acceptor-substituted chromophores can be achieved for a relatively higher polarizability and mean transition energy but a smaller dipole moment. The inclusion of electron correlation at the B3LYP and MP2 levels appreciably enhances both β and γ of aromatic chromophores. However, the NLO responses of quinonoid chromophores are largely underestimated at the B3LYP level compared to that at the the MP2 level due to the overly estimated dipole moment and the underestimation of the polarizability at

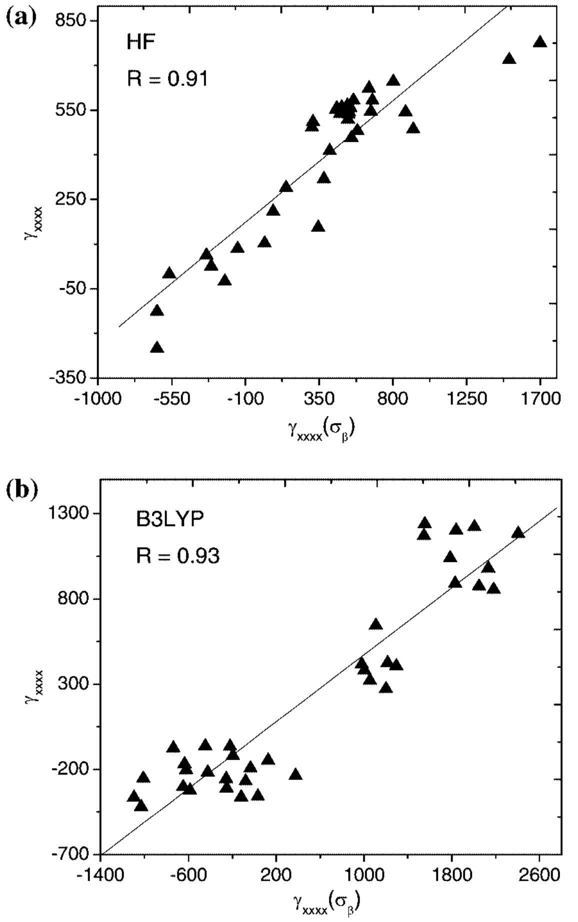


Figure 4. The plot of ab initio calculated γ versus SOS γ (in 10^{-36} esu) (eq 19) with σ_β (eq 15) obtained at the (a) HF and (b) B3LYP levels, respectively.

the DFT level. The use of a ring with a lower degree of aromaticity at the acceptor site causes lowering of γ for aromatic compounds, while it enhances that for quinonoids (sets 3 and 4). The change in the position of the nitrogen atom in the ring and the replacement of the CH group by nitrogen in the conjugative path have been found to markedly influence the NLO responses.

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Supporting Information Available: Table 1 includes the HF- and B3LYP-calculated ground-state dipole moment (μ) and β_{vec} and the B3LYP/6-31G**-calculated standard heats of formation of all of the chosen molecules. Table 2 contains the BHHLYP- and MP2-calculated ground-state dipole moment and polarizability and hyperpolarizabilities of some representative molecules of Scheme 1. This material is available free of charge via the Internet at http://pubs.acs.org.

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