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Theoretical Study of the Effect of Structural Modifications on the Hyperpolarizabilities of Indigo Derivatives

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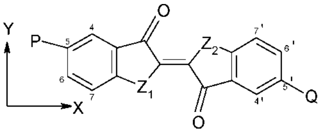
The static first and second hyperpolarizabilities of a number of indigo (In) derivatives, donor−In−donor, acceptor−In−acceptor, and donor−In−acceptor, have been calculated at the B3LYP/6-31+G* level. The various useful relations are obtained from the standard sum-overstate (SOS) expressions with the use of the Thomas−Kuhn (TK) sum rule. The variation of NLO properties, especially the second hyperpolarizability (γ) of indigo compounds, can be satisfactorily explained in terms of ground-state electric moments, linear polarizability (α), and second-order polarizability (β). The noncentrosymmetry arising from replacement of the ring NH of indigo with O and S atoms and also substitution with donor and acceptor at different ring positions of indigo lead to rather significant modulation of γ. The appreciable decrease of third-order polarizability on pyramidalization of the NH_2 group as explained in the present model is equivalent to the decrease of the dipole moment difference and increase of the transition energy in the two-state model.

1. Introduction

Several theoretical and experimental investigations had been carried out to search for potential NLO materials suitable for various opto-electronic applications. Organic charge-transfer compounds with appropriate modifications have been used widely in the design of potential NLO-phores[1−3] because of their relative ease of synthesis, sufficient thermal stability, and varying degree of polarity. Most of the theoretical approaches to understand and interpret the variation of experimental or theoretical results of hyperpolarizabilities were based on the two-state model[4,5] of second-order polarizability and the three-term expression[3] of third-order polarizability obtained from the standard sum-overstate (SOS) expressions.[6,7] In the 2-state model only one of the excited states is assumed to couple strongly with the ground state (ignoring the transition moments with the remaining excited states), while in the three-term γ many other excited states are considered which provide contributions arising from the two-photon processes. It was noted that in most of the dipolar molecules the lowest lying excited state generally can make a dominant contribution to the first hyperpolarizability. The 2-level model, however, fails to account for the origin of β in noncentrosymmetric nonpolar (e.g., octupolar, hexadecapolar) compounds. The three-term expression of cubic polarizability[3] was used earlier to explain its dependence on the ground-state polarization of donor−acceptor-substituted polyenes rather qualitatively. However, the criteria necessary for optimizing the second-order polarizability does not necessarily fit while optimizing the third-order polarizability. It seems that there remain sufficient scopes of theoretical analysis pertaining the structure−property correlations for the second hyperpolarizability. Recently Kuzyk et al.[8,9] derived alternative SOS expressions of NLO properties which do not contain the dipole moment term and are appropriate especially for nondipolar molecules. In the present investigation, we intend to find analytical expressions of static NLO parameters, especially the third-order property in terms of ground-state electric moments and lower order polarizabilities which can provide insight into the structure−property correlations for different molecular systems of interest. The work is essentially based on the idea developed in our earlier paper.[10]

SCHEME 1



P and Q = NH_2 (D) / NO_2 (A); Z_1 and Z_2 = NH/O/S

In order to examine the present formalism, we considered a new kind of chromophore system based on indigo (Schemes 1 and 3) whose charge-transfer characteristics seem to be different from that of the usual donor−acceptor-substituted compounds. The trans form of indigo is centrosymmetric nonpolar. Hence, the possible structural modifications on it may lead to significant variation of NLO responses. Although quite a number of experimental and theoretical studies on the structure and spectroscopic properties of indigo, thioindigo, and their derivatives[11−13] were performed, their NLO properties, however, have not yet been investigated. Therefore, a thorough and systematic study of their NLO responses may reveal the general qualitative features of structure−property correlations. For this purpose, three different class of 5,5′-substituted indigo (In) compounds have been considered: D−In−D, A−In−A, and (D/A)−In−(A/D). Our emphasis will be given to rationalize the variation of γ in terms of the lower order polarizabilities and electric moments rather than to predict the absolute value of the property.

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2. Computational Methods

2.1. Electronic Structure and Properties. The ground-state equilibrium geometry of the selected molecules (Scheme 1) was optimized fully and also with the constraint of a planar structure at the B3LYP level using the 6-31+G* basis set. The former results in a quasi-planar structure (with a dihedral angle of ~177 ° between the N atom of NH_2 and the rings). Molecules of Scheme 3 are, however, fully optimized at the same level, and the equilibrium structures were found slightly out of plane due to the presence of the NH_2 group. Each fully optimized structure corresponds to an energy minimum on the potential-energy hypersurface as confirmed by real frequencies obtained for all normal modes of vibration. The equilibrium structure and electric multipole moments were calculated using the Gaussian 03 program packages.[14]

The static linear and nonlinear polarizabilities of each molecule were computed at the B3LYP/6-31+G*//B3LYP/6-31+G* level in the finite field (FF) scheme. Although the magnitude of the hyperpolarizabilities is sensitive[15] to the choice of the exchange and correlation functionals, the present DFT scheme was noted[10] to give satisfactory correlations for a variety of chromophore systems and showed a nearly identical trend of NLO parameters as obtained at the MP2 level. Thus, meaningful structure−property correlations can be found for the chosen indigo derivatives. Calculation of the NLO parameters was carried out using the GAMESS program.[16]

The vector part of first hyperpolarizability has been represented[1] as

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

The axial component β_i was calculated using the following expression

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

2.2. Variants of Static Hyperpolarizabilities from Standard SOS Expressions. Using the Thomas−Kuhn (TK) sum rule[8] the linear polarizability in the SOS scheme

$$\alpha_{xx} = 2\sum_{m \neq g}\frac{\mu_{gm}\mu_{mg}}{\Delta E_{mg}} \tag{3}$$

can be expressed as

$$\alpha_{xx} = \frac{N_e}{\Delta E^2} \tag{4}$$

where ΔE is the mean transition energy obtained under closure approximation and N_e is the total number of electrons of a molecule. As in our previous work,[10] ΔE has been calculated (eq 4) from the valence electrons and the mean polarizability of a molecule. The B3LYP-calculated ΔE and the hardness parameter η (= 1/2 ($\varepsilon_{\text{LUMO}} - \varepsilon_{\text{HOMO}}$))[17] of molecules in Table 1 were noted to bear a fairly good correlation ($R = 0.90$). The stronger charge-transfer (CT) interaction, in general, corresponds to the smaller value of η or ΔE.

The axial component of static SOS β[6,7] under the closure approximation of the transition energy can be written as

$$\beta_{xxx} = \frac{6}{\Delta E^2}\left[\sum_{m \neq g}\mu_{gm}(\mu_{mm} - \mu_{gg})\mu_{mg} + \sum_{m \neq g}\sum_{n \neq m,g}\mu_{gm}\mu_{mn}\mu_{ng}\right] \tag{5}$$

where the μ_{ij} terms denote the x component of the transition moment integral and μ_{gg} is the x component (μ_x) of the ground-state dipole moment. Equation 5 can also be rewritten explicitly in two terms as the octupolar (first) and quadrupolar (second) contributions. For noncentrosymmetric nonpolar

TABLE 1: B3LYP/6-31+G*//B3LYP/6-31+G*-Calculated Mean Excitation Energy (ΔE, eV), Ground-State Dipole Moment (μ, D), Static Linear (α, 10^{-23} esu) and Nonlinear Optical Parameters (β, 10^{-30} esu and γ, 10^{-36} esu), and $\Theta_{xx}^2/\Delta E^3$ (in 10^2 D^2-$Å^2$/eV^3) of Molecules of Scheme *1* in Planar Structures[a]

Z_1	Z_2	P	Q	ΔE	μ_g	μ_x	α_{xx}	β_{xxx}	β_{vec}	γ_{xxxx}	$\Theta_{xx}^2/\Delta E^3$
NH	NH	H	H	16.58	0.000	0.000	5.70	0.01	0.02	162.5	252.6
NH	O	H	H	17.12	1.407	0.797	5.24	4.12	7.42	167.9	199.3
S	S	H	H	16.31	0.000	0.000	5.93	0.00	0.00	214.8	243.0
NH	NH	A	A	17.18	0.010	0.003	7.76	0.04	0.05	501.9	1162.1
NH	O	A	A	17.81	1.462	1.171	6.99	3.79	3.29	406.1	939.9
O	O	A	A	18.56	0.000	0.000	6.36	0.01	0.03	346.6	779.3
NH	S	A	A	17.16	0.830	0.830	7.79	0.95	15.4	561.4	1161.9
S	S	A	A	17.08	0.000	0.000	7.91	0.04	0.20	621.4	1208.4
S	O	A	A	17.79	1.045	0.304	6.93	7.92	9.75	437.2	966.1
NH	NH	D	D	16.40	0.000	0.000	7.04	0.01	0.04	827.2	158.4
NH	O	D	D	16.93	1.383	0.485	6.41	30.23	42.05	651.9	121.8
O	O	D	D	17.67	0.012	0.009	5.79	0.01	0.03	476.1	84.9
NH	S	D	D	16.36	2.320	0.624	7.03	16.43	17.39	724.9	137.5
S	S	D	D	16.30	0.008	0.001	7.08	0.02	0.05	665.6	121.5
S	O	D	D	16.96	0.946	0.257	6.26	11.83	20.06	525.8	112.8
NH	NH	A	D	16.72	10.38	9.87	7.55	65.37	86.99	875.7	501.7
NH	O	A	D	17.34	10.31	10.08	6.76	32.35	41.72	466.6	406.5
NH	O	D	A	17.28	9.448	8.395	6.83	67.73	94.90	873.2	514.5
O	O	A	D	18.07	9.133	8.74	6.16	35.72	43.54	568.5	312.2
NH	S	A	D	16.71	10.36	10.30	7.46	49.48	69.41	649.6	457.6
NH	S	D	A	16.68	9.424	8.835	7.60	74.18	83.98	1014.4	663.8
S	S	A	D	16.65	9.427	9.37	7.62	59.09	64.37	846.7	482.2
S	O	A	D	17.34	9.233	8.962	6.72	40.91	40.40	585.1	440.2
S	O	D	A	17.32	9.209	8.878	6.64	48.08	69.09	694.6	473.6

[a] Substitution at the 6,6′ positions of indigo. $Z_1 = Z_2 =$ NH, P = Q = A: $\Delta E = 17.34$, $\mu_g = 0.002$, $\mu_x = 0.000$, $\alpha_{xx} = 6.77$, $\beta_{xxx} = 0.006$, $\gamma_{xxxx} = 452.5$, and $\Theta_{xx}^2/\Delta E^3 = 520.28$. $Z_1 = Z_2 =$ NH, P = A, Q = D: $\Delta E = 16.74$, $\mu_g = 10.500$, $\mu_x = 5.554$, $\alpha_{xx} = 6.50$, $\beta_{xxx} = 14.86$, $\gamma_{xxxx} = 310.9$, and $\Theta_{xx}^2/\Delta E^3 = 349.10$.

molecules β depends on the octupolar term the second term being zero.

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

Considering the generalized TK sum rule for $m \neq p$ and simplifying it one gets the following relations[10]

$$\sum_{n=g}^{\infty}(\Delta E_{nm} + \Delta E_{np})\mu_{mn}\mu_{np} = 0 \tag{7}$$

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

$$\sum_{n\neq g}^{\infty}\{2\Delta E_{ng} - (E_m + E_p - 2E_g)\}\mu_{mn}\mu_{np} = (\Delta E_{mg} + \Delta E_{pg})\mu_{mg}\mu_{gp}$$

For m = g the last expression becomes

$$\sum_{n\neq g}^{\infty}\{2\Delta E_{ng} - \Delta E_{pg}\}\mu_{gn}\mu_{np} = \Delta E_{pg}\mu_x\mu_{gp} \quad \text{as } \Delta E_{gg} = 0$$

Under closure approximation this equation can be written as

$$\sum_{n\neq g}^{\infty}\mu_{gn}\mu_{np} = \frac{1}{2k'' - 1}\mu_x\mu_{gp} = k\mu_x\mu_{gp} \tag{8}$$

where $k'' = \Delta E_{ng}/\Delta E$ and $k = 1/(2k'' - 1)$. Thus, the sign and magnitude of k depend on the relative energy spacing of excited states of a molecule around their mean energy and should be different for substantially varying charge-transfer chromophores.

Approximating $\mu_{np}/\mu_{gp} \approx \mu_{ng}/\mu_{gg}$, eq 8 becomes

$$\sum_{n\neq g}^{\infty}\mu_{gn}\mu_{ng} = k\mu_x^2 \text{ or } \sum_{n\neq g}^{\infty}|\mu_{ng}|^2 = k\mu_x^2 \tag{9}$$

Another useful relation to simplify the higher order terms can be obtained by multiplying both sides of eq 8 with μ_{pg} and taking a summation over the index p

$$\sum_{n\neq g}^{\infty}\sum_{p\neq g}^{\infty}\mu_{gn}\mu_{np}\mu_{pg} = k\mu_x\sum_{p\neq g}^{\infty}\mu_{gp}\mu_{pg} \tag{10}$$

Using eq 10, eq 6 can be reduced to

$$\beta_{xxx} = \frac{6}{\Delta E^2}\left(1 - \frac{1}{k}\right)\sum_{m\neq g}\sum_{n\neq g}\mu_{gm}\mu_{mn}\mu_{ng} = \frac{K}{\Delta E^2}\sum_{m\neq g}\sum_{n\neq g}\mu_{gm}\mu_{mn}\mu_{ng} \tag{11}$$

where $K = 6(1 - 1/k)$ is assumed to be a constant for a series of molecular systems having identical structural characteristics. Equation 11 is applicable for both polar and nonpolar noncentrosymmetric (i.e., octupolar symmetry) molecular systems. An alternative expression of β can also be obtained from eqs 10 and 3 as follows

$$\beta_{xxx} = \frac{6(k-1)\mu_x}{\Delta E^2}\sum_{m\neq g}|\mu_{mg}|^2$$

$$\beta_{xxx} = 3(k-1)\frac{\mu_x\alpha_{xx}}{\Delta E} \tag{12}$$

Using eqs 3 and 9, eq 12can also be written in the following form

$$\beta_{xxx} = \frac{3(k-1)}{2k}\frac{\alpha_{xx}}{\mu_x}\frac{2k\mu_x^2}{\Delta E} = \frac{3(k-1)}{2k}\frac{\alpha_{xx}^2}{\mu_x} = \frac{K}{4}\frac{\alpha_{xx}^2}{\mu_x} \tag{13}$$

Equations 12 and 13 indicate that the two-term expressions[10] of β_{xxx} obtained in our previous work are equivalent to each other. Both eqs 12 and 13 are strictly applicable to dipolar molecules. As expected for centrosymmetric cases eq 12 predicts $\beta = 0$.

The another expression of β_{xxx} which is applicable for all molecular systems, in general, can be obtained by approximating the octupolar term of eq 11 as the one-electron octopole moment Ω_{xxx}[18,19]

$$\beta_{xxx} = C\frac{\Omega_{xxx}}{\Delta E^2} \tag{14}$$

where C is a constant.

Let us consider the standard SOS expression of the axial component of third-order polarizability (γ_{xxxx})

$$\gamma_{xxxx} = 24\left[\sum_{m\neq g}\sum_{n\neq g}\sum_{p\neq g}\frac{\mu_{gm}(\mu_{mn} - \mu_{gg}\delta_{mn})(\mu_{np} - \mu_{gg}\delta_{np})\mu_{pg}}{\Delta E_{gm}\Delta E_{gn}\Delta E_{gp}} - \sum_{m\neq g}\sum_{n\neq g}\frac{\mu_{gm}\mu_{mg}\mu_{gn}\mu_{ng}}{\Delta E_{gm}\Delta E_{gn}^2}\right] \tag{15}$$

To compute γ using eq 15 the energy, dipole moment, and transition moments of many excited electronic states are to be known before hand. Moreover, for octupolar molecular species eq 15 is not appropriate to evaluate γ. With the help of the sum rules it is possible to transform the lower order terms in eq 15 into a fully dipole-free expression having only the hexadecapolar term and the higher order term into the lower order terms leading to various equivalent expressions. A little manipulation of summation terms in eq 15 leads to the following expression

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

The last three summation terms can be reduced to the first term with the help of eqs 8−10 as follows

$$\sum_{m\neq g}\mu_{gm}\mu_{mg}\mu_{gg}^2 = \frac{\mu_x}{k}\sum_{m\neq g}\sum_{n\neq g}\mu_{gm}\mu_{mn}\mu_{ng} = \frac{1}{k^2}\sum_{m\neq g}\sum_{n\neq g}\sum_{p\neq g}\mu_{gm}\mu_{mn}\mu_{np}\mu_{pg} \tag{17}$$

$$2\mu_x\sum_{m\neq g}\sum_{n\neq g}\mu_{gm}\mu_{mn}\mu_{ng} = \frac{2}{k}\sum_{m\neq g}\sum_{n\neq g}\sum_{p\neq g}\mu_{gm}\mu_{mn}\mu_{np}\mu_{pg} \tag{18}$$

$$\sum_{m\neq g}\sum_{n\neq g}\mu_{gm}\mu_{mg}\mu_{gn}\mu_{ng} = \sum_{m\neq g}\mu_{gm}\mu_{mg}\sum_{n\neq g}\mu_{gn}\mu_{ng} = k\mu_x^2\sum_{m\neq g}\mu_{gm}\mu_{mg} = \frac{1}{k}\sum_{m\neq g}\sum_{n\neq g}\sum_{p\neq g}\mu_{gm}\mu_{mn}\mu_{np}\mu_{pg} \tag{19}$$

Here, μ_{gg} corresponds to μ_x. Thus, using eqs 17−19 eq 16 can be written in compact form as

$$\gamma_{xxxx} = \frac{24}{\Delta E^3}\left[\sum_{m\neq g}\sum_{n\neq g}\sum_{p\neq g}\mu_{gm}\mu_{mn}\mu_{np}\mu_{pg}\left(1 - \frac{3}{k} + \frac{1}{k^2}\right)\right] = \frac{24k'}{\Delta E^3}\left[\sum_{m\neq g}\sum_{n\neq g}\sum_{p\neq g}\mu_{gm}\mu_{mn}\mu_{np}\mu_{pg}\right] \tag{20}$$

where $k' = (1 - 3/k + 1/k^2)$. Thus, both the second- and third-order polarizability can be calculated from eqs 11 and

20, respectively, by knowing only the constant k and the transition moment integrals. We, however, instead of calculating the transition moment integrals replace them with the lower order polarizabilities and ground-state electric moments. From eq 20 various equivalent expressions can be obtained as given below

$$\gamma_{xxxx} = \frac{24kk'}{\Delta E^3}\left[\sum_{m\neq g} |\mu_{mg}|^2 \sum_{n\neq g} |\mu_{ng}|^2\right] \text{(from eq 19)} \tag{21}$$

$$\gamma_{xxxx} = \frac{6kk'}{\Delta E}\alpha_{xx}^2 \text{ (using eq 3)} \tag{22}$$

$$\gamma_{xxxx} = \frac{24kk'}{\Delta E^3}\mu_x \sum_{m\neq g}\sum_{n\neq g} \mu_{gm}\mu_{mn}\mu_{ng} \text{(from eq 18)} = \frac{24kk'}{K\Delta E}(\mu_x\beta_{xxx}) \text{(from eq 11)} \tag{23}$$

$$\gamma_{xxxx} = \frac{12k'}{K\mu_x}\left(\frac{2k\mu_x^2}{\Delta E}\right)\beta_{xxx} \text{(by rearranging eq 23)} = \frac{12k'}{K}\left(\frac{\alpha_{xx}\beta_{xxx}}{\mu_x}\right) \text{(from eq 9)} \tag{24}$$

Replacing β_{xxx} in eq 24 in terms of α and μ from eq 13 one can get the following expression

$$\gamma_{xxxx} = 12k'\left(\frac{\alpha_{xx}}{\mu_x}\right)\frac{\alpha_{xx}^2}{4\mu_x} = 3k'\left(\frac{\alpha_{xx}^3}{\mu_x^2}\right) \tag{25}$$

Another useful relation between the second hyperpolarizability and lower order polarizabilities can be obtained by making use of eqs 12 and 23 as follows

$$\gamma_{xxxx} = \frac{24kk'}{K\Delta E}(\mu_x\beta_{xxx}) = \frac{24kk'}{K}\left(\frac{\beta_{xxx}}{3(k-1)\alpha_{xx}}\right)\beta_{xxx} = \frac{48k'}{K^2}\left(\frac{\beta_{xxx}^2}{\alpha_{xx}}\right) \tag{26}$$

An alternative expression of γ which may be useful for molecules having significant CT interaction ($\mu_x \neq 0$ and also $\beta_{xxx} \neq 0$) is obtained from eqs 8−10 and 16 as follows

$$\gamma_{xxxx} = \frac{24}{\Delta E^3}\left[\sum_{m\neq g} k^2\mu_x^2|\mu_{mg}|^2 + \mu_x^2\sum_{m\neq g}|\mu_{mg}|^2 - 2k\mu_x^2\sum_{m\neq g}|\mu_{mg}|^2 - \sum_{m\neq g}|\mu_{mg}|^2\sum_{n\neq g}|\mu_{ng}|^2\right]$$

$$\gamma_{xxxx} = \frac{24}{\Delta E^3}\left[\mu_x^2(k-1)^2\sum_{m\neq g}|\mu_{mg}|^2 - \sum_{m\neq g}|\mu_{mg}|^2\sum_{n\neq g}|\mu_{ng}|^2\right]$$

$$\gamma_{xxxx} = \left[12(k-1)^2\frac{\alpha_{xx}\mu_x^2}{\Delta E^2} - 6\frac{\alpha_{xx}^2}{\Delta E}\right]$$

$$\gamma_{xxxx} = \left[\frac{4(k-1)}{\Delta \mathrm{E}}\mu_x\beta_{xxx} - 6\frac{\alpha_{xx}^2}{\Delta E}\right] \tag{27}$$

Equation 27 is appropriate for the case when the $\mu\beta$ term is dominant and α is also significant. These equivalent expressions of third-order polarizability can be used to rationalize the variation of γ for molecules with varying polarity. Equations 22 and 26 having no dipole moment term are applicable for both polar and nonpolar molecules, while eqs 23−25 and 27 are appropriate for dipolar species.

γ_{xxxx} can also be expressed in terms of one-electron multipole moments,[18] Φ_{xxxx}(hexadecapole) and Θ_{xx}(traced quadrupole[20]), as follows

$$\gamma_{xxxx} = K_1\frac{\Phi_{xxxx}}{\Delta E^3} \text{(from eq 20)} \tag{28}$$

$$\gamma_{xxxx} = K_2\frac{\Theta_{xx}^2}{\Delta E^3} \text{(from eq 22)} \tag{29}$$

In the above equations, K_1 and K_2 are constants. These expressions of γ are applicable for both polar and nonpolar molecules as the higher electric moments of the later in contrast to dipole moment are nonzero in general.

3. Results and Discussion

The variation of the B3LYP-calculated static NLO properties of the chosen indigo derivatives, both polar and nonpolar, will be discussed in terms of the ground-state electric moments and the lower order polarizabilities. The nature of the interdependence and the extent of correlation among the various electronic parameters will be justified using the relations obtained in the framework of the standard SOS expressions. Special emphasis

TABLE 2: B3LYP/6-31+G*//B3LYP/6-31+G*-Calculated Mean Excitation Energy (ΔE, eV), Ground-State Dipole Moment (μ, D), Static Linear (α, 10^{-23} esu) and Nonlinear Optical Parameters (β, 10^{-30} esu and γ, 10^{-36} esu), and $\Theta_{xx}^2/\Delta E^3$ (in 10^2 D^2-Å^2/eV^3) of Molecules of Scheme *1* in Quasi-Planar Structures

Z_1	Z_2	P	Q	ΔE	μ_g	μ_x	α_{xx}	β_{xxx}	β_{vec}	γ_{xxxx}	$\Theta_{xx}^2/\Delta E^3$
NH	NH	D	D	16.47	0.005	0.000	6.92	0.00	0.02	668.9	216.1
NH	O	D	D	16.99	1.386	0.561	6.31	24.43	34.34	550.7	167.2
NH	S	D	D	16.41	2.130	0.682	6.94	12.34	12.11	608.9	191.4
S	S	D	D	16.33	0.002	0.001	7.02	0.00	0.01	565.1	174.8
S	O	D	D	16.99	0.761	0.191	6.43	12.01	17.91	505.2	140.8
NH	NH	A	D	16.77	9.504	8.982	7.46	55.97	74.99	737.5	546.6
NH	O	A	D	17.36	9.552	9.358	6.83	30.66	38.45	450.2	433.9
NH	O	D	A	17.34	8.609	7.523	6.74	57.08	80.30	738.3	545.6
O	O	A	D	18.10	8.407	7.991	6.12	31.17	38.34	482.0	343.4
NH	S	A	D	16.73	9.619	9.515	7.42	44.81	63.91	579.5	503.5
NH	S	D	A	16.74	8.588	7.968	7.51	63.79	70.78	874.2	699.2
S	S	A	D	16.67	8.712	8.606	7.56	52.77	57.28	743.9	528.7
S	O	A	D	17.36	8.499	8.326	6.92	38.14	36.23	582.2	453.0
S	O	D	A	17.35	8.517	8.278	6.83	46.40	61.05	669.6	508.3

will be given to rationalize the variation of the second hyperpolarizability.

3.1. NLO Properties of Molecules in Scheme 1 (Tables 1 and 2). The calculated mean transition energy (ΔE), ground-state total dipole moment (μ_g) and its x component (μ_x), the component of linear polarizability (α_{xx}), second-order polarizability (β_{xxx}), and third-order polarizability (γ_{xxxx}) in conjunction with $\Theta_{xx}^2/\Delta E^3$ obtained at the planar structure of molecules in Scheme 1 have been presented in Table 1. The same quantities obtained for the same molecules at the quasi-planar structure have also been reported in Table 2. For molecules in Scheme 1 the calculated $\mu_x \approx \mu_g$ (see Tables 1 and 2) in general. The H−In−H-, A−In−A-, and D−In−D-type chromophores have both dipole moment and first hyperpolarizability nearly zero in most cases. In a few cases, the calculated β_{xxx} values are significant even though $\mu_x \approx 0$, which may arise from the octupolar contribution (eq 6). The donor−acceptor-substituted indigo compounds, however, possess significant dipole moment and also β values. A good linear correlation is noted between β_{xxx} and $\mu_x\alpha_{xx}/\Delta E$ (Figure 1a) for molecules of Table 1. For the polar molecules (fourth set in Table 1) β_{xxx} also bears a nice correlation with α_{xx}^2/μ_x (Figure 1b). The octupolar contribution increases with increasing β value as shown in the plot β_{xxx} vs $\Omega_{xxx}/\Delta E^2$ (Figure 1c).

It is to be noted that the larger β_{xxx} arising from the noncentrosymmetric D−In−D compared to that of the analogous A−In−A may be attributed to the stronger CT interaction in the former as indicated by their smaller value of ΔE. As can be noted from eq 16 for such nondipolar species only the hexadecapolar term (first term) and the last term ($\propto$ linear polarizability) survive. Therefore, the smaller ΔE and smaller α should lead to higher second hyperpolarizability. The substantially larger value of γ_{xxxx} is thus predicted for D−In−D compounds compared to A−In−A. For molecules in either of the sets, D−In−D or A−In−A, the variation of γ_{xxxx} follows the relative trend with α_{xx} and ΔE (eq 22). The apparent discrepancy noted in some cases (D−NH−NH−D, D−NH−S−D, and D−S−S−D) may be resolved if one considers (eq 4) ΔE. For the nonpolar species γ_{xxxx} also shows a fairly regular trend with $\Theta_{xx}^2/\Delta E^3$ as expected from eq 29. γ_{xxxx} of A−In−A chromophores decreases/increases on gradual substituting of the ring NH groups of indigo with O/S. This happens because on replacing NH by O/S the α_{xx} value decreases/increases while ΔE (eq 22) shows a reverse trend. However, for D−In−D systems γ_{xxxx} decreases when the NH groups of indigo are gradually substituted by either a O and S atom. Substitution with O leads to a decrease of α_{xx} and increase of ΔE, which according to eq 22 should lower the γ_{xxxx} value. The justification with sulfur substitution has been explained above.

The third kind of chromophores like (A/D)−In−(D/A) possess appreciable μ and β values. While comparing the relative trend of γ it is better to look for those quantities which show significant variation so that one can easily rationalize it using the appropriate expression of γ (eqs 22−29). The interchange of the donor−acceptor pair strongly modulates both β and γ in the case of NH···O and NH···S compounds. For such dipolar species the variation of β_{xxx} and γ_{xxxx} due to interchange of the substituent pair follows eqs 13 and 25, respectively. For both polar and nonpolar compounds γ_{xxxx} shows a fair correlation with $\alpha_{xx}^2/\Delta E$ (Figure 2a). Besides this the second hyperpolarizability of the donor−acceptor-substituted species also show other interesting correlations: linear with $\mu_x\beta_{xxx}/\Delta E$ (Figure 2b) and $\alpha_{xx}\beta_{xxx}/\mu_x$ (Figure 2c), respectively, which are consistent with eqs 23 and 24.

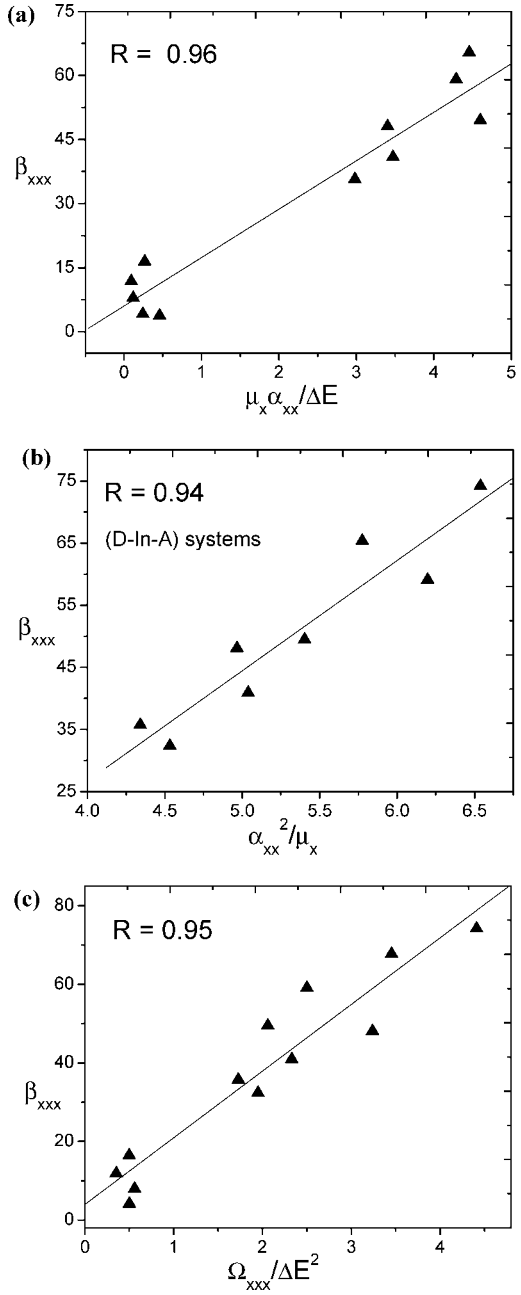


Figure 1. Plot of (a) β_{xxx} versus $\mu_x\alpha_{xx}/\Delta E$ (eq 12), (b) β_{xxx} versus α_{xx}^2/μ_x (eq 13), and (c) β_{xxx} versus $\Omega_{xxx}/\Delta E^2$ (eq 14) for molecules of Table 1.

When both NH groups of the A−In−D system are replaced by O γ lowers substantially, which can be attributed to the significant lowering of α and increase of ΔE (eq 22). However, replacement of both NH groups by S atoms results in a smaller decrease of γ, which is indicated by the rather small variation of lower order polarizabilities and mean transition energy. It is interesting to note that when the NH group at the acceptor site is replaced by the O atom the γ value does not change; however, when it is replaced by the S atom strong enhancement of γ occurs. The latter may be ascribed to an increase of α and β but decrease of μ (see eq 24). However, replacement of one NH group by either O or S at the donor site leads to appreciable lowering of both β and γ, which may arise from the significant decrease of α and increase of μ (eqs 13 and 25). The pattern of variation of γ for three distinct kinds of indigo derivatives shows a rather remarkable identical trend with $\Phi_{xxxx}/\Delta E^3$ and $\Theta_{xx}^2/\Delta E^3$, respectively (Figure 3a and 3b).

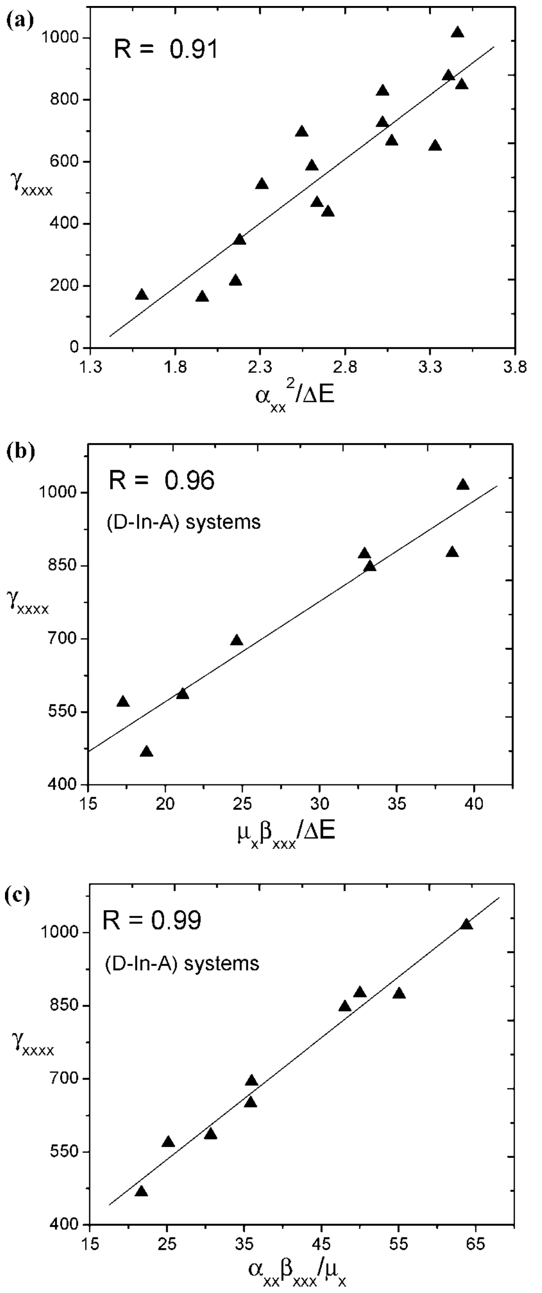


Figure 2. Plot of (a) γ_{xxxx} versus $\alpha_{xx}^2/\Delta E$ (eq 22), (b) γ_{xxxx} versus $\mu_x\beta_{xxx}/\Delta E$ (eq 23), and (c) γ_{xxxx} versus $\alpha_{xx}\beta_{xxx}/\mu_x$ (eq 24) for molecules of Table 1.

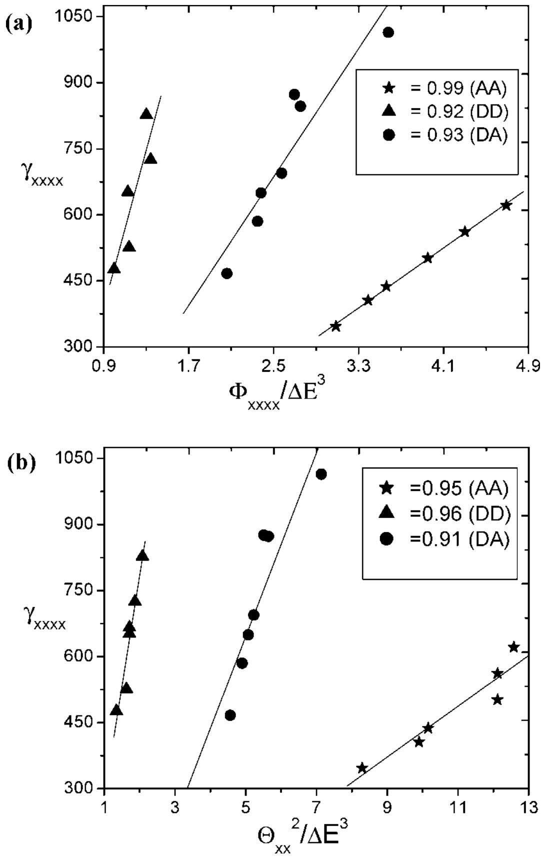


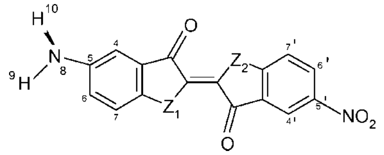
Figure 3. Plot of (a) γ_{xxxx} versus $\Phi_{xxxx}/\Delta E^3$ (eq 28) and (b) γ_{xxxx} versus $\Theta_{xx}^2/\Delta E^3$ (eq 29).

It is worthwhile to mention that the relative order of γ in the following pair of D–A-substituted molecules, 2 < 4, 1 < 6 and 3 > 7 (fourth-set in Table 1), can be reasonably explained using eqs 26 and 27. In order to examine the substitution effect at the 6,6′ positions (versus 5,5′ positions) of indigo on the NLO properties we considered two acceptors (A–A) and a donor–acceptor pair (D–A) at these positions, respectively (see footnote of Table 1). As can be seen the calculated γ_{xxxx} of 6,6′-substituted molecules are substantially smaller than the corresponding 5,5′-substituted derivatives (Table 1), which can be accounted for by the relatively lower value of α associated with the former.

The calculated ground-state total dipole moment and polarizabilities (Table 2) of molecules in Scheme 1 obtained at the fully optimized quasi-planar structure are found to be lower than that of the corresponding planar structure (Table 1). In this respect, γ (compared to β) shows rather significant lowering. The decrease of NLO responses may be attributed to the reduced CT interaction (as indicated by an increase of ΔE) arising from the nonplanar NH_2 group. The D–In–D systems in Table 2 have nearly zero dipole moment, and the calculated γ_{xxxx} value decreases on gradual replacement of NH groups of indigo with either the S or O atom. This primarily arises from the lowering of α_{xx} and increase of ΔE (eq 22). For thio compounds, as noted above, one should consider eq 4 for ΔE. The calculated γ also shows a nice trend with $\Theta_{xx}^2/\Delta E^3$ (eq 29) for the D–In–D species. For dipolar molecules this trend is, however, violated in some cases. The donor–acceptor-substituted indigos analogous to the corresponding planar isomers (Table 1) possess appreciable values of μ, β, and γ compared to the corresponding nonpolar compounds. The lowering of β at the quasi-planar geometry may be accounted for by the relatively smaller value of μ and α (eq 12), while that of γ arises from the significant lowering of β relative to α (see eq 26). The variation of γ of (A/D)–In–(D/A) species (Table 2) on replacement of the NH group with O and S and the substitution effect due to donor–acceptor follow exactly the same qualitative trend as noted for the planar structures (Table 1).

It is interesting to note that a small variation in the twist angle ($\tau_{7-6-5-8}$, Scheme 2) by about 3° between the nitrogen atom of NH_2 and the adjacent ring markedly lowers the γ value of donor-substituted indigo compounds, D–In–D and (D/A)–In–(A/D) (Table 2 versus Table 1). The variation of the twist angle on NLO properties of intramolecular charge-transfer (ICT) chromophores, especially the twisted ICT (TICT) molecular systems, has recently been investigated in depth by Brown et al.[21,22] and others.[23] In this spirit, it would be worthwhile to examine whether further increasing of the twist angle (pyrami-

SCHEME 2



dalization of the NH$_2$ group) will lead to still further lowering of γ. The slight twisting, however, should change the nature of hybridization of the N atom of the NH$_2$ group from sp^2 in the planar structure to sp^3 in the nonplanar geometry. This causes mixing of the nitrogen p orbital having the lone-pair electron with the s orbital and should reduce the donor strength in the ground state but favor the dipole transition of charge from the donor to the π^* antibonding MO. The value of the transition moment integral and hence the oscillator strength is, therefore, expected to be increased as a result of pyramidalization, which may have a significant impact on the NLO responses. To explore this aspect, we considered two molecules, (H$_2$N)−NH−O−(NO$_2$) and (H$_2$N)−NH−S−(NO$_2$) (Scheme 2), and calculated their NLO properties at different twist angles, 180°, 177°, 174°, 171°, and 168°. The geometry at each twist angle has been further optimized. The calculated results showed that the NLO properties, especially γ (Table 3), fall sharply at 177°, thereafter β remains almost insensitive while γ shows a slight rise on going from 177° to 174°, but it becomes invariant beyond 174°. To explain this sort of variation of NLO properties on increasing pyramidalization of the donor moiety the commonly used 2-state model (TSM)[4,5] has been invoked

$$\alpha_{xx} \propto \frac{f_{eg}}{\Delta E_{eg}^2} \tag{30}$$

$$\beta_{xxx} \propto \frac{\Delta\mu_{eg} f_{eg}}{\Delta E_{eg}^3} \tag{31}$$

$$\gamma_{xxxx} \propto (D - N) \tag{32}$$

$$D \propto \frac{\Delta\mu_{eg}^2 f_{eg}}{\Delta E_{eg}^4} N \propto \frac{f_{eg}^2}{\Delta E_{eg}^5} \tag{33}$$

The TSM γ consists of two terms, dipolar (D) and negative (N). In eqs 30−33 ΔE_{eg} is the transition energy gap between the ground and the lowest lying ICT state, $\Delta\mu_{eg}$ is the dipole moment difference between the ground and the excited ICT state, and f_{eg} is the corresponding oscillator strength. The calculated gas-phase electronic properties of the lowest energy singlet excited ICT state of two molecules in Scheme 2 at three twist angles are presented in Table 4. It is to be noted that both the calculated quantities ΔE_{eg} and f_{eg} for each molecule increase gradually on going from the planar to the twisted structure. The significant change, however, occurs at 177°. The dipole moment difference is highest at 180° and lowest at 177°, which makes the dipolar term maximum and minimum at 180° and 177°, respectively. In contrast, the negative term is highest at 177° and lowest at 180° due to the greater increase of oscillator strength (~10 times in atomic unit) relative to the transition energy on twisting. Thus, the overall magnitude of γ_{xxxx} as expected from eq 32 is found to be highest at the planar geometry compared to those obtained at the nonplanar structure. The present finding of the lowering of NLO properties of ICT molecular systems due to increasing pyramidalization of NH$_2$, however, may not be obeyed in general.[24] The similar plots of β as in Figure 1a and γ as in Figure 2c were also obtained with good correlations for the two molecules (Table 3) at different twist angles.

In order to get an explicit expression of the constant k one can use eqs 3 and 9 to obtain the following relation appropriate for polar molecules

$$k = \frac{\Delta E \alpha_{xx}}{2\mu_x^2} \rho \tag{34}$$

The parameter ρ takes care of the angular orientation of the donor orbital and hence the extent of overlap with the π acceptor, $\rho \propto S(0)\cos(\theta)$, where $S(0)$ is the overlap at $\theta_{6-5-8-9} = 0°$ (Scheme 2) in the planar case. For the chosen nonplanar compounds in Table 2, $\theta \approx 28°$. For both the planar and the nonplanar D−In−A compounds the value of k has been found to lie within ~10−14 au. However, for each molecule $k_{\text{planar}} \approx k_{\text{nonplanar}}$. This has also been confirmed from the ratio $k_{\text{planar}}/k_{\text{nonplanar}} \approx 1.0$ as obtained from the slopes of the plots β vs $\mu_x\alpha_{xx}/\Delta E$ and $(\alpha_{xx})^2/\mu_x$ (eqs 12 and 13) separately for planar and nonplanar cases. For the planar nonpolar molecules of Table 1 a rough estimate of k for D−In−D obtained from the plot like in Figure 2a was found to be ~1.63 times of that obtained for A−In−A, which may be due to their different charge-transfer characteristics.

For dipolar compounds, the quantity $(k - 1)\mu_x$ can bear an important physical significance. This follows from the combination of eqs 30 and 31, which leads to the following expression that is similar to eq 12

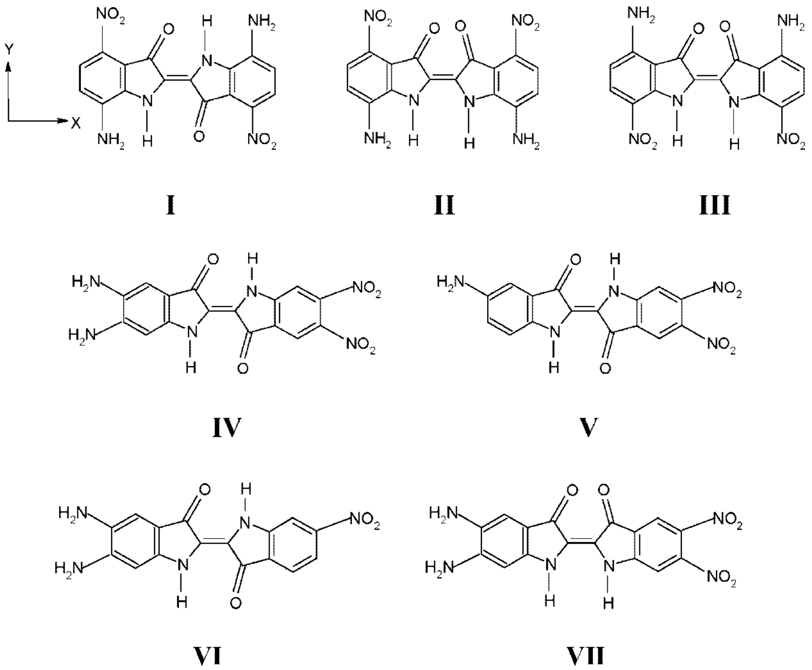
$$\beta_{xxx} \propto \frac{\Delta\mu_{eg}\alpha_{xx}}{\Delta E_{eg}} \tag{35}$$

Thus, in our model $|(k - 1)\mu_x| \propto |\Delta\mu_{eg}|$ and since both TSM β and γ (eqs 31−33) depend on the $|\Delta\mu|$ term it is reasonable to find the larger value of NLO responses of planar D−In−A (Table 1) compared to those of nonplanar isomers (Table 2).

3.2. NLO Properties of Molecules in Scheme 3 (Table 5). The calculated value of the mean transition energy (ΔE), the axial components of the ground-state dipole moment (μ_i), linear polarizability (α_{ii}), first hyperpolarizability (β_{iii}), and second hyperpolarizability (γ_{iiii}) along with β_{vec} for molecules of Scheme 3 have been presented in Table 5. The direction of CT in molecules I−III lies along the Y axis, while for molecules IV−VII CT takes place along both the X and Y axes, which has also been obtained from their calculated dipole moments. The variation of the axial component of β, in general, follows eq 12. The variation of γ, however, shows a rather different trend with respect to the structural changes. It should be noted that the appreciable enhancement of γ occurs along the direction (with $\mu = 0$) which is orthogonal to the donor−acceptor dipole pairs (at 4,7 and 4′,7′ positions). On the other hand, the appreciably larger γ is predicted along the direction associated with the higher dipole moment arising from the donor−acceptor pairs at the 5,5′ and 6,6′ positions.

For each of the molecules, I−III, the largest value of γ (by about an order of magnitude) is predicted along the X axis, which is associated with the largest value of α but zero dipole moment. For such molecular species, the axial variation of γ follows eq 22. This equation can also be used to explain the variation of the axial component of γ for each of the molecules IV−VII. This kind of dependence between the axial components of second hyperpolarizability and linear polarizability was also noted earlier by Kamada et al.[25] For the later compounds (excepting VII) γ also varies as $\alpha\beta/\mu$ (eq 24). Among the molecules IV−VII the largest longitudinal CT interaction along

SCHEME 3



the X axis takes place in V, which is indicated by comparing its inter-ring CC bond length (1.364 Å) with that (~1.362 Å) of IV, VI, and VII. This enhanced CT interaction leads to the highest β and γ values for molecule V.

4. Conclusions

In the present investigation it has been shown that the standard SOS expressions of both the first and second hyperpolarizabilities can be reduced to a single dipole-free term which involves only the transition moments. These have further been reduced to various equivalent expressions relating the ground-state electric moments and the lower order polarizabilities of a molecule by means of the TK sum rule. These simple relations allow one to reasonably compare and correlate the ab-initio-calculated NLO properties of both polar and nonpolar chromophore systems, especially for larger molecules, without calculating the spectroscopic quantities as needed in the standard SOS expressions, which may require rather huge computational costs. The variation of hyperpolarizabilities of different types

TABLE 3: B3LYP/6-31+G*//B3LYP/6-31+G*-Calculated Mean Excitation Energy (ΔE, eV), Ground-State Dipole Moment (μ, D), and Static Linear (α, 10^{-23} esu) and Nonlinear Optical Parameters (β, 10^{-30} esu and γ, 10^{-36} esu) of Two Molecules of Scheme *2* at Different Twist Angles ($\tau_{7\text{-}6\text{-}5\text{-}8}$, deg)

Z_1	Z_2	τ	ΔE	μ_g	μ_x	α_{xx}	β_{xxx}	β_{vec}	γ_{xxxx}
NH	O	180	17.28	9.448	8.395	6.83	67.73	94.90	873.2
		177	17.34	8.609	7.523	6.74	57.08	80.30	738.3
		174	17.34	8.638	7.673	6.83	58.83	79.98	772.0
		171	17.34	8.664	7.704	6.83	58.46	79.57	771.2
		168	17.33	8.689	7.736	6.83	58.15	79.23	762.4
NH	S	180	16.68	9.424	8.835	7.60	74.18	83.98	1014.4
		177	16.74	8.588	7.968	7.51	63.79	70.78	874.2
		174	16.74	8.626	8.058	7.54	64.05	70.50	886.7
		171	16.73	8.643	8.082	7.55	63.65	70.05	884.8
		168	16.73	8.668	8.115	7.55	63.37	69.78	880.5

TABLE 4: CIS/6-31+G*//B3LYP/6-31+G*-Calculated Gas-Phase Dipole Moment (μ_e, D) of the Lowest Energy Singlet ICT State, Dipole Moment Difference Between the Excited ICT State and Ground-State ($\Delta\mu_{eg}$, D), Transition Energy (ΔE_{eg}, eV), and Oscillator Strength (f_{eg}, au) of the Singlet Excited State of Two Molecules of Scheme *2* at Three Twist Angles ($\tau_{7\text{-}6\text{-}5\text{-}8}$, deg)

Z_1	Z_2	τ	μ_e	μ_e^x	$\Delta\mu_{eg}^x$	ΔE_{eg}	f_{eg}
NH	O	180	14.587	12.045	3.395	3.376	0.3384
		177	13.338	10.838	3.315	3.474	0.3672
		174	13.365	11.068	3.65	3.478	0.3678
NH	S	180	13.725	12.018	2.746	3.309	0.3446
		177	12.312	10.700	2.732	3.399	0.3792
		174	12.332	10.804	3.183	3.401	0.3799

TABLE 5: B3LYP/6-31+G*//B3LYP/6-31+G*-Calculated Mean Excitation Energy (ΔE, eV) and the Axial Components[a] of Ground-State Dipole Moment (μ, D), Static Linear (α, 10^{-23} esu) and Nonlinear Optical Parameters (β, 10^{-30} esu and γ, 10^{-36} esu) of Molecules of Scheme *3*

molecule	ΔE	μ_i	α_{ii}	β_{iii}	β_{vec}	γ_{iiii}
I	17.82	0.09	7.44	0.223	1.98	541.6
		2.37	1.94	0.271		15.7
		0.19	5.34	0.066		114.3
II	18.66	0.00	6.69	0.050	26.43	564.8
		17.9	4.75	15.56		87.1
		0.02	1.98	0.006		17.3
III	17.73	0.00	7.77	0.032	3.62	528.5
		8.38	5.34	23.04		40.9
		0.03	1.75	0.014		10.2
IV	17.27	11.88	7.65	39.10	88.19	498.9
		9.12	6.01	27.54		294.2
		0.75	2.00	0.238		12.2
V	17.22	10.96	7.77	76.93	116.95	1157.0
		7.23	5.29	14.92		319.5
		1.84	1.93	0.415		11.4
VI	16.87	6.04	6.88	26.53	85.20	486.3
		7.89	5.87	36.57		346.0
		0.03	1.70	0.038		11.7
VII	17.88	13.14	5.74	40.48	83.69	205.5
		7.34	6.86	16.07		652.2
		1.01	2.03	0.302		13.6

[a] The three successive values against each molecule stand for the axial components x, y and z, respectively.

of indigo compounds has been satisfactorily explained by the present approach. The effect of increasing pyramidalization of the NH_2 group on the NLO properties of the indigo compounds can also be satisfactorily explained by the present model.

Calculation of the linear polarizability alone or electric multipole moments is sufficient to allow one to compare and determine the potential third-order NLO-phores. This investigation also demonstrated that for the chosen indigo derivatives the magnitude of γ depends largely on α. The present analysis can hopefully be extended to other kinds of NLO-phores.

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