Effect of charge and spin multiplicity on hyperpolarizabilities of donor-acceptor substituted polyenes

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Theoretical studies of the ground state structure and nonlinear optical (NLO) properties of a number of donor-acceptor substituted singlet and triplet (neutral) and doublet (mono-positive and mono-negative) polyenes have been carried out. The variation of NLO property of the investigated molecules has been explained by using previously derived relationships between the different order polarizabilities and ground state dipole moment obtained in the framework of the standard sum-over-state expressions of Orr-Ward-Bishop and the generalized Thomas-Kuhn sum rule. The effect of charge and spin multiplicity on the molecular hyperpolarizabilities have been discussed in terms of relative changes of polarizability and ground state dipole moment. Among the investigated polyenes, the isotropic polarizability and the second-hyperpolarizability are predicted to be larger for the doublet anions in which the NH_2 group is pyramidal. The position of nitrogen atom in the π-conjugative path strongly modulates the magnitudes of both the first- and second-hyperpolarizabilities of the investigated polyenes.

Keywords: Theoretical chemistry, Ground state structure, Nonlinear optical properties, Hyperpolarizabilities, Charge, Spin multiplicity, Sum-over-state expressions, Polyenes

Several theoretical and experimental investigations have been carried out to search for potential NLO-materials suitable for various opto-electronic applications. Organic chromophores with varying structural and charge transfer (CT) characteristics have been used extensively in the design of potential NLO-phores. Because of the presence of delocalizable π electrons[1-4], successive use of light alkali metals have significant effects on the second polarizability[5] Quantum chemical calculations and analysis[6-11] have been found to be indispensable to guide synthetic efforts of NLO materials in the elucidation of structure-property relationships as well as to provide mechanism for optimizing the hyperpolarizabilities. Quite a large number of *ab initio* DFT and post-HF calculations have been performed to evaluate the polarizabilities and hyperpolarizabilities of various closed- and open-shell species[1-3]. The electron correlation effect has been found[12-15] to play a significant role in the evaluation of higher-order polarizabilities.

Nakano *et al.* reported[16-19] that the second-hyperpolarizability (γ) of open-shell model nonlinear optical systems depends largely on the spin multiplicity and diradical character compared to the conventional closed-shell NLO chromophores. They explained the spatial contribution of electrons to the second-hyperpolarizability by using the γ density (third-order derivative of electron density with respect to the applied electric fields) analysis[20]. Since the removal of spin contamination and inclusion of electron correlation are essential for calculating hyperpolarizabilities of open-shell systems the spin-unrestricted hybrid density functional theory (DFT) has been used popularly[16-19] to calculate their NLO properties. Hu *et al.* made a comparative study of the calculated[21] α and γ for neutral and charged, closed- and open-shell *trans*-polyacetylene (PA) chains, $C_{2n}H_{2n+2}$, $C_{2n-1}H_{2n+1}$, $C_{2n-1}H^+_{2n+1}$, $C_{2n}H^+_{2n+2}$ and $C_{2n}H^{2+}_{2n+2}$ and predicted that the two neutral PA chains $C_{2n}H_{2n+2}$ and $C_{2n-1}H_{2n+1}$ have similar value of α and γ, while charged doped systems all have larger NLO responses than the neutral ones. The two singly charged PA chains $C_{2n-1}H^+_{2n+1}$ and $C_{2n}H^+_{2n+2}$ possess much larger α and γ than the doubly charged $C_{2n}H^{2+}_{2n+2}$ while the formers have negative γ value. The UCCSD calculated results[22] of linear and non-linear optical properties of neutral π-conjugated pyrrole radical (C_4H_4N) in the doublet, quartet and sextet states shows the variation of β_{tot} in the order

$\beta_{sextet} > \beta_{doublet} > \beta_{quartet}$ and that of $<\gamma>$ as $\gamma_{quartet} > \gamma_{sextet} > \gamma_{doublet}$. It has also been noted that the variation of γ follows the same trend as α. The radical ions (polarons) generated in the electrochemical doping[23] of poly(bithiophene) polymer and in the Raman excitations[24] of solid 2-methyl-4-nitroaniline (MNA) possess hperpolarizabilities which are almost one order of magnitude larger compared to their neutral counterpart.

The SOS scheme of Orr-Ward-Bishop (OWB)[25,26] relating hyperpolarizabilities to the spectroscopic property of a molecule has been used popularly to explain the origin of NLO properties. For chromophores with dominant longitudinal CT interaction the variation of first-hyperpolarizability (β) can be explained by the two-state model (TSM)[27,28]. The three-term SOS expression[4] has been satisfactorily used to explain the variation of second-hyperpolarizability of a number of donor-acceptor substituted closed-shell polyenes. An interesting correlation between the third-order polarizability (γ) and the polarizability (α) was noted earlier[22,29-33] but no theoretical justification was given to explain this relationship. We have, recently, proposed a new method of analysis[34-38] which can provide a number of relationships between the polarizabilities of different order and the ground state electric multipole moments in the framework of the standard SOS expressions of NLO coefficients and the Thomas-Kuhn (TK) sum rule (relating transition dipole moments to transition energies)[39,40]. These relationships have been used to explain the variation of NLO responses of various kind of closed-shell intramolecular charge transferring molecular systems. Such relationships between different polarizabilities may be useful to theoreticians as well as experimentalists to rationalize the variation of higher-order NLO responses in terms of lower-order polarizabilities and hence to optimize the hyperpolarizability. The general validity of these relationships may be justified by applying them to both the closed-shell as well as open-shell molecular species. This prompted us to consider a number of donor-acceptor substituted polyenes with varying structural conformations (Schemes 1–4) for different spin multiplicities: singlet and triplet (neutrals) and radical ions (doublet cations and doublet anions) to make a systematic and comparative study of static first- and second-hyperpolarizabilities in terms of polarizability and ground state dipole moment by

employing the various relationships obtained in our previous works. The chosen molecules belong to a class of electron-donor and electron-acceptor compounds. A number of experimental[41,42,43] and theoretical[38,44,45] studies of NLO properties of linear polyenes with varying donor and acceptor substituent closely related to that of Schemes 1 and 4 can be found in the literature. For the investigated molecules and ions the longitudinal component of NLO parameters is the axial component lying along the donor-acceptor groups that is taken as the *x*-axis.

**Theoretical and Computational Methods**

The ground state geometry of polyenes (Schemes 1–4) with varying charge and spin multiplicities: neutral singlets (nS) and neutral triplets (nT), uni-positive doublets (nP) and uni-negative doublets (nN) have been fully optimized by employing the RB3LYP method for closed-shell species and UB3LYP method for open-shell species for the 6-311++G** basis set. The present DFT method consists of the hybrid exchange-correlation functional (Becke + Slater + HF exchange and LYP + VWN5 correlations)[46-48]. The
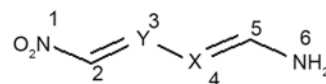
a: X = C, Y = C; b: X = C, Y = N; c: X = N, Y = C; d: X = N, Y = N
Scheme 1
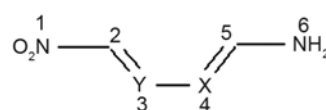
a: X = C, Y = C; b: X = C, Y = N; c: X = N, Y = C; d: X = N, Y = N
Scheme 2
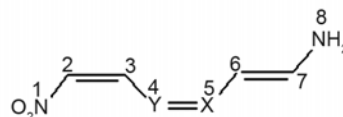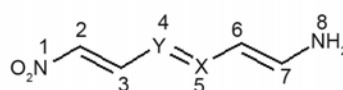

a: X = C, Y = C; b: X = C, Y = N; c: X = N, Y = C; d: X = N, Y = N
Scheme 3

a: X = C, Y = C; b: X = C, Y = N; c: X = N, Y = C; d: X = N, Y = N
Scheme 4

optimized structures correspond to the energy minima in the potential hyper-surfaces which have been confirmed by real frequencies obtained for all the normal modes in the vibrational calculations. The important optimized angles and dihedral angles of the chosen molecules are listed in the Schemes S1-S4 (Supplementary Data). Among the investigated molecules the negatively charged doublet polyenes have ∠HNH angles fairly close to that (about 108°) of NH_3 molecule. It can be seen that most of the structures are not perfectly planar. The linear and non-linear polarizabilities are calculated at the B3LYP/6-311++G** and UB3LYP/6-311++G** levels using the respective optimized geometry. The UB3LYP method correctly predicts the eigenvalue of $\hat{S}$ for the studied open-shell polyenes. In our recent work[38], it has been noted that the B3LYP functional with 6-311++G** can give hyperpolarizabilities of *p*-nitro aniline (PNA) molecule which closely agree with the experimental results. Thus, the present DFT method should give reliable values of NLO properties of the investigated polyenes.

The Cartesian components of static dipole polarizability (α_{ij}) and first-hyperpolarizability (β_{ijk}) of each molecule are computed analytically using the following expressions at the B3LYP/6-311++G** level. The components of dipole second-hyperpolarizability (γ_{ijkl}) are, however, calculated by numerical differentiation of first-hyperpolarizability as implemented in the G09 program suite[49]. Numerical accuracy has been tested by varying the field amplitude around the default value 0.00033 au.

$$\alpha_{ij} = \left(\frac{\partial \mu_i}{\partial F_j} \right) \qquad \qquad \dots (1)$$

$$\beta_{ijk} = \left(\frac{\partial^2 \mu_i}{\partial F_j \partial F_K} \right) \qquad \qquad \dots (2)$$

$$\gamma_{ijkl} = \left(\frac{\partial^3 \mu_i}{\partial F_j \partial F_k \partial F_l} \right) = \left(\frac{\partial \beta_{ijk}}{\partial F_l} \right) \qquad \dots (3)$$

The mean linear polarizability ($<\alpha>$) is calculated as one third of the trace of linear polarizability tensor.

$$\alpha_{av} = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \qquad \dots (4)$$

The vector-part of second-order polarizability (β_{vec} or $\beta_{\parallel}$)[1] as calculated in this work is given by,

$$\beta_{\parallel} = \frac{1}{5}(\sqrt{\beta_x^2 + \beta_y^2 + \beta_z^2} \qquad \dots (5)$$

where β_i,s are the components of β vectors. For example β_x is given by

$$\beta_x = \beta_{xxx} + \frac{1}{3}\sum_{j \neq x}(\beta_{xjj} + \beta_{jxj} + \beta_{jjx}) \qquad \dots (6)$$

The orientationally average second-hyperpolarizability ($<\gamma>$) has been calculated from the following expression[1],

$$<\gamma> = \frac{1}{5}\left\{ \begin{array}{c} \gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} \\ +2(\gamma_{xxyy} + \gamma_{yyzz} + \gamma_{xxzz}) \end{array} \right\} \qquad \dots (7)$$

In most of the earlier theoretical studies the variation of hyperpolarizabilities among related chromophores was satisfactorily explained in terms of simple two-level and three-level models. However, according to the perturbation expression of NLO coefficients the magnitude of hyperpolarizabilities depends on the extent of coupling between the ground and excited states, and also between different excited states which could provide significant two-photon contributions. Thus the state wise analysis seems to be rather difficult task while explaining the higher-order electric response properties, in general. Therefore, the following alternative method of analysis has been sought for which could provide useful structure-property correlations.

In the later approach, the standard sum-over-states (SOS) expressions of hyperpolarizabilities obtained from the time-dependent perturbation theory are reduced to much simpler expressions by employing the generalized TK sum rules and the Unsöld approximation[50] of mean transition energy.

The axial component of β for the second harmonic generation and γ for third harmonic generation along the molecular dipolar axis, x are given below.

$$\beta_{xxx}(-2\omega;\omega,\omega)(\text{SHG}) =$$

$$6\sum_{m \neq g}\sum_{n \neq g}\frac{\mu_{gm}(\mu_{mn} - \mu_{gg}\delta_{mn})\mu_{ng}}{(\Delta E_{gm} - 2\hbar\omega - i\Gamma_{gm})(\Delta E_{gn} - \hbar\omega - i\Gamma_{gn})}$$

$$\dots (8)$$

$$\gamma_{xxxx}(-3\omega;\omega,\omega,\omega)(\text{THG}) =$$

$$24\left[\sum_{m \neq g}\sum_{n \neq g}\sum_{p \neq g}\frac{\mu_{gm}(\mu_{mn} - \mu_{gg}\delta_{mn})\frac{(\mu_{np} - \mu_{gg}\delta_{np})\mu_{pg}}{(\Delta E_{gm} - 3\hbar\omega - i\Gamma_{gm})}}{(\Delta E_{gn} - 2\hbar\omega - i\Gamma_{gn})(\Delta E_{gp} - \hbar\omega - i\Gamma_{gp})} - \right.$$

$$\left. \sum_{m \neq g}\sum_{p \neq g}\frac{\mu_{gm}\mu_{mg}\mu_{gp}\mu_{pg}}{(\Delta E_{gm} - 3\hbar\omega - i\Gamma_{gm})(\Delta E_{gp} - \hbar\omega - i\Gamma_{gp})(\Delta E_{gp} + \hbar\omega - i\Gamma_{gp})} \right]$$

$$\dots (9)$$

where ω is the frequency of the perturbing radiation field. The factor Γ in the above equations is necessary for calculating the NLO components at the resonance limit corresponding to each excited state. The static response properties correspond to $\omega = 0$. In the following, are given the expressions where the higher-order polarizabilities (Eqs.(2) and (3)) are related to the lower-order polarizabilities, ground state dipole moment and the number of electrons. These relationships will be used to discuss the variation of NLO properties among the investigated molecules.

$$\beta_{xxx} \propto \frac{\mu_x \alpha_{xx}^{3/2}}{\sqrt{N}} \text{ or } \beta_{xxx} \propto \frac{\mu_g <\gamma>^{3/2}}{\sqrt{N}} \qquad \dots (10)$$

$$\gamma_{xxxx} \propto \frac{\alpha_{xx}^3}{\mu_x^2} \text{ or } <\gamma> \propto \frac{\mu_g <\alpha>^{3/2}}{\sqrt{N}} \qquad \dots (11)$$

$$\gamma_{xxxx} \propto \frac{\alpha_{xx}\beta_{xxx}}{\mu_x} \text{ or } <\gamma> \propto \frac{<\alpha>\beta_{vec}}{\mu_g} \qquad \dots (12)$$

The equivalent dipole-free expressions of second-hyperpolarizability are the followings.

$$\gamma_{xxxx} \propto \frac{\beta_{xxx}^2}{\alpha_{xx}} \text{ or } <\gamma> \propto \frac{\beta_{vec}^2}{<\alpha>} \qquad \dots (13)$$

$$\gamma_{xxxx} \propto \frac{\alpha_{xx}^{5/2}}{\sqrt{N}} \text{ or } <\gamma> \propto \frac{<\alpha>^{5/2}}{\sqrt{N}} \qquad \dots (14)$$

The above linear relationships is expected to be valid for a series of related molecules at a given method. All calculations were carried out by using the G09 program[49].

Results and Discussion

The UB3LYP/6-311++G** calculated longitudinal components (x-components for the present molecular species) of dipole moment, polarizibility, first-and second-hyperpolarizibilities along with the mean polarizability, vector-part of first-hyperpolarizability ($\beta_{\parallel}$) and the second-hyperpolarizability of the investigated polyenes (Schemes 1–4) have been reported in Table 1. The molecules represented in Table 1 belong to a particular Scheme (1/2/3/4) in the order, a: (X = Y = C), b: (X = C, Y = N), c: (X = N, Y = C) and d: (X = N, Y = N), respectively. The molecules in a group belong to a particular category (a, b, c, d) in different spin states (neutral singlet (S)/ neutral triplet (T)/ positive doublet (P)/ negative doublet (N)). For example a molecule labeled as "2bT" indicates that the molecule belongs to Scheme 2, category b with triplet spin multiplicity (T). In all cases, the predominant charge transfer (CT) as indicated by the dipole moment takes place along the x-axis. Also for the chosen molecules the plots of $<\alpha>$ versus α_{xx}, $\beta_{\parallel}$ *versus* β_{xxx} and $<\gamma>$ versus γ_{xxxx} are found to be linear (excepting for the neutral singlets). For the singlet molecules the longitudinal components of response quantities are used in the plots while for molecules of higher spin

Table 1 — B3LYP/ 6-311++G** calculated dipole moment, polarizibility, first-hyperpolarizibility and second-hyperpolarizibility of donor-acceptor substituted polyenes (Schemes 1–4) in the neutral singlet (S), neutral triplet (T), doublet positive (P) and doublet negative (N)

Molecule	μ_x (Debye)	μ_g (Debye)	α_{xx} (au)	$<\alpha>$ (au)	β_{xxx} (au)	$\beta_{\parallel}$ (au)	γ_{xxxx} (10^4 au)	$<\gamma>$ (10^4 au)
1aS	7.8	9.7	157.49	97.6	-760.5	1239.5	0.92	1.89
1aT	11.0	11.1	218.2	111.9	-2861.6	1667.4	-5.77	0.39
1aP	13.3	13.3	175.6	92.4	3273.2	2081.6	41.69	9.40
1aN	8.9	9.2	228.4	122.7	-7110.4	5168.7	639.50	166.9
1bS	8.2	9.3	168.7	92.9	1845.5	1358.8	3.57	2.21
1bT	7.6	7.9	194.7	103.9	-1222.7	679.3	5.33	2.21
1bP	12.2	12.5	149.3	81.9	-1205.5	773.1	22.20	4.95
1bN	8.7	9.1	204.7	112.9	-1900.5	1542.9	117.37	32.08
1cS	8.0	9.2	138.3	88.0	-321.6	748.9	2.64	2.38
1cT	7.4	7.4	175.9	97.7	-254.8	142.0	13.15	3.92
1cP	11.4	11.4	171.7	89.9	-2903.5	1878.9	16.60	4.33
1cN	8.8	8.9	232.8	122.5	-8809.8	6155.1	707.30	177.46
1dS	8.2	8.3	143.9	81.5	-1528.0	930.9	8.83	2.98
1dT	7.1	7.2	172.6	94.2	2059.2	1150.4	31.86	7.45
1dP	11.8	12.0	146.2	78.0	-1546.1	976.5	29.29	6.43
1dN	9.2	9.3	195.5	108.2	-4000.2	2832.5	175.77	45.89
2aS	7.8	9.5	129.8	93.8	-1002.9	1243.8	2.42	1.92
2aT	10.2	10.2	194.5	106.1	-2710.5	1578.3	-0.30	1.57

(contd.)

Table 1 — B3LYP/ 6-311++G** calculated dipole moment, polarizibility, first-hyperpolarizibility and second-hyperpolarizibility of donor-acceptor substituted polyenes (Schemes 1–4) in the neutral singlet (S), neutral triplet (T), doublet positive (P) and doublet negative (N) (*contd.*)

Molecule	μ_x (Debye)	μ_g (Debye)	α_{xx} (au)	$<\alpha>$ (au)	β_{xxx} (au)	$\beta_{\parallel}$ (au)	γ_{xxxx} (10^4 au)	$<\gamma>$ (10^4 au)
2aP	13.1	14.1	162.2	89.0	-3103.0	1942.7	39.33	8.66
2aN	8.7	8.7	213.9	120.2	5443.5	4091.9	426.98	111.89
2bS	8.4	8.8	133.9	88.3	-1536.7	1420.5	6.05	2.84
2bT	7.9	8.0	127.1	84.4	-178.7	182.9	2.80	1.56
2bN	8.5	8.5	189.0	109.1	-2545.4	2034.3	149.63	41.09
2cS	7.1	8.5	105.8	82.1	-514.8	553.2	3.65	2.32
2cT	6.7	7.0	155.0	93.4	692.9	376.1	35.59	8.46
2cP	8.7	8.8	144.5	83.3	235.3	201.5	1.07	0.54
2cN	7.7	7.8	216.2	118.6	6503.4	4715.7	459.34	117.69
2dT	6.9	7.4	125.2	81.2	-330.6	257.7	3.35	1.59
2dN	9.2	9.4	168.9	101.2	-9685.4	6544.7	688.25	165.99
3aS	9.7	10.8	276.2	144.0	2994.7	2280.4	9.27	4.06
3aT	11.8	12.1	329.1	160.7	6102.6	3662.8	-0.39	1.54
3aP	15.0	15.3	264.1	132.9	2481.5	1550.6	32.54	7.42
3aN	10.3	10.6	338.4	170.7	-5059.6	3386.6	220.35	60.68
3bS	6.8	7.2	159.6	111.5	331.2	417.1	5.51	2.63
3bT	9.4	10.2	311.5	155.3	9921.3	6001.4	35.12	9.21
3bP	12.1	12.6	261.9	136.6	-3303.2	2300.0	5.87	2.62
3bN	10.2	10.5	344.7	172.2	-4401.1	3538.1	404.33	113.91
3cS	7.7	9.9	217.0	140.5	3842.1	2847.2	8.97	3.89
3cT	10.7	10.9	247.4	131.0	-2377.4	1443.7	10.15	4.05
3cP	13.8	14.3	240.1	122.5	834.4	459.5	31.26	7.28
3cN	8.9	9.6	311.9	159.6	-1392.2	1095.9	66.95	19.93
3dS	7.2	9.8	187.0	114.6	593.1	632.8	5.54	3.04
3dN	8.9	10.2	291.1	152.9	2149.3	1476.5	49.81	17.60
4aS	8.8	11.6	254.8	153.6	2001.4	3413.0	4.40	6.10
4aT	12.8	12.9	372.4	173.2	8220.9	4889.9	2.60	2.45
4aP	16.9	17.0	295.3	148.8	-1931.3	1261.5	23.94	5.79
4aN	11.3	11.4	396.4	188.8	6954.0	4663.1	350.10	87.43
4bS	8.1	12.1	226.3	140.0	1080.9	2301.2	6.81	6.65
4bT	11.8	11.8	376.7	172.9	9392.6	5564.9	-19.18	-1.82
4bP	15.9	15.9	314.2	147.1	-5710.5	3576.3	71.54	16.02
4bN	10.7	10.8	388.3	184.2	3278.6	2435.1	238.54	61.93
4cS	7.9	10.7	148.4	149.5	1839.9	3925.3	9.90	6.54
4cP	16.6	16.8	289.0	138.5	-5111.1	3192.7	90.19	19.45
4cN	10.1	10.5	366.1	177.7	1762.7	1428.4	76.38	22.27
4dS	8.9	11.7	229.3	140.4	1170.4	2255.1	3.93	5.61
4dT1	10.0	10.1	266.5	135.3	4035.2	2469.8	31.95	8.24
4dT2	8.8	9.2	265.5	135.0	2679.4	1732.8	24.73	7.22
4dP1	16.3	16.3	269.7	129.8	2969.3	1869.3	52.19	11.71
4dP2	11.2	11.6	268.0	131.1	996.1	878.1	4.39	2.44
4dN	9.7	9.8	359.2	173.0	658.2	834.6	56.85	18.57

multiplicity the corresponding mean values are used. Regarding the basis set superposition error (BSSE), we have noted[38] that for *p*-nitro aniline (PNA) molecule which is a prototypical donor-acceptor molecule, the B3LYP/6-311++G** calculated longitudinal component β_{xxx} (15.084E-30 esu) shows an excellent agreement with the corresponding MP2 (15.019E-30 esu) and experimental values (15.438E-30 esu). In view of this, we think that 6-311++G** basis set used in the present work is

appropriate and for the small donor-acceptor organic molecules considered in the present work, it seems that the BSSE effect on the calculated hyperpolarizabilities would be insignificant.

NLO properties of molecules (Scheme 1) with different spin states

Among the singlet molecules of Scheme 1, it can be seen that for 1bS (X = C, Y = N) (versus 1aS) in which one carbon atom at the acceptor (NO_2) side is replaced by one nitrogen atom both the linear polarizability (α_{xx}) and first-hyperpolarizability (β_{xxx}) increases. However, when one carbon in the donor (NH_2) side is replaced by a nitrogen atom (1cS) both α_{xx} and β_{xxx} decreases while replacing both the central carbon atoms by nitrogen atoms (1dS) results in further increase of α_{xx} and β_{xxx} compared to 1cS. The calculated μ_x remains almost unchanged. The variation of first-hyperpolarizability is consistent with Eq. (10). The maximum value of γ_{xxxx} is obtained for molecule 1dS.

In the case of triplet polyenes, the $<\alpha>$ and μ_g values decrease which lowers $\beta_{\parallel}$ on gradual replacement of carbon atom of the central C-C bond (Y = X = C) with nitrogen atom. However, $<\gamma>$ shows a regular increasing trend predicting the maximum value for 1dT (X = Y = N). The larger value of γ_{xxxx} obtained for molecule 1dT compared to that of 1aT arises from the relatively smaller value of μ_x of the former (see Eq. 11).

The dipole moment of positive doublets compared to the neutral singlets and triplets and negative doublets are found to be substantially larger. It can be seen that on replacing the carbon atom(s) of the chain $<\alpha>$, $\beta_{\parallel}$ and $<\gamma>$ of positive doublets decrease significantly predicting the maximum of these quantities for molecule 1aP (X = Y = C). The maximum $<\gamma>$ corresponds to maximum of $<\alpha>\beta_{\parallel}/\mu_g$ and also of $\beta_{\parallel}^2/<\alpha>$ (see Eqs (7) and (8). The ground state dipole moment of negative doublets is nearly identical. The $<\alpha>$, $\beta_{\parallel}$ and $<\gamma>$ values obtained for the anions are significantly larger compared to molecules of other spin states. The largest β and γ are obtained for the molecule 1cN (X = N, Y = C). Again, the largest $<\gamma>$ of 1cN or the smallest $<\gamma>$ of 1bN may be justified by following the relative variations of $<\alpha>$ and $\beta_{\parallel}$ (see Eqs 7 and 8).

NLO properties of molecules (Scheme 2) with different spin states

The singlet polyenes under this scheme follow the similar trend as noted for the singlet molecules of Scheme 1. Here, the variations of α_{xx} and β_{xxx} are same. The maximum β_{xxx} corresponds to the maximum α_{xx} and maximum μ_x values and is fairly consistent with Eq. 10. The variation of γ_{xxxx} and $<\gamma>$ follows the relation in Eq. 12 predicting the maximum value for the molecule 2bS (X = C, Y = N).

In the case of triplets, the replacement of one or both C atoms by N atom(s) (2aT versus 2bT, 2cT and 2dT) significantly lowers (by an order of magnitude) $\beta_{\parallel}$ which may arise from the substantial decrease of mean polarizability. The magnitude of $<\gamma>$ obtained for molecules 2aT, 2bT and 2dT are rather small which is, however, significant for 2cT (X = N and Y = C). It should be noted that on replacing carbon with nitrogen (2cP vs. 2aP) substantially reduces the magnitudes of hyperpolarizabilities which can be explained by the relative variations of the polarizability and the ground state dipole moment. For the negative doublets, both $\beta_{\parallel}$ and $<\gamma>$ exhibit an identical pattern of variation predicting the maximum values for the polyene 2dN (X = N and Y = N). The largest $<\gamma>$ corresponds to largest $<\alpha>$ and $\beta_{\parallel}$ and smallest μ_g while the minimum $<\gamma>$ corresponds to the substantially smaller value of $\beta_{\parallel}$ (see Eqs 7 and 8).

NLO properties of molecules (Scheme 3) with different spin states

The molecules of Scheme 3 differ from that of Schemes 1 and 2 in the number of double bonds and their orientations. The variation of the electric response properties obtained for singlet molecules of Scheme 3 follows an exactly opposing trend as noted for molecules of Schemes 1 and 2. When one carbon in the acceptor side is replaced by nitrogen, the polarizability decreases significantly but when the carbon in the donor side is replaced by nitrogen polarizability increases. This arises from the extent of electron delocalization of nitrogen lone pair of NH_2. As can be seen in Scheme 3, the position of the double bonds in this conformation leads to accumulation of electron density on the electronegative N atom (3bS) which results in the lowering of α_{xx}, β_{xxx} and γ_{xxxx} and the corresponding mean values. But for molecule 3cS having nitrogen atom in the donor side favors the longitudinal electron delocalization which in turn strongly enhances the first-hyperpolarizability. The rather comparable second-hyperpolarizability of molecules 3aS and 3cS may be justified by means of Eq. (11).

Amongst the triplet molecules, the largest values of both $\beta_{\parallel}$ and $<\gamma>$ are predicted for molecule 3bT

(X = C, Y = N) which is contrary to the relative order predicted for the singlets. This rather larger $\beta_\parallel$ along with the relatively smaller μ_g value accounts for its largest value of second-hyperpolarizability. The relatively much larger first-hyperpolarizability of 3aP compared to that of 3cP arises from the larger μ_g and $<\alpha>$ of the former (see Eq. 10). However, the identical value of γ_{xxxx} or $<\gamma>$ of the two molecules may be explained by means of Eq. (11).

In the case of negative doublets, both $<\alpha>$ and $<\gamma>$ exhibits similar trend. The introduction of nitrogen atom in the polyene chain results in rather significant lowering of both first- and second-hyperpolarizability. Thus the largest magnitudes of both $\beta_\parallel$ and $<\gamma>$ are predicted for the polyene 3aN (X = Y = C) and the lowest for 3bN (X = C, Y = N) which is fairly consistent with Eqs (7) and (8).

NLO properties of molecules (Scheme 4) with different spin states

It can be seen that the molecules of Scheme 4 differs from that of Scheme 1 by the length of conjugative path. For the singlet species, both μ_x and α_{xx} follows almost identical pattern of variation. Although γ_{xxxx} shows significant variations the calculated $<\gamma>$ values do not vary noticeably which is reflected by the larger (smaller) variation of α_{xx} ($<\alpha>$). The maximum values of α_{xx} and β_{xxx} are obtained for molecule 4aS (X = Y = C) while the largest value of γ_{xxxx} is predicted for molecule 4cS in which one carbon in the donor side is replaced with nitrogen. For the neutral triplets β_{xxx} is predicted to be the largest compared to the other molecules under this scheme. The relatively larger (4aT and 4bT) and smaller (4dT1 and 4dT2) values of first-hyperpolarizability arises from the larger and the smaller values of polarizability (see Eq. 10), respectively. For comparable values of α the larger β of 4dT1 compared to that of 4dT2 may be due to the relatively smaller dipole moment.

The doublet cations under this scheme possess substantially larger values of dipole moment. The molecule 4bP (X = C, Y = N) has maximum α_{xx} and β_{xxx}. The larger magnitude of γ_{xxx} and $<\gamma>$ of molecules 4bP and 4cP may be attributed to the rather larger values of β_{xxx} (see Eqs 7 and 8). The substantially larger differences (by about one order of magnitude) of hyperpolarizabilities of molecules 4dP1 and 4dP2 may be ascribed to the significant difference of their ground state dipole moment for comparable linear polarizability. It is interesting to note that all

the quantities μ_g, $<\alpha>$, $\beta_\parallel$ and $<\gamma>$ show a gradual decreasing trend on going from 4aN to 4dN. The maximum values of these quantities are obtained for molecule 4aN (X = Y = C) while the minimum values are predicted for molecule 4dN (X = Y = N) which are consistent with the present model expressions.

In order to find the most general trend of the molecular first- and second-hyperpolarizability for the chosen polyenes with a definite spin multiplicity these properties are plotted against the related quantities in Eqs (5)–(10). For the singlet species no definite trend of β has been noted. The calculated mean second-hyperpolarizability of singlet polyenes, however, bears a linear relation (Fig. 1 a&b). The cubic polarizability of doublet polyene cations show a nice linear correlation (Fig. 2) which is consistent with Eq. (12). The plots obtained for the negatively charged polyenes (Fig. 3 a&b) indicate that the
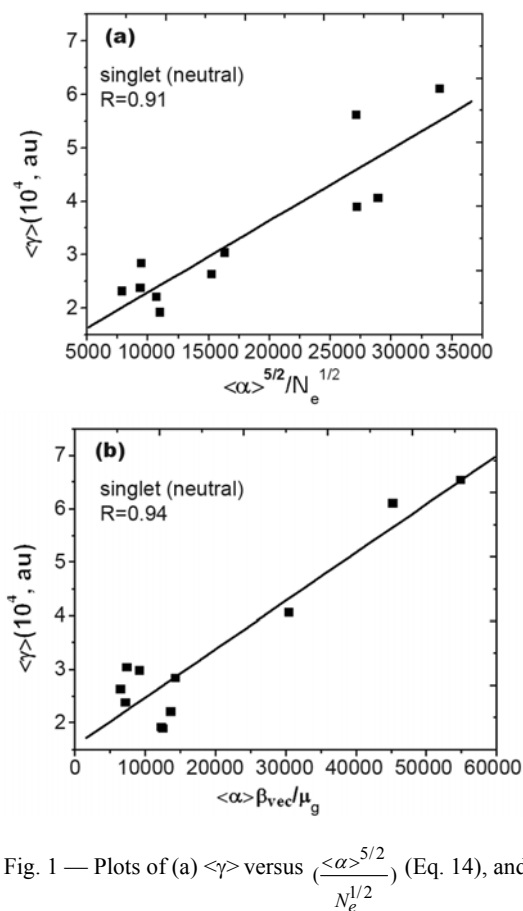

Fig. 1 — Plots of (a) $<\gamma>$ versus $\left(\dfrac{<\alpha>^{5/2}}{N_e^{1/2}}\right)$ (Eq. 14), and,

(b) $<\gamma>$ versus $\left(\dfrac{<\alpha>\beta_{vec}}{\mu_g}\right)$ (Eq. 12) obtained for the

singlet polyenes at the B3LYP level for the 6-311++G** basis set.

second hyperpolarizability strongly correlates with the lower-order polarizabilities and ground state dipole moment. However, as a supplement to the present study the dependence of hyperpolarizabilities on the electronic transition dipole moment and the transition energy associated with the most intense linear transition has been examined. For this purpose, TD-B3LYP/6-311++G** calculations have been carried out for all the chosen polyenes. The results of these spectroscopic quantities are listed in Tables S1–S4 (Supplementary Data). We have noted that the analytically calculated second-hyperpolarizability obtained for the singlet polyenes bears a linear relationship with the non-dipolar two-state[51]
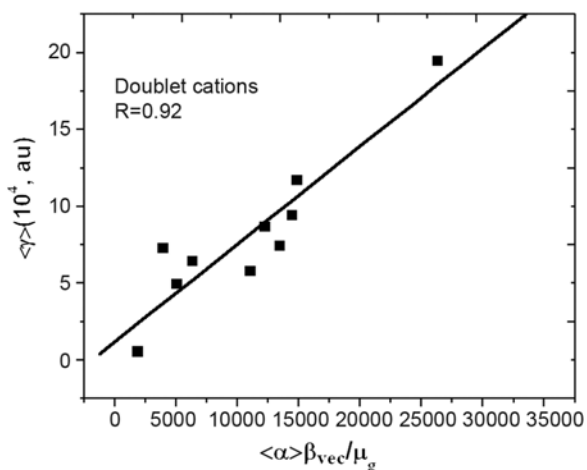
Fig. 2 — Plot of $<\gamma>$ versus $\left(\dfrac{<\alpha> \beta_{vec}}{\mu_g} \right)$ (Eq. 12) obtained for the doublet polyene cations at the B3LYP level for the 6-311++G** basis set.

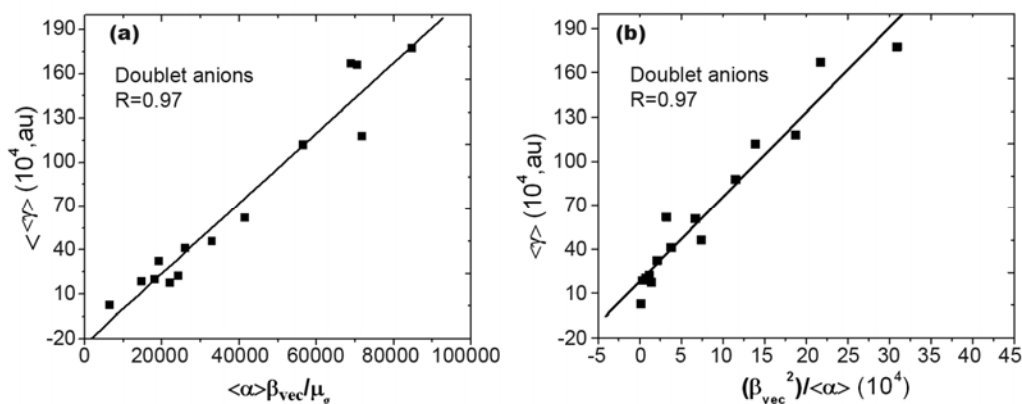contributions (see Fig. 4) which indicates that the transition energy can play a significant role in the modulation of response property of singlet polyenes. This linear correlation although has been noted to some extent for the doublet polyene cations no such linear plots are obtained in the case of other polyene radicals.

Comparison of NLO properties of neutral, cationic and anionic polyenes (Schemes 1–4).

For ployenes with (X = C, Y = C) and (X = C, Y = N), γ_{xxxx} and $<\gamma>$, in general, decrease on passing from the singlet spin state to the triplet state which then increase in the positive doublet and become maximum in the negative doublet state. Barring a few, $<\gamma>$ value of polyenes having (X = N, Y = C) and (X = N, Y = N) in the conjugation path shows a gradually increasing trend in the order singlet < triplet < positive doublet < negative doublet. The largest second-hyperpolarizability obtained for the negative polyenes may be correlated to the pyramidalization of the NH_2 group (the $\angle$HNH angle being very close to 108°). It can be noted that for polyenes under Schemes 1 and 2 the maximum value of β_{xxx} is predicted for the negative doublets while for polyenes belonging to Schemes 3 and 4 the largest value of β_{xxx} is obtained for the neutral triplets. In the former this arises from the invariably larger value of α_{xx} while in the case of later this originates from the significantly larger ground state dipole moment and linear polarizability which is fairly consistent with Eq. (10).

The μ_g values of the neutral singlets and negative doublets are rather comparable varying within a narrow margin. Now, let us consider the neutral
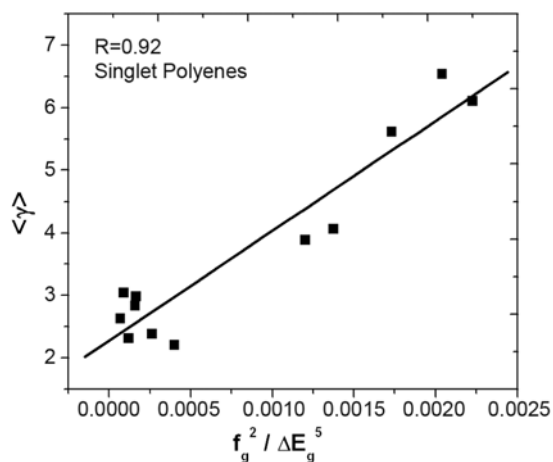

Fig. 3 — Plots of (a) $<\gamma>$ versus $\left(\dfrac{<\alpha> \beta_{vec}}{\mu_g} \right)$ (Eq. 12), and, (b) $<\gamma>$ versus $\left(\dfrac{\beta_{vec}^2}{<\alpha>} \right)$ (Eq. 13) obtained for the doublet polyene anions at the B3LYP level for the 6-311++G** basis set.

Fig. 4 — Plot of $<\gamma>$ versus $\left(\dfrac{f_{ng}^2}{\Delta E_{gn}^5} \right)$ obtained for the singlet polyenes at the B3LYP level for the 6-311++G** basis set.

singlet and negative doublet polyenes to explain the variation of $<\gamma>$ among them. In Scheme 1, the larger $<\gamma>$ of the negatively charged doublets compared to the neutral singlets can be understood by considering the relative changes of linear and quadratic polarizabilities (see Eqs 6–9). The ground start dipole moment (μ_g) of both the singlet and negative doublets being comparable the variation of second-hyperpolarizability of these molecular species may be explained in terms of $<\alpha>$ (related to the extent of one-photon absorption) and $\beta_\parallel$ (relating to both one and two-photon absorptions) which are predicted larger for the doublet anions but with respect to $<\alpha>$ the enhancement of $\beta_\parallel$ is much higher indicating significant two photon contribution. For molecules of Scheme 2, the variation of $\beta_\parallel$ and $<\gamma>$ between the neutral singlets and negative doublets can be explained in a similar way as in Scheme 1. However, the variation of $<\gamma>$ of polyenes in Scheme 3, can be explained in terms of the lower-order polarizabilities. For molecule 3cN (X = N and Y = C) the increase of $<\gamma>$ compared to that of 3cS may be explained solely by the substantial increase of linear polarizability (see Eq. 13). For molecules 4cS and 4cN (X = N, Y = C) and 4dS and 4dN (X = N, Y = N) (Scheme 4), the spin state dependence of second-hyperpolarizability can be rationalized in term of polarizability (Eq. 14).

Let us now compare the electric response properties between the neutral singlets and positive doublets. In Scheme 1, the magnitude of $<\alpha>$ of the positive doublets decreases or varies within a narrow margin when compared to that of the neutral singlets. However, the ground state dipole moment of the doublet cations is found to be invariably larger. This accounts for an increase of $\beta_\parallel$ (except for 1bS and 1bP). The increasing value of the quantity $\beta_\parallel^2/<\alpha>$ indicates that the two-photon absorption makes a greater contribution in the positive doublets which has also been reflected by the larger $<\gamma>$ values compared to that of the singlets. In Scheme 2, molecule 2aP (compared to 2aS) (X = C and Y = C) possesses relatively smaller $<\alpha>$ but larger μ_g which accounts for its larger $\beta_\parallel$ (with greater two-photon contribution indicated by larger $\beta_\parallel^2/<\alpha>$) and $<\gamma>$. For molecules 2cS and 2cP (X = N and Y = C) $<\alpha>$ and μ_g values are almost identical which indicates one-photon contribution to be comparable. The relatively larger $\beta_\parallel$ of 2cS should, therefore, arise from the greater two-photon contribution while the smaller $<\gamma>$ of 2cP may be attributed to the smaller $\beta_\parallel^2/<\alpha>$ value which implies the smaller two-photon contribution. In Scheme 3, the substantial lowering of $\beta_\parallel$ but increase of $<\gamma>$ obtained for the doublet cations 3aP (vs. 3aS) (X = C and Y = C) and 3cP (vs. 3cS) (X = N and Y = C) cannot be explained by the present model expressions. In Scheme 4, the greater longitudinal component of β of the doublet cations arises from the larger μ_x and α_{xx} values (Eq. 10). The larger α_{xx} also results in rather larger γ_{xxxx} of the doublet cations compared to the singlets (see Eq. 14). The comparison of $\beta_\parallel$ between the positive doublets and the neutral singlets can be satisfactorily explained in term of the average polarizability.

Conclusions

In the present investigation, sixty electron donor-electron acceptor substituted polyenes with varying paths of conjugation and spin multiplicities have been considered for the comparative theoretical study of their NLO properties. The hyperpolarizabilities of a polyene system are found to be highly sensitive to its spin multiplicity and charge. Amongst the chosen polyenes, the relatively larger values of hyperpolarizabilities are obtained for the radical ions, especially for the doublet anions. The longitudinal component of γ of most of the later species is found to be of the order of 10^6 au. The maximum $\beta_\parallel$ is obtained for the doublet anion 2dN (X = N, Y = N) while the maximum $<\gamma>$ is predicted for the doublet anion 1cN (X = N, Y = C). The variation of NLO properties has been satisfactorily explained in terms of the ground

state dipole moment and linear polarizability. In many cases, the variation of quadratic and cubic polarizabilities follows the same trend as shown by the linear polarizability. For polyenes having comparable linear polarizability, the relatively larger first-hyperpolarizability may be ascribed to the greater two-photon contribution. The magnitude of second-hyperpolarizability of the radical ions is found to depend largely on the relative magnitudes of ground state dipole moment and linear polarizability. The doublet cations possess significantly larger values of ground state dipole moment. The presence of nitrogen atom in the π-conjugative path strongly modulates the longitudinal component of both first- and second-hyperpolarizabilities of the investigated polyene radicals irrespective of their spin states. Amongst the doublet polyene cations, those containing one nitrogen atom in the chain, 4bP (X = C, Y = N) and 4cP (X = N, Y = C) possess significantly larger second-hyperpolarizability. The present investigation illustrates that by suitable modification of the π-conjugative path and the proper choice of spin multiplicity the magnitude of hyperpolarizabilities of donor-acceptor substituted polyenes can be greatly enhanced which should bear a close relationship with the polarizability and the ground state dipole moment.

Supplementary Data

Supplementary data associated with this article, viz geometrical parameters and spectroscopic quantities (Schemes S1–S4 and Tables S1–S4, are available in the electronic form at http://www.niscair.res.in/jinfo/ijca/IJCA_56A(07)756-766_SupplData.pdf.

Acknowledgement

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