Maximizing the first hyperpolarizability ($\beta$) of conjugated push-pull charge transfer molecules: Tuning of charge transfer and electron correlation effects

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A two-atom two-orbital Huckel like model has been proposed to predict analytically the possible variations of the first hyperpolarizability ($\beta$) of intramolecular organic charge transfer systems when the system parameters change. The model identifies some parameters which can be tuned to achieve the maximization of $\beta$. They include donor-acceptor interaction strength (hopping term), donor and acceptor strength (ionization potential of the donor and electron affinity of the acceptor), state of hybridization of the donor orbital, etc. A simple modification of the same basic model that includes electron interaction explicitly throws some light on the possible role of electron correlation in the emergence of high nonlinear optical response when the other system parameters are favourably tuned.

1 Introduction

Materials exhibiting second order nonlinear optical (NLO) properties are increasingly becoming the target of contemporary research due to their wide range of applications in telecommunication, data storage-retrieval systems, information processing applications, optical switches, etc. Desirable NLO properties are exhibited by conjugated organic molecules with terminal donor and acceptor groups. Such molecules are generally known to possess low energy charge transfer (CT) states with attendant high dipole moment and exhibit large second ($\beta$) or third ($\gamma$) order nonlinearities. Various theoretical models, mainly at the semi-empirical molecular orbital level, have been constructed in an effort to identify the factors that favour the emergence of high nonlinearities or modify them.

In a previous study on a series of intramolecular charge transfer (ICT) molecules, we have found that the orientation of the lone pair of electrons on the donor moiety, the ionization potential of the donor (IP$_D$) and the electron affinity of the acceptor (EA$_A$) groups play a crucial role in modulating the first hyperpolarizability. If the push measuring scale for modeling the ease of donor(D)→acceptor (A) electron transfer is defined as

$$\delta = IP_D (1 - eEA_A)^{-1}$$

where, $e$ is an electron demand factor created by the acceptor, it has been found that $\beta$ passes through a maximum as a function of $\delta$. It essentially means that for a series of ICT molecules the maximization of $\beta$ demands a judicious choice of an acceptor for a good donor so that an effective push-pull parameter ($\delta$) in the appropriate range can be generated.

In the present paper, we have tried to develop a more generalized two-electron two-orbital model to identify some other factors (neglected in the model of reference 9) which control the maximization of $\beta$. The present model includes a possibility of $s$-$p$ mixing of donor orbitals. Our main objective is to explore whether a particular disposition of the donor orbitals can maximize $\beta$ when an appropriate pair of donor and acceptor have been chosen. An analysis is also made of the possible effects of conjugation length. The penultimate section of this article discusses the role of electron correlation in shaping $\beta$ values with reference to the same two-electron two-orbital model augmented by explicit inclusion of electron repulsion terms.

2 The Model

We consider the intramolecular charge transfer molecule to be of the form shown in Scheme 1. It has a donor (D) and an acceptor (A) unit at the opposite ends of a conjugated ring system. We start by recognizing two different modes of intramolecular charge transfer. Then, the quantum of D→A electronic charge transfer is determined among other...
things by the effective electronegativity difference between the donor and the acceptor. This may be called the ionic mode of charge transfer. The strength of the conjugative interaction or the so-called hopping interaction between D and A mediated by the intervening conjugated ring is another factor responsible for charge transfer. We may call it the covalent mode of charge transfer. Considering the intervening n-electron bridge to be homogeneous, the following two-level model containing all the essential ingredients for modeling the basic intramolecular charge transfer process, may be proposed.

Let us consider a diatomic species placed in an electrostatic field applied along the internuclear axis A→B (Scheme 2). The atoms are separated from one another by a distance of 2R. The donor atom B is supposed to have two orbitals s and p, which could be hybridized to form sp hybrid orbitals. If e be the strength of the applied field then the field-modified energy eigenvalues and eigenvectors could be obtained by solving the following secular equation:

\[
\begin{vmatrix}
H_{11} - e & H_{12} \\
H_{21} & H_{22} - e
\end{vmatrix} = 0
\]

Here, the field-modified Hamiltonian may be written as

\[
\hat{H}(a.u.) = H_0 - \hat{r} \cdot \hat{E}
\]

The molecular orbitals \(\psi\) are formed by linear combination of the orbitals \(\phi_{A}\) and \(\phi_{B}\).

\[\psi = c_{A}\phi_{A} + c_{B}\phi_{B}\]

with \(\phi_{A} = |s^A\rangle\) and \(\phi_{B} = \cos \theta |s^A\rangle + \sin \theta |p_{x}^B\rangle\),

where s and p are Slater-type orbitals on the donor. The matrix elements appearing in Eq. (2) can then be written as

\[
H_{11} = \langle \phi_{A} | \hat{H} | \phi_{A} \rangle = \langle s^A | \hat{H}_0 | s^A \rangle - e \langle s^A | \hat{R} | s^A \rangle = U_{s} - Re = U_{s} - Re
\]

\[
H_{12} = \eta = H_{21} = \langle \phi_{A} | \hat{H} | \phi_{B} \rangle = \eta_{s} \cos \theta + \eta_{p} \sin \theta
\]

\[
H_{22} = \langle \phi_{B} | \hat{H} | \phi_{B} \rangle = U_{p} \cos^2 \theta + U_{p} \sin^2 \theta = eR \sin 2\theta
\]

The terms \(U_{s}\) and \(U_{p}\) are defined similarly as in Eq. (3). The last term in Eq. (5) arises from the \(\langle s^A | \hat{R} | p_{x}^B \rangle\) type of matrix elements. Using Slater-type atomic orbitals its magnitude turns out to be \((5/\sqrt{3})\zeta^{1} \cdot k\) being the exponent of the STOs on the atom B and \(k\) in Eq. (5) is \(5/\sqrt{3}\).

The field-modified energy eigenvalues obtained by solving Eq. (2) are given by

\[
E_{\pm}(e) = \varsigma (U + U_{D}) + Ke \psi \pm \sqrt{2\varepsilon(\sigma K + 2\sigma R) + \varepsilon ^{2} K + 2R)}
\]

The explicit expressions for \(U_{D}, \sigma\) and K are

\[
U_{D} = U_{s} \cos^2 \theta + U_{p} \sin^2 \theta
\]

\[
\sigma = U - U_{D}
\]

The energy \(E\) can be expanded in a power series in the field strength (e) as

\[
E_{\pm}(e) = E(0) + (\delta E/\delta e) de + \frac{1}{2!}(\delta^2 E/\delta e^2) de^2
\]

\[+ \frac{1}{3!}(\delta^3 E/\delta e^3)de^3 + \ldots \]

Thus from the expression of \(E_{\pm}(e)\) we can calculate \(\beta\) by taking the limiting value of the third derivative of energy with respect to the field strength.
\[ \beta = (\delta^2 E / \delta \delta^2)_{\theta=0} \]  \quad \ldots \quad (9)

Introducing the constant \( C = K + 2R \), the expression for \( \beta \) turns out to be
\[ \beta = 6C \eta^2 \sigma (\sigma^2 + 4\eta^2)^{-3/2} \]  \quad \ldots \quad (10)

3 Extremization of \( \beta \) values

The analytical expression for \( \beta \) as deduced in the previous section may be utilized to predict the possible variations of \( \beta \) with respect to changes in \( \theta \) in the internuclear separation \( R \) and other important parameters in the model (\( \sigma, \eta \)). For a particular set of \( \sigma \) and \( \eta \) values, \( \beta \) computed for different values of \( \theta \) is seen to pass through a distinct maximum, around a \( \theta \) value of 15-20 degrees (Fig. 1). The position of this maximum shows only a weak \( R \)-dependent shift towards lower \( \theta \)-values; \( \beta_{\text{max}} \), however, attains higher values with the increase of \( R \). This observation can be substantiated from our previous MNDO calculations on a real TICT molecule (DMABN). It has been found that pyramidalization of the donor-\( \text{N(CH}_3)_2 \) group brings about an increase in \( \beta \)-value from \( 5.25 \times 10^{-30} \) esu \([-\text{N(CH}_3)_2 \text{planar}] \) to \( 5.286 \times 10^{-30} \) esu \([-\text{N(CH}_3)_2 \text{pyramidal}] \).

It may be worthwhile to examine how the topographical and electronic properties of the donor modulate \( \beta \) when the effect of donor orbital hybridization is switched off in our model. The situation is achieved by setting \( \theta = 0 \). Under this situation it turns out that
\[ \beta = 48\eta^2 R^3 (\sigma^2 + 4\eta^2)^{-3/2} \]  \quad \ldots \quad (11)

Equation (11) may be used to predict variations of \( \beta \) with respect to different parameters used to model the system. It is seen that for different sets of \( R \) and \( \eta \) values, \( \beta \) always shows a minimum (Fig. 2a) as a function of \( \sigma \). This is also true for the variation of \( \beta \) with respect to \( \eta \) (Fig. 2b). It is to be noted further that when the values of \( \eta \) and \( \sigma \) are simultaneously very low, computed values of \( \beta \) turn out to be high at the maximum. This situation cannot, of course, occur in the case of conjugated systems. It might be realizable in weakly bound atomic clusters in which the hopping interaction \( \eta \) is expected to be very small. Thus for sodium atoms adsorbed as films on rhenium, huge second order polarizabilities have been experimentally observed. Although surface has a role to play in the enhancement of the second order response in these systems, the low \( \beta \) and \( \eta \) values could certainly be an additional causative factor vindicating the prediction of our model.

Fig. 1 — Variation of the first hyperpolarizability (\( \beta \)) with change in hybridization angle (\( \theta \)) at different internuclear separations (\( R \)): (a) 2.0 (b) 2.5 (c) 3.0 a.u.

Fig. 2a — Variation of \( \beta \) with respect to \( \sigma \) at different \( \eta \) values: (a) 0.01 (b) 0.1 (c) 0.2 a.u. The internuclear separation (\( R \)) is kept fixed at 2.0 a.u.

Fig. 2b — Variation of \( \beta \) with respect to \( \eta \) at different \( \sigma \) values: (a) 0.01 (b) 0.1 (c) 0.2 a.u. The internuclear separation (\( R \)) is fixed at 2.0 a.u.
of $\beta$ to variations of $\sigma$ could be explained analytically by evaluating the first and second derivatives of $\beta$ with respect to $\sigma$. The maximization condition turns out to be $\sigma = \pm \eta$, for which

$$\delta^2 \beta / \delta \sigma^2 = 1920 \sigma^4 R \left( \sigma^2 + 4 \eta^2 \right)^{-3/2} \ldots (12)$$

is negative. This means that $|\beta|$ is actually maximized at $\sigma = \eta$ with a value $48(5^{1/2})R/\eta^2$. Analogous treatment, setting $\delta \beta / \delta \eta = 0$, provides the value $\eta = \sigma/6^{1/2}$ and $\delta^2 \beta / \delta \eta^2$ given by

$$\delta^2 \beta / \delta \eta^2 = 96 \sigma R^3 \left( \sigma^2 + 4 \eta^2 \right)^{-3/2}$$

$$\left( \sigma^4 - 420 \sigma^2 \eta^2 + 96 \eta^4 \right) \ldots (13)$$

is less than zero. It implies that $|\beta|$ would be maximized at $\eta = \sigma/6^{1/2}$ with the value $8(3/5)^{1/2} R^3/\sigma^2$.

The variation of $\beta$ with respect to $R$ at various sets of $\sigma$ and $\eta$ values shows an altogether different trend. Fig. 2(c) indicates that $\beta$ increases sharply and monotonically illustrating the $n$-th power dependence of $\beta$ on $R$. The dependence of $\beta$ on $R$ is well documented in the literature $^{12,13}$. Table 1 contains a few such examples where, with fixed donors and acceptors, the experimental $\beta$ values increase with the increase in conjugation length—as predicted by our model. As would be seen from the Table, when the donor is $-\text{N}(\text{CH}_3)_2$ and the acceptor group is $-\text{NO}_2$, the $\beta$ value increases from $12 \times 10^{26}$ esu (DMA) to $63 \times 10^{26}$ esu (DANS). In the cases of DACP and DACS, the $\beta$ value also shows remarkable rise with an increase in the conjugation length (Table 1). The observed increase in the magnitude of $\beta$ with the increase in conjugation length ($R$) may not be the end of the story.

In fact, Morley and Pugh have recently shown $^{12,13}$ that for $\alpha$-dimethyloamino-$\omega$-nitrophenylinc and the related $\alpha$-dimethyloamino-$\omega$-nitropolyenic $n$-mers, the hyperpolarizability per unit volume passes through a maximum with increase in the chain length. In the examples given in Table 1, the conjugation length is probably not large enough for the observed $\beta$ to reach the maximum or go beyond it. Equation (11) of our model, however, predicts monotonic increase in $\beta$ with the increase in conjugation length. It may be noted that $\eta$ in our model is a measure of the effective hopping interaction between the donor and the acceptor orbitals mediated by the intervening conjugative chain or ring. If one assumes that $\eta = \eta_0 e^{-p(R-R_0)}$ where $\eta_0$ depends only on the nature of the conjugation path, $R_0$ is the critical chain length beyond which $\eta$ begins to change perceptibly and $p$ is a characteristic of the conjugation path, Eq. (11) predicts

$$\beta = 48\sigma \eta_0^2 R^3 \exp\left[-2p(R-R_0)\right]$$

$$\left[ \sigma^4 + 4 \eta_0^4 \exp(-2pR) \right]^{1/2} \ldots (14)$$

The exponential term in Eq. (14) would prevent the monotonic growth of $\beta$ with $R$. It remains to be seen how $R$-dependence of this kind could creep into $\eta$.

### 4 Strength of electron correlation and maximization of $\beta$

Recent theoretical investigations using high level ab-initio calculations have indicated that electron correlation might play a role in influencing the observed $\beta$ values of molecular systems $^{14,15}$. We may, therefore, venture to examine whether our simple model can be generalized to ascertain whether electron correlation has any role in the $\beta$ maximization. The Hückel like two-electron two-orbital model discussed in Section 3.0 is obviously inadequate to tackle this problem, but with minor

<table>
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<tr>
<th>Molecule</th>
<th>Code</th>
<th>Donor Group</th>
<th>Acceptor Group</th>
<th>$\beta$ (10$^{26}$ esu)$^4$</th>
</tr>
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<tr>
<td>DMA</td>
<td>DACP</td>
<td>$-\text{N}(\text{CH}_3)_2$</td>
<td>$-\text{NO}_2$</td>
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<tr>
<td>DANP</td>
<td>DACS</td>
<td>$-\text{N}(\text{CH}_3)_2$</td>
<td>$==\text{C(\text{CN})}_2$</td>
<td>64</td>
</tr>
<tr>
<td>DANS</td>
<td>DACS</td>
<td>$-\text{N}(\text{CH}_3)_2$</td>
<td>$-\text{NO}_2$</td>
<td>55</td>
</tr>
</tbody>
</table>

$^4$Reference 18

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Fig. 2c—Variation of $\beta$ with respect to $R$ at different sets of values of $\sigma$ and $\eta$ for $\sigma = 0.1$, $\eta = 0.1$ (a) $\sigma = 0.2$, $\eta = 0.1$ (c) $\sigma = 0.2$, $\eta = 0.05$ (d) $\sigma = 0.2$, $\eta = 0.2$ (e) $\sigma = 0.01$, $\eta = 0.01$. All values are in a.u.
modification this model can include the electron-electron interaction explicitly. We can then invoke configuration-interaction (CI) to account for electron correlation. For the sake of simplicity as well as for staying close to our original model we will restrict our investigation to the level of zero differential overlap (ZDO) approximation. We consider the two atoms A and B to be situated on the X-axis at a distance \( R \) from each other. The vectors \( r_{A1}, r_{B1}, r_{A2}, r_{B2} \) denote the positions of the electrons 1 and 2 relative to the nuclei A and B. The interelectronic distance is denoted by \( \sim 2 \).

If \( Z_A \) and \( Z_B \) be the atomic numbers of the respective atoms, the total Hamiltonian of the system can be written as

\[
H_0 = h_1 + h_2 + \frac{1}{r_{12}} \quad \ldots (15)
\]

with \( h_1 = \left( \frac{V_1^2 + Z_A^2}{r_{A1}} \right) \) and \( h_2 = \left( \frac{V_2^2 + Z_B^2}{r_{B2}} \right) \).

Denoting \( \chi_A \) and \( \chi_B \) as the atomic orbitals on the atoms A and B respectively, the full CI wave function can be written as

\[
\Psi = C_0 \psi_0 + C_1 \psi_1 + C_2 \psi_2 \quad \ldots (16)
\]

\( C_0, C_1 \) and \( C_2 \) are the CI coefficients and \( \psi_0, \psi_1 \) and \( \psi_2 \) are the single determinant wave functions for the ground, singly-excited and doubly-excited configurations.

\[
\psi_0 = |\phi(1)\phi(2)|
\]

\[
\psi_1 = \frac{1}{\sqrt{2}} [ |\phi(1)\phi(2)| + |\phi(2)\phi(1)| ]
\]

\[
\psi_2 = |\phi(2)\phi(2)|
\]

where \( \phi_1 \) and \( \phi_2 \) in Eq. (17) are MOs which are linear combinations of \( \chi_A \) and \( \chi_B \) as given below

\[
\phi_1 = C'_a \chi_A + C'_b \chi_B
\]

\[
\phi_2 = C'_a \chi_A + C'_b \chi_B
\]

such that \( <\phi_1|\phi_1> = <\phi_2|\phi_2> = 1 \) and \( <\phi_1|\phi_2> = 0 \). If the electric field is applied in the direction of the X-axis (internuclear axis), the field modified energy may be expressed as

\[
E' = \langle \psi | H | \psi \rangle = \langle \psi | H_0 | \psi \rangle + \varepsilon (\psi | R | \psi) \quad \ldots (19)
\]

By setting \( \delta E' = 0 \), we can determine the set of field modified CI coefficients \( C'_0, C'_1 \) and \( C'_2 \). There will be off-diagonal terms involving \( R \) in the modified CI equation. The CI problem has been solved under the ZDO approximation for several field strengths and distances. For such calculations, apart from the \( U_a \) and \( U_b \) parameters (\( U_a = <\chi_A|h_A|\chi_A> \), etc.), the electron interaction terms \( \gamma_{aa}, \gamma_{bb} \) (one centre), \( \gamma_{ab} \) (two-centre), \( \eta_{ab} \) (hopping) are required explicitly. We also need the MO expansion coefficients. They can be obtained from a self-consistent calculation on the field-free ground state (\( \phi_0 \)) or even from perturbation theory. Since we are looking for the nature of effects that electron correlation would have on \( \beta \) maximization through a model calculation, an approximate choice of the relevant MO expansion coefficients would serve the purpose. Approximating \( C_a \) perturbatively as \( \beta_a/\sigma \), where \( \sigma = U_a - U_b \), the other coefficients may be calculated using the normalization and orthogonality conditions of \( \phi_1 \) and \( \phi_2 \) [\( C'_a^{-2} + C'_b^{-2} = 1 \), \( C'_a^{-2} + C'_b^{-2} = 1 \), \( C'_a, C'_b = 0 \)]. Since \( \xi_{ab} = \eta_{ab}/\gamma_{ab} \) \[ \gamma_{ab} = (\gamma_{aa} + \gamma_{bb})/2 \] can be considered as a measure of the strength of electron correlation, we have plotted the calculated value of the first hyperpolarizability \( \beta \), against \( \sigma \)

Fig. 3(a & b) — Variation of \( \beta \) with respect to \( \sigma \) at different strengths of electron correlation (\( \xi_{ab} \)). The curves 1 to 7 are for \( \xi_{ab} \) values of 0.39, 0.41, 0.44, 0.47, 0.50, 0.54, 0.58 respectively. The inset shows the variation of \( \beta_{\max} \) with respect to \( \xi_{ab} \).
values at various fixed values of $\xi_{ab}$. Figure 3 shows that the computed $\beta$ passes through a maximum against $\sigma$ for every value of $\xi_{ab}$ when plotted against $\sigma$. The $\sigma$ values range between 0.35 to 1.0 a.u. It is to be noted further that the maximum values of $\beta$ observed for different values of $\xi_{ab}$ also pass through a maximum (see inset of Fig. 3b). The results indicate that electron correlation strength does have an important role in the maximization of $\beta$ values even when $\sigma$ or $\eta$ or both are in the appropriate ranges. It is relatively easy to extend the models proposed here for analyzing third order non-linear response, too.

5 Conclusions

We have presented here a simple two-atom two-orbital model to investigate the role played by different factors in maximizing $\beta$ values of ICT type organic molecules. The maximization conditions for $\beta$ predict that it depends not only on the alignment of the lone pair orbital of the donor, but also on the conjugation length ($R$), hopping matrix element ($\eta_{ab}$) and the relative electron releasing powers of the donor as well as the acceptor moieties ($\sigma$). When configuration interaction is included in the form of single and double excitations in the model, an optimal strength of electron correlation is seen to exist for maximization of $\beta$ for a specific choice of $\eta$ and $\sigma$ values. The proposed models are theoretically very simple and explain a number of interesting observations concerning $\beta$-maximization which have been borne out earlier by experiments. Further refinement of the model can be rewarding. An extension of the model to frequency dependent polarizabilities is underway.

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