

Molecular Polarizability and First Hyperpolarizability of Octupolar Molecules: Donor-Substituted Triphenylmethane Dyes

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Abstract: Molecular polarizabilities and hyperpolarizabilities of a series of octupolar molecules that are donor-substituted triphenylmethane dyes are calculated. The four-state model of an octupolar molecule is used to describe the nonlinear optical properties of this type of molecules. As the charge-transfer character of the ground state is increased by using a strong donor, both the molecular polarizability and first hyperpolarizability increase monotonically. These patterns are in strong contrast with those exhibited by the linear push-pull polyene. On the basis of these results, it is suggested that a common strategy to maximize the molecular polarizability can also be used to optimize the first hyperpolarizability in the case of octupolar molecules such as triphenylmethane dyes.

1. Introduction

Nonlinear optical properties of a conjugated polyene have been extensively studied both theoretically and experimentally.^{1–4} These molecules typically exhibit large optical nonlinearities so that they could be used as a variety of optical and optoelectronic devices. Particularly the push-pull polyene containing electron-donating and -accepting groups with a conjugated polyene linker has been paid much attention.^{5–14} It was found that the bond-length-alternation is a characteristic feature strongly correlated with the nonlinear optical properties. As was shown by Marder and co-workers and several groups,^{5–13} it is possible to optimize the desired NLO property by choosing a proper pair of electron-donating and -accepting groups or

changing the solvent polarity. Despite that these linear push-pull polyenes exhibit large NLO properties, it was found that their large permanent dipole moments are problematic on crystallization from a materials standpoint. To overcome this difficulty, it was suggested that the octupolar molecule with zero permanent dipole moment can be of use as an alternative NLO molecule.^{15–17} For instance, TATB (1,3,5-triamino-2,4,6-trinitrobenzene) has been studied theoretically as well as experimentally by Bredas et al.¹⁸ and Joffre et al.¹⁹ by means of ab initio and PPP (Pariser-Parr-Pople) model calculations. As expected from the geometry of the molecule, the ground state does not have a permanent dipole moment and the first excited state is 2-fold degenerate. In addition to the dipole mechanism for NLO response, which plays a key role in the NLO response of the linear push-pull polyene, they show that the triangle mechanism, that is a sequence of transitions (the ground state → one of the 2-fold degenerate excited states → the other excited state → the ground state), is a crucial contribution to the NLO response of the octupolar molecule.¹⁹ Although detailed numerical calculations of the NLO properties of TATB were presented, there does not exist a simple theoretical model for the NLO properties of the octupolar molecule, which is capable of predicting the general trends of NLO properties in relation to the molecular structure. In this paper, we present a four-state model for the octupolar molecule such as crystal violet (CV) (see Figure 1). In section 2, the theoretical model is briefly summarized. The relationship between the conventional bond-length-alternation coordinate and the electronic structure of the octupolar molecule is discussed in section 3. Numerical calculations of the NLO properties of triphenylmethane (TPM) dyes and dis-

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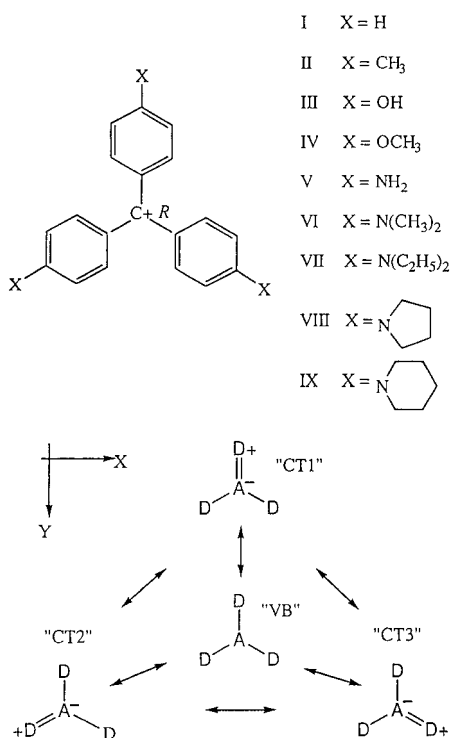


Figure 1. Donor-substituted triphenylmethane dyes shown with the list of substituents. *R* denotes the central carbon and the 1-carbon atom of a benzene ring. One VB configuration and three CT configurations are pictorially drawn, and they are coupled to one another via two finite transfer matrix elements, *t* and *T*. The molecular coordinate system is also shown.

cussions with a few concluding remarks are given in sections 4 and 5, respectively.

2. Four-State Model for a Guanidinium-Type Molecule

Recently the four-state model Hamiltonian, which is particularly designed to describe the electronic structure of the octupolar molecule, was investigated.²⁰ In this section, we briefly recapitulate the main results for the sake of clarity as well as for later use. Although in refs 20 the second hyperpolarizability γ of octupolar molecule was also discussed, we shall focus on the polarizability and first hyperpolarizability in this paper and will present a complete description of γ with several series of octupolar molecules elsewhere. In the next section, we shall extend this model to include the bond-length-alternation (BLA) coordinate. Assuming that the electronic wave functions of the triphenylmethane (TPM) dyes can be approximately represented by the linear combinations of the four basis functions, e.g., a valence-bond (VB) configuration and three charge-transfer (CT) configurations (see Figure 1), we consider the following model Hamiltonian

$$H = \begin{pmatrix} E_{\text{VB}} & -t & -t & -t \\ -t & E_{\text{CT}} & -T & -T \\ -t & -T & E_{\text{CT}} & -T \\ -t & -T & -T & E_{\text{CT}} \end{pmatrix} \quad (1)$$

where the diagonal elements are the Coulomb energies of each configuration. *t* and *T* denote the transfer integrals between VB and CT configurations and between any two CT configurations. The eigenvalues of eq 1 are

$$E_g = \frac{1}{2}(E_{\text{VB}} + E_{\text{CT}} - 2T) - \frac{1}{2}[(V - 2T)^2 + 12t^2]^{1/2}$$

$$E_{e1} = E_{e2} = E_{\text{CT}} + T$$

$$E_f = \frac{1}{2}(E_{\text{VB}} + E_{\text{CT}} - 2T) + \frac{1}{2}[(V - 2T)^2 + 12t^2]^{1/2} \quad (2)$$

where

$$V \equiv E_{\text{CT}} - E_{\text{VB}}$$

As can be seen in eqs 2, there exist 2-fold degenerate excited states denoted as $|e1\rangle$ and $|e2\rangle$. The subscript "g" in eq 2 means the ground state. There is an additional excited-state denoted as $|f\rangle$. The existence of the doubly degenerate excited states is in good agreement with the theoretical results discussed in refs 18 and 19. Corresponding eigenfunctions are given by the linear combinations of the four basis configurations, i.e.

$$\Psi_g = (1 - 3l)^{1/2} \phi_{\text{VB}} + \sum_{j=1}^3 l^{1/2} \phi_{\text{CT},j}$$

$$\Psi_{e1} = -2^{-1/2} (\phi_{\text{CT},1} - \phi_{\text{CT},3})$$

$$\Psi_{e2} = -\frac{1}{\sqrt{6}} (\phi_{\text{CT},1} - 2\phi_{\text{CT},2} + \phi_{\text{CT},3})$$

$$\Psi_f = (1 - 3m)^{1/2} \phi_{\text{VB}} - \sum_{j=1}^3 m^{1/2} \phi_{\text{CT},j} \quad (3)$$

where

$$l \equiv \frac{1}{6} - \frac{V - 2T}{6\sqrt{(V - 2T)^2 + 12t^2}}$$

$$m \equiv \frac{1}{6} + \frac{V - 2T}{6\sqrt{(V - 2T)^2 + 12t^2}} \quad (4)$$

The magnitude of *l* represents the CT character of the ground state, that is to say, as *l* increases, the electronic structure of the ground state becomes close to the linear combination of the three CT configurations without the VB configuration wave function. In eq 4, *m* represents how large the CT character of the nondegenerate second excited state $|f\rangle$ is. From the definition of *l*, one can show that *l* varies from 0 to $1/3$ as *V*, the energy difference between the CT and VB configurations, varies from $-\infty$ to ∞ . In the limit of *l* = 0, the electronic ground state becomes close to the electronic structure of the VB configuration, and in this case, the charge of the central carbon is close to a unit. This limit can be approximately realized by substituting three weak donors in a TPM dye molecule. On the other hand, if *l* approaches $1/3$, the electronic ground state becomes fully charge-transferred so that the donor site develops charge of $1/3$ (see Figure 2). This limiting case is when the donor strength is very large. For a real molecule, the CT character is between 0 and $1/3$, and as demonstrated in this paper by quantum chemistry calculation for most of TPM dye molecules, *l* varies over a limited range around 0.15.

To obtain the analytic expressions of α and β , we shall invoke the usual approximations, $\langle \phi_{\text{VB}} | \hat{\mu} | \phi_{\text{CT},j} \rangle = 0$ and $\langle \phi_{\text{CT},j} | \hat{\mu} | \phi_{\text{CT},k} \rangle = 0$ (for $j \neq k$), where $\hat{\mu}$ is the electric dipole operator.²¹ Then,

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the transition dipole matrix elements and permanent dipole moments can be obtained as

$$\begin{aligned} \mathbf{M}_{g,e1} &= -\frac{l^{1/2}\mu}{2\sqrt{2}}(\sqrt{3}, 3, 0) \\ \mathbf{M}_{g,e2} &= \frac{3l^{1/2}\mu}{2\sqrt{6}}(\sqrt{3}, -1, 0) \\ \mathbf{M}_{e1,e2} &= \frac{\mu}{4\sqrt{3}}(\sqrt{3}, 3, 0) \\ \mathbf{M}_{e1} &= -\frac{\mu}{4}(\sqrt{3}, -1, 0) \\ \mathbf{M}_{e2} &= \frac{\mu}{4}(\sqrt{3}, -1, 0) \end{aligned} \quad (5)$$

where $\mathbf{M}_{g,e1}$ is, for instance, the transition dipole matrix element between $|g\rangle$ and $|e1\rangle$ and \mathbf{M}_{e1} denotes the permanent dipole moment of $|e1\rangle$ state. To obtain eqs 5 we assume that the dipole moments of the three CT configurations shown in Figure 1 are $(0, \mu, 0)$, $(\sqrt{3}\mu/2, -\mu/2, 0)$, and $(-\sqrt{3}\mu/2, -\mu/2, 0)$, respectively. Note that the direction of the y axis is opposite to that in refs 20. Here μ is the absolute magnitude of the dipole moment of a CT configuration, and μ should not be confused with the electric dipole operator $\hat{\mu}$. By using these results and sum-over-state expressions of α and β , we find

$$\alpha_{xx} = \alpha_{yy} = \frac{3l\mu^2}{\Delta} \quad (6a)$$

$$\alpha_{xy} = \alpha_{yx} = 0 \quad (6b)$$

$$\beta_{yyy} = 4.5\frac{l\mu^3}{\Delta^2} \quad (6c)$$

$$\beta_{yxx} = \beta_{xyx} = \beta_{xyx} = -4.5\frac{l\mu^3}{\Delta^2} \quad (6d)$$

$$\beta_{xxx} = 0 \quad (6e)$$

$$\beta_{xyy} = \beta_{yyx} = \beta_{yyx} = 0 \quad (6f)$$

All other tensor elements with z indices vanish within our model. The transition energy gap between the ground state and the doubly degenerate excited state is denoted as Δ :

$$\Delta \equiv E_{e1} - E_g = \frac{1}{2}(V + 4T) + \frac{1}{2}\sqrt{(V - 2T)^2 + 12t^2} \quad (7)$$

The above relationships among the β -tensor elements are in exact agreement with the general properties that should be satisfied by the D_{3h} -symmetric molecule. Note that, to calculate the β -tensor elements, one should consider four sequential optical transition processes, (i) $|g\rangle \rightarrow |e1\rangle \rightarrow |e1\rangle \rightarrow |g\rangle$, (ii) $|g\rangle \rightarrow |e2\rangle \rightarrow |e2\rangle \rightarrow |g\rangle$, (iii) $|g\rangle \rightarrow |e1\rangle \rightarrow |e2\rangle \rightarrow |g\rangle$, and (iv) $|g\rangle \rightarrow |e2\rangle \rightarrow |e1\rangle \rightarrow |g\rangle$.²⁰ The first two optical processes involve the permanent dipole moments of the two excited states, whereas the last two processes involve transition dipole moment between $|e1\rangle$ and $|e2\rangle$. Particularly the two contributions from iii and iv are called as triangle mechanism in the literatures.^{18,19} On the basis of the four-state model, it is shown that the two diagonal tensor elements of α , α_{xx} and α_{yy} , are identical, whereas the two off-diagonal elements, α_{xy} and α_{yx} , vanish. Furthermore,

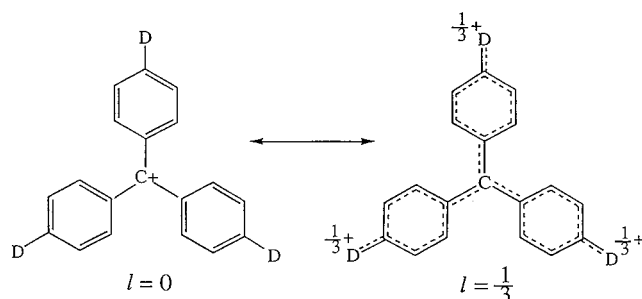


Figure 2. Two limiting cases of the electronic structure of the TPM dye molecule. In case when $l = 0$, the charge-transfer state does not contribute to the electronic structure so that in this limit the central carbon has a unit positive charge. In contrast, when the donor strength is very large so that the CT character l equals $1/3$, the π -electrons are delocalized all over the molecule. In this limit, the three donors bear positive charges of $1/3$. In a real TPM dye, the ground-state electronic structure should be between these two limits.

only four out of 27 β -tensor elements do not vanish and the relationships among the four elements were established above. From eqs 6, as discussed in ref 20a, we find that the nonzero elements of both α and β tensors increase monotonically as the CT character, l , of the ground state increases. These patterns are in strong contrast with those observed in the push-pull polyene.^{5-11,21,22} Here it should be mentioned that, even though our model Hamiltonian assumes D_{3h} symmetry for an octupolar molecule, most of the guanidinium-type molecules such as TPM dyes have D_3 symmetry instead. For example, the crystal violet (CV) contains three phenyl rings with out-of-plane rotations by the steric effect between neighboring phenyl rings so that the symmetry of CV is reduced to D_3 . Therefore, strictly speaking the β -tensor elements with z indices such as β_{zzz} are not zero. Nevertheless these components should be very small in comparison to the in-plane β 's such as β_{yyy} , etc.

In summary, both α and β increase monotonically, as the CT character of the ground state is increased by changing the electron-donating group in a given TPM dye molecule. In other words, the optical nonlinearities should increase as the donor strength is increased. This will be confirmed in the following section by numerically calculating β with a semiempirical method (AM1 parametrization). Also the relationships among the tensor elements discussed above will be verified.

3. Bond-Length-Alternation Coordinate

In the previous section, we discussed the results obtained from the model Hamiltonian eq 1. It should be noted that the model does not contain information on the bond-length-alternation, which has been used extensively to describe the electronic structure of a push-pull polyene.^{5-11,21,22} Therefore we find it necessary to include the bond-length-alternation coordinate in our model Hamiltonian. From the molecular structure of the TPM dyes in Figure 1, we identify three branches of conjugation linkers. Let us denote the three BLA coordinates of each branch as Q_1 , Q_2 , and Q_3 . To construct a reasonable model including these BLA coordinates, we follow the same procedure used to model the linear push-pull polyene by Lu et al. in ref 21. Since the bond-length difference between a double bond and a single bond in *trans*-1,3,5,7-octatetraene was estimated to be 0.12 Å,²³ each BLA coordinate Q_1 , Q_2 , and Q_3 can vary from -0.12 to 0.12 Å. Particularly, the BLA coordinate of the VB configuration of a push-pull polyene was assumed to be -0.12 Å,

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whereas that of the CT configuration was 0.12 Å.²¹ We shall use these notions to model the BLA coordinate that is appropriate for the octupolar molecule, such as TPM dyes.

From the symmetry of the molecular structure, one should consider the following vibrational potential function

$$V(Q_1, Q_2, Q_3) = \sum_{i=1}^3 \frac{1}{2} k_0 (Q_i - Q_i^0)^2 - \sum_{i=1}^3 \sum_{j=i+1}^3 k' Q_i Q_j \quad (8)$$

where k_0 is the force constant that was estimated to be 33.55 eV/Å². The mode coupling force constant is denoted as k' . From the normal-mode analysis, one can identify three normal modes, that are, a totally symmetric stretching mode (q_S) and 2-fold degenerate asymmetric stretching modes (q_{A1} and q_{A2}):

$$\begin{aligned} q_S &= \frac{1}{\sqrt{3}}(Q_1 + Q_2 + Q_3) \\ q_{A1} &= \frac{1}{\sqrt{2}}(-Q_1 + Q_3) \\ q_{A2} &= \frac{1}{\sqrt{6}}(-Q_1 + 2Q_2 - Q_3) \end{aligned} \quad (9)$$

The corresponding force constants will be denoted as k_S ($=k_0 - 2k'$), k_{A1} ($=k_0 + k'$), and k_{A2} ($=k_0 + k'$), respectively. From the symmetry species of the three normal modes, the q_S mode is Raman-active but IR-inactive, and both q_{A1} and q_{A2} modes are IR-active.

When the octupolar molecule is identical to the fictitious VB configuration (see Figure 1), the equilibrium BLA coordinates are $Q_{1,VB}^0 = Q_{2,VB}^0 = Q_{3,VB}^0 = -0.12$ Å. On the other hand, those of the CT1 configuration are $Q_{1,CT1}^0 = 0.12$ Å and $Q_{2,CT1}^0 = Q_{3,CT1}^0 = -0.12$ Å, respectively, and so on. Considering the three normal modes defined in eqs 9, we suggest that the model Hamiltonian eq 1 should be modified as

$$H = \begin{pmatrix} h_{VB} & -t & -t & -t \\ -t & h_{CT1} & -T & -T \\ -t & -T & h_{CT2} & -T \\ -t & -T & -T & h_{CT3} \end{pmatrix} \quad (10)$$

where

$$\begin{aligned} h_{VB} &= E_{VB} + \frac{1}{2} k_S (q_S - q_{S,VB}^0)^2 + \frac{1}{2} k_{A1} (q_{A1} - q_{A1,VB}^0)^2 + \\ &\quad \frac{1}{2} k_{A2} (q_{A2} - q_{A2,VB}^0)^2 \\ h_{CT1} &= E_{CT} + \frac{1}{2} k_S (q_S - q_{S,CT1}^0)^2 + \frac{1}{2} k_{A1} (q_{A1} - q_{A1,CT1}^0)^2 + \\ &\quad \frac{1}{2} k_{A2} (q_{A2} - q_{A2,CT1}^0)^2 \\ h_{CT2} &= E_{CT} + \frac{1}{2} k_S (q_S - q_{S,CT2}^0)^2 + \frac{1}{2} k_{A1} (q_{A1} - q_{A1,CT2}^0)^2 + \\ &\quad \frac{1}{2} k_{A2} (q_{A2} - q_{A2,CT2}^0)^2 \\ h_{CT3} &= E_{CT} + \frac{1}{2} k_S (q_S - q_{S,CT3}^0)^2 + \frac{1}{2} k_{A1} (q_{A1} - q_{A1,CT3}^0)^2 + \\ &\quad \frac{1}{2} k_{A2} (q_{A2} - q_{A2,CT3}^0)^2 \end{aligned} \quad (11)$$

In eqs 11, the corresponding values of q_S^0 , q_{A1}^0 , and q_{A2}^0 are

$$q_S^0 = \frac{k_0}{\sqrt{3}k_S} (Q_1^0 + Q_2^0 + Q_3^0)$$

$$q_{A1}^0 = \frac{k_0}{\sqrt{2}k_{A1}} (-Q_1^0 + Q_3^0)$$

$$q_{A2}^0 = \frac{k_0}{\sqrt{6}k_{A2}} (-Q_1^0 + 2Q_2^0 + Q_3^0) \quad (12)$$

Using the model Hamiltonian 10, one can describe the vibrational contributions to the nonlinear optical properties of the octupolar molecule (see refs 24 and 25 for detailed discussion on the vibrational contributions to the NLO properties of the linear push-pull polyene within the VB-CT model). Also a variety of vibrational characteristics, such as IR and Raman intensities of the normal modes related to the three BLA coordinates, can be studied, as was investigated by Cho for the push-pull polyene.²⁶ The vibrational characteristics as well as the solvation effects on the NLO properties of the octupolar molecule will be presented elsewhere.

Although we considered three vibrational degrees of freedom in the extended model Hamiltonian, eq 10, the equilibrium values, q_{A1}^{eq} and q_{A2}^{eq} , at the potential minimum of the molecule approximately described by eq 10 are found to be zero. This result can be easily understood from the fact that the equilibrium BLA coordinates, Q_1^{eq} , Q_2^{eq} , and Q_3^{eq} , at the potential minimum are all identical due to the symmetry. Therefore it is possible to establish the relationship between the CT character, l , and the equilibrium BLA coordinate by taking into account the symmetric stretching mode only. Denoting q_S^{eq} as the q_S coordinate at the ground-state potential minimum, we find that q_S^{eq} is related to the equilibrium BLA coordinate of each branch as

$$q_S^{\text{eq}} \cong \sqrt{3} Q^{\text{eq}} \quad (13)$$

where the mode coupling constant, k' , is assumed to be negligibly smaller than k_0 . From the analytic expression for the ground-state energy obtained from eq 10 and the definition of l in eq 4, we find

$$\text{BLA} = Q^{\text{eq}} \cong 0.24l - 0.12 \text{ \AA} \quad (14)$$

This is a crucial relationship showing how the electronic structure represented by the CT character l is related to the BLA coordinate, Q^{eq} , of a conjugated polyene bridge. Furthermore it is noted that the relationship given in eq 14 is identical to that observed in the linear push-pull polyene within the VB-CT model discussed by Lu et al.; see eq 16b in ref 21, and note that f in ref 21 is the CT character of the ground state of a given push-pull polyene.²¹ Consequently it is suggested that *the conventional analysis of the NLO properties of the push-pull polyene in terms of the BLA coordinate can also be used to describe the NLO properties of the octupolar molecule.* For instance, if l is zero, the BLA coordinate is -0.12 Å, and this is the limit when the electronic structure of the octupolar molecule is close to the VB configuration shown in Figure 1. On the other hand, if l is $1/3$ as the other limit, the BLA coordinate is -0.04 Å. If we assume that the bond-order-alternation (BOA) is approximately linearly proportional to the BLA, this value, -0.04 Å, for the BLA means that the bond-order of the shorter bond among the two neighboring bonds in

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Table 1. Various Structural Properties of a Series of TPM Dye Molecules (AM1)

X	R (Å)	Z _c	φ (deg)	Δ (eV)	V (eV)	l
–H	1.43647 (1.44946) ^a	0.3191 (0.174) ^a	30.8737 (34.731) ^a	2.3546	4.6833	0.1211
–CH ₃	1.43532 (1.44727) ^a	0.3102 (0.166) ^a	30.7079 (34.242) ^a	2.2801	4.4028	0.1307
–OH	1.43336 (1.44506) ^a	0.3034 (0.152) ^a	30.7671 (34.021) ^a	2.1858	4.0801	0.1470
–OCH ₃	1.43339 (1.44462) ^a	0.3012 (0.149) ^a	30.6328 (33.442) ^a	2.1732	4.0400	0.1408
–NH ₂	1.43118 (1.44215) ^a	0.2875 (0.137) ^a	30.4151 (33.491) ^a	2.0511	3.6690	0.1652
–N(CH ₃) ₂	1.43092 (1.44156) ^a	0.2834 (0.132) ^a	30.2917 (33.244) ^a	1.9994	3.5242	0.1673
–N(C ₂ H ₅) ₂	1.43074	0.2835	30.2941	1.9913	3.5019	0.1688
–pyrrolidine	1.43063	0.2809	30.3036	1.9849	3.4844	0.1698
–piperidine	1.43062	0.2811	30.2139	1.9827	3.4786	0.1698

^a The molecular geometry was obtained by using the 6-31G basis set, whereas the molecular polarizability and hyperpolarizability were calculated with the STO-3G basis set.

a conjugated bridge is $5/3$ and the bond order of the longer one is $4/3$. Here it should be noted that the BLA coordinate of the octupolar molecule, such as TPM dyes, can only vary from -0.12 to -0.04 Å because of the symmetry. This is a crucial difference from the linear push–pull polyene whose BLA coordinate can vary from -0.12 to 0.12 Å. Perhaps this is the main reason the octupolar molecule shows distinctively different NLO properties in comparison to the push–pull polyene. We shall use eq 14 to estimate the CT character of a given TPM dye molecule in the following section.

4. Molecular Polarizability and First Hyperpolarizability of Triphenylmethane Dyes

As can be seen in Figure 1, the central carbon of a TPM dye is positively charged so that this central carbocation acts as an acceptor. Three donors in a given TPM dye molecule are connected to the central acceptor by the conjugated polyenes, i.e., three phenyl rings. Due to the steric hindrance between neighboring phenyl rings, each one rotates by approximately 30° , as can be confirmed by the geometry optimization.

As the donor strength is increased from hydrogen atom to piperidine, the CT character in the electronic ground state, l , should increase. We observe several evidences related to this trend. First of all, the bond length denoted as R in Figure 1 decreases, as the donor strength is increased (Table 1). This is because the double-bond character of R increases, as the donor strength is increased. Also, the charge of the central carbon atom, denoted as Z_c , should decrease, as the charge delocalization is favored by a strong electron-donating group. This behavior is also clearly observed in the numerical results (see Table 1). Another interesting feature is the reduction of the distortion, dihedral angle, ϕ , of a benzene ring (see Figure 1) for a strong donor. All of these observations manifest the increasing CT character of the ground state. In Table 1, we also present ab initio calculation results of R , Z_c , and ϕ , where the 6-31G basis was used to optimize the molecular geometry. Despite that the AM1 results deviate from the ab initio values, the overall trends of these quantities with respect to donor strength are still observed.

Although it is desirable to obtain the value l from the ground-state geometry of a given TPM dye by directly using eq 14, a caution is needed for the TPM dyes. The reason is because the electron localization effect induced by the internal rotational barriers among the three benzene rings strongly competes with the natural electron delocalization effect by the charge-transfer processes. Therefore, unlike the linear push–pull polyene having no such an internal barrier hindering π -electron delocalization, in the case of TPM dyes the BLA coordinate may not be a completely reliable parameter linearly correlated with the electronic structure represented by the CT character, l . It is strongly suggested that a further investigation with the

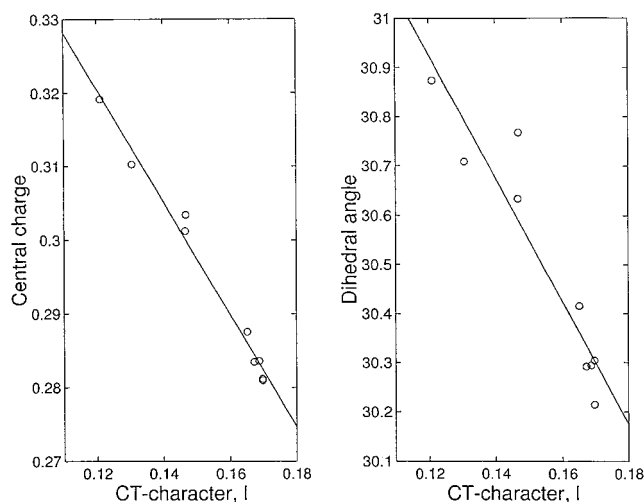


Figure 3. (left) Charge magnitude of the central carbon, Z_c , plotted as a function of the CT character, l . (right) Dihedral angle along the bond R plotted with respect to l .

modification of the model Hamiltonian including the internal rotational degrees of freedom in the future. In this paper, as an approximation, we shall assume that the relationship between the BLA coordinate and the CT character given in eq 14 is applicable to the TPM dyes.

To estimate the BLA coordinate Q^{eq} from the semiempirical calculation result, we shall focus on the bond length R . It should be noted that the length of a carbon–carbon single bond is known to be about 1.451 Å. As the donor strength increases, the bond length R deviates from this value as was confirmed by the calculations listed in Table 1. Then we make an approximation that the BLA coordinate can be calculated as

$$Q^{\text{eq}} \cong 2(\bar{R} - R) \text{ \AA} \quad (15)$$

where \bar{R} is the average of the single and double bond lengths, that is, $\bar{R} = (1.451 + 1.331)/2$ Å. Then using eqs 14 and 15 with the calculated value R , we can evaluate the CT character l (see the last column of Table 1). As expected, l increases as the donor strength increases.

To show the relationships of Z_c and ϕ with the CT character, l , we plot them with respect to l in Figure 3. It is interesting to note that they are almost linearly proportional to l so that one could use these parameters to describe the electronic structure of a TPM dye.

It is also interesting to note the general trend of the transition energy gap between the ground state and the first excited state. As the donor strength is increased, the transition energy gap, Δ , decreases (see Table 1). On the basis of the numerical results presented so far, we conclude that the mobile π -electrons

Table 2. Molecular Polarizability Tensor Elements of CV in esu (10^{-25} esu) (AM1)

α_{xx}	785	α_{yx}	-26	α_{zx}	121
α_{xy}	-26	α_{yy}	802	α_{zy}	134
α_{xz}	122	α_{yz}	134	α_{zz}	270

Table 3. Molecular First Hyperpolarizability Tensor Elements of CV in esu (10^{-30} esu) (AM1)

β_{xxx}	24	β_{yxx}	-142	β_{zxx}	-27
β_{xxy}	-146	β_{yyx}	-11	β_{zyx}	-37
β_{xxz}	-25	β_{yzx}	-35	β_{zxx}	-13
β_{xyx}	-143	β_{yyx}	-13	β_{zyx}	-32
β_{xyy}	-10	β_{yyy}	147	β_{zyy}	31
β_{xxx}	-35	β_{yyz}	29	β_{yzx}	-1
β_{xxz}	-24	β_{yzx}	-35	β_{zxx}	-4
β_{xxy}	-29	β_{yzy}	25	β_{zzy}	4
β_{xxz}	-13	β_{yzz}	-2	β_{zzz}	-3

can be delocalized over a wide range of the molecule, as the electron donor strength is increased. This is the key aspect for an octupolar molecule having large α and β .

In Table 2, the α -tensor elements of CV are presented as a representative example among the TPM dyes. Despite that the data of other TPM dye molecules are not presented in this paper, they all exhibit similar patterns. As predicted by eq 6a, the two diagonal elements, α_{xx} and α_{yy} , are almost identical, and the two off-diagonal elements, α_{xy} and α_{yx} , are negligibly small in comparison to the diagonal ones. The β -tensor elements of CV are listed in Table 3. As shown by eqs 6c and 6d, the absolute magnitudes of the four tensor elements, β_{yxx} , β_{xyx} , β_{xxy} , and β_{yyy} , are almost identical and these four elements are the dominant contributions to β . Furthermore, the signs of β_{yxx} , β_{xyx} and β_{xxy} are opposite to that of β_{yyy} , which also confirms the relationship given in eq 6c. These calculation results are consistent with the symmetry requirements, as expected from the Kleinman symmetry. The static $|\beta_{yyy}|$ value was estimated to be 92×10^{-30} esu by using the HRS (hyper-Rayleigh scattering) method.¹⁶ This value is in good agreement with the AM1-calculated value, 147×10^{-30} esu (see Table 3).

On the basis of the relationships, eqs 6, among the β -tensor elements, we find that

$$\beta_x \equiv \sum_j \beta_{xij} = 0$$

$$\beta_y \equiv \sum_j \beta_{yij} = 0 \quad (16)$$

Although these quantities obtained by AM1 calculation are not exactly zero, they are indeed negligibly small compared to the four major elements.

We summarize the numerical calculations of polarizabilities and hyperpolarizabilities of a series of the TPM dyes in Table 4. Particularly the yy and yyy components of α and β tensors are listed. In the last column of Table 4, $||\beta||$ values of the TPM dyes are listed. It is expected that, from eq 7, $||\beta||$ should satisfy the following relationships:

$$||\beta|| \equiv \left(\sum_{i,j,k} \beta_{ijk}^2 \right)^{1/2} = 2\beta_{yyy} = -2\beta_{xxy} = -2\beta_{xyx} = -2\beta_{yxx} = 9 \frac{l\mu^3}{\Delta^2} \quad (17)$$

Indeed, the numerical results confirm these relationships. This result can serve as another evidence showing that the model Hamiltonian eq 1, though it is too crude to provide quantitative

Table 4. α_{yy} and β_{yyy} of a Series of TPM Dye Molecules in esu (AM1)

substituent	α_{yy} (10^{-25} esu)	β_{yyy} (10^{-30} esu)	$ \beta $ (10^{-30} esu)
-H	407 (274) ^a	25 (~ 1) ^a	55
-CH ₃	507 (337) ^a	51 (21) ^a	107
-OH	506 (352) ^a	57 (28) ^a	123
-OCH ₃	593 (428) ^a	70 (39) ^a	157
-NH ₂	607 (398) ^a	91 (41) ^a	191
-N(CH ₃) ₂	802 (515) ^a	147 (63) ^a	310
-N(C ₂ H ₅) ₂	929	169	362
-pyrrolidine	956	180	405
-piperidine	948	184	395

^a The molecular geometry is optimized with Gaussian 6-31G, whereas the molecular polarizability and hyperpolarizability are calculated with the STO-3G basis set.

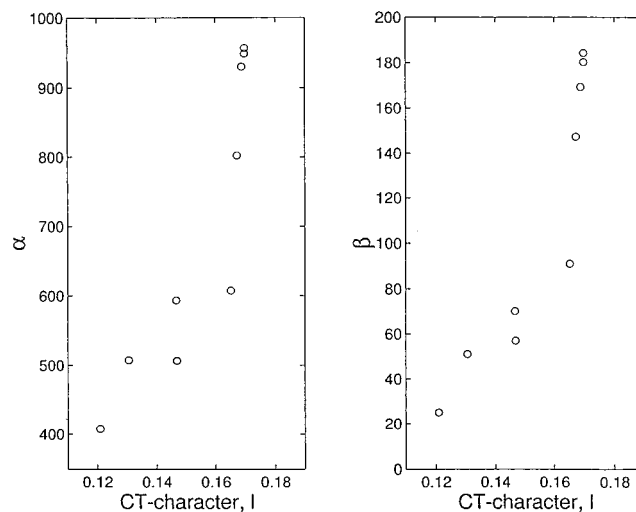


Figure 4. Both α_{yy} and β_{yyy} of a series of TPM dye molecules plotted with respect to l . The units are specified in Table 4. Both of them monotonically increase as the donor strength is increased. See the text for detailed discussions.

information, can capture the essential physics of the NLO responses of octupolar molecules such as TPM dyes.

From Table 4, one can find the general trends of α and β of the TPM dyes with respect to the donating strength varying from H to piperidine. On the basis of the AM1-level calculation, α of the piperidine-substituted TPM dye is two times larger than that of the triphenylmethane ion and β of the piperidine-substituted TPM dye is 7 times larger than that of the TPM dye itself. This observation suggests that the NLO properties of the octupolar molecule can be dramatically increased by the strong donor, in comparison to the linear optical response. It is also noted that both α and β increase monotonically, as the donor strength is increased. To make this statement clear, we plot α and β as a function of the CT character, l , in Figure 4. This pattern is in complete agreement with the theoretical model discussed in section 2. It should also be noted that these patterns are in marked contrast with those of the linear push-pull polyene, where α and β show quite different behaviors as the CT character of the ground state increases.

5. Discussion and a Few Concluding Remarks

For an oscillating electric field, the mobile π -electrons can adiabatically follow the external field. Therefore these oscillating electrons induce an electric dipole as $\mu^{(1)}_{\text{ind}}(t) \approx \alpha E(t)$. This is a classical Drude-type interpretation of the first-order optical response when the electric field frequency is off-resonant. In this case, the magnitude of this response equals to the

molecular polarizability. If the molecular structure accommodating these mobile electrons is spatially large, the polarizability is generally large. In the case of the TPM derivatives, it is clearly the central carbocation that plays a crucial role in bridging the three branches of conjugated systems to make the spatial dimension of the conjugation increase. If the central carbon atom is not cationic so that the further resonance structures among the three branches are prohibited, this molecule would be identical to the case of independent three conjugated polyenes. Furthermore they would not exhibit such a large nonlinear optical response observed in this paper. Precisely because of these additional charge-transfer processes making the mobile electrons delocalized over the whole molecule, the TPM dye molecules exhibit a completely different nonlinear optical response.

On the basis of the numerical results with theoretical analyses presented in section 4, we find that there are a few distinctive features in the NLO properties of the octupolar molecule compared to those of the linear push-pull polyene. The most important but apparent difference between the push-pull polyene and the octupolar molecule is the molecular symmetry, that is to say, the former does not have a certain symmetry whereas the latter does. Because of the symmetry, we found that the equilibrium BLA coordinate of each conjugation branch varies from -0.12 to -0.04 Å; note that the BLA coordinate of the push-pull polyene can vary from -0.12 to 0.12 Å depending on the donor-acceptor pair or solvent polarity.²⁷ Bearing this fact in mind, we first make a comparison of α of the push-pull polyene with that of the TPM dye. As the CT character of the ground state increases, α of the push-pull polyene shows nonmonotonic behavior. More specifically, as the BLA approaches to zero, α reaches a maximum and, as the absolute magnitude of the BLA increases, α decreases. On the other hand, in the case of the TPM dye, as the CT character of the ground state increases, α increases monotonically. Consequently, the strategy of maximizing α is fairly straightforward in this case, as demonstrated in Table 4. Second, let us consider the general pattern of β of the push-pull polyene in comparison with that found in a series of the TPM dyes. In the former case, as the BLA increases from negative to positive values, β

increases and reaches a maximum and decreases to a minimum and then increases again toward zero. Therefore, it was suggested that a meticulous control of the BLA has to be achieved to attain maximum β for the push-pull polyene. In contrast, the TPM dyes exhibit a rather monotonic pattern, that is to say, as the donor strength is increased (this is identical to approximately saying that as the bond length R decreases), β increases continuously. Therefore, the same strategy used to increase α can also be applied to do β in the case of the octupolar molecule such as TPM dyes. Perhaps this is the most striking feature found in this paper. It is not entirely clear whether all types of octupolar molecules other than TPM dyes exhibit these patterns studied in this paper.

Finally we summarize the main results with a few concluding remarks. The four-state model was extended by including the harmonic BLA coordinates. The relationship between the CT character and the BLA coordinate was established, so we suggested that one can use the conventional way of analyzing the NLO properties in terms of the equilibrium BLA coordinate to interpret those of the octupolar molecule. We also presented semiempirical calculations of the NLO properties of TPM dyes to compare them with the four-state model predictions. Despite that the "gas-phase" calculation is known to underestimate the degree of charge separation, the semiempirical calculations should be of use in obtaining semiquantitative results. Within this numerical error, we found that the simple four-state model successfully describes the general trends (Figure 4) of the linear and nonlinear optical responses of these molecules. As the donor strength is increased from hydrogen atom to piperidine, the CT character of the ground state, α , and β increase monotonically. Even though the four-state model is too crude to provide quantitative information on the NLO responses of the octupolar molecule, it is believed that this model should be useful for providing a simple guideline for predicting the general trends of the NLO properties of the octupolar molecule with respect to the CT character as well as the BLA.

Unlike the linear push-pull polyene, the octupolar molecule exhibits a completely different trend of β when the CT character of the ground state changes. To provide further convincing evidences for the results observed in this paper, detailed investigations with *ab initio* methods and experimental measurements of β of a variety of TPM dye molecules and other types of octupolar molecules should be carried out in the future.

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(27) Although we have only focused on a series of octupolar molecules, donor-substituted triphenylmethane dyes, a variety of other types of octupolar molecules are currently under investigation both theoretically and experimentally by the collaboration with organic chemists. We have found that most of the real octupolar molecules that can be synthesized in the lab are likely to belong to the range of BLA considered in this paper. However, if the magnitude of the charge separation is larger than e , where e is the electron charge, one may expect to see different NLO responses in comparison to those presented in this paper. Despite this possibility, it is difficult to find such a strong donor or acceptor in reality. Therefore, the argument that the BLA of the octupolar molecule is rather limited to the range from -0.12 to -0.04 Å is highly likely to be acceptable in general.