

Nonlinear Optical (NLO) Properties of the Octupolar Molecule: Structure–Function Relationships and Solvent Effects

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Nonlinear optical (NLO) properties of two series of octupolar molecules are investigated to establish the structure–NLO-property relationships by carrying out the *ab initio* (HF/6-31G) calculations of the molecular polarizability (α), the first hyperpolarizability (β), and the second hyperpolarizability (γ). It is found that, as the charge-transfer character of the ground state increases by introducing a stronger donor, (i) the absolute BLA value decreases and (ii) α , β , and γ increase. Thus, the design strategy to maximize the NLO properties of the octupolar molecule is established. Also, the solvation-induced effects on the NLO properties are studied by using the self-consistent reaction field (SCRF) method. As the solvent polarity increases, α , β , and γ increase monotonically. These observations are in good agreement with the predictions based on the valence-bond three-charge-transfer model.

1. Introduction

Despite that the molecular nonlinear optical properties of various push–pull polyenes have been extensively studied,^{1–13} the crystallization problem was considered to be a serious obstacle in utilizing this type of nonlinear optical (NLO) molecules for the purpose of devices.^{14,15} Recently, the octupole-type molecules have been paid much attention,^{14–21} since they do not have a permanent dipole moment so that a new principle of crystal engineering can be used to design octupolar nonlinear optical materials.^{22,23}

In contrast with the push–pull polyene showing nonmonotonic NLO properties with respect to the bond length alternation (BLA),^{5–11,24–26} it was recently found that both α and β of the octupolar molecule monotonically increase as the ground state charge-transfer (CT) character increases.^{20,27} In practice, by introducing stronger donor and acceptor and by lengthening the conjugation bridge, one can achieve this goal. Lee et al. carried out semiempirical (AM1) calculation of α and β of the donor-substituted triphenylmethane (TPM) dyes to confirm these theoretical predictions made by using the valence-bond three-charge-transfer (VB-3CT) model.²⁰ In this paper, we consider two series of octupolar molecules shown in Figure 1, where D represents the electron-donating group. The type-I octupolar molecules contain the same central acceptor as the crystal violet, that is the carbocation, and three donating groups are connected to the central acceptor via conjugated polyene bridges, whereas in the series of octupolar compounds of type-II the central acceptor is a trinitrobenzene group and the bridge is the conjugated polyyne. Since these two types of molecules do not have a strong steric hindrance between any two neighboring branches, they serve as the ideal prototype octupolar molecules suitable for the establishment of the structure–NLO-property relationship in terms of the BLA.

Although the general trends of α and β of a specific series of TPM dyes were already explored in ref 20, there exist a few shortcomings in the previous studies. The first is originated from

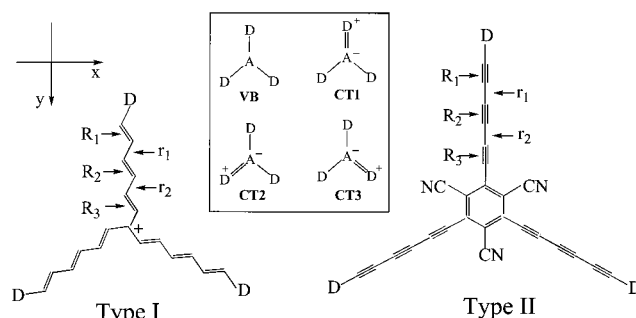


Figure 1. Two types of octupolar molecules are drawn. The molecular coordinate system is also shown. D and A denote the electron-donating and -accepting groups, respectively. Three charge-transfer (CT) configurations with a valence-bond (VB) configuration are pictorially shown in the middle panel.

the fact that the TPM dye molecules having three benzene rings attached to the central carbocation rotate by 30 degrees because of the steric hindrance. Therefore, the charge delocalization effect is in strong competition with the charge localization process induced by the internal rotational barrier. Consequently, it was not possible to obtain the quantitative relationship between the BLA of the three branches and the NLO properties. Second, in addition to α and β of the TPM dyes considered in ref 20, the second hyperpolarizability γ of the two types of octupolar molecules shown in Figure 1 with respect to their ground state structures will be investigated in this paper. Third, the solvation effect on the NLO properties of the octupolar molecule is investigated by using the self-consistent reaction field (SCRF) method.

2. Ab Initio Calculations of the Molecular Polarizability and First and Second Hyperpolarizabilities

The molecular structures of the two series of octupolar molecules in Figure 1 are fully optimized with the 6-31G basis in the GAMESS package.²⁸ Most of the optimized structures have the C_3 symmetry element, but some of them have slightly

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TABLE 1: The BLA, Central Charges (Mulliken and Lowdin Charges), α_{yy} , β_{yyy} , and γ_{yyyy} of the Type-I Octupolar Molecules Calculated with 6-31G Basis Set

donors	BLA (Å)	Mulliken	Lowdin	α_{yy} (10^{-23} esu)	β_{yyy} (10^{-29} esu)	γ_{yyyy} (10^{-34} esu)
H	-0.09811 (-0.1052) ^a	0.1448	0.1714	8.405 (5.485) ^a	12.80 (13.30) ^a	7.646
CH ₃	-0.09140 (-0.09845) ^a	0.1433	0.1661	9.826 (6.419) ^a	17.05 (17.67) ^a	11.13
OH	-0.08713 (-0.08973) ^a	0.1422	0.1625	9.641 (6.338) ^a	18.28 (19.29) ^a	11.04
OCH ₃	-0.08382 (-0.08697) ^a	0.1412	0.1597	11.10 (7.218) ^a	22.83 (23.42) ^a	15.13
NH ₂	-0.06892 (-0.07280) ^a	0.1387	0.1508	11.18 (7.322) ^a	24.66 (25.80) ^a	12.89
N(Me) ₂	-0.06173 (-0.06753) ^a	0.1368	0.1438	13.46 (8.667) ^a	32.55 (32.88) ^a	19.16
N(Et) ₂	— (-0.06686) ^a	—	—	— (9.545) ^a	— (37.21) ^a	—
pyrrolidine	-0.06025 (-0.06039) ^a	0.1363	0.1426	15.11 (10.05) ^a	37.09 (39.80) ^a	22.98

^a These values are calculated by using the 6-31G basis set in the Gaussian 94 program with FF method.

TABLE 2: The BLA, α_{yy} , β_{yyy} , and γ_{yyyy} of Type-II Octupolar Molecules (Calculations with the 6-31G Basis Set)

donors	BLA (Å)	α_{yy} (10^{-23} esu)	β_{yyy} (10^{-29} esu)	γ_{yyyy} (10^{-34} esu)
H	-0.17309	7.27	1.303	2.915
CH ₃	-0.17048	8.32	2.143	3.928
OH	-0.16888	7.80	2.293	3.707
OCH ₃	-0.16725	8.87	2.522	4.727
NH ₂	-0.1632	8.57	4.149	5.922
N(Me) ₂	-0.1614	11.24	5.186	8.948

distorted structures, that is to say, the conjugated polyene bridges in the type-I molecules slightly rotate out of the molecular plane. Despite these deviations from the ideal D_{3h} symmetry, the general trends of the NLO properties are not significantly altered by these structural distortions. Their NLO properties are evaluated by using the finite-field (FF) method.^{2b}

A. BLA vs. NLO Properties. From the optimized structures, the corresponding BLA values are estimated and listed in Tables 1 and 2. The definition of the BLA is given as

$$Q^{\text{eq}} = \frac{1}{3} \sum_{i=1}^3 R_i - \frac{1}{2} \sum_{j=1}^2 r_j \quad (1)$$

where the bond lengths, R_i and r_i , were defined in Figure 1. Because of the C_3 symmetry, the three BLA coordinates of each conjugation bridge are identical. The calculated values of α_{yy} , β_{yyy} , and γ_{yyyy} of the type-I and -II molecules are listed in Tables 1 and 2, respectively. Here it is assumed that the octupolar molecule lies on the $[x,y]$ -plane. In Figures 2 and 3, α_{yy} , β_{yyy} , and γ_{yyyy} are plotted with respect to the equilibrium BLA value estimated from the optimized molecular geometry. As predicted by the VB-3CT model described in refs 20 and 27, the NLO properties increase as the donor strength increases. All other tensor elements can be estimated by using the relationships among the tensor elements

$$\begin{aligned} \alpha_{xx} &= \alpha_{yy} \\ \beta_{yyy} &= -\beta_{yxx} = -\beta_{xyx} = -\beta_{xxy} \\ \gamma_{yyxx} &= \gamma_{xyxx} = \gamma_{xyxy} = \gamma_{xyyx} = \gamma_{xyxy} = \gamma_{xyxy} = \\ &= \frac{1}{3} \gamma_{xxxx} = \frac{1}{3} \gamma_{yyyy} \end{aligned} \quad (2)$$

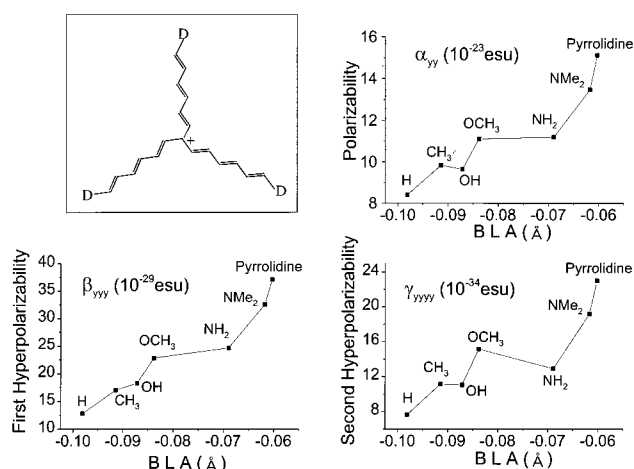


Figure 2. α_{yy} , β_{yyy} , and γ_{yyyy} of the type-I octupolar molecules are plotted with respect to the BLA.

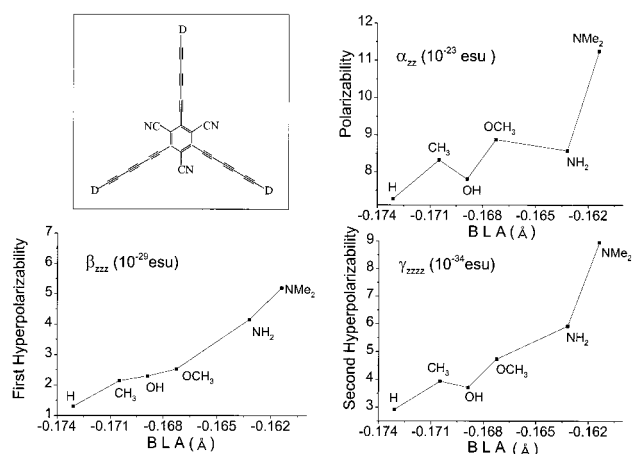


Figure 3. α_{zz} , β_{zzz} , and γ_{zzzz} of the type-II octupolar molecules are plotted with respect to the BLA.

Although the other tensor elements of a real octupolar molecule in Figure 1 are not strictly zero due to the slight deviation from the ideal D_{3h} symmetry, it is confirmed that they are negligibly smaller than the tensor elements listed in eq 2. In order to confirm the relationships among the tensor elements of γ , six representative tensor elements of γ of the type-I molecule with donor of NH₂ are presented in Table 3.

TABLE 3: Six Tensor Elements of γ of Type-I Octupolar Molecule with Donor of NH₂ (in esu)^a

(10 ⁻³⁴ esu)					
γ_{xxxx}	12.69	γ_{yyyy}	12.89	γ_{zzzz}	-0.0093
γ_{xxyy}	4.072	γ_{xxzz}	0.0413	γ_{yyzz}	0.00503

^a The molecular geometry is optimized by using the 6-31G basis, and the dipole-based finite-field method is used to calculate γ .

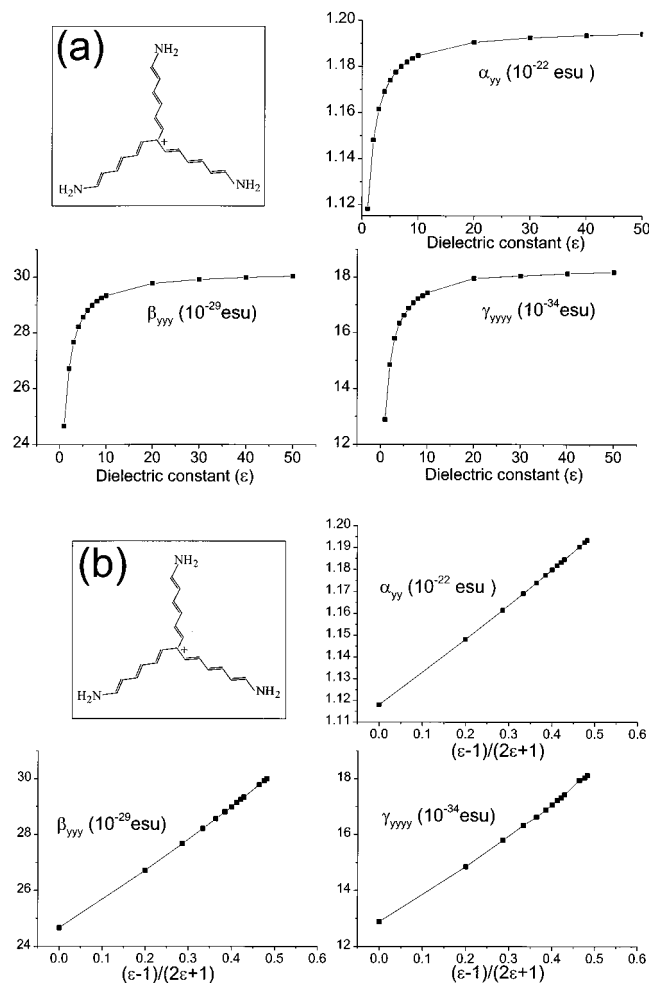


Figure 4. (a) α_{yy} , β_{yyy} , and γ_{yyyy} of the type-I octupolar molecule with $D = \text{NH}_2$ are plotted with respect to the solvent dielectric constant, ϵ . (b) These values are plotted with respect to the Onsager function, $(\epsilon - 1)/(2\epsilon + 1)$.

In Table 1, the BLA, α_{yy} , and β_{yyy} of the type-I octupolar molecules calculated by using the Gaussian 94 program²⁹ with the 6-31G basis set are also presented. The two calculation results with both Gaussian 94 and GAMESS programs are in good agreement with one another.

B. Solvation-Induced Effects. For the type-I compound with NH₂ donors, the solvation-induced effects on the NLO properties are investigated by using the SCRF method,³⁰ and the calculated values are plotted in Figure 4a and b. As the solvent polarity or equally the solvent dielectric constant increases, α_{yy} , β_{yyy} , and γ_{yyyy} increase monotonically. This is mainly due to the fact that the degree of charge delocalization increases as the solvent polarity increases. Note that α_{yy} , β_{yyy} , and γ_{yyyy} show almost linear dependence on the Onsager function, $(\epsilon - 1)/(2\epsilon + 1)$.

3. Discussion

In the case of the linear push-pull polyene, depending on the electron donor and acceptor strengths the BLA changes from

negative to positive.¹⁰ This electronic structure change is sometimes noted as a transition from one phase to the other. This kind of phase transition is possible since the molecular structure of the push-pull polyene is asymmetric. Then, the key to achieve an optimization of the desired NLO property is to precisely choose the right donor and acceptor groups. For instance, the absolute magnitude of γ along the CT axis reaches a maximum value when the BLA equals zero.^{10,24} This is the case of the cyanine-type molecules. On the other hand, β is zero when the BLA equals zero. Therefore, one has to use a different strategy to optimize different NLO properties. On the other hand, the NLO properties of the octupolar molecules studied in this paper show quite monotonic behaviors. Why? The answer can be found by noting the symmetry of the octupolar molecules. Unlike the push-pull polyene, the octupolar molecule has a C_3 symmetry element. Therefore, the BLAs of the three conjugation bridges have to be identical in the electronic ground state geometry. For instance, consider the type-I molecules. In the electronic ground state, the central carbocation has a charge less than a unity since this charge is distributed over the entire molecule. As the donor strength increases from H to pyrrolidine, the extent of the charge distribution or CT character from central cation to peripheral donors increases. The linear relationship between the central acceptor charge and the BLA for the type-I octupolar molecules, shown in Figure 5, supports this idea. However, one cannot expect to see the full changes of the BLA from a negative value to a positive value in this case of the octupolar molecule: note that depending on the definition of the BLA it could be from positive to negative, but we shall use the definition in eq 1 throughout this paper. In comparison to the linear push-pull polyene, the range of the BLA exhibited by the octupolar molecule is thus limited. The ranges of the BLA for the polyene and polyyne bridges in the case of the octupolar molecules are approximately estimated to be from -0.12 to -0.04 Å and from -0.175 to -0.117 Å, respectively.³¹ This aspect is perhaps the main reason why the octupolar molecules exhibit rather monotonic behaviors in the NLO properties.

In order to provide the basic idea on the patterns observed in the ab initio calculations, let us start from the perturbation theory expressions for the static α_{yy} , β_{yyy} , and γ_{yyyy} ³²

$$\begin{aligned}
 \alpha_{yy} &\propto \sum_{m \neq g} \frac{\mu_{gm}^y \mu_{mg}^y}{E_{mg}} \\
 \beta_{yyy} &\propto \sum_{m \neq g} \sum_{n \neq g} \frac{\mu_{gm}^y \bar{\mu}_{mn}^y \mu_{ng}^y}{E_{mg} E_{ng}} \\
 \gamma_{yyyy} &\propto \sum_{m \neq g} \sum_{n \neq g} \sum_{p \neq g} \frac{\mu_{gm}^y \bar{\mu}_{mn}^y \bar{\mu}_{np}^y \mu_{pg}^y}{E_{mg} E_{ng} E_{pg}} - \sum_{m \neq g} \sum_{n \neq g} \frac{\mu_{gm}^y \mu_{mg}^y \mu_{gn}^y \mu_{ng}^y}{E_{mg} E_{ng} E_{ng}} \quad (3)
 \end{aligned}$$

where μ_{mg}^y is the y component of the transition dipole matrix element between $|g\rangle$ and $|m\rangle$ states. $\bar{\mu}_{mn}^y \equiv \mu_{mn}^y - \mu_{gm}^y = \mu_{mn}^y$, where the second equality is obtained by noting that the ground state permanent dipole moment of the octupolar molecule is zero. E_{mg} is the energy difference between $|m\rangle$ and $|g\rangle$, i.e., $E_{mg} = E_m - E_g$. In the case of the octupolar molecule, there exist twofold degenerate excited states so that the optical transitions contributing to β_{yyy} contain so-called triangle processes.^{15,18,20,27} On the basis of the VB-3CT model, it was found that, as the donor and acceptor strengths increase, (i) the energy

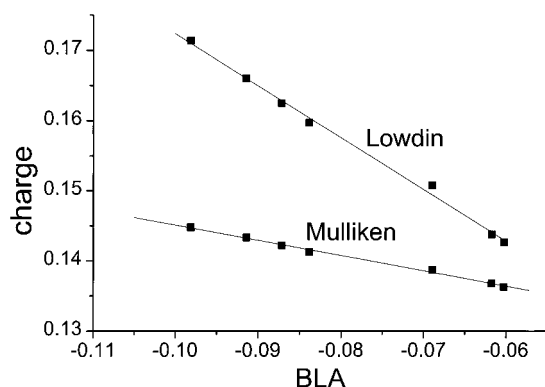


Figure 5. The Lowdin and Mulliken charges at the central acceptor of the type-I molecules are plotted with respect to the BLA.

gap between the ground $|g\rangle$ and twofold degenerate excited states $|e\rangle$ monotonically decreases and (ii) the transition dipole matrix element between $|g\rangle$ and $|e\rangle$ monotonically increases. These two contributions to α_{yy} and β_{yyy} in eq 3 combine to produce the increasing patterns observed in the ab initio calculation results in Figures 2 and 3.

These observations are in good agreement with the previous works on the NLO properties of the TPM dyes.²⁰ In this case, however, the steric hindrance-induced rotations of the benzene rings to form the propeller structure prohibit the full electron delocalization of the mobile π -electrons. On the other hand, the type-I molecules are relatively free from those steric effects. Therefore, the NLO properties of the type-I molecules are expected to be larger than those of the TPM dyes, and indeed this expectation is confirmed by the ab initio calculation. For instance, β_{yyy} of the crystal violet was estimated to be 92×10^{-30} esu by using the HRS (hyper-Rayleigh scattering) method¹⁵ and 150×10^{-30} esu by the AM1 semiempirical calculation,²⁰ whereas that of the type-I molecule with donors of $N(CH_3)_2$ is 330×10^{-30} esu. In the cases of the polyyne bridge type-II octupolar molecules, their NLO properties are smaller than those of the TPM dyes. However, the numerical results shown in Figure 3 clearly show that the same patterns found in the polyene bridge octupolar molecules can be observed in the polyyne bridge octupolar molecules, and also they provide other evidences on the validity of the simple VB-3CT model.²⁷

We next consider the second hyperpolarizability. As shown by using the VB-3CT model, there exist the relationships among the tensor elements of the second hyperpolarizability (see eq 2), and those are quantitatively confirmed (see Table 3). Furthermore, by noting the increasing patterns of γ_{yyyy} for the two types of octupolar molecules, it is concluded that as the charge-transfer character of the ground state increases the second hyperpolarizability also increases. However, a caution is needed in making this general statement. As can be seen in eq 3, there are two distinctive contributions to γ_{yyyy} . If the three states, that are the ground state $|g\rangle$ and twofold degenerate excited states $|e1\rangle$ and $|e2\rangle$, are only taken into account, the first summation in the expression for γ_{yyyy} in eq 3 contains a term associated with the optical transition process such as $|g\rangle \rightarrow |e1\rangle \rightarrow |e2\rangle \rightarrow |e1\rangle \rightarrow |g\rangle$ and $|g\rangle \rightarrow |e2\rangle \rightarrow |e1\rangle \rightarrow |e2\rangle \rightarrow |g\rangle$. On the other hand, a few typical terms contributing to γ_{yyyy} negatively are associated with the processes such as $|g\rangle \rightarrow |e1\rangle \rightarrow |g\rangle \rightarrow |e1\rangle \rightarrow |g\rangle$, $|g\rangle \rightarrow |e2\rangle \rightarrow |g\rangle \rightarrow |e2\rangle \rightarrow |g\rangle$, etc. From the ab initio calculation results, γ_{yyyy} is found to be positive so that the former types of optical transition process involving transitions between the two degenerate excited states are dominant contributions to γ_{yyyy} of the octupolar molecules studied in this paper. However, as the CT character (or donor-acceptor

strengths) increases further, γ_{yyyy} may exhibit a turnover behavior.^{27b} Thus, a more detailed investigation along this line is required.

If an octupolar molecule is dissolved in the polar solvent, the CT configuration is likely to be more strongly solvated by the polar solvent. Which in turn makes the CT character in the ground state increase. Then, as a result of the change of the ground state electronic structure getting close to a strongly charge-transferred geometry, α_{yy} , β_{yyy} , and γ_{yyyy} would increase. These expectations are confirmed by the ab initio calculations with the SCRF method (see Figure 4a and b). The quasilinear dependencies of α_{yy} , β_{yyy} , and γ_{yyyy} on the Onsager function $(\epsilon - 1)/(2\epsilon + 1)$ shown in Figure 4b suggest that the dipolar reaction field interaction with the chromophore could be the dominant contribution in the solvation process of the octupolar molecules. This is in good agreement with the observation made by Luo et al. (see below).^{17b,21} In summary, if the solvent polarity increases, the NLO properties would exhibit increasing patterns. It is hoped that these predictions are confirmed experimentally in near future.

Before we close this section, the results presented in this paper are compared with the works reported previously. Sastre et al.¹⁹ measured the first hyperpolarizabilities of subphthalocyanine (SubPcs) derivatives and found that $\langle \beta^2(0) \rangle^{1/2}$ of nitrosubstituted SubPcs is almost 6 times larger than that of SubPcs with no acceptors. It should be mentioned that these compounds have a central donor instead of an acceptor and also belong to the octupolar molecule. By noting that the principle role of the three strong acceptors in the nitrosubstituted SubPcs is to increase the CT character of the electronic ground state, their observations can be described by the same logic used in the present investigation. As another example, Greve et al.³³ studied several NLO molecules with effective multidirectional charge-transfer transitions. They found that the periphery-to-center charge-transfer (PC-CT) transition is responsible for the large third-order NLO responses from octupolar molecules. They observed these trends by carrying out semiempirical calculations. Here also the simple VB-3CT model can basically capture the essential physics behind these phenomena. Within this model the ground state wave function can be expressed as the linear combination of the four basis configurations, e.g., VB, CT1, CT2, and CT3 configurations shown in Figure 1, that is to say, $|g\rangle = \sqrt{1-3I}\phi_{VB} + \sqrt{I}(\phi_{CT1} + \phi_{CT2} + \phi_{CT3})$ where ϕ_{VB} and ϕ_{CTj} (for $i = 1, 2, 3$) denote the wave functions of the VB and j th CT configurations, respectively.²⁷ On the other hand, the twofold degenerate excited state wave functions are determined by the linear combinations of the CT configurations only, such as $|e1\rangle = \sqrt{2}(\phi_{CT3} - \phi_{CT1})$ and $|e2\rangle = \sqrt{1/6}(2\phi_{CT2} - \phi_{CT1} - \phi_{CT3})$. Therefore the optical transition from $|g\rangle$ to $|e1\rangle$ (or $|e2\rangle$) involves a strong charge-transfer transition from the central acceptor to the donors, and this interpretation is in good agreement with the observation of Greve et al.³³ Finally, Luo, Cesar, and Ågren studied the solvent effects on β of the tricyanomethanide molecular anion in solution^{17b} and recently Luo, Norman, and Ågren also presented similar numerical results on TATB (1,3,5-triamino-2,4,6-trinitrobenzene) by using the Onsager reaction field method.²¹ They also found that α and β increase as the solvent polarity increases. However, the molecules they considered are too small to draw a general conclusion, and furthermore the solvent effect on γ was not investigated previously.

4. Summary

The results presented in this paper differ from the previous work²⁰ in several ways, i.e., (1) unlike the TPM dyes, the two

types of octupolar molecules studied in this paper have minimal steric hindrance effects between neighboring branches, (2) the ab initio methods instead of semiempirical ones were employed in the present calculations, (3) the quantitative relationship between γ_{yyy} and BLA was also established, (4) the octupolar molecules with polyene bridges were studied, and (5) the solvent effects on the NLO properties were investigated. On the basis of the theoretical results presented in this paper, a few characteristic features of the octupolar molecules were found and they are (1) α , β , and γ increase as the CT contribution to the ground state increases, (2) the equilibrium BLA coordinate of the octupolar molecule varies in a limited range because of the molecular symmetry, and (3) the CT character in the ground state is almost linearly proportional to the equilibrium BLA.

Overall, it is found that the BLA concept used in establishing the structure–NLO-property relationships of the linear push–pull polyene still plays a crucial role in understanding the NLO properties of the octupolar molecule. Conclusively, the design strategy to maximize the NLO properties of the octupolar molecule is believed to be clarified. It is hoped that these general trends and quantitative results are confirmed experimentally in the near future.

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