Molecular Design for Octupolar Nonlinear Optical Systems: An ab Initio Study of First Hyperpolarizabilities of Symmetrically Heteroaromatic-Substituted Triazines

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An ab initio coupled perturbed Hartree−Fock study has been performed to investigate the hyperpolarizabilities β of a series of heteroaromatic-substituted *sym*-triazines in the frame of a tensorial formalism. Effects of donor or acceptor substitution and electron correlation on the octupolar triazines have also been explored. Geometric effects have been considered in a set of calculations by using fully optimized and planar structures. It is found that the effects of the deviations from the planarity on β are very small. Octupolar triazines containing pyrrole derivatives have larger β than the corresponding analogues containing furan and thiophene derivatives, and NO_2 or NH_2 substitution strongly affects β of octupolar benzene-substituted triazine. An additive model is introduced to evidence specific contributions to β arising from the multipolar symmetry. The β tensor of a multipolar system is dissected into two separate tensor representation, an additive term β^A representing the tensorial sum of the dipole units' β and a term β^I representing interactions between the dipole units constituting the multipole. The results indicate that when the acceptor groups (NO_2) are introduced into octupolar triazines containing pyrrole and furan derivatives, the effects of the interaction term exceed that of the additive term and greatly enhance the magnitudes of β, contrasted with unsubstitution. It is also seen that incorporating the donor groups (NH_2) into the octupolar molecules not only significantly enhances β^A but also β^I, compared with unsubstitution and NO_2 substitution. The electron correlation has a large influence on the magnitude of the hyperpolarizabilities.

1. Introduction

The design and development of organic conjugated materials with large optical nonlinearities have attracted considerable attention because of their potential applications in photonic devices.[1−6] The optimization of molecules exhibiting large nonlinear optical (NLO) responses is the primary step for designing and synthesizing materials for NLO applications. In general, these molecules are pull−push π-conjugated systems, which contain a conjugated linker segment capped by a donor group at one end and an acceptor group at the other end.[5] Thus, many studies have concentrated on the effects of many donor and acceptor groups as well as various nature and length of conjugated bridges on the NLO properties.[7−19] Such molecules are highly anisotropic dipole structures such as *p*-nitroaniline derivatives, pull−push polyenes, and donor−acceptor stilbenes, in which the optical nonlinearities are intimately associated with quasi-one-dimensional charge transfer. Although they often exhibit extremely large NLO polarizabilities, a number of drawbacks have come to be identified for their dipole character: a high tendency toward unfavorable aggregation, difficult noncentrosymmetric crystallization, and small off-diagonal tensor components.

Octupolar molecules that have been recognized only recently as potentially useful for NLO applications can circumvent the aforementioned disadvantages because these nonpolar molecules combine excellent second-order NLO characteristics with a strict cancellation of all vectorial properties.[20,21] A few years ago, on the basis of experimental evidence as well as on general tensorial and quantum mechanical considerations, it has been proposed[22−24] that two- and three-dimensional stereochemistry offers new possibilities for the design and synthesis of optically nonlinear molecules, in which charge transfer is multidirectional rather than dipolar in character. This is the so-called "octupolar" or more general "multipolar" origin. Octupolar nonlinearities have already been demonstrated in several molecular systems.[23−26] Lately, much more attention has been paid to the NLO responses of the octupolar molecules.[22−43]

NLO applications require thermally robust materials exhibiting large optical nonlinearities. Typical organic conjugated systems such as substituted polyenes and polyynes often have high molecular polarizabilities, but their thermal and chemical stability are low. Although incorporation of benzene rings into the push−pull polyenes such as substituted stilbene can enhance their thermal and chemical stability,[44] this decreases or saturates molecular polarizabilities. The reduction or saturation of molecular polarizabilities may result from the aromatic delocalization energy of the benzene ring. To overcome the above shortcoming, one may replace the benzene rings with easily delocalizable five-membered heteroaromatic rings.[45−47] Much work[48−58] has shown that five-membered heteroaromatic stilbenes have higher linear and nonlinear optical polarizabilities than the corresponding aryl analogues. These investigations on the push−pull heteroaromatic stilbenes presented some significant results: (i) the increment of the electron density in the conjugated linker between the donor and acceptor ends can give rise to large hyperpolarizability;[55] (ii) replacing one of the aryl rings of stilbene with a heteroaromatic ring typically has a different effect on the donor versus acceptor end;[55,57] (iii) the electron-rich or electron-poor nature of the five-membered aromatic heteroring can affect the strength of the donor or

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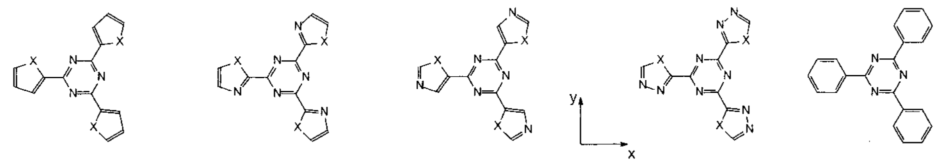
CHART 1



Ia: X=S
Ib: X=O
Ic: X=NH

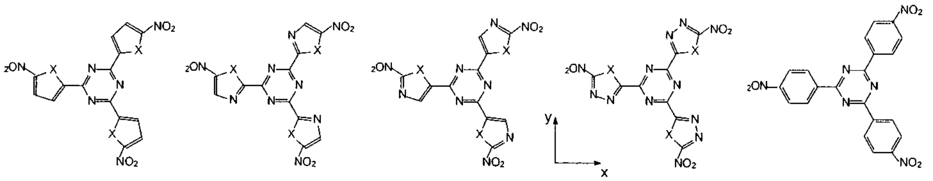
Id: X=S
Ie: X=O
If: X=NH

Ig: X=S
Ih: X=O
Ii: X=NH

Ij: X=S
Ik: X=O
Il: X=NH

Im

CHART 2



IIa: X=S
IIb: X=O
IIc: X=NH

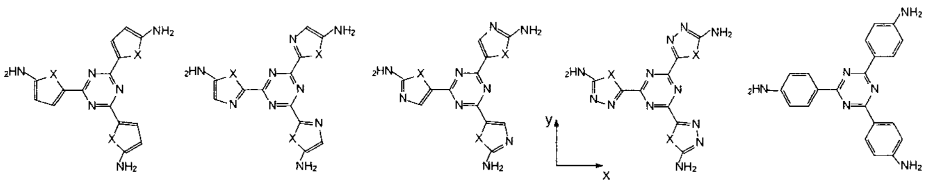
IId: X=S
IIe: X=O
IIf: X=NH

IIg: X=S
IIh: X=O
IIi: X=NH

IIj: X=S
IIk: X=O
IIl: X=NH

IIm

CHART 3



IIIa: X=S
IIIb: X=O
IIIc: X=NH

IIId: X=S
IIIe: X=O
IIIf: X=NH

IIIg: X=S
IIIh: X=O
IIIi: X=NH

IIIj: X=S
IIIk: X=O
IIIl: X=NH

IIIm

acceptor through inductive effects;[55,57] and (iv) because of the inherent dipolar nature of thiazole, the relative orientation of the thiazole ring in the substituted stilbene dramatically influences the hyperpolarizability.[58] Despite the growing interest in the five-membered heteroaromatic-containing NLO molecules, a detailed study of the structure−property relationships for octupolar molecules containing five-membered aromatic heterorings is lacking.

Recently, Ray and Das[31] have shown that the symmetrically substituted triazines have larger first hyperpolarizabilities than the corresponding benzene analogues. In this paper, we report a systematic study of the first hyperpolarizabilities of a series of octupolar triazines containing a wide variety of five-membered aromatic heterorings by using ab initio molecular orbital method. Our main purpose here is to investigate the important role of aromatic heterorings in the design of efficient octupolar NLO molecules and discuss the differences of that between the octupolar and dipolar systems.

The computational method is summarized in section 2. In section 3, we first investigate the first hyperpolarizabilities β of a series of octupolar substituted triazines (Ia $\sim$ Im) shown in Chart 1 then present how the substitution of donor or acceptor groups affect the β of the octupolar triazines (Ia$\sim$Im) illustrated in Charts 2 (IIa$\sim$IIm) and 3 (IIIa$\sim$IIIm), and finally the electron correlation dependences of β for the octupolar triazines (Ia$\sim$Im) are explored. The summary is formulated in section 4.

2. Computational Method

The molecular structures in Charts 1−3 are fully and partially optimized at the restricted Hartree−Fock (RHF) ab initio level with the 6-31G basis set in the Gaussian 94 program.[59] The tensor components of the static first hyperpolarizability are analytically calculated by using the coupled perturbed Hartree−Fock (CPHF) method.[60,61] The electron correlation effects are evaluated in the framework of the second-order Møller−Plesset (MP2) perturbation theory by the finite field (FF) method[62] employing an energy expansion. The total energy E of the molecule under the influence of a static external electric field F can be written as a Taylor series expansion of the field:

$$E(F) = E(0) - \mu_i F_i - \alpha_{ij} F_i F_j/2 - \beta_{ijk} F_i F_j F_k/6 - ... \quad (1)$$

where $E(0)$ and μ_i are the energy and the dipole moment of the molecule in the absence of F, respectively. α_{ij} and β_{ijk} are the tensor components of the static electric dipole polarizability and first hyperpolarizability, respectively. The calculations for the NLO properties using the 6-31G basis set have been performed using the HONDO 95.6 electronic structure package.[63] The geometries used for the electron correlation calculations are planar optimized structures at the RHF level with 6-31G.

Zyss et al.[22−24,29] have developed and discussed the tensorial nature of the first hyperpolarizability for octupolar molecules. Within this framework, the first hyperpolarizability tensor can be decomposed into two components $\beta_{J=1}$ and $\beta_{J=3}$, the dipolar and octupolar contributions:

$$\beta = \beta_{J=1} \oplus \beta_{J=3} \quad (2)$$

$$||\beta||^2 = ||\beta_{J=1}||^2 + ||\beta_{J=3}||^2 \quad (3)$$

To decompose the β tensor attached to a planar tensor in irreducible components, two schemes leading to different results

TABLE 1: First Hyperpolarizabilities and Their Tensor Elements of Fully and Limitedly Optimized Geometries of Octupolar Heteroaromatic-Substituted Triazines I Calculated by the CPHF Method Using the 6-31G Basis Set[a]

	full geometry optimization					limited geometry optimization in the (*X*,*Y*) plane				
molecules	β_{xxx}	β_{xyy}	β_{yyy}	β_{yxx}	$\|\|\beta\|\|$	β_{xxx}	β_{xyy}	β_{yyy}	β_{yxx}	$\|\|\beta\|\|$
Ia	8.0731	−8.0732	0.7121	−0.7121	16.209	3.8427	−3.8432	7.1357	−7.1353	16.209
Ib	−8.7912	8.7912	3.2150	−3.2150	18.721	9.3526	−9.3527	0.1837	−0.1837	18.709
Ic	10.525	−10.525	8.6394	−8.6394	27.232	−13.244	13.245	3.1237	−3.1263	27.217
Id	6.4055	−6.4055	0.6284	−0.6284	12.873	6.3349	−6.3370	1.2265	−1.2244	12.908
Ie	−3.4638	3.4638	6.0732	−6.0731	13.983	−5.5932	5.5941	4.1994	−4.1928	13.984
If	−5.6424	5.6423	10.166	−10.166	23.253	10.971	−10.974	3.8408	−3.8418	23.249
Ig	5.6351	−5.6351	−1.7512	1.7512	11.802	4.0950	−4.0959	4.2586	−4.2582	11.817
Ih	−10.096	10.096	7.3526	−7.3526	14.868	3.8750	−3.8744	6.3496	−6.3490	14.876
Ii	−5.5731	5.5731	8.8964	−8.8964	20.996	−7.1848	7.1850	7.6521	−7.6522	20.993
Ij	0.6926	−0.6926	3.4360	−3.4360	7.0102	−1.8268	1.8269	2.9930	−2.9928	7.0127
Ik	2.4414	−2.4415	3.5870	−3.5870	8.6780	4.3336	−4.3330	−2.1472	2.1337	8.6768
Il	2.5872	−2.5872	6.5379	−6.5379	14.062	−0.9845	0.9846	6.9460	−6.9662	14.070
Im	5.5305	−5.5309	4.4884	−4.4880	14.245	−2.4088	2.4092	6.7027	−6.7020	14.244

[a] All of the values are given in 10^{-30} esu.

may be followed. The following expressions may be applicable for the case of a 2-D planar system with no further symmetric assumptions:

$$||\beta^{2D}_{J=1}||^2 = 3/4[(\beta_{XXX} + \beta_{XYY})^2 + (\beta_{YYY} + \beta_{YXX})^2] \quad (4)$$

$$||\beta^{2D}_{J=3}||^2 = 1/4[(\beta_{XXX} - 3\beta_{XYY})^2 + (\beta_{YYY} - 3\beta_{YXX})^2] \quad (5)$$

whereas for the case of a 3-D system, the following relationships are obtained:

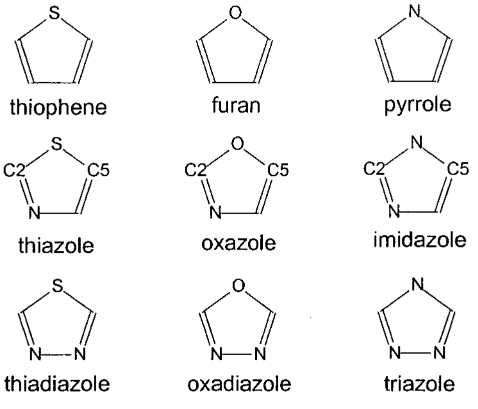
$$||\beta^{3D}_{J=1}||^2 = 3/5[(\beta_{XXX} + \beta_{XYY})^2 + (\beta_{YYY} + \beta_{YXX})^2] \quad (6)$$

$$||\beta^{3D}_{J=3}||^2 = 2/5(\beta^2_{XXX} + \beta^2_{YYY} + 6\beta^2_{YXX} + 6\beta^2_{XYY} - 3\beta_{YXX}\beta_{YYY} - 3\beta_{XYY}\beta_{XXX}) \quad (7)$$

The 2-D approach constrains the hyperpolarizabilities to lie exclusively in the (*X*,*Y*) molecular plane, whereas in the 3-D approach, planar molecules are embedded in 3-D space with *Z* containing tensorial products sustaining out-of-plane polarizabilities.

3. Results and Discussion

3.1. First Hyperpolarizabilities of Heteroring-Substituted *sym*-Triazines. The molecules (Ia∼Im) shown in Chart 1 are derived from octupolar triazines substituted by a variety of five-membered aromatic heterorings. The benzene-substituted compound is listed for comparison. Table 1 presents the calculated values of the hyperpolarizabilities and their tensor elements for both fully optimized and planar structures of these molecules.



Molecular structures of aromatic heterorings

Geometric effects have been considered in a set of calculations by using fully optimized and planar structures. The β values for planar geometries are evaluated by using eqs 3−5, and that for fully optimized geometries are obtained by employing eqs 3, 6, and 7. It is seen from Table 1 that the effects of the deviations from the planarity on β are very small. Therefore one may think that the octupolar molecules present planar structures and the factors that affect β may be electronic in nature. These tensor components for optimized and planar structures approximately have the following relationships:

$$\left.\begin{aligned}\beta_{xxx} &= -\beta_{xyy}\\ \beta_{yyy} &= -\beta_{yxx}\end{aligned}\right\} \quad (8)$$

As a consequence, the octupolar molecules (Ia∼Im) may present an isotropic β tensor.

Andraud et al.[42] have pointed out that the charge transfer in the polyenoctupoles does occur not only from the peripheral donors toward the central phenyl ring but also to some extent between the different branches of the molecule. Therefore, we should not only consider β tensor of an octupole from that of its dipolar components but also evaluate the specific contribution of the octupolar symmetry to β. An additive model,[42] generally applicable to multipolar systems, is introduced to evidence specific contributions to β arising from the multipolar symmetry. In this framework, the β tensor is dissected into two separate tensor representation, an additive term β^{A} representing the tensorial sum of the dipole units' β and a term β^{I} representing interactions between the dipole units constituting the multipole:

$$\beta = \beta^{A} \oplus \beta^{I} \quad (9)$$

$$\beta^{A} = \sum_i \beta^{(i)} \quad (10)$$

The tensor $\beta^{(i)}$ of each dipole unit may be decomposed into dipolar and octupolar components $\beta^{(i)}_{J=1}$ and $\beta^{(i)}_{J=3}$, and then eq 10 becomes eq 11:

$$\beta^{A} = \beta^{A}_{J=1} \oplus \beta^{A}_{J=3} = \sum_i \beta^{(i)}_{J=1} \oplus \sum_i \beta^{(i)}_{J=3} \quad (11)$$

The octupolar molecules may be defined as three independent 1-D units displayed in Figure 1; thus, eq 11 can be rewritten as eq 12 where $\beta^{1D}_{J=1}$ and $\beta^{1D}_{J=3}$ represent the dipolar and octupolar contributions of the 1-D unit, respectively, and $\theta = 120°$:[23]

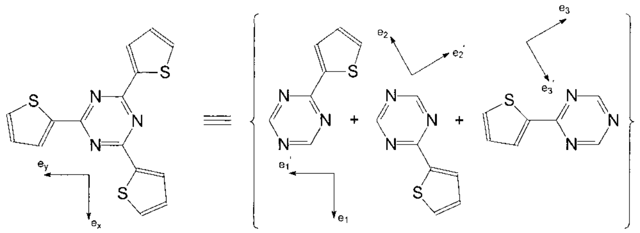


Figure 1. Definition of the independent units constituting the octupolar molecule Ia. The same is true of other octupolar molecules Ib−Im, II, and III.

$$\beta^{A} = (\beta^{1D}_{J=1} \oplus \beta^{1D}_{J=3})(1 + \cos 3\theta + \cos 6\theta) = 3(\beta^{1D}_{J=1} \oplus \beta^{1D}_{J=3}) \qquad (12)$$

For the case of a 2-D planar system, the norm of a tensor β and its dipolar and octupolar components $\beta_{J=1}$ and $\beta_{J=3}$ can be expressed as eqs 3, 4, and 5, respectively, with no further symmetric assumptions. Thus the norm of β^{A} can be defined by eq 13:

$$||\beta^{A}||^2 = 3(\beta^{1D}_{xxx})^2 + 3(\beta^{1D}_{yyy})^2 + 9(\beta^{1D}_{xyy})^2 + 9(\beta^{1D}_{yxx})^2 \qquad (13)$$

The interaction term β^{I} can now be obtained from the difference between the tensor β and β^{A} according to eq 9, and its norm is expressed by eq 14:

$$||\beta^{I}||^2 = ||\beta||^2 - ||\beta^{A}||^2 = ||\beta^{2D}_{J=1}||^2 + ||\beta^{2D}_{J=3}||^2 - ||\beta^{A}||^2 \qquad (14)$$

According to eqs 13 and 14, the norms of β^{A} and β^{I} are calculated by using the CPHF method with the 6-31G basis set for the planar optimized geometries of the octupolar molecules I, II, and III. The results are displayed in Table 2.

The main results shown in Table 1 are as follows: (i) octupolar pyrrole-substituted triazine (Ic) has a larger β than the corresponding furan analogue (Ib), and yet β of Ib is larger than that of its thiophene analogue (Ia). The same is true of a series of the homologous derivatives (cf. If, Ie, and Id; Ii, Ih, and Ig; Il, Ik, and Ij); (ii) for pyrrole and its derivatives, octupolar triazine containing pyrroles (Ic) display a larger β than the analogues of pyrrole derivatives (If (Ii), Il). This holds for a series of the homologous derivatives (cf. Ib and Ie (Ih), Ik; Ia and Id (Ig), Ij); (iii) the substitution positions of the thiazole, oxazole, and imidazole rings in the octupolar triazines determine their β values (Id vs Ig, Ie vs Ih, If vs Ii); (iv) octupolar benzene-substituted triazine (Im) exhibits a larger β than the corresponding thiazole analogues (Id, Ig, and Ij) as well as Ie, Ik, and Il.

The triazine ring is electron-deficient and may act as an acceptor. Thus, including donors into a triazine should be more favorable for the charge transfer and hence increase the NLO response. For the series of pyrrole, furan, and thiophene, they are all electron-rich systems, and the order in which the electron densities varies is pyrrole > furan > thiophene;[57,58] hence, the β values for the 1-D dipole units of the molecules (Ia−Ic) increase in the following order: Ic > Ib > Ia. These suggestions are supported by the calculated results shown in Table 2. It is also found that the order of $||\beta^{I}||$ is same as that of $||\beta^{A}||$. Therefore, the β values for the molecules (Ia−Ic) vary in the following order: Ic > Ib > Ia. Similar conclusions are also true for the homologous derivatives (cf. If > Ie > Id; II > Ih > Ig; Il > Ik > Ij). In the same way, the order of β increase for octupolar triazines containing pyrrole and its derivatives (cf. Ic > If (Ii) > Il) are attributed to the variation of the electron densities of the heterorings and the multipolar symmetry. The same is also true of a series of the homologous derivatives (cf. Ib > Ie (Ih) > Ik; Ia > Id (Ig) > Ij).

TABLE 2: First Hyperpolarizabilities $||\beta^{A}||$ and $||\beta^{I}||$ for Octupolar Molecules I, II, and III Calculated by the CPHF Method Using the 6-31G Basis Set[a]

	molecules I		molecules II		molecules III	
no.	$\|\|\beta^{A}\|\|$	$\|\|\beta^{I}\|\|$	$\|\|\beta^{A}\|\|$	$\|\|\beta^{I}\|\|$	$\|\|\beta^{A}\|\|$	$\|\|\beta^{I}\|\|$
a	11.612	11.308	6.1154	10.522	33.894	26.578
b	13.897	12.526	10.891	19.569	32.215	18.855
c	20.561	17.833	16.053	28.575	38.720	28.419
d	8.0566	10.084	4.8300	7.9007	29.514	27.217
e	9.4619	10.296	7.7882	14.197	26.869	19.073
f	16.331	16.552	11.970	22.155	35.476	28.310
g	7.6051	9.0439	5.7906	9.0417	23.319	20.848
h	9.6363	11.333	8.9558	16.009	21.944	16.177
i	14.534	15.148	13.378	22.762	28.114	22.256
j	3.8764	5.8439	4.1569	5.5960	16.288	17.335
k	5.0284	7.0711	5.3201	9.7226	13.954	12.507
l	9.0539	10.769	9.9242	13.213	19.932	18.416
m	10.626	9.4855	0.5442	1.0760	32.900	24.652

[a] All of the values are given in 10^{-30} esu.

Thiazole rings have two kinds of different substitution positions in a octupolar triazine: (i) the C2 atoms of thiazoles are adjacent to a triazine ring (cf. Id) and (ii) the C5 atoms of thiazoles are adjacent to a triazine ring (cf. Ig). π-electron densities at carbons C2 and C5 of a thiazole ring are different: the former is electron-poor, acting as an auxiliary acceptor, and the latter is electron-rich, as an auxiliary donor.[58] Thus, attaching thiazoles to an octupolar triazine at C2 (cf. Id) ("matched" case[58]) leads to a larger β for the 1-D dipole units than at C5 (cf. Ig) ("mismatched" case[58]). This agrees with the observations displayed in Table 2. The variation of $||\beta^{I}||$ also presents the same trend; thus, Id presents a larger β value than Ig. Similar situations are found for the imidazole analogues (cf. If vs Ii). The only exception is the oxazole analogues (cf. Ie vs Ih).

3.2. Substitution by Acceptor Groups (NO_2). In this section, we examine effects of acceptor (NO_2) substitution on β of the octupolar triazines shown in Chart 2 (IIa∼IIm). The results are shown in Table 3. Geometric effects have been considered in the same way, and similar conclusions are also drawn.

The leading results displayed in Table 3 are as follows: (i) when acceptor groups (NO_2) are attached to the octupolar molecules I, the β values of the molecules containing thiophene derivatives and benzenes (IIa, IId, IIg, IIj, and IIm) decrease, whereas that of the molecules containing furan and pyrrole derivatives (IIb, IIe, IIh, and IIk and IIc, IIf, IIi, and IIl) increase; (ii) the substitution positions of the thiazole, oxazole, and imidazole rings in the triazines determine their β values (IId vs IIg, IIe vs IIh, IIf vs IIi); (iii) the NO_2-substituted molecules containing pyrrole derivatives (IIc, IIf, IIi, and IIl) have higher β values than the corresponding molecules containing furan and thiophene derivatives (IIb, IIe, IIh, and IIk and IIa, IId, IIg, and IIj); and (iv) the NO_2-substituted molecule containing benzenes (IIm) has the smallest β among these substituted molecules.

Thiophene is an electron-rich system. When acceptor groups (NO_2) are attached to the C5 atoms of thiophenes in the molecule Ia, the donor ability of thiophenes should be reduced and hence lead to a reduction in β for the 1-D dipole units. The results in Table 2 confirm the viewpoint. It is also found that the order of $||\beta^{I}||$ is same as that of $||\beta^{A}||$. Therefore, Ia has a larger β than IIa. Similar conclusions are also true for the homologous derivatives (cf. Id > IId, Ig > IIg, Ij > IIj, Im > IIm). However, for the NO_2-substituted molecules containing furan derivatives, the instance is opposite (cf. IIb > Ib, IIe > Ie, IIh > Ih, IIk > Ik). In Table 2, it can be seen that $||\beta^{A}||$ vary in the following

TABLE 3: First Hyperpolarizabilities and Their Tensor Elements of Fully and Limitedly Optimized Geometries of NO_2-Substituted Octupolar Triazines II Calculated by the CPHF Method Using the 6-31G Basis Set[a]

	full geometry optimization					limited geometry optimization in the (*X*,*Y*) plane				
molecules	β_{xxx}	β_{xyy}	β_{yyy}	β_{yxx}	$\|\|\beta\|\|$	β_{xxx}	β_{xyy}	β_{yyy}	β_{yxx}	$\|\|\beta\|\|$
IIa	−2.1946	2.1924	5.6791	−5.6789	12.175	−5.7378	5.7379	2.0248	−2.0263	12.170
IIb	−7.7009	7.7011	8.1241	−8.1249	22.389	−11.017	11.022	1.9916	−1.9852	22.396
IIc	16.383	−16.383	0.6906	−0.6906	32.794	0.3719	−0.3782	16.386	−16.382	32.775
IId	1.4289	−1.4288	4.4035	−4.4035	9.2591	−3.4564	3.4549	−3.0834	3.0816	9.2602
IIe	2.5353	−2.5344	7.6881	−7.6887	16.191	−1.2452	1.2497	7.9961	−8.0009	16.193
IIf	−11.285	11.285	5.5771	−5.5767	25.175	−9.1675	9.1697	8.6267	−8.6298	25.182
IIg	−3.1863	3.1865	4.3160	−4.3158	10.729	−5.3628	5.3653	−0.2061	0.2030	10.737
IIh	−2.4449	2.4467	−8.8332	8.8345	18.333	−4.4720	4.4758	−8.0074	8.0059	18.344
IIi	10.025	−10.025	−8.5882	8.5882	26.401	−13.005	13.006	−2.2639	2.2629	26.403
IIj	−3.2696	3.2696	−1.1989	1.1988	6.9649	−2.2971	2.2972	−2.6212	2.6215	6.9711
IIk	−5.0279	5.0280	2.3252	−2.3253	11.079	−1.3719	1.3711	5.3690	−5.3692	11.083
IIl	−2.6866	2.6866	7.7970	−7.7967	16.493	−3.4947	3.4960	7.4873	−7.4862	16.525
IIm	−0.2784	0.2807	0.2534	−0.2510	0.7530	0.2478	−0.2455	0.2768	−0.2772	0.7412

[a] All of the values are given in 10^{-30} esu.

TABLE 4: First Hyperpolarizabilities and Their Tensor Elements of Fully and Limitedly Optimized Geometries of NH_2-Substituted Octupolar Triazines III Calculated by the CPHF Method Using the 6-31G Basis Set[a]

	full geometry optimization					limited geometry optimization in (X, Y) plane				
molecules	β_{xxx}	β_{xyy}	β_{yyy}	β_{yxx}	$\|\|\beta\|\|$	β_{xxx}	β_{xyy}	β_{yyy}	β_{yxx}	$\|\|\beta\|\|$
IIIa	10.217	−10.217	18.948	−18.948	43.055	18.831	−18.833	10.448	−10.447	43.072
IIIb	3.1837	−3.1837	18.383	−18.383	37.314	−6.1409	6.1427	17.625	−17.623	37.327
IIIc	−23.976	23.976	−1.3219	1.3220	48.024	20.138	−20.136	13.085	−13.086	48.030
IIId	19.663	−19.663	3.8308	−3.8306	40.065	20.001	−20.005	−1.6734	1.6712	40.148
IIIe	−13.739	13.739	9.1064	−9.1064	32.966	14.822	−14.824	7.1921	−7.1880	32.950
IIIf	4.2099	−4.2102	22.295	−22.295	45.379	22.154	−22.154	4.9182	−4.9220	45.388
IIIg	−15.306	15.306	3.1195	−3.1195	31.242	0.9274	−0.9280	15.613	−15.612	31.280
IIIh	−4.0716	4.0716	12.999	−12.999	27.244	10.081	−10.081	9.1746	−9.1750	27.262
IIIi	−10.835	10.835	14.270	−14.270	35.835	−6.6508	6.6533	16.647	−16.650	35.858
IIIj	3.1400	−3.1400	11.471	−11.471	23.785	−0.9246	0.9244	11.855	−11.859	23.787
IIIk	−0.3641	0.3642	9.3667	−9.3667	18.748	−8.4578	8.4555	4.0363	−4.0345	18.739
IIIl	−13.173	13.173	3.3067	−3.3068	27.164	6.2540	−6.2577	12.041	−12.040	27.137
IIIm	−14.931	14.931	14.130	−14.129	41.114	−13.283	13.284	15.687	−15.687	41.111

[a] All of the values are given in 10^{-30} esu.

order, Ib > IIb, and $||\beta^{I}||$ vary in the opposite order. Moreover, the effect of $||\beta^{I}||$ is larger than that of $||\beta^{A}||$; thus IIb has a higher β than Ib. An analogous explanation may be applied to IIe vs Ie, IIh vs Ih, and IIk vs Ik.

Attaching acceptor groups (NO_2) to the C2 atoms of the thiazole rings in IIg should augment the acceptor ability of NO_2 and increase β for the 1-D dipole units. Similarly, appending NO_2 to the C5 atoms of the thiazole rings in IId should have the opposite effect. Actually, both $||\beta^{A}||$ and $||\beta^{I}||$ of IIg are higher than those of IId (see Table 2). The molecule IIg is hence predicted to display a higher β than IId. The same is true of the oxazole and imidazole analogues (cf. IIh vs IIe and IIi vs IIf).

Pyrrole derivatives have higher electron densities than furan and thiophene derivatives[57] and may more effectively afford electrons to the conjugated segment.[57] It can be seen from Table 2 that the molecules containing pyrrole derivatives have larger $||\beta^{A}||$ and $||\beta^{I}||$ than the corresponding molecules containing furan and thiophene derivatives. Thus, the molecules (IIc, IIf, IIi, and IIl) present higher β than the corresponding molecules (IIb, IIe, IIh, and IIk and IIa, IId, IIg, and IIj).

3.3. Substitution by Donor Groups (NH_2). In this section, we examine effects of donor (NH_2) substitution on β of the octupolar triazines shown in Chart 3 (IIIa∼IIIm). The results are shown in Table 4. Geometric effects have been considered in the same way, and similar conclusions are also drawn.

The primary results presented in Table 4 are as follows: (i) the NH_2-substituted octupolar molecules have higher β values than the corresponding unsubstituted and NO_2-substituted analogues I and II; (ii) the substitution positions of the thiazole, oxazole, and imidazole rings in the octupolar triazines determine their β values (IIId vs IIIg, IIIe vs IIIh, IIIf vs IIIi); (iii) the NH_2-substituted molecules containing pyrrole derivatives (IIIc, IIIf, IIIi, and IIIl) have higher β values than the corresponding molecules containing thiophene derivatives (IIIa, IIId, IIIg, and IIIj), and the latter series have larger β values than the corresponding molecules containing furan derivatives (IIIb, IIIe, IIIh, and IIIk); (iv) the NH_2-substituted octupolar molecule containing benzenes (IIIm) has a fairly large β value among the octupolar molecules (III).

The variation trends of β for the NH_2-substituted octupolar molecules can be rationalized by applying the same elements obtained from the above sections. Appending donor groups (NH_2) to the C5 atoms of heterorings in the octupolar molecules (III) should enhance the donor ability of heterorings. This will increase the transfer of electron densities from the peripheral heterorings toward the central triazine ring and lead to the increases of the NLO responses. This is in accord with the variation behavior of $||\beta^{A}||$ displayed in Table 2. The results in Table 2 also show that III have higher $||\beta^{I}||$ than I and II. The octupolar molecules III hence display relatively larger β values than the corresponding I and II. Attaching donor groups (NH_2) to the C5 atoms of a series of thiazole derivatives can augment the donor ability of NH_2[58] and hence increase β. Similarly, appending NH_2 to the C2 atoms should have the opposite effect. This agrees with the results in Table 2.

The results here present that incorporating the donor groups (NH_2) into the octupolar molecules not only enhances the norm $||\beta^{A}||$ of additive term but only the norm $||\beta^{I}||$ of the interaction

TABLE 5: First Hyperpolarizabilities and Their Tensor Elements of Planar Optimized Geometries of Octupolar Heteroaromatic-Substituted Triazines I Calculated by the SVD Fit to the RHF and MP2 Energy Expansions Using the 6-31G Basis Set[a]

	CPHF	RHF/FF	MP2/FF				
molecules	$\|\|\beta\|\|$	$\|\|\beta\|\|$	β_{xxx}	β_{xyy}	β_{yyy}	β_{yxx}	$\|\|\beta\|\|$
Ia	16.209	16.144	5.1136	−5.1139	9.3797	−9.3808	21.367
Ib	18.709	18.697	11.345	−11.344	0.1923	−0.1947	22.692
Ic	27.217	27.241	−17.752	17.752	3.7060	−3.7111	36.271
Id	12.908	12.793	7.9257	−7.9298	2.6753	−2.6631	16.735
Ie	13.984	13.905	−5.8675	5.8700	5.0415	−5.0323	15.466
If	23.249	23.222	13.416	−13.418	5.2322	−5.2334	28.803
Ig	11.817	11.791	4.3834	−4.3862	4.9583	−4.9590	13.240
Ih	14.876	14.865	4.1456	−4.1429	7.1257	−7.1244	16.484
Ii	20.993	21.002	−9.6739	9.6762	8.7818	−8.7797	26.131
Ij	7.0127	6.9759	−2.9765	2.9758	1.9989	−1.9995	7.1704
Ik	8.6768	8.6476	3.9065	−3.9057	0.5236	−0.5243	7.8817
Il	14.070	14.036	−2.3151	2.3141	7.5822	−7.5869	15.862
Im	14.244	14.163	−2.9573	2.9539	8.2150	−8.2172	17.464

[a] All of the values are given in 10^{-30} esu.

term, compared with the unsubtitution and NO_2 substitution. This suggests that the charge-transfer character from the ambient donors toward the central triazine ring and between the different branches of the molecules increase by introducing the donor groups (NH_2) relative to unsubtitution and NO_2 substitution. These observations are fully consistent with those previously studied by others.[39,43]

3.4. Electron Correlation Effects. In this section, our main concern is to investigate whether the variation trends of β for the molecules I at the CPHF level shown in Table 1 are well reproduced by the correlation calculated results as well as electron correlation effects. For the NO_2- and NH_2-substituted octupolar molecules, electron correlations are not considered because the computer times are very expensive. That we select the octupolar molecules I as an example to explore electron correlations thus appears to be a good compromise between computation efficiency and accuracy. The hyperpolarizabilities and their tensor elements of the molecules I are calculated by the singular value decomposition (SVD) fit[65] to the RHF and MP2 energy expansions using 6-31G basis set. The results are listed in Table 5. For the sake of comparison, we also present the corresponding values evaluated by the CPHF analytical approach with the same basis set. Provided the numerical procedure employed is valid, this method must give results equivalent to those obtained by the RHF/FF approach.

It is seen from Table 5 that the RHF/FF β values are indeed found to be in full agreement with the CPHF results. This shows that the numerical accuracy of the FF method is correct. These tensor components of β for Ia∼Im approximately have the eq 8. Thus, the MP2/FF results also validate that these octupolar molecules may present an isotropic β tensor. In addition, the variation trends of β for Ia∼Im shown in Table 1 are similarly confirmed by the correlation calculated results here.

As expected, the impact of electron correlation is very important on β. For the molecules containing thiophene, thiazole, and pyrrole rings (Ia, Ic, and Id), β values are increased by over 30%, compared with the HF results. We also observe an increase in β for the molecules Ib, If, Ii, and Im by about 22%. For other molecules, the correlation effects are relatively small. This is fully in accord with other works.[66−70]

4. Summary

In this work, we have performed ab initio calculations to study the hyperpolarizabilities β of a series of octupolar triazines (Ia−Im) in the frame of a tensorial formalism. Effects of donor or acceptor substitution and electron correlation on Ia−Im have also been explored. Geometric effects have been considered in a set of calculations by using fully optimized and planar structures.

It is found that the octupolar molecules present planar structures. Octupolar triazines containing pyrrole derivatives have larger β values than the corresponding analogues containing furan and thiophene derivatives. Because of the unsymmetrical nature of thiazole, oxazole, and imidazole, the substitution positions of these heterorings in the octupolar triazines determine the magnitudes of their β values. NO_2 or NH_2 substitution strongly affects β values of octupolar benzene-substituted triazine.

When the acceptor groups (NO_2) are incorporated into the octupolar molecules (I), some of the laws describing the NLO properties of the 1-D dipolar systems cannot be applied to predict β variations. An additive model is introduced to evidence specific contributions to β arising from the multipolar symmetry. In this framework, the β tensor of a multipolar system is dissected into two separate tensor representation, an additive term β^A representing the tensorial sum of the dipole units' β and a term β^I representing interactions between the dipole units constituting the multipole. For the molecules I containing furan and pyrrole derivatives, the effects of $||\beta^I||$ exceed those of $||\beta^A||$ and thereby determine the magnitudes of β (cf. IIb vs Ib, IIe vs Ie, IIh vs Ih, IIk vs Ik).

We have shown that incorporating the donor groups (NH_2) into the molecules (I) not only enhances $||\beta^A||$ but also $||\beta^I||$, compared with unsubstitution and NO_2 substitution. This suggests that the charge-transfer character from the ambient donors toward the central triazine ring and between the different branches of the molecules increase by introducing the donor groups.

This work also presents that the variation trends of β for Ia∼Im at the CPHF level are well confirmed by the correlation results and the electron correlation has a large influence on the magnitude of β.

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