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An Ab Initio Study on the First- and Third-Order Polarizabilities of the Octupolar Heteroaromatic-Substituted Triazines

Weihua Zhu and Guo-shi Wu*

Department of Chemistry, Tsinghua University, Beijing 100084, China

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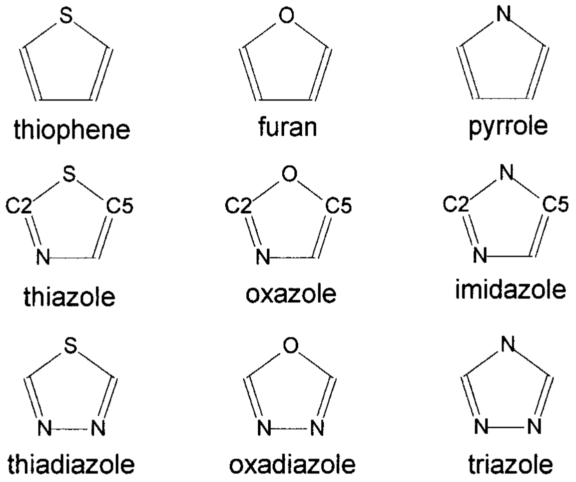
The first- and third-order polarizabilities of a series of octupolar heteroaromatic-substituted triazines have been investigated by using the ab initio coupled perturbed Hartree−Fock (CPHF) method. Effects of donor or acceptor substitution have also been considered. Finally, we have explored the impact of electron correlation on the molecular polarizabilities of these octupolar triazines at the Møller−Plesset second-order perturbation (MP2) theory level. The results show that octupolar triazines containing thiophene derivatives have larger first-order polarizabilities than the corresponding analogues containing furan and pyrrole derivatives, and yet octupolar triazines containing pyrrole derivatives exhibit larger third-order polarizabilities than other ones. Attaching acceptor groups (NO_2) to these octupolar molecules results in an increase of the first- and third-order polarizability values of NO_2-substituted octupolar molecules in comparison with the corresponding unsubstitution. Similar conclusions hold for the NH_2-substituted situation. The effects of acceptor substitution on the first-order polarizabilities exceed these of donor substitution; nevertheless, for the third-order polarizabilities, the situation reverses. These observations are supported by the predictions based on the valence-bond three-charge-transfer model. With the introduction of the electron correlation correction, the first-order polarizabilities do not increase much, whereas the third-order polarizabilities significantly increase.

1. Introduction

Despite the fact that organic pull−push π-conjugated molecules exhibiting large nonlinear optical (NLO) responses have been extensively studied,[1−14] 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. These problems were thought to be a serious obstacle in applying this kind of NLO molecules for the purpose of photonic devices. Octupolar molecules that have been recognized as potentially useful for NLO applications can circumvent the aforementioned disadvantages.[15] Recently, much more attention has been paid to the NLO responses of the octupolar molecules.[16−30]

NLO applications require thermally robust materials exhibiting large optical nonlinearities. In general, incorporation of benzene and five-numbered heteroaromatic rings into the typical push−pull π-systems such as substituted stilbene can increase their thermal and chemical stability,[31] Much work[32−42] has shown that five-numbered heteroaromatic stilbenes have higher second-order polarizabilities than the corresponding aryl analogues. Lately, several studies[22,27,29,30] have reported the second-order polarizabilities of octupolar systems containing benzene and aromatic heterorings. Despite intensive investigations, the evaluation of the third-order polarizability in octupolar molecules is still an ongoing problem. Therefore, it is necessary to investigate the important role of aromatic heterorings in the design of efficient octupolar molecules for the third-order NLO applications.

In this paper, we report a systematic study of the first- and third-order polarizabilities of a series of octupolar triazines containing a wide variety of five-numbered aromatic heterorings by using ab initio molecular orbital method.



The octupolar systems we consider are displayed in Figure 1. The objectives of this work are the following: (i) to analyze the effects of aromatic heterorings on the first- and third-order polarizabilities (α and γ) of octupolar sym-substitued triazines (Ia−Im); (ii) to display how the substitution of donor groups affects α and γ of the octupolar triazines (IIa−IIm); (iii) to exhibit how the substitution of acceptor groups affects α and γ of the octupolar triazines (IIIa−IIIm), (iv) to consider the impact of electron correlation on α and γ of the octupolar triazines (Ia−Im).

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* Corresponding author.

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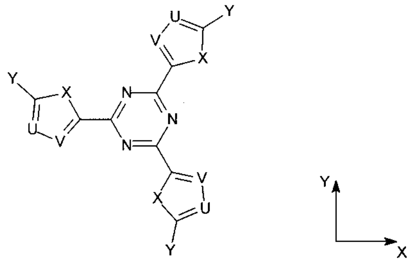

	U=CH V=CH	U=CH V=N	U=N V=CH	U=N V=N	U=CH V=CH
Y=H	Ia: X=S Ib: X=O Ic: X=NH	Id: X=S Ie: X=O If: X=NH	Ig: X=S Ih: X=O Ii: X=NH	Ij: X=S Ik: X=O Il: X=NH	Im: X=HC=CH
Y=NO_2	IIa: X=S IIb: X=O IIc: X=NH	IId: X=S IIe: X=O IIf: X=NH	IIg: X=S IIh: X=O IIi: X=NH	IIj: X=S IIk: X=O IIl: X=NH	IIm: X=HC=CH
Y=NH_2	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: X=HC=CH

Figure 1. Molecular structures of heteroaromatic-substituted *sym*-triazines (Ia−Im), NO_2-substituted octupolar triazines (IIa−IIm), and NH_2-substituted octupolar triazines (IIIa−IIIm).

2. Computational Details

Ab initio molecular orbital calculations of NLO responses provide useful information on the capacity of NLO materials at the molecular level. Almost all ab initio studies of molecular polarizabilities for large systems have been made only at the Hartree−Fock level,[12,27b,30a] and only a few studies for small molecules are devoted to the electron correlation effects on NLO properties,[30b,43] due mainly to their excessive computation time. The molecular structures in Figure 1 are fully optimized at the restricted Hartree−Fock (RHF) ab initio level with the 6-31G basis set in the Gaussian 94 program.[44] The individual components of the static first- and third-order polarizability are analytically calculated by using the coupled perturbed Hartree−Fock (CPHF) method.[45,46] The electron correlation effects are evaluated in the framework of the second-order Møller−Plesset (MP2) perturbation theory by the finite field (FF) method[47] employing an energy expansion. The finite electric field values range from 10^{-2} to 10^{-3} atomic units.[47] 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:

$$E(F) = E(0) - \mu_i F_i - \alpha_{ij} F_i F_j/2 - \beta_{ijk} F_i F_j F_k/6 - \gamma_{ijkl} F_i F_j F_k F_l/24 - \cdots \quad (1)$$

where $E(0)$ and μ_i are the energy and the dipole moment of the molecule in the absence of F, respectively. α_{ij}, β_{ijk}, and γ_{ijkl} are the tensor components of the static first-, second-, and third-order polarizability, respectively. The calculations for the NLO properties using the 6-31G basis set have been performed using the HONDO 95.6 electronic structure package.[48] Although the influence of the quality of the basis set is very important on the third-order polarizabilities,[49,50] the size of the molecules studied here quite obviously excludes the possibility of using a larger basis set. Therefore, we expect to provide only a quality picture. The geometries used for the electron correlation calculations are fully optimized structures at the RHF level with 6-31G.

The calculated tensors are transformed to mean scalar values by applying

$$\alpha = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3 \quad (2)$$

$$\gamma = (\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + 2\gamma_{xxyy} + 2\gamma_{xxzz} + 2\gamma_{yyzz})/5 \quad (3)$$

TABLE 1: The First-Order Polarizabilities and Their Individual Components of Heteroaromatic-Substituted Octupolar Triazines I Calculated by the CPHF Method Using 6-31G Basis Set[a]

molecules	α_{xx}	α_{yy}	α_{zz}	α
Ia	41.7260	41.7261	10.7166	31.3896
Ib	34.4066	34.4066	8.2147	25.6760
Ic	38.0135	38.0136	8.5010	28.1760
Id	38.0581	38.0581	10.6611	28.9257
Ie	30.3188	30.3188	8.1343	22.9240
If	33.7444	33.7444	8.3800	25.2896
Ig	38.0854	38.0854	10.5747	28.9152
Ih	30.8404	30.8404	8.1217	23.2675
Ii	33.8529	33.8529	8.3805	25.3621
Ij	34.4247	34.4247	10.3514	26.4002
Ik	27.0389	27.0389	7.8313	20.6363
Il	29.5724	29.5724	8.0812	22.4087
Im	44.3311	44.3299	9.6728	32.7779

[a] All the values are given in Å^3.

TABLE 2: The Third-Order Polarizabilities and Their Individual Components of Heteroaromatic-Substituted Octupolar Triazines I Calculated by the CPHF Method Using 6-31G Basis Set[a]

molecules	γ_{xxxx}	γ_{yyyy}	γ_{zzzz}	γ_{xxyy}	γ_{xxzz}	γ_{yyzz}	γ
Ia	51.9175	51.9172	0.1881	17.3056	0.2166	0.2166	27.9001
Ib	50.7236	50.7234	0.0896	16.9078	0.2134	0.2134	27.2412
Ic	63.7287	63.7288	0.0832	21.2439	0.1934	0.1934	34.1600
Id	46.9950	46.9543	0.1798	15.6513	0.2034	0.2034	25.2410
Ie	42.4157	42.4163	0.0850	14.1387	0.2068	0.2068	22.8044
If	60.5420	60.5418	0.0838	20.1806	0.1628	0.1628	32.4360
Ig	37.6120	37.6120	0.1971	12.5374	0.2520	0.2520	20.3008
Ih	35.2725	35.2723	0.1111	11.7575	0.2426	0.2426	19.0283
Ii	44.2926	44.3935	0.1080	14.7642	0.2365	0.2365	23.8335
Ij	28.2080	28.2081	0.1625	9.4027	0.2207	0.2207	15.2533
Ik	24.2632	24.2632	0.0643	8.0878	0.2092	0.2092	13.1206
Il	34.9707	34.9702	0.0584	11.3538	0.1985	0.1985	18.8214
Im	47.7493	47.7465	0.0913	15.9162	0.3191	0.3191	25.9392

[a] All the values are given in 10^{-36} esu.

3. Results and Discussion

3.1. First- and Third-Order Polarizabilities of Heteroring-Substituted *sym*-Triazines. The molecules (Ia−Im) shown in Figure 1 are derived from octupolar triazines substituted by a variety of five-numbered aromatic heterorings. The benzene-substituted compound is listed for comparison. Tables 1 and 2 list the calculated values of the first- and third-order polarizabilities and their individual elements. These tensor components approximately have the following relationships:[27b]

$$\begin{gathered}\alpha_{xx} = \alpha_{yy} \\ \gamma_{xxxx} = \gamma_{yyyy} = 3\gamma_{xxyy} \\ \gamma_{xxzz} = \gamma_{yyzz}\end{gathered} \quad (4)$$

All other tensor elements can be estimated by using the relationships among these tensor components

$$\begin{gathered}\gamma_{xxyy} = \gamma_{yyxx} = \gamma_{xyxy} = \gamma_{xyyx} = \gamma_{yxyx} = \gamma_{yxxy} \\ \gamma_{xxzz} = \gamma_{zzxx} = \gamma_{xzxz} = \gamma_{xzzx} = \gamma_{zxzx} = \gamma_{zxxz} \\ \gamma_{yyzz} = \gamma_{zzyy} = \gamma_{yzyz} = \gamma_{yzzy} = \gamma_{zyzy} = \gamma_{zyyz}\end{gathered} \quad (5)$$

The leading results shown in Table 1 are (i) octupolar thiophene-substituted triazine (Ia) has a larger α than the corresponding pyrrole analogue (Ic), and yet α of Ic are larger than that of its furan analogue (Ib). The same is true of a series of the homologous derivatives (cf. Id, If, Ie; Ig, Ii, Ih; Ij, Il, Ik); (ii) for thiophene and its derivatives, octupolar triazine containing thiophenes (Ia) displays a larger α than the analogues of thiophene derivatives (Id (Ig), Ij). This holds for a series of the homologous derivatives (cf. Ib and Ie (Ih), Ik; Ic and If (Ii), Il); (iii) the substitution positions of the thiazole, oxazole, and imidazole rings in the octupolar triazines have a little effect on their α values (Id vs Ig, Ie vs Ih, If vs Ii); (iv) octupolar benzene-substituted triazine (Im) exhibits the largest α values among these octupolar heteroring-substituted triazines.

An important localization of the π-charge on the oxygen atom of furan, nitrogen atom of pyrrole, and sulfur atom of thiophene leads to a π-charge deficit on these aromatic heterorings. Therefore, the heteroatoms play the role of π-electron acceptors and anchor part of the π-electron cloud, which limit the capacity of π-charge delocalization. For the series of furan, pyrrole, and thiophene, since the electronegativities of oxygen, nitrogen, and sulfur decrease in the following order: O > N > S,[51] their order in which the capacity of π-charge delocalization varies is thiophene > pyrrole > furan. Thus, the α values for the octupolar molecules (Ia−Ic) vary in the following order: Ia > Ic > Ib. Similar conclusions are also true for the homologous derivatives (cf. Id > If > Ie; Ig > Ii > Ih; Ij > Il > Ik). In the same way, the order of α increase for octupolar triazines containing thiophene and its derivatives (cf. Ia > Id (Ig) > Ij) is attributed to the variation in the heteroatom's numbers of the heterorings and the multipolar symmetry. The same is also true of a series of the homologous derivatives (cf. Ib > Ie (Ih) > Ik; Ic > If (Ii) > Il).

The carbon atoms of benzene ring have smaller electronegativities than the heteroatoms of the five-numbered aromatic heterorings, and this may improve the capacity of π-charge delocalization. Hence octupolar benzene-substituted triazine (Im) has the largest α values among these octupolar triazines containing aromatic heterorings.

The main results shown in Table 2 are (i) octupolar pyrrole-substituted triazine (Ic) has a larger γ than the corresponding thiophene analogue (Ia), and yet γ of Ia is larger than that of its furan analogue (Ib). The same is true of a series of the homologous derivatives (cf. If > Id > Ie; Ii > Ig > Ih; Il > Ij > Ik); (ii) for pyrrole and its derivatives, octupolar triazine containing pyrroles (Ic) displays a larger γ than the analogues of pyrrole derivatives (If (Ii), Il). This holds for a series of the homologous derivatives (cf. Ia and Id (Ig), Ij; Ib and Ie (Ih), Ik); (iii) the substitution positions of the thiazole, oxazole, and imidazole rings in the octupolar triazines determine their γ values (Id vs Ig, Ie vs Ih, If vs Ii); (iv) octupolar benzene-substituted triazine (Im) exhibits a larger γ than the corresponding thiazole and oxazole analogues (Id, Ig, Ij and Ie, Ih, Ik) as well as Ii and Il.

Optical nonlinearities in dipolar molecules are intimately associated with quasi-one-dimensional charge transfer. Different from a dipolar system, charge transfer in an octupolar system is multidirectional rather than dipolar in character. The charge transfer occurs not only from the peripheral ends toward the center but also to some extent between the different branches of the octupolar molecule. The multidirectional charge-transfer thus determines NLO property of the octupolar molecule. For the series of thiophene, furan, and pyrrole, although their π-charge delocalization capacity varies in the following sequence: thiophene > pyrrole > furan, the charge transfer between the different branches of the octupolar molecules (Ia−Ic) may dominate over that from the peripheral ends toward the center, and increase in the following order: Ic > Ia > Ib. Therefore, the γ values for the molecules vary in the following order: Ic > Ia > Ib. Similar explanations hold for a series of the homologous derivatives (cf. If > Id > Ie; Ii > Ig > Ih; Il > Ij > Ik). As such, the order of γ increase for octupolar triazines containing pyrrole and its derivatives (cf. Ic > If (Ii) > Il) is attributed to the variation in the heteroatom's numbers of the heterorings and the multipolar symmetry. The same is also true of a series of the homologous derivatives (cf. Ia > Id (Ig) > Ij; Ib > Ie (Ih) > Ik).

TABLE 3: The First-Order Polarizabilities and Their Individual Components of NO_2-Substituted Octupolar Triazines II Calculated by the CPHF Method Using 6-31G Basis Set[a]

molecules	α_{xx}	α_{yy}	α_{zz}	α
IIa	53.1993	53.1980	12.3676	39.5883
IIb	45.5521	45.5521	9.8570	33.6537
IIc	49.9928	49.9928	10.1532	36.7129
IId	48.7414	48.7414	12.3097	36.5975
IIe	40.8331	40.8331	9.7721	30.4793
IIf	44.5544	44.5544	10.0141	33.0410
IIg	48.8751	48.8751	12.2409	36.6637
IIh	41.3313	41.3307	9.6950	30.7857
IIi	44.8939	44.8939	9.9431	33.2436
IIj	44.4420	44.4420	12.0166	33.6335
IIk	36.9287	36.9287	9.4145	27.7573
IIl	39.4855	39.4854	9.6394	29.5368
IIm	54.7389	54.7389	11.3642	40.2802

[a] All the values are given in Å^3.

TABLE 4: The Third-Order Polarizabilities and Their Individual Components of NO_2-Substituted Octupolar Triazines II Calculated by the CPHF Method Using 6-31G Basis Set[a]

molecules	γ_{xxxx}	γ_{yyyy}	γ_{zzzz}	γ_{xxyy}	γ_{xxzz}	γ_{yyzz}	γ
IIa	97.8083	97.7967	0.1954	32.5993	0.2181	0.2181	52.3743
IIb	88.3114	88.3129	0.1035	29.4374	0.1614	0.1614	47.2496
IIc	115.2207	115.2201	0.0994	38.4067	0.0511	0.0511	61.5116
IId	76.2441	76.2445	0.1854	25.4147	0.2707	0.2707	40.9172
IIe	64.2666	64.2612	0.0948	21.4207	0.2392	0.2392	34.4842
IIf	89.2914	89.910	0.0964	29.7639	0.1581	0.1581	47.7678
IIg	72.6943	72.6945	0.2084	24.2317	0.3249	0.3249	39.0720
IIh	64.6395	64.6262	0.1192	21.5439	0.2846	0.2847	34.7223
IIi	86.3091	86.3089	0.1148	28.7697	0.2163	0.2163	46.2275
IIj	46.7692	46.7693	0.1739	15.5897	0.3390	0.3390	25.2495
IIk	38.1300	38.1299	0.0734	12.7100	0.2947	0.2947	20.5864
IIl	53.9127	53.9124	0.0669	17.9707	0.2767	0.2767	28.9881
IIm	84.3422	84.3012	0.0964	28.1088	0.3348	0.3349	45.2594

[a] All the values are given in 10^{-36} 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); (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; the latter is electron-rich, as an auxiliary donor.[42] Thus, attaching thiazoles to an octupolar triazine at C2 (cf. Id) ("matched" case[42]) leads to a larger γ values than at C5 (cf. Ig) ("mismatched" case[42]). Thus Id displays a larger γ than Ig. Similar situations are found for the imidazole and oxazole analogues (cf. If vs Ii and Ie vs Ih).

3.2. Effects of Acceptor Group (NO_2) Substitution. In this section, we examine the effects of acceptor (NO_2) substitution on α and γ of the octupolar triazines shown in Figure 1 (IIa−IIm). The results are shown in Tables 3 and 4.

The leading results displayed in Table 3 are (i) when acceptor groups (NO_2) are attached to the octupolar molecules I, all the α values of the molecules II increase, compared with the corresponding unsubstituted case; (ii) the substitution positions of the thiazole, oxazole, and imidazole rings in the triazines have a little effect on their α values (IId vs IIg, IIe vs IIh, IIf vs IIi); (iii) the NO_2-substituted molecules containing thiophene derivatives (IIa, IId, IIg, IIj) have higher α than the corresponding molecules containing furan and pyrrole derivatives (IIb, IIe, IIh, IIk and IIc, IIf, IIi, IIl); (iv) NO_2-substituted molecule containing benzenes (IIm) has the highest α values among these substituted molecules.

Molecular polarizability calculated by the CPHF method should be equivalent to that obtained by the perturbation theory expansion. To display the fundamental pictures on the trends observed in the CPHF calculations, it is convenient to employ the sum over state (SOS) representation. The perturbation expression for the static first-order polarizability can be written as[52]

$$\alpha_{xx} \propto \sum_{m \neq g} \frac{\mu^{x}_{gm} \mu^{x}_{mg}}{E_{gm}} \tag{6}$$

where μ^{x}_{gm} is the x component of the transition dipole matrix element between the ground state $|g\rangle$ and excited state $|m\rangle$. E_{gm} is the energy difference between states $|m\rangle$ and $|g\rangle$. In the case of the octupolar molecule, there exist doubly degenerate excited states. On the basis of the valence-bond three-charge-transfer (VB-3CT) model,[25,27] it was found that, as the acceptor strengths increase, (i) the energy gap between the ground state $|g\rangle$ and doubly degenerate excited states $|m\rangle$ monotonically decreases; (ii) the transition dipole matrix element between $|g\rangle$ and $|m\rangle$ monotonically increases. These two contributions to α_{xx} in eq 6 combine to result in an increase of α_{xx}. Hence, attaching acceptor groups (NO_2) to the octupolar molecules I increases all the α values of the molecules II, compared with the corresponding unsubstituted case.

The main results shown in Table 4 are (i) when acceptor groups (NO_2) are attached to the octupolar molecules I, all the γ values of the molecules II increase, compared with the corresponding unsubstituted case; (ii) the substitution positions of the thiazole, oxazole, and imidazole rings in the octupolar triazines have a little effect on their γ values (IId vs IIg, IIe vs IIh, IIf vs IIi); (iii) NO_2-substituted molecules containing pyrrole derivatives (IIc, IIf, IIi, IIl) have higher γ than the corresponding molecules containing furan and thiophene derivatives (IIb, IIe, IIh, IIk and IIa, IId, IIg, IIj); (iv) octupolar benzene-substituted triazine (IIm) exhibits a larger γ than the corresponding thiazole and oxazole analogues (IId, IIg, IIj and IIe, IIh, IIk) as well as IIl.

As done for α, the perturbation theory expression for the static third-order polarizability can be expressed as[52]

$$\gamma_{xxxx} \propto \sum_{m \neq g} \sum_{n \neq g} \sum_{p \neq g} \frac{\mu^{x}_{gm} \bar{\mu}^{x}_{mn} \bar{\mu}^{x}_{np} \mu^{x}_{pg}}{E_{gm} E_{gn} E_{gp}} - \sum_{m \neq g} \sum_{n \neq g} \frac{\mu^{x}_{gm} \mu^{x}_{mg} \mu^{x}_{gn} \mu^{x}_{ng}}{E_{gm} E_{gn} E_{gn}} \tag{7}$$

where $\bar{\mu}^{x}_{mn} = \mu^{x}_{mn} - \mu^{x}_{gg}$, the ground-state permanent dipole moment of the octupolar molecule is zero. As shown in eq 7, there exist two distinctive contributions to γ_{xxxx}. Provided only the ground state $|g\rangle$ and doubly degenerate excited states $|e_1\rangle$ and $|e_2\rangle$ are considered to contribute to the description of the third-order polarizability, the first summation in eq 7 contains a term associated with the optical transition processes such as $|g\rangle \rightarrow |e_1\rangle \rightarrow |e_2\rangle \rightarrow |e_1\rangle \rightarrow |g\rangle$ and $|g\rangle \rightarrow |e_2\rangle \rightarrow |e_1\rangle \rightarrow |e_2\rangle \rightarrow |g\rangle$; on the other hand, a few typical terms contributing to γ_{xxxx} negatively are associated with the processes $|g\rangle \rightarrow |e_1\rangle \rightarrow |g\rangle \rightarrow |e_1\rangle \rightarrow |g\rangle$, $|g\rangle \rightarrow |e_2\rangle \rightarrow |g\rangle \rightarrow |e_2\rangle \rightarrow |g\rangle$, etc. When acceptor groups (NO_2) are attached to the octupolar molecules I, it can be found from Table 4 that the γ_{xxxx} values of the octupolar molecules II is positive. One may thus envision that the former types of optical transition process involving transition between the doubly degenerate excited states are dominant contributions to γ_{xxxx}. These suggestions are supported by the calculated results.

TABLE 5: The First-Order Polarizabilities and Their Individual Components of NH_2-Substituted Octupolar Triazines III Calculated by the CPHF Method Using 6-31G Basis Set[a]

molecules	α_{xx}	α_{yy}	α_{zz}	α
IIIa	50.3131	50.3131	11.5588	37.3950
IIIb	41.8884	41.8883	8.9699	30.9155
IIIc	45.4130	45.4129	9.2533	33.3597
IIId	46.8262	46.8262	11.5627	35.0717
IIIe	37.8920	37.8920	8.9588	28.2476
IIIf	41.3081	41.3081	9.1795	30.5986
IIIg	45.8682	45.8681	11.3166	34.3510
IIIh	37.5084	37.5084	8.6398	27.8855
IIIi	40.4889	40.4889	8.9226	29.9668
IIIj	41.8297	41.8296	11.1218	31.5937
IIIk	33.2700	33.2700	8.3819	24.9740
IIIl	35.8107	35.8106	8.6455	26.7556
IIIm	52.2450	52.2442	10.5398	38.3430

[a] All the values are given in Å^3.

TABLE 6: The Third-Order Polarizabilities and Their Individual Components of NH_2-Substituted Octupolar Triazines III Calculated by the CPHF Method Using 6-31G Basis Set[a]

molecules	γ_{xxxx}	γ_{yyyy}	γ_{zzzz}	γ_{xxyy}	γ_{xxzz}	γ_{yyzz}	γ
IIIa	118.3002	118.3000	0.1985	39.4333	0.3124	0.3124	63.3829
IIIb	100.5092	100.5095	0.1063	33.5032	0.2901	0.2901	53.8583
IIIc	113.9786	113.9777	0.0974	37.9926	0.2911	0.2911	61.0406
IIId	127.0848	127.0833	0.1862	42.3605	0.1843	0.1843	67.9625
IIIe	104.8019	104.8023	0.0984	34.9340	0.1741	0.1741	56.0534
IIIf	126.3038	126.3059	0.0933	42.1019	0.1516	0.1516	67.5027
IIIg	81.8152	81.8147	0.2232	27.2716	0.4739	0.4739	44.0584
IIIh	69.8367	68.8368	0.1319	23.2789	0.4473	0.4473	37.6304
IIIi	84.0632	84.0632	0.1248	28.0211	0.4545	0.4545	45.2223
IIIj	73.2953	73.2956	0.1873	24.4320	0.3461	0.3461	39.4053
IIIk	59.5253	59.5258	0.0896	19.8420	0.3078	0.3078	32.0112
IIIl	78.7951	78.7939	0.0811	26.2647	0.3159	0.3159	42.2927
IIIm	115.7964	115.7961	0.1001	38.5988	0.4429	0.4429	62.1323

[a] All the values are given in 10^{-36} esu.

3.3. Effects of Donor Group (NH_2) Substitution. In this section, we examine the effects of donor (NH_2) substitution on α and γ of the octupolar triazines shown in Figure 1 (IIIa−IIIm). The results are shown in Tables 5 and 6.

The leading results listed in Table 5 are (i) the NH_2-substituted octupolar molecules have higher α values than the corresponding unsubstituted analogues I, but have smaller α values than the corresponding NO_2-substituted analogues II; (ii) the substitution positions of the thiazole, oxazole, and imidazole rings in the octupolar triazines have a little effect on their α values (IIId vs IIIg, IIIe vs IIIh, IIIf vs IIIi); (iii) the NH_2-substituted molecules containing thiophene derivatives (IIIa, IIId, IIIg, IIIj) have higher α than the corresponding molecules containing pyrrole derivatives (IIIc, IIIf, IIIi, IIIl), and the latter series have larger α than the corresponding molecules containing furan derivatives (IIIb, IIIe, IIIh, IIIk); (iv) NH_2-substituted octupolar molecule containing benzenes (IIIm) has the largest α values among the octupolar molecules (III).

The variation trends of α for the NH_2-substituted octupolar molecules can also be rationalized by applying the VB-3CT model.[25,27] Therefore, appending donor groups (NH_2) to the octupolar molecules I also results in an increase of the α values in comparison with the corresponding unsubstitution.

The main results shown in Table 6 are (i) the NH_2-substituted octupolar molecules have higher γ 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 γ values (IIId vs IIIg, IIIe vs IIIh, IIIf vs IIIi); (iii) the NH_2-substituted molecules containing thiophene derivatives (IIIa, IIId, IIIg, IIIj) have higher γ than the corresponding molecules containing pyrrole derivatives (IIIc, IIIf, IIIi, IIIl), and the latter series have larger γ than the corresponding molecules containing furan derivatives (IIIb, IIIe, IIIh, IIIk), moreover, the series (IIId, IIIe, and IIIf) have the highest γ among the corresponding other series of analogues; (iv) octupolar benzene-substituted triazine (IIIm) exhibits a larger γ than two series of analogues (IIIg, IIIh, IIIi and IIIj, IIIk, IIIl) as well as IIIb, IIIc, IIIe.

When donor groups (NH_2) are attached to the octupolar molecules I, it can be found from Table 6 that the γ_{xxxx} values of the octupolar molecules III are positive. Therefore, the optical transition process involving transition between the doubly degenerate excited states may be dominant contributions to γ_{xxxx}. These suggestions show that incorporating donor groups (NH_2) into the octupolar molecules I increases all the γ values of the molecules III.

Attaching donor groups (NH_2) to the C5 atoms of the thiazole rings in IIId should augment the donor ability of NH_2 and increase γ. Similarly, appending NH_2 to the C2 atoms of the thiazole rings in IIIg should have the opposite effect. The molecule IIId is hence predicted to display a higher γ than IIIg. The same is true of the oxazole and imidazole analogues (cf. IIIe vs IIIh and IIIf vs IIIi).

3.4. Electron Correlation Effects. In this section, our main concern is to investigate whether the variation trends of α and γ for the molecules I at CPHF level shown in Tables 1 and 2 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 since 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 first- and third-order polarizabilities of the molecules I are calculated by the singular value decomposition (SVD) fit[53] to the RHF and MP2 energy expansions using 6-31G basis set. The results are listed in Table 7. For the sake of comparison, we also give 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 FF approach.

It is seen from Table 7 that the RHF/FF α and γ 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. The variation trends of α and γ for Ia−Im shown in Tables 1 and 2 are fully confirmed by the MP2/FF correlation calculated results here.

The first-order polarizabilities do not increase much with the consideration of the electron correlation correction. From the HF to MP2 results, the first-order polarizability values are increased by a maximum of 7.3%. As expected, the impact of electron correlation is very important on the third-order polarizabilities. For the molecules containing thiophene and thiazole rings (Ia and Id), γ values are increased by over 80% compared with HF results. We also observe an increase in γ for the molecules Ib, Ig, Ih, Ii, Ij, and Il by over 70%. For other molecules, the correlation effects exceed 60%. These results are fully in accord with other works.[54−58] As the molecules studied here are large and the basis set is small, the true size of electron correlation effects is beyond the scope of the present investigation.

TABLE 7: The First- and Third-Order Perpolarizabilities of Octupolar Heteroaromatic-Substituted Triazines I Calculated by the SVD Fit to the RHF and MP2 Energy Expansions Using 6-31G Basis Set[a]

	CPHF		RHF/FF		MP2/FF	
molecules	α	γ	α	γ	α	γ
Ia	31.3896	27.9001	31.3869	27.7930	33.1095	50.7994
Ib	25.6760	27.2412	25.6755	27.1892	26.5615	46.4347
Ic	28.1760	34.1600	28.1731	34.1855	30.2357	57.7504
Id	28.9257	25.2410	28.9295	25.0855	30.5291	45.6400
Ie	22.9240	22.8044	22.9239	22.7345	23.5186	37.5048
If	25.2896	32.4360	25.2904	32.4874	26.9370	54.8611
Ig	28.9152	20.3008	28.9171	20.1937	30.4321	35.6674
Ih	23.2675	19.0283	23.2688	18.9993	23.8522	32.5529
Ii	25.3621	23.8335	25.3619	23.8431	26.9960	40.6812
Ij	26.4002	15.2533	26.3994	15.1884	27.5859	26.7174
Ik	20.6363	13.1206	20.6347	13.0530	20.7361	21.1995
Il	22.4087	18.8214	22.4107	18.8372	23.4704	32.2108
Im	32.7779	25.9392	32.7789	25.6636	34.2215	43.3412

[a] All the α and γ values are given in $Å^3$ and 10^{-36} esu, respectively.

4. Synopsis

We have reported an ab initio study on the first- and third-order polarizabilities of a series of octupolar heteroaromatic-substituted triazines. Our calculations have addressed the important role of the five-numbered aromatic heterorings in the design of efficient first- and third-order polarizability for octupolar molecules. Effects of donor or acceptor substitution on these octupolar triazines have also been investigated. The valence-bond three-charge-transfer model has been employed to explain these observations. Finally, we have explored the impact of electron correlation on the molecular polarizabilities of these octupolar triazines at MP2 level.

The results indicate that octupolar triazines containing thiophene derivatives have larger first-order polarizabilities than the corresponding analogues containing furan and pyrrole derivatives. The substitution positions of the thiazole, oxazole, and imidazole rings in the octupolar triazines have a little effect on their first-order polarizability values. Octupolar benzene-substituted triazine exhibits the largest first-order polarizabilities among these octupolar triazines.

When acceptor groups (NO_2) are attached to these octupolar molecules, all the first-order polarizability values of NO_2-substituted octupolar molecules increase, compared with the corresponding unsubstituted case. Similar conclusions hold for the NH_2-substituted situation. The effects of acceptor substitution on the first-order polarizabilities exceed these of donor substitution.

This work shows that octupolar triazines containing pyrrole derivatives present larger third-order polarizabilities than the corresponding analogues containing furan and thiophene derivatives. The substitution positions of the thiazole, oxazole, and imidazole rings in the octupolar triazines determine their third-order polarizability values. Octupolar benzene-substituted triazine exhibits fairly larger third-order polarizabilities among these octupolar triazines.

Attaching acceptor groups (NO_2) to these octupolar molecules increases all the third-order polarizability values of NO_2-substituted octupolar molecules in comparison with the corresponding unsubstitution. The same is true for the NH_2-substituted case. The effects of donor substitution on the third-order polarizabilities exceed these of acceptor substitution.

It is also found that the MP2/FF correlation calculated results fully confirm the variation trends of α and γ for these octupolar molecules. With the introduction of the electron correlation correction, the first-order polarizabilities do not increase much, whereas the third-order polarizabilities significantly increase.

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