

## Theoretical Studies on the Nonlinear Optical Properties of Octupolar Tri-s-triazines

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**Abstract:** The first-, second-, and third-order static and frequency-dependent polarizabilities of a series of octupolar tri-s-triazines have been investigated by using the ab initio coupled perturbed Hartree–Fock (CPHF) method. Effects of substitution have also been considered. The results show that  $\alpha$ ,  $\beta$ , and  $\gamma$  values for octupolar tri-s-triazines are much larger than those for s-triazine in both static and frequency-dependent cases. Attaching groups containing  $\pi$  systems such as azide and ethenyl to the tri-s-triazine molecule results in a significant increase of first-, second-, and third-order polarizabilities. Our calculations suggest that the octupolar tri-s-triazines may be prospective candidates for nonlinear optical materials.

### Introduction

Molecules possessing large nonlinear optical (NLO) properties have been intensively investigated for potential applications in the areas of integrated optics and other sections of materials science.<sup>1–3</sup> As is well-known, second-order NLO compounds show great promise in their application in photonic devices such as high-speed electrooptic (E–O) modulators and switches, owing to their large E–O coefficients, ultrafast response times, and ease of processing into thin films.<sup>4,5</sup> On the other hand, third-order NLO properties provide the basic means for light controlling with light in all optics, as in optical bistability and phase conjugation. Furthermore, the understanding of all-optical switching, modulating, and computing devices is important in modern optical technology, and NLO materials with large third-order nonlinear susceptibilities are indispensable for such devices. For example, if a material has a high third-order nonlinear susceptibility, it can generate a strong conjugate wave in optical phase-conjugate wave generation devices, and the length of the resonator for reaching the bistable region in

optical bistable devices can be much reduced. Our present research is focused on the development of NLO molecules with large nonlinearity, high thermal stability, and good processability.<sup>6,7</sup>

The traditional materials with enhanced molecular second-order NLO coefficients are those with extended  $\pi$ -systems and significant molecular dipoles. Although there are many examples of dipolar molecules exhibiting extremely large hyperpolarizabilities, several limitations prevent them from being a candidate for NLO materials, such as the NLO efficiency-transparency tradeoff, and the proclivity of dipolar molecules to adopt centrosymmetric packing in the solid state.<sup>8</sup> Octupolar molecules, which combine nonlinear optical properties with a strict cancellation of all vectorlike observable dipole moment,<sup>8–11</sup> overcome these problems due to the presence of a 3-fold symmetry axis in octupolar 1,3,5-substituted aromatic ring systems. Such a 3-fold axis may lead to better transparency characteristics,<sup>11</sup> and the lack of a molecular dipole enhances the prospects of noncentrosymmetric crystal packing.

In the 1990s, Zyss and co-workers introduced octupolar molecules for second-order nonlinear optics.<sup>8,9</sup> Since the development of hyper-Rayleigh scattering techniques, the hyperpolarizabilities of octupolar molecules, such as tri-cyanomethanide ion, tetraorganotin compounds, and sym-

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metrically substituted benzenes and triazines as well as tertiary amines, have been evaluated experimentally.<sup>12–17</sup> In 1999, Humphrey et al. first reported data exploring the third-order NLO potential of an organometallic octupolar compound.<sup>18</sup> In 1995, Ray and Das measured the first hyperpolarizabilities of some symmetrically substituted triazines and compared them with those of the corresponding symmetrically substituted benzenes. It was found that the octupolar triazines have quadratic polarizabilities higher than the corresponding octupolar benzenes.<sup>19</sup> In 2002, Wu investigated the first- and third-order polarizabilities of a series of octupolar heteroaromatic-substituted triazines using ab initio methods. It was revealed that these triazines have high polarizabilities.<sup>20</sup> In a recent study, we calculated the geometric and electronic structures of some symmetrically substituted tri-*s*-triazines<sup>21</sup> and found that the octupolar tri-*s*-triazines molecules possess high thermal stability. In this work, we report NLO data for these octupolar compounds using ab initio molecular orbital method.

## Methods

The geometries of all symmetrically substituted tri-*s*-triazines studied in this work were optimized at the B3LYP/aug-cc-pVDZ level of theory using the software package Gaussian 98.<sup>22</sup> The calculations for the NLO properties were performed using the HONDO 99.9 set of programs.<sup>23</sup> Static polarizabilities as well as the first- and second-order hyperpolarizability components were calculated analytically using the coupled perturbed Hartree–Fock (CPHF) method.<sup>24</sup> The Buckingham type expansion<sup>25</sup> was used in the CPHF calculation:

$$E = E^{(0)} - \mu_i^{(0)} F_i - \frac{1}{2} \alpha_{ij} F_i F_j - \frac{1}{6} \beta_{ijk} F_i F_j F_k - \frac{1}{24} \gamma_{ijkl} F_i F_j F_k F_l - \dots$$

where  $E$  is the energy of a molecule under the electric field  $F$ ,  $E^{(0)}$  is the unperturbed energy of a free molecule,  $F_i$  is the vector component of the electric field in the  $i$ th direction, and  $\mu_i$ ,  $\alpha_{ij}$ ,  $\beta_{ijk}$ , and  $\gamma_{ijkl}$  denote the dipole moment, linear polarizability, and first- and second-order hyperpolarizabilities, respectively. Each of the subscripts  $i$ ,  $j$ ,  $k$ , and  $l$  represents the index of the Cartesian axes  $x$ ,  $y$ , and  $z$ . To provide additional useful information to experimentalists, we also calculated the frequency-dependent polarizabilities and hyperpolarizabilities using the time-dependent CPHF method.<sup>26</sup> The 1064 nm line of Nd:YAG laser is used in our calculation since the second-harmonic generation (SHG) experiments are usually performed at this fundamental wavelength.

It is well-known that splitting valence basis sets with additional diffuse and polarization functions can be employed to correct the underestimation, especially for the  $\gamma$ -tensor components. Hurst et al.<sup>24</sup> reported that the 6-31G functions plus one p and one d function (6-31G plus lp1d) is a reliable basis set which yields quality  $\beta$  and  $\gamma$  values of polyene systems, even though it is not a very big basis set. In this work, we selected Pople's standard 6-31++G(d,p) basis set in the CPHF calculations. The reliability of this method can be justified since it has been applied to a variety of molecules

and has achieved good results.<sup>20,27</sup> So far *s*-triazine derivatives have not been extensively investigated for NLO applications. Only a few important *s*-triazine derivatives have been synthesized and their second harmonic generation properties measured. But these derivatives are too large to be dealt with the CPHF/6-31++G(d,p) method. Instead, we calculated the (hyper)polarizability of benzene and compared our computational results with the available experimental data. The calculated  $\alpha$  (64.5 au) is very close to the experimental value of 71.5 au.<sup>28</sup> For the calculated  $\gamma$  (13 241 au, dcKerr 632.8 nm), we also find satisfactory agreement with the measured value (12 800 au, dcKerr 632.8 nm).<sup>29</sup> Hence the theoretical methods adopted in this work should be reliable.

The calculated tensors were transformed to mean scalar values by applying the following equations.

$$\alpha = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$$

$$\langle \gamma \rangle = \frac{1}{5}(\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + 2\gamma_{xxyy} + 2\gamma_{xxzz} + 2\gamma_{yyzz})$$

Zyss et al.<sup>8,9,11,30</sup> have developed and discussed the tensorial nature of the second-order polarizability for octupolar molecules. Within their framework, the second-order polarizability tensor can be decomposed in two components  $\beta_{J=1}$  and  $\beta_{J=3}$ , the dipolar and octupolar contributions, respectively.

$$\beta = \beta_{J=1} \otimes \beta_{J=3}$$

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

For 2-D planar systems, the following expressions apply:

$$\|\beta_{J=1}\|^2 = 3/4[(\beta_{xxx} + \beta_{xyy})^2 + (\beta_{yyy} + \beta_{yxx})^2]$$

$$\|\beta_{J=3}\|^2 = 1/4[(\beta_{xxx} - 3\beta_{xyy})^2 + (\beta_{yyy} - 3\beta_{yxx})^2]$$

## Results and Discussion

### Static First-, Second-, and Third-Order Polarizabilities.

The octupolar tri-*s*-triazines studied in this work shown in Figure 1 are derived from symmetrical substitution of hydrogen atoms by various groups in tri-*s*-triazine. The *s*-triazine molecule is also displayed for comparison. The geometric structures of these molecules were discussed in detail in our previous work.<sup>21</sup> Tables 1–3 list the calculated values of the static first-, second-, and third-order polarizabilities and their individual components for all six tri-*s*-triazines shown in Figure 1. The tensor components listed in these tables have the following approximate relationships:

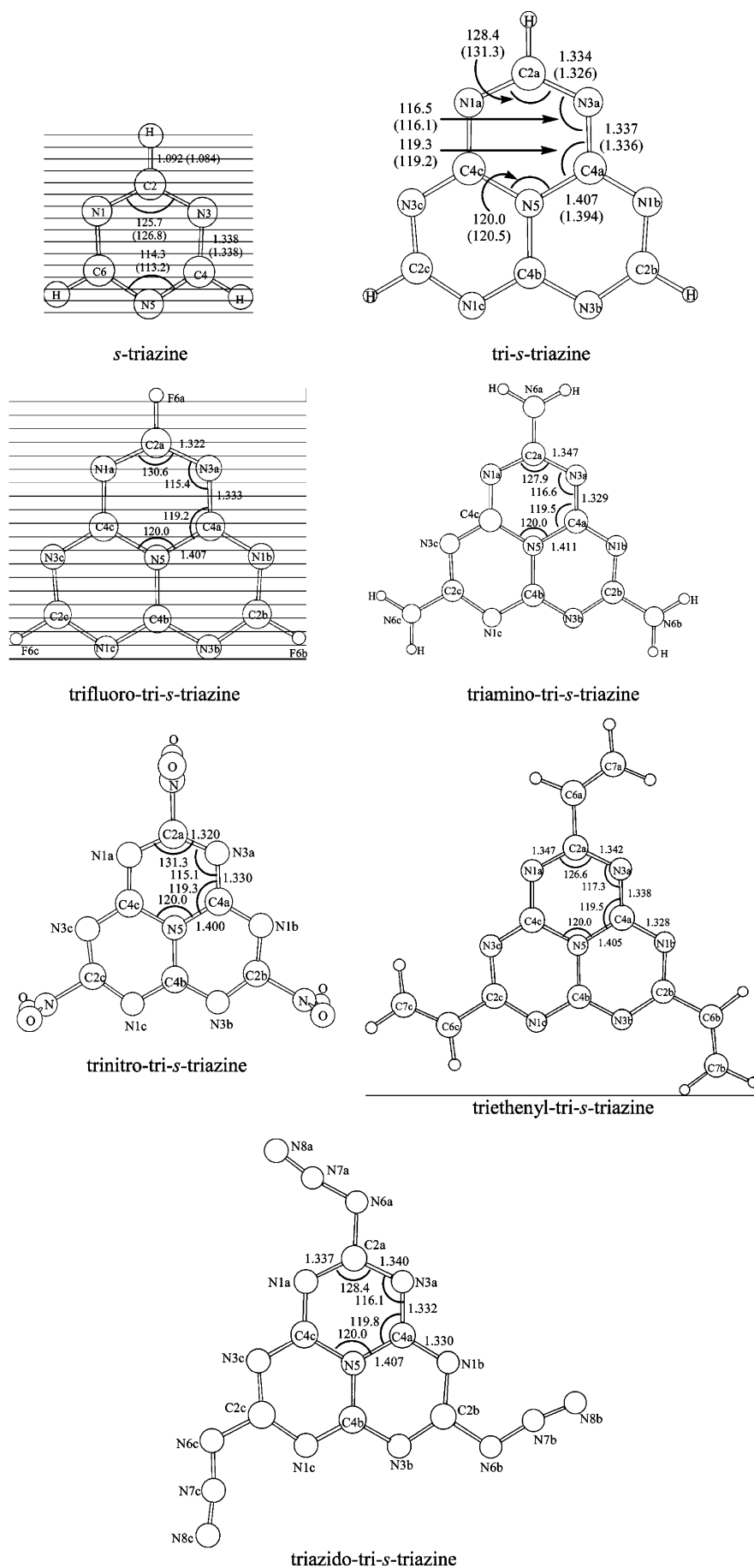
$$\alpha_{xx} = \alpha_{yy}$$

$$\beta_{xxy} = -\beta_{yyy}$$

$$\gamma_{xxxx} = \gamma_{yyyy} = 3\gamma_{xxyy}$$

$$\gamma_{xxzz} = \gamma_{yyzz}$$

In all the molecules investigated in this work, the axial component  $\alpha_{zz}$  of  $\alpha$  along the  $C_{3v}$  axis is smaller than the



**Figure 1.** Optimized molecular structures for *s*-triazine and octupolar tri-*s*-triazines with bond lengths in Å and angles in degrees. Experimental data for *s*-triazine and tri-*s*-triazine are given in parentheses.

**Table 1.** Static First-Order Polarizabilities ( $\text{\AA}^3$ ) and Their Individual Components of *s*-Triazine and Octupolar Tri-*s*-triazines

molecule	$\alpha_{xx}$	$\alpha_{yy}$	$\alpha_{zz}$	$\alpha$
<i>s</i> -triazine	8.3265	8.3265	4.3104	6.9878
tri- <i>s</i> -triazine	19.5108	19.5108	7.7516	15.5911
trifluoro-tri- <i>s</i> -triazine	19.3357	19.3357	7.6744	15.4486
triamino-tri- <i>s</i> -triazine	25.2204	25.2204	9.9322	20.1243
trinitro-tri- <i>s</i> -triazine	26.1252	26.1200	17.7568	23.3340
triethenyl-tri- <i>s</i> -triazine	37.9127	37.9127	13.3907	29.7387
triazido-tri- <i>s</i> -triazine	36.7575	36.7574	11.3723	28.2958

nonaxial components  $\alpha_{xx}$  and  $\alpha_{yy}$ . As expected, the polarizability  $\alpha$  of tri-*s*-triazine is larger (by a factor of 2.2) than that of *s*-triazine. The average  $\alpha$  of the parent molecule tri-*s*-triazine is 15.5911  $\text{\AA}^3$ . Upon substitution, the average  $\alpha$  decreases slightly to 15.4486  $\text{\AA}^3$  in the fluoro derivative but increases significantly to 20.1243, 23.3340, 28.2958, and 29.7387  $\text{\AA}^3$  for the amino, nitro, azido, and ethenyl derivatives, respectively. It is noted that, when the substituent contains  $\pi$  system such as azide and ethenyl, the  $\alpha$  value of the tri-*s*-triazine derivative is nearly twice as that of the parent molecule. The fluorine atom plays the role of  $\pi$ -acceptor and drains part of the  $\pi$ -electron cloud from the rings, which in turn decreases the degree of  $\pi$ -charge delocalization. Hence the fluoro-substituted tri-*s*-triazine has the smallest  $\alpha$  value.

When we turn to the second-order polarizability  $\beta$ , we notice that the  $\|\beta\|$  value for the parent tri-*s*-triazine molecule is  $459.2260 \times 10^{-32}$  esu, which is almost 8 times larger than that of *s*-triazine ( $64.6887 \times 10^{-32}$  esu). By symmetry, the nonzero tensors of  $\beta$  in tri-*s*-triazine and its fluoro and amino derivatives, all with  $D_{3h}$  symmetry, are  $\beta_{yyy}$  and  $\beta_{xxy}$ . However, for the nitro, ethenyl, and azide derivatives, all with  $C_{3h}$  symmetry, the nonzero  $\beta$  tensors are  $\beta_{xxx}$ ,  $\beta_{yyy}$ ,  $\beta_{xxy}$ , and  $\beta_{xyy}$ . With tri-*s*-triazine as a reference, the  $\|\beta\|$  value

increases slightly in fluoro and nitro derivatives but increases by about 3–5 times in amino, azido, and ethenyl derivatives. This shows that the substituent containing  $\pi$  system enhances the second-order polarizability  $\|\beta\|$  drastically.

The averaged third-order polarizabilities  $\langle\gamma\rangle$  of the *s*-triazine, tri-*s*-triazine, and its derivatives are listed in Table 3. Using *s*-triazine as a reference, the  $\langle\gamma\rangle$  value of tri-*s*-triazine increases by about 2-fold. However, comparing with the parent tri-*s*-triazine, trifluoro-tri-*s*-triazine decreases by about 25%, while the other derivatives experience an increase of 1 order of magnitude.

In summary, when compared with the parent molecule, all substituted tri-*s*-triazines, except the fluoro derivative, experience an increase, sometimes even by several orders of magnitude, for the static first-, second-, and third-order polarizabilities.

**Frequency-Dependent First-, Second-, and Third-Order Polarizabilities.** From a qualitative point of view, tuning up the frequency of the external electric field induces an increase of delocalizability, allowing a stronger electron mobility in the aromatic systems. This simple model leads to a practical explanation of the frequency dispersion pattern found in tri-*s*-triazines.

The frequency-dependent  $\alpha$  and  $\beta$  values are reported in Table 4, where the laser frequency 1064 nm was used as a standard. For polarizability  $\alpha$ , comparing the last column of Table 1 with the second column of Table 4, the effect of frequency dispersion is very small. But for second-order polarizability  $\beta$ , comparing the last column of Table 2 with the third and fourth columns of Table 4, frequency dispersion enhances the  $\beta$  value by 10% and more. In particular, the increase is more pronounced when electron-donating or  $\pi$ -bonding substituents are involved. Also, the increase for SHG  $\beta(-2\omega; \omega, \omega)$  is more prominent than that for electrooptic pockels effect (EOPE)  $\beta(-\omega; 0, \omega)$ . Compared with the static value, for the ethenyl derivative,  $\beta(-2\omega; \omega,$

**Table 2.** Static Second-Order Polarizabilities ( $10^{-32}$  esu) and Their Individual Components of *s*-Triazine and Octupolar Tri-*s*-triazines

molecule	$\beta_{xxx}$	$\beta_{yyy}$	$\beta_{xxy}$	$\beta_{xyy}$	$\ \beta\ $
<i>s</i> -triazine		32.3444	−32.3443		64.6887
tri- <i>s</i> -triazine		−229.6120	229.6133		459.2260
trifluoro-tri- <i>s</i> -triazine		−282.5875	282.5871		565.1744
triamino-tri- <i>s</i> -triazine		−632.9766	632.9786		1265.9562
trinitro-tri- <i>s</i> -triazine	−248.8180	265.8763	−265.9148	248.6477	728.1550
triethenyl-tri- <i>s</i> -triazine	276.1715	−1018.2450	1018.2460	−276.1698	2110.0658
triazido-tri- <i>s</i> -triazine	162.1427	−1019.7733	1019.7743	−162.1436	2065.1679

**Table 3.** Static Third-Order Polarizabilities ( $10^{-39}$  esu) and Their Individual Components of *s*-Triazine and Octupolar Tri-*s*-triazines

molecule	$\gamma_{xxxx}$	$\gamma_{yyyy}$	$\gamma_{zzzz}$	$\gamma_{xxyy}$	$\gamma_{xxzz}$	$\gamma_{yyzz}$	$\langle\gamma\rangle$
<i>s</i> -triazine	2657.8618	2657.8703	1730.1931	885.9296	676.2007	676.2029	2304.5183
tri- <i>s</i> -triazine	6036.2210	6036.6554	2478.1237	2012.2301	1241.5368	1241.5300	4708.3188
trifluoro-tri- <i>s</i> -triazine	4638.8088	4639.2272	1873.7772	1546.4137	845.5892	845.5909	3525.4001
triamino-tri- <i>s</i> -triazine	13385.3187	13386.4202	3664.2631	4462.1743	1706.9594	1706.9679	9237.6411
trinitro-tri- <i>s</i> -triazine	8403.6906	8401.1645	951.2307	2800.4181	952.1211	952.0732	5433.4621
triethenyl-tri- <i>s</i> -triazine	44783.0373	44783.2771	10353.5549	14927.7331	4283.2492	4283.2457	29381.6605
triazido-tri- <i>s</i> -triazine	31072.2844	31071.7690	2688.5543	10357.2748	1757.4668	1757.4676	18515.4052

**Table 4.** Frequency-Dependent ( $\lambda = 1064$  nm) First- ( $\text{\AA}^3$ ) and Second-Order ( $10^{-32}$  esu) Polarizabilities of s-Triazine and Octupolar Tri-s-triazines

molecule	$\alpha (-\omega, +\omega)$	$\ \beta\  (-2\omega; \omega, \omega)$	$\ \beta\  (-\omega; 0, \omega)$
s-triazine	7.0462	71.0365	66.6595
tri-s-triazine	15.7928	512.9644	529.8788
trifluoro-tri-s-triazine	15.6171	616.0259	581.22425
triamino-tri-s-triazine	20.3787	1435.5371	1318.2964
trinitro-tri-s-triazine	23.6296	813.2688	754.5485
triethenyl-tri-s-triazine	30.3280	2644.1821	2265.4672
triazido-tri-s-triazine	28.7613	2437.2169	2176.6892

**Table 5.** Frequency-Dependent ( $\lambda = 1064$  nm) Third-Order ( $10^{-39}$  esu) Polarizabilities of s-Triazine and Octupolar Tri-s-triazines

molecule	$\gamma (-3\omega; \omega, \omega, \omega)$	$\gamma (-2\omega; 0, \omega, \omega)$	$\gamma (-\omega; \omega, \omega, -\omega)$	$\gamma (-\omega; 0, 0, \omega)$	$\gamma (0; 0, \omega, -\omega)$
s-triazine	2857.1075	2555.7084	2470.8334	2382.8672	2378.8438
tri-s-triazine	7003.7833	5329.7833	5164.3859	4899.9057	4889.4697
trifluoro-tri-s-triazine	4502.7955	3918.5818	3828.9645	3649.5615	3647.7562
triamino-tri-s-triazine	12844.0528	10663.8378	10336.4123	9690.8679	9728.7243
trinitro-tri-s-triazine	8334.8171	6094.7383	5972.8161	5646.8307	5659.3228
triethenyl-tri-s-triazine	55269.1883	38363.5500	35562.8818	31994.5338	32094.7608
triazido-tri-s-triazine	30792.1488	23025.3981	21757.3120	19873.1236	19952.7164

**Table 6.** Natural Atomic Charges of the Atoms in Tri-s-triazine Ring for Octupolar Tri-s-triazines

	tri-s-triazine				
	trifluoro-	triamino-	trinitro-	triethenyl-	triazido-
N1	-0.55	-0.57	-0.61	-0.52	-0.55
C2	0.36	0.91	0.66	0.65	0.47
N3	-0.55	-0.57	-0.61	-0.51	-0.56
C3a	0.68	0.69	0.69	0.70	0.69
N4	-0.55	-0.57	-0.61	-0.51	-0.55
C5	0.36	0.91	0.66	0.63	0.47
N6	-0.55	-0.57	-0.61	-0.51	-0.56
C6a	0.68	0.69	0.69	0.70	0.69
N7	-0.55	-0.57	-0.61	-0.51	-0.55
C8	0.36	0.91	0.66	0.64	0.47
N9	-0.55	-0.57	-0.61	-0.51	-0.56
C9a	0.68	0.69	0.69	0.70	0.69
N9b	-0.47	-0.48	-0.51	-0.46	-0.48
total	-0.65	0.90	-0.12	0.49	-0.33

$\omega$ ) is increased by 25%. For the azide and amino derivatives, the corresponding enhancements are 18% and 13%, respectively. For  $\beta (-\omega; 0, \omega)$  values, a similar trend is detected. This means that, as the static  $\beta$  values increase, so do the frequency dispersion effects.

For the third-order polarizabilities of tri-s-triazines, five different optical processes are considered: third-harmonic generation (THG)  $\gamma (-3\omega; \omega, \omega, \omega)$ , electric-field-induced second-harmonic generation EFISH  $\gamma (-2\omega; 0, \omega, \omega)$ , degenerate four-wave mixing DFWM  $\gamma (-\omega; \omega, \omega, -\omega)$ , electric-field-induced Kerr effect EFIKE  $\gamma (-\omega; 0, 0, \omega)$ , and electric-field-induced optical rectification EFior  $\gamma (0; 0, \omega, -\omega)$ . The calculated values of the third-order polarizability  $\gamma$  for the aforementioned processes are tabulated in Table 5, where only the averaged scalar values  $\langle\gamma\rangle$  are listed. As can be seen from this table, the effect of frequency dispersion on  $\gamma$  is very strong, with the trend  $\gamma (-3\omega; \omega,$

**Table 7.** HOMO and LUMO Energies and the Their Gaps for Octupolar Tri-s-triazines

molecule	$E_{\text{HOMO}}$ (eV)	$E_{\text{LUMO}}$ (eV)	$\Delta E_{\text{LUMO-HOMO}}$ (eV)
tri-s-triazine	-7.32	-3.40	3.92
trifluoro-tri-s-triazine	-8.14	-3.64	4.50
triamino-tri-s-triazine	-6.44	-1.52	4.92
trinitro-tri-s-triazine	-8.91	-4.85	4.06
triethenyl-tri-s-triazine	-6.84	-3.19	3.65
triazido-tri-s-triazine	-7.48	-3.34	4.14

$\omega, \omega) > \gamma (-2\omega; 0, \omega, \omega) > \gamma (-\omega; \omega, \omega, -\omega) > \gamma (0; 0, \omega, -\omega) \approx \gamma (-\omega; 0, 0, \omega)$  for all studied molecules. Again, as expected, the derivatives containing  $\pi$ -bonding substituents, such as ethenyl and azide groups, have the largest frequency-dependent third-order polarizability. Also, as the static  $\gamma$  values increase, so do the frequency dispersion affects. Taking triethenyl-tri-s-triazine as an example,  $\gamma (-3\omega; \omega, \omega, \omega)$ ,  $\gamma (-2\omega; 0, \omega, \omega)$ ,  $\gamma (-\omega; \omega, \omega, -\omega)$ ,  $\gamma (0; 0, \omega, -\omega)$ , and  $\gamma (-\omega; 0, 0, \omega)$  increase by 88%, 31%, 21%, 9%, and 9%, respectively.

**Ground-State Net Charges and Energy Levels.** The ground-state net charge distribution of the tri-s-triazines studied in this work was analyzed by means of the natural bond orbital (NBO) model.<sup>31-34</sup> The natural atomic charges of the atoms in the tri-s-triazine ring are listed in Table 6. The results indicate that the total net charge of the fused ring for the tri-s-triazine molecule is -0.65 and that all substituents decrease the magnitudes of negative charges of the ring. These results imply that there is partial electron transfer from the rings to the substituents. This transfer is more pronounced for the fluoro and nitro derivatives, where the total net charges of the ring become positive. As a result of the charge transfer, the  $\alpha$ ,  $\beta$ , and  $\gamma$  values in triamino-tri-s-triazine, trinitro-tri-s-triazine, triethenyl-tri-s-triazine, and triazido-tri-s-triazine molecules are much greater than that



**Table 8.** Static First-Order Polarizabilities ( $\text{\AA}^3$ ) and Their Individual Components of Triethenyl-tri-*s*-triazine, Triazido-tri-*s*-triazine, and Their Configurations

molecule	$\alpha_{xx}$	$\alpha_{yy}$	$\alpha_{zz}$	$\alpha$
triethenyl-tri- <i>s</i> -triazine	37.9127	37.9127	13.3907	29.7387
triethenyl-tri- <i>s</i> -triazine-30 <sup>a</sup>	31.4639	19.9353	36.4698	29.2897
triethenyl-tri- <i>s</i> -triazine-60 <sup>a</sup>	32.5031	18.5031	33.4127	28.1396
triethenyl-tri- <i>s</i> -triazine-90 <sup>a</sup>	28.5112	24.4644	29.3246	27.4334
triazido-tri- <i>s</i> -triazine	36.7575	36.7574	11.3723	28.2958
triazido-tri- <i>s</i> -triazine-30 <sup>b</sup>	35.4912	13.3622	35.4744	28.1093
triazido-tri- <i>s</i> -triazine-60 <sup>b</sup>	32.4198	17.3844	32.3598	27.3880
triazido-tri- <i>s</i> -triazine-90 <sup>b</sup>	30.5213	24.2214	25.7043	26.8157

<sup>a</sup> Three N1–C2–C6–C7 dihedrals are 30°, 60°, and 90°, respectively. <sup>b</sup> Three N1–C2–N6–N7 dihedrals are 30°, 60°, and 90°, respectively.

**Table 9.** Static Third-Order Polarizabilities ( $10^{-39}$  esu) and Their Individual Components of Triethenyl-tri-*s*-triazine, Triazido-tri-*s*-triazine, and Their Configurations

molecule	$\gamma_{xxxx}$	$\gamma_{yyyy}$	$\gamma_{zzzz}$	$\gamma_{xxyy}$	$\gamma_{xxzz}$	$\gamma_{yyzz}$	$\gamma$
triethenyl-tri- <i>s</i> -triazine	44783.0373	44783.2771	10353.5549	14927.7331	4283.2492	4283.2457	29381.6605
triethenyl-tri- <i>s</i> -triazine-30 <sup>a</sup>	27273.2289	11475.0252	80337.7657	8989.0430	11870.8883	5359.7104	26330.1226
triethenyl-tri- <i>s</i> -triazine-60 <sup>a</sup>	2649.5188	6143.9387	27637.2076	3350.2628	8351.7971	3401.2846	18007.4708
triethenyl-tri- <i>s</i> -triazine-90 <sup>a</sup>	11981.5824	7753.9653	13130.8486	4020.2897	4645.3995	3893.5861	11596.9894
triazido-tri- <i>s</i> -triazine	31072.2844	31071.7690	2688.5543	10357.2748	1757.4668	1757.4676	18515.4052
triazido-tri- <i>s</i> -triazine-30 <sup>b</sup>	28777.3275	3398.8258	28823.6385	1954.6754	9620.8997	1897.6983	17589.2677
triazido-tri- <i>s</i> -triazine-60 <sup>b</sup>	21667.6432	4080.1100	21437.4695	2005.1426	7297.3843	2146.9824	14016.8483
triazido-tri- <i>s</i> -triazine-90 <sup>b</sup>	14865.2099	6947.8452	8648.6290	3463.8451	3606.3176	3639.6542	10376.2636

<sup>a</sup> Three N1–C2–C6–C7 dihedrals are 30°, 60°, and 90°, respectively. <sup>b</sup> Three N1–C2–N6–N7 dihedrals are 30°, 60°, and 90°, respectively.

observed in tri-*s*-triazine molecule, while, in the trifluoro-tri-*s*-triazine molecule, the  $\beta$  value increases and both the  $\alpha$  and  $\gamma$  values decrease.

The energies of HOMO and LUMO and the gaps between them for the molecules investigated are summarized in Table 7. When compared with the parent molecule, the HOMO and LUMO energy levels decrease in fluoro and nitro derivatives, while they increase in amino and ethenyl substitutions. The energy gap decreases only in triethenyl-tri-*s*-triazine, in which the substituent is a very effective  $\pi$ -donating system. Owing to this small energy gap, the triethenyl-tri-*s*-triazine molecule possesses the largest  $\alpha$ ,  $\beta$ , and  $\gamma$  values.

**$\pi$ -Conjugation Effects.** From the previous analysis, it should be noted that the substituents with  $\pi$ -donating group could enhance the (hyper)polarizabilities of tri-*s*-triazines dramatically. We now examine the role of  $\pi$ -conjugation between the substituent R group and the parent tri-*s*-triazine ring. In general, the most stable conformation of triethenyl-tri-*s*-triazine and triazido-tri-*s*-triazine adopts a planar geometry in order to achieve conjugation between the R group and the parent ring. Examination of the molecular orbitals reveals that the  $\pi$  orbital of the ring is composed of  $2p_z$  orbitals of nitrogen and carbon atoms on the ring, and the  $\pi$  orbitals of ethenyl and azido groups are also composed of  $2p_z$  orbitals of the atoms in the groups. The conjugation between the groups and the parent ring extends the delocalization of the electrons in the molecule. Hence triethenyl-tri-*s*-triazine and triazido-tri-*s*-triazine have the largest (hyper)polarizabilities.

It is possible that this conjugation will be destroyed to a large extent when rotation around the dihedral angles N1–

C2–C6–C7 of triethenyl-tri-*s*-triazine and N1–C2–N6–N7 of triazido-tri-*s*-triazine deviate significantly from 0°. When we rotated the three equivalent dihedral angles N1–C2–C6–C7 of triethenyl-tri-*s*-triazine and N1–C2–N6–N7 of triazido-tri-*s*-triazine to 30°, 60°, and 90° and calculated the (hyper)polarizabilities of these configurations, the results listed in Tables 8 and 9 were obtained. As can be seen from these tables, the (hyper)polarizabilities decrease with the increase of the dihedrals, which weakens the conjugation between the substituents and the ring. Even under such conditions, the (hyper)polarizabilities of all these configurations are still much larger than those of other substituted tri-*s*-triazines.

## Conclusions

We have reported an ab initio study on the first-, second-, and third-order static and frequency-dependent polarizabilities of a series of octupolar tri-*s*-triazines. Our calculations show that octupolar tri-*s*-triazines have much larger  $\alpha$ ,  $\beta$ , and  $\gamma$  values than *s*-triazine, both in static and frequency-dependent cases. The  $\pi$ -containing substituents such as azide and ethenyl result in a significant increase of first-, second-, and third-order polarizabilities. Based on our results, these octupolar tri-*s*-triazines can be classified as a new family of NLO materials.

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