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Masayoshi Nakano [a] & Kizashi Yamaguchi [a]
[a] Department of Chemistry, Faculty of Science, Osaka University, Osaka, 560, Japan
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THEORETICAL STUDIES FOR THIRD-ORDER HYPERPOLARIZABILITIES OF ALTERNANT AND CONDENSED-RING CONJUGATED SYSTEMS I

MASAYOSHI NAKANO AND KIZASHI YAMAGUCHI
Department of Chemistry, Faculty of Science, Osaka University, Osaka 560, Japan

Abstract Static third-order hyperpolarizabilities(γ) for neutral, ion radical and ion states of centrosymmetric systems are calculated by the use of the *ab initio* method. The dependences of basis sets and electron correlation effects on the γ values for allyl systems are examined. It is found that the extended basis set with diffuse *p* and *d* functions and Møller-Plesset second-order perturbation (MP2) method are necessary for reasonable descriptions of at least relative tendencies for these charged states of allyl. We also show that triafulvalene (alternant conjugated system) exhibits positive γ value, while the anion radical state of pentalene (condensed-ring conjugated system) does negative one by the *ab initio* MP2 calculations using 6-31G+*pd*($\zeta_{p,d}$=0.05).

INTRODUCTION

Recently, considerable attention has been given to third-order nonlinear optical effects on organic substances. Many theoretical calculations of γ, which is the origin of macroscopic third-order nonlinear optical effects, are carried out.[1-14] From the time-dependent perturbational analysis of nonlinear optical processes, it is well known that the π–conjugated noncentrosymmetric systems tend to possess large positive γ values. Previously, we presented the three-type approximation[1,3,5] in which virtual excitation processes describing the γ can be divided into three types: (I) ($\gamma > 0$), (II)' ($\gamma < 0$) and (III)' ($\gamma > 0$). The three-type approximation shows that the signs and magnitudes of γ for centrosymmetric systems are determined from the detailed balance between types (II)' and (III)'. We reformulated the *N* state three-type approximate formula by the use of the ground and excited state polarizabilities and the ratio of excitation energies as follows.[1]

$$\gamma^{(\mathrm{I})+(\mathrm{II})'+(\mathrm{III})'} = \frac{1}{2}\sum_{n=1}^{N}\left\{\frac{\alpha_0(n)}{E_{n0}}\left[\frac{(\Delta\mu_{n0})^2}{E_{n0}} + \frac{1}{2}\sum_{m(\neq n)=1}^{N}\left(\alpha_n(m)r(m,n) - [1-r(m,n)]\frac{\alpha_0(n)}{N-1}\right)\right]\right\}. \quad (1)$$

Here, $\alpha_0(n)$ is the contribution of the nth excited states to the ground state polarizability α_0 and $\alpha_n(m)$ is the contribution of the mth excited states to the nth excited state polarizability α_n. The factor $r(m,n)$ is the ratio of excitation energy E_{mn} to E_{n0}. The first and second terms of Eq. (1) correspond to the type (I) and type (II+III)', respectively. The centrosymmetric system (type (I)=0), whose N value is large and whose $r(m,n)$ is not close to 0 (nondegenerate), tends to exhibit a positive γ value, whereas that with numerous near-degenerate excited states has a possibility of exhibiting not only positive but also negative γvalues. Furthermore, in the limiting case with the smallest N value (N=3), Eq. (1) can be reduced to the three-state three-type approximate formula;[1]

$$\gamma^{(I)+(II)'+(III)'} = \frac{1}{2}\frac{\alpha_0}{E_{n0}}\left(\frac{(\Delta\mu_{n0})^2}{E_{n0}} + \frac{1}{2}\left[\alpha_n r - \alpha_0(1-r)\right]\right), \tag{2}$$

where the first term represents the type (I) and the second term does to the type (II+III)'. The formula shows that the centrosymmetric three state systems have negative γvalues in the case of $[\alpha_n > 0$ and $\alpha_n / \alpha_0 < E_{n0} / E_{mn}]$ or $\alpha_n < 0$. The condition seems to be feasible to be achieved for the centrosymmetric systems with large ground state polarizability $\alpha_0(>\alpha_n)$. Therefore, we investigate three charged states (neutral, ion radical and ion states) of centrosymmetric alternant and condensed-ring conjugated model systems with large polarizability α_0.

First, we have to check the basis set and electron correlation dependences of theγ values in order to choose appropriate size basis sets and correlation methods before calculating the γvalues of alternant and condensed-ring systems. In this end, the γ values of neutral, cation and anion states of allyl are examined with respect to the various basis sets and electron correlation methods. The γvalues are calculated by the finite-field (FF) method using the coupled Hartree-Fock (CHF) + electron correlation (MPn, coupled-cluster(CC)) methods.[15] In the first step, the restricted HF (RHF) and the unrestricted HF (UHF) methods are used for closed and open shell systems, respectively. In this study, the *ab initio* calculations are performed by using GAUSSIAN 92 program package.[16]

Second, as models of alternant and condensed-ring conjugated systems, main components of γvalues for neutral, ion radical and ion states of triafulvalene and pentalene are calculated by the methods selected above. We discuss the results in relation to various charged states, molecular structures and correlation effects.

γ VALUES OF NEUTRAL, CATION AND ANION STATES OF ALLYL

We investigate main components of $\gamma(\gamma_{xxxx})$ for neutral (a), cation (b) and anion (c) states of allyl shown in Figure 1. In the case, according to the three-type approximation, the systems have a possibility to exhibit negative γ_{xxxx} values except positive ones. The geometry of each charged state of allyl is fully optimized by the *ab initio* HF calculations using 6-31G** basis set. The basis sets used for calculations of γ_{xxxx} are STO-3G, 6-31G, 6-31G**, 6-31+G (ζ_{sp}=0.0438), 6-31G+*d* (ζ_d=0.05), 6-31G+*pd* (ζ_p=0.05, ζ_d=0.05) and 6-31G+*pdd* (ζ_p=0.05, ζ_d=0.2, ζ_d=0.05). We also examine the effects of electron correlations on γ_{xxxx} values. The applied correlation methods are MP2, MP3, MP4DQ(including double(D) and quadruple(Q) excitations), MP4SDQ(including single(S), double(D) and quadruple(Q) excitations), MP4SDTQ(including single(S), double(D), triple(T) and quadruple(Q) excitations), CCSD(including single(S) and double(D) excitations) and CCSD(T) (including single(S), double(D) and triple(T) excitations). We use 0.01 a.u. for neutral and cation states, while use 0.005 a.u. for anion states as the minimum electric field (F^x) in the FF method. The γ_{xxxx} value is obtained by the numerical differentiation of total energy E with respect to the field F^x as follows.

$$\gamma_{xxxx} = -\{56E(0) - 39[E(F^x) + E(-F^x)] + 12[E(2F^x) + E(-2F^x)] - [E(3F^x) + E(-3F^x)]\} / 6(F^x)^4 \quad (3)$$

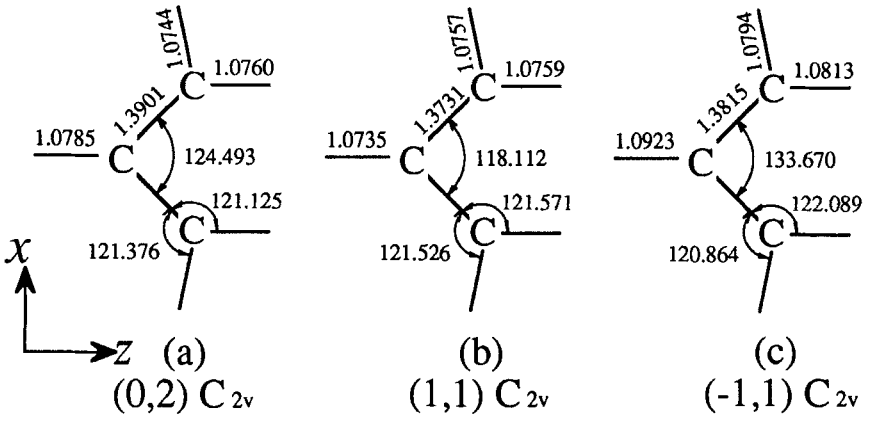

FIGURE 1 Structures of neutral (a), cation (b) and anion (c) allyl systems optimized by *ab initio* HF method using 6-31G**. Bond lengths [Å] and bond angles [°] are shown. Numbers in parentheses depict charge and spin multiplicity, respectively.

Figure 2 shows variations of γ_{xxxx} of neutral (a), cation (b) and anion (c) states of allyl with basis sets and electron correlations. First, as for the neutral allyl (a), the basis sets excluding diffuse *p* and *d* functions (STO-3G, 6-31G and 6-31G**) are found to give small $|\gamma_{xxxx}|$ and exhibit small electron correlation effects on γ values. In contrast, extended basis sets including diffuse *p* and/or *d* functions (6-31+G, 6-31G+*d*, 6-31G+*pd* and 6-31G+*pdd*) provide large $|\gamma_{xxxx}|$ and exhibit similar tendencies of correlation effects with each other. Therefore, it is concluded that variations of $|\gamma|$ with electron correlation effects cannot be reproduced correctly using the basis sets without diffuse *p* and *d* functions. It is also found that the $|\gamma_{xxxx}|$ values increase with the size of basis set till the 6-31G+*pd*(ζ_p=0.05, ζ_d=0.05), while the 6-31G+*pdd* in which the tight *d*(ζ_d=0.2) function is added to the 6-31G+*pd* , tends to fall the $|\gamma_{xxxx}|$ values slightly. The MP2 correlation effects on γ values are found to be largest and be positive in sign. The change of γ_{xxxx} from MP2 to MP4 is found to be small. The effects of S, D and Q excitations decrease the $|\gamma_{xxxx}|$, while those of T increase the $|\gamma_{xxxx}|$ slightly. The CCSD method, in which the S and D excitation effects are included until the infinite order, is found to give considerably smaller $|\gamma_{xxxx}|$ than those of MP4. This suggests that higher-order (beyond the fourth-order) correlation corrections are needed to evaluate the $|\gamma_{xxxx}|$ quantitatively. The $|\gamma_{xxxx}|$ values by CCSD(T) method are shown to be slightly increased against the CCSD method due to the T excitation effects.

Second, the basis set and electron correlation dependences of γ_{xxxx} for allyl cation (b) are examined. As shown in Figure 2, the γ_{xxxx} values by all basis sets and correlation methods are negative in sign in contrast to those of neutral allyl (a). The behaviors of γ_{xxxx} with the correlation effects are all similar regardless of their used basis sets. The differences in the magnitudes of γ_{xxxx} and the tendencies of variations of γ_{xxxx} with the correlation effects are shown to be smaller than those of neutral allyl (a). This seems to be caused by the unnecessity of diffuse *p* and *d* functions in describing cation states. On the other hand, the changes of γ_{xxxx} of allyl cation (b) with electron correlations are much larger than those of neutral allyl (a). It is revealed that the correlation effects contribute to the increase of $|\gamma_{xxxx}|$ from MP2 to MP4DQ, while S and T excitation effects in MP4 contribute to the decrease of $|\gamma_{xxxx}|$. It is also found that the γ_{xxxx} values of CCSD are close to the MP4SDQ values and the CCSD(T) tends to decrease the $|\gamma_{xxxx}|$ due to the T excitation effects. For allyl cation (b), although each order correlation effect is considerably large, the CCSD(T) values are shown to be close to the MP2 values eventually.

Third, the γ_{xxxx} values of allyl anion (c) are investigated. As can be seen from the variations of γ_{xxxx} shown in Figure 2, the basis set dependence is largest among three

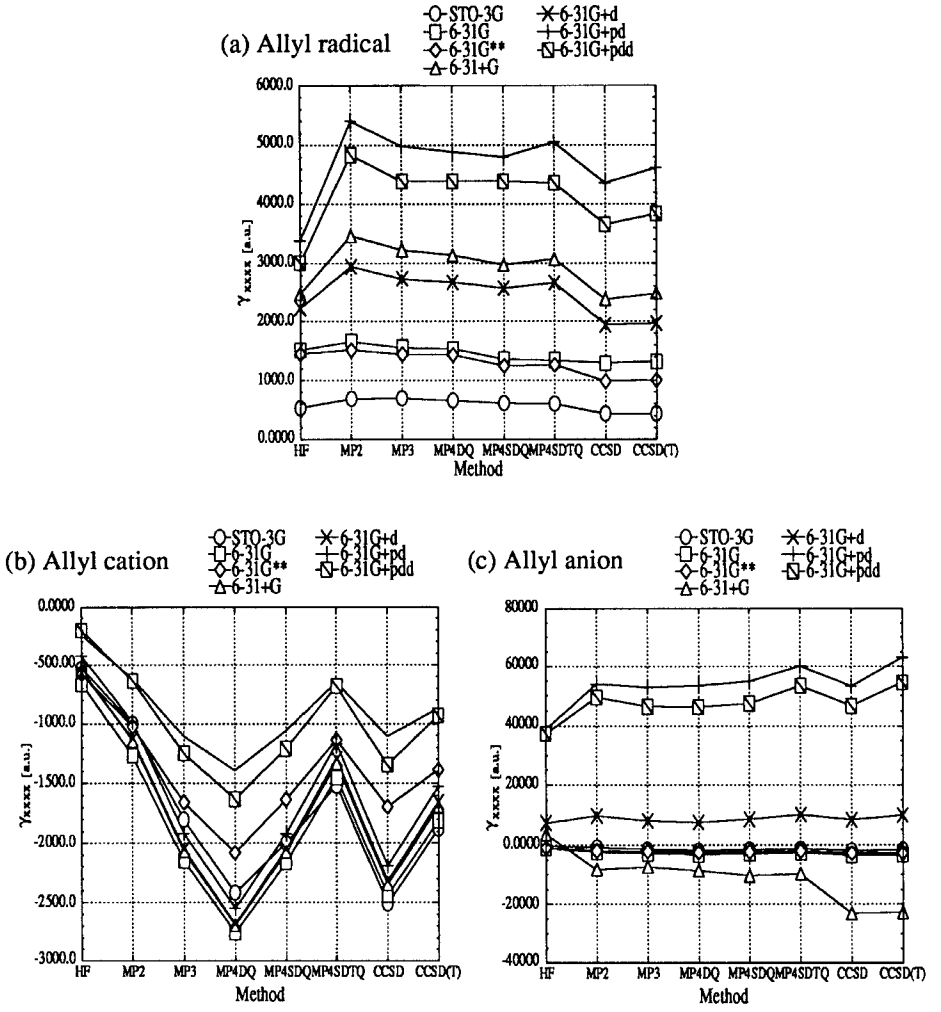

FIGURE 2 Basis set and electron correlation dependences of γ_{xxxx} for neutral (a), cation (b) and anion (c) states of allyl systems.

charged states (a)-(c). This seems to be a result predicted from the necessity of diffuse *p* and/or *d* functions in describing anion states. It is found that the γ_{xxxx} values using the basis sets without both diffuse *p* and *d* functions come to be small negative values and the variations of γ_{xxxx} with correlation effects are also small. Although the 6-31+G basis set is usually available for describing anion states, that is found to be unavailable for

reproducing at least the tendencies of γ values of anion states: the γ_{xxxx} value using 6-31+G at the HF level is shown to give the positive small value, whereas higher-order correlation methods fall off the γ_{xxxx} to negative values. On the other hand, all correlation methods using the 6-31G+*d* are shown to provide the positive γ_{xxxx} values, but the magnitudes of γ_{xxxx} and the correlation effects are relatively small. These results indicate that the extended basis sets only including either diffuse *p* or *d* function cannot provide reasonable tendencies of γ for anion states. The methods using 6-31G+*pd* basis set are found to give sufficiently large $|\gamma_{xxxx}|$ and large electron correlation effects on γ_{xxxx} values. The addition of tight $d(\zeta_d=0.2)$ function tends to slightly decrease the $|\gamma_{xxxx}|$ as well as the case of the neutral allyl (a). It is found that the electron correlation effects are mainly incorporated in the MP2 correction and higher-order correlation effects only provide small changes of γ_{xxxx}.

The γ_{xxxx} values of three charged states of allyl for each basis set are plotted in Figure 3. As shown in the graphs, the double zeta (DZ) type basis set augmented by diffuse *p* and *d* ($\zeta_p=0.05$, $\zeta_d=0.05$) and the MP2 correlation methods must be used at least to describe the relative tendencies of the systems. Particularly, both the diffuse *p* and *d* functions are essential for describing the qualitative tendency of the anion state.

The order in the magnitude of γ_{xxxx} values of allyl systems is obtained as $|\gamma(\text{anion})| >> |\gamma(\text{neutral})| > |\gamma(\text{cation})|$. It is shown that the signs of γ_{xxxx} are positive for neutral (a) and anion (c) states of allyl systems, while the sign of γ_{xxxx} is negative for allyl cation (b). In the next section, the γ values of alternant and condensed-ring conjugated systems are investigated by the use of the MP2 correlation methods using the DZ + diffuse *p* and *d* basis set.

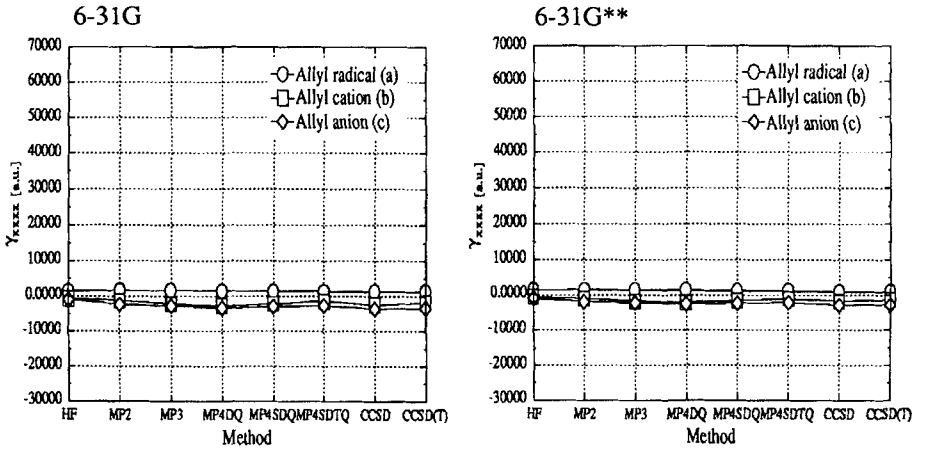

FIGURE 3 Electron correlation dependences of γ_{xxxx} for three charged states (neutral (a), cation (b) and anion (c)) of allyl in each basis set.

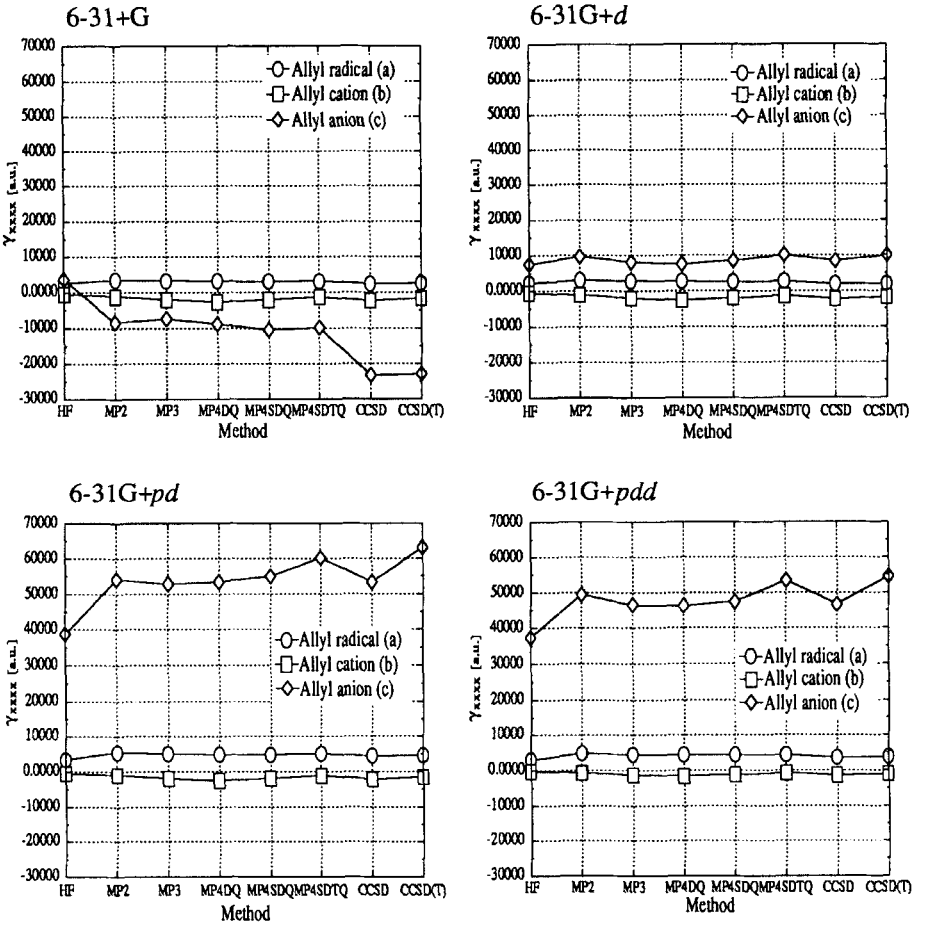

FIGURE 3 (Continued)

MAIN COMPONENTS OF γ FOR ALTERNANT AND CONDENSED-RING CONJUGATED SYSTEMS

Table I gives the static γ_{zzzz} (main component) values of triafulvalene (d) and pentalene (e) shown in Figure 4 calculated by CHF+MP2 method using 6-31G+pd(ζ_p=0.05, ζ_d=0.05) basis set. The geometries for three states (neutral, ion radical and ion states) of the systems are optimized by the HF method using 6-31G** basis set.

The sign of γ_{zzzz} value of cation radical states of triafulvalene (d-2) as a model of alternant conjugated system is shown to be inverted between HF and MP2 methods. For the other charged states (d-1) and (d-3), it is found that the MP2 and HF methods

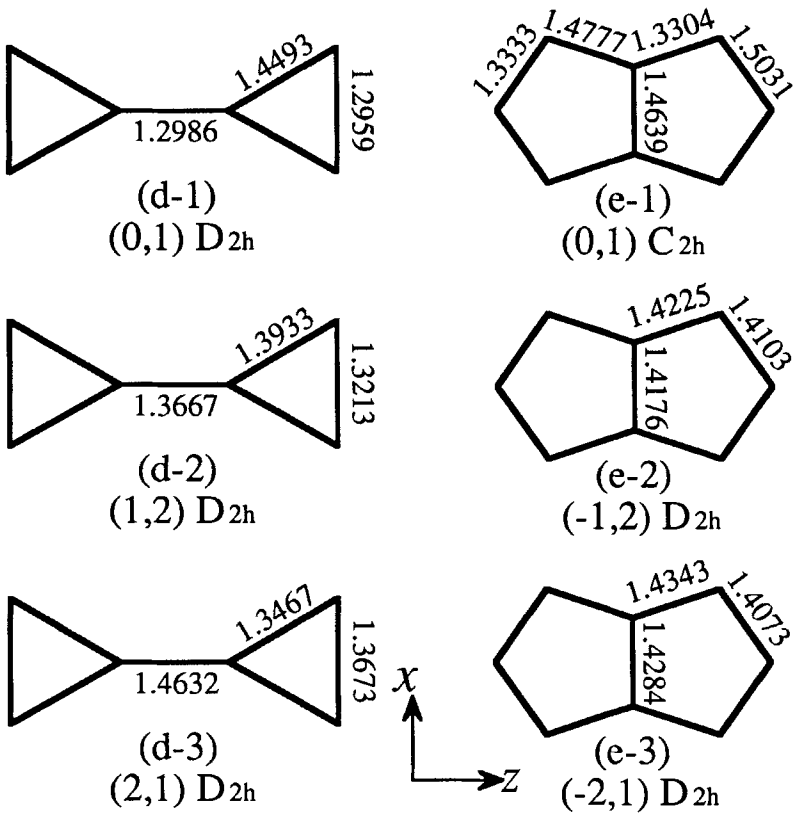

FIGURE 4 Calculated bond lengths [Å] of three charged states (neutral, ion radical and ion) of alternant and condensed-ring cinjugated systems ((d) triafulvalene and (e) pentalene) using 6-31G** . Numbers in parentheses depict charge and spin multiplicity, respectively.

TABLE I γ_{zzzz} [a.u.] values of triafulvalene (d) and pentalene (e) calculated by the HF and MP2 methods using 6-31G+*pd* basis set.

System (charge, multiplicity)	Symmetry	HF	MP2
(d-1) (0,1)	D_{2h}	12000	17300
(d-2) (1,2)	D_{2h}	-12600	10600
(d-3) (2,1)	D_{2h}	866	1390
(e-1) (0,1)	C_{2h}	4350	9330
(e-2) (-1,2)	D_{2h}	-11700	-105000
(e-3) (-2,1)	D_{2h}	177000	329000

give positive γ_{zzzz} values though the magnitudes of γ_{zzzz} are much enhanced in the MP2 in contrast to the HF method. The order in the magnitudes of γ_{zzzz} at the MP2 level is obtained as $|\gamma(\text{neutral})| > |\gamma(\text{cation})| >> |\gamma(\text{dication})|$ which shows that the systems with larger number of electrons possess larger $|\gamma_{zzzz}|$ values.

As for the anion radical states of pentalene (e-2), which is a model of condensed-ring conjugated systems, it is interesting that both the HF and MP2 methods provide negative γ_{zzzz} values. Furthermore, the $|\gamma_{zzzz}|$ values are shown to be extremely enhanced at MP2 level against the HF level. The electron correlation effects are found to be also large for neutral (e-1) and dianion (e-3) states. The order in the magnitudes of γ_{zzzz} is obtained as $|\gamma(\text{dianion})| > |\gamma(\text{anion})| >> |\gamma(\text{neutral})|$. The relations between the magnitude of γ_{zzzz} of pentalene (e) and the number of π-electrons are similar with those of triafulvalene (d).

RESULTS AND DISCUSSION

On the basis of the three-type approximation, the centrosymmetric systems with larger ground state polarizability α_0 than the excited polarizability α_n have a possibility of exhibiting larger negative γ values. In this study, the γ values of neutral, ion radical and ion states of alternant and condensed-ring conjugated systems were examined by the *ab initio* CHF + electron correlation methods using extended basis sets. From the results of neutral (a), cation (b) and anion (c) states of allyl systems, it is found that the double zeta (DZ) + diffuse p and d (ζ_p=0.05, ζ_d=0.05) basis sets are at least necessary for describing the relative tendencies of the three states of allyl systems (a)-(c). For the allyl cation (b), it is found that the electron correlation effects are very large and that the γ_{zzzz} values come to be negative in sign. This seems to be caused by larger mobility of π-electrons of allyl cation (b) due to the resonating-valence states than that of neutral allyl (a), which tends to enhance the type (II) contribution ($\gamma > 0$). On the other hand, for the anion state of allyl (c), the diffuse orbitals are used by the excessive electrons to enhance the polarization in the presence of the external electric field, so that the $|\gamma|$ values are seen to be enlarged where the type (III) (including higher excited states) seems to become important.

From the results by the HF and MP2 calculations of alternant and condensed-ring conjugated systems (triafulvalene (d) and pentalene (e)), the electron correlation effects on γ_{zzzz} (main component) values are found to be extremely large for ion radical systems (d-2) and (e-2); the sign of γ for cation radical state of triafulvalene (d-2) is inverted between HF and MP2 methods, while the magnitude of γ dramatically

increase for the anion radical states of pentalene (e-2). The behaviors of γ seem to be due to the mobility of electrons as well as the case of allyl cation (b). However, the γ_{xxxx} value of cation radical state of triafulvalene (d-2) is not negative in sign in contrast to that of anion radical state of pentalene (e-2). Therefore, we must perform the *ab initio* calculations with higher-order electron correlation corrections (beyond the second-order ones) in order to confirm the tendencies of γ for alternant and condensed-ring conjugated systems. Particularly, the condensed-ring systems are very interesting since they are involved in fullerenes. From the results obtained here, the poly anion radical states of fullerenes ,*e.g.*, C_{60}^{n-} and C_{70}^{n-}, are expected to possess large negative γ values and exhibit large correlation effects on γ values. In order to confirm the predictions, *ab initio* calculations with the moderate-size extended basis sets (DZ + diffuse *p* and *d*) including the MP and CC correlations for large-size alternant and condensed-ring conjugated systems will be also performed in the next paper II.

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