

Molecular Design for Organic Nonlinear Optics: Polarizability and Hyperpolarizabilities of Furan Homologues Investigated by Ab Initio Molecular Orbital Method[†]

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Static polarizabilities and hyperpolarizabilities have been calculated for the furan homologues including furan (C₄H₄O), thiophene (C₄H₄S), selenophene (C₄H₄Se), and tellurophene (C₄H₄Te), at the Hartree–Fock and various correlation levels by ab initio molecular orbital methods. The influence of substitution with heavy atoms on the molecular properties of the homologues was examined theoretically. In the calculations for molecules with Se and Te atoms, the contribution of core electrons in the atoms was estimated using effective core potential (ECP) methods. With the calculation for the thiophene molecule, effectiveness of the use of the ECP method was examined, and the ECP method was found to give the (hyper)polarizability values similar to those obtained considering all electrons for the molecule. The calculated results show that substitution of the heteroatom with heavy atoms systematically increases the individual components of the polarizability, α , and second hyperpolarizability, γ . On the other hand, this does not give systematic variations on the first hyperpolarizability, β . The variation of these values depending on the homologues was examined in terms of the perturbation expansion formula and was explained by the energy levels of the electronic excited states in the valence states. The second hyperpolarizability values calculated, including electron correlation effect, are well correlated with the observed electronic components of nonlinear optical susceptibilities, $\chi^{(3)}$, obtained using optical Kerr effect experiments, which have been done in our laboratory. However, some discrepancy is observed between the theoretical and the experimental values for the homologues with heavier heteroatoms. Possible causes for the discrepancy are discussed in detail.

1. Introduction

In the past decade, advances in computer technology and methodology of molecular orbital (MO) calculation make it possible to calculate response properties due to higher-order perturbation in molecular systems within a realistic computation time. Studies on MO calculation of first and second hyperpolarizabilities have been performed extensively with increasing importance of molecular nonlinear optics for laser wavelength conversion, ultrafast electrooptical and optical–optical switching, and basic research of optical physics. MO calculation can be a good tool for obtaining some insight into molecular property; each tensor component of hyperpolarizability can be assessed directly, unlike optical experiments in which the property is obtained as macroscopic quantity. Usually, a macroscopic quantity cannot be directly converted to a microscopic one due to intermolecular or collective effects. Therefore, calculation of molecular hyperpolarizabilities and comparison of the results with corresponding experimental results are of importance in establishing the structure–property relationship and estimating the amount of such effects on molecular optical nonlinearity.

Furan and its homologues, such as thiophene, selenophene, and tellurophene, are an important series of molecules with regard to organic nonlinear optical materials. They are the simplest five-membered cycles with a π -electron system and a hetero (non-carbon) atom in their rings. Effects of the extended π -electron conjugation system on third-order optical nonlinearity have been extensively studied for thiophene and its oligomers and polymers by several research groups.¹ On the other hand, the heteroatom in the five-membered ring provides π electrons to its conjugation system, and therefore, in addition to the difference in binding energy of valence electrons, the heteroatom with different electronegativity modulates the π -electron system, which must influence its polarizability and hyperpolarizabilities.

We have been interested in the role of the heteroatom in the conjugation ring and its effect on nonlinear optical properties.^{2,3} We have extensively studied the ultrafast third-order nonlinear optical responses for several furan homologues by optically heterodyned optical Kerr effect (OHD-OKE) experiments.^{4–8} The third-order responses are known to consist of several contributions arising from distinct physical origins, such as electronic third-order nonlinear polarization and light-induced polarizability changes coupling with several inter- and intramolecular modes of nuclear motion. We have focused on quantitatively separating the third-order responses into the individual physical processes^{4–7} and extracted the contributions originating from electronic nonlinear polarization.⁶ The separated electronic contributions are the quantities that correspond to the second

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hyperpolarizability obtained by MO calculations. On the other hand, we have searched for an appropriate approximation level for calculating the second hyperpolarizability of organic molecules by ab initio MO method.⁹ For the carbon disulfide molecule, we have made comprehensive ab initio calculations at the various correlation levels.¹⁰ We previously presented our results of comparison between the experimentally obtained electronic contributions and our preliminary MO calculations, to elucidate the effects of heteroatoms (X) on their third-order nonlinearity in terms of heavy atom substitution.^{6,11}

In this article, we present the complete results of our ab initio calculation on heavy-atom substitution of furan homologues (C₄H₄X) for furan (X = O), thiophene (X = S), selenophene (X = Se), and tellurophene (X = Te). The calculation results, in various correlation levels, for (linear) polarizability and first and second hyperpolarizabilities are presented. Comparison of orientational-averaged second hyperpolarizability data with the experimental results is also shown. Differences between the calculations and the experiments, with regard to convention of hyperpolarizability and physical processes, were fully considered prior to the comparison.

2. Calculation Method

Polarizability and hyperpolarizability are defined throughout this article as coefficients of the next Taylor expansion of the total electric dipole moment, μ_{total} , with respect to the applied electric field, F

$$\mu_{\text{total}} = \mu + \alpha F + \beta FF/2 + \gamma FFF/6 + \dots \quad (1)$$

where μ is the permanent electric dipole moment, α is the linear polarizability, β is the first hyperpolarizability, and γ is the second hyperpolarizability. Accordingly, the total energy $E(F)$ under the electric field, F , can be expressed by

$$E(F) = E(0) - \mu F - \alpha FF/2 - \beta FFF/6 - \gamma FFFF/24 - \dots \quad (2)$$

Here, we describe the calculation method used in this study. The Gaussian 92 program¹² was used for ab initio molecular orbital calculations throughout this study. The polarizability, α , and first hyperpolarizability, β , at the Hartree–Fock (HF) level are readily obtained by the coupled perturbed HF (CPHF) method with the optional routine of the Gaussian program. As described in the previous papers,^{9,11} the static second hyperpolarizability, γ , at the HF level can be calculated by the finite-field (FF) methods using the following equation for the numerical first-order derivative of the first hyperpolarizability values, β

$$\gamma_{ijj} = [45\{\beta_{ijj}(F_j) - \beta_{ijj}(-F_j)\} - 9\{\beta_{ijj}(2F_j) - \beta_{ijj}(-2F_j)\} + \{\beta_{ijj}(F_j) - \beta_{ijj}(-F_j)\}]/60F_j \quad (3)$$

with $i, j = x, y, z$. Individual $\beta_{ijj}(F_j)$ values can be obtained by the routine in the Gaussian program under the application of a uniform electric field on a molecule. In this case, the minimum finite electric field value, F_j , was set at 0.0025 atomic units (au).⁹

Other than the HF method, the electron-correlation effects on the properties were also examined by a variety of theoretical models, including Møller–Plesset (MP n , $n = 2-4$) and coupled cluster (CC) methods, where we considered contributions from different excitation types. For this purpose, the individual components of the μ , α , β , and γ values at the correlation calculations were obtained by using the following equations for

the numerical first-, second-, third-, and fourth-derivatives, respectively, of the total energy, E , when applying the uniform finite electric field on the molecule.

$$\mu_i = -[45\{E(F_i) - E(-F_i)\} - 9\{E(2F_i) - E(-2F_i)\} + \{E(3F_i) - E(-3F_i)\}]/60F_i \quad (4)$$

$$\alpha_{ii} = [490E(0) - 270\{E(F_i) + E(-F_i)\} + 27\{E(2F_i) + E(-2F_i)\} - 2\{E(3F_i) + E(-3F_i)\}]/180F_i^2 \quad (5)$$

$$\beta_{iii} = [13\{E(F_i) - E(-F_i)\} - 8\{E(2F_i) - E(-2F_i)\} + \{E(3F_i) - E(-3F_i)\}]/8F_i^3 \quad (6)$$

$$\begin{aligned} \beta_{ijj} = & [38\{E(F_j) - E(-F_j)\} - 4\{E(2F_j) - E(-2F_j)\} - \\ & 20\{E(F_i, F_j) - E(F_i, -F_j) + E(-F_i, F_j) - E(-F_i, -F_j)\} + \\ & \{E(2F_i, F_j) - E(2F_i, -F_j) + E(-2F_i, F_j) - E(-2F_i, -F_j)\} + \\ & 2\{E(F_i, 2F_j) - E(F_i, -2F_j) + E(-F_i, 2F_j) - \\ & E(-F_i, -2F_j)\}]/24F_i^2 F_j \quad (7) \end{aligned}$$

$$\gamma_{iiii} = -[56E(0) - 39\{E(F_i) + E(-F_i)\} + 12\{E(2F_i) + E(-2F_i)\} - \{E(3F_i) + E(-3F_i)\}]/6F_i^4 \quad (8)$$

$$\begin{aligned} \gamma_{ijij} = & -[72E(0) - 38\{E(F_i) + E(-F_i) + E(F_j) + \\ & E(-F_j)\} + 2\{E(2F_i) + E(-2F_i) + E(2F_j) + E(-2F_j)\} + \\ & 20\{E(F_i, F_j) + E(F_i, -F_j) + E(-F_i, F_j) + E(-F_i, -F_j)\} - \\ & \{E(2F_i, F_j) + E(2F_i, -F_j) + E(-2F_i, F_j) + E(-2F_i, -F_j) + \\ & E(F_i, 2F_j) + E(F_i, -2F_j) + E(-F_i, 2F_j) + \\ & E(-F_i, -2F_j)\}]/12F_i^2 F_j^2 \quad (9) \end{aligned}$$

with $i, j = x, y, z$. In this case, the minimum finite electric field values F_i and F_j were set at 0.005 atomic units.^{10,11}

Basis sets used for the furan and thiophene molecules in the present calculation were the 6-31G+*pd*, 6-31G+*pdd*, and 6-31G(3*d*)+*pd* used in the previous calculations, where the standard orbital exponents were used for the (3*d*) polarization functions.^{10,11} Because the computation time for the calculations considering all electrons becomes unrealistic for selenophene and tellurophene molecules, all of the values were estimated by substituting the effect of the inner electrons of selenium and tellurium atoms with the effective core potential (ECP), thereby minimizing computation time. Generally, valence electrons in outer regions of the molecules, rather than inner electrons, have been considered to play more essential roles for polarizability and hyperpolarizability. This gives a firm basis for the validity of using the ECP method for calculation of (hyper)polarizability. However, there have been few studies on the effectiveness of the ECP method for calculation of those electric response properties.^{13,14} In this study, the LANL1DZ+*pd* and LANL1DZ+*pdd* sets were used for selenium and tellurium atoms in the selenophene and tellurophene molecules.^{11,15,16}

To examine the effectiveness of the ECP methods, the calculation results were compared for both methods using ECP with LANL1DZ+*pd* and the all-electron method with 6-31G+*pd* for the sulfur atom in the calculation of thiophene. Later, good agreement will be shown by comparison of the second hyperpolarizability values.

The orbital exponents of the augmented diffuse orbitals were determined by the same procedure as previously described.^{11,15} The molecular geometries used for the correlation calculations

TABLE 1: Total Energy, Dipole Moment, and Individual Components of the Polarizability of Furan (C_4H_4O) Calculated with 6-31G+*pd*, 6-31G+*pdd*, and 6-31G(3*d*)+*pd* Basis Sets^a

| method | $E(+228)$ | μ_z | α_{xx} | α_{yy} | α_{zz} | α_s | $\Delta\alpha$ |
|-------------------------------|------------|----------------|---------------|---------------|---------------|---------------|----------------|
| 6-31G+ <i>pd</i> | | | | | | | |
| HF | -0.5342479 | 0.49688 (1.00) | 50.529 (1.00) | 30.064 (1.00) | 49.333 (1.00) | 43.309 (1.00) | 19.894 |
| MP2 | -1.0235976 | 0.40578 (0.82) | 52.283 (1.03) | 31.738 (1.06) | 49.359 (1.00) | 44.460 (1.03) | 19.250 |
| MP3 | -1.0346875 | 0.44267 (0.89) | 50.598 (1.00) | 30.950 (1.03) | 48.522 (0.98) | 43.357 (1.00) | 18.697 |
| MP4D | -1.0493643 | 0.45066 (0.91) | 49.874 (0.99) | 30.650 (1.02) | 48.661 (0.99) | 43.062 (0.99) | 18.647 |
| MP4DQ | -1.0426824 | 0.44672 (0.90) | 50.085 (0.99) | 30.752 (1.02) | 48.521 (0.98) | 43.119 (1.00) | 18.600 |
| MP4SDQ | -1.0495741 | 0.43764 (0.88) | 50.799 (1.01) | 31.091 (1.03) | 49.333 (1.00) | 43.741 (1.01) | 19.017 |
| MP4SDTQ | -1.0698813 | 0.42212 (0.85) | 51.801 (1.03) | 31.596 (1.05) | 49.009 (0.99) | 44.135 (1.02) | 18.964 |
| CCSD | -1.0505391 | 0.44689 (0.90) | 50.705 (1.00) | 30.911 (1.03) | 49.135 (1.00) | 43.583 (1.01) | 19.058 |
| CCSD(T) | -1.0695950 | 0.43138 (0.87) | 51.662 (1.02) | 31.438 (1.05) | 49.532 (1.00) | 44.211 (1.02) | 19.248 |
| 6-31G+ <i>pdd</i> | | | | | | | |
| HF | -0.5609546 | 0.38512 (1.00) | 53.862 (1.00) | 33.962 (1.00) | 51.015 (1.00) | 46.280 (1.00) | 18.640 |
| MP2 | -1.1234617 | 0.30503 (0.79) | 56.024 (1.04) | 35.459 (1.04) | 51.689 (1.01) | 47.724 (1.03) | 18.777 |
| MP3 | -1.1345532 | 0.33361 (0.87) | 54.251 (1.01) | 34.651 (1.02) | 50.813 (1.00) | 46.572 (1.01) | 18.127 |
| MP4D | -1.1503679 | 0.34461 (0.89) | 53.610 (1.00) | 34.352 (1.01) | 50.952 (1.00) | 46.304 (1.00) | 18.076 |
| MP4DQ | -1.1398543 | 0.33926 (0.88) | 53.842 (1.00) | 34.462 (1.01) | 50.852 (1.00) | 46.385 (1.00) | 18.071 |
| MP4SDQ | -1.1476175 | 0.33139 (0.86) | 54.527 (1.01) | 34.729 (1.02) | 51.623 (1.01) | 46.960 (1.01) | 18.518 |
| MP4SDTQ | -1.1744062 | 0.31479 (0.82) | 55.512 (1.03) | 35.285 (1.04) | 51.372 (1.01) | 47.390 (1.02) | 18.508 |
| CCSD | -1.1474087 | 0.33635 (0.87) | 54.436 (1.01) | 34.603 (1.02) | 51.423 (1.01) | 46.821 (1.01) | 18.511 |
| CCSD(T) | -1.1723771 | 0.32207 (0.84) | 55.369 (1.03) | 35.067 (1.03) | 51.842 (1.02) | 47.426 (1.02) | 18.788 |
| 6-31G(3 <i>d</i>)+ <i>pd</i> | | | | | | | |
| HF | -0.6447448 | 0.27928 (1.00) | 53.493 (1.00) | 34.282 (1.00) | 50.648 (1.00) | 46.141 (1.00) | 17.958 |
| MP2 | -1.4417216 | 0.23504 (0.84) | 55.673 (1.04) | 34.985 (1.02) | 51.104 (1.01) | 47.254 (1.02) | 18.824 |
| MP3 | -1.4559601 | 0.25435 (0.91) | 53.878 (1.01) | 34.080 (0.99) | 50.426 (1.00) | 46.128 (1.00) | 18.318 |
| MP4D | -1.4740384 | 0.26532 (0.95) | 53.305 (1.00) | 33.862 (0.99) | 50.585 (1.00) | 45.917 (1.00) | 18.236 |
| MP4DQ | -1.4536311 | 0.25971 (0.93) | 53.607 (1.00) | 33.960 (0.99) | 50.520 (1.00) | 46.029 (1.00) | 18.300 |
| MP4SDQ | -1.4624393 | 0.25158 (0.90) | 54.086 (1.01) | 34.134 (1.00) | 51.010 (1.01) | 46.410 (1.01) | 18.606 |
| MP4SDTQ | -1.5023428 | 0.23625 (0.85) | 55.128 (1.03) | 34.666 (1.01) | 50.858 (1.00) | 46.884 (1.02) | 18.696 |
| CCSD | -1.4615109 | 0.25367 (0.91) | 54.101 (1.01) | 34.124 (1.00) | 50.923 (1.01) | 46.383 (1.01) | 18.593 |
| CCSD(T) | -1.4980768 | 0.24150 (0.86) | 54.900 (1.03) | 34.479 (1.01) | 51.254 (1.01) | 46.878 (1.02) | 18.864 |

^a Numbers in parentheses are ratios to the Hartree–Fock values (atomic units).

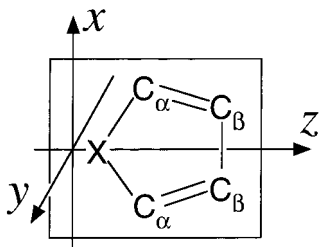


Figure 1. Molecular fixed Cartesian coordinates used in the present calculation for furan homologues C_4H_4X ($X = O, S, Se, Te$).

were those optimized by the HF method for each basis set unless otherwise described. The optimized geometries have C_{2v} symmetry for all of the basis sets used for the four molecules. The optimized geometries are summarized in Table 1S of the Supporting Information. The molecular coordinates used for representing the tensor components are given in Figure 1.

3. Results and Discussion

3.1. Dipole Moment, μ , and Polarizability, α . Because both the dipole moment, μ , and the linear polarizability, α , are the most fundamental electric response properties, calculation of these values has provided a good basis for discussing the reliability of the calculation of the electronic states with various theoretical models in the field of quantum chemistry.^{17,18} Recently, Christiansen et al.¹⁹ discussed the polarizability of the furan molecule with highly sophisticated approximation methods. Here, prior to our later detailed discussions of second hyperpolarizability, we briefly mention the calculation results of the dipole moment and polarizability with the approximation levels used in the present study. Tables 1–4 show the results for the dipole moment and polarizability of the homologues.

The orientationally averaged value of the polarizability, α_s , and anisotropy, $\Delta\alpha$, in the tables are defined as the following equations

$$\alpha_s = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3 \quad (10)$$

$$\Delta\alpha = [(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2]/2]^{1/2} \quad (11)$$

The tables show that the absolute values of the dipole moment decrease with the larger basis set, irrespective of the molecules. Similarly, the absolute values become smaller with inclusion of the electronic correlation of higher levels. This means that the wave functions at lower approximation tend to overestimate the charge separation in a molecule for the homologues. Table 5 shows the results from the CCSD(T) method, which can be considered the closest approximation within the theoretical models used in the present study, with presently available experimental values.

For the calculation of dipole moment, both the basis set and electronic correlation are important to produce the most accurate results. On the contrary, for the calculation of polarizability, the selection of the basis set is more essential as revealed for several organic molecules previously.⁹ The effect of the electron correlation is at most 5% even at the individual component level. It is expected that selection of better basis sets will make the effect of the electron correlation less than that found for the present results.

The experimental values of the refractive indices are chosen to be compared with the present results of polarizability of the homologues. The physical constants necessary for obtaining the experimental polarizabilities from the refractive indices are summarized in Table 6. Table 7 shows the comparison of the

TABLE 2: Total Energy, Dipole Moment, and Individual Components of the Polarizability of Thiophene (C₄H₄S) Calculated with 6-31G+*pd*, 6-31G+*pdd*, and 6-31G(3*d*)+*pd* Basis Sets^a

| method | $E(+551)$ | μ_z | α_{xx} | α_{yy} | α_{zz} | α_s | $\Delta\alpha$ |
|-------------------------------|------------|----------------|---------------|---------------|---------------|---------------|----------------|
| 6-31G+ <i>pd</i> | | | | | | | |
| HF | -0.1976793 | 0.52654 (1.00) | 62.997 (1.00) | 37.613 (1.00) | 71.456 (1.00) | 57.355 (1.00) | 30.506 |
| MP2 | -0.6266174 | 0.36008 (0.68) | 65.469 (1.04) | 40.449 (1.08) | 72.674 (1.02) | 59.531 (1.04) | 29.295 |
| MP3 | -0.6463825 | 0.40506 (0.77) | 63.477 (1.01) | 39.698 (1.06) | 71.801 (1.00) | 58.325 (1.02) | 28.856 |
| MP4D | -0.6595226 | 0.41799 (0.79) | 62.888 (1.00) | 39.389 (1.05) | 71.671 (1.00) | 57.983 (1.01) | 28.909 |
| MP4DQ | -0.6525936 | 0.41243 (0.78) | 63.069 (1.00) | 39.529 (1.05) | 71.595 (1.00) | 58.065 (1.01) | 28.767 |
| MP4SDQ | -0.6578317 | 0.40565 (0.77) | 63.865 (1.01) | 39.851 (1.06) | 72.508 (1.01) | 58.741 (1.02) | 29.307 |
| MP4SDTQ | -0.6761493 | 0.38041 (0.72) | 64.862 (1.03) | 40.419 (1.07) | 72.469 (1.01) | 59.250 (1.03) | 29.005 |
| CCSD | -0.6600535 | 0.41733 (0.79) | 63.708 (1.01) | 39.762 (1.06) | 72.316 (1.01) | 58.595 (1.02) | 29.217 |
| CCSD(T) | -0.6779664 | 0.40014 (0.76) | 64.800 (1.03) | 40.379 (1.07) | 72.929 (1.02) | 59.369 (1.04) | 29.343 |
| 6-31G+ <i>pdd</i> | | | | | | | |
| HF | -0.2174462 | 0.47007 (1.00) | 66.920 (1.00) | 43.601 (1.00) | 75.173 (1.00) | 61.898 (1.00) | 28.361 |
| MP2 | -0.7408605 | 0.32566 (0.69) | 70.049 (1.05) | 45.990 (1.05) | 77.108 (1.03) | 64.383 (1.04) | 28.258 |
| MP3 | -0.7604607 | 0.37208 (0.79) | 67.891 (1.01) | 45.188 (1.04) | 76.236 (1.01) | 63.105 (1.02) | 27.830 |
| MP4D | -0.7755711 | 0.38244 (0.81) | 67.393 (1.01) | 44.891 (1.03) | 76.106 (1.01) | 62.796 (1.01) | 27.898 |
| MP4DQ | -0.7637777 | 0.37648 (0.80) | 67.624 (1.01) | 45.041 (1.03) | 76.107 (1.01) | 62.924 (1.02) | 27.812 |
| MP4SDQ | -0.7697725 | 0.37097 (0.79) | 68.329 (1.02) | 45.245 (1.04) | 76.904 (1.02) | 63.493 (1.03) | 28.361 |
| MP4SDTQ | -0.7958017 | 0.34832 (0.74) | 69.341 (1.04) | 45.870 (1.05) | 76.972 (1.02) | 64.061 (1.03) | 28.075 |
| CCSD | -0.7705621 | 0.37717 (0.80) | 68.172 (1.02) | 45.162 (1.04) | 76.731 (1.02) | 63.355 (1.02) | 28.278 |
| CCSD(T) | -0.7955160 | 0.36190 (0.77) | 69.211 (1.03) | 45.667 (1.05) | 77.343 (1.03) | 64.074 (1.04) | 28.494 |
| 6-31G(3 <i>d</i>)+ <i>pd</i> | | | | | | | |
| HF | -0.3079695 | 0.31166 (1.00) | 66.086 (1.00) | 43.803 (1.00) | 74.406 (1.00) | 61.432 (1.00) | 27.407 |
| MP2 | -1.0989340 | 0.20930 (0.67) | 69.030 (1.04) | 44.900 (1.03) | 75.622 (1.02) | 63.184 (1.03) | 28.014 |
| MP3 | -1.1206086 | 0.23998 (0.77) | 66.876 (1.01) | 43.987 (1.00) | 74.873 (1.01) | 61.912 (1.01) | 27.765 |
| MP4D | -1.1394512 | 0.24680 (0.79) | 66.426 (1.01) | 43.844 (1.00) | 74.825 (1.01) | 61.698 (1.00) | 27.752 |
| MP4DQ | -1.1170814 | 0.24044 (0.77) | 66.754 (1.01) | 43.954 (1.00) | 74.869 (1.01) | 61.859 (1.01) | 27.762 |
| MP4SDQ | -1.1249167 | 0.23867 (0.77) | 67.184 (1.02) | 44.051 (1.01) | 75.306 (1.01) | 62.180 (1.01) | 28.089 |
| MP4SDTQ | -1.1669358 | 0.21832 (0.70) | 68.321 (1.03) | 44.615 (1.02) | 75.496 (1.01) | 62.811 (1.02) | 27.992 |

^a Numbers in parentheses are ratios to the Hartree–Fock values (atomic units).

TABLE 3: Total Energy, Dipole Moment, and Individual Components of the Polarizability of Selenophene (C₄H₄Se) Calculated with 6-31G+*pd* and 6-31G+*pdd* Basis Sets and ECP Methods^a

| method | $E(+162)$ | μ_z | α_{xx} | α_{yy} | α_{zz} | α_s | $\Delta\alpha$ |
|--|------------|----------------|---------------|---------------|---------------|---------------|----------------|
| 6-31G+ <i>pd</i> for C, ECP (LANL1DZ+ <i>pd</i>) for Se | | | | | | | |
| HF | -0.7243520 | 0.40362 (1.00) | 68.202 (1.00) | 42.324 (1.00) | 81.091 (1.00) | 63.872 (1.00) | 34.196 |
| MP2 | -1.1368962 | 0.23565 (0.58) | 70.972 (1.04) | 45.637 (1.08) | 82.679 (1.02) | 66.429 (1.04) | 32.795 |
| MP3 | -1.1566843 | 0.27791 (0.69) | 68.905 (1.01) | 45.016 (1.06) | 81.754 (1.01) | 65.225 (1.02) | 32.291 |
| MP4D | -1.1700915 | 0.28813 (0.71) | 68.340 (1.00) | 44.704 (1.06) | 81.549 (1.01) | 64.864 (1.02) | 32.332 |
| MP4DQ | -1.1634251 | 0.28443 (0.70) | 68.525 (1.00) | 44.875 (1.06) | 81.499 (1.01) | 64.966 (1.02) | 32.163 |
| MP4SDQ | -1.1686540 | 0.27841 (0.69) | 69.363 (1.02) | 45.196 (1.07) | 82.512 (1.02) | 65.690 (1.03) | 32.783 |
| MP4SDTQ | -1.1867122 | 0.25506 (0.63) | 70.378 (1.03) | 45.781 (1.08) | 82.551 (1.02) | 66.237 (1.04) | 32.444 |
| CCSD | -1.1710329 | 0.28968 (0.72) | 69.190 (1.01) | 45.159 (1.07) | 82.288 (1.01) | 65.546 (1.03) | 32.616 |
| CCSD(T) | -1.1887547 | 0.27386 (0.68) | 70.358 (1.03) | 45.834 (1.08) | 83.039 (1.02) | 66.410 (1.04) | 32.760 |
| 6-31G+ <i>pdd</i> for C, ECP (LANL1DZ+ <i>pdd</i>) for Se | | | | | | | |
| HF | -0.7452576 | 0.36884 (1.00) | 72.060 (1.00) | 49.004 (1.00) | 85.536 (1.00) | 68.867 (1.00) | 31.998 |
| MP2 | -1.2497224 | 0.19084 (0.52) | 75.500 (1.05) | 51.712 (1.06) | 87.875 (1.03) | 71.696 (1.04) | 31.834 |
| MP3 | -1.2696440 | 0.24102 (0.65) | 73.266 (1.02) | 51.021 (1.04) | 86.950 (1.02) | 70.413 (1.02) | 31.408 |
| MP4D | -1.2849884 | 0.25088 (0.68) | 72.783 (1.01) | 50.709 (1.03) | 86.755 (1.01) | 70.082 (1.02) | 31.479 |
| MP4DQ | -1.2734982 | 0.24547 (0.67) | 73.028 (1.01) | 50.892 (1.04) | 86.799 (1.01) | 70.239 (1.02) | 31.376 |
| MP4SDQ | -1.2794134 | 0.23924 (0.65) | 73.769 (1.02) | 51.090 (1.04) | 87.667 (1.02) | 70.842 (1.03) | 31.979 |
| MP4SDTQ | -1.3049552 | 0.21589 (0.59) | 74.799 (1.04) | 51.734 (1.06) | 87.831 (1.03) | 71.455 (1.04) | 31.661 |
| CCSD | -1.2803175 | 0.24553 (0.67) | 73.606 (1.02) | 51.026 (1.04) | 87.491 (1.02) | 70.708 (1.03) | 31.877 |
| CCSD(T) | -1.3048838 | 0.22985 (0.62) | 74.717 (1.04) | 51.571 (1.05) | 88.251 (1.03) | 71.513 (1.04) | 32.127 |

^a Numbers in parentheses are ratios to the Hartree–Fock values (atomic units).

orientationally averaged α_s values by the present CCSD(T) method with experimental values obtained from refractive indices by using the Lorentz–Lorenz eq (12)

$$(n^2 - 1)/(n^2 + 2) = 4\pi N_A d\alpha_s / 3M_w \quad (12)$$

where n is the refractive index, N_A is Avogadro's number, d is the density, and M_w is the molecular weight. The agreement is excellent despite the presence of the frequency dispersion in the experimental refractive indices.

Basically, results of the present calculation well-reproduce the observed values for both the dipole moment and polariz-

ability, and the approximation level of the present calculation is sufficient to reproduce those observed values.

The anisotropy of the polarizability has been measured by the depolarization of Rayleigh or Raman scattering.²⁰ Recently, it has been recognized that the third-order nonlinear susceptibility, $\chi^{(3)}$, obtained by DFWM method using a laser with a pulse width larger than picosecond level is directly related to the anisotropy of the polarizability, $\Delta\alpha$, originating from the molecular reorientation.^{15,21} This effect is the dominant contribution to the $\chi^{(3)}$ values observed for the anisotropic molecule. Keshari et al.²² previously compared the experimental $\chi^{(3)}$ values obtained by a DFWM method using picosecond laser with the

TABLE 4: Total Energy, Dipole Moment, and Individual Components of the Polarizability of Tellurophene (C₄H₄Te) Calculated with 6-31G+*pd* and 6-31G+*pdd* Basis Sets and ECP Methods^a

| method | <i>E</i> (+161) | μ_z | α_{xx} | α_{yy} | α_{zz} | α_s | $\Delta\alpha$ |
|--|-----------------|----------------|---------------|---------------|----------------|---------------|----------------|
| 6-31G+ <i>pd</i> for C, ECP (LANL1DZ+ <i>pd</i>) for Te | | | | | | | |
| HF | -0.5537462 | 0.18099 (1.00) | 77.818 (1.00) | 53.047 (1.00) | 97.832 (1.00) | 76.232 (1.00) | 38.858 |
| MP2 | -0.9653664 | 0.04120 (0.23) | 81.171 (1.04) | 57.295 (1.08) | 100.544 (1.03) | 79.670 (1.05) | 37.522 |
| MP3 | -0.9842054 | 0.07962 (0.44) | 78.972 (1.01) | 56.859 (1.07) | 99.219 (1.01) | 78.350 (1.03) | 36.697 |
| MP4D | -0.9979667 | 0.08626 (0.48) | 78.372 (1.01) | 56.515 (1.07) | 98.858 (1.01) | 77.915 (1.02) | 36.677 |
| MP4DQ | -0.9912649 | 0.08565 (0.47) | 78.598 (1.01) | 56.755 (1.07) | 98.882 (1.01) | 78.078 (1.02) | 36.491 |
| MP4SDQ | -0.9967215 | 0.07913 (0.44) | 79.543 (1.02) | 57.105 (1.08) | 100.134 (1.02) | 78.927 (1.04) | 37.276 |
| MP4SDTQ | -1.0150967 | 0.05970 (0.33) | 80.633 (1.04) | 57.724 (1.09) | 100.376 (1.03) | 79.578 (1.04) | 36.972 |
| CCSD | -0.9993258 | 0.08865 (0.49) | 79.353 (1.02) | 57.139 (1.08) | 99.800 (1.02) | 78.764 (1.03) | 36.956 |
| CCSD(T) | -1.0174406 | 0.07502 (0.41) | 80.678 (1.04) | 57.924 (1.09) | 100.853 (1.03) | 79.818 (1.05) | 37.200 |
| 6-31G+ <i>pdd</i> for C, ECP (LANL1DZ+ <i>pdd</i>) for Te | | | | | | | |
| HF | -0.5704348 | 0.21104 (1.00) | 81.929 (1.00) | 60.367 (1.00) | 103.959 (1.00) | 82.085 (1.00) | 37.753 |
| MP2 | -1.0753054 | 0.02939 (0.14) | 85.722 (1.05) | 63.413 (1.05) | 107.446 (1.03) | 85.527 (1.04) | 38.135 |
| MP3 | -1.0945450 | 0.08442 (0.40) | 83.360 (1.02) | 62.947 (1.04) | 106.080 (1.02) | 84.129 (1.02) | 37.372 |
| MP4D | -1.1104005 | 0.08987 (0.43) | 82.834 (1.01) | 62.577 (1.04) | 105.693 (1.02) | 83.702 (1.02) | 37.362 |
| MP4DQ | -1.0985667 | 0.08738 (0.41) | 83.126 (1.01) | 62.827 (1.04) | 105.855 (1.02) | 83.936 (1.02) | 37.283 |
| MP4SDQ | -1.1046780 | 0.07962 (0.38) | 83.947 (1.02) | 62.990 (1.04) | 106.911 (1.03) | 84.616 (1.03) | 38.050 |
| MP4SDTQ | -1.1307725 | 0.05922 (0.28) | 85.059 (1.04) | 63.694 (1.06) | 107.355 (1.03) | 85.370 (1.04) | 37.814 |
| CCSD | -1.1057618 | 0.08365 (0.40) | 83.766 (1.02) | 62.924 (1.04) | 106.700 (1.03) | 84.464 (1.03) | 37.926 |
| CCSD(T) | -1.1309505 | 0.06837 (0.32) | 85.008 (1.04) | 63.515 (1.05) | 107.788 (1.04) | 85.437 (1.04) | 38.347 |

^a Numbers in parentheses are ratios to the Hartree–Fock values (atomic units).

TABLE 5: Experimental and Calculated Values of Dipole Moment (atomic units)

| molecule | calculations (CCSD(T)) | | | experiment ^a | |
|----------------------------------|------------------------|--------------|--------------------------|-------------------------|--------------|
| | + <i>pd</i> | + <i>pdd</i> | (3 <i>d</i>)+ <i>pd</i> | in benzene | gas phase |
| C ₄ H ₄ O | 0.43138 | 0.32207 | 0.24150 | 0.28 (0.72) | 0.26 (0.66) |
| C ₄ H ₄ S | 0.40014 | 0.36190 | 0.21832 | 0.21 (0.54) | 0.21 (0.53) |
| C ₄ H ₄ Se | 0.27386 | 0.22985 | - | 0.20 (0.52) | 0.15 (0.39) |
| C ₄ H ₄ Te | 0.07502 | 0.06837 | - | 0.18 (0.46) | 0.075 (0.19) |

^a Fringuelli, F.; Marino, G.; Taticchi, A. *Adv. Heterocycl. Chem.* **1977**, *21*, 119. Numbers in parentheses are in Debye (D). 1 au = 8.478418 × 10⁻³⁰ cm = 2.541765 × 10⁻¹⁸ Fr cm = 2.541765 D.

TABLE 6: Physical Constants for Experimental Polarizability

| molecule | mol wt (g/mol) | density (g/cm ³) | refractive index <i>n</i> _D | polarizability | |
|----------------------------------|----------------|------------------------------|--|--------------------------------------|---------------|
| | | | | (10 ⁻²⁴ cm ³) | (atomic unit) |
| C ₄ H ₄ O | 68.08 | 0.9514 ^a | 1.4214 ^a | 7.1998 | 48.587 |
| C ₄ H ₄ S | 84.14 | 1.0649 ^a | 1.5289 ^a | 9.6588 | 65.181 |
| C ₄ H ₄ Se | 131.04 | 1.5251 ^b | 1.5642 ^b | 11.0820 | 74.785 |
| C ₄ H ₄ Te | 179.68 | 2.13 ^b | 1.6844 ^b | 12.7014 | 85.713 |

^a *CRC Handbook of Chemistry and Physics*, 79th ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 1998. ^b Fringuelli, F.; Marino, G.; Taticchi, A. *Adv. Heterocycl. Chem.* **1977**, *21*, 119.

TABLE 7: Experimental and Calculated Values of Polarizability (atomic units)

| molecule | calculations (CCSD(T)) | | | experiment |
|----------------------------------|------------------------|--------------|--------------------------|------------|
| | + <i>pd</i> | + <i>pdd</i> | (3 <i>d</i>)+ <i>pd</i> | |
| C ₄ H ₄ O | 44.211 | 47.426 | 46.878 | 48.59 |
| C ₄ H ₄ S | 59.369 | 64.074 | 62.811 | 65.18 |
| C ₄ H ₄ Se | 66.410 | 71.513 | - | 74.78 |
| C ₄ H ₄ Te | 79.818 | 85.437 | - | 85.71 |

calculated second hyperpolarizability, γ . However, those $\chi^{(3)}$ values should be compared with the anisotropy of polarizability, $\Delta\alpha$. By using the calculated $\Delta\alpha$ values and the equation γ (orient) = 2($\Delta\alpha$)²/(135*k*_B*T*) (where *k*_B = Boltzmann constant, *T* = absolute temperature), they could obtain the order-of-magnitude agreement in the comparison. In our previous paper,⁷ the anisotropy of the calculated polarizability was used for estimating the preexponential factors of the orientational time-correlation factors for the homologues.

Here we will examine the physical mechanism concerning determination of the α value, to discuss the origin of the difference in α among the different components and among the different homologues, because it will be important also for the discussion of β and γ values. Although we use the CPHF or FF methods for obtaining (hyper)polarizability in this study, values obtained by these methods should be equivalent to those obtained by the perturbation expansion formula, which includes the orbital relaxation due to the applied electric field. Therefore, to discuss the relation between the calculated values and the electronic excited states contributing to the properties, it is convenient to employ the sum over state (SOS) representation.

The perturbation expansion for the *ii*-component (*i* = *x, y, z*) of the static polarizability, α_{ii} , can be written as

$$\alpha_{ii} = 2 \sum_n \frac{(\mu_{ng}^i)^2}{E_{ng}} \quad (13)$$

where *E*_{*ng*} means the energy difference between the ground state and *n*th excited state and μ_{ng}^i is the matrix elements of the transition moment, which directly expresses the transition-probability density between the ground and excited states. The molecular structure of the furan homologues has the *C*_{2*v*} symmetry, and the electric dipole operators μ_x , μ_y , and μ_z along the *x*-, *y*-, and *z*-directions belong to the *b*₂, *b*₁, and *a*₁ symmetry species, respectively, in the present coordinate system shown in Figure 1. Therefore, the excited states from the ground *A*₁ state that are symmetry-allowed through the μ_x , μ_y , and μ_z are the *B*₂, *B*₁, and *A*₁ states, respectively. For the π -conjugated systems treated here the lower excited states appear by π - π^* transition. Because the symmetry species of the π - π^* excited states is *B*₂ or *A*₁,²³ the transition moments concerning the π - π^* transition are limited to μ_x and μ_z . The reason the α_{xx} component of furan is smaller than that of the other homologues is because the transition energy between the excited *B*₂ and the ground states is larger for furan than that of the homologues.²³ As the heteroatom becomes heavier, the α_{zz} component is larger, which corresponds to the fact that the energy level of the excited *A*₁ state becomes lower. Moreover, the contribution of α_{zz} to the orientationally averaged α_s values overcomes that of α_{xx} values as the heteroatom becomes heavier. This is well-correlated with

TABLE 8: Individual Components of the First Hyperpolarizability of Furan (C₄H₄O) Calculated with 6-31G+*pd*, 6-31G+*pdd*, and 6-31G(3*d*)+*pd* Basis Sets^a

| method | β_{xxz} | β_{yyz} | β_{zzz} | β_z |
|-------------------------------|---------------|----------------|----------------|-----------------|
| 6-31G+ <i>pd</i> | | | | |
| HF | 11.505 (1.00) | -28.193 (1.00) | -38.404 (1.00) | -55.092 (1.00) |
| MP2 | -1.420 | -43.847 (1.56) | -52.074 (1.36) | -97.340 (1.77) |
| MP3 | -2.408 | -39.222 (1.39) | -52.351 (1.36) | -93.980 (1.71) |
| MP4D | -6.754 | -39.325 (1.39) | -55.080 (1.43) | -101.159 (1.84) |
| MP4DQ | -7.108 | -39.957 (1.42) | -56.590 (1.47) | -103.656 (1.88) |
| MP4SDQ | -6.834 | -42.405 (1.50) | -58.862 (1.53) | -108.101 (1.96) |
| MP4SDTQ | -0.043 | -42.409 (1.50) | -55.021 (1.43) | -97.473 (1.77) |
| CCSD | -6.946 | -43.055 (1.53) | -66.096 (1.72) | -116.097 (2.11) |
| CCSD(T) | -4.962 | -45.829 (1.63) | -69.157 (1.80) | -119.948 (2.18) |
| 6-31G+ <i>pdd</i> | | | | |
| HF | 19.293 (1.00) | -33.636 (1.00) | -51.425 (1.00) | -65.768 (1.00) |
| MP2 | 9.634 (0.50) | -44.980 (1.34) | -59.927 (1.17) | -95.273 (1.45) |
| MP3 | 8.142 (0.42) | -40.551 (1.21) | -58.988 (1.15) | -91.397 (1.39) |
| MP4D | 4.550 (0.24) | -40.567 (1.21) | -60.379 (1.17) | -96.396 (1.47) |
| MP4DQ | 4.226 (0.22) | -41.129 (1.22) | -61.451 (1.19) | -98.353 (1.50) |
| MP4SDQ | 4.353 (0.23) | -43.057 (1.28) | -63.559 (1.24) | -102.264 (1.55) |
| MP4SDTQ | 10.695 (0.55) | -43.447 (1.29) | -61.319 (1.19) | -91.071 (1.43) |
| CCSD | 4.974 (0.26) | -43.232 (1.29) | -67.532 (1.31) | -105.790 (1.61) |
| CCSD(T) | 7.044 (0.37) | -45.532 (1.35) | -70.349 (1.37) | -108.837 (1.65) |
| 6-31G(3 <i>d</i>)+ <i>pd</i> | | | | |
| HF | 22.385 (1.00) | -34.464 (1.00) | -48.637 (1.00) | -60.716 (1.00) |
| MP2 | 14.961 (0.67) | -44.651 (1.30) | -54.387 (1.12) | -84.077 (1.38) |
| MP3 | 13.173 (0.59) | -39.368 (1.14) | -52.546 (1.08) | -78.741 (1.30) |
| MP4D | 10.678 (0.48) | -38.734 (1.12) | -52.518 (1.08) | -80.574 (1.33) |
| MP4DQ | 10.299 (0.46) | -39.673 (1.15) | -53.738 (1.10) | -83.112 (1.37) |
| MP4SDQ | 10.189 (0.46) | -40.531 (1.18) | -54.908 (1.13) | -85.251 (1.40) |
| MP4SDTQ | 14.930 (0.67) | -42.628 (1.24) | -54.826 (1.13) | -82.524 (1.36) |
| CCSD | 10.584 (0.47) | -40.691 (1.18) | -57.501 (1.18) | -87.609 (1.44) |
| CCSD(T) | 11.035 (0.49) | -43.000 (1.25) | -60.700 (1.25) | -92.665 (1.53) |

^a Numbers in parentheses are ratios to the Hartree–Fock values (atomic units).

the fact that the energy level of the excited A₁ state becomes lower than that of the B₂ state for tellurophene. From these considerations, it is found that the energy difference between the ground and excited states in the denominator of eq 13 is the major factor for determining the values of the α_{xx} and α_{zz} components. On the other hand, for the smallest α_{yy} component, all of the matrix elements of μ related to the valence $\pi-\pi^*$ transitions are zero, and there is no symmetry-allowed transition. Therefore, it is considered that higher excitations, including the $\sigma-\pi^*$ transition or transition to continuum, should contribute to the α_{yy} values.

Thus, it is found theoretically that the individual components of α of these homologues are increased when the heteroatoms are substituted with heavier atoms. Variation of the main component of α and variation of these values depending on the homologues can be explained by the energy levels of the electronic excited states in the valence states. This kind of consideration will be more important for discussion of the β and γ values.

3.2. First Hyperpolarizability, β . Tables 8–11 show the individual components of the β values calculated in the present study. Here β_z in the tables is the next z -component of the β vector, and it can be compared with observed values.

$$\beta_z = \beta_{xxz} + \beta_{yyz} + \beta_{zzz} \quad (14)$$

Compared to the α value, the β values vary significantly depending on selection of the basis sets and inclusion of electron correlation. Even the sign of the β value can sometimes change.

At the Hartree–Fock level, the β_{yyz} and β_{zzz} values increase by augmenting the semi-diffuse functions for all of the homologues, while the β_{xxz} values move to the positive direction except for the tellurophene molecule. By including the electron

correlation, the β_{xxz} and β_{zzz} values of the homologues move to the negative direction independent of the basis sets, while the β_{yyz} component increases its value except for furan. Thus, at first glance, improvement of the wave functions does not seem to systematically influence the individual components of β .

To the best of our knowledge, no experimental observation of the β values of furan homologues by the electric-field-induced second harmonics (EFISH) or hyper Rayleigh scattering (HRS) methods has yet been published. Our present calculation indicates that the individual components of β do not show the clear correlation with the weight of the heteroatoms as shown in the α or γ values, and that thiophene should give the smallest absolute value of β among the homologues and tellurophene is expected to have the β value one order larger than the other molecules.

Similar to the α value, the iiz component ($i = x, y, z$) of β can also be written by the following perturbation expansion.

$$\beta_{iiz} = 2 \sum_n \frac{(\mu_{ng}^i)^2 \Delta\mu_{ng}^z + 2\mu_{ng}^i \mu_{ng}^z \Delta\mu_{ng}^i}{(E_{ng})^2} \quad (15)$$

Here the diagonal approximation is adopted according to Morrell et al.²⁴ Most important here is the term $\Delta\mu_{ng}^i$ ($= \mu_{in} - \mu_{ig}$) in the numerator, which determines the sign of each component of β , where μ_{in} is the dipole moment in the i -direction of the n th excited-state symmetry-allowed through the operator μ_i . Note that the coordinate system shown in Figure 1 is defined so that the dipole moment, μ_z , of the homologues in the ground state has a positive value.

From the calculation of β_{zzz} of furan, it is found that the dipole moment, μ_z , in the excited A₁ state has a larger absolute value, with the same sign, than that in the ground A₁ state. Contrary

TABLE 9: Individual Components of the First Hyperpolarizability of Thiophene (C₄H₄S) Calculated with 6-31G+*pd*, 6-31G+*pdd*, and 6-31G(3*d*)+*pd* Basis Sets^a

| method | β_{xxz} | β_{yyz} | β_{zzz} | β_z |
|-------------------------------|----------------|---------------|---------------|---------------|
| 6-31G+ <i>pd</i> | | | | |
| HF | -14.075 (1.00) | 3.776 (1.00) | 12.831 (1.00) | 2.532 (1.00) |
| MP2 | -14.171 (1.01) | 6.148 (1.63) | -34.438 | -42.461 |
| MP3 | -16.644 (1.18) | 10.800 (2.86) | -32.181 | -38.026 |
| MP4D | -20.492 (1.46) | 10.777 (2.85) | -35.837 | -45.552 |
| MP4DQ | -19.772 (1.40) | 10.874 (2.88) | -39.461 | -48.359 |
| MP4SDQ | -19.568 (1.39) | 10.099 (2.67) | -36.332 | -45.802 |
| MP4SDTQ | -13.532 (0.96) | 8.611 (2.28) | -33.163 | -38.085 |
| CCSD | -22.434 (1.59) | 11.952 (3.17) | -48.031 | -58.514 |
| CCSD(T) | -20.377 (1.45) | 9.799 (2.60) | -49.450 | -60.028 |
| 6-31G+ <i>pdd</i> | | | | |
| HF | -4.305 (1.00) | 10.018 (1.00) | 31.519 (1.00) | 37.233 (1.00) |
| MP2 | -5.299 (1.23) | 13.499 (1.35) | -5.311 | 2.889 (0.08) |
| MP3 | -7.129 (1.66) | 19.324 (1.93) | 0.076 | 12.271 (0.33) |
| MP4D | -10.121 (2.35) | 18.192 (1.82) | -1.844 | 6.228 (0.17) |
| MP4DQ | -9.738 (2.26) | 18.791 (1.88) | -5.064 | 3.989 (0.11) |
| MP4SDQ | -9.123 (2.12) | 18.045 (1.80) | -3.476 | 5.446 (0.15) |
| MP4SDTQ | -4.450 (1.03) | 16.999 (1.70) | -2.846 | 9.703 (0.26) |
| CCSD | -11.853 (2.75) | 18.907 (1.89) | -10.226 | -3.171 |
| CCSD(T) | -10.616 (2.47) | 16.953 (1.69) | -13.390 | -7.054 |
| 6-31G(3 <i>d</i>)+ <i>pd</i> | | | | |
| HF | -6.753 (1.00) | 5.733 (1.00) | 36.332 (1.00) | 35.311 (1.00) |
| MP2 | -5.631 (0.83) | 6.867 (1.20) | 3.690 (0.10) | 4.925 (0.14) |
| MP3 | -8.868 (1.31) | 12.159 (2.12) | 10.408 (0.29) | 13.698 (0.39) |
| MP4D | -12.024 (1.78) | 10.508 (1.83) | 10.637 (0.29) | 9.120 (0.26) |
| MP4DQ | -11.194 (1.66) | 11.321 (1.97) | 7.058 (0.19) | 7.185 (0.20) |
| MP4SDQ | -10.594 (1.57) | 10.486 (1.83) | 9.192 (0.25) | 9.084 (0.26) |
| MP4SDTQ | -5.090 (0.75) | 10.904 (1.90) | 7.697 (0.21) | 13.511 (0.38) |

^a Numbers in parentheses are ratios to the Hartree–Fock values (atomic units).

TABLE 10: Individual Components of the First Hyperpolarizability of Selenophene (C₄H₄Se) Calculated with 6-31G+*pd* and 6-31G+*pdd* Basis Sets and ECP Methods^a

| method | β_{xxz} | β_{yyz} | β_{zzz} | β_z |
|--|---------------|---------------|---------------|----------------|
| 6-31G+ <i>pd</i> for C, ECP (LANL1DZ+ <i>pd</i>) for Se | | | | |
| HF | -3.230 (1.00) | 42.882 (1.00) | 57.607 (1.00) | 97.258 (1.00) |
| MP2 | -0.166 | 54.489 (1.27) | -9.203 | 45.120 (0.46) |
| MP3 | -1.099 | 62.000 (1.45) | -2.446 | 58.454 (0.60) |
| MP4D | -5.369 | 61.451 (1.43) | -6.952 | 49.130 (0.51) |
| MP4DQ | -4.199 | 62.133 (1.45) | -11.199 | 46.734 (0.48) |
| MP4SDQ | -3.830 | 62.566 (1.46) | -5.009 | 53.727 (0.55) |
| MP4SDTQ | 1.946 | 60.377 (1.41) | -2.817 | 59.505 (0.61) |
| CCSD | -7.230 | 66.485 (1.55) | -17.646 | 41.609 (0.43) |
| CCSD(T) | -5.138 | 65.227 (1.52) | -18.005 | 42.084 (0.43) |
| 6-31G+ <i>pdd</i> for C, ECP (LANL1DZ+ <i>pdd</i>) for Se | | | | |
| HF | 1.859 (1.00) | 56.628 (1.00) | 78.474 (1.00) | 136.961 (1.00) |
| MP2 | 2.212 | 64.542 (1.14) | 26.536 (0.34) | 93.290 (0.68) |
| MP3 | 2.460 | 74.634 (1.32) | 37.179 (0.47) | 114.273 (0.83) |
| MP4D | -1.595 | 72.346 (1.28) | 34.038 (0.43) | 104.789 (0.77) |
| MP4DQ | -0.661 | 73.759 (1.30) | 30.302 (0.39) | 103.400 (0.75) |
| MP4SDQ | 0.081 | 73.216 (1.29) | 35.084 (0.45) | 108.381 (0.79) |
| MP4SDTQ | 5.010 | 72.028 (1.27) | 35.172 (0.45) | 112.209 (0.82) |
| CCSD | -3.175 | 74.940 (1.32) | 28.357 (0.36) | 100.121 (0.73) |
| CCSD(T) | -1.872 | 73.355 (1.30) | 26.956 (0.34) | 98.439 (0.72) |

^a Numbers in parentheses are ratios to the Hartree–Fock values (atomic units).

to furan, the dipole moment, μ_z , in the excited A₁ state for the selenophene and tellurophene molecules has a smaller value than that in the ground A₁ state, or even the opposite sign. Thiophene has the intermediate character of β among them, and its dipole moment is almost the same for the ground and excited states.

Recently, Larsen et al.²⁵ calculated the α , β , and γ values of the BH molecule using full configuration interaction (CI) and variant CC methods. They pointed out that even the highly sophisticated CCSD wave function gives a large error for the β value, while it can give more precise α and γ values. As mentioned above, this originates from the fact that the sign of

β values cannot be determined solely by the property of the ground state. On the other hand, the α value always has the positive sign in the ground state of molecules and the γ value tends to be positive since the term contributing to the positive sign is dominant for the stable molecule. Accordingly, it is considered that β values do not seem to show the systematic variation. However, once the sign of β is determined, then the energy denominator in eq 15 should become more dominant for the increase or decrease of the calculated values.

3.3. Second Hyperpolarizability, γ . The main purpose of the present study is to obtain accurate theoretical values of the second hyperpolarizability and to examine the physical mechanism in the observed γ value obtained for the homologues using the optical Kerr effect (OKE) method.^{5,6} Tables 12–15 show the calculated second hyperpolarizability, γ , for the homologues. Here, for the correlated results, the last digit in every γ component under 10 au was neglected due to the lack of stability which may have occurred in the numerical differentiation. The orientationally averaged γ_s values in the tables were obtained as follows:

$$\gamma_s = (\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + 2\gamma_{xxyy} + 2\gamma_{xxzz} + 2\gamma_{yyzz})/5 \quad (16)$$

This value can be directly compared to the electronic component of the experimental Kerr coefficients observed for the liquid phase.

Variation of the γ values due to improvement of the wave function is more straightforward than variation of the β values. First, we discuss the effect of the improvement of the basis set on the calculated γ value at the HF level. Replacing the basis set from the +*pd* function with that from the +*pdd* function tends to reduce the γ value, except the component concerning the z-direction of furan. However, proceeding to the (3*d*)+*pd* function increases the components except γ_{zzzz} . Therefore, there seems to be little difference between the results with +*pd* and

TABLE 11: Individual Components of the First Hyperpolarizability of Tellurophene (C₄H₄Te) Calculated with 6-31G+*pd* and 6-31G+*pd*d Basis Sets and ECP Methods^a

| method | β_{xxz} | β_{yyz} | β_{zzz} | β_z |
|---|---------------|----------------|----------------|----------------|
| 6-31G+ <i>pd</i> for C, ECP (LANL1DZ+ <i>pd</i>) for Te | | | | |
| HF | 41.232 (1.00) | 144.441 (1.00) | 162.588 (1.00) | 348.260 (1.00) |
| MP2 | 50.465 (1.22) | 171.091 (1.18) | 49.488 (0.30) | 271.044 (0.78) |
| MP3 | 52.966 (1.28) | 183.999 (1.27) | 68.118 (0.42) | 305.083 (0.88) |
| MP4D | 47.738 (1.16) | 182.862 (1.27) | 61.780 (0.38) | 292.380 (0.84) |
| MP4DQ | 49.820 (1.21) | 184.457 (1.28) | 56.737 (0.35) | 291.015 (0.84) |
| MP4SDQ | 51.233 (1.24) | 187.297 (1.30) | 67.748 (0.42) | 306.278 (0.88) |
| MP4SDTQ | 56.315 (1.37) | 183.118 (1.27) | 67.024 (0.41) | 306.457 (0.88) |
| CCSD | 46.436 (1.13) | 193.616 (1.34) | 54.132 (0.33) | 294.184 (0.84) |
| CCSD(T) | 48.995 (1.19) | 193.609 (1.34) | 54.535 (0.34) | 297.139 (0.85) |
| 6-31G+ <i>pd</i> d for C, ECP (LANL1DZ+ <i>pd</i> d) for Te | | | | |
| HF | 35.249 (1.00) | 169.910 (1.00) | 192.512 (1.00) | 397.671 (1.00) |
| MP2 | 34.545 (0.98) | 183.598 (1.08) | 97.369 (0.51) | 315.512 (0.79) |
| MP3 | 39.451 (1.12) | 201.710 (1.19) | 120.249 (0.62) | 361.409 (0.91) |
| MP4D | 33.725 (0.96) | 197.480 (1.16) | 115.657 (0.60) | 346.863 (0.87) |
| MP4DQ | 35.523 (1.01) | 200.319 (1.18) | 110.664 (0.57) | 346.506 (0.87) |
| MP4SDQ | 36.204 (1.03) | 199.906 (1.18) | 119.830 (0.62) | 355.939 (0.90) |
| MP4SDTQ | 41.280 (1.17) | 198.394 (1.17) | 117.254 (0.61) | 356.928 (0.90) |
| CCSD | 31.624 (0.90) | 202.713 (1.19) | 113.169 (0.59) | 347.506 (0.87) |
| CCSD(T) | 32.646 (0.93) | 201.680 (1.19) | 113.184 (0.59) | 347.510 (0.87) |

^a Numbers in parentheses are ratios to the Hartree–Fock values (atomic units).**TABLE 12: Individual Components of the Second Hyperpolarizability of Furan (C₄H₄O) Calculated with 6-31G+*pd*, 6-31G+*pd*d, and 6-31G(3d)+*pd* Basis Sets^a**

| method | γ_{xxxx} | γ_{yyyy} | γ_{zzzz} | γ_{xyxy} | γ_{xxzz} | γ_{yyzz} | γ_s |
|----------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|--------------|
| 6-31G+ <i>pd</i> | | | | | | | |
| HF | 15191 (1.00) | 12046 (1.00) | 5040 (1.00) | 6923 (1.00) | 2159 (1.00) | 3438 (1.00) | 11463 (1.00) |
| MP2 | 18590 (1.22) | 14600 (1.21) | 7810 (1.55) | 8360 (1.21) | 3750 (1.74) | 4750 (1.38) | 14940 (1.30) |
| MP3 | 16950 (1.12) | 13410 (1.11) | 6640 (1.32) | 7460 (1.08) | 3310 (1.53) | 4190 (1.22) | 13380 (1.17) |
| MP4D | 16260 (1.07) | 12700 (1.05) | 6810 (1.35) | 7050 (1.02) | 3250 (1.51) | 4070 (1.18) | 12900 (1.13) |
| MP4DQ | 16580 (1.09) | 13010 (1.08) | 6910 (1.37) | 7200 (1.04) | 3370 (1.56) | 4150 (1.21) | 13190 (1.15) |
| MP4SDQ | 17080 (1.12) | 13560 (1.13) | 7760 (1.54) | 7570 (1.09) | 3450 (1.60) | 4440 (1.29) | 13870 (1.21) |
| MP4SDTQ | 18340 (1.21) | 14660 (1.22) | 7440 (1.48) | 8260 (1.19) | 3620 (1.68) | 4630 (1.35) | 14690 (1.28) |
| CCSD | 16950 (1.12) | 13440 (1.12) | 7860 (1.56) | 7540 (1.09) | 3390 (1.57) | 4470 (1.30) | 13810 (1.20) |
| CCSD(T) | 18010 (1.19) | 14490 (1.20) | 8480 (1.68) | 8210 (1.19) | 3650 (1.69) | 4820 (1.40) | 14870 (1.30) |
| 6-31G+ <i>pd</i> d | | | | | | | |
| HF | 13518 (1.00) | 11804 (1.00) | 5223 (1.00) | 6492 (1.00) | 2528 (1.00) | 3447 (1.00) | 11096 (1.00) |
| MP2 | 16590 (1.23) | 13670 (1.16) | 7680 (1.47) | 7630 (1.18) | 3850 (1.52) | 4550 (1.32) | 14000 (1.26) |
| MP3 | 14680 (1.09) | 12100 (1.03) | 6460 (1.24) | 6540 (1.01) | 3310 (1.31) | 3900 (1.13) | 12150 (1.09) |
| MP4D | 14130 (1.05) | 11480 (0.97) | 6570 (1.26) | 6200 (0.96) | 3230 (1.28) | 3770 (1.09) | 11720 (1.06) |
| MP4DQ | 14440 (1.07) | 11770 (1.00) | 6680 (1.28) | 6340 (0.98) | 3340 (1.32) | 3870 (1.12) | 12000 (1.08) |
| MP4SDQ | 14910 (1.10) | 12190 (1.03) | 7460 (1.43) | 6640 (1.02) | 3460 (1.37) | 4110 (1.19) | 12600 (1.14) |
| MP4SDTQ | 16050 (1.19) | 13350 (1.13) | 7250 (1.39) | 7320 (1.13) | 3650 (1.44) | 4340 (1.26) | 13460 (1.21) |
| CCSD | 15210 (1.13) | 12640 (1.07) | 7990 (1.53) | 7060 (1.09) | 3840 (1.52) | 4770 (1.38) | 13440 (1.21) |
| CCSD(T) | 16500 (1.22) | 13930 (1.18) | 8760 (1.68) | 7690 (1.18) | 4260 (1.69) | 5340 (1.55) | 14750 (1.33) |
| 6-31G(3d)+ <i>pd</i> | | | | | | | |
| HF | 14407 (1.00) | 12550 (1.00) | 4956 (1.00) | 7293 (1.00) | 2645 (1.00) | 3576 (1.00) | 11788 (1.00) |
| MP2 | 16900 (1.17) | 13880 (1.11) | 7130 (1.44) | 8120 (1.11) | 3760 (1.42) | 4540 (1.27) | 14150 (1.20) |
| MP3 | 14570 (1.01) | 12020 (0.96) | 5910 (1.19) | 6730 (0.92) | 3130 (1.18) | 3780 (1.06) | 11960 (1.01) |
| MP4D | 13980 (0.97) | 11410 (0.91) | 5850 (1.18) | 6400 (0.88) | 3000 (1.13) | 3610 (1.01) | 11450 (0.97) |
| MP4DQ | 14370 (1.00) | 11770 (0.94) | 6040 (1.22) | 6580 (0.90) | 3130 (1.18) | 3740 (1.05) | 11820 (1.00) |
| MP4SDQ | 14740 (1.02) | 12030 (0.96) | 6540 (1.32) | 6790 (0.93) | 3240 (1.22) | 3880 (1.09) | 12220 (1.04) |
| MP4SDTQ | 16150 (1.12) | 13370 (1.07) | 6730 (1.36) | 7600 (1.04) | 3560 (1.35) | 4280 (1.20) | 13420 (1.14) |
| CCSD | 14920 (1.04) | 12220 (0.97) | 6700 (1.35) | 6910 (0.95) | 3310 (1.25) | 3970 (1.11) | 12440 (1.06) |
| CCSD(T) | 16940 (1.18) | 13870 (1.11) | 7370 (1.49) | 6890 (0.94) | 3630 (1.37) | 4290 (1.20) | 13560 (1.15) |

^a Numbers in parentheses are ratios to the Hartree–Fock values (atomic units).

(3d)+*pd* sets at the Hartree–Fock level. However, inclusion of electron correlation reveals that there is appreciable difference between the two sets. As found for carbon disulfide previously,¹⁰ a poor basis set tends to overestimate the effect of electron correlation. Also, when moving from MP2 to MP3 to MP4, we see slight variation in the γ values, but it can be observed that the result with the MP2 method well-simulates the MP4SDTQ or CCSD(T) results. Total electron correlation effect on the second hyperpolarizability is estimated to be around 30% at the γ_s value of the homologues, irrespective of the compounds.

Here we will mention the reliability and validity of the use of the ECP method for calculation of the second hyperpolarizability. For comparison with the ECP method, in the correlation calculation considering all electrons, both methods including all excitations from core electrons and approximating with frozen cores were applied for the calculation of γ of the thiophene molecule with the +*pd* basis set. The results are listed in Table 16 with those by ECP methods. In this case, the calculations were made with the same orbital exponent for the augmented diffuse functions and for the same molecular

TABLE 13: Individual Components of the Second Hyperpolarizability of Thiophene (C₄H₄S) Calculated with 6-31G+*pd*, 6-31G+*pdd*, and 6-31G(3*d*)+*pd* Basis Sets^a

| method | γ_{xxxx} | γ_{yyyy} | γ_{zzzz} | γ_{xyxy} | γ_{xxzz} | γ_{yyzz} | γ_s |
|-------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|--------------|
| 6-31G+ <i>pd</i> | | | | | | | |
| HF | 15965 (1.00) | 13445 (1.00) | 14749 (1.00) | 6623 (1.00) | 4024 (1.00) | 6391 (1.00) | 15647 (1.00) |
| MP2 | 21610 (1.35) | 18020 (1.34) | 22080 (1.50) | 9350 (1.41) | 6930 (1.72) | 9380 (1.47) | 22610 (1.45) |
| MP3 | 18980 (1.19) | 16690 (1.24) | 20270 (1.37) | 8100 (1.22) | 6330 (1.57) | 8600 (1.35) | 20400 (1.30) |
| MP4D | 18760 (1.18) | 16180 (1.20) | 20260 (1.37) | 7910 (1.19) | 6300 (1.57) | 8480 (1.33) | 20110 (1.29) |
| MP4DQ | 19030 (1.19) | 16510 (1.23) | 20600 (1.40) | 8050 (1.22) | 6460 (1.61) | 8610 (1.35) | 20480 (1.31) |
| MP4SDQ | 19890 (1.25) | 17240 (1.28) | 21890 (1.48) | 8500 (1.28) | 6610 (1.64) | 9110 (1.43) | 21490 (1.37) |
| MP4SDTQ | 20800 (1.30) | 18060 (1.34) | 21750 (1.47) | 9020 (1.36) | 6740 (1.67) | 9260 (1.45) | 22130 (1.41) |
| CCSD | 19760 (1.24) | 17380 (1.29) | 22610 (1.53) | 8480 (1.28) | 6660 (1.66) | 9220 (1.44) | 21690 (1.39) |
| CCSD(T) | 21160 (1.33) | 18560 (1.38) | 23890 (1.62) | 9240 (1.40) | 7020 (1.74) | 9750 (1.53) | 23130 (1.48) |
| 6-31G+ <i>pdd</i> | | | | | | | |
| HF | 14222 (1.00) | 13079 (1.00) | 14219 (1.00) | 6742 (1.00) | 3576 (1.00) | 6522 (1.00) | 15040 (1.00) |
| MP2 | 19050 (1.34) | 16470 (1.26) | 20190 (1.42) | 8920 (1.32) | 5870 (1.64) | 8890 (1.36) | 20620 (1.37) |
| MP3 | 16030 (1.13) | 14760 (1.13) | 18120 (1.27) | 7360 (1.09) | 5170 (1.45) | 8020 (1.23) | 18000 (1.20) |
| MP4D | 16010 (1.13) | 14320 (1.09) | 17960 (1.26) | 7250 (1.08) | 5110 (1.43) | 7870 (1.21) | 17750 (1.18) |
| MP4DQ | 16270 (1.14) | 14650 (1.12) | 18340 (1.29) | 7390 (1.10) | 5270 (1.47) | 8020 (1.23) | 18120 (1.20) |
| MP4SDQ | 17070 (1.20) | 15110 (1.16) | 19470 (1.37) | 7740 (1.15) | 5450 (1.52) | 8360 (1.28) | 18950 (1.26) |
| MP4SDTQ | 17880 (1.26) | 16100 (1.23) | 19660 (1.38) | 8310 (1.23) | 5610 (1.57) | 8650 (1.33) | 19760 (1.31) |
| CCSD | 16730 (1.18) | 15030 (1.15) | 19550 (1.37) | 7620 (1.13) | 5350 (1.50) | 8310 (1.27) | 18770 (1.25) |
| CCSD(T) | 18180 (1.28) | 16210 (1.24) | 20650 (1.45) | 8100 (1.20) | 5660 (1.58) | 8720 (1.34) | 20000 (1.33) |
| 6-31G(3 <i>d</i>)+ <i>pd</i> | | | | | | | |
| HF | 14461 (1.00) | 13544 (1.00) | 14109 (1.00) | 7091 (1.00) | 3761 (1.00) | 6961 (1.00) | 15548 (1.00) |
| MP2 | 18540 (1.28) | 16240 (1.20) | 19220 (1.36) | 9000 (1.27) | 5770 (1.53) | 9010 (1.29) | 20310 (1.31) |
| MP3 | 15360 (1.06) | 14180 (1.05) | 16730 (1.19) | 7190 (1.01) | 4880 (1.30) | 7870 (1.13) | 17230 (1.11) |
| MP4D | 15380 (1.06) | 13770 (1.02) | 16290 (1.15) | 7130 (1.01) | 4710 (1.25) | 7630 (1.10) | 16880 (1.09) |
| MP4DQ | 15720 (1.09) | 14170 (1.05) | 16860 (1.19) | 7310 (1.03) | 4930 (1.31) | 7870 (1.13) | 17400 (1.12) |
| MP4SDQ | 16230 (1.12) | 14370 (1.06) | 17490 (1.24) | 7500 (1.06) | 5040 (1.34) | 7980 (1.15) | 17830 (1.15) |
| MP4SDTQ | 17310 (1.20) | 15720 (1.16) | 18610 (1.32) | 8240 (1.16) | 5500 (1.46) | 8670 (1.25) | 19290 (1.24) |

^a Numbers in parentheses are ratios to the Hartree–Fock values (atomic units).

TABLE 14: Individual Components of the Second Hyperpolarizability of Selenophene (C₄H₄Se) Calculated with 6-31G+*pd* and 6-31G+*pdd* Basis Sets and ECP Methods^a

| method | γ_{xxxx} | γ_{yyyy} | γ_{zzzz} | γ_{xyxy} | γ_{xxzz} | γ_{yyzz} | γ_s |
|--|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|--------------|
| 6-31G+ <i>pd</i> for C, ECP (LANL1DZ+ <i>pd</i>) for Se | | | | | | | |
| HF | 17269 (1.00) | 18432 (1.00) | 22013 (1.00) | 7331 (1.00) | 5450 (1.00) | 9076 (1.00) | 20286 (1.00) |
| MP2 | 23990 (1.39) | 24600 (1.33) | 31580 (1.43) | 10520 (1.44) | 8920 (1.64) | 12750 (1.40) | 28910 (1.43) |
| MP3 | 21030 (1.22) | 23660 (1.28) | 29690 (1.35) | 9270 (1.26) | 8320 (1.53) | 12020 (1.32) | 26720 (1.32) |
| MP4D | 20880 (1.21) | 23100 (1.25) | 29600 (1.34) | 9100 (1.24) | 8300 (1.52) | 11880 (1.31) | 26430 (1.30) |
| MP4DQ | 21180 (1.23) | 23550 (1.28) | 30090 (1.37) | 9270 (1.26) | 8480 (1.56) | 12040 (1.33) | 26880 (1.33) |
| MP4SDQ | 22230 (1.29) | 24420 (1.32) | 31580 (1.43) | 9780 (1.33) | 8700 (1.60) | 12650 (1.39) | 28100 (1.39) |
| MP4SDTQ | 23110 (1.34) | 25160 (1.37) | 31540 (1.43) | 10260 (1.40) | 8790 (1.61) | 12800 (1.41) | 28700 (1.41) |
| CCSD | 22070 (1.28) | 24970 (1.35) | 32540 (1.48) | 9820 (1.34) | 8780 (1.61) | 12920 (1.42) | 28520 (1.41) |
| CCSD(T) | 23710 (1.37) | 26400 (1.43) | 34240 (1.56) | 10640 (1.45) | 9240 (1.70) | 13610 (1.50) | 30270 (1.49) |
| 6-31G+ <i>pdd</i> for C, ECP (LANL1DZ+ <i>pdd</i>) for Se | | | | | | | |
| HF | 15319 (1.00) | 17928 (1.00) | 19409 (1.00) | 7624 (1.00) | 4613 (1.00) | 8879 (1.00) | 18978 (1.00) |
| MP2 | 21150 (1.38) | 22410 (1.25) | 27010 (1.39) | 10310 (1.35) | 7310 (1.58) | 11630 (1.31) | 25820 (1.36) |
| MP3 | 17720 (1.16) | 20990 (1.17) | 24740 (1.27) | 8660 (1.14) | 6570 (1.42) | 10830 (1.22) | 23110 (1.22) |
| MP4D | 17710 (1.16) | 20370 (1.14) | 24420 (1.26) | 8530 (1.12) | 6500 (1.41) | 10620 (1.20) | 22760 (1.20) |
| MP4DQ | 18040 (1.18) | 20850 (1.16) | 24980 (1.29) | 8710 (1.14) | 6700 (1.45) | 10820 (1.22) | 23270 (1.23) |
| MP4SDQ | 18990 (1.24) | 21320 (1.19) | 26240 (1.35) | 9090 (1.19) | 6920 (1.50) | 11210 (1.26) | 24200 (1.28) |
| MP4SDTQ | 19860 (1.30) | 22450 (1.25) | 26640 (1.37) | 9730 (1.28) | 7080 (1.53) | 11530 (1.30) | 25130 (1.32) |
| CCSD | 18700 (1.22) | 21320 (1.19) | 26360 (1.36) | 8980 (1.18) | 6860 (1.49) | 11160 (1.26) | 24080 (1.27) |
| CCSD(T) | 20140 (1.31) | 22460 (1.25) | 27800 (1.43) | 9630 (1.26) | 7240 (1.57) | 11640 (1.31) | 25480 (1.34) |

^a Numbers in parentheses are ratios to the Hartree–Fock values (atomic units).

geometry. From Table 16, we can see that these three methods show good agreement within a few percent at component levels with almost all approximation models. This means that the ECP methods can well-simulate the γ values with the all-electron methods. Therefore, it is believed that the present ECP results for selenophene and tellurophene should give the γ values which can be compared directly to those with the all-electron method for other homologues. Although the results are not shown, for the μ , α , and β values, the same similarity can be observed at the individual components obtained by the three methods.

Comparison of the γ values among the homologues shows that, as was the case for α , every component of γ is increased

as the heteroatom becomes heavier. This demonstrates that the substitution of the heteroatom with heavier atoms is effective for improving nonlinear optical properties, which well-correlates with the experimental values shown later. Among the individual components, variation of the components concerning the z -axis is more prominent than variation of the other components. Later in this paper, this will also be discussed in terms of the related excited states.

In our laboratory we have obtained experimental γ values, which correspond to the purely electronic part of the $\chi^{(3)}$ value, by the OKE method for the furan homologues treated here. In a previous paper,⁶ we have already reported preliminary

TABLE 15: Individual Components of the Second Hyperpolarizability of Tellurophene (C₄H₄Te) Calculated with 6-31G+*pd* and 6-31G+*pdd* Basis Sets and ECP Methods^a

| method | γ_{xxxx} | γ_{yyyy} | γ_{zzzz} | γ_{xyyy} | γ_{xzzz} | γ_{yyzz} | γ_s |
|--|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|--------------|
| 6-31G+ <i>pd</i> for C, ECP (LANL1DZ+ <i>pd</i>) for Te | | | | | | | |
| HF | 20881 (1.00) | 36036 (1.00) | 38128 (1.00) | 10701 (1.00) | 8947 (1.00) | 16299 (1.00) | 33388 (1.00) |
| MP2 | 29650 (1.42) | 46670 (1.30) | 52420 (1.37) | 15250 (1.43) | 13610 (1.52) | 21240 (1.30) | 45790 (1.37) |
| MP3 | 26190 (1.25) | 47060 (1.31) | 50110 (1.31) | 14040 (1.31) | 12910 (1.44) | 20640 (1.27) | 43710 (1.31) |
| MP4D | 26000 (1.25) | 46180 (1.28) | 49930 (1.31) | 13780 (1.29) | 12900 (1.44) | 20430 (1.25) | 43260 (1.30) |
| MP4DQ | 26430 (1.27) | 47050 (1.31) | 50720 (1.33) | 14060 (1.31) | 13140 (1.47) | 20670 (1.27) | 43990 (1.32) |
| MP4SDQ | 27830 (1.33) | 48270 (1.34) | 52760 (1.38) | 14720 (1.38) | 13520 (1.51) | 21500 (1.32) | 45670 (1.37) |
| MP4SDTQ | 28830 (1.38) | 48910 (1.36) | 52740 (1.38) | 15250 (1.43) | 13570 (1.52) | 21670 (1.33) | 46290 (1.39) |
| CCSD | 27740 (1.33) | 50000 (1.39) | 54070 (1.42) | 14990 (1.40) | 13510 (1.51) | 21690 (1.33) | 46430 (1.39) |
| CCSD(T) | 29830 (1.43) | 51990 (1.44) | 56640 (1.49) | 16030 (1.50) | 14130 (1.58) | 22600 (1.39) | 48790 (1.46) |
| 6-31G+ <i>pdd</i> for C, ECP (LANL1DZ+ <i>pdd</i>) for Te | | | | | | | |
| HF | 18640 (1.00) | 33413 (1.00) | 31140 (1.00) | 10714 (1.00) | 7085 (1.00) | 14392 (1.00) | 29515 (1.00) |
| MP2 | 26130 (1.40) | 39800 (1.19) | 41970 (1.35) | 14290 (1.33) | 10580 (1.49) | 17570 (1.22) | 38550 (1.31) |
| MP3 | 22160 (1.19) | 39600 (1.19) | 39140 (1.26) | 12670 (1.18) | 9730 (1.37) | 16940 (1.18) | 35920 (1.22) |
| MP4D | 22010 (1.18) | 38320 (1.15) | 38540 (1.24) | 12360 (1.15) | 9630 (1.36) | 16630 (1.16) | 35220 (1.19) |
| MP4DQ | 22510 (1.21) | 39290 (1.18) | 39470 (1.27) | 12690 (1.18) | 9880 (1.39) | 16920 (1.18) | 36050 (1.22) |
| MP4SDQ | 23720 (1.27) | 39580 (1.18) | 40970 (1.32) | 13080 (1.22) | 10180 (1.44) | 17360 (1.21) | 37100 (1.26) |
| MP4SDTQ | 24850 (1.33) | 41240 (1.23) | 41760 (1.34) | 13970 (1.30) | 10370 (1.46) | 17780 (1.24) | 38420 (1.30) |
| CCSD | 23270 (1.25) | 39890 (1.19) | 41050 (1.32) | 12990 (1.21) | 10100 (1.43) | 17340 (1.20) | 37020 (1.25) |
| CCSD(T) | 25080 (1.35) | 41340 (1.24) | 43190 (1.39) | 13820 (1.29) | 10620 (1.50) | 17990 (1.25) | 38890 (1.32) |

^a Numbers in parentheses are ratios to the Hartree–Fock values (atomic units).

TABLE 16: Individual Components of the Second Hyperpolarizability of Thiophene (C₄H₄S) Calculated with 6-31G+*pd* Basis Set and ECP Method^a

| method | γ_{xxxx} | γ_{yyyy} | γ_{zzzz} | γ_{xyyy} | γ_{xzzz} | γ_{yyzz} | γ_s |
|---|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|--------------|
| 6-31G+ <i>pd</i> full electron | | | | | | | |
| HF | 15965 (1.00) | 13445 (1.00) | 14749 (1.00) | 6623 (1.00) | 4024 (1.00) | 6391 (1.00) | 15647 (1.00) |
| MP2 | 21610 (1.35) | 18030 (1.34) | 22060 (1.50) | 9350 (1.41) | 6930 (1.72) | 9380 (1.47) | 22600 (1.44) |
| MP3 | 18970 (1.19) | 16700 (1.24) | 20270 (1.37) | 8100 (1.22) | 6330 (1.57) | 8600 (1.35) | 20400 (1.30) |
| MP4D | 18760 (1.18) | 16190 (1.20) | 20260 (1.37) | 7910 (1.19) | 6300 (1.57) | 8480 (1.33) | 20120 (1.29) |
| MP4DQ | 19030 (1.19) | 16520 (1.23) | 20590 (1.40) | 8050 (1.22) | 6450 (1.60) | 8600 (1.35) | 20470 (1.31) |
| MP4SDQ | 19880 (1.25) | 17250 (1.28) | 21850 (1.48) | 8510 (1.28) | 6600 (1.64) | 9100 (1.42) | 21480 (1.37) |
| MP4SDTQ | 20780 (1.30) | 18060 (1.34) | 21740 (1.47) | 9020 (1.36) | 6730 (1.67) | 9250 (1.45) | 22110 (1.41) |
| CCSD | 19780 (1.24) | 17390 (1.29) | 22580 (1.53) | 8490 (1.28) | 8720 (2.17) | 9210 (1.44) | 22520 (1.44) |
| CCSD(T) | 21220 (1.33) | 18590 (1.38) | 23850 (1.62) | 9240 (1.40) | 9390 (2.33) | 9750 (1.53) | 24090 (1.54) |
| 6-31G+ <i>pd</i> frozen core | | | | | | | |
| HF | 15965 (1.00) | 13445 (1.00) | 14749 (1.00) | 6623 (1.00) | 4024 (1.00) | 6391 (1.00) | 15647 (1.00) |
| MP2 | 21610 (1.35) | 18020 (1.34) | 22080 (1.50) | 9350 (1.41) | 6930 (1.72) | 9380 (1.47) | 22610 (1.45) |
| MP3 | 18980 (1.19) | 16690 (1.24) | 20270 (1.37) | 8100 (1.22) | 6330 (1.57) | 8600 (1.35) | 20400 (1.30) |
| MP4D | 18760 (1.18) | 16180 (1.20) | 20260 (1.37) | 7910 (1.19) | 6300 (1.57) | 8480 (1.33) | 20110 (1.29) |
| MP4DQ | 19030 (1.19) | 16510 (1.23) | 20600 (1.40) | 8050 (1.22) | 6460 (1.61) | 8610 (1.35) | 20480 (1.31) |
| MP4SDQ | 19890 (1.25) | 17240 (1.28) | 21890 (1.48) | 8500 (1.28) | 6610 (1.64) | 9110 (1.43) | 21490 (1.37) |
| MP4SDTQ | 20800 (1.30) | 18060 (1.34) | 21750 (1.47) | 9020 (1.36) | 6740 (1.67) | 9260 (1.45) | 22130 (1.41) |
| CCSD | 19760 (1.24) | 17380 (1.29) | 22610 (1.53) | 8480 (1.28) | 6660 (1.66) | 9220 (1.44) | 21690 (1.39) |
| CCSD(T) | 21160 (1.33) | 18560 (1.38) | 23890 (1.62) | 9240 (1.40) | 7020 (1.74) | 9750 (1.53) | 23130 (1.48) |
| 6-31G+ <i>pd</i> for C, ECP (LANL1DZ+ <i>pd</i>) for S | | | | | | | |
| HF | 15901 (1.00) | 13385 (1.00) | 15271 (1.00) | 6512 (1.00) | 4095 (1.00) | 6270 (1.00) | 15662 (1.00) |
| MP2 | 21600 (1.36) | 17880 (1.34) | 22590 (1.48) | 9190 (1.41) | 6990 (1.71) | 9210 (1.47) | 22570 (1.44) |
| MP3 | 19000 (1.19) | 16670 (1.25) | 20940 (1.37) | 7990 (1.23) | 6430 (1.57) | 8520 (1.36) | 20500 (1.31) |
| MP4D | 18800 (1.18) | 16180 (1.21) | 20910 (1.37) | 7810 (1.20) | 6400 (1.56) | 8390 (1.34) | 20220 (1.29) |
| MP4DQ | 19070 (1.20) | 16510 (1.23) | 21250 (1.39) | 7950 (1.22) | 6560 (1.60) | 8520 (1.36) | 20580 (1.31) |
| MP4SDQ | 19910 (1.25) | 17210 (1.29) | 22520 (1.47) | 8390 (1.29) | 6710 (1.64) | 9010 (1.44) | 21570 (1.38) |
| MP4SDTQ | 20790 (1.31) | 18000 (1.34) | 22410 (1.47) | 8880 (1.36) | 6830 (1.67) | 9150 (1.46) | 22180 (1.42) |
| CCSD | 19810 (1.25) | 17440 (1.30) | 23290 (1.53) | 8350 (1.28) | 6770 (1.65) | 9170 (1.46) | 21830 (1.39) |
| CCSD(T) | 21240 (1.34) | 18650 (1.39) | 24600 (1.61) | 9080 (1.39) | 7150 (1.75) | 9720 (1.55) | 23280 (1.49) |

^a Numbers in parentheses are ratios to the Hartree–Fock values (atomic units).

comparison of the experimental values with the Hartree–Fock calculation for furan, thiophene, and selenophene. Table 17 shows the comprehensive comparison between the present theoretical calculations and the experimental values. Among the experimental values, the γ value for tellurophene has been measured very recently.⁸ The table shows that by including the higher electron-correlation effects the calculated results are in good agreement with the observed values when the heteroatom is light. In particular, the agreement for the furan molecule is excellent. However, as the heteroatom becomes heavier, the experimental values exceed the calculated ones. The possible

causes of this discrepancy are (1) frequency dispersion, (2) basis set deficiency, and (3) relativistic effect.

Among the possible causes, the most plausible is frequency dispersion, because the present calculation corresponds to the value at the limit of the zero frequency of the light, and does not consider the frequency dispersion. Even though our measurements were done at 800 nm in the transparent region for the furan homologues, some dispersion cannot be avoided. For homologues with heavier heteroatoms, the energy level of the excited states becomes lower and the influence of the dispersion should be more prominent.²³ To examine the effect of the

TABLE 17: Comparison between the Orientationally Averaged Second Hyperpolarizabilities Obtained by the Present Ab Initio Calculations and OKE Experiment^a

| molecule | calculation ^b | | | | experiment ^c |
|----------------------------------|--------------------------|-----------------------|---------|-----------------------|-------------------------|
| | Hartree–Fock | | CCSD(T) | | |
| | au | 10 ⁻³⁶ esu | au | 10 ⁻³⁶ esu | |
| C ₄ H ₄ O | 11096 | 5.6(1.0) | 14750 | 7.4(1.0) | 7.5(1.0) |
| C ₄ H ₄ S | 15040 | 7.6(1.4) | 20000 | 10.1(1.4) | 13.2(1.7) |
| C ₄ H ₄ Se | 18978 | 9.6(1.7) | 25480 | 12.8(1.7) | 17.2(2.3) |
| C ₄ H ₄ Te | 29515 | 14.9(2.7) | 38890 | 19.5(2.6) | 37.5(5.0) |

^a Numbers in parentheses are ratios to the values for furan molecule.

^b Present results, 6-31G+*pad*, ECP for Se and Te. ^c Measured at 790 nm. See references 5 and 8.

dispersion, we have already made frequency-dependent calculations of the second hyperpolarizability by using the time-dependent Hartree–Fock (TDHF) method, and found a larger dispersion for tellurophene than for the other homologues, which can account for part of the discrepancy. Some preliminary results will be published in a separate paper.²⁶

The second reason for the discrepancy is the possibility that the basis set is not yet sufficient for the heavier atoms. Klinkhammer and Pyykkö²⁷ pointed out that for the molecules with Te atoms the role of the f orbital is important for accurately estimating the intermolecular interaction. In general, as for the intermolecular interaction, the electron distribution in the outer region of a molecule can be important also for estimating the second hyperpolarizability. However, our preliminary calculation of γ further augmenting a diffuse f orbital does not show appreciably different results with or without the f orbital (results not shown). Therefore, we do not feel at present that the influence of the f orbital is large in this case.

The third reason is the possible relativistic effect. There has been little study of the relativistic effect on response properties such as (hyper)polarizability of molecules.^{28,29} The relativistic effect may be approximated by the ECP used in the present calculations.¹⁶ However, from the formula of perturbation expansion the transitions which are spin-forbidden in nonrelativistic approximation can be allowed. Transition properties of this kind cannot be approximated only by the ECP, and this effect may not be ignored for the response property calculations.

As done for the α and β values, the perturbation expansion for γ can be expressed as follows:

$$\gamma_{iiii} = 24 \sum_{n \neq g} \left[\frac{(\mu_{ng}^i \Delta \mu_{ng}^i)^2}{(E_{ng})^3} - \frac{(\mu_{ng}^i)^4}{(E_{ng})^3} + \sum_{m \neq n, g} \frac{(\mu_{ng}^i)^2 (\mu_{mn}^i)^2}{(E_{ng})^2 E_{mg}} \right] \quad (17)$$

$$\gamma_{ijij} =$$

$$4 \sum_{n \neq g} \left[\frac{4\mu_{ng}^i \mu_{ng}^j \Delta \mu_{ng}^i \Delta \mu_{ng}^j + (\mu_{ng}^i \Delta \mu_{ng}^j)^2 + (\mu_{ng}^j \Delta \mu_{ng}^i)^2}{(E_{ng})^3} - \frac{6(\mu_{ng}^i \mu_{ng}^j)^2}{(E_{ng})^3} + \sum_{m \neq n, g} \frac{4\mu_{ng}^i \mu_{mn}^i \mu_{ng}^j \mu_{mn}^j + (\mu_{ng}^i \mu_{mn}^i)^2 + (\mu_{ng}^j \mu_{mn}^j)^2}{(E_{ng})^2 E_{mg}} \right] \quad (18)$$

Here, in order to simplify the analysis, we adopt the three-type approximation proposed by Nakano et al.³⁰ and by Brédas et

al.³¹ The first term in the equations contributes positively to the total γ , where the difference of the dipole moments in the ground and excited states, $\Delta \mu_{ng}^i$, is important. Note that for the furan homologues this term can remain only in the components concerning the z -component. The second term also concerns only two levels but contributes negatively to the total γ . The last term concerns three states and contributes positively.

As mentioned before, components concerning the z -axis such as γ_{zzzz} or γ_{xxxx} are very much enhanced with substitution of heavier heteroatoms. For example, the γ_{zzzz} value of tellurophene is about five times that of furan, whereas the γ_{xxxx} value of tellurophene is smaller than twice that of furan. We can develop discussions similar to that done for the α value; that is, we can relate this to the two lowest excited states in the π -conjugated systems. Because the symmetry species for the two lowest excited states are B₂ and A₁,²³ the nonzero transition moments concerning the π - π^* transition are limited to μ_x and μ_z , respectively. Also, the transition moment between the two excited states is limited to μ_x . By using these relations from symmetry consideration and the three-state approximation, eqs 17 and 18 can be reduced as:

$$\gamma_{zzzz} = 24 \left[\frac{(\mu_{qg}^z \Delta \mu_{qg}^z)^2}{(E_{qg})^3} - \frac{(\mu_{qg}^z)^4}{(E_{qg})^3} \right] \quad (19)$$

$$\gamma_{xxxx} = 24 \left[-\frac{(\mu_{pg}^x)^4}{(E_{pg})^3} + \frac{(\mu_{pg}^x)^2 (\mu_{qp}^x)^2}{(E_{pg})^2 E_{qg}} \right] \quad (20)$$

$$\gamma_{xxzz} = 4 \left[\frac{(\mu_{pg}^x \Delta \mu_{pg}^z)^2}{(E_{pg})^3} + \frac{(\mu_{qg}^z \mu_{pg}^x)^2}{(E_{qg})^2 E_{pg}} \right] \quad (21)$$

where p and q denote the B₂ and A₁ excited states, respectively.

By considering the energy difference between the ground and the symmetry-allowed excited states, E_{qg} , in the denominator of eq 19 as the major factor, the large enhancement in the γ_{zzzz} value can be accounted for. Again, this corresponds to the fact that the energy level of the A₁ excited state becomes lower as the heteroatom becomes heavier.²³ Actually, the enhancement in the γ_{zzzz} value gives good correlation to the cubic inverse of E_{qg} , rather than that of E_{pg} .⁸

However, the major contributing term can be different depending on the tensor component. For the γ_{zzzz} component, it is very probable that the contribution from the positive two-state term, i.e., the first term in eq 19, is large. On the other hand, for the γ_{xxxx} component, the three-state term, i.e., the second term in eq 20, is considered to be the primary contributor because the obtained values are positive. In the case for the γ_{xxzz} component, both of these terms in eq 21 may contribute. The evaluation of the concerning transition moments is necessary to know the relative importance of the terms in eq 21.

Other tensor components, which concern the y -direction, vanish under the three-state approximation using π -character states. However, the calculated values are nonzero. This disagreement suggests that the non- π character states, such as the σ - π^* transition or transition to continuum states, considerably contribute to the tensor components concerning the y -direction.

4. Conclusions

In this study we made theoretical calculations of polarizability and hyperpolarizability of furan homologues and discussed physical mechanisms contributing to these values. As a result,

were revealed that, for the polarizability, α , and the second hyperpolarizability, γ , the energy difference between the ground and the symmetry-allowed excited states is the major factor in determining the values. On the other hand, for the first hyperpolarizability, β , the difference in the dipole moment, μ , between the two states can be the more important factor. These characteristics may be common for the response properties of other molecules with asymmetric direction such as furan homologues.

This work mainly concerned the effect of the heavy atom on the (hyper)polarizability in a series of homologues. The calculated results show that substitution of heteroatoms with heavier atoms is effective for the enhancement of the second hyperpolarizability, γ . Also of interest is the influence of π -conjugation on the polarizability and hyperpolarizability for these homologues. As for the second hyperpolarizability, we have already completed sufficient discussion of the problem by comparison between the furan and tetrahydrofuran homologues.¹¹

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Supporting Information Available: Table 1S, optimized geometries of furan homologues for each basis set (1 page). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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