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Theoretical Study on Diradical Characters and Nonlinear Optical Properties of 1,3-Diradical Compounds

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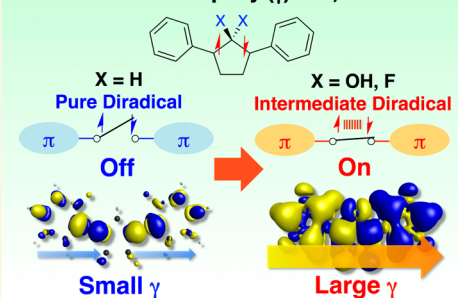
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S Supporting Information

ABSTRACT: We investigate the relationships between the diradical character (y) and nonlinear optical (NLO) properties of open-shell 1,3-diradical compounds using the broken-symmetry density functional theory method. The 2,2-substituent effects on the structure–property relationship are clarified for several 1,3-diphenylcyclopentane-1,3-diyl derivatives, which are known as the systems with weak or intermediate π -single-bonding characters. The parent 1,3-diphenylcyclopentane-1,3-diyl (**1a**: X = H) is found to be almost pure diradical ($y \sim 1$) owing to the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). The energy gap is determined by the balance of the through-space coupling with the through bond coupling effect. On the other hand, the introduction of the electron-withdrawing substituents X at the C2 position of cyclopentane-1,3-diyls (**1b**: X = OH, **1c**: X = F) is found to decrease the y -value owing to the effects of additional through-bond interactions. As a result, **1b** and **1c** are found to have intermediate y . Static second hyperpolarizabilities (γ) of **1b** and **1c** are found to be enhanced by a factor of ~ 4.5 and ~ 6.4 , respectively, compared with those of the pure singlet diradical **1a** and those of the triplet **1a–1c**. From the analysis of the third-order responses of electron density, the introduction of the 2,2-substituents is found to enhance the field-induced third-order polarizations over the whole system. We also investigate the effects of asymmetric donor/acceptor substitutions at the *para* positions of phenyl rings on the response properties. Although the asymmetric donor/acceptor substitutions have no significant impact on y in the present systems, they are found to provide the increase of γ from the corresponding nonsubstituted analogues. The present results have revealed strong correlation between the π -bonding character (diradical character) and third-order NLO properties in the real 1,3-diradical compounds. On the basis of the theoretically predicted correlation in the real systems, NLO measurements are speculated to be utilized as a new probe of the unique chemical bonding nature in such localized diradical compounds, which is one of the fundamental subjects in chemistry.

Correlation between Diradical Character and Third-Order NLO Property (γ) in 1,3-Diradicals



I. INTRODUCTION

Open-shell singlet species involving singlet di/multiradicals are known to be highly reactive, which originates in the unpaired or weakly bound electrons with antiparallel spins. Among the open-shell singlet species, singlet diradicals (and diradicaloids) are usually found as reaction intermediates, transition-state species, and metastable species,^{1–22} though there have been several singlet diradicaloids with high thermodynamic stability. Chemical and electronic structures of singlet diradicals have been investigated so far to achieve fundamental understanding of the nature of chemical bonding, and to expand the metastable chemical species that we can handle and observe experimentally. To this end, various quantitative evaluations of the diradical nature have been investigated for a long time. Among them, “diradical character (y)” has been widely employed as a theoretically defined chemical index of diradical nature.^{23,24} y is originally defined as twice the weight of the antibonding double excitation configuration in the ground-state

wave function, and it takes a value from 0 (closed-shell state) to 1 (pure diradical state).^{1,23–25} On the basis of the definition, $1 - y$ is regarded as one of the definitions of effective bond order.²⁵ In this regard, y is a useful index for discussing instability of chemical bond in the singlet ground state.²⁵

On the other hand, because y is defined from the weight of the excitation configuration, we can relate y with excitation properties for the low-lying excited states as well.^{26,27} From this point of view, we have theoretically clarified excitation energies and transition dipole moments in terms of y , by using the valence configuration interaction (VCI) method based on the symmetric^{26–29} and asymmetric³⁰ two-site diradical model. As a result, we have theoretically found the relationship between y and molecular second-hyperpolarizability γ (third-order non-

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linear optical [NLO] properties at the molecular scale); i.e., open-shell molecules with intermediate γ have significantly larger γ -values than those in the closed-shell ($\gamma = 0$) and pure diradical states ($\gamma \sim 1$).^{26–30} So far, lots of efficient design guidelines for molecular systems with high NLO properties have been proposed by both theoretically and experimentally.^{31–42} Most guidelines have focused on the chemical modifications, e.g., extension of π -conjugation length, introduction of donor/acceptor substitutions etc., of thermally stable closed-shell molecular species. On the basis of the so-called “ γ – γ correlation”, a new paradigm of NLO molecular designs using open-shell singlet species with intermediate γ has risen for realizing highly active open-shell NLO systems,^{43–54} which have the potential to be superior to conventional closed-shell NLO molecular systems.

Chemical structures that exhibit intermediate γ -values can be designed and realized on the basis of conventional chemical concepts, e.g., the resonance structure that is characterized by both open-shell (diradical) form and closed-shell form. Such systems are also characterized by small energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), which leads to the decrease in aromaticity and in excitation energy. To date, on the basis of the γ – γ correlation, experimental measurements of large two-photon absorption (TPA; third-order NLO phenomenon) cross sections have been reported for several delocalized singlet diradicals involving *ortho*- and/or *para*-quinoid structures, such as polycyclic aromatic hydrocarbons (PAHs),^{46–51} tetracyanoquinodimethane derivatives,^{52,53} bis-(acridine) dimer,⁵⁴ etc. These studies have not only raised the potential of open-shell molecular systems as novel NLO materials but also deepened the fundamental understanding of the correlation between the ground-state open-shell singlet character and magnetic interaction^{26,27,55} and other excitation properties like singlet fission.^{56–58}

In contrast to the recent rapid progress in studies on the delocalized diradicals mentioned above, studies on the γ – γ correlation in localized diradicals have been limited so far because such species are usually unstable and have short lifetimes. Molecular materials composed of localized diradicals with high thermostability are therefore considered to be difficult to realize. On the other hand, a wide-range tuning of diradical character for these compounds together with improving their kinetic stability are challenging issues from the viewpoint of understanding and analyzing the chemical bond nature of such transient species as well as of expanding the number of possible open-shell singlet species. In this study, therefore, as a prototypical localized diradical, we investigate 1,3-diradical compounds that are usually observed as the transition structure in the homolytic bond-cleavage and -formation reaction processes of cyclic compounds.^{1–4} 1,3-Diradical compounds are expected to have a small HOMO–LUMO gap because of the balance between the weak through-space (TS) interaction of the $p\pi$ AOs on the C_1 and C_3 sites and the weak through bond (TB) interaction of the ψ_s with the pseudo- π -orbital of CH_2 at the C_2 position (Figure 1, central part).^{59–61} Because of this feature, most of 1,3-diradical compounds tend to have small singlet–triplet (ST) energy gap and to be the ground-state triplet.^{62–65}

So far, several synthetic strategies have been proposed to increase the lifetime of 1,3-diradicals in the singlet state. As an example, long-lived 1,3-diphenyloctahydropentalene-1,3-diyl derivatives, which are generated as intermediate species

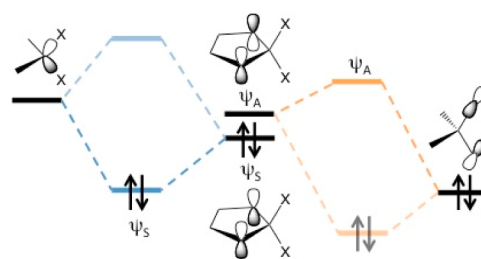


Figure 1. Structure of cyclopentane-1,3-diradical and the mechanism of increase of the HOMO–LUMO gap by the through-bond orbital interactions (hyper- and spiro-conjugations, shown by the left- and right-hand side diagrams, respectively).

obtained by the photodenitrogenation of the related cyclic azoalkanes, have been predicted and achieved by the introduction of electron-withdrawing substitution groups X (such as, X = OR and F) at the C_2 site (Figure 1).^{60,61,66–73} These intermediates are available within the lifetimes of $\sim 1 \mu s$ at room temperature, and the UV–vis spectroscopic investigations were also performed under low temperature glassy matrix conditions to characterize their chemical and electronic structures. The increase of the lifetime was explained by the contributions of the TB interaction with the pseudo- π -orbital of CX_2 in addition to the weak TS interaction between the radical sites.^{9,69–75} The TB interaction is the so-called hyper-conjugation mechanism, where the vacant σ^* -orbital for the C–X bonds, σ^*_{CX} , interacts with the bonding $p\pi$ -orbital, which results in the stabilization of the HOMO level (Figure 1, left-hand side diagram). In addition to the hyper-conjugation, we need to consider effects of another TB interaction, which is called spiro-conjugation. In this case, the 2p nonbonding atomic orbital (AO) on X atom, n_X , interacts with the antibonding $p\pi^*$ -orbital, which results in the destabilization of the LUMO level (Figure 1, right-hand side diagram). Judging from the relative positions of σ^*_{CX} and n_X levels, the hyper- and spiro-conjugation interactions were predicted to be dominant for systems with X = F and X = OR, respectively.⁷⁵ This π -bonding character between the spatially separated two radical sites is referred to as the “ π -single-bonding” character.⁹ Several long-lived intermediate species with different π -single-bonding characters have been studied experimentally by using the low-temperature and transient spectroscopic analyses as well as the NMR and EPR measurements.⁹ Furthermore, *para* donor and/or acceptor substituent effects on the lifetimes of 2,2-dimethoxy-1,3-diphenylcyclopentane-1,3-diyl derivatives were investigated theoretically and experimentally.⁷¹ Compared to the nonsubstituted reference compound, mono- and disubstituted compounds were found to show slightly longer lifetimes.^{64,71,76,77} The relationship between the lifetime and the ST energy gap of the *para* substituted systems was examined as well. Introduction of donor and/or acceptor groups to the conjugated systems are known to be an efficient way to modulate their optical response properties as well through the change of electronic structures.

Because the localized 1,3-diradical compounds are known as a prototypical real open-shell compounds, investigations on the γ – γ correlation in the real 1,3-diradical compounds are expected to further deepen the fundamental understanding of the relationship between the chemical structures and optical response signals. In this regards, 2,2-substituent effects on the diradical character and NLO properties of 1,3-diradical compounds would be interesting topics from both the

theoretical and experimental viewpoints. Actually, generation and isolation of these localized diradicals under low temperature matrix condition have made it possible to study their electronic structures by using several spectroscopic measurement analyses. These results suggest the possibility of NLO measurements of such thermally unstable localized diradical species under a certain condition. We therefore investigate the correlation among the chemical species X of the 2,2-substituents, diradical character y , linear polarizability α , and second hyperpolarizability γ of the parent 1,3-diphenylcyclopentane-1,3-diyl (**1a**: X = H) and of its derivatives (Figure 2).

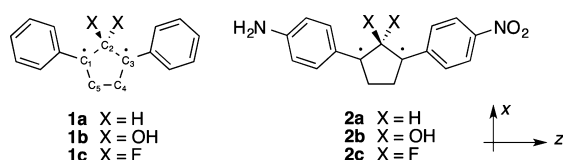


Figure 2. Structures of symmetric (**1a–1c**) cyclopentane-1,3-diyl derivatives and corresponding asymmetric donor/acceptor substituted systems (**2a–2c**).

Here, the group X = OH (**1b**) and F (**1c**) are considered as the 2,2-substituents. In addition, we also examine the asymmetric donor/acceptor substitution effects on y , α , and γ of the 1,3-diradical compounds from the viewpoint of asymmetric diradicaloids, where the degree of asymmetric electron distribution, i.e., “asymmetry”, is predicted to further enhance the optical responses as compared to the symmetric diradicaloids.³⁰ The *para*-disubstituted 1,3-diphenylcyclopentane-1,3-diyl derivatives (**2a–2c**) with $-\text{NH}_2/-\text{NO}_2$ groups have been studied as compared to the nonsubstituted analogues (Figure 2).

II. CALCULATION METHODS

Figure 2 shows the calculated molecular systems. Geometry optimizations for the lowest singlet and triplet states were performed at the UB3LYP/6-311G* level of approximation. No symmetry constraint was imposed during the geometry optimization. After that, frequency analyses were performed to confirm stable minimum structures. Because broken-symmetry solution for the singlet state is known to suffer from the spin-contamination effect, which affects the ST energy gaps, we have employed the approximate spin-projection scheme, which can effectively remove the spin-contamination effect in the low-spin state energy, proposed by Yamaguchi.^{25,78,79} The singlet energy after the approximate spin-projection is expressed by

$$^S E^{\text{AP}} = ^S E + \frac{\langle S^2 \rangle_S}{\langle S^2 \rangle_T - \langle S^2 \rangle_S} (^S E - ^T E) \quad (1)$$

Here, $\langle S^2 \rangle_X$ and $^X E$ represent the expectation value of the spin-squared operator and the total energy for the spin state X (=S, T) at the optimized geometry of the singlet state, respectively. This approximate projection scheme is known to be applicable to the evaluation of adiabatic ST energy gap of various localized diradical compounds.^{25,78,79} The single point energy calculations for the ST energy gap were performed at the UB3LYP/6-31+G* level of theory using the UB3LYP/6-311G* optimized geometries. The HOMO–LUMO energy gap for the lowest singlet-state geometry, $\Delta \varepsilon_{\text{HL}}$, was evaluated at the RB3LYP/6-31+G* level of approximation.

Diradical character y of the lowest singlet state was calculated from the occupation number of the lowest unoccupied natural orbital (LUNO)^{80,81} obtained using the long-range corrected (LC-)UBLYP exchange–correlation functional⁸² along with the 6-31+G* basis set. Here, the range-separating parameter μ in the LC scheme was set to be 0.33 bohr^{−1}, which is known to well reproduce the excitation energies and transition properties for several organic molecules.⁸² Within the calculation of optical response properties, we set the coordinate axis so that the linear line going through the C₁ and C₃ atoms is parallel to z-axis. The longitudinal (z-axis) component of static polarizability α ($\equiv \alpha_{zz}$) and second hyperpolarizability γ ($\equiv \gamma_{zzzz}$) were calculated by the finite-field (FF) method⁸³ using the total energies obtained at the LC-UBLYP/6-31+G* level of approximation. In the FF approach, the static α - and γ -values were numerically evaluated using the differentiation formula,

$$\alpha_{zz} = \frac{1}{(F^z)^2} \{E(F^z) - 2E(0) + 2E(-F^z)\} \quad (2a)$$

and

$$\gamma_{zzzz} = \frac{1}{36(F^z)^4} \{E(3F^z) - 12E(2F^z) + 39E(F^z) - 56E(0) + 39E(-F^z) - 12E(-2F^z) + E(-3F^z)\} \quad (2b)$$

respectively, where $E(F^z)$ represents the total energy of the system in the presence of the static electric field with the amplitude of F^z . The B convention⁸⁴ was employed in the definition of the hyperpolarizability. The applicability of the LC-UBLYP exchange–correlation functional ($\mu = 0.33$ bohr^{−1}) for the evaluation of the (hyper)polarizabilities of organic open-shell compounds has been reported in our previous paper.^{85,86} In the previous study, we have also investigated the basis set dependence of γ -values of singlet diradical systems by employing the *p*-quinodimethane model.⁸⁷ By comparing the reference results using large basis sets (e.g., aug-cc-pVDZ and aug-cc-pVTZ), we found the Pople-type 6-31G basis set along with the polarization and diffuse functions on carbon atoms give both qualitative and (semi)quantitative results for the y – γ correlation. On the other hand, taking account of the polarization and diffuse functions on hydrogen atoms is found to have small impact on the amplitudes of γ of such π -diradical systems with medium size. Accordingly, in the present study, we employed the 6-31+G* basis set for the evaluation of γ . The convergence criterion for the total energy was set to be 10^{−10} au. We employed several static field amplitudes so that the relative numerical errors for the γ -values become about ~1%.

To discuss the spatial contributions of electrons to the optical response properties, we performed the (hyper)polarizability density analysis.⁸⁸ From the expansions of the dipole moment and of the charge density function $\rho(\mathbf{r}, \mathbf{F})$ in a power series of applied electronic field \mathbf{F} , α and γ can be expressed by⁸⁸

$$\alpha_{zz} = \int r^z \rho_z^{(1)}(\mathbf{r}) d\mathbf{r} \quad (3a)$$

and

$$\gamma_{zzzz} = \frac{1}{3!} \int r^z \rho_{zzz}^{(3)}(\mathbf{r}) d\mathbf{r} \quad (3b)$$

where

$$\rho_z^{(1)}(\mathbf{r}) = \left. \frac{\partial \rho(\mathbf{r}, \mathbf{F})}{\partial F^z} \right|_{F=0} \quad (4a)$$

and

$$\rho_{zzz}^{(3)}(\mathbf{r}) = \left. \frac{\partial^3 \rho(\mathbf{r}, \mathbf{F})}{\partial F^z \partial F^z \partial F^z} \right|_{F=0} \quad (4b)$$

Here, z represents the z -axis component of the electron coordinate. The first-order (third-order) derivative of electron density with respect to the applied electric fields, $\rho_z^{(1)}(\mathbf{r})$ [$\rho_{zzz}^{(3)}(\mathbf{r})$], is referred to as static $\alpha(\gamma)$ -density.⁸⁸ The α (γ)-density map represents the relative phase and magnitude of change in the first-order (third-order) charge densities between two spatial points with positive and negative $\alpha(\gamma)$ -densities. The relationship between $\alpha(\gamma)$ and its density $\rho_z^{(1)}(\mathbf{r})$ [$\rho_{zzz}^{(3)}(\mathbf{r})$] is explained by considering a simple example: a pair of localized $\alpha(\gamma)$ -densities with positive and negative values. The sign of the contribution to $\alpha(\gamma)$ is positive when the direction from positive to negative $\alpha(\gamma)$ -density coincides with the positive direction of the coordinate axis. The sign becomes negative in the opposite case. Moreover, the magnitude of the contribution associated with this pair of $\alpha(\gamma)$ -densities is proportional to the density amplitudes multiplied by the distance between them. Because the positive and negative $\alpha(\gamma)$ -densities correspond to the increase and decrease of field-induced first-order (third-order) charge densities, respectively, we can understand the spatial contributions of first-order (third-order) polarization from the $\alpha(\gamma)$ -density map. All the calculations were performed using the Gaussian 09 program package.⁸⁹

III. RESULTS AND DISCUSSION

Structural Features and Diradical Characters. We first discuss the calculation results of systems **1a–1c**. In Table 1, we

Table 1. Selected Atomic Distances R [Å], and Dihedral Angles D [deg] in the UB3LYP/6-311G* Optimized Geometries of the Singlet and Triplet States

	1a (X = H)		1b (X = OH)		1c (X = F)	
	singlet	triplet	singlet	triplet	singlet	triplet
$R(C_1-C_2)$	1.508	1.505	1.512	1.521	1.481	1.500
$R(C_2-C_3)$	1.508	1.505	1.512	1.521	1.481	1.500
$R(C_1-C_3)$	2.396	2.397	2.379	2.408	2.366	2.411
$D(C_2-C_1-C_4-C_5)$	12.99	13.64	0.23	14.21	0.08	14.82
$D(C_2-C_3-C_5-C_4)$	12.89	13.61	0.42	14.25	0.12	14.83

compare the results of selected interatomic distances R , and dihedral angles D of the optimized geometries of the singlet and triplet states. The molecular structures of **1a** in the singlet and triplet states are found to be very close to each other. Actually, we obtained almost the same interatomic distances and dihedral angles of the five-membered ring of the compounds for each spin state (Table 1). In contrast, in **1b** and **1c**, the optimized geometries of the singlet and triplet states are found to be different from each other. For example, the atomic distances $R(C_1-C_2)$ of **1b** and **1c** in the singlet state (1.512 Å for **1b** and 1.481 Å for **1c**) are slightly shorter than those in the triplet state (1.521 Å for **1b** and 1.500 Å for **1c**). The interatomic distance $R(C_1-C_3)$ of the singlet state is found to be shorter in **1b** (2.379 Å) and in **1c** (2.366 Å) than in **1a**

(2.396 Å). Such decreases of $R(C_1-C_3)$ in **1b** and **1c** were not obtained for the optimized geometry of the triplet state. In the systems with the electron-withdrawing 2,2-substituents, the TB interactions (hyper- and spiro-conjugations) are predicted to assist the π -bonding character between the C_1 and C_3 sites. The TB interactions are also expected to affect the structural planarity. Actually, although the dihedral angle $D(C_2-C_1-C_4-C_5)$ of **1a** in the singlet state is more than 10°, which indicates the nonplanar structure of the five-membered ring, the dihedral angle for **1b** and **1c** is found to be close to 0°. As a result, **1b** and **1c** have almost planar structures in the singlet state (see also Figure S1 in Supporting Information for side views of these systems). On the other hand, all the systems in the triplet state are found to have nonplanar structures.

Table 2 summarizes the calculation results of $\Delta\epsilon_{HL}$ and ΔE_{ST} . At the RB3LYP/6-31+G* level of approximation, $\Delta\epsilon_{HL}$

Table 2. Calculation Results for HOMO–LUMO Gap $\Delta\epsilon_{HL}$, Singlet–Triplet Energy Gap ΔE_{ST} , Diradical Character y , Linear Polarizability α , and Second Hyperpolarizabilities γ in the Singlet and Triplet States of **1a–1c**

	$\Delta\epsilon_{HL}$ [eV]	ΔE_{ST} [kcal/mol]	y	α [au]		γ [10^5 au]	
				singlet	triplet	singlet	triplet
1a	0.79	0.44	0.97	311	311	0.42	0.41
1b	1.46	−5.75	0.72	348	326	1.9	0.53
1c	1.68	−8.79	0.64	355	319	2.7	0.60

of **1a** (0.79 eV) was smaller than 1 eV. The results for **1b** (1.46 eV) and **1c** (1.68 eV) are about twice as large as that of **1a**. The increase of $\Delta\epsilon_{HL}$ was predicted to affect the ΔE_{ST} results of the 1,3-diradical compounds. Actually, the ΔE_{ST} value of **1a** is a small positive value, which means that the ground state is the triplet, whereas those of **1b** and **1c** are found to be negative, which means that these have the singlet ground states. Because the singlet state is relatively stabilized by the introduction of the electron-withdrawing 2,2-substituents, we are interested in the qualitative evaluation of π -bonding character in the singlet state from the calculation of y . The calculated y -values of **1a–1c** in the singlet state are also shown in Table 2. As expected from the localized nature of electrons in 1,3-diradical systems and the small HOMO–LUMO energy gap, y of **1a** is found to be close to 1 ($y = 0.97$), which means that the electronic structure of **1a** is almost pure diradical state. In other words, the π -bonding character for this system is negligible. On the other hand, **1b** ($y = 0.72$) and **1c** ($y = 0.64$) are found to have intermediate diradical character values, which indicate the intermediate π -bonding characters of **1b** and **1c** in the singlet state owing to the presence of the electron-withdrawing 2,2-substituents. These differences of y -values, i.e., π -bonding character, between **1a** and **1b/1c** substantiate the structural differences between them mentioned in the previous paragraph.

To discuss the 2,2-substituent effects on the bonding characters, we compared the frontier natural orbitals of **1a–1c**. Figure 3 shows spatial distributions and occupation numbers of the HONO and LUNO in the singlet state evaluated at the LC-UBLYP/6-31+G* level of approximation. Note that, in the present study, y is evaluated as the occupation number of the LUNO. As expected, we obtained the π -bonding character between the p-orbitals on the C_1 and C_3 sites for the HONO. For **1a**, it is found that the bonding region of the HONO (the white mesh region) extended over the C_1 and C_3

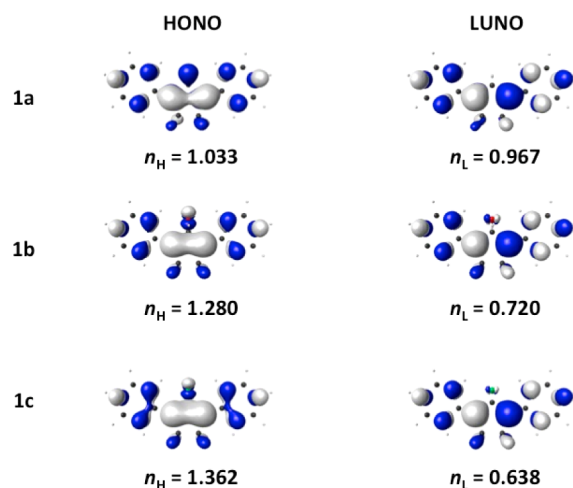


Figure 3. Spatial distributions of the HONO and LUNO of 1a–1c along with their occupation numbers (denoted as n_H and n_L , respectively). White and blue meshes represent isosurfaces with contour values of ± 0.03 au, respectively.

sites is not distributed on the C_2 site. On the other hand, the bonding regions of the HONO for 1b and 1c are found to extend around C_2 site to some extent. When the maps of 1a and 1b/1c are compared, the bonding region is more extended for 1b/1c than for 1a. Such difference in the spatial distributions of bonding region is considered to originate in the difference of the degree of hyper-conjugation effect. For the LUNO, we obtained the π -antibonding character between the p-orbitals on the C_1 and C_3 sites. In the LUNOs of 1b and 1c, it is also found that there are small distributions on the O(F) atoms, which originate in the p_z -orbital of the O(F) atoms. This is considered to be due to the spiro-conjugation effect. Actually, such a contribution cannot be obtained for the LUNO of 1a ($X = H$). From the isosurface map, the distributions on the O atoms are slightly larger than those on the F atoms of 1c. In summary, the introduction of the electron-withdrawing 2,2-substituents X is found to increase the π -bonding character of the 1,3-diradical compounds through the TB interactions (hyper- and spiro-conjugations).

Optical Response Properties. In the previous subsection, we discussed the 2,2-substituent effects on the chemical and electronic structures of 1,3-diradical compounds. As a result, 1b and 1c with electron-withdrawing substituents are found to have intermediate γ -values. Here, we focus on the optical response properties of 1,3-diradical compounds. The present 1,3-diradical compounds are composed of the terminal π -conjugation parts (phenyl groups) linked with the central 1,3-diradical part. One of the most efficient strategies for enhancing the NLO properties is known to be the extension of the π -conjugation length.^{31–42} Therefore, the electronic coupling between both-end phenyl groups is considered to be important for determining their optical response properties. Because we have already found that the coupling between the p π -electrons on C_1 and C_3 can be tuned by the 2,2-substituents X, we expect that the coupling between both-end phenyl groups are also tuned by the 2,2-substituents X, which are thus expected to provide significant effects on the NLO properties. In Table 2, we also summarized the calculation results of the linear polarizabilities α and the second hyperpolarizabilities γ of 1a–1c. As expected from the geometric features and the electronic structures, the α -values of 1a in the singlet and triplet states are

found to be almost equal to each other. The α -values of 1b and 1c in the singlet state are about 112% and 114% of the reference α -value of 1a with the pure diradical nature, respectively. That is, the α -values are slightly enhanced by the introduction of the electron-withdrawing substituents. On the other hand, the α -values of 1b and 1c in the triplet state are found to be close to the value of 1a. Therefore, the electron-withdrawing 2,2-substituents are considered to have slight effects on the linear optical responses of the 1,3-diradical compounds in the ranges from intermediate to large γ -values.

In contrast to the results of α , we obtained significant γ and spin-state dependences of γ . Again, the γ -values of 1a in the singlet and triplet states are found to be almost similar to each other because of their similar electronic structures, i.e., negligible and non C_1 – C_3 π -bondings, respectively. In the singlet state, the γ -values of 1b ($\gamma = 0.72$) and 1c ($\gamma = 0.64$) with intermediate γ are found to be about 4.5 and 6.4 times as large as that of 1a with the pure diradical nature ($\gamma = 0.97$). Of course, 1b and 1c have the electronegative atoms (O and F), the electron-withdrawing feature of which may directly contribute to the enhancement of the γ -values in some degree. However, the γ -values of 1b and 1c in the triplet state are only about 130% and 146% of that of 1a. Judging from these results, the enhancement of γ -values of 1b and 1c in the singlet state is mainly attributed to the intermediate diradical nature of these systems. The electron-withdrawing 2,2-substituents are thus considered to affect indirectly to the enhancement of the γ -values through the modulations of π -bonding character of the 1,3-diradical part. These results revealed that the strong correlation between the π -bonding characters and third-order NLO properties of 1,3-diradical compounds. In other words, large third-order NLO signals of 1,3-diradical compounds in comparison with that of a reference compound may be treated as a signature of the existence of the intermediate C_1 – C_3 π -bonding character in the 1,3-diradical moiety.

To further discuss the relationship between the electronic structure and the response properties of 1,3-diradical compounds, we here show the results of α - and γ -density analyses. Figure 4 shows the isosurface maps of the α -densities, i.e., the increase and decrease of charge density proportional to

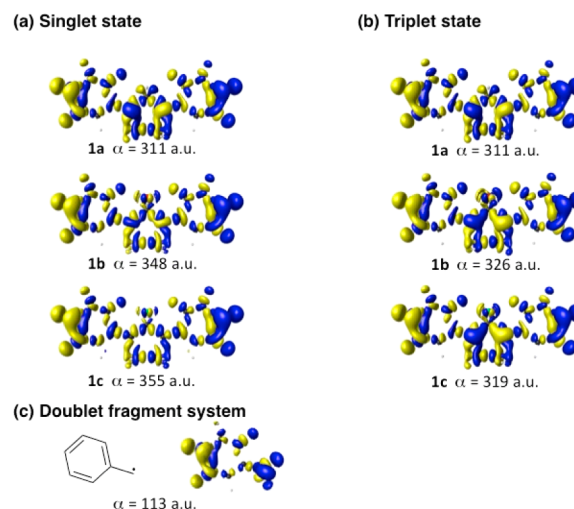


Figure 4. Maps of α -density of singlet state (a) and triplet state (b) of the 1,3-diradical compounds, 1a–1c, and that of the benzyl radical (c). Yellow and blue meshes represent positive and negative α -densities with contour values of ± 0.1 au, respectively.

F^z , of **1a–1c** in the singlet and triplet states (Figure 4a,b). Spatial distributions of the α -density of **1a** in the singlet and triplet states are found to be almost similar to each other, which corresponds to the similar α -values of each spin state of **1a**. It is found that large positive and negative α -densities appear around the edges of both-end phenyl groups, which give a primary positive contribution to α . In addition to the primary contributions, small positive and negative α -densities due to the σ -electrons can be observed over the molecule. These positive and negative σ -electron contributions are found to appear alternately, and thus to almost cancel each other. On the other hand, the π -electrons on the C_1 and C_3 sites are found to contribute negatively to the total α . Such negative contributions of π -electrons on the C_1 and C_3 sites are also observed in the maps of **1b** and **1c** in the triplet state. It is found that the negative π -electron contributions on the C_1 and C_3 sites in the singlet state are reduced gradually when γ decreases. Indeed, the negative π -electron contributions in **1c** almost disappear. To clarify the origin of the negative π -electron contributions, we also calculated α and its density of a benzyl radical, which constitutes the left-hand side of 1,3-diphenylcyclopentane-1,3-diyl (Figure 4c). The geometry of this doublet fragment system was taken from that of the singlet **1a** by eliminating the irrelevant atoms and then attaching two hydrogen atoms to C_1 . As seen from the α -density map, primary positive and negative α -densities due to π -electrons are distributed around the left-hand edge of the phenyl-group and the $-\text{CH}_2$ radical site, respectively. This feature is similar to that of singlet **1a**, whereas for singlet **1b** and **1c**, the negative π -electron α -densities on the $-\text{CH}_2$ radical site are significantly reduced. This implies that for singlet **1a**, the left- and right-hand benzyl radical moieties are well decoupled, resulting in the negative π -electron contributions to the α of the C_1 and C_3 sites, whereas that for singlet **1b** and **1c**, the π -electrons are somewhat delocalized from the one benzyl radical side to the other side, leading to the primary positive π -electron contribution to the α of the both-end phenyl rings. This difference in π -electron delocalization features for **1a–1c** turns out to substantiate that in the γ -values. For the triplet states, all the α -densities are very similar to that of singlet **1a**. However, by comparing the maps of singlet **1a** and **1b/1c**, we found that the primary difference of the spatial distributions of α -density only around the five-membered ring, and that the α -density distributions on the both-end phenyl rings are almost unchanged. This indicates that the 2,2-substituent effect on the first-order response of π -electron density is local.

Next, we examine the substituent effects on the γ -densities. We compared the maps of **1a–1c** in the singlet and triplet state (Figure 5a,b). As seen from the maps, π -electrons provide dominant contributions to the third-order response. Similar to the results of α -density, spatial distributions of γ -density of **1a** in the singlet and triplet states are almost the same, which corresponds to their similar γ -values and indicates that the nearly pure diradical state ($\gamma \sim 1$) exhibits effective decoupling between the left- and right-hand benzyl radical moieties similar to that for the triplet state. In the maps of **1a**, positive and negative regions of γ -densities are distributed on the both-end phenyl rings. The γ -densities on the phenyl groups contribute positively to the total γ . It is found that the γ -density distributions of **1b** and **1c** in the triplet state are similar to those of **1a**, except for the slight γ -density distributions on O(F) atoms. These results are in agreement with the fact that the γ -values of these systems are almost similar to each other. In

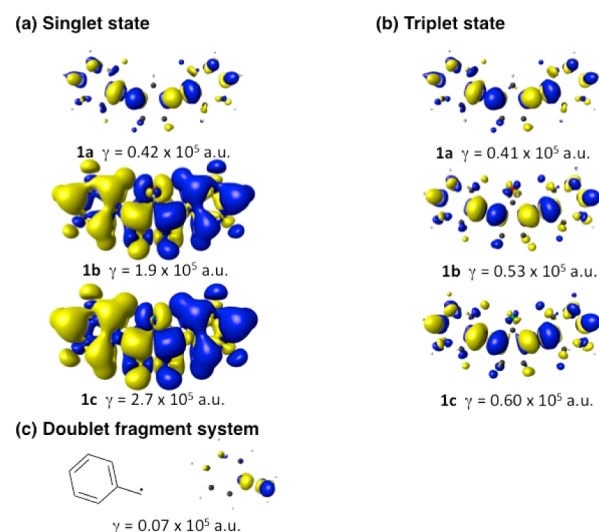


Figure 5. Maps of γ -density of singlet (a) and triplet state (b) of the 1,3-diradical compounds, **1a–1c**, and that of the benzyl radical (c). Yellow and blue meshes represent positive and negative γ -densities with contour values of ± 100 au, respectively.

these cases, the γ -densities on the C_1 and C_3 sites are found to contribute negatively to the γ , the feature of which is the same as that of the α -densities. We therefore calculated γ and its density of a benzyl radical to clarify the origin of the negative contributions (Figure 5c). As seen from the γ -density map of this doublet fragment system, the positive and negative γ -densities appear primarily on the exocyclic C–C bond region. In particular, the negative γ -densities appear on the $-\text{CH}_2$ radical site. Although the γ -density on the phenyl ring of the fragment system is slightly small, the feature of the spatial distributions is similar to that of the left-hand side of **1a**. In contrast to the results of α -density, it is found that the amplitudes of the γ -densities of **1b** and **1c** in the singlet state are significantly enhanced in the whole region of the systems. Furthermore, large positive and negative γ -densities are well separated on each side of the system. This result indicates that significant third-order polarization over the system is induced in **1b** and **1c** in the singlet state.

In contrast to the case of the first-order response, it should be noted that the substituent effect on the third-order response is expected to be nonlocal. Actually, the 2,2-substituents are found to induce significant third-order response of π -electron densities on the both-end phenyl rings. Such a significant nonlocal effect is predicted to be caused by the enhancement of the virtual excitation processes between low- and high-lying excited states (described by the extended wave functions) due to the intermediate γ -values. Similar significant nonlocal enhancement of the third-order response in open-shell molecular systems with intermediate open-shell character has been obtained previously in the open-shell slipped-stacked aggregates composed of diphenalenyl-diradical compounds,⁹⁰ where the strong covalent-like intermolecular interactions between the open-shell monomers induce significant third-order polarization over the aggregates. In the present case, it is shown that the intermediate π -bonding (intermediate diradical character) between the C_1 and C_3 sites is the origin of the significant third-order polarization over the molecule.

Asymmetric Donor/Acceptor Substitution Effects on Electronic Structures and Optical Response Properties of 1,3-Diradicals. In a previous study, we have theoretically

Table 3. Calculation Results for HOMO–LUMO Gap $\Delta\epsilon_{\text{HL}}$, ΔE_{ST} , γ , α , and γ in the Singlet and Triplet States of Asymmetric Donor/Acceptor Substituted Systems, **2a–2c**

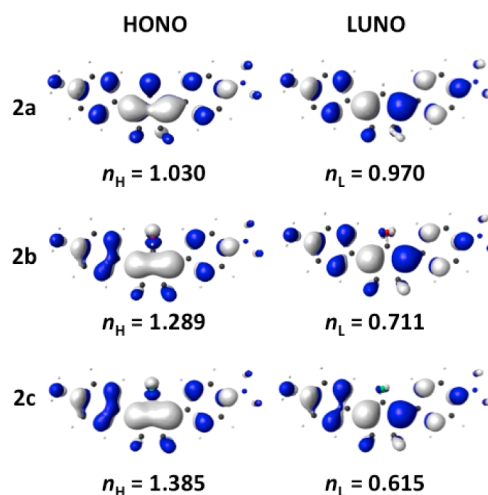
	$\Delta\epsilon_{\text{HL}}$ [eV]	ΔE_{ST} [kcal/mol]	γ	α [au]		γ [10^5 au]	
				singlet	triplet	singlet	triplet
2a	0.70	0.40	0.97	420 (1.35) ^a	420 (1.35) ^a	1.8 (4.3) ^a	1.8 (4.4) ^a
2b	1.33	−5.82	0.71	481 (1.38) ^a	440 (1.35) ^a	9.1 (4.8) ^a	2.4 (4.5) ^a
2c	1.54	−8.96	0.62	509 (1.43) ^a	433 (1.36) ^a	14 (5.2) ^a	2.7 (4.5) ^a

^aValues in round parentheses represent the increase ratio of (hyper)polarizabilities with respect to the corresponding symmetric systems, **1a–1c**.

revealed the effect of introducing asymmetric electron distribution on the (hyper)polarizabilities of open-shell singlet systems on the basis of the two-site asymmetric model, where the factor of asymmetry is introduced.³⁰ We found the decrease of diradical character (y_{A}) in an asymmetric system as compared with that (y_{S}) in the corresponding symmetric system. The γ of an asymmetric system with a large asymmetry was found to be enhanced extraordinarily in the intermediate y_{A} region. Even in a system with a moderate asymmetry, we can expect significant enhancement of γ .³⁰ In practice, the introduction of asymmetry to a symmetric system can be achieved by the external physical perturbations (e.g., application of static electric field) or by the chemical modifications (e.g., donor/acceptor substitutions).⁹¹ However, there have been few examples of real asymmetric diradical systems. On the other hand, the effects of donor and/or acceptor substitution on the singlet–triplet energy gap, ΔE_{ST} , and lifetime of the singlet intermediate of 1,3-diphenylcyclopentane-1,3-diyl derivatives have been studied both experimentally and theoretically.^{37,38} The introduction of donor and/or acceptor groups at the *para* positions of phenyl groups was found to enhance ΔE_{ST} slightly, so that the singlet state becomes more stable. We therefore investigate the asymmetric donor/acceptor substitution effects on γ , α , and γ of the 1,3-diradical compounds. Here, we employ a pair of donor/acceptor substituents, $-\text{NH}_2$ and $-\text{NO}_2$, at the *para* positions of terminal phenyl groups (**2a–2c** in Figure 2) and then compare the calculation results with each other and with the nonsubstituted analogues **1a–1c**. Actually, donor/acceptor substitutions are known as the efficient strategies to enhance the NLO properties of closed-shell π -conjugated systems. We therefore focus on the cooperative effect of intermediate γ and asymmetric donor/acceptor disubstitutions on the optical response properties of 1,3-diradical systems.

Table 3 shows the calculation results of $\Delta\epsilon_{\text{HL}}$, ΔE_{ST} , and γ . From the comparison of the results with those of **1a–1c**, $\Delta\epsilon_{\text{HL}}$ is found to slightly decrease by the asymmetric donor/acceptor substitution. The effect of donor/acceptor substituents on $\Delta\epsilon_{\text{HL}}$ is slightly larger for the systems with the electron-withdrawing 2,2-substituents [1.46 eV (**1b**) vs 1.33 eV (**2b**) and 1.68 eV (**1c**) vs 1.54 eV (**2c**)] than for the reference system [0.79 eV (**1a**) vs 0.70 eV (**2a**)]. As expected, it is found that the results of ΔE_{ST} are also slightly influenced by the donor/acceptor substitutions. The ΔE_{ST} of **2a** was positive value, and thus the system is the ground-state triplet. On the other hand, the ΔE_{ST} of **2b** and **2c** are found to be negative, and thus these systems are predicted to be ground-state singlet. In these systems, the ST gap becomes slightly large compared to that of the corresponding nonsubstituted systems **1b** and **1c**.

Figure 6 shows plots of the HONO and LUNO for **2a–2c**. It is found that the spatial distributions of both these frontier NOs are delocalized over the whole region of the system involving the terminal donor and acceptor groups at the given contour

**Figure 6.** Spatial distributions of the HONO and LUNO of **2a–2c** along with their occupation numbers (denoted as n_{H} and n_{L} , respectively). White and blue meshes represent isosurfaces with contour values of ± 0.03 au, respectively.

value. The feature of spatial distributions indicates that the asymmetries in **2a–2c** introduced by the terminal donor/acceptor substitution are moderate. Actually, the diradical characters γ of **2a–2c** that correspond to y_{A} are nearly close to those of the corresponding nonsubstituted systems **1a–1c** that corresponds to y_{S} . As a result, **2a** is almost pure diradical in the singlet state, whereas **2b** and **2c** have an intermediate diradical nature. This moderate effect on γ can be explained by the mutually remote *para* positions of donor/acceptor substituents; i.e., there is a phenyl ring between the donor (acceptor) and the C_1 (C_3) radical site. The donor and acceptor orbitals are considered to interact directly with those of the phenyl groups. It is therefore expected that the electron-donating and -withdrawing abilities on the p-electrons on the C_1 and C_3 sites are considerably shielded by the π -orbitals on the phenyl rings. Nevertheless, it is expected from the VCI results that an asymmetric open-shell singlet system with intermediate y_{A} and moderate asymmetry still exhibits the enhancement of γ -value as compared to the reference symmetric open-shell singlet system.

In Table 3, we also summarize the calculation results of α and γ in the singlet and triplet states of **2a–2c**. By comparing the results with those of the corresponding nonsubstituted systems, **1a–1c**, we found the α -values increase about 130–140% for all systems. This is predicted to be due to the increase of molecular size as well as the electron-donating and -withdrawing natures of the donor and acceptor. In Table 3, we also show the increase ratio of α defined as $\alpha(2x)/\alpha(1x)$ [$x = \text{a, b, and c}$]. From the results, the ratios of α of **2a** in the singlet (135%) and triplet (135%) states are found to almost coincide with each other. The ratios are slightly enhanced for

2b (138%) and **2c** (143%) in the singlet state with intermediate γ . Because the ratios of **2b** (135%) and **2c** (135%) in the triplet state are nearly equal to that of **2a**, there is a very small synergy effect of intermediate γ and asymmetric donor/acceptor substitution on α , though the increase ratio is slight in this case.

Next, we compare the results of γ . Here, we also defined the increase ratio for γ as $\gamma(2x)/\gamma(1x)$ [$x = a, b$, and c]. As seen from the results, the γ -values show about 400–500% increase by the introduction of the asymmetric donor/acceptor substituents. It is found that the ratio of γ of **2a** in the singlet state (430%) is similar to that in the triplet state (440%). The ratios of **2b** (480%) and **2c** (520%) in the singlet state are found to be larger than that of **2a**, though those in the triplet state remain about 450%. Asymmetric donor/acceptor substitutions at the *para* positions are therefore considered to provide at least a 430–450% increase of γ , regardless of the difference in the π -bonding character between the C_1 and C_3 sites. This primary contribution in the increase of γ is predicted to be caused by the enhancement of the virtual excitation contribution via the low-lying excited state (described by the wavefunction with the charge transfer character from the donor to the acceptor). Judging from the results of **2b** and **2c** in the singlet state, however, it should be noted that there is a small synergy enhancement effect of intermediate γ and asymmetric donor/acceptor substitution on γ ; i.e., the enhancement ratio of γ of the asymmetric systems to the symmetric counterparts tends to increase as approaching intermediate γ region: 4.3 for **a** [$\gamma = 0.97$ for **1a** and **2a**] \rightarrow 5.2 for **c** [$\gamma = 0.64$ (**1c**), 0.62(**2c**)]. This feature coincides with our prediction in the previous study for systems with moderate asymmetry.³⁰ As a result, the γ of **2c** with intermediate γ and donor/acceptor substitutions is found to be more than 30 times as large as that of the parent compound **1a**.

To clarify the spatial contributions of electrons to the response, we also performed the α - and γ -density calculations. Figure 7 shows the α -density maps of **2a–2c** in the singlet and triplet states (Figure 7a,b). As expected from the α -values, spatial distributions of α -densities of **2a** in the singlet and triplet states are almost similar to each other. Large positive and negative α -densities are found to appear on the $-\text{NH}_2$ and

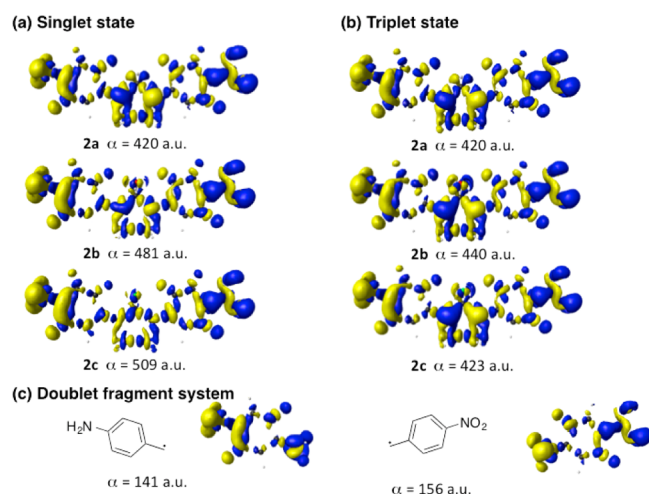


Figure 7. Maps of α -density of singlet state (a), triplet state (b) for **2a–2c**, and that for the doublet fragment systems (c). Yellow and blue meshes represent positive and negative α -densities with contour values of ± 0.1 au, respectively.

$-\text{NO}_2$ groups as well as around the edges of the phenyl rings. These positive and negative α -densities provide primary positive contributions to α . In addition, small positive and negative α -densities originating in the polarization of σ -electrons can be observed over the molecule. Similar to the case of nonsubstituted systems, these σ -electron contributions are expected to be almost canceled each other. It is also found that the π -electrons on the C_1 and C_3 sites contribute negatively to the total α . Again, such negative contributions of π -electrons on the C_1 and C_3 sites are observed in the maps of **2b** and **2c** in the triplet state, whereas the negative π -electron contributions are reduced for **2b** and **2c** in the singlet state. We also calculated α and its density of the fragment systems, which constitute the left- and right-hand side of the *para*-disubstituted 1,3-diphenylcyclopentane-1,3-diyl (Figure 7c). The α -density maps of these doublet fragment systems are found to be very similar to those of the left- and right-hand sides of **2a**, respectively. Therefore, the negative contributions of α -densities on the C_1 and C_3 sites are predicted to originate in the weak or negligible π -bonding characters on the C_1 and C_3 sites. In this case, the difference of the spatial distributions of α -density appears only around the five-membered ring. Even in the presence of the donor/acceptor groups, the effect of 2,2-substituents on the first-order response of electron density is found to be limited within the five-membered ring.

Finally, we compare the results of the γ -density maps of **2a–2c** in Figure 8. From the spatial features of the γ -density maps,

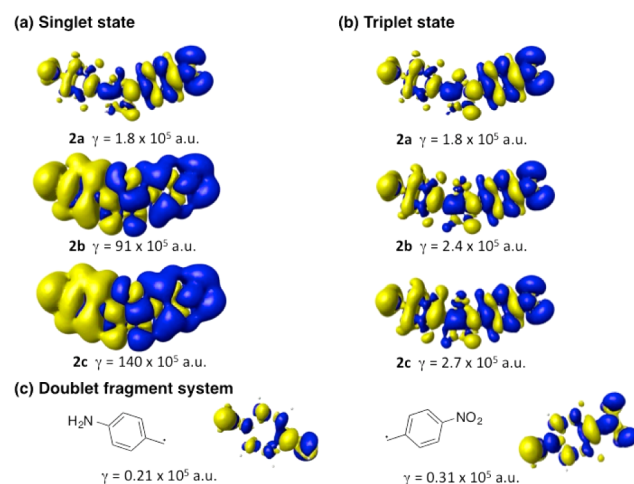


Figure 8. Maps of γ -density of singlet state (a), triplet state (b) for **2a–2c**, and that for the doublet fragment systems (c). Yellow and blue meshes represent positive and negative γ -densities with contour values of ± 100 au, respectively.

the π -electrons are found to provide dominant contributions to γ . Spatial distributions of the γ -density maps in the singlet and triplet states are shown to be almost the same for **2a** (Figure 8a,b). Although the amplitudes of γ -densities of **2a** become larger than those of **1a**, the positive and negative γ -densities for **2a** appear alternately, and thus these contributions considerably cancel each other. In particular, the γ -densities on the C_1 and C_3 site pair are found to contribute negatively to the total γ . Similar features of the γ -densities on the C_1 and C_3 sites are observed for **2b** and **2c** in the triplet state as well. As mentioned in the parent diradical case, this negative contribution is a common feature for systems in which the π -electron coupling between the C_1 and C_3 sites are considerably small. This is

supported by the result of the doublet fragment systems, where negative γ -density distribution is observed on the radical sites (Figure 8c). Despite the presence of the negative contributions, the γ -density map of **2a** shows a larger field-induced polarization effect from the one side to the other side the molecule than that of **1a**. As mentioned before, this is predicted to be caused by the enhancement of the virtual excitation contribution via the low-lying charge transfer excited state. The field-induced polarization effect is shown to be further enhanced in the γ -density maps of **2b** and **2c** in the singlet states with intermediate y -values. This is ascribed to the field-induced virtual electron transfer between the donor and acceptor groups as well as the intermediate y -values. Namely, when the π -electron coupling between the left- and right-hand sides of the system becomes strong due to the presence of the electron-withdrawing 2,2-substituents, the amount of virtual electron transfer between the donor and acceptor groups tends to be further enhanced. In consequence, the asymmetric donor/acceptor substitution at the *para* positions is expected to have a larger effect on the third-order NLO properties for the 1,3-diradical compounds with intermediate y than that for the pure diradical compounds.

IV. CONCLUSION AND PERSPECTIVES

In this study, we have investigated the relationship between the molecular structure and optical response properties of open-shell 1,3-diradical compounds by using the BS-DFT method. From the calculation results of y , it is found that **1a** ($X = H$) is in the pure diradical state, whereas **1b** ($X = OH$) and **1c** ($X = F$) are in the intermediate diradical state. The decreases in diradical characters of **1b** and **1c** are found to originate in the TB interactions. As predicted from the y - γ correlation, the second hyperpolarizabilities γ of intermediate diradical systems **1b** and **1c** are found to be enhanced significantly compared with that of pure diradical **1a**, though linear polarizabilities α of these systems are similar to each other. Spatial distributions of the α - and γ -densities, which respectively represent linear and third-order responses of charge density function, have revealed that the 2,2-substituents can assist the coupling between the π -electrons of left- and right-hand sides of the systems. In particular, it is found that strong third-order electronic polarizations over the system are induced owing to the intermediate π -bonding character of the 1,3-diradical systems with the 2,2-substituents. The effect of the 2,2-substituents on the third-order response of electron density is therefore found to be nonlocal, which may be possible through the virtual excitation process via the high-lying excited states characterized by extended wave functions.

We have also investigated the effects of asymmetric donor/acceptor substitutions at the *para* positions of the phenyl groups on y , α , and γ . The y -values of donor/acceptor disubstituted systems **2a–2c** are found to be almost unchanged from those of the nonsubstituted analogues **1a–1c**. Thus, the donor/acceptor substituents at the *para* positions have a very small influence on the π -bonding character between the C_1 and C_3 sites. Compared to the result of **1a–1c**, the γ -values of **2a–2c** are found to show 400–500% increase by the introduction of the asymmetric donor/acceptor substituents, regardless of the difference in the π -bonding character between the C_1 and C_3 sites. This increase is primarily caused by the contributions of the virtual excitation process via the low-lying excited states with charge transfer character between the donor and acceptor. It should be noted that, from the result of **2b** and **2c**, there is a

small synergy enhancement effect of the intermediate y and asymmetric charge distributions. It can be concluded that chemical modification such as the introduction of substituents can provide significant changes in the NLO properties of 1,3-diradical compounds through the modulation of their diradical character. The present results therefore revealed the strong correlation between the π -bonding character and third-order NLO properties, i.e., the y - γ correlation, in the real 1,3-diradical compounds.

Recently, experimental means for qualitative and/or quantitative estimations of bonding character (diradical character) between the diradical sites are of great interest^{50,51,92}

in the field of open-shell chemistry, because the bonding character is expected to be strongly correlated to the structures, chemical reactivity, and the physicochemical properties. Indeed, a variety of chemical modifications, such as the introduction of heteroatoms as well as of donor and/or acceptor substituents, have been proposed so far to tune the diradical (bonding) characters of several localized diradical compounds involving 1,3-diradicals.⁴ In experiment, the chemical bond nature for a specific bond has been speculated from the results of optical, vibrational, and magnetic resonance spectroscopies. On the basis of the predicted y - γ correlation in the real 1,3-diradical compounds, NLO measurements are speculated to be utilized for a novel probe of the unique chemical bond nature of open-shell species in the intermediate and/or transition states, in addition to these conventional measurement techniques.

■ ASSOCIATED CONTENT

Supporting Information

Optimized geometries of all the calculated systems in the singlet and triplet states are available as Supporting Information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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