Second Hyperpolarizabilities (γ) of Bisimidazole and Bistriazole Benzenes: Diradical Character, Charged State, and Spin State Dependences

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The second hyperpolarizabilities of bisimidazole- and bistriazole-benzene compounds have been calculated at different levels of approximation to unravel the effects of diradical character as well as of charge and spin multiplicity. The largest second hyperpolarizabilities are associated with intermediate diradical character, provided positive charging does not compensate for this effect. For the neutral diradical bisimidazole compound, the singlet diradical species possesses a second hyperpolarizability two to three times larger than the corresponding triplet, demonstrating the possibility of spin state control of the third-order NLO responses for diradical species.

1. Introduction

So far, most of the organic π-conjugated compounds exhibiting large nonlinear optical and electrooptic effects are closed-shell systems[1] though some pioneering studies have already been carried out on several open-shell systems in view of designing multifunctional materials.[2−5] In recent studies,[6] we have proposed open-shell model nonlinear optical (NLO) systems whose second hyperpolarizabilities (γ) can be drastically changed depending on the spin multiplicity and diradical character. These changes have the same origin as the variation in γ for the dissociation process of the H_2 molecule.[7] Such a dissociation process is classified into three regimes of the strength of electron correlation, i.e., equilibrium-, intermediate-, and long-bond distance regions correspond to weak-, intermediate-, and strong-correlation regimes, respectively. Namely, the systems in the intermediate and somewhat strong correlation regimes tend to exhibit larger γ values than the systems in the weak correlation regime.

In this study, we investigate the static γ values of neutral disubstituted benzene molecules in the singlet state with intermediate and very small diradical characters, i.e., 1,4-bis(imidazole-2-ylidene)cyclohexa-2,5-diene (BI2Y) [Figure 1a] and a related molecule, 1,4-bis(triazole-2-ylidene)cyclohexa-2,5-diene (BT2Y) [Figure 1b], respectively, by various ab initio molecular orbital (MO) and hybrid density functional theory (DFT) calculations. The results are discussed in view of the diradical character dependence of γ. The effect of charging is also examined by comparing the results of BI2Y (singlet) and BT2Y (singlet) with those of $BT2Y^{2+}$ (singlet) and $BI2Y^{2-}$ (singlet). We further address the spin-state dependence of γ values of diradical molecules comparing BI2Y and $BT2Y^{2+}$ in their singlet and triplet spin states. The γ density analysis is used to describe and analyze the spatial contributions of electrons to γ. On the basis of these results, we discuss the possibility of diradical character and spin state control of third-order NLO properties of diradical molecular systems. BI2Y is in fact a simplified analogue of the recently studied 1,4-bis(4,5-diphenylimidazole-2-ylidene)cyclohexa-2,5-diene (BDPI-2Y) where the phenyl groups on the imidazole rings are replaced by H atoms, which has been shown to exhibit thermally excited triplet diradical character, especially when the central cyclohexadiene ring is substituted by four F atoms.[8a] As reported in ref 8b, BDPI-4Y, an isomer of BDPI-2Y, with or without Cl substituents displays a significant increase of the spin concentration with respect to BDPI-2Y, showing the potential of these systems as molecule-based organic magnets. Moreover, in the form of a compressed pellet, delocalized singlet diradical hydrocarbons based on two phenalenyl radicals separated by a *p*-quinodimethane moiety have recently been shown to exhibit the largest single-component electrical conductivity among structurally well-defined neutral hydrocarbon molecules.[9a] This

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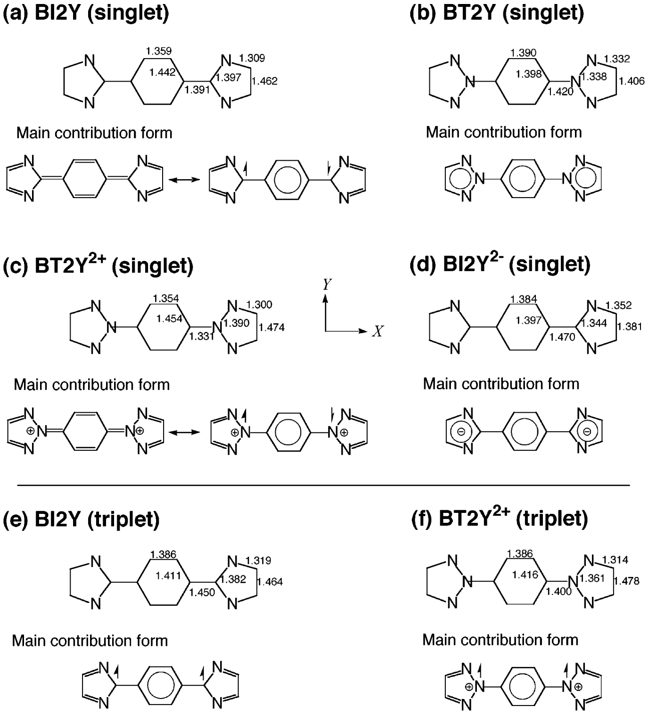

Figure 1. Geometrical structures (bond length [Å]) and coordinate axis of BI2Y (singlet) (a), BT2Y (singlet) (b), BT2Y^{2+} (singlet) (c), BI2Y^{2-} (singlet) (d), BI2Y (triplet) (e), and BT2Y^{2+} (triplet) (f) optimized under the constraint of D_{2h} symmetry by B3LYP/6-31G**. Main contribution (resonance) forms are also shown.

large electrical conductivity was ascertained to nearly degenerate HOMO and LUMO levels[9b] leading to substantial intermolecular interactions. Theoretical investigations have also predicted that the latter phenalenyl-based compound exhibits a rather large second hyperpolarizability, typical of molecules having an intermediate diradical character.[9c] Many other investigations have demonstrated the potential of diradicals in view of preparing electronic, optical, and magnetic materials.[9d−f]

2. Computational Aspects and Structural Properties

2.1. Geometrical Structures and Diradical Character. Figure 1 shows the optimized structures (D_{2h} symmetry) and main contribution (resonance) forms of the six compounds as determined by using the B3LYP method with the 6-31G** basis set. For small systems, B3LYP was found to provide geometries in very close agreement to QCISD.[6b,c] The structure of BI2Y in its singlet ground state is described by two resonance forms, i.e., the quinoid and diradical forms [Figure 1a]. Although the quinoid form has no spin sites, the diradical form presents two antiparallel spins at both-end C sites. In contrast, BT2Y in the singlet ground state is predicted to have a main contribution with a negligible diradical character [Figure 1b]. The doubly positive charged state of BT2Y (singlet), however, recovers some diradical form contribution as shown in the resonance structure [Figure 1c]. Figure 1d shows the optimized geometry of the singlet state of BI2Y^{2-}, which presents an isoelectronic structure to the singlet BT2Y. Indeed, each imidazole ring of BI2Y^{2-} (singlet) tends to possess 6π electrons, so that the diradical character is negligible. By definition, in their triplet state, BI2Y and BT2Y^{2+} have unpaired electrons and the central six-membered rings present a larger aromatic character. The triplet state of BI2Y [Figure 1e] is slightly unstable compared to its singlet analogue [0.1 kcal/mol at the CCSD(T)/6-31G level, 8.9 kcal/mol at the BHandHLYP/6-31G*+p level, and 10.0 kcal/mol at the PUMP2(l=4)/6-31G level (see Section 2.2)], in agreement with recent results on BDPI-2Y.[8a] BT2Y^{2+} (triplet) [Figure 1f] is isoelectronic to BI2Y (triplet). Its open-shell broken-symmetry singlet state is also more stable than the triplet diradical [0.4 kcal/mol at the CCSD(T)/6-31G level, 22.4 kcal/mol at the BHandHLYP/6-31G*+p level, and 31.0 kcal/mol at the PUMP2(l=4)/6-31G level].

TABLE 1: Diradical Character y (calculated by UHF/6-31G*+p) and γ Values[a] ($\times 10^2$ au) for the BI2Y (singlet), BT2Y (singlet), BT2Y^{2+} (singlet), and BI2Y^{2-} (singlet) as Well as Those for BI2Y (triplet) and BT2Y^{2+} (triplet) (see Figure 1)

		6-31G		6-31G*+p
	y	CCSD(T)	BHandHLYP	BHandHLYP
BI2Y (singlet)	0.4227	5244	4844	6534
BT2Y (singlet)	0.0100	434	503	654
BT2Y^{2+} (singlet)	0.2228	405	−344	−489
BI2Y^{2-} (singlet)	0.0106	779	761	1422
BI2Y (triplet)		1924	1960	2116
BT2Y^{2+} (triplet)		−100	−1071	548

[a] The γ values for BI2Y (singlet), BT2Y^{2+} (singlet), BI2Y (triplet), and BI2Y^{2+} (triplet) are calculated by using the spin-unrestricted methods, while for BT2Y (singlet) and BI2Y^{2-} (singlet) spin-restricted methods are employed.

The diradical character y has been estimated from spin-unrestricted Hartree−Fock (UHF) calculations. For a pair of occupied and unoccupied MO's, HOMO-i and LUMO+i, it is defined by the weight of the doubly excited configuration in the multiconfigurational (MC)-SCF theory and is formally expressed in the case of the spin-projected UHF (PUHF) theory as[10]

$$y_i = 1 - \frac{2T_i}{1 + T_i^2} \tag{1}$$

where T_i, the orbital overlap between the corresponding orbital pairs, is determined by using the occupation numbers (n_i) of UHF natural orbitals (UNO):

$$T_i = \frac{n_{\mathrm{HOMO}-i} - n_{\mathrm{LUMO}+i}}{2} \tag{2}$$

Since the PUHF diradical characters amount to 0% and 100% for closed-shell and pure diradical states, respectively, y_i represents the diradical character, i.e., the instability of the chemical bond. This scheme is simple but it reproduces well the diradical character calculated by other methods such as the ab initio configuration interaction (CI) method.[11] The present formula employs the UNOs instead of UDFT NOs, which, using eq 2, lead to underestimated diradical character.

Table 1 gives the diradical characters y calculated from eqs 1 and 2 by using HOMO and LUMO of UNOs for BI2Y, BT2Y, BT2Y^{2+}, and BI2Y^{2-}. In agreement with the analysis of the geometries in terms of main resonance forms, the diradical character of singlet BI2Y (y = 0.4227) is larger than that of singlet BT2Y (y = 0.01) and singlet BI2Y^{2-} (y = 0.01), while the diradical character (y = 0.2228) of BT2Y^{2+} in the singlet state increases as compared to that of neutral BT2Y. Judging from their negligible diradical characters, BT2Y (singlet) and BI2Y^{2-} (singlet) are closed-shell ground-state systems.

2.2. Methods for Calculating and Analyzing the Second Hyperpolarizabilities. The same strategy as in ref 6 has been adopted for computing the γ values, and more precisely the dominant longitudinal component of the static electronic γ (γ_{xxxx}). It relies on the finite field approach,[12] which consists of determining the fourth-order energy derivative with respect to an external electric field. More details about the numerical differentiation procedure can be found in ref 6. Because the present study includes singlet diradical systems, we apply single-reference spin-unrestricted based methods in place of spin-restricted multireference based methods,[10b] which can provide reliable results in principle when sufficiently large active space is considered, but are practically difficult to apply to the large-size molecules in NLO materials. Calculations have been carried out at the Hartree−Fock (HF) level as well as using correlated methods such as the Møller−Plessert *n*th-order perturbation theory schemes [MPn ($n = 2-4$)], the coupled cluster (CC) methods including single and double excitation operators (CCSD), and the CCSD with a perturbative treatment of the triple excitations [CCSD(T)] methods. Spin-unrestricted methods are used for molecules with finite diradical characters [BI2Y (singlet) and BT2Y^{2+} (singlet)] and high-spin systems [BI2Y (triplet) and BT2Y^{2+} (triplet)], while spin-restricted methods are used for closed-shell molecules [BT2Y (singlet) and BI2Y^{2-} (singlet)]. For the spin-unrestricted based methods, we also employ the l-fold spin-projection scheme by Löwdin.[13] On the basis of their reliability for estimating γ of the *p*-quinodimethane models,[6b] a hybrid DFT approach using the BHandHLYP exchange-correlation functional has also been applied in its spin-restricted or spin-unrestricted form according to the nature of the compound.

In addition to the standard 6-31G basis set, the 6-31G*+p basis set with a p exponent of 0.0523 on carbon (C) atoms and 0.0582 on nitrogen (N) atoms is employed to address basis set effects.[6] Indeed, the 6-31G*+p basis set was shown to provide γ values in very close agreement with much larger basis sets, including aug-cc-pvdz and aug-cc-pvtz.[6d] For defining γ, the power series expansion convention (called B) has been adopted.[14]

The spatial contributions of electrons to γ are characterized by using a density analysis[15a] and in particular the third-order derivative of the electron density with respect to the applied electric fields, $\rho^{(3)}(\boldsymbol{r})$, which is referred to as the γ density.[15b,c] The positive and negative values of γ densities multiplied by F^3 correspond respectively to the field-induced increase and decrease in the charge density (in proportion to F^3), which induce the third-order dipole moment (third-order polarization) in the direction from positive to negative γ densities. Therefore, the γ density maps represent the relative phase and magnitude of the contributions to γ from pair of γ densities with positive and negative values. Moreover, the magnitude of the contribution associated with pairs of γ densities is proportional to the distance between them. The γ densities are calculated for a grid of points from field-dependent electron densities. More details about the computational procedure to determine $\rho^{(3)}(\boldsymbol{r})$ can be found in our recent investigations.[6]

All calculations are performed with the Gaussian 98 and 03 program packages.[16]

3. Results and Discussion

3.1. Diradical Character, Charge, and Spin State Effects on γ. Figure 2 displays the γ values as a function of the method for BI2Y (singlet) (a), BT2Y (singlet) (b), BT2Y^{2+} (singlet) (c), BI2Y^{2-} (singlet) (d), BI2Y (triplet) (e), and BT2Y^{2+} (triplet) (f). They are also listed in Table 1 in the case of the CCSD(T) and BHandHLYP methods. The full list of γ values can be found in the Supporting Information.

BI2Y, a neutral singlet diradical molecule with an intermediate diradical character, exhibits a much larger γ value than BT2Y, a neutral closed-shell molecule with a similar π-conjugation length. These results are consistent with previous studies with model diradical compounds, i.e., *p*-quinodimethane and twisted ethylene.[6] When BT2Y (singlet) has a +2 charge, it presents an intermediate diradical character, which is expected to be accompanied by an increase in γ. Nevertheless, with use of the reference CC and DFT methods, the γ values of BT2Y^{2+} and BT2Y present similar amplitude. This results from the balance between the charge and diradical effects. Indeed, the introduction of charge enhances the negative contributions to γ, as observed in small closed-shell polyenes bearing a charged soliton defect[6f] as well as in high-spin radical π-conjugated molecules such as the C_6H_8 radical cation.[3a] The 80% magnitude enhancement of γ for BI2Y^{2-} (singlet) as compared to BT2Y (singlet) originates from the double negative charge, which leads to an increase of type III (positive) contributions[3] involving high-lying excited states with extended spatial distributions. With respect to BI2Y (singlet), the introduction of doubly negative charges significantly reduces the diradical character and therefore the γ value.

To elucidate the spin-state effects on γ for diradical systems, the triplet states of BI2Y and BT2Y^{2+} are investigated. For BI2Y, going from the singlet to the triplet state leads to a reduction of γ by a factor of 3. This significant impact can be related to the difference of the field-induced electron fluctuation effects between the singlet and triplet states. In the singlet state, the MOs associated with the unpaired electrons can overlap whereas, due to Pauli principle, they are localized in the triplet state. This difference between the singlet and triplet states is reduced in the region with large y value because the overlap between diradical distributions becomes negligible for both spin states. Moreover the energy difference between the singlet and triplet ground states of BI2Y is rather small (see Section 2.1), so that the γ value for the ground state of BI2Y thermally includes contributions from the triplet state. In the case of BT2Y^{2+}, unraveling the effects of the singlet−triplet transition is more difficult because of the delicate balance between positive and negative contributions to γ, which leaves undetermined the sign of the γ. At least both CCSD(T) and BHandHLYP methods predict an increase of the negative contributions to γ (or a decrease of the positive term) when going to higher spin state.

Figure 3 shows the γ density distributions for BI2Y (singlet) (a), BT2Y (singlet) (b), BI2Y^{2-} (singlet) (c), and BI2Y (triplet) (d) obtained at the BHandHLYP/6-31G*+p level of approximation. As is often the case, π- and σ-electrons lead to contributions of mutually opposite sign but the π-electron contribution is by far the largest. Then, the resulting positive contribution is mostly associated with both-end five-membered rings whereas in the middle benzene ring, positive and negative contributions cancel each other. The γ density plots substantiate the above discussion in the sense it reflects the enhancement of γ for BI2Y (singlet) as compared to BI2Y^{2-} (singlet), BI2Y (triplet), and BT2Y (singlet). They also evidence the impact of charging BI2Y^{2-} compared to BT2Y since both compounds are closed-shell systems. In BI2Y (triplet), in addition to reduced γ densities over the whole system, the γ density distribution in the middle benzene ring is smaller than that for its singlet analogue as a result of the Pauli principle between the parallel radical spins on both-end five-membered rings.

3.2. Electron Correlation and Basis Set Effects on γ. Basis set effects were investigated at the HF, MP2, and BHandHLYP levels of approximation by considering the change in γ induced by adding to the 6-31G basis set a set of diffuse and a set of polarization functions to obtain the 6-31G*+p basis set (Table 1 and Supporting Information). For the molecules presenting a

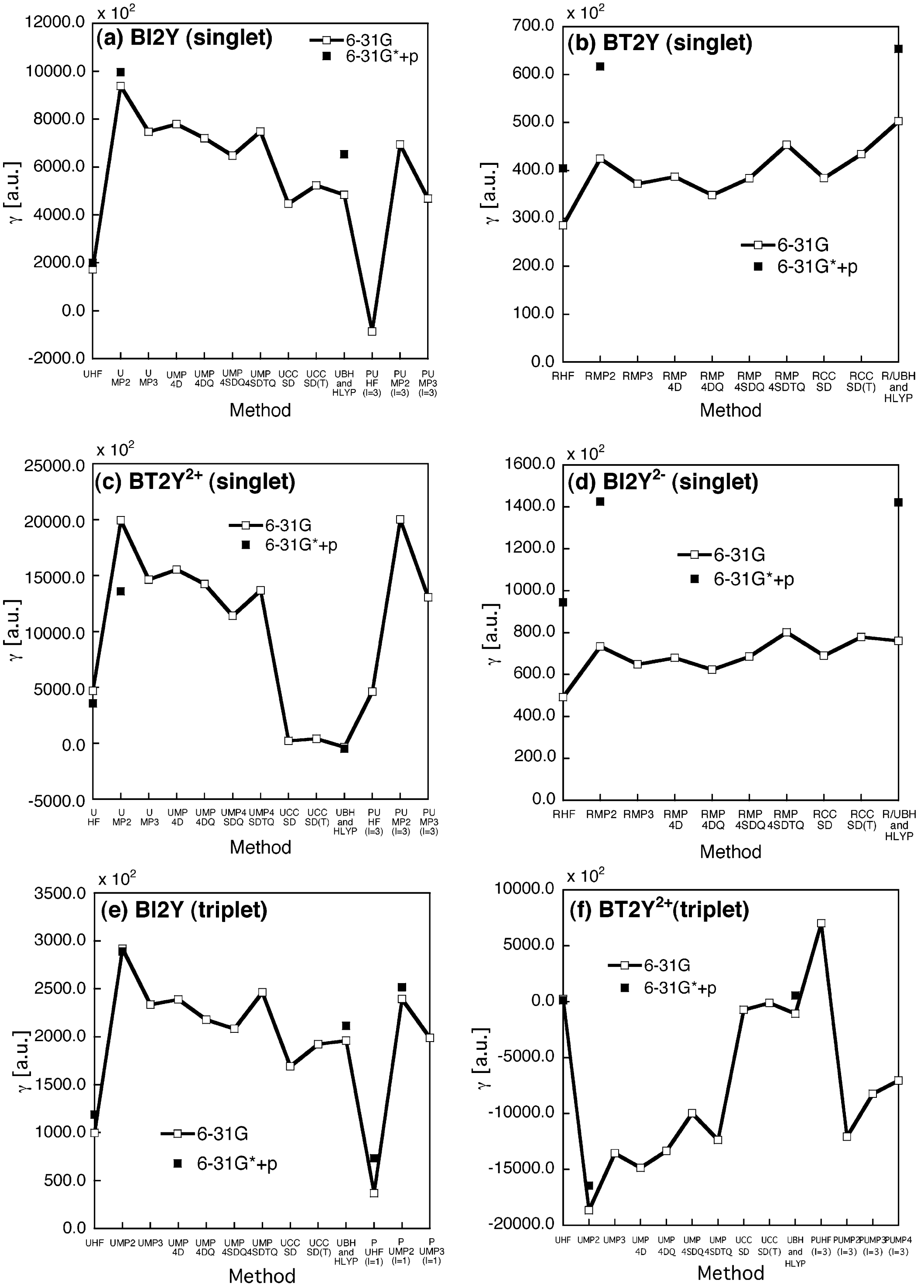

Figure 2. Calculation method dependence of γ [au] for BI2Y (singlet) (a), BT2Y (singlet) (b), BT2Y^{2+} (singlet) (c), BI2Y^{2-} (singlet) (d), BI2Y (triplet) (e), and BT2Y^{2+} (triplet) (f). The 6-31G basis set is used for all the calculation results, while the 6-31G*+*p* basis set is also used at the HF, MP2, and BHandHLYP levels of approximation.

nonnegligible diradical character, enlarging the basis set can lead to increase or decrease of the γ amplitude, which remains smaller than 42%. For BI2Y, the effect is an increase ranging from 6% to 35%. For BT2Y^{2+}, γ is positive and decreases by 24% and 32% at the HF and MP2 levels, respectively, whereas γ is negative at the BHandHLYP level and its amplitude increases by 42% upon enlarging the basis set. For closed-shell systems, the basis set effects are more important and range from 30% to 45% for BT2Y and from 87% to 94% for BI2Y^{2-}. The large increase in the latter case is consistent with the anionic nature of the system and its larger requirement in basis set functions. The basis set dependence of γ is the smallest for the triplet state of BI2Y and the γ variations from 6-31G to 6-31G*+*p* amount to 19%, −1%, and 8% at the HF, MP2, and BHandHLYP levels of approximation, respectively. This relatively small basis set dependence is related to the localized nature of the radical orbitals due to the Pauli principle. In the case of BT2Y^{2+} (triplet), the basis set effects are, however, a bit larger than those for BI2Y(singlet). They attain −49%, −12%, −21%, and 0.3% with the HF, MP2, PUHF(l=1), and

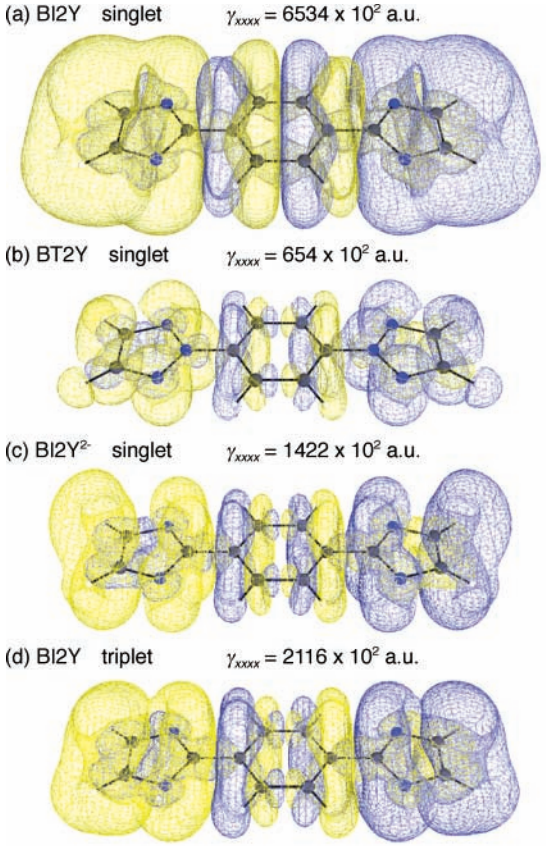

Figure 3. BHandHLYP/6-31G*+p γ density distributions as well as γ values for BI2Y (singlet) (a), BT2Y (singlet) (b), BI2Y^{2-} (singlet) (c), and BI2Y (triplet) (d). The yellow and blue meshes represent positive and negative γ densities with iso-surfaces with ±50 au, respectively.

PUMP2(l=1) methods of calculation. By using the hybrid BHandHLYP functional, the amplitude is reduced by a factor of 2 and γ changes sign. This substantial difference is due to the necessity of including d-polarization functions in the basis set. Indeed, with use of the 6-31G, 6-31G*, 6-311G, 6-311G*, and 6-31G*+p basis sets, the γ value amounts to -1071×10^2, 262×10^2, -481×10^2, 415×10^2, and 548×10^2 au, respectively. Thus, except for BT2Y^{2+} (triplet), the 6-31G and 6-31G*+p basis sets provide similar qualitative insights on the γ variations with the diradical character, charge, and spin multiplicity.

The electron correlation effects are mostly discussed by using the 6-31G basis set results. As for the basis set effects, for singlet states, electron correlation effects depend on the diradical nature. In the case of systems having diradical character (BI2Y and BT2Y^{2+}) by going from the HF to MP2 level the γ value increases substantially but is reduced upon adding further electron correlation corrections. For the neutral species (BI2Y), the HF γ value is three times smaller than its CCSD(T) analogue whereas for the charged species (BT2Y^{2+}), the CCSD(T) result is 10 times smaller. Similar behaviors have been evidenced for model π-conjugated systems in their doublet state.[6] Such remarkable decreases in γ values at the high-level electron correlation levels suggest the relative increase of negative contribution (type II [2]) to γ, the feature of which is also observed in γ for the C_6H_8 radical cation (doublet).[6] An alternative to reduce the overestimation associated with the MP scheme consists of projecting out the higher spin components. Indeed, the γ value of BI2Y amounts to 6944×10^2 au at the PUMP2(l=3) level and 4682×10^2 au at the PUMP3(l=3) level with respect to 9387×10^2 au at the MP2 level, 7477×10^2 au at the MP3 level, and 5244×10^2 au at the CCSD(T) level. However, as for the C_6H_8 radical cation,[6] for BT2Y^{2+} (y = 0.22), spin projected (l = 3) MP schemes hardly improve the UMP results. This confirms that spin-contamination-free higher order electron correlation schemes are necessary for obtaining reliable γ values of charged radical systems. For the closed-shell compounds, the MP2 method provides a good estimate of the γ with respect to highly correlated methods, which is in agreement with other investigations.[17] For BT2Y, the CCSD(T) value is only 2% larger than the MP2 analogue whereas for BI2Y^{2-} the difference amounts to 6%.

For BI2Y in its triplet state, the electron correlation dependence of γ is qualitatively similar to that of its singlet analogue, though the amplitude of variation is much larger for the singlet. Again the MP2 method overshoots the γ values due to spin contaminations, which are reduced by using spin projection or coupled cluster approaches. The electron correlation dependence of γ of BT2Y^{2+} (triplet) is the mirror image of the electron correlation effects in its singlet analogue (as well as for BI2Y singlet and triplet). In other words, the magnitudes of the effects are similar but their signs are opposite. In particular, the MP2 value is very large and negative (-18645×10^2 au) while including electron correlation effects at the CCSD and CCSD(T) levels of approximation gives values of -713×10^2 and -100×10^2 au, respectively. Projecting out the spin contamination corrects only partly for the amplitude overestimation and leads to the following γ amplitudes: -12075×10^2 [PUMP2(l=3)], -8234×10^2 [PUMP3(l=3)], and -7031×10^2 au [PUMP4(l=3)].

Table 1 shows also that the UBHandHLYP method reproduces well the CCSD(T) γ values for four compounds, the problematic cases being BT2Y^{2+} in both singlet and triplet ground states. This is consistent with the ability of the BHandHLYP XC functional to reproduce the CCSD(T) γ values of the neutral C_5H_7 radical and p-quinodimethane models but contrasts with its efficiency in the case of the C_6H_8 radical cation.[6] Nevertheless, despite this good agreement for these compounds, care should be taken with regard of the behavior of conventional DFT schemes when considering large extended π-conjugated systems.[18]

4. Conclusions and Outlook

The second hyperpolarizabilities of bisimidazole and bistriazole benzene compounds have been calculated at different levels of approximation to unravel the effects of diradical character as well as of charge and spin multiplicity. Intermediate diradical character turns out to be associated with enhanced second hyperpolarizability, provided positive charging does not compensate for this effect. For the neutral diradical bisimidazole compound, the singlet diradical species possesses a second hyperpolarizability two to three times larger than the corresponding triplet, demonstrating the possibility of spin state control of the third-order NLO responses for diradical species. The situation is more complex for the charged diradical bistriazole compound because, for both its singlet and triplet states, the second hyperpolarizability depends strongly on the level of inclusion of electron correlation. The comparison of the two closed-shell systems leads to the expected conclusion of the largest second hyperpolarizability for the system bearing a doubly negative charge. Moreover, looking at the basis set effects, except for the charged bistriazole compound in its triplet state, the 6-31G and 6-31G*+p basis sets provide similar qualitative insights on the γ variations with the diradical character, charge, and spin multiplicity. It is consequently predicted that for singlet diradical systems, the addition of a set of diffuse polarization *p* functions to a standard split-valence basis set is necessary at least for obtaining semiquantitative γ values, in particular for negatively charged systems, whereas for triplet diradical systems such basis set extension does not give an important effect except for the charged triplet system, in which a set of *d*-polarization functions is essential for obtaining reliable γ values.

Current directions of investigations encompass (i) addressing the effects of counterions in the case of the charged compounds, (ii) investigating the amplitude of the singlet−triplet gap[8] as a function of the substituents, and (iv) evaluating dynamic γ and vibrational effects on γ, as well as (v) measuring the NLO responses of these compounds.

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Supporting Information Available: Complete listing of γ data for BI2Y (singlet), BT2Y (singlet), BT2Y^{2+} (singlet), BI2Y^{2-} (singlet), BI2Y (triplet), and BT2Y^{2+} (triplet). This material is available free of charge via the Internet at http://pubs.acs.org.

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