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Challenging Compounds for Calculating Hyperpolarizabilities: *p*-Quinodimethane Derivatives

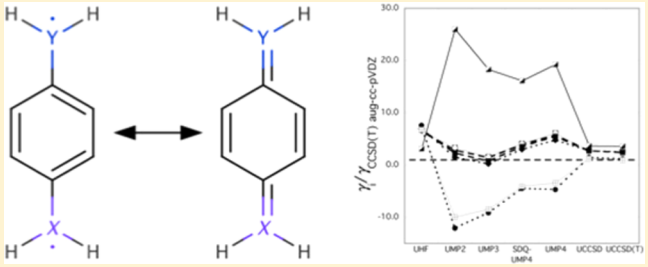
Marc de Wergifosse,[†] Frédéric Wautelet,[‡] Benoît Champagne,*[,†] Ryohei Kishi,[§] Kotaro Fukuda,[§] Hiroshi Matsui,[§] and Masayoshi Nakano[§]

[†]Laboratoire de Chimie Théorique, Unité de Chimie Physique Théorique et Structurale, and [‡]Plateforme Technologique en Calcul Intensif, University of Namur, rue de Bruxelles, 61, B-5000 Namur, Belgium

[§]Department of Materials Engineering Science, Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka 560-8531, Japan

Supporting Information

ABSTRACT: The hyperpolarizabilities of three *p*-quinodimethane derivatives with low diradical character have been evaluated. As electron correlation effects rule the electric field response properties, wave function and density functional theory-based methods have been compared to benchmark values calculated with the coupled cluster method including single and double excitations as well as perturbative estimate of the triples [CCSD(T)]. The basis set effects have been further assessed. This study shows that the determination of the second hyperpolarizability with the CCSD method provides results in closest agreement with the CCSD(T) reference values. The use of MP2 level of theory performs well for the closed-shell compound but not for open-shell ones. Spin-projection UMP3 and UMP4 methods reproduce well UCCSD(T) values for the *p*-quinodimethane but not for the charged compound. Without spin projection correction, density functional theory with a large range of exchange-correlation functionals does not perform well for these systems. Similar effects have been observed for the polarizability and first hyperpolarizability, although these effects are smaller.



I. INTRODUCTION

Electron correlation plays a central role in the prediction of the molecular nonlinear optical properties, the first (β) and the second (γ) hyperpolarizabilities.[1−5] The situation is even more crucial in the case of open-shell systems.[6−8] Two major types of methods are currently employed for computing accurately the β and γ responses of molecules, ab initio methods, where electron correlation effects can be systematically included, order by order in the perturbation theory expansion of the electron−electron interactions,[9−15] and density functional theory (DFT) approaches where the exchange-correlation (XC) functionals are improved step by step, by accounting for physical constraints/rules or by better reproducing sets of experimental data.[16−21] The first category is often limited to small compounds due to the related huge computational requirements, whereas they enable one to obtain benchmark results that can be used to assess the reliability of the XC functionals. On the other hand, DFT methods can be applied to large systems, but their use raises the question of the choice of XC functional. This issue is not trivial. First, the XC requirements differ for small molecules like the reference NLO molecules and for extended systems like polymer chains or large donor−acceptor π-conjugated systems. In the first class of molecules, key issues to describe the hyperpolarization phenomena are related to the description of the most delocalizable and external part of the electron distribution as well as of (hyper)polarization effects.[14,20,22] In the second class, the dominant part of the response is no more attributed to the outer part of the electron distribution but rather to the molecular units/moieties (hyper)polarization and to charge transfer,[23,24] which requires a proper treatment of intramolecular long-range delocalization. As it has been evidenced for about 15 years, conventional XC functionals, local density approximation (LDA) and generalized gradient approximation (GGA), fail dramatically to reproduce these latter effects, and this was attributed to the lack of a field-induced counteracting term in the response part of the exchange functional.[25] Several solutions to this problem have been proposed, including the use of exact exchange within the optimized effective potential (OEP),[26] self-interaction free functionals,[17−19] and long-range corrected (LR) functionals.[16,27] Although these approaches correct DFT results for shortsightedness and can better describe the evolution of the hyperpolarizabilities with the system size, to some extent they remain unsatisfactory because the correlation issue remains unsolved. In the case of LR functionals, this correlation issue was already evidenced by a study on the second hyperpolarizabilities of polydiacetylene and polybutatriene chains where the LC-BLYP functional overshoots the CCSD(T) γ values, in particular for the longer chains.[28]

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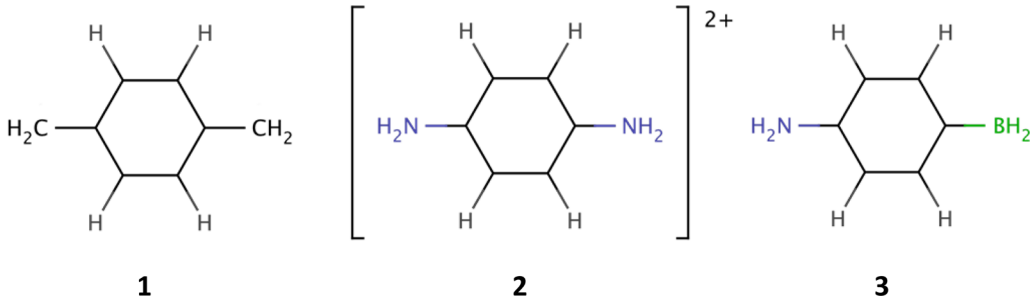

Figure 1. Structures of the three compounds.

This article deals with the evaluation of the second hyperpolarizability of three challenging open-shell molecules, where electron correlation effects govern the electric field response properties. They encompass *p*-quinodimethane (**1**) and two derivatives where the $CH_2^{\bullet}$ terminal units are formally replaced by two $NH_2^{+\bullet}$ (**2**), or by one $NH_2^{+\bullet}$ and one $BH_2^{-\bullet}$ (**3**) (Figure 1). This study addresses the choice of a suitable basis set and the description of electron correlation. So, it goes beyond recent works where γ of **1** has been calculated with rather small basis sets,[6] which are not always suitable to describe accurately the second hyperpolarizability, especially in the case of poorly polarized sets.[29,30] Electron correlation is treated using the Møller−Plesset (MP) perturbation theory approach in its unrestricted form, and the effects of spin contamination are assessed using spin-projected approaches. Our benchmark values are obtained at the coupled cluster level including all single and double excitations (CCSD) as well as after including a perturbative estimate of the triples [CCSD(T)]. Within DFT, some conventional and less conventional XC functionals are employed, and their performance is tested with respect to the UCCSD(T) data. Besides γ, this Article also analyzes the polarizability (α) and first hyperpolarizability (β), of which the estimates depend also on the inclusion of static and dynamic electron correlations. Some of these models belong to the class of "open-shell singlet" species, which have recently attracted much attention due to their unique structural, optical, and magnetic properties.[31−33]

This article is organized as follows. The next section briefly describes the key computational and theoretical aspects, whereas the results are presented and discussed in section III before conclusions are drawn in section IV.

II. THEORETICAL AND COMPUTATIONAL APPROACHES

The geometrical structures were fully optimized with density functional theory (DFT) and the UB3LYP XC functional in combination with the 6-311G* basis set. The polarizabilities (α), first (β), and second (γ) hyperpolarizabilities were calculated using the finite field approach,[34] which consists of the second-, third-, and fourth-order numerical differentiations of the energy with respect to the applied external electric field, respectively. In all of the FF calculations, the Romberg or Richardson method was employed in combination with selected field amplitudes [$\pm 2^k$ 0.0004 or $\pm(\sqrt{2})^k$ 0.0004 with k going from 0 to 5] so as to achieve a numerical accuracy within 1% or less on the γ values, while for β and α the accuracy attains at least 0.1% and 0.01%, respectively. The use of this method is particularly important for obtaining a stable γ value when large basis sets with many diffuse functions are employed. Tight convergence on the density matrices and on the energies (10^{-10} to 10^{-12} au) was thus mandatory to meet the requested accuracy. The (hyper)-polarizabilities were evaluated at different levels of approximation with unrestricted methods, including the Hartree−Fock (HF) method, the Møller−Plesset perturbation theory approach truncated to second (MP2), third (MP3), and fourth (MP4) orders as well as SDQ-MP4, and the coupled cluster approach including all single and double excitations with [CCSD(T)] and without (CCSD) a perturbative estimate of the triples. A range of basis sets was employed: the standard 6-31G, 6-31G(d), 6-311G(d), 6-31+G(d), 6-311++G(2df,p), aug-cc-pVDZ, and aug-cc-pVTZ basis set as well as the 6-31G(d) basis set augmented with one set of diffuse p functions [ζ = 0.0523, 0.0582, and 0.0447, for C, N, and B, respectively], which is denoted 6-31G(d)+p. Note that in the standard 6-31+G(d) basis set, a set of sp diffuse functions is included, with ζ = 0.0438, 0.0639, and 0.0315, for C, N, and B, respectively.

The s-fold spin-projection scheme was also employed.[35] It consists of removing the successive spin contamination contributions from the UHF and UMPn energies. At the UHF level, s = 6 spin projections were carried out exactly, whereas at the UMPn (n = 2−4) levels they were done in an approximate way up to s = 4 following ref 36. No projection method was used for the coupled cluster energies because these methods are known to suffer less from spin contamination. After the successive removals of the spin contamination contributions, the S^2 expectation value drops to 0.001 or less, which is the exact value for a singlet wave function.

Unrestricted DFT calculations with a selection of XC functionals were performed to probe the effect of the functional and particularly the role of HF exchange: BLYP, B3LYP, BHandHLYP, CAM-B3LYP, LC-BLYP (μ = 0.33), LC-BLYP (μ = 0.47), B98, and B2PLYP. BLYP, B3LYP, and BHandHLYP XC functionals include 0%, 20%, and 50% of HF exchange, respectively. CAM-B3LYP and LC-BLYP are standard range-separated functionals, which contain 65% and 100% of HF exchange at large interelectronic distances. In these functionals, using the Ewald partitioning, the electron−electron repulsion operator is partitioned in a short-range and a long-range part. The long-range exchange is described by HF exchange, whereas different local and nonlocal DFT functionals are used for the short-range part. The transition between short- and long-range is dictated by the range-separating parameter μ. For LC-BLYP, two range-separated parameters were used, the original one (μ = 0.33) and the default (μ = 0.47) in Gaussian 09. Still, these are not universal constants, and the results depend on μ. For instance, from comparison with CC results, in the case of diradical species, a μ = 0.3−0.5 value is adequate for calculating γ of organic compounds like *p*-quinodimethane and pentalene, whereas for dimetal compounds a larger μ = 0.7−0.9 value is required.[37,38]

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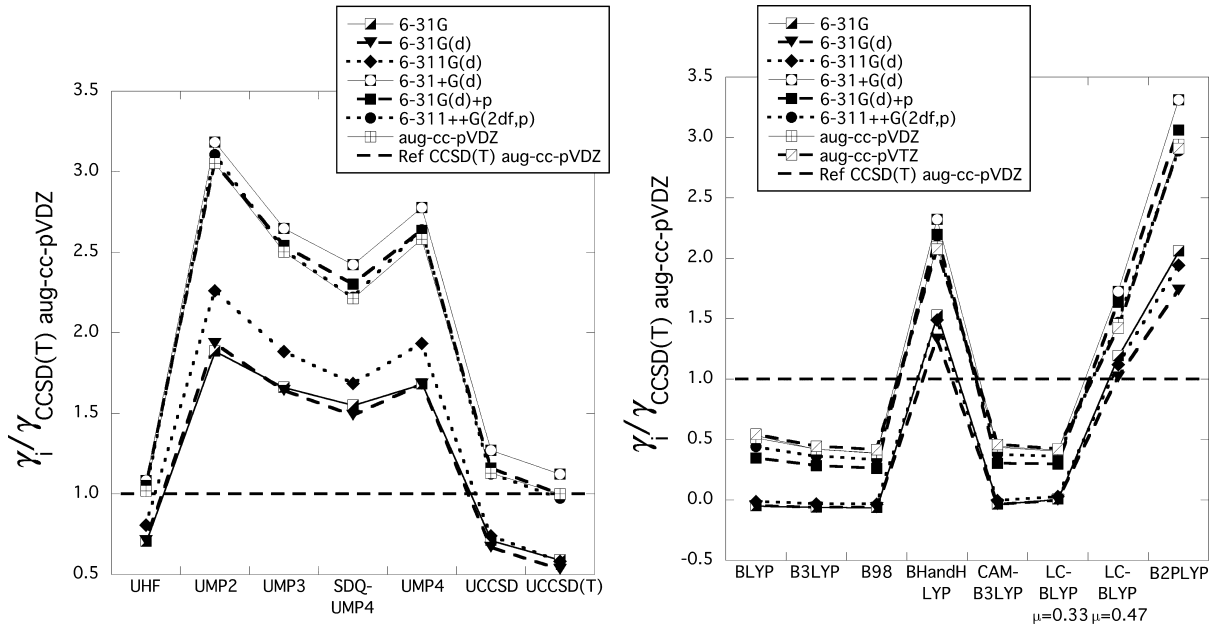

Figure 2. Basis set and electron correlation effects on the second hyperpolarizability of molecule **1**. Lines are guides for the eyes. The left figure compares wave function correlated schemes to UCCSD(T) results as a function of the basis set, whereas the right figure concentrates on DFT XC functionals.

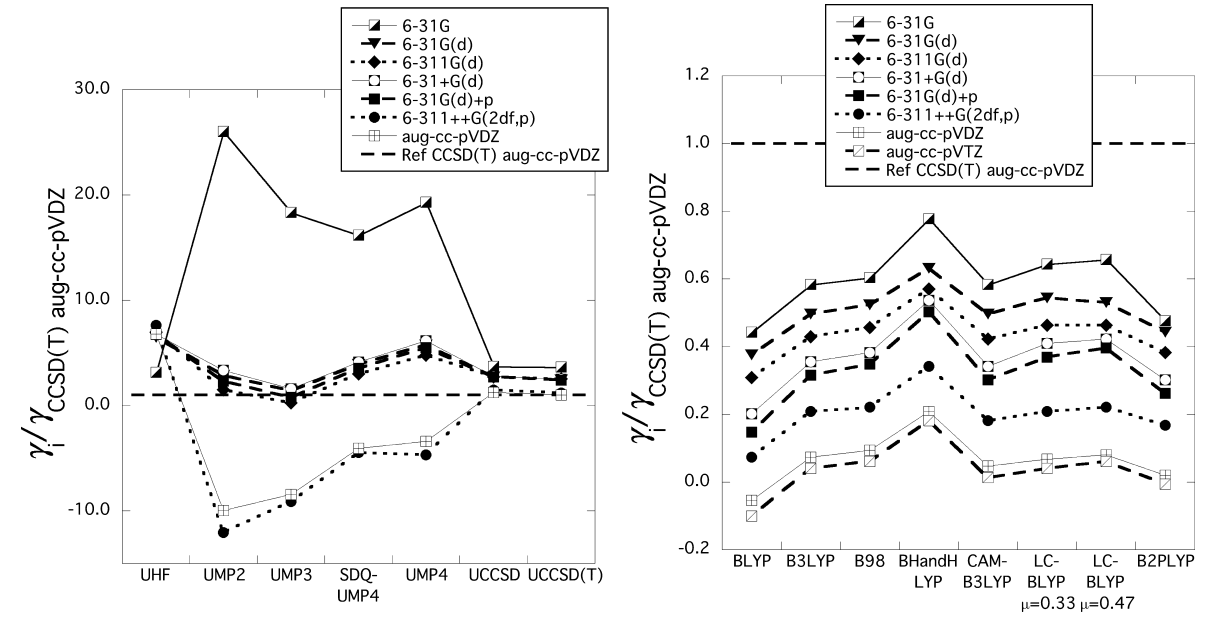

Figure 3. Basis set and electron correlation effects on the second hyperpolarizability of molecule **2**.

The calculations were restricted to the diagonal longitudinal component, $\alpha_{zz} = \alpha, \beta_{zzz} = \beta, \gamma_{zzzz} = \gamma$ (with z the long axis), which are by far dominant in this particular case due to electron delocalization, but for other systems, the relative magnitude of other γ components may vary considerably.[39] The T convention was used to define β and γ. All of the calculations were performed with the Gaussian 09 package[40] as well as with homemade codes to perform the Romberg iterations.

III. RESULTS AND DISCUSSION

III.A. Wave Function Methods. The UMPn, UCC, and UDFT γ values calculated using different basis sets are presented in Figures 2−4 for compounds **1**−**3**, respectively. Additional values, obtained at the PUHF, PUMP2, PUMP3, and PUMP4 levels with large basis sets, are sketched in Figure 5. Table 1 lists the UHF/6-31+G(d) diradical character as well as those γ values determined at different levels of calculation in comparison to the reference γ values, obtained at the UCCSD(T) level with the aug-cc-pVDZ basis set.

The second hyperpolarizability of **1** is underestimated when using basis sets, which do not contain diffuse functions [6-31G, 6-31G(d), 6-311G(d)], whereas adding one set of diffuse p functions is sufficient to provide γ values in close agreement with those obtained with the aug-cc-pVDZ basis set. So, the difference between the 6-311++G(2df,p) and aug-cc-pVDZ γ values is negligible (a maximum of 3%). Note that the 6-31G(d)+p basis set provides results in better agreement with aug-cc-pVDZ than 6-31+G(d), which is attributed to the different exponents of the

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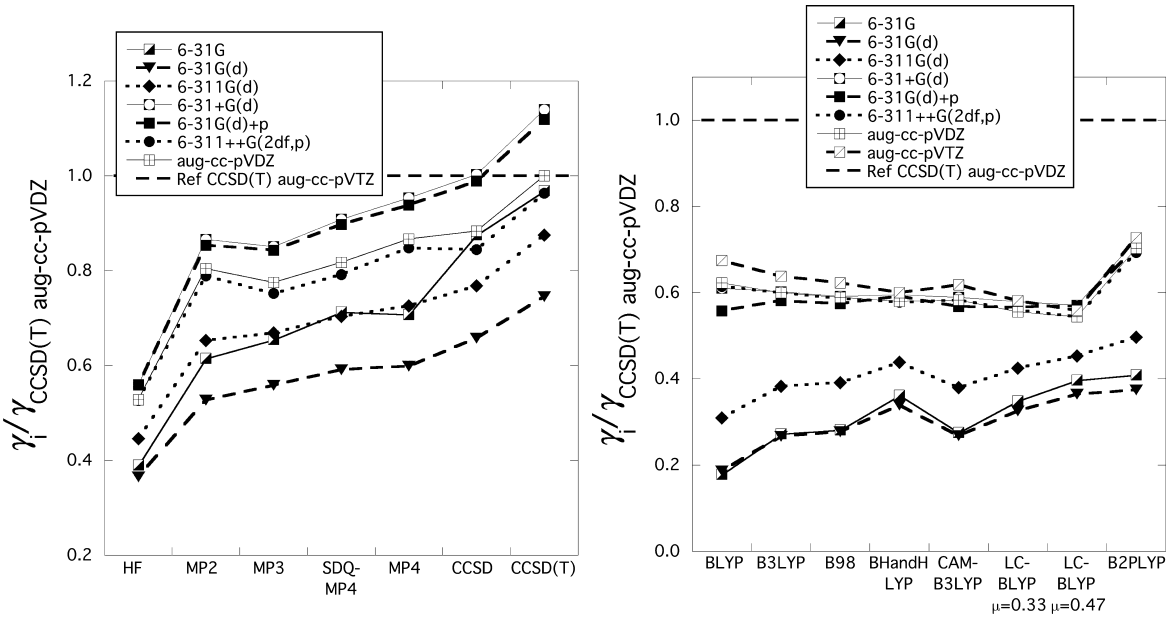

Figure 4. Basis set and electron correlation effects on the second hyperpolarizability of molecule **3**.

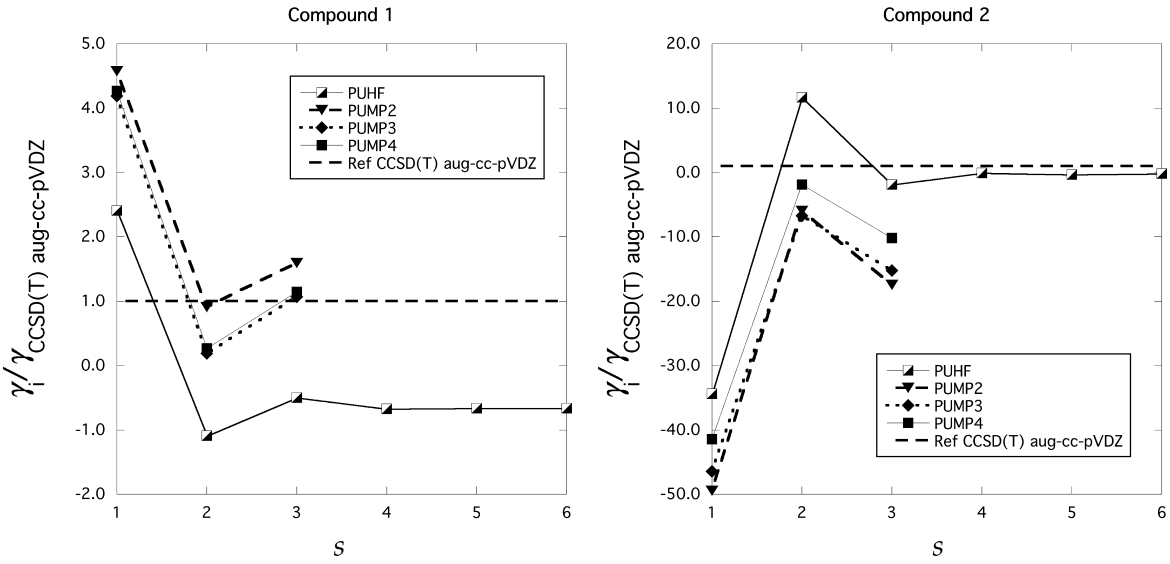

Figure 5. Spin-projected UHF, UMP2, UMP3, and UMP4 results obtained with the aug-cc-pVDZ basis set for compounds **1** and **2** as a function of the order of the spin projection(s).

diffuse basis functions. For this compound having a rather small diradical character (Table 1), electron correlation effects are negligible if noticing that the UHF values are close to the UCCSD(T) ones, but the situation is more complex. Indeed, on the one hand, the UCCSD values are only 20% larger than the UCCSD(T) results and provide therefore a good estimate. The UMP2, UMP3, SDQ-UMP4, and UMP4 schemes overestimate γ by more than 100%, highlighting the impact of spin contaminations. On the other hand, the PUMP2 method with $s = 3$ (2400×10^2 au) leads to a better agreement with the reference UCCSD(T)/aug-cc-pVDZ value (1500×10^2 au) than the UMP2 method (4580×10^2 au). The agreement gets even better at the PUMP3 and PUMP4 levels ($s = 3$) with values of 1600×10^2 and 1700×10^2 au, respectively. Note also that the PUHF value (-997×10^2 au) is far from the reference value, demonstrating the amplitude of electron correlation effects. Thus, for compound **1**, provided spin contamination is removed, the electron correlation contributions to γ converge quite rapidly with the order of perturbation theory.

Compound **2** is a dication with very small diradical character. It displays a negative UCCSD(T) γ value, about 1 order of magnitude smaller than compound **1**. When using too small basis sets, the UCCSD and UCCSD(T) γ amplitudes are overestimated by up to a factor of 2−3. Contrary to the case of compound **1**, the addition of diffuse functions has a rather limited impact on γ, smaller than the effect of including polarization functions. Electron correlation effects as described by the unrestricted Møller−Plesset scheme are poorly estimated, leading to errors on both the sign and the magnitude of γ. Employing the corresponding spin-projected methods does not improve the situation. Indeed, spin projection corrections typically lead to increases of the γ values by about 1000×10^2 au for $s = 3$, and therefore the agreement with UCCSD(T) gets even worse. Only the UCCSD method can approach the

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Table 1. UHF/6-31+G(d) Diradical Characters and aug-cc-pVDZ γ Values (in 10^2 au) Calculated at Different Levels of Calculation for Compounds 1−3

γ	**1** (U)	**2** (U)	**3** (R)
y	0.145	0.061	0.000
HF	1530	−1013	774
MP2	4580	1483	1179
MP3	3750	1255	1136
SDQ-MP4	3320	605	1198
MP4	3870	509	1271
CCSD	1690	−185	1300
CCSD(T)	**1500**	**−149**	**1470**
PUHF/s = 6	−997	20	
PUMP2/s = 3	2400	2600	
PUMP3/s = 3	1600	2300	
PUMP4/s = 3	1700	1500	

UCCSD(T) results, demonstrating that for this compound with a small γ value, the third-order response depends strongly on electron correlation.

The "zwitterionic" compound **3** displays a closed-shell character and a positive γ value similar to that of **1**. The effects of basis sets are however very unusual. At the HF level, the γ value increases in the order 6-31G(d) < 6-31G < 6-311G(d) < 6-311++G(2df,p) < aug-cc-pVDZ < 6-31+G(d) < 6-31G(d)+p. At the MP2 level, this order becomes 6-31G(d) < 6-31G < 6-311G(d) < 6-311++G(2df,p) < aug-cc-pVDZ < 6-31G(d)+p < 6-31+G(d), whereas at the CCSD(T) level it is 6-31G(d) < 6-311G(d) < 6-311++G(2df,p) < 6-31G < aug-cc-pVDZ < 6-31G(d)+p < 6-31+G(d). With the exception of the performance of the 6-31G basis set, which is too small, these results show the need for a balance between diffuse and polarization functions and the fact that the basis set effects are the same at most levels of approximation, as evidenced also by the almost parallel lines in Figure 4. Contrary to the open-shell systems, the MP2 scheme already recovers 80% of the CCSD(T) γ response. The MP4 scheme performs slightly better [86% of CCSD(T) value], whereas the CCSD value differs by only 12%.

III.B. Density Functional Theory Calculations. We now turn to the comparisons between DFT results obtained with different functionals and the reference UCCSD(T) values. Note that because the diradical character is small for compounds **1** and **2**, all XC functionals do not lead to unrestricted solutions. In fact, for compound **2** (y = 0.061), all of the solutions are restricted, while for compound **1** (y = 0.145) only BHandHLYP, LC-BLYP with μ = 0.47, and B2PLYP give unrestricted solutions.

From the comparisons sketched in Figures 2−4, the major conclusion is the nonexistence of a XC functional, which is able to reproduce the UCCSD(T) γ values of the three compounds. In the case of compound **1**, those functionals with zero or small amount of HF exchange (BLYP, B3LYP, B98) as well as LC-BLYP(μ = 0.33) and CAM-B3LYP predict too small values, off by at least a factor of 2 when using the aug-cc-pVDZ and aug-cc-pVTZ basis sets. On the other hand, the XC functionals, which lead to unrestricted solutions, LC-UBLYP(μ = 0.47) and UBHandHLYP, overestimate γ by about 50% and 100%, respectively, whereas UB2PLYP leads to even larger values, consistent with the huge γ overestimation noted in Section III.A at the UMP2 level. These DFT calculations further substantiate the conclusions drawn above on the basis set requirements; that is, diffuse functions are important to describe the third-order field response of **1**. In the case of compound **2**, as there is no unrestricted solutions, all DFT results strongly underestimate γ, and this underestimation grows when the basis set gets more flexible. Using the aug-cc-pVDZ basis set, BHandHLYP gives the closest γ value to UCCSD(T), but it is off by 79%. For compound **3**, all DFT XC functionals underestimate γ by 25−50%. The γ values closest to CCSD(T) are obtained with the B2PLYP XC functional where the value is 10% under the MP2 one. Provided the basis set is large enough, larger amounts of HF exchange are associated with smaller γ values, with a typical decrease by 15% from BLYP to LC-BLYP(μ = 0.47).

The DFT calculations have also enabled one to assess the quality of the aug-cc-pVDZ basis set with respect to aug-cc-pVTZ. Considering the results obtained with the BHandHLYP XC functional, the aug-cc-pVDZ/aug-cc-pVTZ ratio amounts to 1.011, 1.148, and 0.966 for compounds **1**, **2**, and **3**, respectively. The above analysis of the performance of DFT XC functionals to calculate γ of different compounds has to be contrasted with previous studies assessing whether DFT could qualitatively describe the change in γ as a function of the diradical character. In that case, it was found that the BHandHLYP XC functional reproduces the UCCSD(T) versus y curve, although it underestimates γ, especially for large y values, and slightly overestimates γ, for small y values, whereas LC-BLYP(μ = 0.33) exhibits a similar reliability. However, improvement can be obtained by using an approximate spin-projected scheme, as shown in the case of LC-BLYP(μ = 0.47) calculations on *p*-quinodimethane.[41]

The present set of compounds covers a broad range of *p*-quinodimethane derivatives with quite different responses, as those that can be modeled by the valence CI model described in refs 42 and 43. Indeed, the second hyperpolarizability does not depend solely on the diradical character but also on the charge. The largest response is attributed to both compounds **1** and **3**. **1** has an intermediate diradical character, whereas **3** is closed shell, zwitterionic, and asymmetric. The dicationic compound **2** has the smallest diradical character and also the smallest response. Both the charge and the diradical character appear to be important parameters to explain and more importantly to tune the γ response.

III.C. Polarizability and First Hyperpolarizability. It is further interesting to analyze the performance of the different levels of approximation as well as of the projection corrections for the lower-order properties, α and β, the latter being different from zero only for compound **3**. The results are listed in Table 2.

Table 2. α and β Values Calculated at Different Levels of Calculation with the aug-cc-pVDZ Basis Set[a]

	α			β
	1 (U)	**2** (U)	**3** (R)	**3** (R)
HF	143	142	142	−1340
MP2	213	138	158	−1930
MP3	198	137	154	−1880
SDQ-MP4	194	137	156	−1980
MP4	205	140	160	−2100
CCSD	185	135	155	−2100
CCSD(T)	**189**	**136**	**159**	**−2300**
PUHF/s = 6	114	127		
PUMP2/s = 4	184	124		
PUMP3/s = 4	167	124		
PUMP4/s = 4	174	127		

[a]All values are given in au.

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As was observed in other studies, the higher the order of the electric field response is, the larger the effects of electron correlation and the spin contamination are. In the case of the polarizability, for compound **1**, the UMPn values are already in good agreement with the reference UCCSD(T) result, but the agreement is further improved when removing spin contamination by using the projected schemes, in particular at second order. Contrary to its second hyperpolarizability, the polarizability of compound **2** is little modified by electron correlation. In addition, the unrestricted MPn values are already in good agreement with UCCSD(T), and removing the spin contamination does not lead to any noticeable improvement. Similarly to compound **2**, the CCSD(T) polarizability of compound **3** is accurately estimated at the MP2 level, and further inclusion of electron correlation has a negligible impact. The error introduced by using (U)CCSD instead of (U)CCSD(T) amounts to −2.2%, −0.8%, and −2.6%, for compounds **1**−**3**, respectively.

Looking now at the first hyperpolarizability of compound **3**, its CCSD(T)/aug-cc-pVDZ value attains −2300 au. Again, like for α and γ, the MP2 level is already suitable to provide a good estimate of β, with an error of 16%, whereas at the MP4 level this error reduces to 9%, like at the CCSD level.

In summary, the spin-projected technique provides improvements for the polarizability of the neutral compound **1**, whereas for compound **2** the spin projection corrections are negligible. Finally, the MP2 method provides good estimates for α and β of compound **3**.

IV. CONCLUSIONS AND OUTLOOK

The second hyperpolarizability of *p*-quinodimethane derivatives has been calculated at different levels of approximation in combination with a large range of basis sets. The main conclusions are (i) the CCSD method provides results in the closest agreement with the CCSD(T) reference values with CCSD/CCSD(T) ratios amounting to 0.85, 1.26, and 0.88 for compounds **1**−**3**, respectively, (ii) the MP2 level of approximation performs well for the closed-shell compound **3** but not for the open-shell systems **1** and **2**, (iii) for compound **1**, the projected UMP3 and UMP4 methods enable to reproduce the unrestricted CCSD(T) value but not for the charged compound **2** where high-order electron correlation effects are needed to predict the sign of γ, and (iv) without spin projection correction, density functional theory with a broad range of XC functionals does not perform well for these systems with low diradical character, in particular for the charged species. Qualitatively, similar effects have been observed for the lower order properties (polarizability and first hyperpolarizability), although the effects are smaller.

■ ASSOCIATED CONTENT

Supporting Information

Atomic Cartesian coordinates of the B3LYP/6-311G* optimized geometries. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: benoit.champagne@unamur.be.

Notes

The authors declare no competing financial interest.

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