

Electron correlation effects on the first hyperpolarizability of push–pull π -conjugated systems

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The first hyperpolarizability (β) of representative push–pull π -conjugated compounds has been calculated at several levels of approximation to assess the effects of electron correlation. First, the 6-31+G(d) basis set has been shown to give the best balance between accuracy and computational resources for a polyene linker whereas for polyene linker, the 6-31G(d) basis set is already an optimal choice. As a result of cancellations between higher order contributions, the MP2 method turns out to be the method of choice to predict β of push–pull π -conjugated systems since it closely reproduces the values obtained with the reference CCSD(T) scheme. Moreover, the SDQ-MP4 and CCSD approaches provide rarely improved estimates over MP2 while the MP4 method does not represent an improvement over MP4-SDQ or the SCS-MP2 method, over MP2. Among density functional theory exchange-correlation functionals, LC-BLYP is reliable when characterizing the changes of first hyperpolarizability upon enlarging the π -conjugated linker or upon changing the polyene linker into a polyene segment. Nevertheless, its reliability is very similar to what can be achieved with the Hartree–Fock method and the MP2 scheme is by far more accurate. On the other hand, the BLYP, B3LYP, and BHandHLYP functionals perform quantitatively better in a number of cases but the trends are poorly described. This is also the case of the B2-PLYP and mPW2-PLYP functionals, which are often the most accurate, though they underestimate the increase of β when going from polyene to polyene linkers and overestimate the enhancement of β with chain length.

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I. INTRODUCTION

The design of multifunctional compounds has often been focusing on molecules and materials displaying exceptional nonlinear optical (NLO) responses.¹ Conversely, the NLO signatures are detected to reveal the presence and the evolution of molecular and supramolecular structures, such as in second-harmonic imaging microscopy based on fluorescent proteins or in chiral crystal identification.² In these multidisciplinary approaches, theoretical tools can be highly relevant, not only for selecting the most performing compounds but also for interpreting the underlying physico-chemical phenomena. This requires, of course, the use of accurate and rapid prediction tools. Nevertheless, even after several decades of intensive research,³ the prediction and the interpretation of the hyperpolarizabilities remain an ambitious and tremendous task for quantum chemistry. Indeed, many aspects still need to be considered to provide efficient guidelines for designing new systems with targeted nonlinear optical responses, in particular for the most promising systems build from π -conjugated and aromatic linkers with donor and acceptor moieties.

Among these aspects to master in theoretical investigations, several works have addressed the vibrational contributions⁴ or the effects of the surrounding⁵ while in this article, we focus on the electron correlation,^{6–10} in particular,

with the aim of predicting the first hyperpolarizability, β , of push–pull π -conjugated systems. The effects of electron correlation on the hyperpolarizabilities are indeed far from being negligible, as demonstrated by several recent investigations. Nowadays, for small polyatomic molecules, the most efficient and accessible description is given by coupled cluster singles and doubles calculations with a perturbative estimate of triples [CCSD(T)] but, in general, this method cannot be routinely applied to large systems. Hierarchies of lower levels of approximation, including the Hartree–Fock (HF) and density functional theory (DFT) methods, have been proposed but comparisons with coupled cluster results are quite rare. Among these, a recent CCSD study due to Hammond and Kowalski¹¹ showed that the CAMB3LYP exchange-correlation (XC) functional outperforms the B3LYP, PBE0, and PBE XC functionals with respect to the CCSD result, for evaluating the polarizability and the first hyperpolarizability of acetonitrile while comparisons with the HF, CCS, and CC2 methods demonstrate the key role of electron correlation. In the case of *p*-nitroaniline, the prototype push–pull π -conjugated system, the best agreement is found with the B3LYP XC functional whereas CAMB3LYP underestimates it by about 15%. Moreover, Ref. 11 shows that for *p*-nitroaniline these XC functionals perform better than the CC2 scheme (overestimation by 30%) or the HF scheme (underestimation by 43%). In their recent work, Suponitsky *et al.*¹² showed that two DFT functionals with a larger fraction of Hartree–Fock exchange (BMK and especially M05-2X)

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provide the best agreement to experiment, in comparison with the MP2 method. They also highlighted that all hybrid DFT functionals, in their study, overestimate the hyperpolarizability of D- π -A molecules while they recommended using the M05-2X functional as a systematic prediction tool for β . On the other hand, it has been recognized since a decade that the performance of DFT with LDA, GGA, and hybrid XC functionals will generally deteriorate when considering larger systems due to the XC potential shortsightedness.¹³ So far, several solutions have been proposed, under the form of the optimized effective potential (OEP) (Ref. 14) or long-range corrected XC functionals¹⁵ but these solutions are not completely satisfactory. On the other hand, Møller–Plesset second-order perturbation theory (MP2) can now routinely be applied to systems with a hundred of atoms or more, which opens the way to investigate systems of interest for NLO applications. This approach was favored in several of our recent investigations combining measurements and simulations¹⁶ because for model systems (NH₂–CH=CH–CH=CH–NO₂ and NH₂–CH=CH–CH=CH–CH=CH–NO₂), the MP2 scheme provides first hyperpolarizability values in close agreement with the CCSD(T) results.¹⁷ Nevertheless, for polybutatriene chains, the MP2 approach was found to overestimate the second hyperpolarizability by more than a factor of 2 with respect to CCSD(T) for chains containing at least 16 C atoms.¹⁸ Note that such MP2/CC comparisons also raise the question of the basis set effects. In Ref. 17, the relationships between the MP2 and CCSD(T) results were found rather similar when using the 6-31G(d), 6-31+G(d), cc-pVDZ, and aug-cc-pVDZ basis sets. This is however not always the case, in particular, when considering smaller compounds. Thus, in Ref. 11, at the CCSD level, the importance of using very large basis sets to calculate the first hyperpolarizability has been reaffirmed, with the d-aug-cc-pV5Z basis set considered to provide reference values. So, for acetonitrile and chloroform, Hammond and Kowalski have shown that the d-aug-cc-pVTZ leads to accurate results whereas for *p*-nitroaniline, the Sadlej POL basis set leads to results in close agreement with more extended Dunning basis sets. They have further substantiated the fact that molecules of similar size but different chemical compositions may behave in a much different manner with respect to basis set convergence. Finally, as expected, in the case of *p*-nitroaniline the evaluation of the properties with respect to the basis set is far less demanding.

In a number of cases, long-range corrected XC functionals have appeared appealing to describe the hyperpolarizabilities of π -conjugated systems because the errors observed with LDA and GGA are reduced for a large part.^{13,14} These studies have therefore naturally concluded that, after improving the exchange part of the functional, the correlation part should also be improved. One of these strategies has consisted in adding MP2 correlation to the pure DFT correlation, leading therefore to double hybrid XC functionals.¹⁹ Several improvements have been highlighted upon using the double hybrid B2-PLYP functional, for example, in the case of harmonic and anharmonic vibrational frequencies or in the prediction of the barrierless reaction of the benzenium–ethene complex to the ethyl-1H-benzene cation.^{20,21} This method has also been extended without any further empirical adjustment to electronic

excited states in the framework of time-dependent density functional theory or the closely related Tamm–Dancoff approximation (TDA-DFT).²² Other investigations²³ have been carried out but not in the case of first hyperpolarizability determinations. Then, the new mPW2-PLYP double hybrid XC functional²⁴ outperforms the B2-PLYP functional in the computation of thermodynamic properties of large molecules. This functional gives accurate predictions for both the excitation and emission energies of substituted *p*-quaterphenylenes nanofibers.²⁵

In addition to the MP2 scheme, we focus here also on two other Møller–Plesset perturbation theory schemes to calculate the first hyperpolarizabilities, the fourth order Møller–Plesset (MP4) method and the spin-component-scaled Møller–Plesset second-order perturbation theory (SCS-MP2) method, which has been recently proposed by Grimme.²⁶ The SCS-MP2 scheme consists in a separate scaling of the parallel and antiparallel spin components of the MP2 energy expression and, therefore, it can be applied without additional cost to the ordinary MP2 method. The SCS-MP2 method has already demonstrated good reliability for a wide range of molecular properties, including energies of reaction, molecular geometries, harmonic frequencies, noncovalent interactions, heats of formation, as well as excitation energies.²⁷ Preliminary results on the polarizability and second hyperpolarizability of model H₂ chains have also investigated the SCS-MP2 reliability.²⁸ All these results call therefore for further investigations of electron correlation effects on the first hyperpolarizability of push–pull π -conjugated systems and for the assessment of MP2 and new DFT schemes with respect to CCSD(T).

In order to carry out this investigation on electron correlation effects, six donor/acceptor (D/A) π -conjugated systems were selected (Fig. 1). The donor (dimethylamino) and acceptor (nitro) groups are among the strongest donating and accepting groups. π -conjugated linkers of different lengths and natures were considered: a polyene segment of four or six double bonds forms the backbone of compounds **a** and **c**, whereas in compounds **b** and **d**, it is a polyene segment with four or six double bonds, respectively. In **e** and **f**, the linker is made of two aromatic rings, either two phenyl or two thiophene rings. As a result of electron delocalization along the π -conjugated backbone, the longitudinal component of the first hyperpolarizability, $\beta_{xxx} = \beta_L = \beta$, is by far the largest tensor component. Thus, in the following, we just considered this longitudinal component of the static first hyperpolarizability.

The paper is organized as follows. The methods and the computational scheme are summarized in Sec. II. Section III presents and discusses the results, whereas Sec. IV concludes and draws some perspectives.

II. THEORETICAL AND COMPUTATIONAL ASPECTS

The geometries were optimized at the DFT level using the B3LYP XC functional and the 6-311G(d) basis set. The longitudinal (*x*) direction is defined by one of the principal inertial axes. For compounds **a**, **c**, and **e**, this axis is passing by the two nitrogens of the substituents while for molecules **b**, **d**, and **f**, this axis passes nearby the midpoint of the C–N bonds.

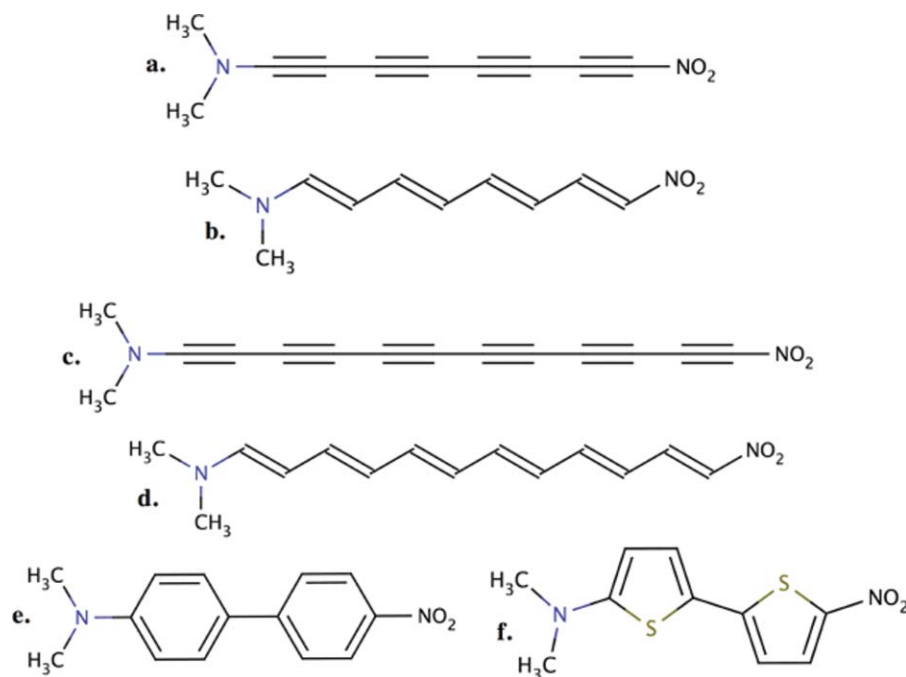


FIG. 1. Chemical structures of the a–f D/A π -conjugated systems: **a**, dimethyl(8-nitroocta-1,3,5,7-tetraen-1-yl)amine; **b**, dimethyl(8-nitroocta-1,3,5,7-tetraen-1-yl)amine; **c**, dimethyl(12-nitrododeca-1,3,5,7,9,11-hexayn-1-yl)amine; **d**, dimethyl(12-nitrododeca-1,3,5,7,9,11-hexaen-1-yl)amine; **e**, *N,N*-dimethyl-4-(4-nitrophenyl)aniline; **f**, *N,N*-dimethyl-5-(5-nitrothiophen-2-yl)thiophen-2-amine.

The finite field (FF) procedure²⁹ was used to evaluate the static longitudinal first hyperpolarizability at the different levels of approximation. These encompass MO based methods: (i) the Hartree–Fock method, (ii) the Møller–Plesset second- and fourth-order perturbation theory approaches (MP2 and MP4), (iii) the spin-component-scaled Møller–Plesset second-order perturbation theory (SCS-MP2) method, (iv) the coupled cluster method including the singles and the doubles (CCSD), and (v) the coupled cluster method including the singles and the doubles and a perturbative estimate of the triple excitations (CCSD(T)), as well as DFT schemes with a range of XC functionals: (i) the GGA BLYP functional, (ii) the hybrid B3LYP and BHandHLYP functionals, which contain 20% and 50% of HF exchange, respectively, (iii) the long-range corrected LC-BLYP functional ($\mu = 0.47$), and (iv) the double hybrid B2-PLYP functional (53% E_X^{GGA} , 47% E_X^{HF} , 73% E_C^{GGA} , and 27% E_C^{MP2}) and mPW2-PLYP (55% E_X^{GGA} , 45% E_X^{HF} , 75% E_C^{GGA} , and 25% E_C^{MP2}). The $\mu = 0.47$ value in LC-BLYP is a reoptimized parameter to minimize the errors in the atomization energies of molecules in the G2 set³⁰ and is the default in GAUSSIAN 09. To achieve an accuracy of 1–10 a.u. on the first hyperpolarizability values, special care was given to the choice of threshold in the iterative procedures. In the SCF calculations, the convergence parameter N , which implies a convergence of 10^{-N} on the energy and $10^{-(N+2)}$ on the wavefunction, was set to 10. On the other hand, in the CC calculations, the convergence parameter M , which implies a convergence of 10^{-M} on the energy and $10^{-(M+2)}$ on the wavefunction, was set to 9. In the latter case, going from $M = 9$ to $M = 10$ did not lead to any relevant difference (<0.05 a.u.) on β . The general finite difference expression for a third-order

derivative reads

$$\beta^{0,k} = \frac{2[E(2^k E) - E(-2^k E)] - [E(2^{k+1} E) - E(-2^{k+1} E)]}{2(2^k E)^3},$$

where E , the energy, is evaluated for different field amplitudes. To remove higher-order contaminations in the FF differentiation, the Romberg procedure was applied in combination with field amplitudes ranging from ± 0.0004 to ± 0.0064 a.u., i.e., $E = 0.0004$ a.u. and $k = 0-4$ in the previous equation. The iterative Romberg expression reads:

$$\beta^{n,k} = \frac{4^n \beta^{n-1,k} - \beta^{n-1,k+1}}{4^n - 1},$$

where n is the order of the iteration. Several atomic basis sets were employed, starting from the 6-31G(d) valence double- ζ + polarization basis set and then adding an additional set of valence functions [6-311G(d)] or a set of diffuse functions [6-31+G(d)]. Much larger basis sets, including the 6-311++G(2df,p), aug-cc-pVDZ, and aug-cc-pVTZ basis sets, were also employed at the SCF and MP2 levels of approximation. In addition, the Z3PolX basis set due to Benkova *et al.*³¹ was selected. The ZmPolX [where m denotes the number of primitive GTOs (Gaussian Type Orbitals) in the contracted polarization] basis sets are reduced-size polarized basis sets, which result from the truncation of the original PolX basis sets³² without any major loss of accuracy when calculating the molecular electric properties. This ZmPolX basis sets have primarily been tailored to well reproduce the molecular dipole moments and the dipole polarizabilities but recent calculations have also demonstrated their performance for calculating the NLO properties.¹¹ Simultaneously, the dipole moment and polarizability data remain at almost the same

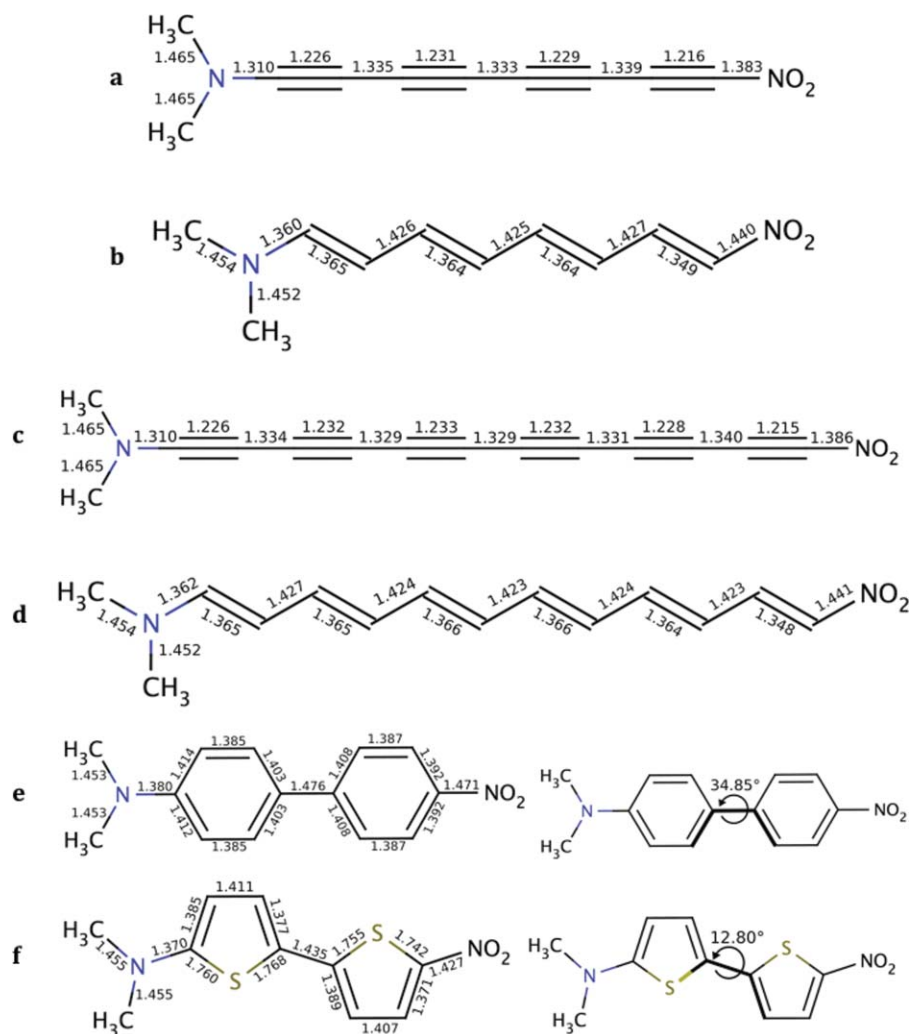


FIG. 2. Principal interatomic distances (Å) for the set of six D/A π -conjugated systems. For compounds **e** and **f**, the dihedral angle between the two cycles has also been given.

level of accuracy as in the case of the original PolX basis set, which is most comparable to the d-aug-cc-pVDZ set in the Dunning series, despite being approximately two-thirds of the size. This paper will further assess the performance of the Z3PolX basis set in the case of the first hyperpolarizability of large D/A π -conjugated systems.

All reported β values are given in a.u. [$1 \text{ a.u. of } \beta = 3.6213 \times 10^{-42} \text{ m}^4 \text{ V}^{-1} = 3.2064 \times 10^{-53} \text{ C}^3 \text{ m}^3 \text{ J}^{-2} = 8.639 \times 10^{-33} \text{ esu}$] within the T convention. All calculations were performed using the GAUSSIAN 03 and 09 program packages.^{33,34}

III. RESULTS AND DISCUSSION

A. Optimized geometries

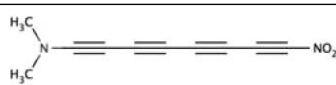
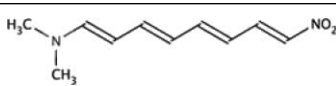
The principal geometrical characteristics of the six D/A π -conjugated systems are shown in Fig. 2, i.e., the principal interatomic distances and the dihedral angles between the two cycles for molecules **e** and **f**. In the latter cases, the steric constraint between the two cycles prevents the π -conjugated pathway to be planar. Thus, these two molecules are less conjugated than the others. As expected, the average bond length

alternation (BLA) is smaller for the polyene linker (0.06 Å for **b** and **d**) than for the polyyne linkers (0.11 Å for **a** and 0.10 Å for **c**). In the case of compounds **e** and **f**, the inter-ring BLA amounts to 0.07 and 0.05 Å, whereas the intraring BLA is much smaller and attains only 0.02 and 0.03 Å, respectively. The smaller inter-ring BLA for compound **f** can be related to the smaller dihedral angle (12.8° for **f** vs 34.9° for **e**) and therefore a better electron conjugation.

B. Basis set effects

The smaller D/A molecules **a** and **b** are used to investigate the basis set effects on β . Due to basis set compensation effects, basis set effects on the other and larger compounds are expected to be smaller. The results are listed in Table I. The addition of a supplementary set of valence basis functions from the 6-31G(d) to the 6-311G(d) basis set has a rather small effect on β , with a decrease of β not larger than 1.5%, for all levels of calculation. On the other hand, the addition of diffuse functions has a larger effect. At the HF level, going from the 6-31G(d) to the 6-31+G(d) basis set results in an increase of β by about 10% but this increase is about

TABLE I. Basis set effects on the static longitudinal first hyperpolarizability of compounds **a** and **b**, at different levels of calculation. The values in parentheses correspond to the ratios, at a given level of approximation, with the respect to the corresponding aug-cc-pVDZ, 6-311++G(2df,p), and aug-cc-pVTZ basis sets.

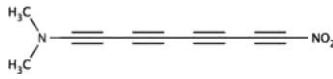
							
	6-31G(d)	6-311G(d)	6-31+G(d)	Z3PolX	aug-cc-pVDZ	6-311++G(2df,p)	aug-cc-pVTZ
Number of basis functions	222	270	278	288	376	518	782
HF	8151 (0.90) (0.91) (0.91)	8151 (0.90) (0.91) (0.91)	9077 (1.00) (1.02) (1.01)	9429 (1.04) (1.05) (1.05)	9089	8946	8966
MP2	13 255 (0.87) (0.88) (0.88)	13 068 (0.86) (0.87) (0.87)	15 576 (1.02) (1.04) (1.03)	16 011 (1.05) (1.07) (1.06)	15 258	14 988	15 096
SCS-MP2	12 937 (0.87) (0.89) (0.88)	12 777 (0.86) (0.88) (0.87)	15 121 (1.02) (1.04) (1.03)	15 601 (1.05) (1.07) (1.06)	14 824	14 566	14 653
MP4	13 783	13 607	16 498	16 925			
CCSD	11 490	11 260	13 700	14 069			
CCSD(T)	12 685	12 380	15 628	16 017			
							
	6-31G(d)	6-311G(d)	6-31+G(d)	Z3PolX	aug-cc-pVDZ	6-311++G(2df,p)	aug-cc-pVTZ
Number of basis functions	238	294	294	336	448	574	966
HF	10 138 (0.96) (0.98) (0.98)	10 007 (0.95) (0.96) (0.97)	11 413 (1.08) (1.10) (1.10)	11 207 (1.06) (1.08) (1.08)	10 581	10 389	10 331
MP2	24 206 (0.92) (0.94) (0.93)	24 016 (0.91) (0.93) (0.93)	27 745 (1.06) (1.07) (1.07)	28 126 (1.07) (1.08) (1.09)	26 252	25 847	25 905
SCS-MP2	24 785 (0.93) (0.94) (0.94)	24 619 (0.92) (0.94) (0.93)	28 318 (1.06) (1.08) (1.07)	28 819 (1.08) (1.10) (1.09)	26 763	26 291	26 363
MP4	24 943	24 574	28 574	27 897			
CCSD	21 190	20 874	25 079				
CCSD(T)	21 646	21 549	26 539				

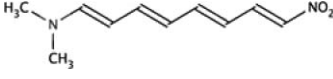
twice larger when using MO correlated methods. Indeed, in the case of compound **a**, the increase of β when going from the 6-31G(d) to 6-31+G(d) basis set amounts to 17% at the MP2 and SCS-MP2 levels, 20% at the MP4 and CCSD levels, and up to 23% for the CCSD(T) method. Similar effects are found for compound **b**, with increases of β by 12.6%, 14.6%, 18.4%, and 22.6% at the HF, MP2, CCSD, and CCSD(T) levels of approximation, respectively. For compound **a**, the β values obtained with the Z3PolX basis set are another 3%–4% larger than the 6-31+G(d) values whereas for compound **b**, the variations are smaller and range from a decrease of β by 2.4% (MP4) to an increase by 1.8% (SCS-MP2).

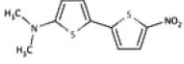
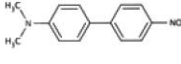
Additional assessments of these medium-size basis sets were then carried out by comparison with more extended ba-

sis sets. The differences in β between these three reference basis sets [aug-cc-pVDZ, 6-311++G(2df,p), and aug-cc-pVTZ] are generally small (less than 2%). In particular, for compound **a**, going from the aug-cc-pVDZ to the aug-cc-pVTZ basis set leads to a decrease by about 1%, while the number of basis functions more than double. The 6-311++G(2df,p) basis set predicts β values, which are slightly smaller than with the aug-cc-pVTZ basis set. For compound **b**, the differences between the 6-311++G(2df,p) and aug-cc-pVDZ basis sets are slightly smaller than for compound **a** while the differences between the 6-311++G(2df,p) and aug-cc-pVTZ basis sets are very small, and smaller than 0.3% at the MP2 and SCS-MP2 levels of approximation. The ratios between the β values for the medium-size basis sets and these reference

TABLE II. Electron correlation effects on the static longitudinal first hyperpolarizability of compounds **a**, **b**, **c**, **e**, and **f**, as estimated by the $\beta(X)/\beta[\text{CCSD(T)}]$ ratios, where X is a lower level of approximation than CCSD(T).

				
	6-31G(d)	6-311G(d)	6-31+G(d)	Z3PolX
HF	0.643	0.658	0.580	0.589
MP2	1.045	1.056	0.997	1.000
SCS-MP2	1.020	1.032	0.968	0.974
MP4	1.086	1.100	1.056	1.057
SDQ-MP4	0.931	0.933	0.881	0.891
CCSD	0.906	0.910	0.877	0.878

			
	6-31G(d)	6-311G(d)	6-31+G(d)
HF	0.464	0.464	0.430
MP2	1.118	1.114	1.045
SCS-MP2	1.145	1.142	1.067
MP4	1.152	1.140	1.076
SDQ-MP4	1.083	1.062	0.999
CCSD	0.980	0.969	0.945

			
	6-31G(d)	6-31G(d)	6-31G(d)
HF	0.663	0.647	0.618
MP2	1.178	0.992	1.026
SCS-MP2	1.187	0.922	0.998
MP4	1.150	1.174	1.084
SDQ-MP4	0.977	0.887	0.892
CCSD	0.928	0.838	0.887

values are given in Table I. For molecule **a**, the closest agreement is obtained with the 6-31+G(d) basis set, with overestimations smaller than 2% or 4% at the HF and MP2/SCS-MP2 levels of approximation, respectively. The Z3PolX basis set gives also good results but the calculations takes longer than with the 6-31+G(d) basis set, due to the slower SCF convergence. For molecule **b**, with respect to the 6-311++G(2df,p) or aug-cc-pVTZ basis sets the 6-31G(d) basis set underestimates less the first hyperpolarizability than the 6-311G(d) basis set while the 6-31+G(d) and Z3PolX basis sets lead to overestimations of similar amplitudes. The results on compound **b** further show that the presence of diffuse functions in the basis set has little impact on the agreement with more complete basis sets. Indeed, although the difference in β between the 6-31G(d) and 6-311G(d) basis sets on one side and the 6-31+G(d) and Z3PolX basis sets on the other side attains 10%–15%, the amplitude of the deviations with respect to the 6-311++G(2df,p) or aug-cc-pVTZ basis set is similar and fluctuates between 5% and 10%.

As intermediate conclusion from this section, one can state that, for evaluating the first hyperpolarizability of molecule **a**, the 6-31+G(d) basis set gives the best balance between accuracy and computational resources whereas for molecule **b**, the 6-31G(d) basis set is already an optimal

choice. Another interesting comment is related to the usual believe that higher order methods require larger basis sets to achieve a converged description of the electron correlation effects. As far as we consider the data reported in Table I, it turns out that (a) the MP2/HF ratios for both compounds **a** and **b** are very stable when going from the smallest 6-31G(d) to the largest aug-cc-pVTZ basis sets with variations smaller than 7% and (b) the variations of the CCSD(T)/MP2 ratios estimated from using the 6-31G(d), 6-311G(d), 6-31+G(d), and Z3PolX basis sets are also within a range of 5%–7%, demonstrating that for the longitudinal first hyperpolarizability of push–pull π -conjugated systems, these basis set effects are not exacerbated.

C. Electron correlation effects using MO based methods

Considering the medium-size basis sets discussed above, the impact of electron correlation on the static longitudinal first hyperpolarizabilities of compounds **a**, **b**, **c**, **e**, and **f** were addressed. Table II reports the corresponding $\beta(X)/\beta[\text{CCSD(T)}]$ ratios, where X is a lower level of approximation than CCSD(T). The HF method systematically underestimates β . Using basis sets lacking diffuse functions,

this underestimation amounts to about 35%–39% for compounds **a**, **c**, **e**, and **f** while 54% for compound **b**. When diffuse functions are included in the basis set, the underestimation increases by 7% for compound **a**, but only by 3% for compound **b**.

Including the lowest order electron correlation correction (MP2) leads to β values in very close agreement with the reference CCSD(T) data. Moreover, the difference between the MP2 and CCSD(T) results is smaller (i) when the basis set contains diffuse functions and (ii) for polyynes rather than polyene linker. Switching to the SCS-MP2 method does not provide a systematic improvement over the MP2 results: for compound **a**, the SCS-MP2 method is in better agreement with respect to the CCSD(T) reference value provided the basis set does not contain diffuse functions. On the other hand, the MP2 method performs better than the SCS-MP2 scheme for molecules **b**, **c**, and to a lesser extent for molecule **f**. For molecule **e**, SCS-MP2 performs slightly better when using the 6-31G(d) basis set.

Except for compound **f**, moving from MP2 to MP4 leads to a small increase of the first hyperpolarizabilities, which results in larger deviations with respect to the CCSD(T) data. Data in Table II also point out the relatively large contribution from the triples, in particular in the case of the polyyne linker, where the CC triple bonds concentrate a large amount of electronic charge. So, for compounds **a** and **c**, removing the fourth-order triples (T4) contribution switches the difference with respect to CCSD(T) from an overestimation by 5%–10% for **a** and 17% for **c** to an underestimation by 7%–12%. This T4 contribution is smaller for compounds **b** and **f**, which also

brings the SDQ-MP4 β values in better agreement with the CCSD(T) results than the MP4 results.

Finally, considering the CCSD results, the main conclusions are (i) the CCSD method underestimates the CCSD(T) β values by up to 16%, (ii) for both compounds **a** and **b**, this difference increases when the basis set includes diffuse functions, and (iii) the agreement with CCSD(T) is better for compound **b** than compound **a**, demonstrating again that the triples contribution is larger for systems with CC triple bonds than for these with CC double bonds.

In view of these results, due to some cancellations between higher order contributions, (i) the MP2 method turns out to be a method of choice to predict the first hyperpolarizabilities of push–pull π -conjugated systems, (ii) the SDQ-MP4 or CCSD approaches provide improved estimates over MP2 only in the case of compounds **b** and **f**, (iii) in comparison to MP4-SDQ, the MP4 method does not constitute an improvement, and (iv) the SCS-MP2 improves over MP2 only in limited cases.

D. Structure–property relationships

Table III lists the β values of the six D/A π -conjugated systems at different levels of approximation. Since the MP4, CCSD, and CCSD(T) calculations require substantial computational resources, in several cases we have considered the MP2 approximation as the reference, because it leads, in view of the precedent subsection, to results in close agreement with the CCSD(T) values.

TABLE III. Static longitudinal first hyperpolarizability for all the D/A π -conjugated systems considered in this study, at different levels of calculation and for different basis sets.

						
	6-31G*					
Number of basis functions	222	238	282	306	298	268
HF	8151	10 138	18 079	28 652	3432	5825
MP2	13 255	24 206	27 704	66 895	5692	10 346
SCS-MP2	12 937	24 785	25 768	66 056	5541	10 429
MP4	13 783	24 943	32 809	68 446	6015	10 102
SDQ-MP4	11 804	23 453	24 791	60 669	4952	8582
	6-311G*					
Number of basis functions	270	294	342	378	366	334
HF	8151	10 007	18 175	28 421	3498	5904
MP2	13 068	24 016	27 814	67 234	5752	10 342
SCS-MP2	12 777	24 619	25 930	66 592	5602	10 429
MP4	13 607	24 574	32 998	68 575	6113	10 113
SDQ-MP4	11 556	22 877	24 809	60 411	4963	8436
	6-31+G*					
Number of basis functions	278	294	354	378	370	332
HF	9077	11 413	19 607	31 701	3895	6693
MP2	15 576	27 745	31 804	75 741	6769	12 393
SCS-MP2	15 121	28 318	29 454	74 657	6555	12 413
MP4	16 498	28 574	38 043	...	...	...
SDQ-MP4	13 766	26 529	28 158	...	...	...

In the case of “short” polyene and polyynes chains, β increases nonlinearly with the number (N) of double/triple bonds. In other words, the first hyperpolarizability reported to the number of double/triple bonds increases with N . Indeed, $\beta(\text{MP2}, 6\text{-}31\text{+G(d)})/N$ amounts to 3894 and 5300 a.u. for **a** and **c** and to 6936 and 12623 a.u. for **b** and **d**, respectively. For a given number of units in the chain, the D/A molecule with doubly bonded π -conjugated linkers displays a larger β value than its triply bonded analog. This can be rationalized in terms of the BLA, following the general relations where β increases with decreasing BLA, attains a maximum for BLA of around 0.05 Å, then, it decreases, becomes negligible, and reverses sign.³⁵ Indeed, the BLA for molecule **d** (or **b**) amounts 0.06 Å, which is close to the value maximizing β , while for molecule **c** (and **a**) we have 0.10 Å (0.11 Å).

For the molecules **e** and **f**, the steric constraint between the two cycles prevents the π -conjugated pathway to be planar. Combined with the effect of ring aromaticity, which hampers electron delocalization from the donor to the acceptor, these two molecules are less conjugated than the others, which explains why they have smaller β values. Between molecules **e** and **f**, molecule **f** presents a larger β value than molecule **e**. This can be rationalized in terms of the amplitude of the dihedral angle between the two cycles. For molecule **f**, the dihedral angle is 12.8° while for the molecule **e**, it raises to 34.9°.

Figures 3 and 4 summarize these structure–property relationships, where β is plotted as a function of the distance between the two nitrogen atoms at the chains ends (Fig. 3) or as a function of the number of the π -electrons in the linker (Fig. 4). These figures also demonstrate that similar conclusions are drawn when using the MP2 and MP4 methods or by employing the 6-31G(d) and 6-31+G(d) basis sets. If adopting the HF and MP2 methods, similar orderings of β values are obtained, though the β underestimation when using the HF method has been shown to be stronger for a polyene linker. This is further evidenced by considering the ratios of β values with respect to compound **a**. At the HF level, the β values are in the ratio 1.00:1.26:2.16:3.49:0.43:0.74 for compounds **a–f**, respectively whereas 1.00:1.78:2.04:4.86:0.43:0.80 at the MP2 level.

E. Assessment of DFT exchange-correlation functionals

The D/A molecules **a**, **b**, **c** and **d** are used for assessing the performance of DFT XC functionals to account for electron correlation effects in the description of the β responses. As already mentioned in the introduction, the performance of traditional and hybrid XC functionals (here: BLYP, BHandHLYP, and B3LYP) will generally deteriorate when considering larger systems. In order to extend this analysis, we also employed the LC-BLYP functional, which is a long-range corrected XC functional, and the B2-PLYP and mPW2-PLYP functionals, which are double hybrid XC functionals,^{19,25} where MP2 correlation is added to the pure DFT correlation. Table IV lists the $\beta(X)/\beta[\text{CCSD(T)}]$ ratios or the $\beta(X)/\beta[\text{MP2}]$ ratio when CCSD(T) calculations are not available.

For compound **a**, among the GGA and hybrid XC functionals, the B3LYP functional is very efficient and only underestimates β by 1% or less, for both the 6-31G(d) and 6-31+G(d) basis sets. Using the BHandHLYP and BLYP functionals provides β values smaller than the CCSD(T) reference by 6%–10% and 13%–15%, respectively. The LC-BLYP functional leads to an underestimation by 19% with the 6-31G(d) basis set or by 20% when adding diffuse functions. The B2-PLYP (mPW2-PLYP) double hybrid XC functional overestimates β by 19% (15%). For molecule **c**, which has a longer polyene chain than **a**, the β values obtained using the 6-31G(d) basis set are now overestimated when using the BLYP (27%), BHandHLYP (10%), and B3LYP (37%) XC functionals. The smallest overestimation is found for the functional with the largest (50%) amount of HF exchange. The LC-BLYP functional does not perform better than BHandHLYP since it underestimates β by 18% while B2-PLYP overestimates it by about 46% and mPW2-PLYP by 38%. Similar trends are observed when using the 6-31+G(d) basis set, even though the MP2 data are used as reference.

Turning now to the polyene linkers and compound **b**, the BLYP, BHandHLYP, B3LYP, and LC-BLYP functionals strongly underestimate β . The only satisfactory values are obtained with the B2-PLYP and mPW2-PLYP functionals, with underestimations around 10%–15%. Again, it is interesting to see the evolution of the method reliability for a push–pull compound with a slightly longer linker, here compound **d**. There is no substantial improvement for the BLYP, BHandHLYP, B3LYP, and LC-BLYP functionals whereas the B2-PLYP and mPW2-PLYP functionals remain accurate. Going from the 6-31G(d) to the 6-31+G(d) basis set has a limited impact on this analysis. Note however that the reliability of the conventional functionals will strongly deteriorate when further enlarging the conjugated linker.^{13,14}

Rather than just considering the absolute value of the hyperpolarizabilities, the predictive power of these methods can also be assessed by considering trends in the hyperpolarizabilities among chemically related species. As a matter of fact, we have considered the ratios between β of chains containing the same number of unsaturated bonds but double versus triple bonds, i.e., $\beta[\mathbf{b}]/\beta[\mathbf{a}]$ and $\beta[\mathbf{d}]/\beta[\mathbf{c}]$, and ratios between chains containing six and four unsaturated bonds of the same nature, i.e., $\beta[\mathbf{c}]/\beta[\mathbf{a}]$ and $\beta[\mathbf{d}]/\beta[\mathbf{b}]$. The results are presented in Table V. The double versus triple bond ratio, estimated by $\beta[\mathbf{b}]/\beta[\mathbf{a}]$ and $\beta[\mathbf{d}]/\beta[\mathbf{c}]$, is larger than 1.5 and increases with the linker size. This increase is reproduced at the HF level but the ratios are underestimated. The performance of B2-PLYP and mPW2-PLYP are similar, while they require the evaluation of cpu-expensive MP2 contributions. Among the DFT schemes, the LC-BLYP functional provides here the best result. On the other hand, the ratios and their evolution with chain length are getting worse when going from BHandHLYP to B3LYP, and to BLYP. When enlarging the π -linker by two unsaturated bonds, the first hyperpolarizability increases by about 100%–125% ($\beta[\mathbf{c}]/\beta[\mathbf{a}] \sim 2.2$). This effect is well reproduced at the HF and LC-BLYP levels whereas the increase is strongly overestimated when using the other functionals. A similar situation occurs for the polyene linker, though in that case the $\beta[\mathbf{d}]/\beta[\mathbf{b}]$ ratio is close to 2.7.

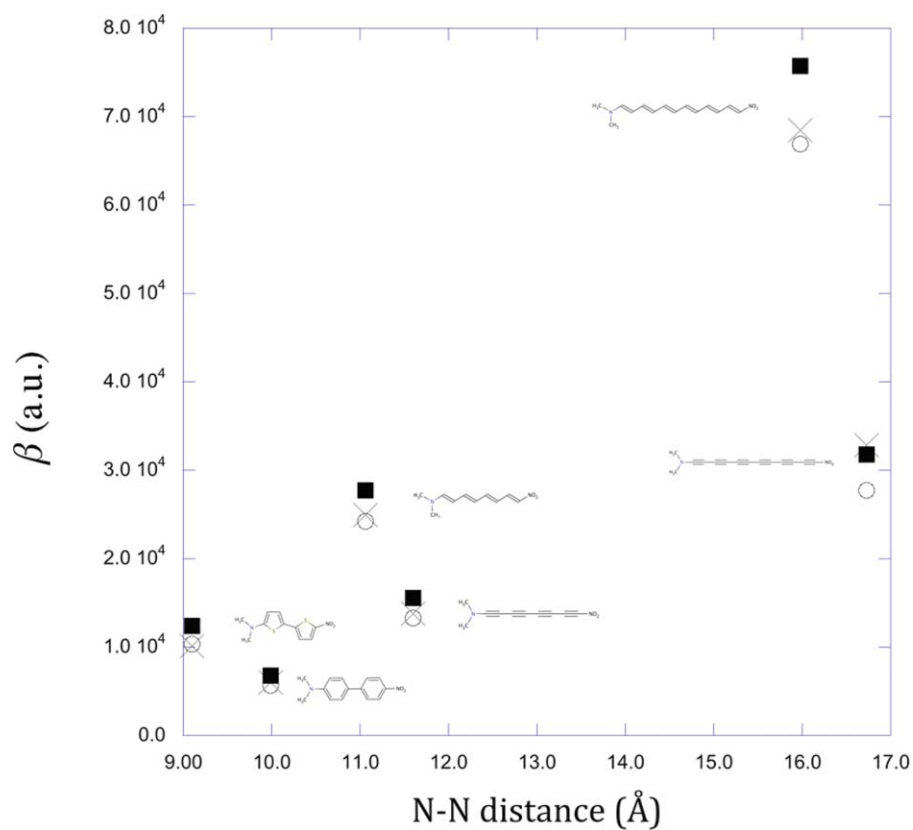


FIG. 3. β as a function of the distance between the two nitrogen atoms at the chain extremities, calculated at different levels of approximation: MP2/6-31+G(d): ■; MP2/6-31G(d): ○; MP4, 6-31G(d): ×.

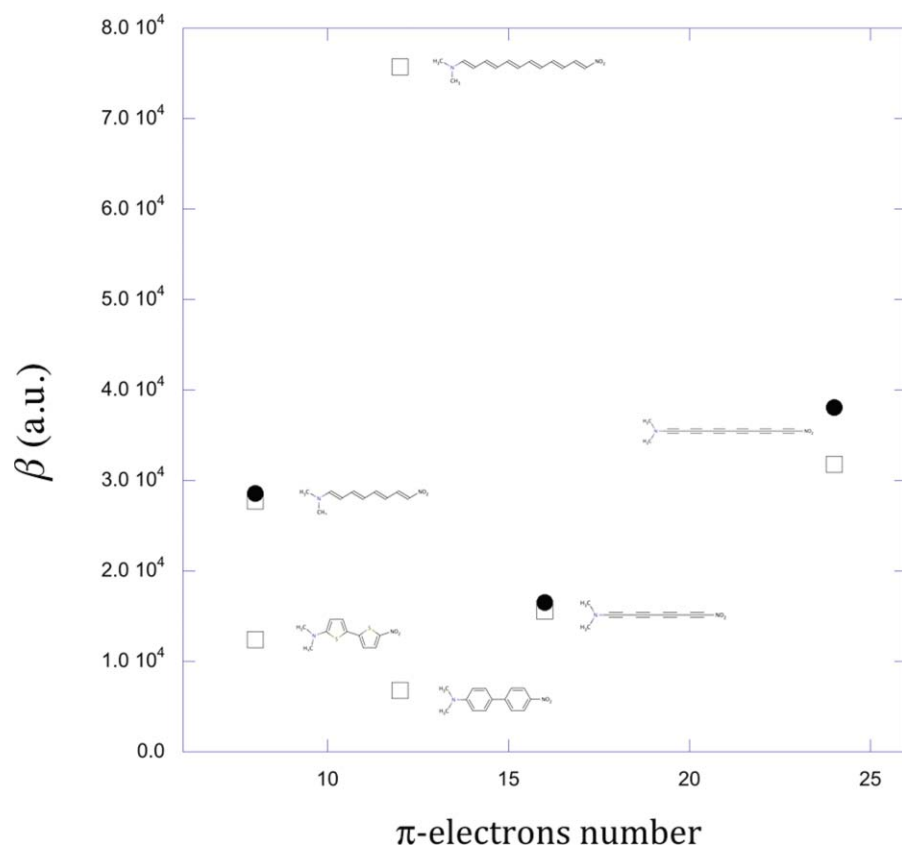


FIG. 4. β as a function of the number of π -electrons in the linker, calculated at different levels of approximation: MP2/6-31+G(d): □; MP4/6-31+G(d): ●.

TABLE IV. Comparison between MO-based and density-based methods to predict the static longitudinal first hyperpolarizability of compounds **a–d**.

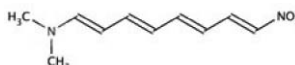
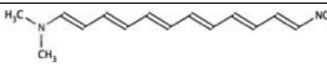
				
	6-31G(d)	$\frac{\beta(X)}{\beta[\text{CCSD(T)}]}$	6-31+G(d)	$\frac{\beta(X)}{\beta[\text{CCSD(T)}]}$
Number of basis functions	222		278	
HF	8151	0.643	9077	0.580
BLYP	10 788	0.850	13 503	0.864
BHandHLYP	11 870	0.936	14 021	0.897
B3LYP	12 684	0.999	15 556	0.995
LC-BLYP	10 316	0.813	12 471	0.798
B2-PLYP	15 121	1.192	18 627	1.192
mPW2-PLYP	14 607	1.151	17 904	1.146
MP2	13 255	1.045	15 576	0.997
CCSD(T)	12 685	1.000	15 628	1.000
				
	6-31G(d)	$\frac{\beta(X)}{\beta[\text{CCSD(T)}]}$	6-31+G(d)	$\frac{\beta(X)}{\beta[\text{CCSD(T)}]}$
Number of basis functions	238		294	
HF	10 138	0.464	11 413	0.430
BLYP	12 341	0.570	14 845	0.559
BHandHLYP	14 067	0.650	16 419	0.619
B3LYP	14 033	0.648	16 706	0.629
LC-BLYP	14 847	0.686	17 824	0.672
B2-PLYP	19 497	0.901	23 199	0.874
mPW2-PLYP	18 907	0.873	22 452	0.846
MP2	24 206	1.118	27 745	1.045
CCSD(T)	21 646	1.000	26 539	1.000
				
	6-31G(d)	$\frac{\beta(X)}{\beta[\text{CCSD(T)}]}$	6-31+G(d)	$\frac{\beta(X)}{\beta[\text{MP2}]}$
Number of basis functions	282		354	
HF	18 079	0.647	19 607	0.631
BLYP	35 504	1.271	44 427	1.397
BHandHLYP	30 853	1.104	35 596	1.119
B3LYP	38 339	1.372	46 598	1.465
LC-BLYP	22 923	0.821	26 612	0.837
B2-PLYP	40 902	1.464	49 205	1.547
mPW2-PLYP	38 235	1.380	46 617	1.464
MP2	27 704	0.992	31 804	1.000
CCSD(T)	27 935	1.000	...	...
				
	6-31G(d)	$\frac{\beta(X)}{\beta[\text{MP2}]}$	6-31+G(d)	$\frac{\beta(X)}{\beta[\text{MP2}]}$
Number of basis functions	306		378	
HF	28 652	0.428	31 701	0.418
BLYP	41 442	0.619	48 946	0.646
BHandHLYP	45 090	0.674	51 580	0.681
B3LYP	47 743	0.714	55 781	0.736
LC-BLYP	40 287	0.602	47 283	0.628
B2-PLYP	64 381	0.962	75 153	0.992
mPW2-PLYP	61 844	0.924	72 135	0.952
MP2	66 895	1.000	75 741	1.000

TABLE V. β ratios at different levels of calculation between different molecules.

6-31G(d)	β [b]	β [d]	β [c]	β [d]
	β [a]	β [c]	β [a]	β [b]
HF	1.243	1.585	2.218	2.826
BLYP	1.144	1.167	3.291	3.358
BHandHLYP	1.185	1.461	2.600	3.205
B3LYP	1.106	1.245	3.023	3.402
LC-BLYP	1.439	1.757	2.222	2.713
B2-PLYP	1.289	1.574	2.705	3.302
mPW2-PLYP	1.294	1.617	2.618	3.271
MP2	1.826	2.415	2.090	2.764
CCSD(T)	1.706	...	2.202	...

6-31G+(d)	β [b]	β [d]	β [c]	β [d]
	β [a]	β [c]	β [a]	β [b]
HF	1.257	1.617	2.160	2.778
BLYP	1.099	1.102	3.290	3.297
BHandHLYP	1.171	1.449	2.539	3.141
B3LYP	1.074	1.197	2.996	3.339
LC-BLYP	1.429	1.777	2.134	2.653
B2-PLYP	1.245	1.527	2.642	3.239
mPW2-PLYP	1.254	1.547	2.604	3.213
MP2	1.781	2.238	2.042	2.730
CCSD(T)	1.698	...	...	...

Therefore, though they generally underestimates the hyperpolarizability values, the HF and DFT/LC-BLYP methods are suitable to describe the variations of β values induced by chemical modifications. On the other hand, the other DFT XC functionals provide for some compounds an accurate β estimate but the trends are poorly described.

IV. FURTHER DISCUSSION, CONCLUSIONS, AND OUTLOOK

In this article, we have investigated the electron correlation effects on the first hyperpolarizabilities of a set of push-pull π -conjugated systems. As a preliminary step, basis set requirements have been tackled, showing that the 6-31+G(d) basis set gives the best balance between accuracy and computational resources for the compounds with alternating single and triple CC bonds whereas for polyene linkers, the 6-31G(d) basis set is already an optimal choice. Among the molecular orbital-based methods to account for electron correlation, the MP2 method turns out to be the method of choice to predict the first hyperpolarizabilities of push-pull π -conjugated systems. Indeed, as a result of cancellations between higher order contributions, it closely reproduces the values obtained with the CCSD(T) scheme, considered here as the reference method. In the case of compounds **b** and **f**, however, the SDQ-MP4 and CCSD approaches provide improved estimates over MP2 but the MP4 method does not represent an improvement over MP4-SDQ. Moreover, the use of a separate scaling of the parallel and antiparallel components of the MP2 energy, as proposed in the SCS-MP2 method, improves over MP2 only in limited cases. Finally, DFT has been employed to provide a further assessment of the reliability of conventional and more recent exchange-correlation

functionals. In particular, the LC-BLYP functional is reliable when characterizing the changes of first hyperpolarizability upon enlarging the π -conjugated linker or upon changing the polyene linker into a polyene segment. Nevertheless, its reliability is very similar to what can be achieved with the Hartree-Fock method while the MP2 scheme is by far more accurate. On the other hand, the BLYP, B3LYP, and BHandHLYP functionals perform quantitatively better in a number of cases but the trends are poorly described. This is also the case of the B2-PLYP and mPW2-PLYP functionals, which are often the most accurate, but they underestimate the increase of β when going from polyene to polyene linkers and they overestimate the enhancement of β with chain length.

We think that these conclusions—which are also supported by more sporadic results on other push-pull π -conjugated systems including molecular switches—can be extended to many DA π -conjugated compounds having a potential for NLO applications. On the other hand, twisted tictoid merocyanine dyes, of which the structure results from the delicate balance between diradical and zwitterionic forms, belong to another category of NLO molecules, which remain a great challenge for theoretical chemistry.³⁶

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