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Assessing the quantum mechanical level of theory for prediction of linear and nonlinear optical properties of push-pull organic molecules

Diego Paschoal · Hélio F. Dos Santos

Abstract In this paper, we assessed the quantum mechanical level of theory for prediction of linear and nonlinear optical (NLO) properties of push-pull organic molecules. The electric dipole moment (μ), mean polarizability ($\langle\alpha\rangle$) and total static first hyperpolarizability (β_t) were calculated for a set of benzene, styrene, biphenyl and stilbene derivatives using HF, MP2 and DFT (31 different functionals) levels and over 71 distinct basis sets. In addition, we propose two new basis sets, NLO-V and aNLO-V, for NLO properties calculations. As the main outcomes it is shown that long-range corrected DFT functionals such as M062X, ωB97, cam-B3LYP, LC-BLYP and LC-ωPBE work satisfactorily for NLO properties when appropriate basis sets such as those proposed here (NLO-V or aNLO-V) are used. For most molecules with β ranging from 0 to 190 esu, the average absolute deviation was 13.2 esu for NLO-V basis sets, compared to 27.2 esu for the standard 6-31 G(2d) basis set. Therefore, we conclude that the new basis sets proposed here (NLO-V and aNLO-V), together with the cam-B3LYP functional, make an affordable calculation scheme to predict NLO properties of large organic molecules.

Keywords Ab initio · Basis set · NLO-V · Polarizability · First hyperpolarizability

D. Paschoal (✉) · H. F. Dos Santos
Núcleo de Estudos em Química Computacional (NEQC),
Departamento de Química, ICE, Universidade Federal de Juiz de Fora,
Campus Universitário,
36.036-330, Juiz de Fora, MG, Brazil
e-mail: diego_paschoal@yahoo.com.br

Introduction

Molecular materials with nonlinear-optical (NLO) response have been the subject of intensive studies because of their potential technological applications in telecommunications, information storage, optical switching and laser technology. These materials interact with electromagnetic fields, generating new fields that are altered in frequency and phase [3–6]. The strength of optical response depends on the electrical properties of the whole material, which for molecules can be related to the polarizability (α, linear response) and hyperpolarizabilities (β, γ, etc. nonlinear responses) [4]. Therefore, these are the properties that should be measured in order to assess the optical potential for molecules. In general they are notably sensitive, making such experiments difficult [7, 8]. In this scenario, theoretical methods based on quantum mechanics theory can be a useful alternative to overcome this drawback and assist experimentalists [9, 10]. Nonetheless, NLO properties are strongly dependent on theoretical approaches, with inclusion of electronic correlation and extended basis set being necessary to achieve satisfactory accuracy [11]. For large molecules, such calculation schemes would not be affordable, in which case simple Hamiltonian and smaller basis sets are desired. Methods based on density functional theory (DFT) are usually used with modified basis sets augmented with diffuse and polarization functions. Among others, the group of Maroulis [12–19] has made an impressive contribution in this direction, reporting notably accurate basis sets for prediction of the electrical properties of small molecules. Furthermore, Maroulis [20–22] has shown the basis set and level of theory dependence for predicting properties such as electric dipole moment, polarizability and first hyperpolarzability. Recently, Rappoport and Furche [23] reported

Table 1 Ab initio methods and density functional theory (DFT) functionals used in the present work. *LDA* Local-density approximation, *GGA* generalized gradient approximation

Ab initio	LDA	GGA	meta-GGA	Hybrid	Long-range
HF	SVWN	mPWLYP	VSXC	mPW1LYP	M06
MP2		mPWPBE	BMK	mPW1PW91	ωB97
		mPWPW91	B97-2	mPW3PBE	cam-B3LYP
		OLYP	BB95	O3LYP	LC-ωPBE
		BLYP		B1B95	LC-BLYP
		BPW91		B3LYP	
		PBEPBE		B3PW91	
		τ-HCTH		PBE1PBE	

Table 2 Gaussian basis sets used for all atoms

Double-zeta	Triple-zeta	Type
6-31 G	6-311 G	Pople[a]
6-31+G	6-311+G	
6-31++G	6-311++G	
6-31 G(d)	6-311 G(d)	
6-31+G(d)	6-311+G(d)	
6-31++G(d)	6-311++G(d)	
6-31 G(d,p)	6-311 G(d,p)	
6-31+G(d,p)	6-311+G(d,p)	
6-31++G(d,p)	6-311++G(d,p)	
6-31 G(2d)	6-311 G(2d)	
6-31+G(2d)	6-311+G(2d)	
6-31++G(2d)	6-311++G(2d)	
6-31 G(2d,p)	6-311 G(2d,p)	
6-31 G+(2d,p)	6-311 G+(2d,p)	
6-31 G++(2d,p)	6-311 G++(2d,p)	
6-31 G(2d,2p)	6-311 G(2d,2p)	
6-31 G+(2d,2p)	6-311 G+(2d,2p)	
6-31 G++(2d,2p)	6-311 G++(2d,2p)	
6-31 G(2df)	6-311 G(2df)	
6-31 G+(2df)	6-311 G+(2df)	
6-31 G++(2df)	6-311 G++(2df)	
6-31 G(2df,p)	6-311 G(2df,p)	
6-31 G+(2df,p)	6-311 G+(2df,p)	
6-31 G++(2df,p)	6-311 G++(2df,p)	
6-31 G(2df,2p)	6-311 G(2df,2p)	
6-31 G+(2df,2p)	6-311 G+(2df,2p)	
6-31 G++(2df,2p)	6-311 G++(2df,2p)	
6-31 G(2df,2pd)	6-311 G(2df,2pd)	
6-31 G+(2df,2pd)	6-311 G+(2df,2pd)	
6-31 G++(2df,2pd)	6-311 G++(2df,2pd)	
cc-pVDZ	cc-pVTZ	Dunning[a]
aug-cc-pVDZ	aug-cc-pVTZ	
Dunning	-	
Thakkar	-	Thakkar[b]
DZP	-	Jorge[c]
-	Sadlej	Sadlej[d]
Ahlrichs-VDZ	Ahlrichs-VTZ	Ahlrichs[a,e]
Def2-SVP	-	Rappoport[f]
NLO	-	Paschoal[g]
NLO-V	-	Present work
aNLO-V	-	

[a] Basis set found in http://bse.pnl.gov/bse/portal [66]; Basis set obtained by

[b] Thakkar et al. [72, 73]

[c] Jorge et al. [74]

[d] Sadlej et al.[75, 76]

[e] Alhrichs et al. [67]

[f] Rappoport et al. [23]

[g] Paschoal et al. [26]

adjusted basis sets where the radial exponents were optimized, seeking to maximize the electronic polarizability. For slightly larger molecules, Suponitsky et al. [24] described an analysis of the effect of some basis sets and DFT functionals to predict β value for para-nitroaniline (PNA) and 4-hydroxy-4′-nitro-stilbene molecules, concluding that standard valence double-zeta basis sets like 6–31 G(d) and BMK [25] functional provide an affordable calculation scheme to predict β for large molecules. This work raises an important point that is the result of the combination of level of theory and basis set. Nowadays, with the advent of DFT approaches, there are plenty of functionals available, and these are somehow organized in an evolutionary line. Although DFT results usually converge quickly with basis set, this is not always true for NLO properties. More recently, Paschoal et al. [26] presented a systematic study on the calculation of electric properties for a series of 36 push-pull substituted benzene derivatives using adjusted atomic basis set and HF, MP2 and B3LYP levels. For the PNA molecule, the error was only 2 % at MP2, with similar accuracy achieved for the other analogues.

Currently, it is well recognized that π-conjugated organic molecules (such as substituted styrene, biphenyl and stilbene derivatives) exhibit intensified NLO responses due mostly to the delocalized electrons in the extended π-orbital systems. Besides, organic molecules with push-pull (donor/acceptor) groups display increased nonlinear responses [1, 2, 6, 27–30]. Thus, in the present work, substituted benzene, styrene, biphenyl and stilbene derivatives are selected as representative molecules to benchmark the calculation schemes for electric properties, namely electric dipole moment (μ), average polarizability ($\langle\alpha\rangle$) and total static first hyperpolarizability (β_t). Standard ab initio levels HF and MP2 were used in addition to 31 DFT variants. We also assess the basis set role from a survey of 71 standard basis sets and three new basis sets, two being proposed in the present work.

Table 3 Adjusted atomic Gaussian basis sets proposed in present work. *GTO* Gaussian-type orbital, *CGTO* contracted Gaussian-type orbital

Atoms	Basis set[a]		Contraction scheme	GTO	CGTO
H	Ahlrichs-VDZ	(4 s)→[2 s]	3,1(s)	4	2
	NLO-V	(6s2p)→[2s1p]	3,3(s); 2(p)	12	5
	aNLO-V	(7s2p)→[3s1p]	3,3,1(s); 2(p)	13	6
B, C, N, O, F	Ahlrichs-VDZ	(7s4p)→[3s2p]	5,1,1(s); 3,1(p)	19	9
	NLO-V	(10s8p2d)→[3s2p1d]	(4,3,3)s; (4,4)p; 2(d)	44	14
	aNLO-V	(11s9p2d)→[4s3p1d]	(4,3,3,1)s; (4,4,1)p; 2(d)	48	18
Si, P, S, Cl	Ahlrichs-VDZ	(10s7p)→[4s3p]	5,3,1,1(s); 5,1,1(p)	31	13
	NLO-V	(14s12p2d)→[4s3p1d]	(6,3,3,2)s; (5,4,3)p; 2(d)	60	18
	aNLO-V	(15s13p2d)→[5s4p1d]	(6,3,3,2,1)s; (5,4,3,1)p; 2(d)	64	22

[a] Exponents of diffuse functions added in aNLO-V basis set: H (s=0.033454307970), B (s=0.02787134995, p=0.02744468288), C (s=0.05610768902, p=0.01821287289), N (s=0.05995211849, p=0.02361875868), O (s=0.10704883082, p=0.016271573530), F (s=0.13529949691, p=0.0180594241), Si (s=0.02969613233, p=0.03390972594), P (s=0.03995890584, p=0.01835410425), S (s=0.05116083061, p=0.02162544986) and Cl (s=0.06364379811, p=0.03338519431)

Theoretical methodology

When a molecule is placed in an uniform static electric field, its electronic energy can be written as a series involving coefficients identified as permanent multipole moments and polarizabilities (Eq. 1) [31–33].

$$E^p = E^0 - \mu_\alpha F_\alpha - \left(\frac{1}{2}\right)\alpha_{\alpha\beta}F_\alpha F_\beta - \left(\frac{1}{6}\right)\beta_{\alpha\beta\gamma}F_\alpha F_\beta F_\gamma$$
$$- \left(\frac{1}{24}\right)\gamma_{\alpha\beta\gamma\delta}F_\alpha F_\beta F_\gamma F_\delta + \cdots \quad (1)$$

Where F_α, F_β, etc. denote the field at the origin. E^0 and μ_α are the energy and the permanent dipole moment, respectively. The quantities $\alpha_{\alpha\beta}$, $\beta_{\alpha\beta\gamma}$, $\gamma_{\alpha\beta\gamma\delta}$ are the dipole polarizability, the first and the second dipole hyperpolarizabilities, respectively. The subscripts represent the Cartesian coordinates.

The electric properties were calculated directly from the CPHF/CPKS [34] methods as implemented in the Gaussian 09 [35] package, where the final quantities are described by Eqs. (2, 3, 4) [31].

$$\mu = \sqrt{\mu_x^2 + \mu_y^2 + \mu_z^2} \quad (2)$$

$$\langle\alpha\rangle = \frac{1}{3}\left(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}\right) \quad (3)$$
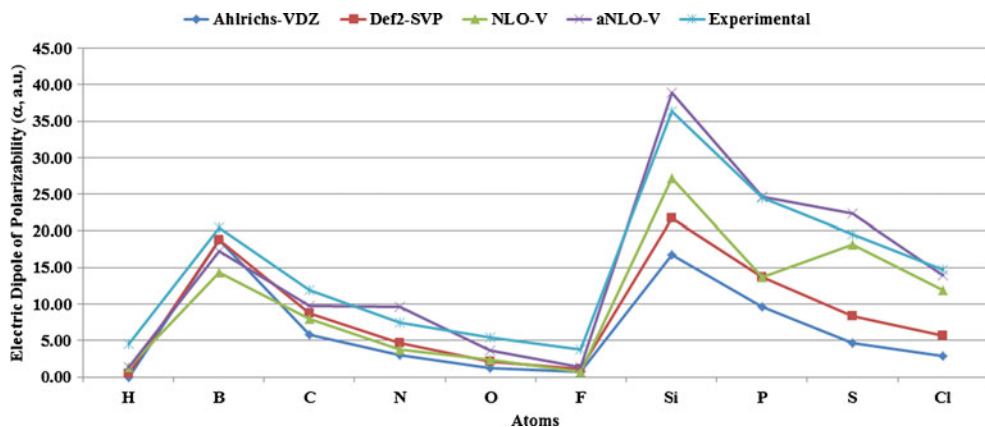
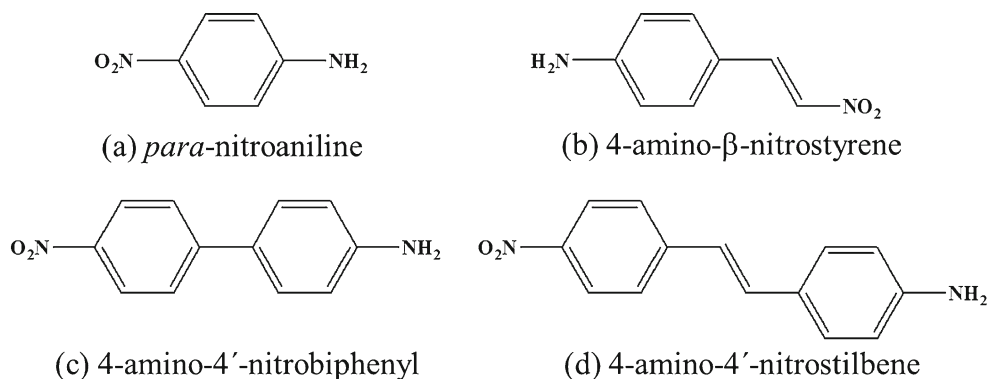$$\beta_t = \sqrt{\beta_x^2 + \beta_y^2 + \beta_z^2} \quad (4)$$

With

$$\beta_i = \beta_{iii} + \sum_{i \neq j}\left(\beta_{ijj} + \beta_{jij} + \beta_{jji}\right) \quad (5)$$

Where i and j run over the molecular Cartesian directions x, y, and z.

Fig. 1 Electric dipole of polarizability (α, a.u.) for all atoms calculated at Hartree-Fock (HF) level. Experimental values can be found at http://cccbdb.nist.gov [77]

Fig. 2 Standard push-pull molecules used in the initial analysis of the work. **a** Benzene-NO$_2$-NH$_2$, **b** styrene-NO$_2$-NH$_2$, **c** biphenyl-NO$_2$-NH$_2$, **d** stilbene-NO$_2$-NH$_2$

(a) *para*-nitroaniline

(b) 4-amino-β-nitrostyrene

(c) 4-amino-4′-nitrobiphenyl

(d) 4-amino-4′-nitrostilbene

The geometries of all molecules studied in this work were fully optimized and characterized as stationary points on the potential energy surface (PES) through harmonic frequency calculations at B3LYP/6-31 G(d). This level has long been proved to be suitable for the geometry of organic molecules.

Calculations of electrical properties were performed at the HF, MP2 [36–40] and DFT (SVWN [41], mPWLYP [42, 43], mPWPBE [42, 44], mPWPW91 [42, 45], OLYP[46], BLYP [43, 47], BPW91 [45, 47], PBEPBE [44], HCTH [48], M06L [49], VSXC [50], τ-HCTH [51], BB95 [47, 52], PBEKCIS [44, 53], B97-2 [54], BMK [25], TPSSh [55], mPW1LYP [42, 43], mPW1PW91 [42, 45], mPW3PBE [42, 44], O3LYP [56], B1B95 [52, 57], B3LYP [43, 58, 59], B3PW91 [45, 58] PBE0 [53, 56], M062X [60], ωB97 [61], cam-B3LYP [62], LC-ωPBE [63], LC-BLYP [43, 47, 64] and B2PLYP [65] functionals) levels (see Table 1).

The basis sets used for all atoms are listed in Table 2, where the new NLO-V is included. The general procedure followed to fit the exponents of the radial (ζ) Gaussian functions and contraction coefficients of NLO-V is detailed bellow.

1. The Ahlrichs [66, 67] valence double-zeta (VDZ) basis set was chosen as reference and fully uncontracted;
2. New sets of functions with the same angular momentum os the existing one were added and the exponents fitted by minimizing the atomic energy at HF level;
3. The resulting basis set was contracted following the protocol described elsewhere [68].
4. Sets of polarizations functions were added and the exponents were fitted following step 2.

The final NLO-V and aNLO-V basis sets are described in Table 3. All calculations were performed with the Gaussian 09 package, revision A.02 [35].

The present paper considers only the electronic contribution in the calculation of the electric properties; however, it should be borne in mind that the vibrational contribution to the total static first hyperpolarizability in many cases is comparable to electronic contribution, as can be seen in the papers of Champagne [69] and Bartkowiak [70].

Results and discussion

The new NLO-V basis set proposed here is described in Table 3 where its valence-double-zeta-polarized (VDZP) character can be seen. The aNLO-V is the augmented NLO-V basis set, modified by inclusion of sets of s and p diffuse functions. In order to evaluate the quality of these new basis sets, we first test them to atoms and compare the results with the parent basis set, Ahlrichs-VDZ, and with the Def2-SVP basis set, radial exponents of which were adjusted to maximize the electronic polarizability. Only the electric dipole of polarizability was calculated at HF level for closed shell atoms and un-restrict-HF (UHF) for open shell atoms. Figure 1 shows the results, where we clearly see the superiority of NLO-V, mainly for second row elements. For these atoms, the agreement between experiment and theory is excellent when aNLO-V is used. The overall relative error was 65 % for Ahlrichs-VDZ, 49 % for Def2-SVP, 41 % for NLO-V and 26 % for aNLO-V basis set. Only for the B atom was the Ahlrichs-VDZ basis set superior (the calculated values are given in Table S1 in the Supplementary Material), and for B, C and N atoms the Def2-SVP presented good results when compared with the NLO-V basis set. Therefore, in this very preliminary test, the NLO-V basis set might be considered well balanced and suitable for more challenging tests including polyatomic molecules. This is described in the next sections, divided into three sequential steps: (1) the level of theory is evaluated using the standard 6-31 G(d) basis set, (2) the best level of theory is then set up and (3) the basis set varied to include 74 basis sets. The two initial steps were carried out for four molecules only, which are usually used as templates for molecular NLO properties, namely the PNA, 4-amino-β-nitrostyrene, 4-amino-4′-nitrobiphenyl and 4-amino-4′-nitrostilbene (Fig. 2). In the last part we discuss the performance of NLO-V and its augmented version to predict larger values of β.
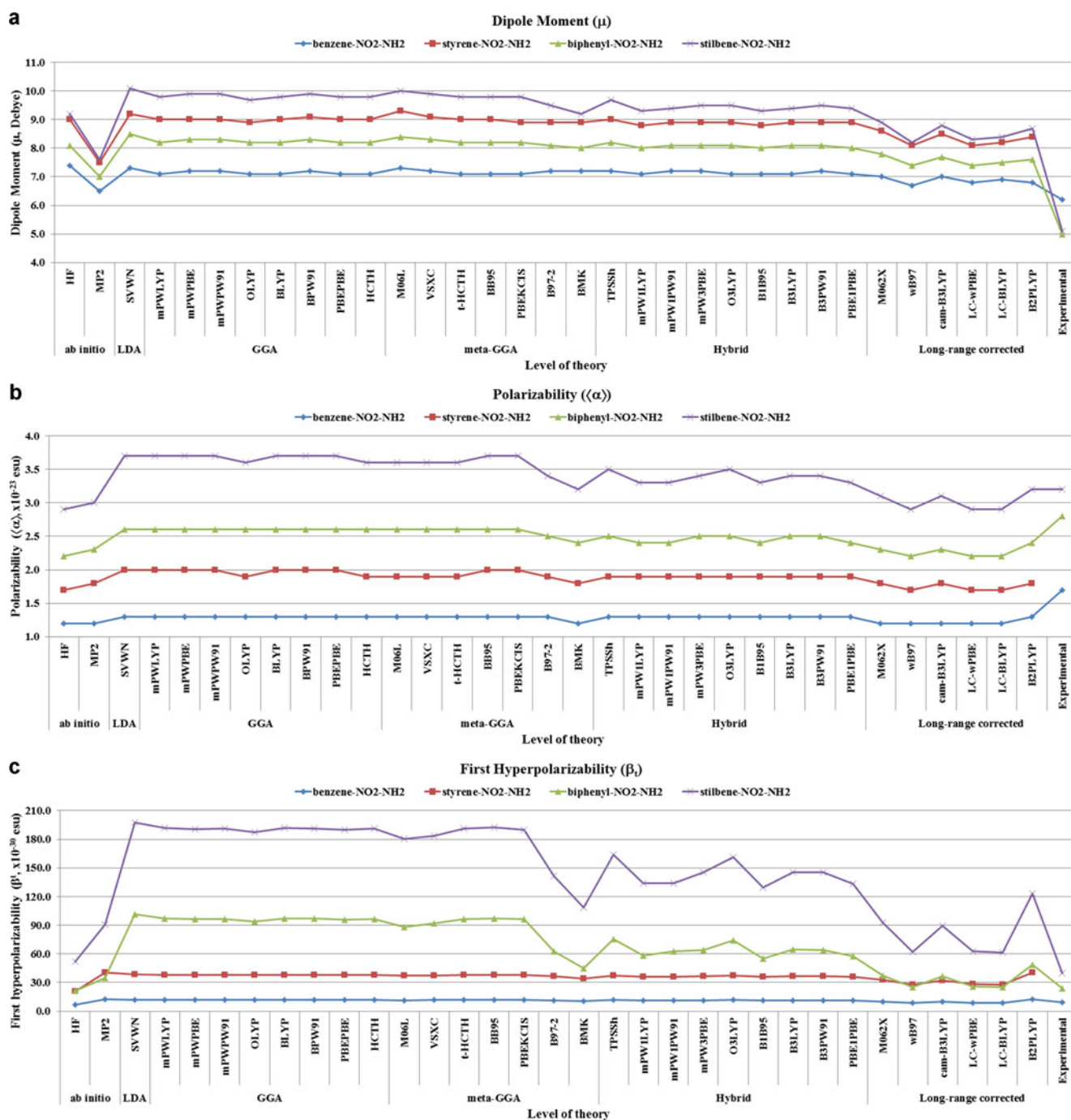
Fig. 3 **a** Calculated values for electric dipole moment (μ), **b** average polarizability (⟨α⟩), **c** total static first hyperpolarizability (β_t) at level of theory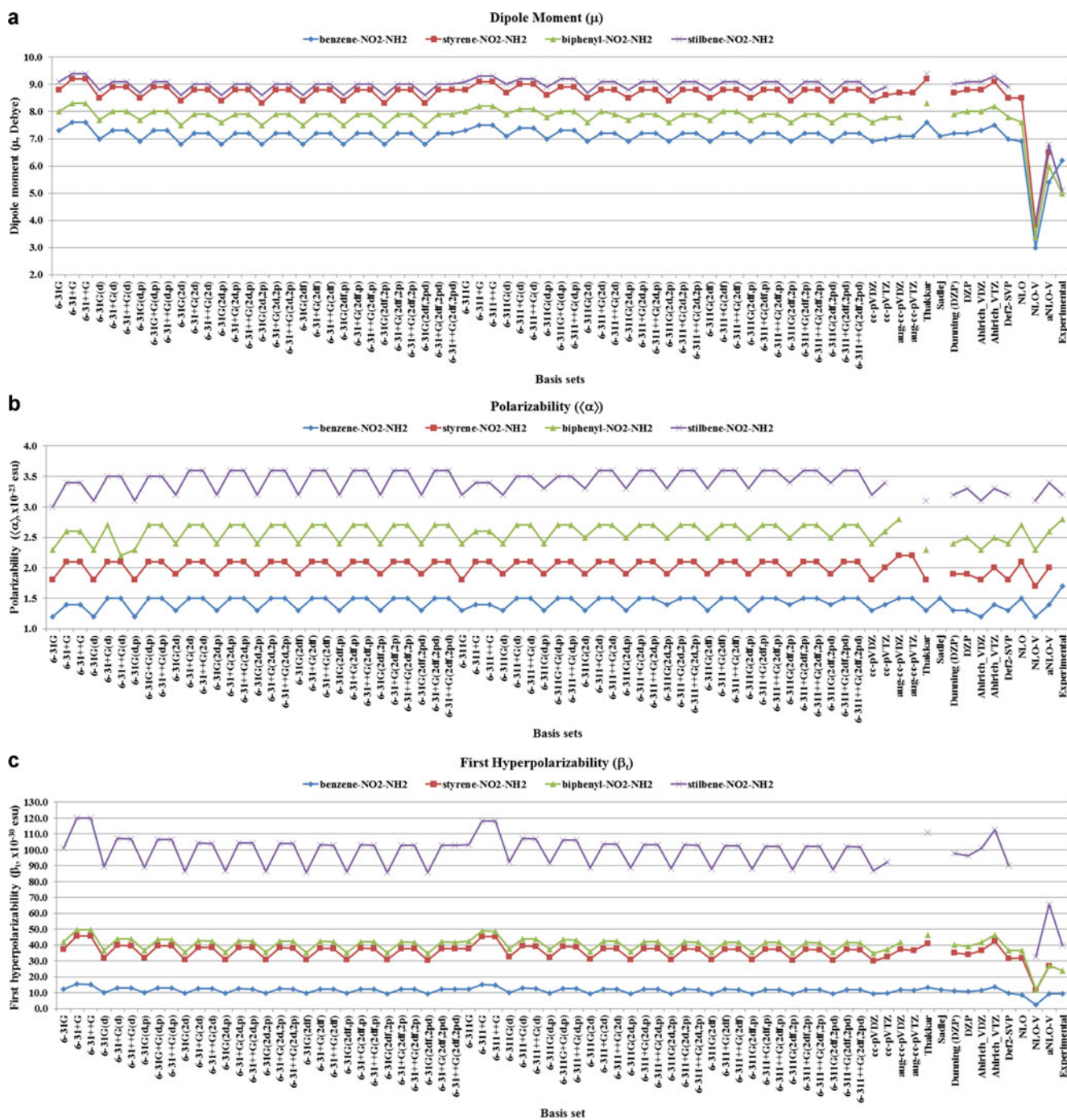/6-31 G(d) for para-nitroaniline, 4-amino-β-nitrostyrene, 4-amino-4′-nitrobiphenyl and 4-amino-4′-nitrostilbene. Experimental values are from Cheng et al. [1, 2]

Level of theory

The electric dipole moment, mean polarizability and total static first hyperpolarizability for the four standard push-pull molecules shown in Fig. 2 were calculated at HF, MP2 and 31 different DFT functionals. All the geometries were optimized at B3LYP/6–31 G(d) level.

The absolute values for the calculated properties are represented in Fig. 3 and given in Tables S2, S3, S4 and S5. As expected, for electric dipole moment and ⟨α⟩ the values are almost constant within the series of DFT functionals. In general, the best results for μ were found at MP2 level, with an estimated error of 5 % (PNA), 40 % (biphenyl) and 49 % (stilbene). Care is needed when relative

Fig. 4 **a** Calculated values for electric dipole moment (μ), **b** average polarizability (⟨α⟩), **c** total static first hyperpolarizability (β_t), at cam-B3LYP/BASIS SET for para-nitroaniline, 4-amino-β-nitrostyrene, 4-amino-4′-nitrobiphenyl and 4-amino-4′-nitrostilbene. Experimental values are from Cheng et al. [1, 2]

error is analyzed for small values. For example, in the case of stilbene, the MP2 electric dipole moment differs from actual value by only 2 a.u. and the relative error is around 50 %. At DFT level, the best results for μ are those from the new long-range corrected functionals, with errors ranging from 8–13 % (benzene), 48–56 % (biphenyl) and 61–75 % (stilbene). In general, a glance at Fig. 3a reveals that the values of long-

range corrected functionals tend to MP2, which is the best level of theory for μ. Regarding polarizability (Fig. 3b), the error was always lower than 30 %, regardless of the level of theory and the molecule considered, reaching excellent agreement with the actual value where stilbene is concerned (0–16 %). As stated previously, long-range corrected functionals work fine, with the best performance among the DFT approaches found for the

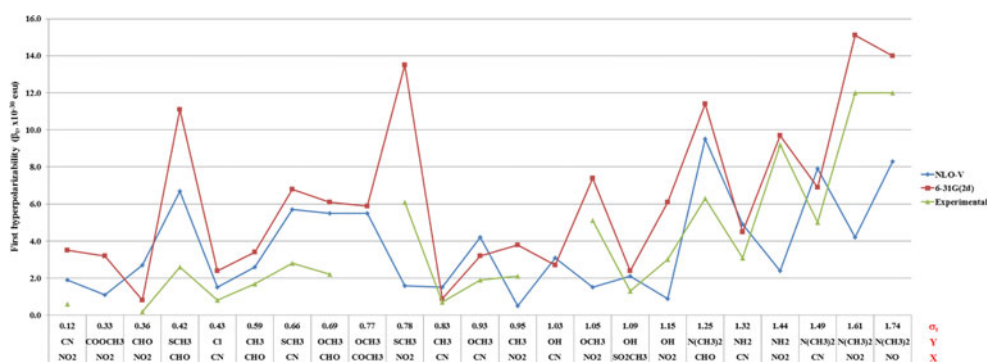**Table 4** Push-pull organic molecules studied in this work

p-disubstituted benzene

disubstituted 4-β-styrene

disubstituted 4-4´-biphenyl

disubstituted 4-4´-stilbene

X	Y	X	Y	X	Y
NO$_2$	CN	NO$_2$	COOCH$_3$	NO$_2$	CHO
CHO	SCH$_3$	CN	Cl	CHO	CH$_3$
CN	SCH$_3$	CHO	OCH$_3$	COCH$_3$	OCH$_3$
NO$_2$	SCH$_3$	CN	CH$_3$	CN	OCH$_3$
NO$_2$	CH$_3$	CN	OH	NO$_2$	OCH$_3$
SO$_2$CH$_3$	OH	NO$_2$	OH	CHO	N(CH$_3$)$_2$
CN	NH$_2$	NO$_2$	NH$_2$	CN	N(CH$_3$)$_2$
NO$_2$	N(CH$_3$)$_2$	NO	N(CH$_3$)$_2$		

BMK meta-GGA functional. This outcome is in line with the previous study by Suponitsky et al. [24]. Lastly, Fig. 3c represents the results for total static hyperpolarizability, which is among the electric properties calculated here the most sensitive and, moreover, the main focus of the present study. For the small value of β_t presented for PNA, the errors are on average 36 % at MP2 level and only 3 % at DFT level, with the long-range corrected functionals LC-ωPBE and LC-BLYP giving the best performance. For the other levels of theory, the error

was larger than 20 %. When biphenyl and stilbene derivatives are addressed the relative error increases significantly. For stilbene derivatives, which present the largest β_t, the lowest deviation was obtained at LC-BLYP, supporting the superiority of long-range corrected functionals.

From previous analysis, a general conclusion can be drawn regarding the best performance of DFT long-range corrected functionals with regard to the electric properties addressed here. Therefore, these are our methods of choice

Fig. 5 Calculated values for total static first hyperpolarizability (β_t) for para-disubsituted benzenes at cam-B3LYP/NLO-V and cam-B3LYP/6-31 G(2d) levels. Experimental values are from Cheng et al. [1, 2]
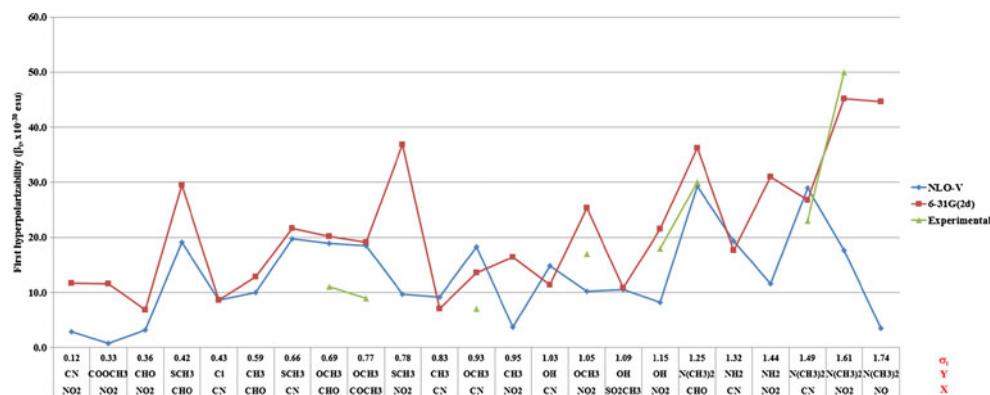
for the next step, which aims to assess the role of basis set. Among those DFT included in Table 1, we choose the cam-B3LYP functional, which maintains the quality of B3LYP for geometries and standard molecular properties and improves significantly the electrical properties predictions.

The basis set

The role of basis set for prediction of electric properties is now addressed using the same molecules in Fig. 2 as a reference. Over 71 standard basis sets available in the literature were tested in addition to our NLO [26] and the two new basis sets proposed here: NLO-V and aNLO-V. The results are plotted in Fig. 4 and quoted in Tables S6, S7, S8 and S9. From Fig. 4 it is clear that there is a periodic behavior throughout the basis sets tested, with a more pronounced variance for the NLO series. For the electric dipole moment (Fig. 4a), we note that the first and second sets of d-polarization functions for heavy atoms play a primary role, with errors found 18 %, 13 % and 10 % for 6-31 G, 6-31 G (d) and 6-31 G(2d), respectively, for PNA. For the other two molecules for which experimental values are available (biphenyl and stilbene), the relative error at 6-31 G(2d) level was around 60 %. The improvement in the basis set by addition of an f-polarization function and/or p and d-functions for H does not cause a sizable change in the electric dipole moment. Diffuse functions and splitting the valence-shell play a minor role, increasing the deviation

slightly. This same trend is also followed by the Dunning correlated-consistent (cc) (cc-pVDZ and cc-pVTZ) and Ahlrichs (VDZ and VTZ) basis sets. For the Def2-SVP basis set, the errors found are of the same order as those found with 6-31 G(d). Our basis sets NLO-V and aNLO-V lead to satisfactory results, with the latter giving the best agreement with experiment (error lower than 40 %). For electric dipole moment, the best performance among the basis sets tested was the aNLO-V followed by 6–31 G(2d).

Conversely, for the mean polarizability, the diffuse functions are important as shown in Fig. 4b, and, in general, the d-polarization functions improve the agreement when combined with diffuse functions. For stilbene derivatives, which present the highest value of $\langle \alpha \rangle$, polarization functions are of paramount importance. For this property, our NLO basis sets present the same accuracy as the standard basis sets.

Lastly, total static first hyperpolarizability is addressed. From Fig. 4c, we note that diffuse functions increase β_t, with the first and second d- and f- polarization functions playing a major role in improving the results. For PNA, which shows the smallest β_t, the error found was 4 % at 6–31 G(2df) level. The NLO basis sets show good results for all molecules, being far superior to the other standard basis sets for stilbene derivative (error of 18 %), which presents the highest value of β_t. For this molecule, the standard basis sets generally overestimate actual values. Therefore, in short, it can be said that, among the standard basis sets, 6–31 G(d), 6–31 G(2d) and Def2-SVP are
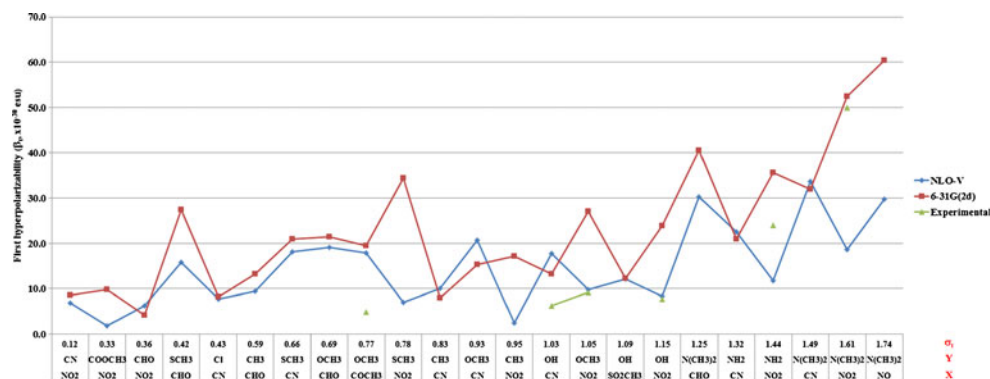
Fig. 8 Calculated values for total static first hyperpolarizability (β_t) for 4-4′-disubstituted stilbenes at cam-B3LYP/NLO-V and cam-B3LYP/6-31 G(2d) levels. Experimental values are from Cheng et al. [1, 2]
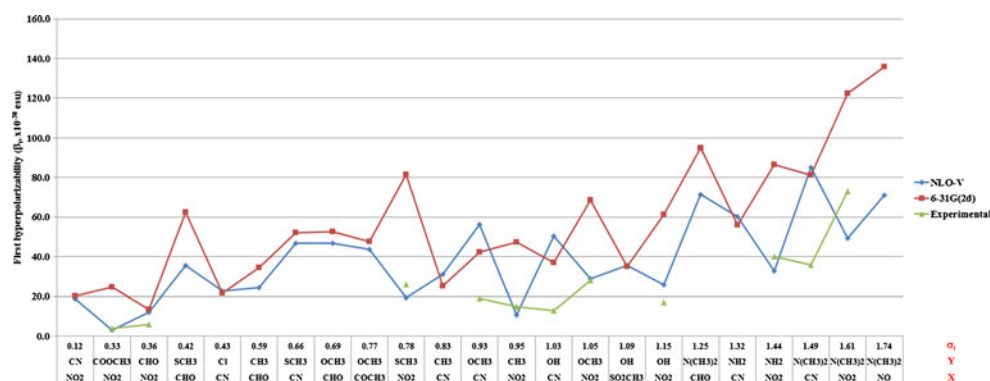
recommended to predict electric properties for large organic molecules, with the best results found using the new NLO-V and aNLO-V basis sets proposed here.

First hyperpolarizability (β) for push-pull organic molecules

In the last part of the present study, we apply our previous conclusions and to a broad series of push-pull molecules as represented in Table 4. Geometries were optimized at B3LYP/6–31 G(d), and the β_t calculated at cam-B3LYP/6–31 G(2d) and cam-B3LYP/NLO-V levels, which were the best calculation schemes found previously.

To analyze the net substituent effect, the electronic Hammett constants [71] for substituent (σ_p) were used. For electron-donating substituents (donor groups) $\sigma_p < 0$ and for electron-withdrawing substituents (acceptor groups) $\sigma_p > 0$.

Table 5 Push-pull disubstituted di- and phenylpolyene oligomers studied in this work

**4-β-disubstituted α-phenylpolyene oligomers**

n = 0, 1, 2, 3

X	Y	X	Y
CHO	OCH$_3$	CHC(CN)$_2$	OCH$_3$
CHO	N(CH$_3$)$_2$	CHC(CN)$_2$	N(CH$_3$)$_2$

α,ω-diphenylpolyene oligomers

n = 1,2,3,4

X	Y	X	Y
CN	OCH$_3$	NO$_2$	N(CH$_3$)$_2$
NO$_2$	OCH$_3$		

Fig. 9 Calculated values for total static first hyperpolarizability (β_t) for 4-β-disubstituted α-phenylpolyenes oligomers at cam-B3LYP/NLO-V, cam-B3LYP/6-31 G(2d) and cam-B3LYP/Def2-SVP levels. Experimental values are from Cheng et al. [1, 2]
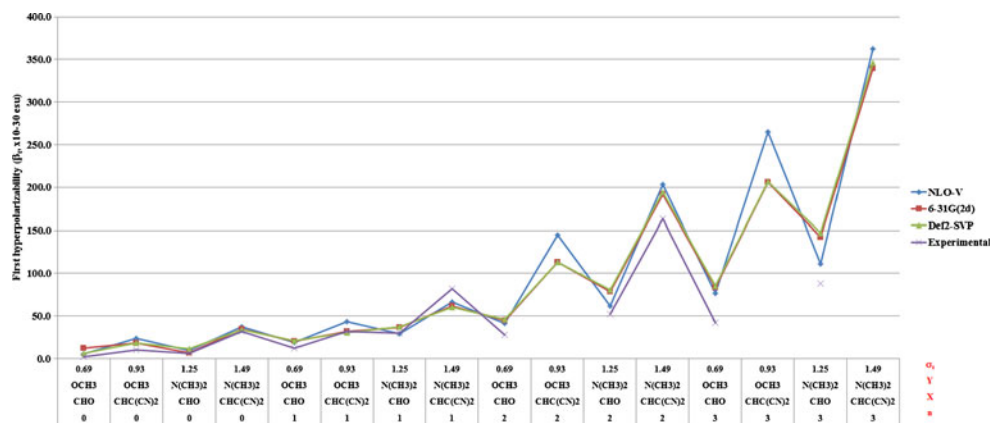
The net electronic effect is given by $\sigma_t = \sigma_p^+ - \sigma_p^-$ (where σ_p^+ is the largest positive parameter (stronger acceptor group) and σ_p^- is the lowest positive value (weaker acceptor group) or the negative value (donor substituent). The results are organized according to increasing value of σ_t.

The para-disubstituted benzenes are first discussed. The β_t values are plotted in Fig. 5 as function of σ_t and also given in Table S10 as Supplementary Material. At first glance, we note that the predicted values follow the same overall trend observed for the experimental data. The average absolute deviation (in esu) was 3.2 for NLO-V and 3.0 for 6-31 G(2d), which is considered satisfactory for the range of experimental values, 0.2–12.0 esu. For 4,β-disubstituted styrenes and 4-4′-disubstituted biphenyls (Figs. 6, 7; Tables S11, S12), only a few experimental values are available. For these molecules, the average absolute deviation was 9.4 (styrene) and 11.6 esu (biphenyl) with the NLO-V basis set and 5.8 (styrene) and 11.6 esu (biphenyl) with the 6–31 G(2d) basis set. For these derivatives the experimental values range from 4.9 to 50.0 esu.

Figure 8 and Table S13 show the predicted β_t values for 4,4′-disubstituted stilbenes. These molecules present the largest β_t among the molecules analyzed here, ranging from 4.0 to 73.0 esu. We observe that, in general, β_t increases with σ_t. The average absolute deviation relative to the experimental values was only 16.6 for NLO-V basis set and 35.4 with 6–31 G(2d) basis set, showing the best performance for NLO-V, mainly for larger values of β_t (see

Fig. 8). Summarizing the previous results it can be stated that, from small to intermediate β_t values, the NLO-V and 6–31 G(2d) basis sets have similar performance; however, for higher β_t values, the NLO-V basis set is superior.

In order to evaluate further the performance of NLO-V basis set, the set of oligomers shown in Table 5 were studied. For these molecules, the experimental values range from 3.5 to 190.0 esu. The results are graphed in Figs. 9 and 10 (and given in Tables S14 and S15). For 4-β-disubstituted α-phenylpolyenes oligomers (Fig. 9) the calculated values with NLO-V, 6–31 G(2d) and Def2-SVP basis sets are in good agreement with experimental values. The average absolute deviation (in esu) was 13.9 for NLO-V, 17.2 for 6-31 G(2d) and 18.3 for Def2-SVP. However, when we consider the calculated values for disubstituted α,ω-diphenylpolyenes oligomers (Fig. 10), which present values greater than phenypolyenes, the calculated values with 6-31 G(2d) and Def2-SVP presented a poorer agreement with experimental value than NLO-V. The absolute deviation was 42.0 for NLO-V, 136.3 for 6-31 G(2d) and 141.2 for Def2-SVP.

Concluding remarks

The present paper reports an in-depth analysis of the role of the level of theory and basis sets for prediction of electric

Fig. 10 Calculated values for total static first hyperpolarizability (β_t) for disubstituted α,ω-diphenylpolyenes oligomers at cam-B3LYP/NLO-V, cam-B3LYP/6-31 G(2d) and cam-B3LYP/Def2-SVP levels. Experimental values are from Cheng et al. [1, 2]
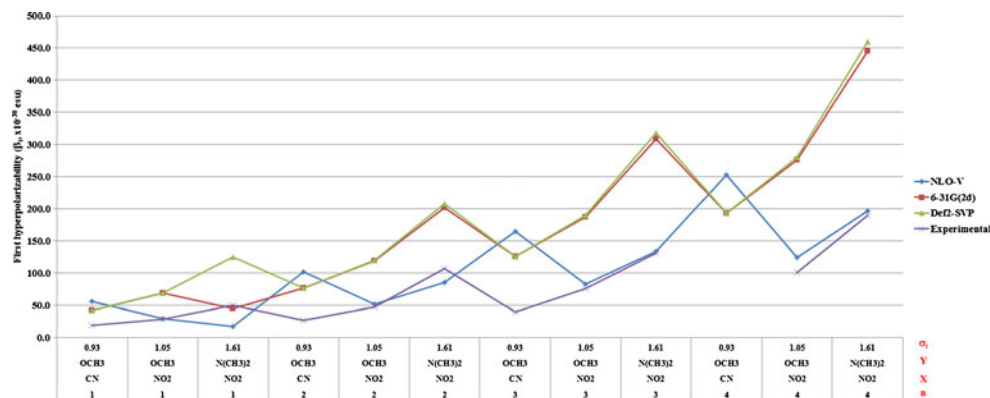
properties of push-pull organic molecules. Within this broad class of compounds, the main representatives were selected, namely *p*-benzene, 4,β-styrene, 4,4′-biphenyl and 4,4′-stilbene derivatives. Among the survey of calculation schemes used, the best overall performance was achieved with long-range corrected functionals (M062X, cam-B3LYP, ωB97, LC-BLYP and LC-ωPBE) when associated with the new basis sets proposed here: NLO-V and aNLO-V. Moreover, the standard split-valance basis set 6–31 G(2d) also led to satisfactory results for linear and NLO properties of small molecules. The superiority of NLO-V is evidenced mainly for molecules with large β_t, such as conjugated organic polymers, which are actually of practical interest in material science.

For the broad class of molecules studied in this work, with β_t values ranging from 0 to 190 esu, the calculated values with NLO-V basis set presented an average absolute deviation of 13.2 esu, which is considered satisfactory for molecules with β_t around 100 esu or larger. Moreover, the size of NLO-V is affordable, allowing calculation of the properties of large molecules, such as small organic polymers which are used commonly as building blocks and prototypes for advanced optical materials.

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