Electronic Hyperpolarizabilities for Donor−Acceptor Molecules with Long Conjugated Bridges: Calculations versus Experiment

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We investigate the molecular first hyperpolarizability (β) for donor/acceptor (D/A) substituted π-conjugated organic molecules with different D/A groups and π-systems (including up to eight π-bonds). The results of the MP2 and density functional theory (PBE0, BMK, M05, M05-2X) calculations are compared to those obtained from experimental data. The goal of this study is to select a protocol with optimal quality/cost ratio to be used for systematic prediction of molecular nonlinear optical (NLO) properties. This goal is closely related to the way in which theoretical βs are compared to experimental ones and to the accuracy and consistency of experimental hyperpolarizabilities used to test theoretical predictions. We found that two DFT functionals with the larger fraction of Hartree−Fock exchange (BMK and especially M05-2X) provide the best agreement to the experiment, comparable to that of the MP2 method. Due to high computational cost of MP2 method, we recommend to use the M05-2X functional as a tool for systematic prediction of molecular hyperpolarizabilities.

1. Introduction

Rational design of effective nonlinear optical (NLO) materials for second harmonic generation requires the understanding how the hyperpolarizability is affected by the molecular structure.[1−6] Numerous experimental and theoretical studies carried out over the last three decades have revealed that the high molecular nonlinearities can be achieved if a molecule contains donor and acceptor (D/A) groups connected through the π-electron delocalized bridge.[7−10] Electron distribution in such D-π-A molecules is extremely sensitive to the applied electric field, which results in strong induced dipole moments and high hyperpolarizability (β). It was shown that the molecular hyperpolarizability is strongly enhanced by elongation of the π-system[11−13] and depends on its aromaticity: the fewer aromatic rings that are used as building blocks of the π-system, the higher the hyperpolarizability observed.[14−19] Unfortunately, an elongation of the π-bridge and decrease of its aromaticity lead to a decrease of the thermal stability and optical transparency.[20,21] Therefore the π-bridge of the optimal NLO molecule usually consists of the aromatic and double-bonded $-(X{=}X)_n-$ fragments ($X =$ CH, N) with two to eight π-bonds (we use a number of π-bonds in the conjugated π-bridge to define its length throughout this article).

The computational methods of quantum chemistry play an important role in the search for molecules with desirable NLO properties and wide wavelength range of optical transparency. A choice of an appropriate level of theory for the calculation of hyperpolarizability is the most significant question. To answer to this question one must take into account a basis set, method of computation, precision of the results obtained (in comparison to experiment), and possibility to handle molecules of practical interest (30−80 atoms) as well as the purpose of investigations. In most cases, use of theoretical calculations is aimed to select the most promising molecules in advance of their synthesis and experimental study. For those goals a semiquantitative or even qualitative level of accuracy is usually sufficient.

The importance of the choice of the basis set was the subject of the discussion in many investigations.[22−29] It was shown that the reliable estimation of molecular hyperpolarizability requires diffuse and polarization functions. In our recent study,[29] we demonstrated that modest 6-31+G* basis set is sufficient for estimation of the relative hyperpolarizabilities. The more serious problem is the choice of the method, and this problem was extensively discussed in the literature.[13,30−34] Comparison to high-quality gas-phase measurements of the hyperpolarizability for small molecules revealed that the quantum chemical approaches based on coupled cluster (CC) theory can produce results of high accuracy.[35−38] However the use of CC methods is restricted to small-size molecules (20−30 atoms at most). Although the MP2 method requires less computational resources,

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it is still too computationally expensive and thus cannot be adopted as a routine tool for computational design of NLO molecules. In addition, MP2 can overestimate the increase of β when going from D/A substituted benzenes to D/A-stilbenes up to 70% or underestimate it up to 10%, as it was shown recently for some cases.[29]

Methods of density functional theory (DFT) are less computationally demanding and present a compromise between computational cost and accuracy of the results. Fast development of DFT and the availability of new functionals make it a promising approach for investigation of molecular NLO properties. However, comparison with MP2 results demonstrates[33] that the B3LYP functional is unreliable for estimation of the molecular first hyperpolarizability. Overestimation by a factor of 2.3 was found for a β ratio of 4-amino-4′-nitrostilbene/*p*NA while an even higher difference (factor of 3.8) was obtained for the ratio of $NH_2-(CH{=}CH)_{12}-NO_2/NH_2-(CH{=}CH)_6-NO_2$. An example of a dramatic failure of the DFT is given by the study of polymethineimine (PMI) homologues.[13] Here, even the sign of β is predicted incorrectly by both HF, pure and hybrid DFT methods. Range-separated hybrids improve the situation to some extent but still predict the wrong sign for the shortest homologues.[13] Analysis of the sum-over-state expression demonstrated the physical origin of this failure. The shape of the β curve was explained as resulting from the competition between two contributions of opposite signs, corresponding to bond charge and bond polarization phenomena.[39]

The reasons for overestimation of molecular hyperpolarizability were shown to be unrelated to the asymptotic behavior of the exchange-correlation potential,[32] as it was suggested previously. Instead, they are rooted in self-interaction error in the exchange part of the density functional,[40−42] which is responsible for overdelocalization of the electron density. This results in incorrect screening of the external electric field[33] and incorrect description of the charge transfer in both ground and excited states.[43] A simplified approach based on a charge-transfer model was recently used to show that self-interaction error results in a decrease of molecular hardness that makes electron redistribution easier.[44] Because these effects are more pronounced at the ends of a D-π-A molecule, the molecules with longer π-systems are more affected by self-interaction error. Although self-interaction corrected DFT functionals seem to give good agreement with MP2 results,[13,45−47] the self-interaction free functionals are not yet implemented in commercially available software tools.

In our recent study on D/A substituted benzenes and stilbenes[29] we have shown that the DFT functionals B3LYP, B972, PBE0, and BMK correctly describe smaller-sized π-conjugated molecules (two π-bonds) while for D/A-stilbenes (five π-bonds) they lead to an overestimation of the molecular hyperpolarizability. Nevertheless, overestimation was systematic, which allowed us to suggest a scaling factor to correct DFT calculations. The hybrid meta-GGA BMK functional overestimates β the least, which was attributed, at least partly, to the larger fraction of the HF exchange. Among three hybrid GGA functionals, the PBE0 appeared to be the best.

The validation of various quantum chemical approaches is based on comparison between the theoretical and experimental results. This task is complicated however by an ambiguity in experimental results.[4,29,48−51] Use of different values of standards and different conventions by experimentalists makes comparison of absolute values of β nearly impossible. We suggested comparing the ratios of the molecular βs (calculated at the same level of theory and measured in the same laboratory, provided that the same standard value and convention factors are utilized). Moreover, close analysis of experimental data shows that even ratios obtained by different experimental groups (even if in the same solution and at the same wavelength) are in fact quite different, despite the cancellation of systematic errors, choice of benchmark molecules, and convention factors.[29,50] This complicates the comparison between the theory and experiment.

As we have mentioned above, the MP2 level of theory can reproduce experiment with the accuracy described by the multiplicative factor of 0.9−1.7. The BMK functional somewhat overestimates the increase in β from benzene to stilbene by the factor of 1.2−2.4. It allowed us to conclude that in general the MP2 results are more accurate, while some large deviations might be attributed to either ambiguity in experimental data or deficiency of the theory (both DFT and MP2). The data clearly show that neither DFT nor MP2 approaches can be used to reproduce experiment quantitatively.

The goal of the present work is to investigate the performance of DFT for D-π-A type molecules with long π-conjugated bridges and to compare these results with the experiment and MP2 (whenever possible). This will allow us to understand the extent to which we can trust the results of such calculations of molecular hyperpolarizability. We expect overestimation of β values by DFT to be systematic and consistent with MP2 and possibly experiment. Such a consistency would make it possible to suggest an appropriate scaling factor to correct DFT hyperpolarizability in order to reproduce the experimental picture at semiqualitative or even quantitative level of accuracy. This should be sufficient for the purpose of the rational design of NLO-active compounds. For the present study we use the PBE0[52] and BMK[53] functionals (that performed the best in our previous study[29]) as well as two new functionals developed by Truhlar's group: M05[54] and M05-2X.[55] The latter includes 56% of HF exchange and is expected to provide better agreement with experiment (less overestimation). These functionals were designed to improve property predictions for organic, organometallic, and noncovalent compounds, including molecular geometry, thermochemistry, and kinetics.

We included HF method in the first part of this study[29] and found it to severely underestimate hyperpolarizability, in agreement with earlier reports. Simple adjustment of the fraction of HF exchange alone may seem to be sufficient to improve hyperpolarizability predictions. However, this adjustment will most likely ruin the predictions the other molecular properties. The development of balanced DFT functional is not an easy task, which clearly extends beyond the scope of our present investigation. In the present study we show that recent development of new exchange-correlation functionals also improves hyperpolarizability predictions, even if that was not the goal of the functional developers. This may be an indication that essential physics is captured in the new functionals.

2. Computational Details

The Gaussian 2003 suite of programs was used to obtain all the numerical results.[56] When a molecule is placed in an electric field of strength E, its dipole moment can be expanded in the Taylor series by the orders of the field strength:

$$\mu_i = \mu_i^{\,0} + \alpha_{ij}E_j + \beta_{ijk}E_jE_k + \gamma_{ijkl}E_jE_kE_l + \ldots \qquad (1)$$

where $\mu_i^{\,0}$ is the dipole moment of the unperturbed molecule (permanent dipole moment), α_{ij} is the linear polarizability, and β_{ijk} and γ_{ijkl} are the first and second hyperpolarizability, respectively. The first hyperpolarizability tensor components are obtained as the second derivatives of the dipole moment with respect to the applied field or as the negative third derivatives of the energy (W) with respect to the applied field:

$$\beta_{ijk} = -\frac{\partial^3 W(E)}{\partial E_i \partial E_j \partial E_k}_{E=0} \tag{2}$$

In Gaussian 2003 this is accomplished numerically with the finite field (FF) approach (Freq=Raman keyword), or analytically with the coupled perturbed Hartree–Fock (CPHF) method (Polar=DCSHG keyword).

From EFISH experiments, the measured quantity is the scalar product of the dipole moment and vectorial part of β ($\mu\beta_{\text{vect}}$). When the dipole moment is available from independent measurements, EFISH results may be reported as β_{vect} on the assumption of the collinearity between μ and β_{vect}. We calculate β_{vect} from tensor components β_{ijk} as

$$\beta_{\text{vect}} = (\beta_x^{\,2} + \beta_y^{\,2} + \beta_z^{\,2})^{1/2}$$

where

$$\beta_j = \frac{1}{3}\sum_{i=1}^{3}(\beta_{jii} + \beta_{iji} + \beta_{iij})$$

$$i,j = x, y, z$$

and then multiply by calculated μ if necessary.

Experimental molecular hyperpolarizability is measured at some wavelength of the incident laser beam (λ). For correct comparison, calculated β values should account for wavelength or frequency dependence (dispersion). Within the Gaussian 2003 program off-resonant dynamic hyperpolarizability is implemented only at the HF level of theory. In the case of DFT and MP2 methods, which do account for electron correlation, we use a multiplicative correction to static correlated property:[24,57,58]

$$\beta_{\text{corr}}(2\omega, \omega, \omega) = \beta_{\text{corr}}(0)\frac{\beta_{\text{HF}}(2\omega, \omega, \omega)}{\beta_{\text{HF}}(0)} = \beta_{\text{corr}}(0)\Delta$$

$$\Delta = \frac{\beta_{\text{HF}}(2\omega, \omega, \omega)}{\beta_{\text{HF}}(0)}$$

where $\beta_{\text{corr}}(0)$ and $\beta_{\text{corr}}(2\omega,\omega,\omega)$ are static and dynamic hyperpolarizabilities at the correlated level of theory and $\beta_{\text{HF}}(0)$ and $\beta_{\text{HF}}(2\omega,\omega,\omega)$ are the same properties calculated at the HF level; Δ is the multiplicative correction factor. Our recent study[29] has revealed that if β values are measured at $\lambda = 1907$ nm of the incident laser beam, the wavelength correction appears to be less than 10% and can be neglected, while for correct comparison to experimental β values obtained at $\lambda = 1064$ nm, it is necessary to take into account frequency dependence; this can increase the ratio of β values by 25–30%.

Four exchange-correction functionals PBE0, BMK, M05, and M05-2X as well as the MP2 method were chosen for this study. Based on our recent recommendations[29] we used the 6-31+G* basis set throughout this study and compared only the ratios of molecular hyperpolarizabilities to avoid the problem related to the standards and convention factors used by experimentalists. Molecular geometries were first optimized at the same theory level as was used for estimation of β. The latter were then calculated at static limit ($\lambda = \infty$, $\omega = 0$) using the FF method implemented in the Gaussian03 (Freq=Raman keyword). Solvation effects were taken into account using the Polarizable Continuum Model (SCRF=IEFPCM with option NoAddSph). When necessary, the wavelength correction was calculated by the CPHF method with analytical derivatives (Polar=DCSHG keyword).

3. Results and Discussion

The following principles were taken into account to choose molecules for the present study. The most widely used donor and acceptor groups (dialkylamino, alkoxy, cyano, and nitro groups and derivatives of barbituric acid) and building blocks of the π-system (benzene, ethylene fragments, and heterocycles such as thiophene and oxazole) were considered. Molecules with different sizes of π-system including up to 8 π-bonds, λ-shaped molecules (including one acceptor and two donor groups), and conformationally locked polyenes are represented among the compounds chosen. We believe that the compounds which are considered in this study contain nearly all common building blocks (connected in different combinations) from which NLO molecules are usually constructed and represent common types of the NLO molecules thereby covering the majority of promising candidates which are interesting for potential applications in nonlinear optics.

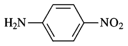
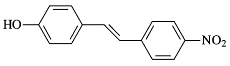
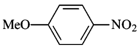
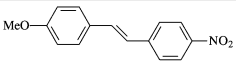
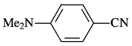
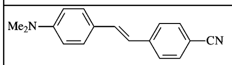
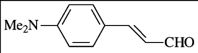
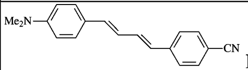
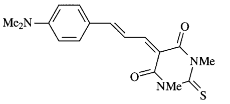
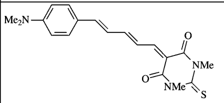
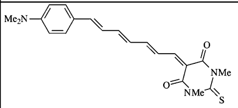
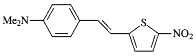
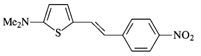
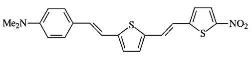
All the molecules considered in this study are grouped into several sets. In each set, experimental molecular hyperpolarizabilities originate from the same research group implying that the benchmarks and conventions remain the same within the given set of molecules. Based on our recent conclusion,[29] only the ratios of molecular hyperpolarizabilities rather than the absolute values are considered throughout the present study. This avoids potential problems related to different conventions and standards used in experimental measurements.

In Table 1 we present calculated β-ratios and compare them with the experimental values for the D/A-substituted benzenes, stilbene analogues, and phenylpolyenes (including those with the thiophene cycle put in place of the phenyl group).

The MP2 method always shows the lowest increase of β when going from molecules with shorter π-bridges to molecules with longer π-bridges. The PBE0 and M05 functionals demonstrate similar behavior leading to dramatic overestimation of β for long-chain molecules while the BMK functional overestimates β to a lesser extent. Much better agreement is observed for the M05-2X functional. These results show that for DFT methods, a decrease of overestimation (improvement of the agreement) is related to an increase of the fraction of HF exchange included in functional: 25% for PBE0, 28% for M05, 42% for BMK, 56% for M05-2X.

In order to investigate how the theoretical results obtained correlate with each other and experiment, we have considered D/A-benzenes and stilbenes from sets **I**–**III**. We expect that relative increase of β estimated by different methods should be consistent. The relative differences of the ratios can be obtained by the expression $(r^{\text{solv}}_{\beta(\mu\beta)}(X - 2))_{\text{Method-1}}/(r^{\text{solv}}_{\beta(\mu\beta)}(X - 2))_{\text{Method-2}}$, where X defines the set (**I**, **II**, or **III**). In applying this expression we find that, for instance, for BMK/M05-2X methods the ratio is within the range of 1.25–1.40 and for MP2/M05-2X methods it remains within the 0.69–0.80 range that does not exceed 15%. This clearly suggests that theoretical methods behave in a similar way. When theoretical β values are compared to experimental

TABLE 1: Comparison of Experimental and Theoretical Ratios of Molecular Hyperpolarizabilities (r_β) or Scalar Products $\mu\beta$ ($r_{\mu\beta}$) for D-π-A Molecules with Different Length of π-System[a]

Set	Molecule with its number	Exp.[b]	PBE0		BMK		M05		M05-2X		MP2	
		r_β^{solv}	r_β	r_β^{solv}	r_β	r_β^{solv}	r_β	r_β^{solv}	r_β	r_β^{solv}	r_β	r_β^{solv}
I	 **I-1 (*p*NA)**											
	 **I-2**	4.1	9.0	9.7	7.5	7.4	8.8	9.5	6.4	5.3	5.3	3.8
		$r_{\mu\beta}^{solv}$	$r_{\mu\beta}$	$r_{\mu\beta}^{solv}$	$r_{\mu\beta}$	$r_{\mu\beta}^{solv}$	$r_{\mu\beta}$	$r_{\mu\beta}^{solv}$	$r_{\mu\beta}$	$r_{\mu\beta}^{solv}$	$r_{\mu\beta}$	$r_{\mu\beta}^{solv}$
II	 **II-1**											
	 **II-2**	8.2	18.4	20.2	16.0	15.8	17.3	19.5	13.5	12.3	11.7	9.8
III	 **III-1**											
	 **III-2**	8.7	17.3	16.4	15.0	12.6	16.3	15.2	12.5	10.1	9.6	7.0
	 **III-3**	4.0	5.0	5.4	4.8	5.3	4.7	4.9	4.5	4.9	4.4	4.8
	 **III-4**	18.1	36.2	37.3	30.7	26.7	33.3	33.6	24.5	19.7	18.5	13.0
IV	 **IV-1**											
	 **IV-2**	2.7	2.5	2.8	2.4	2.8	2.5	2.7	2.3	2.6	2.1	-
	 **IV-3**	6.8	5.1	6.3	4.7	6.1	5.0	6.1	4.2	5.5	3.7	-
V	 **V-1**											
	 **V-2**	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.2	1.1	1.2	-
	 **V-3**	2.3	4.0	4.2	3.4	3.3	3.9	4.0	2.8	2.6	2.6	-

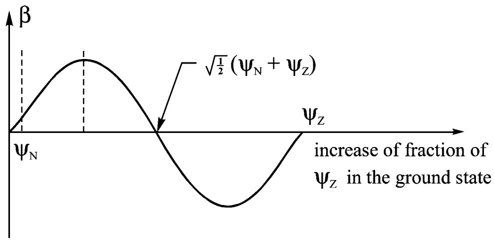
[a] Calculated data are presented for both isolated molecules (r_β or $r_{\mu\beta}$) and those which account for solvation effects (r_β^{solv} or $r_{\mu\beta}^{solv}$); the first molecule of each set ($X - 1$) is taken as a reference; the ratios are obtained by formulas $r_\beta = (\beta_{X-n})/(\beta_{X-1})$ and $r_{\mu\beta} = (\mu\beta_{X-n})/(\mu\beta_{X-1})$, where X is the set number; for compounds measured at 1064 nm, wavelength correction is included in calculated values while for those studied at 1907 nm, ratios of static β values are given (see Computational details section). [b] Experimental measurements are carried out for set **I** in $CHCl_3$ at 1064 nm[59,60] for set **II** in *p*-dioxane at 1064 nm;[61] for set **III** in DMSO at 1907 nm[62,11] for set **IV** in $CHCl_3$ at 1907 nm;[63] and for set **V** in *p*-dioxane at 1907 nm.[64]

ones, the situation becomes more complicated. Experimental increase of β upon elongation of the π-system from benzene to stilbene is overestimated by BMK and M05-2X functionals by 80 and 29% for set **I**, by 93 and 50% for set **II**, and by 45 and 16% for set **III**. The MP2 method underestimates increase of β by 7 and 20% for sets **I** and **III** while it leads to an overestimation of the $\beta_{\mathbf{II-2}}/\beta_{\mathbf{II-1}}$ ratio by 20%. Therefore, the uncertainty range appears to be 48% for BMK, 34% for M05-2X, and 40% for MP2 that is significantly higher than that obtained above for different theoretical methods. We believe that these findings can be attributed to an ambiguity in the experimental data mentioned in the Introduction. The PBE0 and M05 functionals display even bigger uncertainty range.

Molecules **III-3** and **III-4** have three and six π-bond bridges respectively. Pairwise comparison of **III-3** to **III-1** and **III-4** to **III-2** shows that all the DFT methods closely reproduce fourand nearly twofold increase of $\mu\beta$. This allows us to conclude that D-π-A molecules with two to three π-bonds in the bridge connecting D/A substituents represent a group for which any hybrid DFT method can be used to predict relative hyperpolarizability. The same is true for five to six π-bonds containing molecules.

In the case of thiobarbituric acid derivatives (set **IV**), all the DFT methods show nearly the same increase of β upon elongation of the polyene bridge, while MP2 predictions are found to be significantly smaller. Moreover, in contrast to sets **I**−**III**, underestimated $\beta_{\mathbf{IV-3}}/\beta_{\mathbf{IV-1}}$ ratio is observed for all the DFT methods. Unfortunately it is difficult to provide an unequivocal explanation for these findings. This might be due either to deficiency of all theoretical approaches for this particular family of compounds or to experimental errors. The results obtained for set **IV** demonstrate that all the DFT methods

SCHEME 1



reproduce experimental data reasonably well for the molecules with the length of π-system in the range of four to six π-bonds. This is in agreement with data on molecules **III-2** and **III-4** (five and six π-bonds correspondingly) and allows us to include molecules with four π-bonds in π-bridges in the above-defined second group of molecules containing five to six π-bonds in the π-system rather than in the first group of molecules with two to three π-bonds between D/A substituents. One can also see that for molecules **III-2,4** and **IV-1,2,3**, the DFT results are in better agreement with the experiment than the MP2 predictions while opposite is true for **III-1,3** molecules.

Set **V** represents a family of the thiophene-containing molecules. Results on **V-1** and **V-2** are found to be in an agreement with the concept of auxiliary donor/acceptor groups introduced in ref 18. For this pair of molecules, all the methods give the same increase of β, in agreement with experimental measurements. These findings along with data on molecules of sets **III** and **IV** confirm our conclusion[29] that relative increase/decrease of molecular hyperpolarizability in the series of molecules with equal (or slightly different) length of the π-bridge can be well reproduced by any of the hybrid DFT methods.

Comparison of **V-2** and **V-3** shows that the PBE0 and M05 methods overestimate increase of β by a factor of $\sim$2, BMK by 43%, and M05-2X by only 13%. The MP2 performs only slightly better than M05-2X. These results show that **V-3** (which has eight π-bonds in the π-system) should be considered as a separate (third) group.

Another significant question is the solvent effect on hyperpolarizability. The data on the compounds of sets **II** and **V** were measured in nonpolar *p*-dioxane. Based on our calculations, this solvent does not significantly affect the hyperpolarizability ratios: difference is found to be less than 10% and, therefore, solvation effect can be neglected. This is not the case for the polar solvents such as chloroform and DMSO. For more rigorous comparison to the experiment which is carried out in polar solvents, solvation effect should be taken into account.

When solvent was taken into account, the hyperpolarizability ratio increased in some cases, while a reverse situation is observed in other cases. This can be explained in terms of the valence resonance model, considering the dependence of hyperpolarizability on the degree of mixture of the neutral ψ_N and zwitterionic ψ_Z wave functions in the ground state of the given molecule (Scheme 1). The *X* axis can also be represented by the bond length alernation (BLA), bond order alernation (BOA), or other similar parameters (see for instance refs 4, 63).

The D-π-A molecules considered in this study belong to the region shown by the dashed line in Scheme 1. Inclusion of the solvent effect in calculation would, therefore, always lead to increase of β. Nevertheless, because each molecule is characterized by its own unique curve, the relative increase of β upon solvatation (which depends on position of the molecule at the abscissa axis and the shape of curve) appears to be different. The shape of the curve and position of the molecule depend also on the method used.

Results for the other NLO molecules studied here are grouped into three sets and listed in Table 2. It contains molecules with long π-systems including λ-shaped molecules and conformationally locked polyenes. Because of the big size of those molecules, we carried out calculations with BMK and M05-2X functionals only.

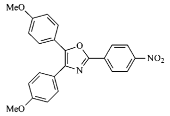
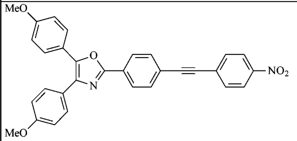
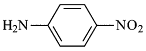
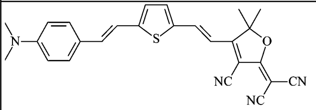
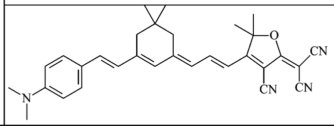
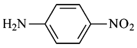
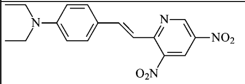
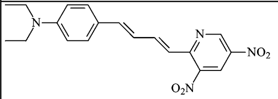
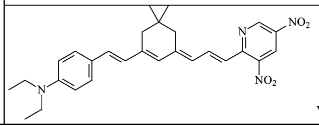
NLO properties of compounds from set **VI** were measured in *p*-dioxane; therefore β values are calculated for isolated (gas-phase) molecules only while solvent effect is taken into account for set **VII**. Set **VIII** represents three compounds that we plan to synthesize and measure their NLO properties. We use our conclusions based on comparison of calculated and experimental results for sets **I**−**VII** to predict hyperpolarizability of **VIII-1**−**VIII-3** in advance of their experimental study.

In molecules **VI-1** and **VI-2**, donor substituents are rotated out of the plane of π-conjugation. Therefore we considered **VI-1,2** as four and seven π-bridged systems. Increase of β is overestimated by BMK and M05-2X methods by 47 and 29%, respectively. These results are in reasonable agreement with ratios for **V-3** and **V-1**. Therefore the **VI-2** molecule can be considered as belonging to the same group as **V-3**.

Set **VII** contains well-known NLO molecules FTC[67,68] and CLD[69] with 8 π-bonds in their π-system in comparison to pNA. The BMK functional overestimates increase of β by ca. 40% while the M05-2X shows ca. 30% overestimation. Again in agreement with previous results on comparison of β values for molecules of the same group, both methods show good agreement of ratio $\beta_{\mathbf{VII\text{-}2}}/\beta_{\mathbf{VII\text{-}1}}$: 22% increase found experimentally is estimated to be 17 and 32% by BMK and M05-2X, respectively.

Comparison of calculated and experimental β-ratios for molecules of sets **I**−**VII** which cover systems with the most frequently used building blocks of NLO molecules and with different length of the π-system shows that one can use existing DFT functionals reliably. In order to do that, one should separate molecules into different groups depending on the length of their π-system. Inside the group, any DFT functional can be used to predict relative hyperpolarizabilities. For comparison of β values for molecules from different groups the best agreement with experiment is observed for the M05-2X functional. Slightly worse agreement is obtained for the BMK functional while PBE0 and M05 methods show more significant overestimation of the increase of β upon elongation of the π-system. An increase of β when going from molecules of group **1** to group **2**, and from group **2** to group **3** is overestimated by M05-2X in the range of 1.09−1.50 (sets **I**−**IV**) and 1.13−1.29 (sets **V**−**VI**), respectively. The BMK functional gives the range of 1.23−1.93 for **1** → **2** (also including data from ref 29) and 1.43−1.47 **2** → **3**. For clarity, we presented β ratios for group **1** to group **2** graphically (Figure 1). Linear fit of these data results in scaling factor that is equal to average overestimation of β (1.13 for M05-2X and 1.46 for BMK). Combining these data with those for set **VII**, an average overestimation for **1** → **3** transition amounts to 29% for M05-2X and 71% for BMK. Therefore the ratios for molecules of the set **VIII** listed in Table 2 should be corrected for average overestimation to give $r_{\beta(\text{VIII-1})}^{\text{M052X}} = 16.8$, $r_{\beta(\text{VIII-1})}^{\text{BMK}} = 14.4$, $r_{\beta(\text{VIII-2})}^{\text{M052X}} = 30.1$, $r_{\beta(\text{VIII-2})}^{\text{BMK}} = 26.0$, $r_{\beta(\text{VIII-3})}^{\text{M052X}} = 52.2$, $r_{\beta(\text{VIII-3})}^{\text{BMK}} = 48.0$, which should be pairwise equivalent, but in fact appear to be slightly different due to uncertainty in the experimental data and, to a lesser extent, due to inaccuracy in the calculated results.

TABLE 2: Comparison of Experimental and Theoretical Ratios of Molecular Hyperpolarizabilities (r_β) or Scalar Products $\mu\beta$ ($r_{\mu\beta}$) for λ-Shaped Molecules, Conformationally Locked Polyenes, and Heterocycle-Containing Molecules

Set		Exp.	BMK	M05-2X
		$r_{\mu\beta}$	$r_{\mu\beta}$	$r_{\mu\beta}$
VI[a]	 **VI-1**			
	 **VI-2**	1.7	2.5	2.2
		r_β^{solv}	r_β^{solv}	r_β^{solv}
VII[b]	 **I-1 (*p*NA)**			
	 **VII-1 (FTC)**	36	51	45
	 **VII-2 (CLD)**	44	60	58
		r_β	r_β	r_β
VIII[c]	 **I-1 (*p*NA)**			
	 **VIII-1**	–	21	19
	 **VIII-2**	–	38	34
	 **VIII-3**	–	82	59

[a] Experimental data measured in *p*-dioxane and extrapolated to infinite frequency are used; calculated data are obtained for isolated molecules at the static limit.[65] [b] Experimental measurements are carried out in $CHCl_3$ at 1907 nm; calculated data including solvatation effect are obtained at the static limit.[66] [c] Calculated data for isolated molecules at static limit.

4. Conclusions

We investigated the applicability of density functional theory to study of the first hyperpolarizability of organic π-conjugated molecules and to provide a computational protocol to be used for rational design of the compounds with large β values. We found that all hybrid DFT functionals used in this study overestimate hyperpolarizability of D-π-A molecules. This overestimation increases with the size of π-system, which is probably related to self-interaction error. The main question addressed here is how significant this discrepancy is in comparison to the more sophisticated theoretical methods and to experiment, and to which extent we can trust the results of DFT calculations. The problem of the choice of the appropriate method is closely related to (1) the way in which theoretical results are compared to experiment, (2) how to interpret the observed disagreement, and (3) how accurate the experimental data are and what accuracy is required from theory.

We considered only hybrid GGA functionals, which are known to provide a better agreement with experiment than pure DFT methods. Our results show that increased fraction of the HF exchange in the functional improves the agreement between theory and experiment. The M05-2X functional (with 56% of the HF exchange) appears to be the best DFT method considered. The BMK functional is less accurate, while PBE0 and M05 functionals overestimate the hyperpolarizability in the longer π-systems considerably. The comparison of calculated and experimental ratios of β demonstrates semiquantitative agreement (in the range of −28% to 20% for MP2, 9% to 50% for M05-2X, 23% to 93% for BMK). Both theoretical deficiencies and experimental uncertainties lead to these inaccuracies. In some cases, nearly quantitative agreement can be obtained while significant errors are observed in other cases. None of the theoretical methods considered in this study can be used for quantitative predictions. The computational study aim was to find potentially useful compounds to be synthesized and studied experimentally; semiquantitative predictions are sufficient. The M05-2X functional provides an accuracy comparable to that of the MP2 method, albeit at a much lower computational cost.

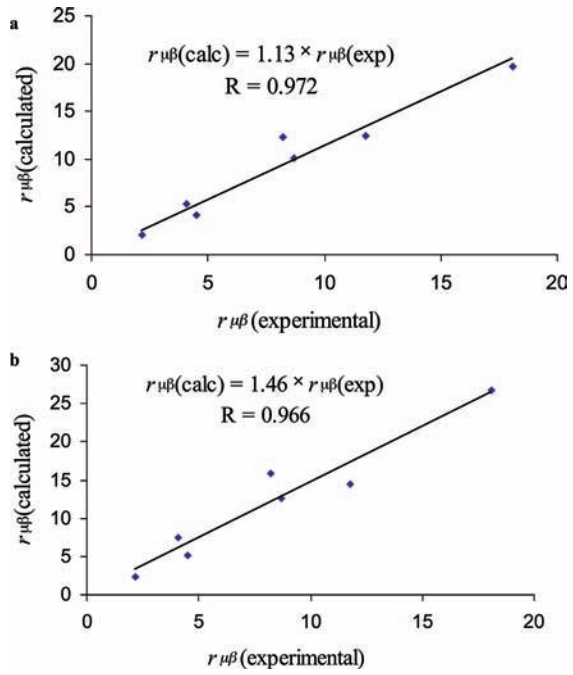


Figure 1. Linear fit of calculated versus experimental β ratios upon elongation of the π-system of molecules from group **1** to group **2**, calculated at M052X/6-31+G* (a) and BMK/6-31+G* (b) theory levels.

The experimentally measured gas phase value of hyperpolarizability is available only for the *p*NA molecule.[70,51,29] Therefore we propose to use *p*NA as the benchmark for quantum chemical calculations of other conjugated molecules. This will allow estimation of absolute value of hyperpolarizability $\beta_{\mathrm{NewMol}}(\lambda)$ (in Taylor convention) at appropriate wavelength λ according to following expression

$$\beta_{\mathrm{NewMol}}(\lambda) = \frac{\beta^{\mathrm{calc}}_{\mathrm{NewMol}}(\lambda)}{\Delta^{p\mathrm{NA}}_{1064}\beta^{\mathrm{calc}}_{p\mathrm{NA}}(\lambda = \infty)}\beta^{\mathrm{exp}}_{p\mathrm{NA}}(\lambda = 1064)\frac{1}{f^{\mathrm{DFT}}_{\mathrm{SC}\text{-}N}}$$

where $\beta^{\mathrm{calc}}_{\mathrm{NewMol}}(\lambda)$ and $\beta^{\mathrm{calc}}_{p\mathrm{NA}}(\lambda{=}\infty)$ are calculated hyperpolarizabilities for the new molecule with appropriate wavelength correction and *p*NA at static limit (which must be obtained at the same level of theory), $\beta^{\mathrm{exp}}_{p\mathrm{NA}}(\lambda{=}1064)$ is the experimental hyperpolarizability of *p*NA measured at 1064 nm, 1787 au (from ref 70), $f^{\mathrm{DFT}}_{\mathrm{SC}\text{-}N}$ is the appropriate scaling factor for the method chosen (N defines the group according to number of π-bonds in the π-system), and $\Delta^{p\mathrm{NA}}_{1064}$ is the wavelength correction factor for $\lambda = 1064$ nm for *p*NA ($\Delta^{p\mathrm{NA}}_{1064} = 1.33$ at HF method). With this expression, an absolute gas phase value of β at the static limit for three proposed NLO molecules (**VIII-1,2,3**) can be predicted at the M05-2X/6-31+G* level of theory: $\beta^{\mathrm{M052X}}_{\mathbf{VIII\text{-}1}} = 23156$ au, $\beta^{\mathrm{M052X}}_{\mathbf{VIII\text{-}2}} = 39997$ au, $\beta^{\mathrm{M052X}}_{\mathbf{VIII\text{-}3}} = 60990$ au.

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