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Computational search for nonlinear optical materials: are polarization functions important in the hyperpolarizability predictions of molecules and aggregates?

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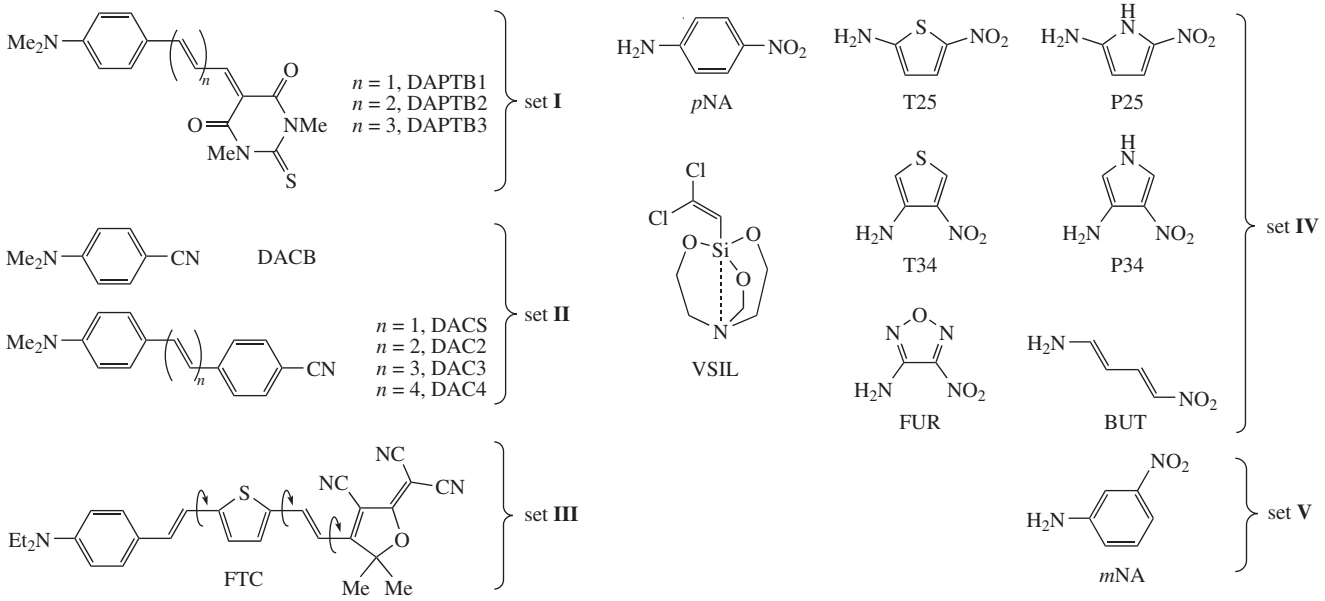
Hyperpolarizability of conjugated molecules with relatively long π-system (three and more double bonds in the π-bridge) and molecular aggregates (composed of the same molecules) can be predicted at the Density Functional Theory level with the 6-31G basis set to within 5–10% (compared to 6-31+G* results), while 6-31G* and especially MIDI! basis sets are much less accurate.

Theoretical estimation of molecular nonlinear optical (NLO) properties is an important part of the systematic search for materials for optoelectronic devices.[1,2] Methods of quantum chemistry are widely used to predict molecular hyperpolarizability (β) for compounds in advance of their synthesis.[3] While the advanced wavefunction theory methods, such as coupled cluster approximations, can predict β with high accuracy,[4,5] they become impractical with the increase of the molecular size. We have recently shown that hybrid Density Functional Theory (DFT) methods based on BMK and, in particular, M05-2X functionals are approaching the accuracy of the MP2 method, when carefully compared to experiment.[6,7] These functionals are superior in accuracy to more common exchange-correlation functionals (such as B3LYP or B97-2) due to increased fraction of Hartree–Fock (HF) exchange.

Another component of a quantum chemical method is the basis set. The choice of the basis appropriate for the prediction of NLO properties was critically addressed by many authors.[6,8–14] The common consensus is that the basis set must contain polarization and diffuse functions for the reliable estimation of β. Our detailed study on basis set dependence of β in *para*-nitroaniline had revealed that diffuse functions are necessary for the description of intra-atomic polarization, while polarization functions are necessary for the description of interatomic polarization.[6] For conjugated organic molecules, the 6-31+G* basis set provides sufficient accuracy to predict relative hyperpolarizabilities, useful in the systematic search for NLO-active molecules.

The goal of this work was to investigate the quality of the hyperpolarizability predictions if the 6-31+G* basis is reduced to 6-31G*, MIDI! and, finally, to 6-31G. Smaller basis sets may be the only option for the large molecules or aggregates.

The test systems are donor–π–acceptor (D-π-A) molecules with different D/A substituents and π-systems (Scheme 1). We divided them into several sets: sets **I** and **II** represent D/A-substituted phenylpolyenes with increasing size of the polyene bridge; set **III** contains eight planar conformations of well-known NLO molecule FTC.[15] Conformational dependence of hyperpolarizability in FTC has been subject of two thorough studies, which have revealed that relative hyperpolarizability varies in the ranges of 1–1.20 (for β_{vec} at BMK/6-31+G*)[16] and 1–1.35 (for β_{HRS} at



Scheme 1

Table 1 Hyperpolarizability ratios obtained with M05-2X functional and different basis sets. The ratio is defined as $r_X^n = \beta_{X-n}/\beta_{X-1}$ relative to the first compound in each set. In addition, $r_{p\mathrm{NA}}^n$ is the ratio of β relative to *p*NA, r_{DACS}^n is the ratio of β relative to DACS. The last three columns list percentage deviations of the results obtained with smaller basis from those obtained with the 6-31+G* basis, $\Delta = 100[r_X^n(\mathrm{basis}) - r_X^n(6\text{-}31{+}G^*)]/r_X^n(6\text{-}31{+}G^*)$.

Set	Ratio	Molecule	6-31+G*	6-31G*	6-31G	MIDI!	Δ(6-31G*)	Δ(6-31G)	Δ(MIDI!)
I	r_{I}^n	BAR1	1.00	1.00	1.00	1.00	0.0	0.0	0.0
		BAR2	2.01	2.03	2.06	2.03	0.9	2.4	1.0
		BAR3	3.47	3.45	3.49	3.40	–0.6	0.6	–1.9
	$r_{p\mathrm{NA}}^n$	BAR1	12.63	14.50	11.96	19.78	14.8	–5.3	56.6
		BAR2	25.37	29.37	24.60	40.11	15.8	–3.0	58.1
		BAR3	43.84	50.04	41.76	67.35	14.1	–4.8	53.6
II	r_{II}^n	DACB	1.00	1.00	1.00	1.00	0.0	0.0	0.0
		DACS	10.21	12.06	11.07	13.13	18.2	8.4	28.7
		DAC2	18.63	22.60	20.18	24.75	21.3	8.3	32.8
		DAC3	28.30	34.69	30.69	37.82	22.6	8.5	33.7
		DAC4	40.25	49.06	43.04	53.18	21.9	6.9	32.1
	r_{DACS}^n	DACS	1.00	1.00	1.00	1.00	0.0	0.0	0.0
		DAC2	1.83	1.87	1.82	1.88	2.7	–0.1	3.2
		DAC3	2.77	2.88	2.77	2.88	3.7	0.0	3.9
		DAC4	3.94	4.07	3.89	4.05	3.2	–1.4	2.7
III[a]	r_{III}^n	FTC(*aas*)	1.00	1.00	1.00	1.00	0.0	0.0	0.0
		FTC(*aaa*)	1.00	0.99	0.98	0.97	–0.7	–2.0	–3.3
		FTC(*ass*)	1.10	1.10	1.11	1.10	0.0	0.6	–0.5
		FTC(*asa*)	1.15	1.14	1.16	1.14	–0.6	1.2	–1.1
		FTC(*sas*)	1.07	1.07	1.10	1.12	0.1	2.9	4.4
		FTC(*saa*)	1.09	1.08	1.09	1.09	–0.6	0.4	0.4
		FTC(*sss*)	1.12	1.12	1.16	1.16	0.4	3.9	4.0
		FTC(*ssa*)	1.17	1.17	1.20	1.19	–0.3	2.8	1.8
IV	r_{IV}^n	*p*NA	1.00	1.00	1.00	1.00	0.0	0.0	0.0
		T25	0.99	0.99	0.93	1.05	–0.6	–6.1	5.7
		P25	0.90	0.89	0.83	0.80	–0.5	–7.0	–10.3
		T34	0.39	0.37	0.40	0.36	–5.3	2.7	–8.1
		P34	0.36	0.35	0.35	0.36	–3.3	–2.8	–2.0
		FUR	0.22	0.23	0.22	0.21	3.2	–0.9	–3.7
		BUT	1.52	1.52	1.46	1.76	–0.4	–4.5	15.5
		VSIL	0.41	0.45	0.36	–	11.4	–12.7	–

[a] *s* and *a* mark relative orientation of double bonds for FTC according to Scheme 1 (*s* for *syn*, *a* for *anti*); FTC(*aas*) conformer corresponds to the most energetically stable one.

RPBE/DNP).[17] D-π-A molecules with the short π-system compiled in set **IV**. Among them are D/A derivatives of benzene, thiophene, pyrrole, furazane, butadiene and dichlorovinyl-substituted silatrane. The latter is known to act as a strong σ-donor while two Cl atoms act as σ-acceptors. This compound is chosen because of its sufficiently high melting point of 181 °C (one of the requirement for NLO applications) and biological activity[18] thereby representing potentially multifunctional material. Set **V** contains aggregates of increasing size (up to eight molecules) of *meta*-nitroaniline (*m*NA), selected from its crystal structure.[19] Each aggregate is formed by weak π–π stacking interactions along the *c* crystallographic direction.

The Gaussian03 program[20] was used for all the calculations. Two functionals BMK[21] and M05-2X[22] and four basis sets 6-31+G(d), 6-31G(d), 6-31G and MIDI! were used for both optimization and finite-field hyperpolarizability calculations (keyword Polar=EnOnly). All molecules were optimized without symmetry constraints and found to be nearly planar to within 1–5° (with one exception of VSIL). Geometry of *m*NA aggregates was taken from its crystal structure.[23] Hyperpolarizability was estimated as numerical negative third derivative of the energy with respect to the applied electric field and reported as the vectorial part

$$\beta_{\mathrm{vect}} = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2}, \text{ where } \beta_j = \frac{1}{3}\sum_{i=1}^{3}(\beta_{jii} + \beta_{iji} + \beta_{iij}),\ i, j = x, y, z.$$

The results are listed in Table 1. We report only the results obtained with the M05-2X functional, as BMK gave fairly similar values. For set **I**, we also calculated the ratios $r_{p\mathrm{NA}}^n = \beta_{\mathrm{I}-n}/\beta_{p\mathrm{NA}}$, while for the family of dimethylamino-cyano-substituted biphenylpolyenes (set **II**) we have additionally presented the ratios of β with DACS as a reference molecule ($r_{\mathrm{DACS}}^n = \beta_{\mathrm{II}-n}/\beta_{\mathrm{II}-2}$ for $n \geq 2$).

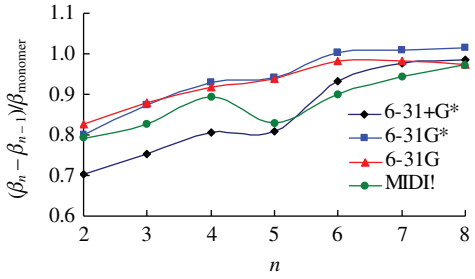


Figure 1 Dependence of relative hyperpolarizability per molecule on the number of molecules in stacking aggregate of *m*NA.

For the following discussion, we separate all compounds into three Groups: set **I** (including values of r_{DACS}^n), and set **III** are combined into Group 1 (D/A-substituted π-conjugated molecules with relatively long π-bridge); sets **IV** and **V** combined into Group 2 (smaller molecules and their stacking aggregates), while set **II** (including $r_{p\mathrm{NA}}^n$ ratios) are separated into Group 3. From Table 1, one can see that the maximum deviation is largest for MIDI! (over 50%), while 6-31G* is more accurate (close to 20%). Surprisingly, the smallest basis 6-31G consistently produces low (less than 10%) deviations from 6-31+G* results. When one takes into account the accuracy of hyperpolarizability obtained with M05-2X/6-31+G* approximation (±30–35%),[7] increase in uncertainty by additional 10% is apparently insignificant. Deviations are more pronounced for Group 2, composed of molecules with short π-systems. This is in line with the general trend: the smaller is the molecule, the more extended basis set should be used for its description. We also observed that a less polarizable π-bridge between D/A substituents requires an extended basis

set. This is exemplified by VSIL, where π-bridge consists of only an ethylene fragment.

The results for *m*NA stacking aggregates are shown in Figure 1. They demonstrate consistency to within 10%. We also predicted the asymptotic limit for infinite 1D stack, relevant to the NLO properties of solid materials. We used a fitting procedure[24] with the following equation: $(\beta_n - \beta_{n-1})/\beta_{\text{monomer}} = a - be^{-Nc}$, where β_n is hyperpolarizability of aggregate of n molecules, and fitting parameter a is asymptotic relative hyperpolarizability. We found this parameter to be 0.99, 1.01, 0.98 or 0.97 for the 6-31+G*, 6-31G*, 6-31G or MIDI! basis set, respectively. Thus, all a values are all within 2% of each other. Using this fact, one can obtain the asymptotic relative value using a small basis set, then calculate β_{monomer} at a higher level of theory and obtain the accurate value of β for the large aggregate, affected by intermolecular interactions.

The results for Group 3, which compares the molecules with long and short π-systems, are also surprising. The basis sets (6-31G* and MIDI!) that contain only polarization functions (meaning that interatomic polarization is correctly described by the basis set, while intra-atomic polarization is taken into account to a lesser extent) produce overestimated β ratios, while 6-31G results in only 10% increase of uncertainty range relative to 6-31+G* basis set. Apparently, this is the result of error cancelation. This is recurring trend, and it can be explored to reduce computational costs of the high throughput screening.

The following conclusions can be drawn from this study. There is general consensus that for correct description of molecular hyperpolarizability one needs to use basis set augmented with both polarization and diffuse functions. However, if the system of interest is large enough, that can lead to convergency problems, basis set reduction can be done safely. We found that, for molecules with relatively long and easily polarizable π-bridges (four and more double bonds between D/A substituents), the use of the 6-31G basis set will lead to a less than 5% error in comparison to the 6-31+G* basis set. Basis set reduction for small molecules can be possible only if all molecules in the test series are characterized by a nearly identical size of the π-bridges. Apparently, such molecules should be investigated with more extended basis sets. The exceptions are molecular aggregates where convergence deteriorates with increased size of the cluster. In such cases, one deals with the same molecule (and apparently with the same π-system), which is slightly perturbed by molecular surrounding. Our results show that, in such cases, the quality of the results is not changed by a reduction of the basis set.

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