

Semiempirical Calculations of First-Order Hyperpolarizabilities: Testing the Performance of Different Methods in Comparison to Experiment

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The performances of three semiempirical program packages for the calculation of frequency-dependent first-order hyperpolarizabilities are tested using a data set of 200 different organic compounds. The methods used are the sum-over-states approaches implemented in VAMP6.0 and CNDOS, and the time-dependent Hartree–Fock (TDHF) method included in MOPAC. For the configuration interaction (CI) calculations in the gas-phase single and pair-double excitation (VAMP–PECI) and single excitation CI (CNDOS–SCI) with two different sizes of the active orbital window are used. In the case of MOPAC and VAMP6.0 the AM1 and PM3 Hamiltonians are used. Although the correlation coefficients, r , obtained are slightly different, all calculational methods are comparably useful for trend predictions in the molecular design of new compounds for nonlinear optical applications. Because of the enormous computational costs, the TDHF method is only feasible for smaller molecules or smaller data sets. To account for solvent effects, the state energies obtained first from gas-phase CI calculations are corrected using the self-consistent-reaction-field (SCRF) approach implemented in VAMP6.0, improving the quality of the results.

Introduction

Organic materials consisting of extended conjugated π systems with enhanced nonlinear optical properties, like special polymers and Langmuir–Blodgett multilayers, have a wide range of potential applications in the fields of optical communications, optical computing, and dynamic image processing.^{1–5}

In the absence of local field effects the nonlinear response of molecule-based materials can be related directly to the corresponding microscopic hyperpolarizabilities of the constituent molecules, for instance second- and third-order bulk susceptibilities to the first- and second-order molecular hyperpolarizability tensors β and γ .⁶ The starting point for the design of new materials for NLO applications is to understand the relationship between the geometric and electronic structure of the molecules in question and their nonlinear response. For more than 10 years computational methods have been important tools in this regard, as they can give a priori information on the nonlinear properties of a molecule.

The ideal computational treatment would employ an exact Hamiltonian in an extensive basis set and an exact computation of the second-order response with full scale correlation. This is normally accomplished at the *ab initio*^{7,8} and possibly also at the density functional levels.^{9,10} Despite increasing computational power such exhausting accuracy still requires high computational costs and is therefore only feasible for smaller molecules or smaller data sets. On the other hand, the aim of many theoretical studies is to find reliable trends for a number of candidate molecules.^{8,11,12} Semiempirical methods are often used for this purpose, because the size or the number of the molecules is often prohibitive for *ab initio* applications.

Many semiempirical approaches have been applied to NLO properties, for example PPP,¹³ CNDOS,^{14,15} INDO,¹⁶ MNDO,¹⁷ AM1,^{18,19} and PM3.^{20,21} If several parametrizations are available, e.g. for CNDOS and INDO, parameters optimized for spectroscopic properties are normally used in NLO studies.^{22–25} ZINDO calculations have been reported to be particularly useful for open shell systems.²⁶

In all of these studies molecular hyperpolarizabilities are computed using either numerical finite field (FF),²⁷ analytical coupled Hartree–Fock (CHF),²⁸ or sum-over-states (SOS) techniques.^{18,29,30} Significant computational advantages of the correction vector method over the conventional SOS technique have recently been demonstrated by Albert¹⁶ and Ramasesha et al.³¹ More recently a time-dependent Hartree–Fock (TDHF)³² scheme has been incorporated into the semiempirical MOPAC program³³ by Kurtz and co-workers. For a recent overview on the computation of second-order optical nonlinearities see ref 34.

The starting point for this investigation was the idea to include the calculation of the second-order hyperpolarizability γ into the semiempirical program package VAMP6.0.³⁵ In a first step we aimed to test the performance and the reliability of the SOS approach included in VAMP,^{18,36} because both the first-order and the second-order hyperpolarizabilities are expressed in terms of state energies, dipole moments, and transition dipole moments. Although good performance of β calculations need not guarantee good performance for γ calculations,^{37,38} it would probably be useless to put any programming effort to the calculation of γ if the program delivers unsatisfactory results for β . Therefore, we decided to use a large data set containing different types of organic compounds with reliable experimentally determined β values to compare these values with the calculated ones.

On the other hand, we want to compare the VAMP–SOS approach with other methods for calculating frequency-depend-

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ent hyperpolarizabilities. Although there have been a large number of publications dealing with the calculation of first-order and second-order hyperpolarizabilities during the past few years, only a few of them compare different semiempirical methods with each other³⁹ or with *ab initio* calculations.^{40,41} To our knowledge only smaller data sets were used for these comparisons. Therefore, we decided to extend this study and use two other popular semiempirical methods, namely a CNDOS–SOS^{42,43} method and the TDHF approach included in MOPAC.³³ Thus we are able to compare the performance of three different parametrizations (AM1, PM3, and CNDOS) as well as that of two different approaches (SOS and TDHF) with respect to the calculation of first-order hyperpolarizabilities.

Computational Methods

All geometries used during this investigation are fully optimized using the AM1 and PM3 Hamiltonians included in VAMP6.0.³⁵ In the case of MOPAC and VAMP6.0 the first-order hyperpolarizabilities are then calculated using AM1 and PM3. In the case of CNDOS we use both the AM1 optimized geometries and the PM3 ones as input for the NLO calculations.

For the sum-over-states approach included in VAMP^{18,35} a singles-plus-pair-doubles CI (PECI) expression¹⁸ and for CNDOS only singly excited CI (SCI)⁴³ are used. To be able to discuss the influence of the size of the active orbital window during the CI calculation on the value of the calculated hyperpolarizability β , we decided to use two different window sizes. After several tests 8 and 20 active orbitals are taken for the SOS calculations.

To make the calculated hyperpolarizabilities comparable to experimental results from EFISHG (electric-field-induced second-harmonic generation) measurements, the scalar products of the total vector values of β and the unit vector along the corresponding dipole moments are calculated from the output data.

The solvent calculations are done using the self-consistent reaction field (SCRf) correction of the state energies within VAMP6.0⁴⁴ and the AM1 parametrization with Peci = 8.

All VAMP and MOPAC calculations are performed on a DEC 3000 (150 MHz) workstation. The CNDOS calculations are done on an Intel Pentium (90 MHz) PC.

Results and Discussion

The data set contains 200 organic compounds, including substituted benzenes, stilbenes, styrenes, biphenyls, and fluorenes. The experimental values were obtained from solution-phase dc EFISHG at a fundamental wavelength of 1.91 μm (0.65 eV).^{45,46}

β is calculated along the direction of the dipole moment in order to be able to compare the results obtained directly with experiment. β is expressed in units of $10^{-36} \text{ cm}^5 \text{ esu}^{-1}$ (esu) throughout the text, figures, and tables.

In the following sections we will discuss the reliability of the different methods with respect to the calculation of the first-order hyperpolarizability.

We will use the expression “trend” in order to describe the agreement between calculation and experiment, especially to what extent the calculations could reproduce the sequence of the measured β values. A reliable trend is most important during the design process of new molecules for nonlinear optical applications.

Before we start to discuss the obtained results we want to say that we are aware of the problems which arise if one tries to compare calculated β values with experiment. This problem has already been addressed by Shelton and Rice in 1994.⁸ The

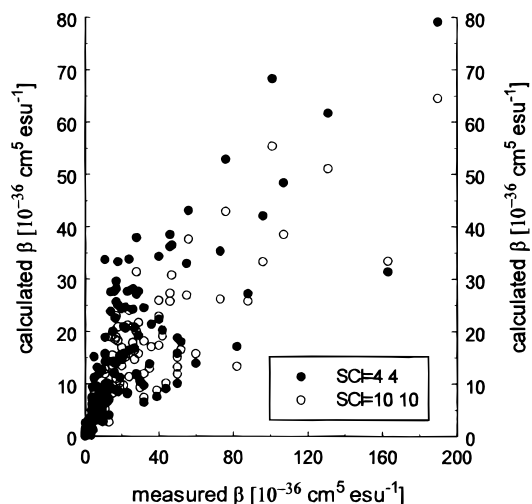


Figure 1. Calculated against measured β values using AM1 optimized structures as input for the CNDOS/SCI calculations. Results obtained by the small (SCI = 4 4) and the large (SCI = 10 10) active orbital window size are shown.

most important point is the fact that there are two different values for the quartz reference which differ by a factor of 0.58. Therefore, we will not discuss the exact magnitude of the values too much, but the correlation coefficients are unaffected by this problem. Merely the slope of the correlation is changed, which does not diminish the predictive power concerning trends. From our point of view the calculational methods should be able to differ between molecules with low or high β values so that they can be used to decide whether a compound is a good NLO compound or not.

First a general comparison is made, before the results will be discussed in more detail.

General Comparisons

Dependence of the Calculated β Values on the Size of the Active Orbital Window. In this section we want to discuss the influence of the size of the active orbital window during the CI calculation on the quality of the calculated β values. Therefore, we use active orbital window sizes of 8 and 20 for the two SOS approaches. The first size is recommended by Clark and Chandrasekhar;¹⁸ the second is chosen according to the results of test calculations performed on 15 molecules, including different benzene, stilbene, fluorene, and acetylene compounds. Starting for 20 active orbitals, the calculated β values became somewhat constant.

In the case of CNDOS–SCI using the AM1 optimized structures as input (CNDOS[AM1]), the correlation coefficients between the calculated and the measured values obtained for the whole data set are 0.80 (standard deviation 16.74) and 0.86 (14.61) for the small (8) and large (20) active orbital number, respectively. For both options the calculated trend for the compounds in the data set reproduces the experimental findings. Larger deviations occur especially for molecules with experimental values lower than 40 esu. The corresponding plots are shown in Figure 1.

It can easily be seen that the calculated hyperpolarizability becomes smaller for the larger active orbital window. The corresponding results for CNDOS–SCI using PM3 optimized structures as input (CNDOS[PM3]) are marginally worse than described above. Correlation coefficients of 0.77 (17.95) for the small and 0.82 (16.04) for the large number of active orbitals are obtained. This situation is shown in Figure 2.

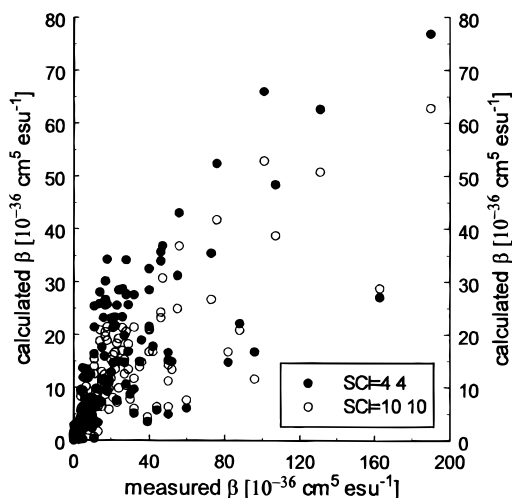


Figure 2. Calculated versus experimental first-order hyperpolarizabilities. Results obtained by CNDOS-SCI [PM3].

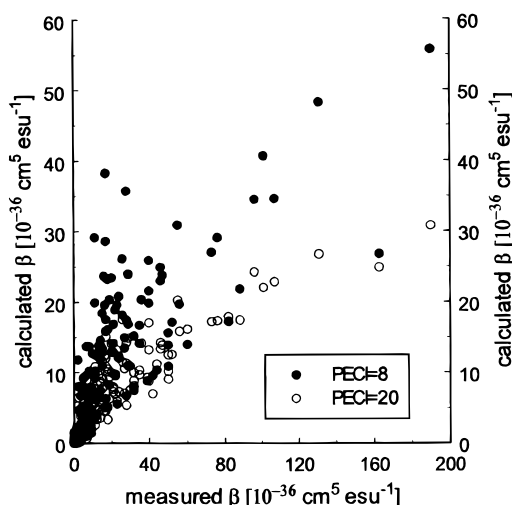


Figure 3. Calculated against measured β values using the VAMP-AM1-PECI approach.

Again the first-order hyperpolarizabilities calculated with 20 active orbitals are normally smaller than those yielded by using 8 active orbitals during the CI calculations.

A comparable situation is given for the VAMP-PECI calculations, with the exception that in this case the PM3 results are marginally better than those obtained using the AM1 Hamiltonian.

For AM1 (Figure 3) correlation coefficients of 0.79 and 0.88 with standard deviations of 16.54 and 13.46 are achieved for the small and the large active orbital window, respectively. The PM3 calculations yield correlation coefficients of 0.82 (15.42) and 0.89 (12.47). The corresponding plots are shown in Figure 4.

It is obvious that the deviation between small (8) and large (20) number of active orbitals is much larger for VAMP-PECI than in the case of CNDOS-SCI.

Although the test set includes compounds with extended π systems, we are able to obtain reliable trends using the small number of active orbitals. In this respect we point out that the calculations using only 8 active orbitals are up to 100 times faster than those using 20 active orbitals.

Comparison between the Different Calculation Approaches. Regarding the TDHF approach implemented in MOPAC for the calculation of frequency-dependent first-order hyperpolarizabilities, nearly identical results for AM1 and PM3

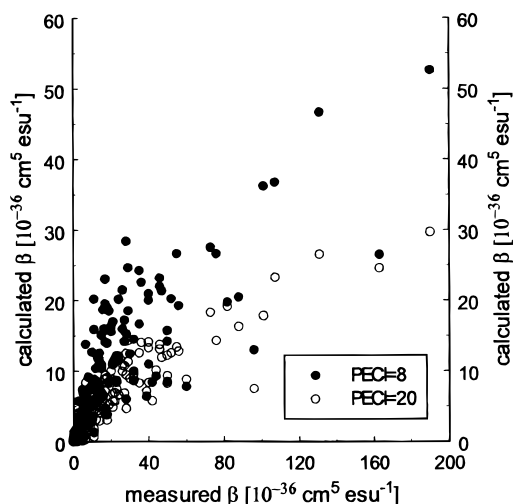


Figure 4. Plot of calculated against measured β values using VAMP-PM3-PECI.

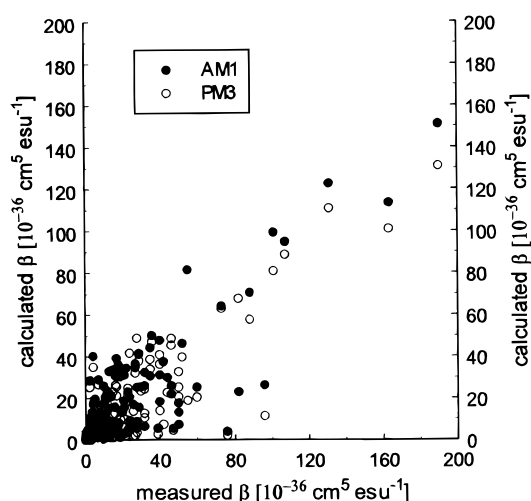


Figure 5. Results obtained by MOPAC-TDHF using AM1 (●) and PM3 (○).

are obtained (Figure 5). The correlation coefficients are 0.85 (14.31) and 0.85 (14.11), respectively. Especially for compounds with measured β values lower than about 40 esu the performance of the MOPAC-TDHF approach is worse than the two SOS methods.

On the other hand the calculated β values for molecules with large measured ones are much closer to experiment than those obtained by VAMP or CNDOS. This is shown in Figure 6.

Another very important aspect is the computational costs of the various approaches. The computational times for five molecules are listed in Table 1, and the corresponding structures are shown in Scheme 1. The fastest method is VAMP-PECI (8), followed by CNDOS-SCI (4 4). The performance of the MOPAC-TDHF approach is only acceptable for the benzene compounds.

Finally the difficulty with the TDHF method is that it estimates the hyperpolarizability as third derivatives of the SCF energy with respect to the applied external field. Hence, as opposed to the sum-over-states method, TDHF is inherently unable to clarify the excited states, related to the hyperpolarizabilities. This is also not straightforward with the correction vector method because this procedure does not require solving for the excited states which is, on the other hand, the reason for its computational efficacy. According to the literature,^{16,31}

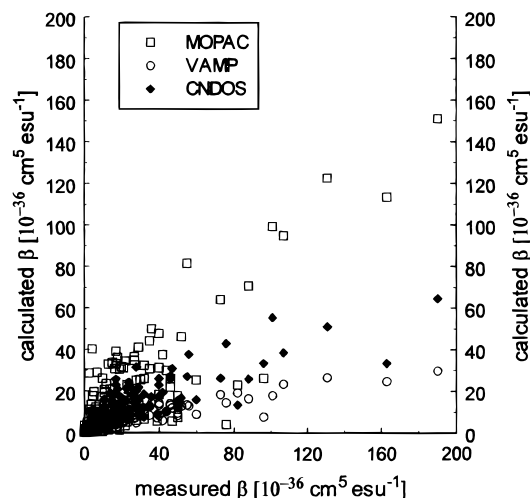


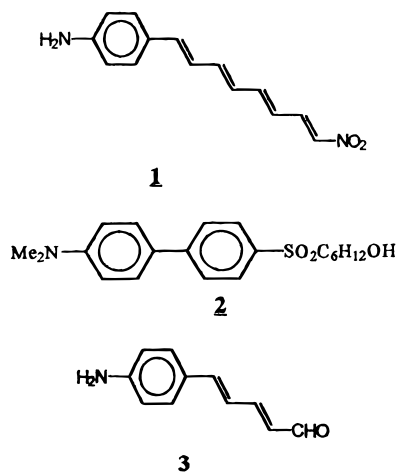
Figure 6. Plot of calculated against measured β values concerning the best results of each of the three semiempirical program packages used. Especially for molecules with measured β -values higher than 40 esu, the MOPAC-TDHF values are closer to experiment than the CNDOS[AM1] and the VAMP-PM3 results.

TABLE 1: Comparison of Computational Times (s) Required by Various Approaches for Five Selected Compounds

compound	VAMP-PECI (SOS)			MOPAC-TDHF	CNDOS-SCI (SOS) ^e	
	PECI = 8	PECI = 20	solvent ^d		CI = 4 4	CI = 10 10
benzene	3.07	1161.11		14.94	5.14	59.91
benzonitrile	3.73	1147.36		39.21	9.06	60.83
1^a	49.56	1547.46	731.84	12 744.13	91.23	142.49
2^b	25.15	1615.18	743.45	12 138.03	84.08	124.82
3^c	8.74	1215.27	285.12	11 07.87	16.50	57.52

^a 1-4'-Aminophenyl-8-nitrooctatetraene. ^b 4-(Dimethylamino)-4'-(6-hydroxyhexyl-1-sulfonyl)biphenyl. ^c 4-(Aminophenyl)butadien-1-aldehyde. Structures are shown in Scheme 1. ^d Calculated for CHCl_3 as a solvent. ^e Note that the CNDOS calculations were done on a PC (Pentium 90 MHz), whereas all other work was done on a DEC workstation.

SCHEME 1



this approach implemented for semiempirical methods appears to be the most efficient one.

To obtain a more detailed picture of the performance of the three methods used, we now discuss the results for the different types of compounds.

Detailed Comparisons

The exact statistical values for each of the following types of compounds and the whole data set are given in Table 2.

The individual results for all compounds and all methods are given in Tables IS-XS.

Substituted Benzenes. For monosubstituted benzenes the agreement between calculated and measured β values is worse for all methods used. None of the tested programs are able to reproduce the measured trends. The best correlation is found for CNDOS[AM1](20), with a correlation coefficient of 0.79 and a standard deviation of 0.53. The experimental values range between 0 and 3 esu with errors around 0.2 esu.

For di- and polysubstituted benzenes as well as for heteroaromatic compounds correlation coefficients higher than 0.90 are obtained, but still the calculations are not able to predict satisfactorily the correct trend. In the case of disubstituted benzenes with measured values between 0.2 and 60 esu CNDOS[AM1](20) ($r = 0.94$; $\text{SD} = 6.41$) and VAMP-AM1-(20) ($r = 0.92$; $\text{SD} = 5.40$) yield the best statistical performance. Both methods, particularly CNDOS[AM1](20), are able to reproduce the experimental NLO activity sequence for compounds with β values higher than about 15 esu, whereas below this value no reliable trend could be obtained. Both MOPAC-TDHF approaches are not able to yield any useful result.

The largest deviations compared to experiment are found for molecules including sulfur-containing substituents (SH, SMe).

For the eight heteroaromatic and polysubstituted benzenes in the data set CNDOS[PM3] gives the best results, followed by VAMP-PM3. Again the MOPAC-TDHF approach is not able to reproduce the experimental findings. The largest deviation between experiment and calculation occurs for the 2-chloro-4-amino-nitrobenzene.

For all benzene derivatives the performance of the three tested methods is not very good. For compounds with β values below 10 esu no program could give reliable trends. Above this value only the two SOS approaches, especially CNDOS, give reasonable trends.

Substituted Stilbenes. For the mono- and disubstituted stilbene compounds the situation is much better than for the benzene derivatives. The experimental β values for this kind of molecule range between 0 and 96 esu. The best results are achieved using VAMP-AM1(20) ($r = 0.89$; $\text{SD} = 9.71$) and CNDOS[AM1](20) ($r = 0.86$; $\text{SD} = 12.02$), whereas MOPAC-PM3 yields the worst results ($r = 0.53$; $\text{SD} = 19.44$). With some exceptions the VAMP and CNDOS calculations are able to give reliable trends compared to experiment. The largest deviations of the SOS calculation from experiment are observed with 4-nitro-4'-julolidinestilbene, the compound with the highest measured β value. VAMP-PM3(8) and (20) as well as CNDOS[PM3] severely underestimate β . For 4-NO₂-4'-OPh stilbene the calculated hyperpolarizability is much too high (VAMP-AM1(8), VAMP-PM3(8), and CNDOS[PM3](8)).

In the case of heteroaromatic and trisubstituted stilbenes the performance of all tested methods becomes worse again. No correlation coefficients higher than 0.77 could be achieved. As for the benzene compounds, we are not able to reproduce the experimental trend satisfactorily.

Substituted Biphenyls, Polyphenyls, and Fluorenes. Very good calculated trends could be obtained for this kind of molecule (experiment between 0 and 55 esu), whereas the statistical values are not that good. The best correlation coefficient is obtained with MOPAC-PM3 ($r = 0.88$; $\text{SD} =$

TABLE 2: Correlation Coefficients (r), Cross Validation Coefficients (CV), and Standard Deviations (SD) Derived from Linear Regression Analyses of the Experimental versus Calculated β -vector Components along the Dipole Moments (CV Measures the Predictive Power of the Regression). Numbers in Parentheses in the Second Column of the Whole Data Set Refer to SCRF Results

statistic values	VAMP (PECI-SOS)						CNDO/S (SCI-SOS)			
	AM1		PM3		MOPAC (TDHF)		AM1 geometry		PM3 geometry	
	8	20	8	20	AM1	PM3	8	20	8	20
Monosubstituted Benzenes										
r	0.35	0.35	0.34	0.16	0.46	0.46	0.38	0.61	0.30	0.52
CV								0.35		0.21
SD								0.67		0.73
Disubstituted Benzenes										
r	0.82	0.92	0.74	0.84	0.81	0.82	0.85	0.94	0.58	0.78
CV	0.66	0.84	0.53	0.69	0.66	0.67	0.62	0.79	0.29	0.50
SD	7.77	5.40	9.05	7.38	7.75	7.71	8.55	6.41	11.72	9.83
Substituted Heteroaromatic and Polysubstituted Benzenes										
r	0.70	0.78	0.95	0.99	0.55	0.73	0.98	0.98	0.97	0.97
CV	0.48	0.58	0.81	0.75	0.19	0.40	0.81	0.83	0.88	0.86
SD	2.14	1.93	1.29	1.48	2.67	2.30	1.33	1.28	1.04	1.13
Mono- and Disubstituted Stilbenes										
r	0.85	0.89	0.68	0.72	0.61	0.53	0.83	0.86	0.59	0.60
CV	0.71	0.78	0.47	0.52	0.31	0.14	0.67	0.72	0.35	0.36
SD	11.07	9.71	15.11	14.25	17.12	19.44	12.96	12.02	18.24	18.07
Heteroaromatic and Trisubstituted Stilbenes										
r	0.76	0.76	0.73	0.77	0.66	0.74	0.75	0.67	0.74	0.61
CV	0.51	0.56	0.54	0.57	0.04	0.11	0.53	0.44	0.53	0.36
SD	6.68	6.33	6.52	6.29	9.36	9.01	5.93	6.43	5.90	6.88
Substituted Biphenyls and Fluorenes										
r	0.58	0.80	0.70	0.87	0.70	0.88	0.57	0.72	0.61	0.68
CV	0.32	0.63	0.49	0.74	0.49	0.76	0.31	0.51	0.37	0.46
SD	10.50	7.81	9.14	6.48	9.13	6.26	11.35	9.59	10.86	10.07
Disubstituted Styrenes and α -Phenylpolyenes										
r	0.93	0.96	0.88	0.92	0.90	0.95	0.91	0.92	0.90	0.94
CV	0.83	0.91	0.75	0.84	0.77	0.87	0.77	0.79	0.73	0.79
SD	16.59	12.01	19.97	16.01	19.37	14.30	19.76	18.75	21.46	18.69
Substituted Diphenylpolyenes										
r	0.96	0.95	0.95	0.97	0.87	0.86	0.94	0.94	0.93	0.93
CV	0.90	0.87	0.90	0.93	0.75	0.73	0.86	0.86	0.86	0.86
SD	15.80	17.47	15.88	13.26	25.69	26.83	19.26	19.56	19.03	19.23
Substituted Tolanes and Diphenylpolyynes										
r	0.36	0.62	0.71	0.89	0.21	0.77	0.76	0.74	0.75	0.72
CV		0.35	0.51	0.75		0.48	0.50	0.48	0.44	0.40
SD		8.77	7.61	5.40		7.85	7.68	7.82	8.12	8.42
Results Concerning the Whole Data Set										
r	0.79 (0.84)	0.88	0.82	0.89	0.85	0.85	0.80	0.86	0.77	0.82
CV	0.61 (0.68)	0.75	0.67	0.78	0.71	0.72	0.65	0.73	0.59	0.67
SD	16.54 (13.47)	13.46	15.42	12.47	14.31	14.11	16.74	14.61	17.95	16.04

6.26); the worst ones with CNDO[AM1](8) ($r = 0.57$; SD = 11.35). The best qualitative trend is achieved by VAMP-PM3(20).

The largest deviations between calculated and measured values occur for the polyphenyl compound containing three or four phenyl rings and a nitro and an amino group as substituents. The β values for these molecules are too high compared to the measured ones. The difference could arise from the difference in the dihedral twist of the phenyl rings; see below. Another problematic compound is the 4-nitro-4'-(dimethylamino)biphenyl, for which the calculated NLO activity is much too low compared to experiment.

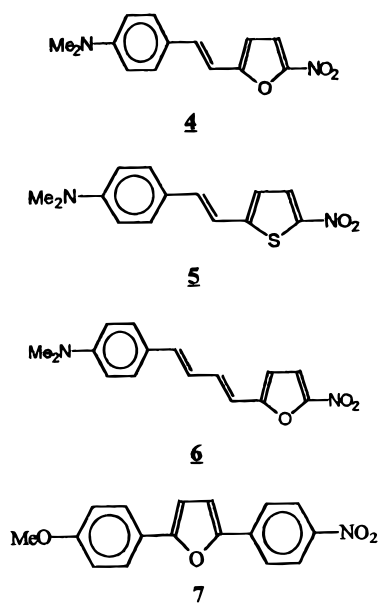
Substituted Styrenes and α -Phenylpolyenes. Compared to the results discussed above the performance of all three tested methods for this type of molecule is nearly perfect. The calculated sequence reproduces the experiment with a few exceptions. Most of the correlation coefficients are above 0.90. VAMP-AM1(20) gives the best results ($r = 0.96$; SD = 12.01) and VAMP-PM3(8) the worst ones ($r = 0.88$; SD = 19.97). In this case the calculations perfectly reproduce the effects of different substituents and different number of double bonds on the first-order hyperpolarizability. No serious deviations occur. The main difference among the three methods is that the

MOPAC values are much closer to the measured ones than the CNDO and VAMP calculated β values. Nevertheless it seems that the SOS approaches as well as the TDHF method are able to allow reliable predictions of the NLO property within this group of compounds.

Substituted Diphenylpolyenes, Tolanes, and Diphenylpolyynes. As for the styrene compounds, the effect of an increasing number of double bonds as well as that of the different types of substituents is reproduced correctly. With the exception of the MOPAC results, the achieved correlation coefficients are higher than 0.90, whereas VAMP-PM3(20) with 0.97 (13.26) gives the best result. MOPAC-PM3 yields with a correlation coefficient of 0.86 (26.83) the worst result. Again the experimental trends are reliably predicted so that for this kind of molecule all three tested methods could be used during the design process of new NLO compounds.

The situation becomes worse for the substituted tolans and diphenylpolyene compounds. Usually, the correlation coefficients obtained are below 0.80 except for VAMP-PM3 with PECI = 20 ($r = 0.89$; SD = 5.40). Neither the SOS methods nor the TDHF approach is able to reproduce the measured sequence satisfactorily. It seems that all methods have problems describing triple bonds correctly.

SCHEME 2



Finally we calculate the first-order hyperpolarizability for four compounds containing pentacyclic heteroaromatic rings. The molecules are shown in Scheme 2. MOPAC-AM1 and VAMP-AM1(20) reproduce the experimental findings.

At the end of this section we want to sum up the results for the gas-phase calculations. Regarding the whole data set VAMP-PM3 (20) yields the best correlation to experiment, followed by VAMP-AM1(20) and CNDOS[AM1](20). Both SOS methods are able to reproduce the experimental sequence reasonably well. The reason for the poor performance of the MOPAC-TDHF method is mainly due to problems with molecules with measured values below 40 esu.

One should also keep in mind that the TDHF is up to 250 times slower than the SOS methods with eight active orbitals and up to 7 times slower than VAMP (PECI = 20).

Another more general aspect is that we used β values calculated for one molecule in the gas-phase energy minimum geometry. Compared to the experimental situation we neglect the influence of the solvent. In general local field effects⁴⁷ caused by dimers or higher aggregates have to be taken into account as a source of differences,^{18,48,49} but with the compounds investigated in this work this problem seems to be less important. We also neglect that the values measured are normally mean values of a number of different rotamers. The influence of different conformers on the calculated first-order hyperpolarizabilities is already discussed in the literature.^{50,51,52} In this respect it is indeed astonishing that the MOPAC-TDHF values are that close to the measured ones.

Solvent Calculations

All calculations described above are done for gas phase, whereas all experimental values were measured in solution or with neat substances. Several investigations have been published that describe the importance of the solvent effects during the calculations of molecular hyperpolarizabilities.^{53,54,55} In this section we also want to investigate the influence of the solvent on the calculated β values, as far as this is possible with the current SCRF methods. Therefore, we perform VAMP-SCRF-PECI calculations^{18,35,44} using eight active orbitals and the AM1 Hamiltonian. This includes a gas-phase CI calculation and a step in which the energies of the different states are

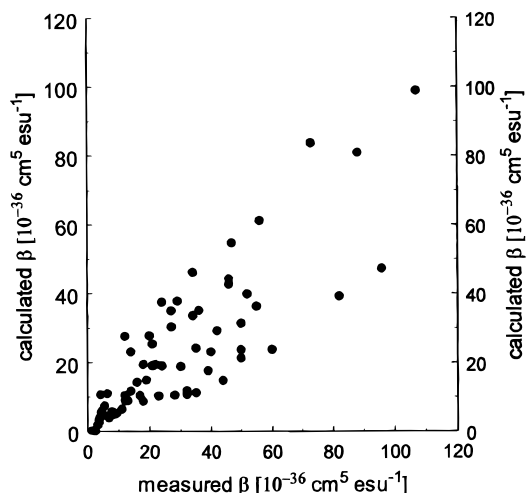


Figure 7. Results obtained by VAMP-AM1-SCRF calculations.

corrected. The effect of the solvent is therefore included by the polarization of the whole molecule and during the correction of the energies.

The β values for all compounds measured in acetone, methylene chloride, or chloroform are recalculated, because these solvents are implemented in VAMP6.0. The correlation coefficient obtained (gas-phase values in parentheses) is 0.84 (0.79), with a standard deviation of 13.47 (16.54). As shown in Figure 7 the calculated β values are now much closer to the measured ones.

The computational costs are up to 16 times lower than for MOPAC-TDHF and about half the cost of Peci calculations using 20 active orbitals.

Two calculational problems arise by using the current SCRF-CI approach. The first one is that at the moment no geometry optimization is possible within this method and we must use gas-phase geometries as input for the SCRF-CI calculations. Some of the larger deviations observed in Figure 8 may be explained by the fact that we have used an inappropriate geometry. The second problem is that sum-over-states methods in general suffer from severe resonances at excitation energies close to half the vertical absorption energies. This is demonstrated in ref 18. During our investigations this problem occurs for all compounds marked with an asterisk in the tables. If one wants to get reliable predictions of NLO properties during the design process of new compounds, one therefore should use small excitation energies in order to avoid this problem.

Conclusions

The major problem with the data set is neither the accuracy of the calculations nor that of the experimental data (although both may eventually be lacking), but rather the difference between isolated molecules in the gas phase and the actual experimental situation. In this respect the performance of all methods used seems to be good enough to obtain a good qualitative trend for compounds during the design process.

The best values concerning the whole data set are obtained by VAMP-PM3-PECI(20) followed by VAMP-AM1-PECI(20) and CNDOS[AM1]-SCI(20).

Despite the fact that the MOPAC-TDHF approach has unexpected high computational costs, even higher than the VAMP-PECI method using the large active orbital window size or the VAMP-SCRF-CI calculations, the method is also unable to give reliable trends for molecules with experimental hyperpolarizabilities below 40 esu.

The results are also in good agreement with those obtained by Matsuzawa and Dixon²⁰ for nearly the same test set by using the finite-field approach. The authors fit the calculated $\beta(0)$ to the measured values and claim that they have obtained a linear fit.

Regarding the different types of organic compounds within the test set, there are mixed performances of the different approaches. The best results are achieved for substituted diphenylpolyenes, styrenes, and α -phenylpolyenes, whereas the most unreliable results are obtained for substituted benzenes and diphenylpolyynes.

It is shown that the quality of the results increases by using SCRF-CI calculations, but still this implementation in VAMP needs some more development.

Further tests will be done using charged compounds and those having larger experimental values.

According to the results discussed above, the calculation of the second-order hyperpolarizability will be implemented into the semiempirical program package VAMP.

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Supporting Information Available: Ten tables with the individual values for all compounds in the data set (21 pages). Ordering information is given on any current masthead page.

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