

Solvent Effects in Molecular Hyperpolarizability Calculations

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Molecular geometries, dipole moments, polarizabilities and first-order hyperpolarizabilities for five classic donor–aromatic π system–acceptor NLO chromophores were calculated, using semiempirical methods (PM3), in both vacuum and solvent environments. Solvent effects on the computed molecular geometries were found to be minimal. Dipole moments calculated for the molecules in vacuo showed good agreement with experimental data obtained in nonpolar solvents, but a substantial solvent dependence was observed for molecules modeled in a polar solvent. This dependence was very pronounced in the calculated first-order hyperpolarizabilities, β , where an increase of a factor as great as 6 was observed upon changing from a vacuum to solvent environment. Hyperpolarizabilities calculated for molecules in solvent were found to be in better agreement with experimental EFISH data than those calculated for molecules in vacuo.

Introduction

The development of novel materials for nonlinear optical (NLO) applications has been a very active area of research for a number of years.^{1–4} In particular, organic NLO materials have shown great promise in the area of photonics due to their useful physical and optical properties. Additionally, they can be easily processed into optical-quality thin films.⁵ Recent advances in this area include the first successful integration of a reflection (Fabry-Perot) etalon onto the surface of a working CMOS chip.⁶

One particularly valuable aspect of the effort to design more efficient NLO materials is the computational modeling of optical and NLO properties of potential NLO chromophores.⁷ By modeling a novel compound's electronic, optical, and NLO properties using either ab initio or semiempirical techniques, it is possible to eliminate the high costs associated with the hit and miss synthetic approach. This also offers the materials scientist the added advantage of quick feedback on a compound's potential usefulness.

Unfortunately, the majority of these calculations have been performed on isolated molecules in vacuo^{7–9} despite solvent effects being well-known throughout chem-

istry¹⁰ and having been shown to be important in the experimental determination of the first-order hyperpolarizability, β .^{11,12} Combining this dependence on the local environment with the solid-state nature of most NLO devices^{1,2,5} reveals the importance of taking solvent and local environmental effects into consideration during computational studies. Bond-length alteration due to solvent has been the center of a great deal of attention in polyene^{13–17} and merocyanine organic NLO systems.^{18,19} A few studies involving the more classic aromatic systems have examined solvent effects.^{11,20–22} These have employed either spherical^{20–22} or ellipsoidal¹¹ cavities located in a continuum dielectric, as first discussed by Onsager.²³ Although this is an improvement over the complete neglect of the solvent, typical NLO chromophores are neither spherical nor ellipsoidal in shape but tend to be long, thin, and flat. This mismatch between the cavity shape and the actual molecular shape introduces a source of error into the computational process. To quantify solvent effects on both linear and nonlinear electronic and optical properties, we have investigated five compounds, 4-nitro-

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aniline, **I**; 1-(*N,N*-dimethylamino)-4-nitrobenzene, **II**; 1-(*N,N*-dimethylamino)-4-[2-(4-nitrophenyl)ethenyl]benzene, **III**; {4-(*N,N*-dimethylamino)phenyl}methylidene}propanedinitrile, **IV**; 2-[(4-nitrophenyl)methylidene]-1,3-dithiole, **V**; in both vacuum and solvent environments using an appropriate, solute-dependent, cavity model.

Methodology

To effectively study the electronic properties of an NLO chromophore through computational techniques, it is imperative that the molecular geometry be correct. Although these geometries may be obtained from X-ray crystallographic data, the choice of compounds available for study would be limited to not only those which have been previously synthesized but also to those whose crystal structures have been determined. The usefulness of the computational approach would thus be restricted to the confirmation of experimental results and would preclude its use as a truly predictive tool. An alternative method is to use molecular geometries obtained through computational geometry optimizations. All of the data reported herein was generated in MOPAC^{24,25} using the PM3 Hamiltonian with specification of the "Precise" keyword.²⁶ The eigenvector following^{27,28} method of convergence was employed as it has been our experience that it performs well when searching for global minima. To ensure that the global minimum was achieved during the optimization process, five distinct nonplanar molecular files were independently created and fully optimized. Convergence to the global minimum, as indicated by a single geometry, was validated through comparison of the five independently calculated geometries and their electronic energy data.

Calculations in solvent employed the COSMO²⁹ algorithm as included in CAChe MOPAC 94³⁰ which is based on MOPAC 6.00.^{24,25} COSMO is a continuum dielectric model based on a conductor-like screening model which allows for the calculation of analytical gradients for a solute-dependent cavity shape. While COSMO does require specification of the dielectric constant of the solvent for the reaction field calculation, neither the solvent cavity shape nor cavity size need to be specified as required by Onsager's classical continuum dielectric theory.²³ The van der Waals radius, for an assumed spherical solvent molecule, is also required as input in order to calculate the solvent accessible surface area of the solute molecule. All reported calculations used the default values of DISEX = 2.0 and NSPA = 42, where DISEX is the maximum distance, in angstroms, of intersegmental interactions and NSPA is the number of surface segments per atom. Solvent radii were calculated by taking half of the maximum molecular length, as determined computationally. The maximum molecular length was defined by the maximum interatomic separation plus the van der Waals radii³¹ of the two terminal atoms.

Calculation of the electronic properties was achieved via the finite-field, FF, method.^{7,32} Since the dipole moment, $\mu(F)_i$, of a molecule located in an external electromagnetic field may be written as

$$\mu(F)_i = \mu(0)_i + \sum_j \alpha_{ij} F_j + \sum_{j,k} \beta_{ijk} F_j F_k + \sum_{j,k,l} \gamma_{ijkl} F_j F_k F_l + \dots$$

where $\mu(0)_i$ is the permanent dipole moment, α_{ij} is the molecular polarizability tensor, β_{ijk} and γ_{ijkl} are the first- and second-order hyperpolarizability tensors, F is the local electric field, and the subscripts i, j, k , and l refer to the molecular axes. It is possible through a simple derivative technique, the FF method, to calculate the higher order terms. This results in the following expressions:

$$\alpha_{ij} = \left. \frac{\partial \mu_i}{\partial F_j} \right|_{F=0}$$

$$\beta_{ijk} = \left. \frac{\partial^2 \mu_i}{\partial F_j \partial F_k} \right|_{F=0}$$

While the derivatives should theoretically be evaluated at zero field strength, the FF method requires the presence of a small static (dc) perturbation field to be applied. In our calculations this field strength was the MOPAC default of 0.001 au. It should also be mentioned at this point that an equally valid method of employing the FF method involves an expansion of the energy, U , of a molecule located in an electric field:

$$U = -\sum_i \mu_i F_i - \sum_{i,j} \alpha_{ij} F_i F_j - \sum_{i,j,k} \beta_{ijk} F_i F_j F_k - \sum_{i,j,k,l} \gamma_{ijkl} F_i F_j F_k F_l + \dots$$

The polarizability and first-order hyperpolarizability now become

$$\alpha_{ij} = - \left. \frac{\partial^2 U}{\partial F_i \partial F_j} \right|_{F=0}$$

$$\beta_{ijk} = - \left. \frac{\partial^3 U}{\partial F_i \partial F_j \partial F_k} \right|_{F=0}$$

where the derivatives are once again at zero field strength. Values of α and β ³³ were calculated using both the dipole moment and the energy derivative methods. The reported values were obtained from the energy derivatives, although the differences between the values obtained via the two methods were negligible.³⁴

Results and Discussion

A comparison of the molecular geometries obtained in vacuo ($\epsilon = 1$) and in solvent, DMSO ($\epsilon = 45$, $r_{\text{solvent}} = 3.43 \text{ \AA}$), reveals that the presence of solvent, even one

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(33) All reported values of β correspond to β_{μ} , the magnitude of β along the direction of the permanent dipole moment.

(34) The values of α calculated for compounds **I–V** were found to be independent of the computational technique, while those for β varied by as much as 1.9% but had an average difference of only 1.2%.

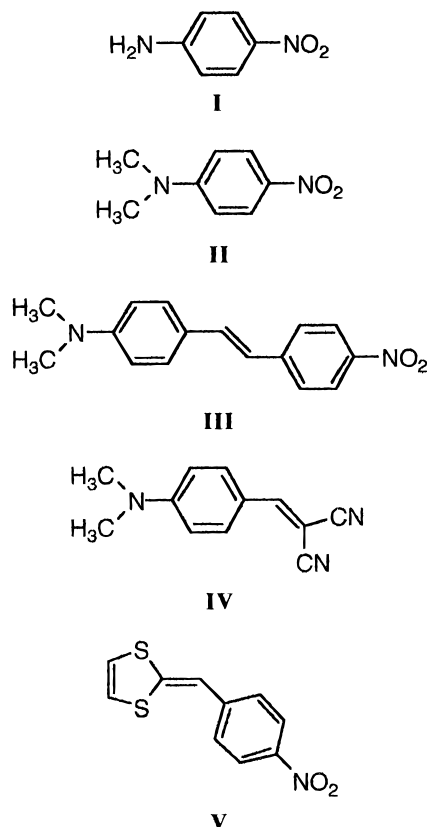


Figure 1. Molecular structures of compounds I–V.

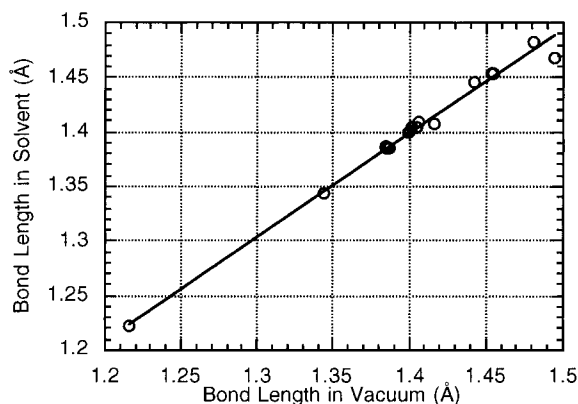


Figure 2. Plot of solvent bond lengths, DMSO ($\epsilon = 45$, $r_{\text{solvent}} = 3.43$ Å), versus vacuum bond lengths for compound **III**. A linear fit of the data yields a slope of 0.953 and a correlation (R^2) of 0.993.

with a high dielectric constant, has very little effect on the optimized geometries. This is illustrated in Figures 2 and 3, where the solvent versus vacuum bond lengths and bond angles are plotted for compound **III**.³⁵ Compound **III** was chosen for closer examination as it was representative of all five compounds. It had the largest data set (i.e., the most number of bond lengths and bond angles) and had a correlation factor which was the median of the five studied.

A linear fit of the bond length data obtained in vacuo and in DMSO, presented in Figure 2, yields a line with slope of 0.953 and correlation (R^2) of 0.993. Similarly,

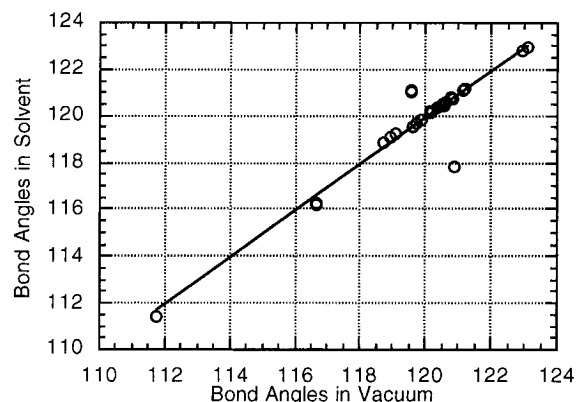


Figure 3. Plot of solvent bond angles, DMSO ($\epsilon = 45$, $r_{\text{solvent}} = 3.43$ Å), versus vacuum bond angles for compound **III**. A linear fit of the data yields a slope of 0.994 and a correlation (R^2) of 0.890. The outlayer below the fitting line corresponds to the O–N–O bond angle of the nitro group while the two outlayers above the line correspond to the two aromatic C–N–O bond angles.

Table 1. Dipole Moment Values^a Calculated in Vacuo, in Solvent and Determined Experimentally^b

compound	μ (vacuum)	μ (solvent)	μ (experimental) ^c
I	6.64	7.48	6.3
II	7.01	7.95	7.1
III	7.75	8.36	7.2
IV	5.53	8.07	8.7
V	6.30	6.80	6.9

^a All dipole moments are in units of debye. ^b Dipole moments were calculated and measured in *p*-dioxane ($\epsilon = 2.209$, $r_{\text{solvent}} = 3.23$ Å) except for compounds **IV** and **V** which were in DMSO ($\epsilon = 45$, $r_{\text{solvent}} = 3.43$ Å). ^c Experimental data is from ref 36.

the corresponding fit of the bond angle data, from Figure 3, results in a slope of 0.994 and correlation of 0.890. This consistency displayed by the bond lengths and bond angles, regardless of their local electronic environment, is attributable to the molecular framework of the compounds studied. All five consist of rigid aromatic core structures which do not easily undergo distortions. This results in virtually no solvent effects on bond lengths of the central structures while small effects are seen for the terminal pendant groups. For example, in going from vacuum to solvent, the aromatic carbon-to-nitro nitrogen bond shows an increase in length of 0.007 Å, from 1.216 to 1.223 Å. This moderate alteration is nearly twice that of any other change in bond length. Similarly, the greatest variation in bond angles also occurs at the terminus of the molecule. The O–N–O bond angle of the nitro group in compound **III** is seen to decrease 3.05°, from 120.90° to 117.85°, which is a factor of 19 larger than the variation of any angle within the aromatic core. Exclusion of the bond lengths and bond angles involving the terminal nitro group from the linear fit increases the correlation for the bond lengths and angles to 0.998 and 0.997, respectively. This is clear indication that the optimized geometries of the rigid aromatic core structures show a negligible solvent dependence.

The dipole moments calculated in solvent for compounds **IV** and **V** are in excellent agreement with the experimental results while the vacuum based calculations yield better agreement for compounds **I–III**. (See Table 1). This is a direct result of the experimental conditions under which the dipole moments were measured and of an underlying assumption of the COSMO

(35) A full list of the optimized bond lengths and bond angles, both in vacuo and in simulated DMSO, is available as supporting information.

(36) Singer, K. D.; Sohn, J. E.; King, L. A.; Gordon, H. M.; Katz, H. E.; Dirk, C. W. *J. Opt. Soc. Am. B* **1989**, *6*, 1339.

Table 2. Molecular Polarizabilities^a Calculated in Vacuo, in Solvent and Determined Experimentally^{a,b}

compound	α (vacuum)	α (solvent)	α (experimental) ^d
I	2.19 (1.00)	3.31 (1.00)	2.2 (1.00)
II	2.72 (1.24)	3.83 (1.16)	2.3 (1.05)
III	5.65 (2.58)	7.49 (2.26)	4.5 (2.05)
IV	4.00 (1.83)	5.60 (1.69)	3.7 (1.68)
V	4.15 (1.89)	5.74 (1.73)	3.9 (1.77)

^a All molecular polarizabilities are in units of 10^{-23} cm³. ^b All molecular polarizabilities were calculated and measured in DMSO ($\epsilon = 45$, $r_{\text{solvent}} = 3.43$ Å). ^c Bracketed values were normalized by dividing by the polarizability of compound **I**. ^d Experimental data is from ref 36.

algorithm. The dipole moments of compounds **I–III** were measured experimentally in *p*-dioxane, a nonpolar solvent ($\epsilon = 2.209$). The good correlation observed between the vacuum-based calculations and experiment is thus expected since the continuum model employed, COSMO, bases its reaction field calculation solely on the dielectric constant of the solvent and, assuming that $\epsilon \neq 1$, the radius of the solvent molecule. For vacuum calculations $\epsilon = 1$ and there is no reaction field calculation to compute, thus a very nonpolar solvent, such as *p*-dioxane, is well modeled by a vacuum-based calculation. Conversely, the dipole moments of compounds **IV** and **V** were measured in the very polar solvent DMSO. Here the solvent is a strong enough dielectric to induce a significant reaction field, thus necessitating the inclusion of solvent effects in the dipole moment calculation.

A significant point which must be addressed is that the vacuum based calculations out performed the COSMO-based calculations for **I–III** even though the simulated solvent was *p*-dioxane, the same as used experimentally. The source of this discrepancy lies in one of the underlying assumptions of the COSMO algorithm.²⁹ The screening energy of a charge distribution in a continuum dielectric scales as³⁷

$$\frac{\epsilon - 1}{\epsilon + x}$$

where x ranges from 0 to 2. The case where $x = 1$ corresponds to a monopole located in front of a planar surface of a dielectric, while $x = 2$ corresponds to a monopole located at infinity relative to a dielectric sphere. The authors of COSMO assume²⁹ that x will lay between 0 and 1 and have set it equal to $1/2$. The results of this assumption is that the algorithm contains an intrinsic error which scales as $1/2\epsilon$. Since this error scales as the reciprocal of the dielectric constant of the solvent, the COSMO algorithm is more accurate at modeling polar than nonpolar solvents. For a very nonpolar solvent, such as *p*-dioxane, this intrinsic error is significant, as seen by the results for compounds **I–III** in Table 1.

A review of the polarizability data, presented in Table 2, indicates that both the vacuum- and solvent-based calculations show the same trends in the polarizabilities (i.e., **III** > **V** > **IV** > **II** > **I**) as measured experimentally. The absolute average error is seen to be greater however for the solvent-based calculations, $\Delta\alpha_{\text{sol}} = 1.874 \times 10^{-23}$ cm³, than for the calculations in vacuo, $\Delta\alpha_{\text{vac}} = 0.426 \times 10^{-23}$ cm³. This indicates that the reaction field

Table 3. First-Order Hyperpolarizabilities^a Calculated in Vacuo, in Solvent and Determined Experimentally^{b-d}

compound	β (vacuum)	β (solvent)	β (experimental) ^c
I	3.11 (1.00)	18.7 (1.00)	9 (1.00)
II	4.12 (1.32)	17.5 (0.96)	12 (1.33)
III	18.6 (5.98)	42.1 (2.25)	52 (5.78)
IV	8.94 (2.87)	27.9 (1.49)	16 (1.78)
V	7.18 (2.31)	20.0 (1.07)	25 (2.78)

^a All hyperpolarizabilities are in units of 10^{-30} cm⁵ esu⁻¹. ^b All hyperpolarizabilities were calculated and measured in DMSO ($\epsilon = 45$, $r_{\text{solvent}} = 3.43$ Å). ^c Bracketed values were normalized to the hyperpolarizability of compound **I**. ^d All values for β are static, i.e., are at zero frequency. Experimental results were measured at $1.356 \mu\text{m}$ except for compound **I** which was measured at $1.58 \mu\text{m}$. Experimental results were extrapolated to zero frequency through use of the two-state model. (See ref 9). ^e Experimental data are from ref 36.

employed in the solvent-based calculation is too great, i.e., the effective dielectric constant of the continuum is actually greater than would be expected for a solvent where $\epsilon = 45$.³⁸ A number of possible explanations exist for this lack of correlation. The first is that COSMO is a continuum model, and although it employs a solute-dependent cavity shape it neglects all directed intermolecular interactions between the solvent and solute. Second, a simulated solvent is defined in COSMO by only two variables, the dielectric constant and solvent radius. Both of these variables are potential sources of error particularly in DMSO since it is not spherical and has two different end groups. Additionally the DMSO used in the experimental work may have had a dielectric constant differing from that used computationally.³⁹

A third way of viewing the data, aside from the relative trends in the data and the absolute values obtained for the polarizability calculations, is to examine the increase in polarizability observed throughout the series of compounds after normalizing by the value obtained for one of the compounds. An analysis of this type may aid in eliminating any systematic errors in the data. To examine such a possibility, the calculated data was normalized by the value of the polarizability obtained from compound **I**. (See the bracketed data presented in Table 2.) This analysis reveals that the ratios of the polarizabilities calculated in solvent are in better agreement with the ratios of the experimental data than are those from the vacuum-based calculations. This may indicate that the polarizabilities calculated in solvent may include systematic errors which result in the observed overestimation of the experimental values. As discussed above, an improper representation of the reaction field may account for this result.

Unlike the polarizabilities, the first-order hyperpolarizabilities calculated in the simulated solvent, Table 3, are in better absolute agreement with the experimental results than are the vacuum based results with the absolute average errors being $\Delta\beta_{\text{sol}} = 8.4 \times 10^{-30}$ cm⁵ esu⁻¹ and $\Delta\beta_{\text{vac}} = 14.4 \times 10^{-30}$ cm⁵ esu⁻¹. A point of potential importance regarding these errors is that all of the vacuum-based calculations underestimated the hyperpolarizabilities while the solvent-based calculations

(38) Windholz, M., Ed. *The Merck Index*, 10th ed.; Merck and Co.: Rahway, NJ, 1983.

(39) Due to the hygroscopic nature of DMSO the value of ϵ , measured at 25 °C, depends on the concentration of contaminating water. The value of $\epsilon = 45$ was obtained from ref 32, while ref 10 reports a value of 46.5.

(37) Böttcher, C. J. F. *Theory of Electric Polarization*; Elsevier: Amsterdam, 1973.

tions overestimated the three smallest values, compounds **I**, **II**, and **IV**, and underestimated the two largest values, compounds **III** and **V**. This fluctuation between under- and overestimating the experimental values may be tied to the overestimation of the molecular polarizabilities and a poor description of the reaction field.

An examination of the relative orders of the hyperpolarizabilities yields rather poor results. Experimentally, the compounds are ordered **III** > **V** > **IV** > **II** > **I**, the solvent-based calculations yield **III** > **IV** > **V** > **I** > **II**, a swapping of **IV** and **V** as well as **I** and **II**, while the calculations in vacuo produced an order of **III** > **IV** > **V** > **II** > **I**, a swapping on **IV** and **V** relative to the experimental results. The fact that neither calculation reproduced the correct order of the measured hyperpolarizabilities is a potentially disturbing result. Although certain quantitative aspects of the semiempirical-FF computational approach may be questionable,⁷ one of its strengths is the ability to qualitatively assess a series of potential NLO chromophores.

A critical review of compounds **I**–**V** reveals that while compounds **I**–**III** show a very close structural relationship, compound **IV** is slightly removed from this series, by replacing the nitro accepting group with a dicyano acceptor, and compound **V** is even further removed as it contains a substantially different donor group containing sulfur. Thus, the swapping of compounds **IV** and **V**, as observed in both sets of calculations, is not necessarily surprising. The switching of **I** and **II**, as observed in the solvent based calculations, cannot be explained by such structural differences. The exact reason for this change in trend is not clear at this point. It must be remembered however that the molecular geometries are fixed and that thermal effects, such as free rotation around single bonds, are not accounted for in our method. The results of the free rotation expected for the amino and nitro groups with respect to the aromatic rings will be evident in the experimentally determined values, through a modification of the hyperpolarizability data. These effects have not been accounted for computationally.

While the solvent-based calculations outperformed those conducted in vacuo when examining the absolute hyperpolarizability values, the opposite is true for the normalized hyperpolarizabilities. (See the bracketed values in Table 3.) Although the source of this error is unclear, it may lie in an erroneous value for compound **I** when calculated in solvent. All of the normalized values for the solvent-based calculations are significantly lower than observed experimentally. A possible explanation of this result would be that the hyperpolarizability calculated for compound **I** may be anomalously large. By normalizing the hyperpolarizability data using the value obtained for compound **II**, instead of compound **I**, the ratios determined for the solvent-based calculations show much better correlation to those measured experimentally, changing from an average difference of $1.48 \times 10^{-30} \text{ cm}^5 \text{ esu}^{-1}$ to $0.86 \times 10^{-30} \text{ cm}^5 \text{ esu}^{-1}$. The analogous ratios for the vacuum-based calculations show a slight increase, from $0.21 \times 10^{-30} \text{ cm}^5 \text{ esu}^{-1}$ to $0.34 \times 10^{-30} \text{ cm}^5 \text{ esu}^{-1}$. This increased

correlation, between the solvent-based calculations and the experimental results, indicates that the calculated hyperpolarizability for compound **I** may indeed lie at the heart of the matter. One explanation would be the lack of inclusion of thermal effects as discussed above. Additionally, an erroneously large β for compound **I** would also account for the poor correlation between the observed trends in the hyperpolarizabilities.

Conclusions

Although the increase in correlation observed between the absolute values of the experimental and solvent-based computational results is moderate, the actual differences between the hyperpolarizabilities calculated in vacuo and in solvent are quite large, up to a factor of 6 with an average difference of a factor of 3.7. The importance of this is that the NLO properties of most NLO chromophores are characterized via electric-field-induced second harmonic generation, EFISH, while in solution. *Thus, a more accurate estimation of the experimental results will require the consideration and presence of solvent effects in the hyperpolarizability calculations, specifically when a polar solvent is involved.* It should also be mentioned however, that the inclusion of these solvent effects can significantly increase the computational expense of a calculation.

In conclusion, we have calculated the linear and nonlinear electronic and optical properties of a number of classic donor-acceptor NLO chromophores both in vacuo and in solution using the COSMO solvent model. Although the presence of the solvent had little effect on the calculated molecular geometries, results from the calculated dipole moments indicate that inclusion of solvent is necessary to properly model the electronic properties of molecules in polar solvents. For nonpolar solvents, such as *p*-dioxane, dipole moment calculations performed in vacuo provide reasonable results. Our first-order hyperpolarizability calculations indicate a very strong solvent dependence. To our knowledge, this is the first time that the COSMO solvent model has been applied to the study of NLO chromophores. Since most computational studies ignore the effects of solvent, large errors in the resulting computed value of β may ensue. The possibility of these errors should be recognized and taken into consideration when using computational results.

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Supporting Information Available: Tables of calculated bond lengths and angles for compounds **I**–**V** and structure of **I**–**IV** (15 pages). Ordering information is given on any current masthead page.

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