Articles

A Solvatochromic Method for Determining Second-Order Polarizabilities of Organic Molecules

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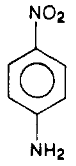
A simple experimental method for determining optical second-order polarizabilities of organic molecules for second harmonic generation (SHG) is developed by using a two-level quantum mechanical model. Required values of excited-state dipole moments are obtained from a solvatochromic method based on the theoretical treatment of McRae. Second-order polarizabilities obtained by this method for a series of compounds compare well with those obtained by the conventional EFISH technique. The solvatochromic method has the important advantage that measurements can be made rapidly with simple equipment available in most chemistry laboratories.

Introduction

There has been much recent interest in organic compounds that show large optical second-order molecular polarizabilities.[1-3] These materials are useful for applications in nonlinear optics (NLO) such as second-harmonic generation (SHG; i.e., doubling the frequency of laser radiation) and electrooptic phase modulation. The common technique for measuring molecular second-order polarizabilities is electric field induced second-harmonic generation (EFISH).[4-6] In this method a DC electric field is applied across a solution of the compound to be tested, a laser beam is passed through the solution, and the intensity of the generated second-harmonic light is measured. Elaborate and expensive instruments seldom found in a chemistry laboratory are required to make these time-consuming measurements. The goal of this work is to devise and test a simpler method for determining second-order polarizabilities so that these important measurements can be made more quickly with equipment available in a typical chemistry laboratory.

The method we have chosen to explore is based on solvatochromism, which is the solvent dependence of the UV-visible absorption (or emission) spectrum of a molecule.[7-12] The advantage of this method is that the only instrumentation required is a dipole-moment apparatus (essentially a capacitance bridge) and a UV-vis spectrometer. In the present work we have measured the second-order polarizabilities of a series of compounds (**1**–**8**) with the conventional EFISH technique and compared the results with those obtained with our solvatochromic method.



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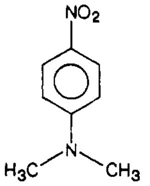

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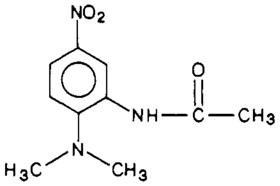

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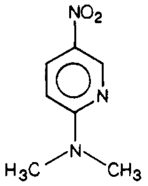

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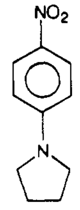

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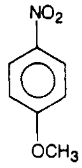

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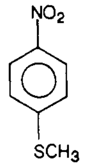

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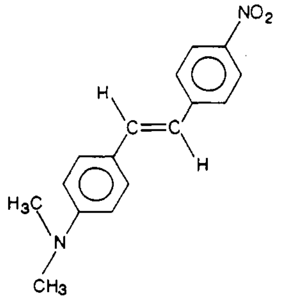

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Theoretical Background

General Considerations.[1-3] When a molecule is placed in an external electric field, DC or optical, a redistribution of electron density results, changing its dipole moment. The induced dipole moment, μ, can be expressed in terms of the permanent, ground-state dipole moment (in the absence of a field), μ_g, and the applied field E by means

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(12) Although solvatochromic methods of determining β have been alluded to in the literature, one has never been described: Buckley, A.; Choe, E.; DeMartino, R.; Leslie, T.; Nelson, G.; Stamatoff, J.; Stuetz, D.; Yoon, H. *Pro. ACS Div. Polym. Mat: Sci. Eng.* **1986**, *54*, 502–509.

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of a power series. In one dimension this can be written:

$$\mu = \mu_g + \alpha E + \beta E^2 + \gamma E^3 + ... \qquad (1)$$

The coefficients of the powers of E are the first-order, second-order, and higher polarizabilities of the molecule; it is these second-order and higher terms, or "nonlinear" terms, that give rise to a number of interesting optical effects in the field of "nonlinear optics." In general the situation is not one-dimensional, in that an electric field applied in one direction can induce a dipole moment in a different direction. In this case eq 1 becomes tensorial and α_{ij} is a first-rank tensor, β_{ijk} is a second-rank tensor, etc.:

$$\mu_i = (\mu_g)_i + \alpha_{ij}E_j + \beta_{ijk}E_jE_k + ... \qquad (2)$$

An important result that can be obtained from eq 2 is that all even-order polarizabilities are zero for centrosymmetric molecules. Hence one immediate requirement for an isolated molecule to be capable of SHG is that it cannot possess a center of symmetry. This restriction applies to bulk media as well, so centrosymmetric crystals are also incapable of SHG.[13]

Quantum Mechanical Treatment.[4,17-20] To obtain theoretical expressions for molecular polarizabilities it is necessary to use the methods of quantum mechanics, specifically time-dependent perturbation theory. The oscillating electric field component of an electromagnetic wave, such as in laser radiation, can be expressed as $E_o \cos \omega t$, where ω is the frequency of the laser light and E_o the peak amplitude of the field. Treating this as a time-dependent perturbation on the molecule, using second-order perturbation theory, gives the following expression for second-order molecular polarizability for SHG (neglecting a damping term which becomes important only when ω is close to a resonant frequency of the molecule):

$$\beta_{ijk}(2\omega) = \frac{1}{2\hbar^2} \sum_{n=0}^{\infty} \sum_{l=0}^{\infty} \left[\mu_{on}{}^{i}(\mu_{nl}{}^{j}\mu_{lo}{}^{k} + \mu_{nl}{}^{k}\,\mu_{lo}{}^{j}) \frac{\omega_{no}\omega_{lo} + 2\omega^2}{(\omega_{no}{}^2 - 4\omega^2)(\omega_{lo}{}^2 - \omega^2)} + \mu_{on}{}^{k}\mu_{nl}{}^{i}\mu_{lo}{}^{j} \frac{\omega_{no}\omega_{lo} - \omega^2}{(\omega_{no}{}^2 - \omega^2)(\omega_{lo}{}^2 - \omega^2)} \right] \qquad (3)$$

where

$$\mu_{pq}{}^{l} \equiv \int \psi_p{}^{*}\hat{\mu}^{l}\,\psi_q \mathrm{d}V$$

and $\hat{\mu}^l$ is the component of the dipole moment operator along axis l, ψ_p and ψ_q are the stationary state wavefunctions of the molecules in states p and q, $\hbar$ is Plank's constant divided by 2π and ω_{pq} is the frequency of transition from state q to state p. Thus second-order polarizability is dependent on the resonant frequencies of the molecule, the permanent and transition dipole moments of the molecule, and the laser frequency.

Treatment of EFISH.[4-6] There is no direct way of measuring the individual components of the polarizability tensors of a single molecule, since a single molecule cannot be isolated and oriented. The standard technique for measuring second-order molecular polarizabilities is EFISH, electric field induced second-harmonic generation. As described in the introduction, the compound to be analyzed is first dissolved in a solvent, ideally one that has a low second-order polarizability. Nonpolar solvents such as 1,4-dioxane, benzene, or hexane satisfy this requirement well. A DC electric field is applied across the solution to induce molecular alignment (coupling to the permanent dipole moment). A laser beam of frequency ω, with electric field component in the same direction as the DC field, is sent through the solution, and the intensity of the generated second-harmonic light (i.e., light of frequency 2ω) is measured. The macroscopic polarization with frequency 2ω can then be computed.

If we choose the X direction as that of the DC and laser fields, statistical mechanical calculations show that (neglecting a small term due to third-order molecular polarizability)[4-6] the X component of the polarization at frequency 2ω, $P_X(2\omega)$, is related to the second-order molecular polarizability by:

$$P_X(2\omega) = (\mu_g\beta_x/5kT)Nf_of_\omega{}^2f_{2\omega}E_X(o)E_X{}^2(\omega) \qquad (4)$$

where $E_X(o)$ is the X component of the DC field, $E_X(\omega)$ is the X component of the laser field, the f terms are local field factors at frequencies zero, ω, and 2ω, N is the number of molecules per unit volume, k is the Boltzman constant, T is absolute temperature, μ_g is the permanent dipole moment of the molecule is the ground state, and β_x, the vector part of the hyperpolarizability tensor, is:

$$\beta_x \equiv \beta_{xxx} + \tfrac{1}{3}(\beta_{xyy} + 2\beta_{yxy} + \beta_{xzz} + 2\beta_{zxz}) \qquad (5)$$

Here the x direction is in the molecular reference frame and is the direction of the permanent dipole moment of the molecule. The local field factors are usually Onsager and Lorenz–Lorentz local field factors, which can be computed from the dielectric constant and refractive index of the solvent. Hence, all quantities are known except for β_x, which can then be calculated from eq 4. Note that EFISH does not measure the individual tensor components β_{ijk}, but measures β_x which is the sum of certain β_{ijk} components (eq 5). To minimize solute–solute interactions, β_x is usually determined at several concentrations and then extrapolated to infinite dilution.

The Two-Level Model.[1,4,17] An alternative approach to determining molecular second-order polarizabilities begins with eq 3. This equation contains complicated summations over all stationary states of the molecule. If one were interested in theoretical calculations, then eq 3 would be acceptable as it stands, since all of the frequencies and dipole moments can be calculated from the wavefunctions of the molecule, which in turn can be computed by means of molecular orbital calculations.[4,18,19] However, eq 3 is not very useful for experimental determinations because most of the quantities involved are not accessible experimentally. To obtain a more tractable equation we adopt the two-level model, an approximation common in quantum theory. In this model all terms in eq 3 beyond the first excited state are ignored; i.e., the infinite sum over all eigenstates is replaced by a sum over only the ground and first excited states.

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For most organic molecules that are of interest for second-harmonic generation the two-level model is a good approximation because the energy difference between the ground and first excited state is considerably less than that between the ground and higher excited states; i.e., there is a first excited state low in energy. Furthermore, both the fundamental and doubled laser frequencies are usually well below the frequencies of transition to the higher excited states. As a consequence, all terms in eq 3 involving these higher excited states are quite small. Typical molecules of interest have an electron-donor group and an acceptor group linked through a π-electron system. As a result, the first excited state is often a low-lying charge-transfer state, usually in the visible or near-UV region of the spectrum. Also, most of these molecules have the donor and acceptor groups located such that the charge transfer takes place primarily along the axis of the permanent ground state dipole moment of the molecule (i.e., the x axis). As a consequence the dominant component of the tensor β_{ijk} is β_{xxx}, often referred to in the literature as β_{CT} (charge transfer). For example, theoretical calculations on PNA 1 (in the vapor) have shown that β_{CT} accounts for 75% of β_x.[21]

Applying the two-level model to eq 3 and setting i, j, and k equal to x results in a relatively simple expression for second-order polarizability:[20]

$$\beta_{xxx}(2\omega) = {}^3\!/_2\hbar^2\mu_{eg}^2(\mu_e - \mu_g)\omega_{eg}^2/(\omega_{eg}^2 - \omega^2)(\omega_{eg}^2 - 4\omega^2) \qquad (6)$$

where ω_{eg} is the frequency of transition from ground to first excited state, μ_{eg} is the transition dipole moment between ground and excited state, μ_g is the permanent dipole moment of the ground state, μ_e is the permanent dipole moment of the excited state, and ω is the laser frequency. This well-known formula for second-harmonic generation has the advantage over eq 3 that all quantities are experimentally accessible. The key to finding a simpler method for analyzing second-order polarizabilities lies in finding simple methods for evaluating ω_{eg}, μ_{eg}, μ_g, and μ_e for solution of eq 6.

Determination of ω_{eg} and μ_{eg}. The frequency of transition, ω_{eg}, can be found simply from the band maximum of the UV–vis absorption spectrum of the molecule. For the purpose of comparison with EFISH, the solvent chosen should be the one used for the EFISH measurements. The transition dipole moment, μ_{eg}, is related to the intensity of the transition and can be gotten from the area under the band by means of eq 7:[7]

$$\text{area} = \int \mathscr{E} M d\omega = 2\pi\omega_{eg}N_o n\mu_{eg}^2 M/3(2.303)\epsilon_o ch \qquad (7)$$

where M = concentration (moles/liter), N_o = Avogadro's number, n = solvent refractive index, $\mathscr{E}$ = molar extinction coefficient, ϵ_o = permittivity of vacuum, c = speed of light in a vacuum, and the integral is over the entire absorption band (MKS units).

Typically the band shape is fairly symmetrical and can be treated as a Lorentzian function.[23] If the extinction coefficient at the maximum and the half width at half maximum are then measured, the area can be found by analytically evaluating the integral in eq 7.

Determination of μ_g and μ_e. The ground-state permanent dipole moment, μ_g, can be determined readily by means of a capacitance bridge. Solutions are prepared at several concentrations, the dielectric constant of each solution is measured, and the dipole moment is then calculated from the Guggenheim–Debye equation:[24]

$$\mu_g^2 = (9kT/4\pi N_o)[3/(\epsilon + 2)(n^2 + 2)](\delta/C) \qquad (8)$$

where ϵ = dielectric constant of solvent, n = refractive index of solvent, C = concentration (mol/cm^3), N_o = Avogadro's number, $\delta = (\epsilon_1 - n_1^2) - (\epsilon - n^2)$, ϵ_1 = dielectric constant of solution, and n_1 = refractive index of solution (CGS units). The value of μ_g is then extrapolated to infinite dilution.

The excited-state dipole moment of the molecule, μ_e, is the most difficult quantity to obtain. The most accurate techniques for determining μ_e make use of electrical dichroism, electrical polarization of fluorescence, or Stark splitting of rotational spectra; these, however, require special equipment.[7-10] A less accurate, but much easier (and thus more suitable to our own goals) method makes use of solvatochromism, which can be defined as the effect of solvent on position, shape, or intensity of the absorption and emission bands of a molecule. In particular, the effect of solvent on the position of the UV–visible absorption maximum, ω_{eg}, can be used to determine μ_e.

Various theoretical treatments of solvatochromic shifts in absorption frequency of a molecule have been developed, most of which are based on a continuum dielectric model in which the solute dipole polarizes surrounding solvent molecules, in turn creating an electric field that perturbs the energy levels of the solute. This perturbing electric field is known as the reaction field and was first described by Onsager.[25] An expression for the solvatochromic shift that we have found useful is that of McRae:[11]

$$(\omega_{eg})_s - \omega_{eg} = A[(n^2 - 1)/(2n^2 + 1)] + B[(\epsilon - 1)/(\epsilon + 2) - (n^2 - 1)/(n^2 + 2)] \qquad (9)$$

$$B = (2/4\pi\epsilon_o\hbar a^3)\mu_g(\mu_g - \mu_e) \qquad (10)$$

where $(\omega_{eg})_s$ = frequency of transition in a solvent, ω_{eg} = frequency of transition in vacuum (dilute vapor), ϵ = dielectric constant of solvent, n = refractive index of solvent, A and B are constants, and a is the radius of a spherical cavity in the solvent occupied by the molecule (MKS units).

Measurement of the absorption maximum in a variety of solvents of known dielectric constant and refractive index permits calculation of constant B from eq 9. The cavity radius a can be estimated by various means.[10] We have assumed that a equals 0.7 times the length of the molecule; this somewhat arbitrary choice gives good fit to McRae's equation and gives values of μ_e that compare well with available literature values, Table III. Solution of eq 10 then gives the dipole-moment difference $(\mu_g - \mu_e)$ from which μ_e can be calculated and compared with literature values. Note that it is only necessary to know the difference term $\mu_g - \mu_e$ to compute β_{xxx} from eq 6. It is the uncertainty in estimating a, as well as the various assumptions made in deriving eq 9, that make the solvatochromic method of calculating μ_e less accurate than electrical dichroism, electrical polarization of fluorescence, or Stark splitting. Nonetheless the data obtained from solvatochromism compare well with those obtained by the more elaborate methods (and application of the solvatochromic method requires only a simple US–vis spectrometer).

In summary, we have presented methods permitting ready determination of ω_{eg}, μ_{eg}, μ_g, and μ_e, which can be used to solve eq 6 for $\beta_{xxx}(2\omega)$.

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Table I. Ground-State Dipole Moments (μ_g) and Second-Order Polarizabilities in Dioxane as Measured by EFISH (β_x) or Solvatochromism (β_{xxx})

		1064 nm		1907 nm	
compd	μ_g, D	β_x[a]	β_{xxx}[a]	β_x[a]	β_{xxx}[a]
1, PNA	7.13	29	17	12	9.6
2, DMNB	7.14	57	22	22	12
3, DAN	8.10	36	16	13	9.5
4, DMNP	5.97	38	23	20	13
5, PNB	7.50	45	34	25	17
6, NMB	5.34	13	5.7	5	4
7, NTA	4.61	23	10.6	16	6.7
8, DANS	7.10[b]	450[c]	323[c]	–	–

[a] All values multiplied by 10^{30} esu. [b] Reference 7. [c] Measured in acetone.[28]

Experimental Methods

Synthetic Methods. All samples utilized were rigorously purified:

PNA, 4-nitroaniline, 1, was Aldrich Gold Label material which was Kugelrohr distilled and then recrystallized from methanol.

DMNB, 4-(dimethylamino)-1-nitrobenzene, 2, was prepared by aromatic nucleophilic substitution reaction between excess aqueous dimethylamine and 1-fluoro-4-nitrobenzene in *N*-methylpyrrolidinone. The product was precipitated with water and recrystallized from ethanol/tetrahydrofuran.

DAN, 3-acetamido-4-(dimethylamino)-1-nitrobenzene, 3, was prepared by acetylation of 3-amino-4-fluoronitrobenzene (purified by column chromatography) with acetic anhydride in chloroform and the resultant intermediate subjected to aromatic nucleophilic substitution reaction with excess dimethylamine in dimethyl sulfoxide. The crude DAN was isolated by precipitation with water and then recrystallized from ethyl acetate.

DMNP, 2-(dimethylamino)-5-nitropyridine, 4, was prepared by aromatic nucleophilic substitution reaction between 2-chloro-5-nitropyridine and excess aqueous dimethylamine in *N*-methylpyrrolidinone. The crude product was isolated by precipitation with water and then twice recrystallized from ethanol.

PNB, 4-pyrrolidinonitrobenzene, 5, was prepared by aromatic nucleophilic substitution reaction between pyrrolidine and 1-fluoro-4-nitrobenzene in *N*-methylpyrrolidinone. The crude product was precipitated with water and then twice recrystallized from ethanol/water.

NMB, 4-nitroanisole, 6, was an Eastman sample that had been recrystallized four times from methanol.

NTA, methyl 4-nitrophenyl sulfide, 7, was an Aldrich 90% tech grade sample that was Kugelrohr distilled to remove an unidentified high-boiling impurity and the distillate crystallized twice from methanol.

DANS, 4-(dimethylamino)-4′-nitrostilbene, 8, was prepared by β-alanine-catalyzed Perkin condensation between 4-(dimethylamino)benzaldehyde and 4-nitrophenylacetic acid. The crude product was crystallized from toluene.

Determination of μ_g. All measurements were carried out in 1,4-dioxane (OmniSolv grade from EM Science), which was used without further purification. The dielectric cell was made of two coaxial stainless steel cylinders of 7-cm length. These cylindrical electrodes were rigidly separated by Teflon spacers at a distance of about 0.8 mm. The electrode assembly was enclosed in a glass tube having a total sample volume of 20 cm^3. The entire enclosed assembly was then placed in a thermostated oil bath at 30.0 ± 0.1 °C. The (air) capacitance of the empty cell was determined to be 51 pF at this temperature. The capacitance (of the cell) was then measured when the cell was filled with pure dioxane and when filled with a series of solutions of each compound using an HP Model 4275A multifrequency LCR meter set to 100 KHz. The dielectric constants of the solutions were determined relative to a reference value of 2.2090 for pure dioxane.[26] The refractive indexes of the dilute solutions were assumed to be equal to that of pure dioxane at 25 °C, 1.4224.[26] The value of μ_g for each compound was then calculated from eq 8, Table I.

Table II. Ultraviolet–Visible Absorption Data for Calculation of the Transition Dipole Moment μ_{eg}

compd	ω_{eg}, cm^{-1}	ϵ	half-width at half-maximum, cm^{-1}	μ_{Eg}, D
PNA, 1	28333	14605	2467	5.08
DMNB, 2	26178	19365	1889	5.34
DAN, 3	27778	9047	2838	4.33
DMNP, 4	27322	21633	2215	5.97
PNB, 5	25773	21542	1948	5.75
NMB, 6	32895	11083	2958	4.50
NTA, 7	29586	16211	2445	5.21
DANS, 8	23148	28359	2716	8.41

Determination of β_x by EFISH. EFISH experiments were performed at fundamental wavelengths of 1.06 and 1.9 μm applying the method described in ref 5 and 6. The 1.06-μm radiation was derived from a Q-switched ND:YAG laser (Quanta Ray DCR-2, repetion rate 10 Hz, pulse duration 15 ns) and the 1.9-μm radiation was obtained by Raman shifting the 1.06-μm radiation in a high-pressure (20 kPa) hydrogen cell. The laser beam was focused by a 40-cm lens into the liquid cell and the generated second harmonic light was then detected by a photomultiplier after blocking the fundamental radiation by appropriate interference filters.

The liquid cell was comprised of two wedge-shaped fused silica (Suprasil) windows mounted on a stainless steel plate. This plate also served as the bottom electrode in the experiment. The windows were of dimensions 20 mm × 16 mm × 4 mm with a wedge angle of 3° providing a liquid compartment of 1–3 mm length. A 20 mm long stainless steel top electrode was used to get an electric field that was homogeneous inside the liquid cell and decayed to zero within the extensions of the cell windows. As a result Maker fringe patterns of uniform amplitude and well-defined nulls were obtained. All parts were assembled using silicon rubber adhesive that proved to be solvent resistant and a good high voltage isolator. The high voltage pulses applied across the cell were of 10-kV amplitude and 5-μs duration yielding an electric field of 25 kV/cm.

A LiIO$_3$ wedge, mounted on the same linear translation stage as the liquid cell, was used for absolute calibration of the second-harmonic signal. It turned out the experimental error of the β_x value obtained was mostly due to this calibration measurement that involved switching back and forth between liquid cell and crystal wedge. Better accuracy was obtained by using a standard solution as a reference instead. We have thus carefully calibrated a solution of 1% (by weight) 2-methyl-4-nitroaniline in dioxane against the reference crystal yielding a value of 3.13(15) × 10^{-13} esu (1.56(8) × 10^{-13} esu) for its nonlinear response coefficient Γ at 1.06 μm (1.9 μm, respectively) fundamental radiation. This solution was then used in all the further experiments for calibration to provide a higher relative accuracy of the hyperpolarizabilities for the various molecules investigated.

A more detailed description of the EFISH measurements will be published elsewhere.[27]

Determination of ω_{eg} and μ_{eg}. With the exception of DANS, 8, all measurements were made in anhydrous, gold label 1,4-dioxane (Aldrich) and used without further purification. Solutions of each compound at four concentrations were prepared, and UV-vis spectra were obtained in the range 200–800 nm using an HP 8452A diode array spectrometer. The value of ω_{eg} for each compound was determined from the position of the lowest energy band maximum, and the half width at half maximum was also measured. The molar extinction coefficient, $\mathcal{E}$, was determined by means of a linear regression fit of the data to Beer's law. From this information, and the refractive index of dioxane, the transition dipole moment, μ_{eg}, was computed from eq 7. The value of μ_{eg} for DANS was determined in electronic grade acetone (Fisher) to permit comparison with a literature value of β_x in this same solvent.[28] The results are summarized in Table II.

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Table III. Solvatochromism Data and Excited-State Dipole Moments μ_e (eq 9)

compd	a, Å	μ_e, D	σ,[a] %	μ_e lit.,[b] D
PNA, **1**	4.4	14.2	9.13	14.0–15.0
DMNB, **2**	4.9	13.1	9.55	12.0–15.0
DAN, **3**	4.9	16.6	5.54	–
DMNP, **4**	4.9	11.8	7.53	–
PNB, **5**	5.4	14.8	9.15	–
NMB, **6**	4.6	10.3	7.66	–
NTA, **7**	4.7	9.4	7.05	–
DANS, **8**	8.7	25.4	4.53	25.0–26.0

[a] Standard deviation for fit of solvatochromism data to the McRae equation as in Figure 1, expressed as percent of spread of experimental frequency shifts. [b] Obtained by electrical dichroism methods.[7]

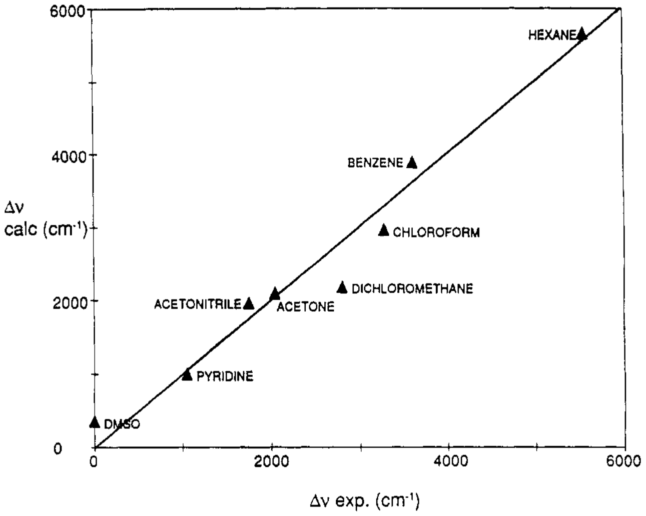

Figure 1. Solvatochromism data for DAN ($\Delta\nu$ relative to 25126 cm^{-1}).

Determination of μ_e and β_{xxx}. For the solvatochromic determinations, all solvents were anhydrous gold label quality purchased from Aldrich and dried for 24 h over 3-Å molecular sieves (4–8 mesh, Aldrich), except for hexane and benzene which were dried over 4-Å sieves. Drying is important since small amounts of water can cause shifts in absorbance maxima. The solvents chosen were those expected to have little or no specific type of interaction either internally or with the solute other than electrostatic dipole–dipole forces. Thus hydroxylic solvents such as water or alcohols were exluded because of their hydrogen-bonding ability. The solvents that were found to be most suitable were hexane, benzene, chlorobenzene, chloroform, dichloromethane, pyridine, acetone, acetonitrile, and dimethyl sulfoxide. Dioxane was not included in the solvatochromic determinations because, as noted previously,[10] it is not adequately described by the simple electrostatic model used here. The dielectric constants and refractive indices for these solvents at 25 °C were obtained from the CRC handbook.[26]

The value of ω_{eg} for each compound in each solvent was measured, and the data were fitted by means of linear regression to eq 9 to yield values of the constants A and B. An estimate of the cavity radius, a, was obtained from a = 0.7(length of molecule), where the molecule length was gotten from adding literature values of the bond lengths.[18,19,26] The value of μ_e was then computed by means of eq 10 (Table III). The data for DAN, **3**, shown in Figure 1 is representative of the fit of the solvatochromic shifts to the McRae equation.

The data for ω_{eg}, μ_{eg}, μ_g, and μ_e were then used to calculate values of β_{xxx} in dioxane from eq 6 for laser wavelengths 1064 and 1907 nm. The results obtained for each compound, along with values of β_x determined by EFISH, are summarized in Table I.

Results and Discussion

For the solvatochromic method to be useful it is important that the solvatochromic shifts be well described by the McRae equation, eq 9, so that the resulting excited state dipole moments, μ_e, will be accurate. The fit of the solvatochromic shifts to the McRae equation is excellent as shown by the plot of calculated vs observed shifts for the example of DAN, **3**, Figure 1; plots of similar quality were observed for the other compounds as shown by the standard deviations of less than 10%, Table III. This same table also shows excellent agreement between the solvatochromic μ_e values and the three known values determined by other methods.

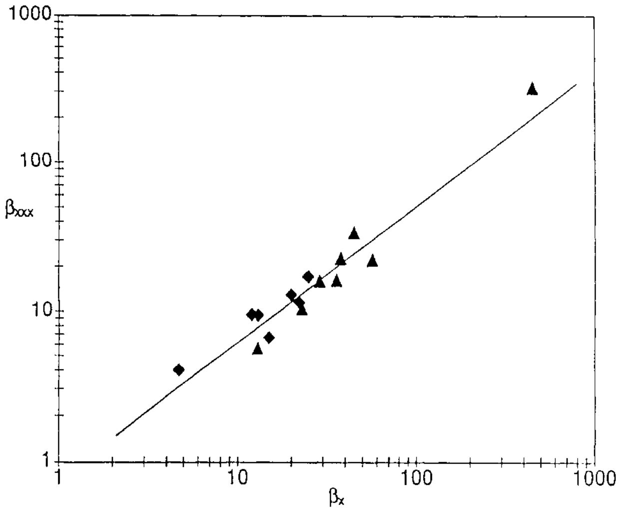

Figure 2. Scatter plot of β_{xxx} vs β_x. Data represented by ▲ is for wavelength 1064 nm and data represented by ◆ is for wavelength 1907 nm.

It appears then that the validity of the present approach will only be limited by the two-level approximation and the degree to which β_{xxx} represents β_x. At 1064 nm, the values of β_{xxx} are generally about half the values of β_x; and at 1907 nm, the values of β_{xxx} are about two-thirds those of β_x. As apparent from eq 5, the values of β_{xxx} are not expected to be equal to those of β_x. They are two different quantities; β_x is the vector part of a tensorial property, whereas β_{xxx} is only one component of the tensor. Furthermore, it should be pointed out that there is often considerable spread in the reported literature values of β_x determined by EFISH for a particular compound. For example, published values of β_x at 1064nm for PNA, **1**, in dioxane range from 16.7 × 10^{-30} esu to 34.3 × 10^{-30} esu.[4] For these reasons a direct comparison of the absolute magnitudes of these two quantities is not very informative. The meaningful result is the comparison of the trend in the values of β_{xxx} with the trend in the values of β_x. As seen from Table I and Figure 2 (a scatter plot of β_{xxx} vs β_x), the trends in these two quantities are in excellent agreement at both laser wavelengths. Thus is seems that β_{xxx} can be used as well as β_x for evaluating the relative merit of small organic molecules for SHG (the value of the method for very large molecules remains to be tested).

In summary, we find that the McRae equation is useful for obtaining good values for excited state dipole moments of organic molecules. Furthermore, the values of β_{xxx} obtained from solvatochromic measurements compare well with the values of β_x obtained by EFISH. Hence we conclude that the solvatochromic method provides the chemist with a very useful and simple alternative to EFISH for analyzing second-order polarizabilities of organic molecules.

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