Dissociation Constants of Weak Organic Acids in Protic Solvents Obtained from Their First Hyperpolarizabilities in Solution

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The first hyperpolarizabilities (β) of some weak aromatic organic acids have been measured in protic solvents by the hyper-Rayleigh scattering (HRS) technique at low concentrations. The measured hyperpolarizability (β_m) varies between the two extreme limits: the hyperpolarizability of the acid form (β_{HA}) at the lower side and that of the basic form (β_{A^-}) at the higher side. The degree of dissociation (α) of the acid in a solvent is related to the measured hyperpolarizability, β_m, by the following relationship: $\beta_m^2 = (1 - \alpha)\beta_{HA}^2 + \alpha\beta_{A^-}^2$. The calculated β's including solvent effects in terms of an Onsager field do not reproduce the experimentally measured hyperpolarizabilities. Other solvent-induced effects like hydrogen bonding and van der Waals interactions seem to influence the first hyperpolarizability and, thus, indirectly the extent of dissociation of these weak acids in these protic solvents.

Introduction

Second-order light scattering in isotropic samples has gathered momentum recently, since accurate first hyperpolarizabilities (β) of molecules as well as solvents can be obtained from hyper-Rayleigh scattering (HRS) intensities in solution.[1−6] It is well-known that some weak organic acids (e.g., 4-(4′-aminophenyl)-azobenzoic acid, 6-aminonicotinic acid, 3-hydroxybenzoic acid, etc.)[7] show high macroscopic second-order nonlinearities in powder form. But their microscopic polarizabilities have not been measured, the primary reason being that the traditional electric-field-induced second-harmonic generation (EFISHG) technique,[8] which requires the application of a strong DC field, cannot be used with these molecules which dissociate partially in solution. The field will cause migration of ionic species rather than dipolar orientation in the direction of the field. The HRS technique, on the contrary, is a nonperturbative technique, and the dependence of the double-quantum Rayleigh scattering intensity on the concentration of the nonlinear optical (NLO) chromophores allows for an accurate determination of β. Ionic molecules in highly polar solvents can be routinely handled for measurements.[9−11]

Using the advantages offered by the HRS technique, in this paper, we present the first systematic results on the second-order NLO coefficients of some aromatic push−pull weak organic acids in various protic solvents. We have chosen different acidic functional groups (which normally act as acceptors) and electron donor groups attached to aromatic moieties of various molecular lengths.

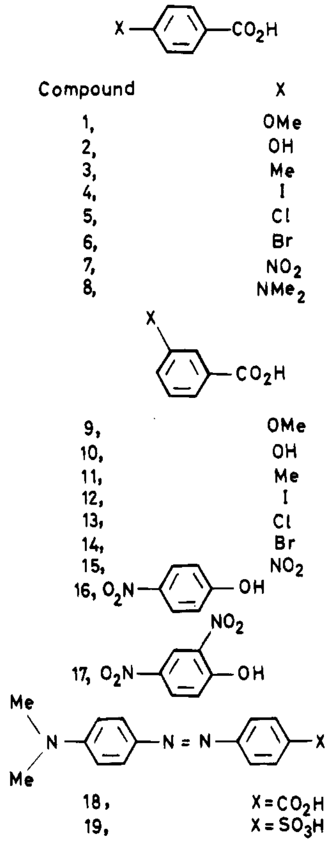

Figure 1. Structures of compounds **1**−**19**.

Experimental Section

Compounds **1**−**19** (Figure 1) were purchased from Aldrich. Solvents were obtained locally and purified through standard procedures. The experimental apparatus for the HRS measurement is described in detail elsewhere.[5] Briefly, the fundamental of a Q-switched Nd:YAG laser (Spectra Physics, 8 ns, ≤12 mJ/pulse) is focused onto a 4 × 4 × 2 cm^3 cell containing the solution of compounds. The scattered second-harmonic light is collected by an efficient optical imaging system at the photocathode of a UV−visible photomultiplier tube. Other linearly scattered frequencies are eliminated first by a low-band-pass filter and finally by a 4 nm bandwidth 532 nm interference filter. A small fraction of the 1064 nm fundamental is directed toward an IR sensitive photomultiplier tube for monitoring the incident light intensity. Gated integrators are used to retrieve the actual intensities of the incident and scattered second-harmonic signal pulses after averaging over 1000 shots. All data are collected at laser powers (≤12 mJ/pulse) well below the threshold for stimulated Raman and Brillouin scattering, self-focusing or self-defocusing, and dielectric breakdown.

The total intensity of the second-harmonic scattered light, $I_{2\omega}$, is given by the following[12,13]

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$$I_{2\omega} = GB^2 I_\omega^2 = G\sum_k N_k|\beta_k|^2 I_\omega^2 \qquad (1)$$

where G depends upon the scattering geometry and contains the average of the products of the direction cosines and the local field corrections including the instrumental factor. I_ω is the incident light intensity, and N_k is the number density of the k-th species, which has the second-order polarizability β_k. For a two-component system, we can write

$$B^2 = N_{\text{solvent}}\beta_{\text{solvent}}^2 + N_{\text{solute}}\beta_{\text{solute}}^2 \qquad (2)$$

and from the $I_{2\omega}/I_\omega^2$ vs N_{solute} plot, β_{solute} is normally obtained. Since low concentrations ($\sim 10^{-6}$ M) of solute are used, it is assumed that the presence of the solute molecules does not change the number density of the solvent molecules, N(solvent), significantly. Terhune et al.[13] calibrated carbon tetrachloride with respect to quartz, using the same HRS technique, and we have calibrated water, methanol, ethanol, propanol, and ethylene glycol with respect to carbon tetrachloride by a method similar to that of Zyss et al.[6] and obtained values of $\beta_{\text{water}} = 0.05 \times 10^{-30}$ esu, $\beta_{\text{ethylene glycol}} = 0.41 \times 10^{-30}$ esu, $\beta_{\text{methanol}} = 0.52 \times 10^{-30}$ esu, $\beta_{\text{ethanol}} = 0.61 \times 10^{-30}$ esu, and $\beta_{\text{propanol}} = 0.48 \times 10^{-30}$ esu.

The widely used eq 2 above is applicable when the concentration of the solute remains unchanged. From this equation the average $\langle\beta_{\text{solute}}^2\rangle$ value is obtained by measuring the incoherent second-harmonic scattering light intensity. The square-root of this quantity gives the measured average first hyperpolarizability, $\langle\beta\rangle$. However, the weak organic acids considered here dissociate in the protic solvents employed in the experiments and a dependence of β on the degree of dissociation (α) is expected. The neutral molecules are weak acids, HA, with first hyperpolarizability β_{HA}. The initial concentration of HA (C_0) and the actual concentration ($C = N_0(1 - \alpha)$, where N_0 is the initial number density of HA) in solution will be different due to the dissociation reflected in the following equilibrium

$$\text{HA} \Leftrightarrow \text{H}^+ + \text{A}^-$$

The conjugated base, A^-, will have another hyperpolarizability β_{A^-} distinctly different from β_{HA}, just as they also have other linear absorption characteristics, and its concentration in solution is given by $N_0\alpha$. In a given solvent the contribution of these two forms (acidic and basic) weighed appropriately with α should satisfy the measured HRS intensity in solution. We rewrite eq 2 in the following way for these weakly acidic molecules

$$B^2 = N_{\text{solvent}}\beta_{\text{solvent}}^2 + N_0(1-\alpha)\beta_{\text{HA}}^2 + N_0\alpha\beta_{\text{A}^-}^2 \qquad (3)$$

The degree of dissociation is not constant and varies with the initial concentration. At an initial concentration of 10^{-6} to 10^{-4} M in ethanol α remains very small[14-16] (e.g., for compound **1**, α varies in the range 0.52×10^{-2} to 0.52×10^{-3}) and the third term in eq 3 may be neglected to obtain

$$B^2 = N_{\text{solvent}}\beta_{\text{solvent}}^2 + N_0(1-\alpha)\beta_{\text{HA}}^2 \qquad (4)$$

From the $I_{2\omega}/I_\omega^2$ vs $N_0(1 - \alpha)$ plot (Figure 2a) β_{HA} is derived, since β_{solvent} is known. The intercept provides G, which may be used for calculating β_{m}, defined as

$$I_{2\omega}/I_\omega^2 = G(N_{\text{solvent}}\beta_{\text{solvent}}^2 + N_0\beta_{\text{m}}^2) \qquad (5)$$

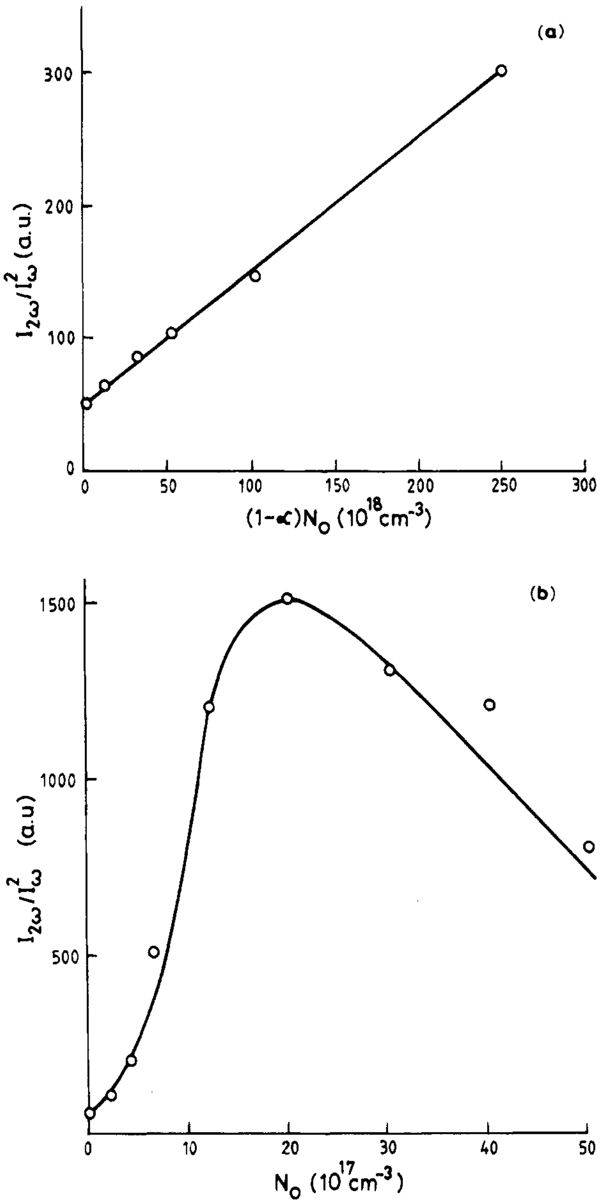

Figure 2. Quadratic coefficient $I_{2\omega}/I_\omega^2$ vs number density of (a) compound **1** in ethanol and (b) compound **18** in alkaline water.

in other solvents. In other words, β_{m}^2 is given by

$$\beta_{\text{m}}^2 = (1-\alpha)\beta_{\text{HA}}^2 + \alpha\beta_{\text{A}^-}^2 \qquad (6)$$

From eq 5 β_{m}^2 is measured as a function of initial concentration, N_0, i.e., in terms of varying α in other solvents. And from the intercepts at $\alpha = 0$ and 1 in the β_{m}^2 vs α plot, β_{HA}^2 and $\beta_{\text{A}^-}^2$, respectively, are obtained.

The above analysis is adequate for weak organic acids which (as well as whose basic counterparts) do not absorb significantly at the incident frequency ω or the second-harmonic frequency 2ω. However, compounds **18** (methyl red) and **19** (methyl orange) absorb in the green, and corrections as suggested by Verbiest et al.[10] are necessary in these cases. Equation 1 may be modified to take into account the absorption at the harmonic frequency, as

$$I_{2\omega} = 10^{-l\{\epsilon_{\text{HA}}(2\omega)N_0(1-\alpha)+\epsilon_{\text{A}^-}(2\omega)N_0\alpha\}}GB^2I_\omega^2 \qquad (7)$$

where $\epsilon(2\omega)$ are the absorption cross sections (in cm^2) of the respective species at the second harmonic frequency and l (in cm) is an effective path length. We obtain Figure 2b for

TABLE 1: Second-Order NLO Coefficients β^{eth} (× 10^{30} esu), of 1–19 Measured by the HRS Technique in Ethanol

compound	μ_g[a]	μ_{eth}[b]	β_g[c]	β^{eth}(calc)	β^{eth}(measd)
1	6.8	9.4	4.1	30	36
2	6.4	9.2	3.8	26	30
3	6.0	9.0	3.3	24	29
4	5.8	8.8	3.0	21	26
5	5.6	8.7	2.8	19	24
6	5.2	8.5	2.7	16	22
7	5.0	8.2	2.0	15	20
8	7.2	10.2	4.8	27	20
9	6.1	8.2	3.2	18	24
10	5.9	8.0	3.1	14	18
11	5.2	7.6	2.9	14	18
12	4.9	7.4	2.6	16	20
13	4.7	7.3	2.4	12	16
14	4.6	7.1	2.3	9	13
15	6.2	9.4	4.2	10	12
16	4.8	7.4	4.6	18	22
17	6.4	9.2	4.8	21	25
18	10.8	15.0	22.8	78	135
19	11.6	16.2	26.2	108	164

[a] Calculated gas phase dipole moment in D. [b] Dipole moment in ethanol in D. [c] First hyperpolarizability in the gas phase (× 10^{30} esu).

compound **18**, which fits 7 taking the path length in our setup as 1 cm. A similar procedure was adopted for methyl orange (**19**). It may be worth noting that it is also possible to obtain a reliable hyperpolarizability for these two dyes using the linear part of Figure 2b (low-concentration results) with eq 1. Compounds **18** and **19** were studied in water in the alkaline pH range, and a drop of 1 M NaOH solution was added to the solution of these compounds before making the β measurement. The measured hyperpolarizabilities are correct within ±5%.

All spectra were recorded in a Hitachi (U-3400) spectrometer at room temperature. For recording the spectrum in the acid form, freshly prepared solutions of **1–19** in ethanol with initial concentrations of 10^{-3} to 10^{-4} M (to achieve $\alpha < 10^{-2}$) were taken. For the absorption spectrum in the basic form, 10^{-6} to 10^{-7} M solutions of the compounds in water were used. For compounds **16**, **18**, and **19**, one drop of 1 M NaOH was added to ensure complete dissociation in solution.

Results and Discussion

The microscopic hyperpolarizabilities (β) of compounds **1–19** in ethanol are listed in Table 1. For compounds **18** and **19** propanol was also used as an additional solvent. All the compounds are substituted weak aromatic acids and exhibit appreciable second-order nonlinearities in solution. For the para- and meta-substituted benzoic acid derivatives, the first hyperpolarizability in a solvent varies according to the strength of the donor groups. For example the OMe group is a better electron donor among the substituents studied in this paper, and we find that *p*-methoxybenzoic acid exhibits the highest value of β among the benzoic acid derivatives. The dimethylamino group is an even stronger donor than the methoxy substituent, but the β value is less for compound **8** due to some other complications which will be addressed later in the discussion. In fact, with this exception the trend in β values for a particular acid series correlates very well with the trend in the Hammett σ-parameters for the substituents. In other words, a better donor in the para position leads to higher second-order nonlinearity in benzoic acids. The para-substituted benzoic acid derivatives have higher β values than the corresponding meta compounds, since the participation of an electron donor in the para position in stabilizing the canonical charge transfer excited state[17] is more than that of one in the meta position. For compounds **18** and **19** the conjugation length between the donor and the acid (acceptor) groups is higher and, consequently, they have higher hyperpolarizabilities. In the case of methyl red (λ_{max} = 441 nm for the acid form and 495 nm for the basic form) and methyl orange (λ_{max} = 438 nm for the acid form and 485 nm for the basic form), the high β value is largely due to the resonance enhancement.

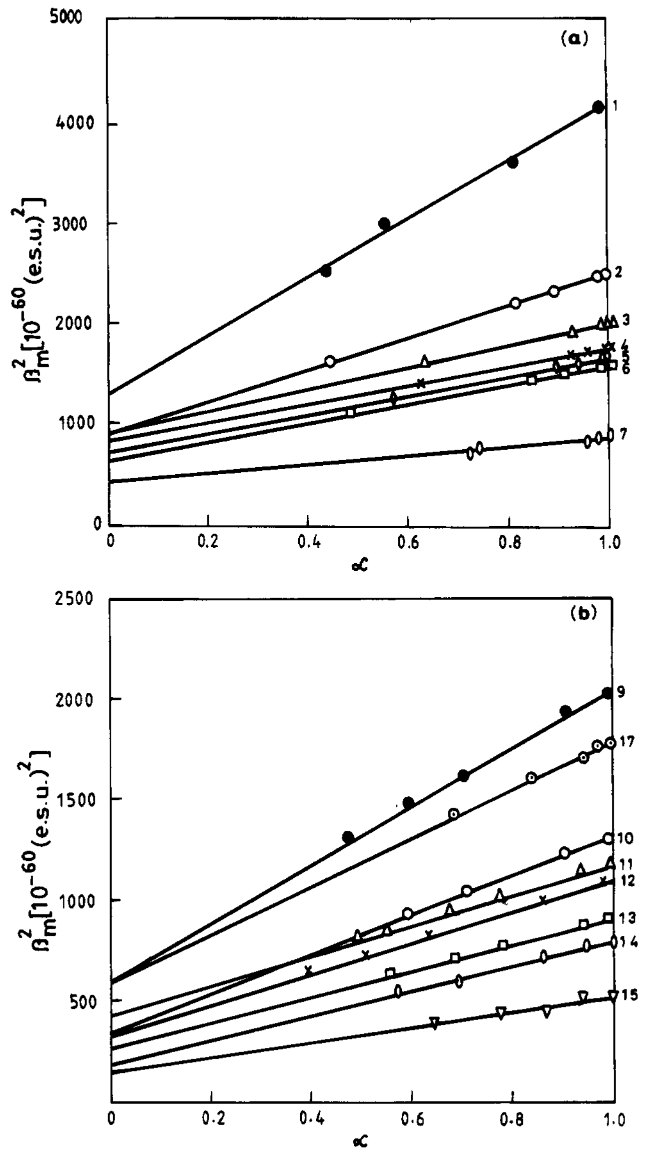

Figure 3. β_m^2 vs α of (a) compounds **1–7** and (b) compounds **9–15** and **17**.

We have carried out quantum chemical calculations on the static β response at the Hartree–Fock (HF) ab initio level using a split valence (6-31G*) basis set using the Gaussian-92 set of programs,[18] after performing a full geometry optimization in the ground state within the AM1 framework.[19] The calculated ground state dipole moment (μ_g) and first-order hyperpolarizability in the gas phase (β_g) for each compound are also listed in Table 1. Although the trend in the calculated gas phase β matches that of the experimental β in these compounds, the gas phase numbers are much lower. This is mainly because the influence of solvation is significant on β and intermolecular interactions are not taken into account in the gas phase computations. To take into account solvent effects, at least partially, we adopted Onsager's self-consistent reaction field approach,[20] as implemented in the Gaussian-92 set of programs. In this approach, the solute dipole is considered to occupy a spherical cavity in a continuum of solvent molecules (medium of dielectric constant D). The molecular dipole moment (μ_g)

TABLE 2: Second-order Nonlinearities (in 10^{-30} esu) of the Acid (β_{HA}) and Basic (β_{A^-}) Forms Obtained in Water and Calculated

compound	β_{HA}	β_{A^-}	β_{calc}^{water}
1	36.2	65.0	36.4
2	30.3	50.0	30.2
3	28.5	44.8	25.8
4	26.4	40.9	25.3
5	24.0	38.9	25.1
6	22.6	36.9	20.4
7	20.8	29.7	14.1
8	20.1	38.2	41.2
9	24.7	45.2	28.1
10	18.8	36.2	24.0
11	18.2	33.4	19.9
12	20.6	34.2	17.2
13	16.3	30.1	15.4
14	13.6	28.2	11.8
15	12.0	22.0	11.1
16	22.8	41.2	18.2
17	24.1	44.1	31.5
18	135.2	185.4	98.0
19	164.6	209.6	112.1

and hyperpolarizability (β_g) were then calculated through the coupled perturbed Hartree–Fock (HF) scheme[9,21] in the presence of the appropriate dielectric. The calculated static hyperpolarizability in ethanol increases approximately 7 times (Table 1) as we increase the dielectric constant 24-fold (from 1 in the gas phase to 24 in ethanol). This actually points out that the dipolar contribution to β in solution is appreciable and cannot be neglected. However, the theoretical value of β calculated within the Onsager model is still lower by a factor of 1.2 than the experimentally measured value. This is not at all surprising, since effects related to electron correlation and frequency dispersion, hydrogen bonding, and ionic interaction are not considered in our calculations.

Also in water the degree of dissociation, α, of these weak acids can be altered by changing the initial concentration, i.e., N_0. For each N_0, we obtain α from pK_a values known in the literature,[14–16,22–27] and β_m is calculated from eq 5. Parts a and b of Figure 3 show the plots of β_m^2 vs α for all the para- and meta-substituted benzoic acids, respectively. The linear nature of the plots confirms the adequacy of eq 6 in describing the relationship between α and the measured hyperpolarizabilities. Compound **16** is not included in Figure 3, since the range of α obtainable in water by varying the initial concentration is limited. Methyl red (**18**) and methyl orange (**19**) molecules are not included, since they absorb light at ~532 nm and after a certain concentration ($\geqslant 10^{-4}$ M) second-harmonic light could not be detected in water.

From the two extreme limits of the α vs β_m^2 plot, i.e., at α = 0 and 1, the values of the first hyperpolarizabilities of the undissociated and dissociated forms of these weak organic acids in water are obtained (Table 2). The calculated hyperpolarizabilities in water are also listed for comparison. The β value for the conjugated base is greater than that of the corresponding undissociated neutral acid form. The conjugated base has an absorption spectrum that is red-shifted with respect to the spectrum of the neutral species (Table 3). This has a positive effect on the value of the first hyperpolarizability, β. This may be understood on the basis of the two-state model which predicts[28] $\beta_0 \propto (\lambda_{max})^n$ where $n \geqslant 3$ and β_0 is the second-order polarizability corrected for dispersion. In fact for para- and meta- (data not shown) substituted benzoic acids and their basic forms, the data (Figure 4) are in agreement with the prediction within some uncertainty. Alternatively, COO^- and SO_3^- are stronger electron-withdrawing groups than COOH or SO_3H and, therefore, it is expected that β_A^- would be greater than β_{HA} in these examples.

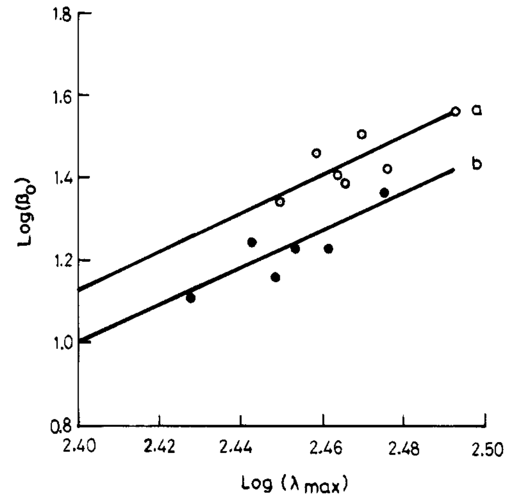

Figure 4. Logarithmic plot of β_0 ($\times 10^{30}$ esu) vs λ_{max} (nm) for *p*-benzoic acid derivatives, **1**–**7**: (a) basic form (unfilled circles); (b) acid form (filled circles). The solid line is a least squares fit through the experimental points, and the calculated slopes are (a) 4.36 and (b) 4.26, respectively.

TABLE 3: Wavelength of Maximum Absorption in the Acidic and Basic Forms of 1–19 in nm

compound	λ_{max}(acid)	λ_{max}(basic)
1	298.6	309.2
2	279.6	294.8
3	276.8	287.4
4	289.4	299.2
5	284.1	290.6
6	280.6	291.8
7	267.8	281.7
8	294.6	310.1
9	287.6	298.2
10	272.8	284.1
11	269.1	274.4
12	284.6	295.2
13	279.2	288.6
14	271.6	282.8
15	261.8	272.6
16	311.0	328.0
17	319.0	332.0
18	441.0	495.0
19	458.0	485.0

Using the β_{HA} and β_{A^-} values in water, we can derive the degree of dissociation of the weak acid at a particular concentration in another protic solvent from eq 6 by measuring the first hyperpolarizability (β_m) at that concentration. From the knowledge of α, the equilibrium constant in that solvent can be easily obtained. Table 4 compares the results for compounds **1**–**19** in two other protic solvents with those obtained from the literature,[14–16,22–27] and the agreement between our equilibrium constant and the literature value is excellent. Therefore, we propose this as an alternate method for measuring the dissociation constant of a weak organic acid in a protic solvent. However, an important caution is necessary at this point before we investigate this phenomenon in more detail. If the weak organic acid exists as a zwitterion in solution, as in compounds **8**, **18**, and **19** in this study, the equilibrium in solution is maintained between the zwitterion and the acid form (i.e., HA). In that event, A^- is no longer the conjugated base. Although we expect that the zwitterion hyperpolarizability (β_{zwi}) is still obtainable from the α = 1 limit, its full implications are not yet clear. It appears from the measured hyperpolarizabilities of compound **8** that the zwitterionic form of the acid (if it exists)

TABLE 4: Equilibrium Constants for Dissociation of 1–19 in Ethylene Glycol and Methanol Calculated from β_m[a]

compound	K_a^{methanol} (10^{-10} M)	$K_a^{\text{ethylene glycol}}$ (10^{-10} M)
1	1.66 (1.67)	39.81 (40.06)
2	1.91 (1.93)	25.11 (25.24)
3	2.88 (2.89)	50.11 (51.20)
4	9.14 (9.32)	143.87 (143.34)
5	9.46 (9.71)	377.50 (379.20)
6	7.94 (8.12)	398.00 (398.90)
7	39.85 (40.00)	794.10 (796.12)
8	12.83 (13.10)	441.85 (443.40)
9	1.58 (1.71)	25.11 (25.43)
10	2.66 (2.74)	125.89 (127.21)
11	13.06 (13.42)	309.00 (311.12)
12	3.16 (3.21)	39.81 (40.06)
13	13.80 (14.03)	398.00 (401.10)
14	14.09 (14.14)	478.00 (481.20)
15	43.05 (45.00)	501.10 (504.00)
16	1.31 (1.35)	21.43 (22.20)
17	137.00 (139.20)	199.50 (201.42)
18	6.30 (6.33)	97.70 (98.13)
19	8.43 (8.50)	118.40 (120.60)

[a] The values in parentheses, derived from ref 14–16 and 22–27, are listed for comparison (see text for details).

has a lower hyperpolarizability than the corresponding conjugated base. This can perhaps be accounted for by the fact that the dimethylamino group becomes an acceptor after capturing a proton from the acidic end of the molecule, resulting in a decrease of its electron-donating strength.

Conclusions

In this paper, we have investigated the first hyperpolarizabilities of some weak aromatic acids in polar protic solvents. These acids dissociate partially in solutions of polar solvents, and by measuring the hyper-Rayleigh scattering intensity in a solvent as a function of the degree of dissociation (by varying the initial concentration), it is possible to obtain the hyperpolarizabilities of the undissociated acid (β_{HA}) and the conjugate base (β_{A^-}). From β_{HA} and β_{A^-} thus derived, the equilibrium constant (K_a) for the acid dissociation in another polar solvent can be easily obtained from the measured hyperpolarizability (β_m) in that solvent. $\beta_m{}^2$ is found to vary linearly with α from our experimental results. Although acids which exist in the zwitterionic form in solution seem to obey the same relationship, more examples of such acids need to be studied before the equations derived here are applicable to them. However, we believe that, for any weak organic acids that dissociate into a proton and a base in protic solvents, hyper-Rayleigh scattering intensity measurements can be used to determine their acid constants.

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