Synthesis and Characterization of Some Pyridinium-*N*-phenoxide Betaine Dyes for Second-Harmonic Generation

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Received February 12, 1990

The synthesis and characterization of some pyridinium-*N*-phenoxide betaine dyes (including Reichardt's dye) for second-harmonic generation (SHG) is described. These dyes are highly solvatochromic, which indicates that they can have large second-order molecular polarizabilities. The effects of substituents on the solvatochromic and optical properties of the betaines are investigated. Also the crystal structure of the betaines is discussed and the molecular geometry in the crystal is compared to that predicted by AM1 calculations. The crystallographic space group of the betaines is found to be centrosymmetric; therefore these dyes are incapable of SHG as crystals. To overcome this obstacle, we have synthesized and characterized a chiral betaine; because of its chirality this compounds must necessarily crystallize in a noncentrosymmetric space group, thereby making it capable of SHG as a crystal. Lastly, the utility of these betaines for SHG in poled polymer films is discussed.

Introduction

In the past 10 years there has been active research into organic compounds for applications in nonlinear optics such as second-harmonic generation (SHG), i.e., frequency doubling of laser radiation.[1] To be of interest for SHG, a compound must possess a reasonably large second-order molecular polarizability (β). On the basis of both theoretical considerations and experimental results, the types of molecular structures that can have large βs are fairly well understood; generally these are structures with electron-donating groups and electron-accepting groups linked through some conjugated π-electron system (e.g., 4-nitroaniline). Molecules with these structures are often highly solvatochromic,[2,3] i.e., their UV–vis absorption spectra are very sensitive to the solvent in which they are placed. Indeed there is a connection between solvatochromism and SHG; those structural features that give rise to large βs also give rise to strong solvatochromism. Recently we have developed a simple experimental method based on solvatochromism for estimating βs of small organic molecules;[4] previously, βs could only be determined by complex methods carried out in physics (optics) laboratories. Because of this connection between solvatochromism and SHG, the search for compounds with large βs should clearly include those that are known to be highly solvatochromic.

Simply because a compound has a large β, however, does not insure that it will be useful for SHG. The quantity β is a molecular property; it indicates that a single isolated molecule of some compound is capable of SHG. It does not guarantee effectiveness of the compound for SHG in bulk form, either crystal or poled polymer film.[5] For any medium to be capable of SHG, it must first be noncentrosymmetric.[6] Unfortunantly many compounds with large βs crystallize in centrosymmetric space groups; in fact, the very structural features that enhance β (i.e., polarity) often increase the likelihood of the molecules packing in a centrosymmetric crystal. Poled polymer films present an alternative but suffer from the disadvantages that it is hard to achieve significant alignment of the dye molecules with the poling field and that the molecules relax to a random (centrosymmetric) arrangement upon removal of the field. The challenge to organic chemists is to design and synthesize materials that can overcome these difficulties.

A promising class of compounds for SHG is the pyridinium-*N*-phenoxide betaine dyes, first studied in depth by Reichardt and Dimroth in the 1960s.[7] These compounds are interesting in that their electronic ground state is a dipolar ion, with the nitrogen atom bearing a positive charge and the oxygen atom bearing a negative charge (1). These dyes have received much attention because they are highly negatively solvatochromic; polar solvents shift their longest wavelength UV–vis absorption band to shorter wavelengths, and nonpolar solvents shift the band to longer wavelengths. The dye 2,6-diphenyl-4-(2,4,6-triphenyl-*N*-pyridinio)phenolate (Reichardt's dye, **2**) is one of the most highly solvatochromic compounds known.[3,8] In water this dye has a maximum at 453 nm and in diphenyl ether it has a maximum at 810 nm, a shift of 357 nm. Because of this pronounced solvatochromism, these betaines have been used for the characterization of solvents in the $E_T(30)$ method of Reichardt and the solvatochromic method of Kamlet, Abraham, and Taft (KAT).[3,8,9]

The strong solvatochromism of the pyridinium-*N*-phenoxide betaines also makes them of interest as dyes for nonlinear optics. The purpose of the present work is to synthesize some of these dyes and evaluate their utility for SHG applications. Specifically, we solvatochromically characterize three pyridinium-*N*-phenoxide betaines and report the synthesis of a new chiral betaine, which, because of its chirality, must necessarily crystallize in a noncentrosymmetric space group.

Results and Discussion

The synthesis of a series of pyridinium-*N*-phenoxide betaine dyes (a total of 32 compounds) was carried out and published by Reichardt and Dimroth in 1963.[7]

The betaine 2,6-diphenyl-4-(2,4,6-triphenyl-*N*-pyridino)phenolate (Reichardt's dye, **2**) was found by these researchers to be of the most interest because it is the most highly solvatochromic of all the dyes they investigated. It is by far the best known of the pyridinium-*N*-phenoxide betaines; the UV–vis absorption spectrum of this dye has been determined in over 270 pure organic solvents, as well as in several mixtures of organic solvents.[3]

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[1] *Nonlinear Optical Properties of Organic Molecules and Crystals*; Chemla, D. S., Zyss, J., Eds.; Academic Press: Orlando, FL, 1987; Vol. 1.

[2] Liptay, W. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 177–188.

[3] Reichardt, C. *Solvent Effects in Organic Chemistry*; Verlag Chemie: Weinheim, 1979; Chapter 6.

[4] Paley, M. S.; Harris, J. M.; Looser, H., Baumert, J. C.; Bjorklund, G. C.; Jundt, D.; Tweig, R. J. *J. Org. Chem.* **1989**, *54*, 3774–3778.

[5] Reference 1, Chapter II-4 and II-7.

[6] Reference 1, Chapter II-1.

[7] Dimroth, K.; Reichardt, C.; Siepmann, T.; and Bohlmann, F. *Justus Liebigs Ann. Chem.* **1963**, *661*, 1–37.

[8] Reichardt, C. *Angew. Chem.*, Int. *Ed. Engl.* **1965**, *4* (1), 29–40.

[9] Kamlet, M. J.; Doherty, R. M.; Abboud. J.-L. M.; Abraham. M. H.; Taft, R. W. *Chem. Tech.* **1986**, 566–76.

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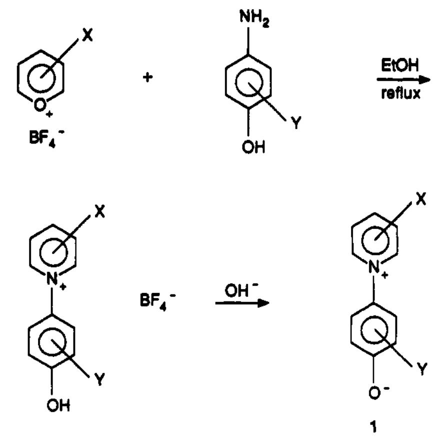

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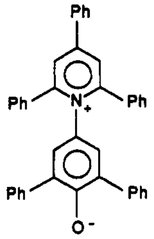

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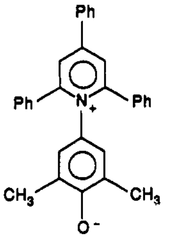

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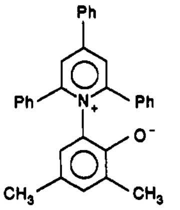

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Characterization of Reichardt's Dye. To determine the potential utility of Reichardt's dye for SHG, we applied the solvatochromic method referred to earlier.[4] This method is applied in two steps. First, the solvatochromic equation of McRae is used to obtain the excited-state dipole moment of the dye (more complex treatments of solvatochromism are available, but this relatively simple method is sufficient for our requirements). Second, the excited-state dipole moment is then used in the two-level model, eq 3, to obtain β_{xxx} for SHG.

Literature values of the maximum of the longest wavelength UV-vis absorption band (the solvatochromic band) of this dye in various solvents (Table I), excluding alcohols and ethers, were fit by multiple linear regression to the McRae equation.[10,11]

$$\nu_s - \nu = A\left[\frac{n^2-1}{2n^2+1}\right] + B\left[\frac{\epsilon-1}{\epsilon+2} - \frac{n^2-1}{n^2+2}\right] \qquad (1)$$

$$B = \left[\frac{2}{4\pi\epsilon_0 h a^3}\right]\vec{\mu}_g(\vec{\mu}_g - \vec{\mu}_e) \qquad (2)$$

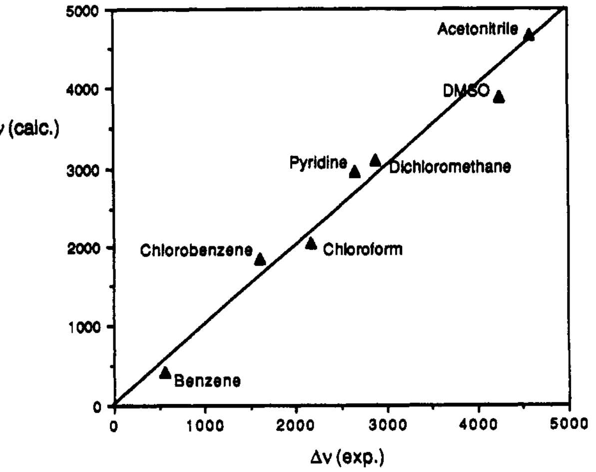
In this equation ν_s is the frequency of transition in a solvent, ν is the frequency of transition in vacuum, ϵ is the static dielectric constant of the solvent, n is the refractive index of the solvent, A and B are constants, μ_g and μ_e are, respectively, the ground- and excited-state dipole moments of the solute, ϵ_0 is the permittivity of vacuum, h is Plank's constant, and a is the radius of the spherical cavity that the solute molecule occupies in the solvent. By measuring ν_s in a variety of solvents with known n and ϵ and fitting the data by linear regression to eq 1, one can obtain values of the constants A and B, as well as ν (however, the uncertainty in the value of ν is greater than that in the values of A and B).

The McRae equation is based solely on an electrostatic model of the solute-solvent and solvent-solvent interactions; no other type of interaction is taken into account.

Table I. Solvatochromic Data (Absorption Maxima) for the Pyridinium-*N*-phenoxide Betaines in Selected Solvents. All Solvents Were Dried over Molecular Sieves (Except for Water)[23]

	betaine					
	2[a]		**3**		**5**	
solvent	λ_{max} (nm)	ν_{max} (cm^{-1})	λ_{max} (nm)	ν_{max} (cm^{-1})	λ_{max} (nm)	ν_{max} (cm^{-1})
water	453	22080	436	22940	402	24880
methanol	516	19380	478	20920	*b*	*b*
ethanol	551	18150	519	19270	476	21010
2-propanol	591	16930	580	17240	522	19160
acetonitrile	625	16000	635	15750	600	16670
acetone	677	14760	660	15150	604	16560
chloroform	731	13680	725	13790	664	15060
dichloromethane	702	14240	685	14600	664	15060
benzene	834	11200	*c*	*c*	804	12440
dimethyl sulfoxide	634	15780	665	15040	616	16230
chlorobenzene	777	12870	790	12660	746	13400
pyridine	706	14170	728	13740	680	14710

[a] Literature values.[3] [b] Maximum not discernable. [c] Dye not soluble.



$$\nu(\text{calc.}) = -11295\left[\frac{n^2-1}{2n^2+1}\right] + 5170\left[\frac{\varepsilon-1}{\varepsilon+2} - \frac{n^2-1}{n^2+2}\right] + 14457\ (\text{cm}^{-1})$$

Figure 1. Solvatochromic data (absorption maxima) for Reichardt's dye, **2**, fit to the McRae equation (eq 1, $\Delta\nu$ relative to 11 500 cm^{-1}).

Hence solvents in which there is some specific interaction between solvent and solute, or between solvent molecules themselves, are not included when fitting data to this equation. Thus hydroxylic solvents, such as alcohols, are excluded because of their hydrogen bonding. Ethers were excluded in the case of the pyridinium-N-phenoxide betaines because they form complexes with these dyes. The constant B from the McRae equation indicates how much the dipole moment of the molecule changes upon going from its electronic ground state to the Frank-Condon excited state, and it can be used to compute the excited-state dipole moment from eq 2, if the ground-state dipole moment is known (assuming that μ_g and μ_e are nearly parallel). The results of the fit of the data for Reichardt's dye to eq 1 are shown in Figure 1.

Using the value of the constant B from the McRae equation for Reichardt's dye (5170), a value of 6.0 Å for the cavity radius, and a calculated value (AM1) of 5.67 × 10^{-29} Coloumb-meters (C-m) for the ground-state dipole moment,[12] we compute, from eq 2, the value of the excited-state dipole moment of Reichardt's dye to be 3.49

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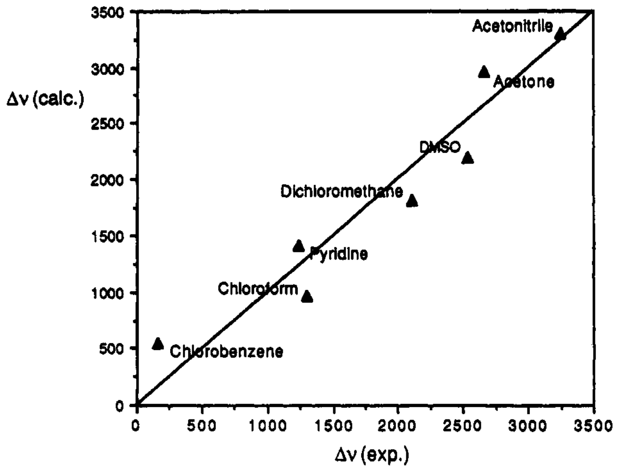
[10] McRae, E. G. *J. Phys. Chem.* **1957**, *61*, 562-572.

[11] Bakhshiev, N. G.; Knyazhanskii, M. I.; Minkin, V. I.; Osipov, O. A.; Seidov. G. V. *Russian Chem. Rev.* **1969**, *3*, 740-754.

[12] Dewar, M. J. S.; Zeobisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.



$$\nu(\text{calc.}) = -20118\left[\frac{n^2-1}{2n^2+1}\right] + 3802\left[\frac{\varepsilon-1}{\varepsilon+2} - \frac{n^2-1}{n^2+2}\right] + 16625\ (\text{cm}^{-1})$$

Figure 2. Solvatochromic data (absorption maxima) for the dimethyl betaine, **3**, fit to the McRae equation (eq 1, $\Delta\nu$ relative to 12 500 cm^{-1}).

$\times 10^{-29}$ C-m. From this and our experimentally determined value of 1.01×10^{-29} C-m for the transition dipole moment (μ_{eg}) of Reichardt's dye in acetonitrile (λ_{max} at 625 nm), we compute, using the two-level model (eq 3), a value of $\beta_{xxx} = 34 \times 10^{-30}$ esu for the second-order polarizability (in acetonitrile) of this dye for SHG at laser wavelength 1064 nm. Note that β is not negative, despite the betaine being negatively solvatochromic, because a term in the denominator is also negative.

$$\beta_{xxx}(2\nu) = \frac{2}{3h^2}\mu_{eg}{}^2\,(\mu_e - \mu_g)\frac{2}{(\nu_{eg}{}^2 - \nu^2)(\nu_{eg}{}^2 - 4\nu^2)} \qquad (3)$$

This is a sizeable β, indicating that Reichardt's dye could indeed be capable of efficient SHG, at least from a molecular standpoint (for MNA, 2-methyl-4-nitroaniline, a well-known compound for SHG, the β in 1,4-dioxane at 1064 nm is around 17×10^{-30} esu).[13]

Characterization of Dimethyl Betaine. We have prepared a dimethyl-substituted betaine, 2,6-dimethyl-4-(2,4,6-triphenyl-*N*-pyridino)phenolate (**3**), essentially Reichardt's dye with the phenyl groups on the phenoxide ring replaced by methyl groups, following much the same procedure that Reichardt and Dimroth used (with a few modifications, see Experimental Section). The purpose of making this compound was to investigate the importance of the phenyl groups to the solvatochromism and second-order polarizability of the pyridinium-*N*-phenoxide betaines by comparing Reichardt's dye to the dimethyl betaine.

As was done with Reichardt's dye, the absorption maximum of the solvatochromic band of the dimethyl betaine was determined in several solvents (Table I), the data were fit to eq 1 (Figure 2), and the constant B was obtained (3802). Using the calculated value (AM1) of 5.31×10^{-29} C-m for the ground-state dipole moment of the dimethyl betaine,[12] and again, a cavity radius of 6 Å, we compute, from eq 2, a value of 3.60×10^{-29} C-m for the excited-state dipole moment of the dimethyl betaine. The transition dipole moment in acetonitrile (λ_{max} at 635 nm) was experimentally determined to be 5.78×10^{-30} C-m. From these dipole moments the β_{xxx} (in acetonitrile) for the dimethyl betaine for SHG at 1064 nm was computed, using eq 3, to be 8.8×10^{-30} esu.

Upon comparison of the results for the dimethyl betaine to those for Reichardt's dye, we see that both dyes are highly negatively solvatochromic. Note that for both dyes the permanent dipole moment in the excited state is less than that in the ground state; this is expected for negatively solvatochromic compounds. We also see that the difference in permanent dipole moments between ground and excited states is nearly the same for the two dyes (the difference for the dimethyl betaine is about 80% of that for Reichardt's dye). Thus the charge distributions in the ground and excited states of these betaines do not appear to be affected much by substitution of methyl groups for the phenyl groups on the phenoxide ring. Note, however, that the transition dipole moment between ground and excited states, a measure of the intensity (probability) of the transition, is quite different for the two dyes; μ_{eg} for Reichardt's dye in acetonitrile is about twice that for the dimethyl betaine in this same solvent. This, in turn, causes β for Reichardt's dye at 1064 nm to be almost four times that for the dimethyl betaine at 1064 nm (both in acetonitrile). Hence replacing the phenyl groups on the phenoxide ring by methyl groups causes only a small decrease in the solvatochromism of these betaines, but causes a significant decrease in both their transition probabilities and second-order polarizabilities.

Examination of the basic structure of the pyridinium-*N*-phenoxide betaines reveals that this structure is exactly of the type expected to be highly solvatochromic and thus have a large β. The phenoxide ring is a good electon donor and the pyridinium ring a good electron acceptor; the large difference in permanent dipole moments between ground and excited states results from electron transfer between these two rings upon excitation.[14] The similarity in the solvatochromism of Reichard's dye and the dimethyl betaine (indicating similar charge distributions in both their ground states and excited states) is probably a consequence of the axial symmetry of these compounds. Even though one might expect conjugation with the phenoxide ring to take place with phenyl groups but not with methyl groups, thereby allowing more charge to be delocalized into the phenyl groups than into the methyl groups, the symmetric location of these groups would cause the effect of this charge on the permanent dipole moments (both ground and excited state) to be largely cancelled out. Furthermore, on the basis of the X-ray crystal structures, the geometry of the betaines prevents effective conjugation even with the phenyl groups (see next section).[14,15] As a consequence, Reichardt's dye and the dimethyl betaine have similar permanent dipole moments in both their ground and excited states and so they exhibit about the same degree of solvatochromism.

The reason for the significant decrease in transition dipole moment upon substitution of methyl groups for the phenyl groups on the phenoxide ring is not clear at the present time. It could result from the aforementioned unlikely possibility that effective conjugation with the phenoxide ring may be occurring with phenyl groups but not with methyl groups (thus affecting the electronic transition moment).

Crystal Structure of the Betaines. A brominated pyridinium-*N*-phenoxide betaine (Reichardt's dye with a bromine atom on the para phenyl group of the pyridinium ring) was synthesized and crystallized, and the crystal structure was determined by using X-ray analysis by

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(13) Teng, C. C.; Garito, A. F. *Phys. Rev.* **1982**, *28*, 6766–6773.

(14) Paley, M. S.; Meehan, E. J.; Smith, C. D.; Rosenberger, F. E.; Howard, S. C.; Harris, J. M. *J. Org. Chem.* **1989**, *54*, 3432–3436.

(15) Allmann, R. Z. *Kristallogr.* **1969**, *128*, 115.

(16) Reference deleted in press.

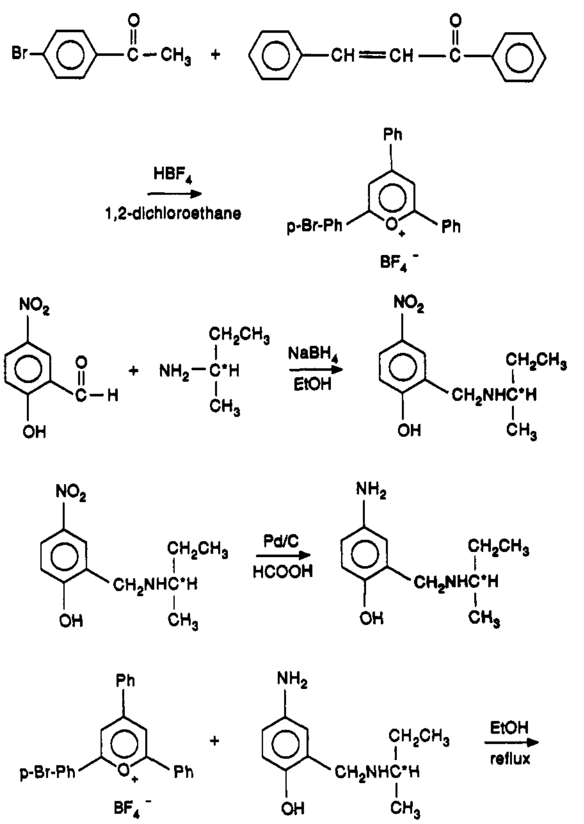
Allmann in 1969.[15] The purpose of the bromine was to provide a heavy atom to simplify determination of the structure. Analysis of the structure revealed that the space group is $P2_1/a$; thus the betaine crystal is centrosymmetric. This is not surprising since it could be expected that the large dipole moment of the betaine (ground state) would induce the molecules to pack in an antiparallel fashion in order to cancel their dipole moments and thereby minimize electrostatic energy. We would expect the same behavior for both Reichardt's dye and the dimethyl betaine (and for that matter, any pyridinium-*N*-phenoxide betaine with a similar type of structure). Because the betaine crystals are centrosymmetric, they are incapable of SHG. Hence the utility of these dyes for SHG applications will be limited to use in poled polymer films (except for chiral betaines, see later section).

We note from the crystal structure of the betaine that the C–O bond is shortened (1.29 Å, almost as short as a double bond), indicating that a significant amount of negative charge must be delocalized into the phenoxide ring in the ground state. On the other hand, the C–N bond between the pyridinium and phenoxide rings is of normal length (1.47 Å), indicating little delocalization of charge between these two rings. This probably results because the pyridinium ring is twisted out of plane by 65° with the phenoxide ring, making effective conjugation between the two rings unlikely. We also note that the para phenyl group of the pyridinium rings is twisted out of plane by 18° and that the other phenyl groups on the pyridinium and phenoxide rings are twisted out of plane by 65–70°, again, making effective conjugation unlikely (except with the para phenyl group on the pyridinium ring). This is consistent with the observation that Reichardt's dye and the dimethyl betaine exhibit similar charge distributions in their ground states and excited states. Interestingly, we observed similar structural features for an ortho-substituted betaine, 2,4-dimethyl-(2,4,6-triphenyl-*N*-pyridinio)phenolate (4), a compound that we have previously synthesized and characterized.[15]

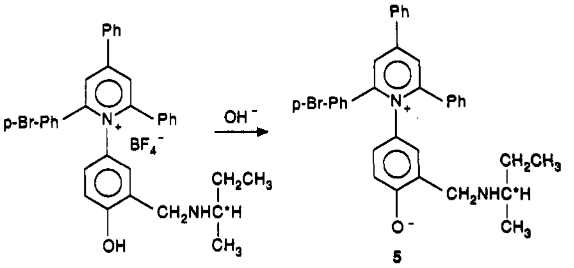
AM1 Calculations on the Betaines. We have used semiempirical AM1 calculations to obtain ground-state dipole moments of the betaines because we do not have apparatus for experimental determination and because AM1 gives excellent agreement with experiment for betaines.[12] The crystal structure of the brominated betaine corroborates the results obtained from these calculations. For Reichardt's dye, AM1 gives a C–O bond length of 1.26 Å and a C–N bond length between the pyridinium and phenoxide rings of 1.43 Å, in good agreement with the X-ray values (within 0.04 Å). In addition, AM1 predicts the pyridinium and phenoxide rings to be twisted out of plane by 89°, which is in reasonable agreement with the X-ray value of 65°. Also, the phenyl groups on the pyridinium and phenoxide rings are predicted to be twisted out of plane by about 90°, again, in reasonable agreement with the X-ray structure. Calculations on the dimethyl betaine and the chiral betaine yielded similar results. One should bear in mind that AM1 determines the structure of an isolated molecule of the betaine and that this structure may be slightly different from that in the crystal. Nonetheless, the qualitative features of the structures determined by the two methods should be similar.

Lastly, we note that the calculated value of 5.31×10^{-29} C-m for the ground-state dipole moment of the dimethyl betaine is in very good agreement with the experimental literature value of 4.9×10^{-29} C-m for the ground-state dipole moment of a di-*tert*-butyl betaine, 2,6-di-*tert*-butyl-4-(2,4,6-triphenyl-*N*-pyridinio)phenolate.[17] This lends credence to the AM1 calculations since nearly equal dipole moments would be expected for these two similar compounds. Hence we use the ground-state dipole moments calculated by AM1 for the betaines with reasonable confidence in the determination of μ_e and β_{xxx} from eqs 2 and 3.

Scheme I



Synthesis and Characterization of Chiral Betaine. To obtain a pyridinium-*N*-phenoxide betaine that could be capable of SHG as a crystal, one possessing a chiral center was synthesized and characterized (the chiral carbon is denoted with an asterisk) **5** (Scheme I). The presence of chirality in the dye insures that the compound will crystallize in a noncentrosymmetric space group; any pure enantiomer of a chiral compound must necessarily crystallize in a noncentrosymmetric space group. The synthesis of this betaine required four steps; again, the bromine was included to provide a heavy atom to simplify determination of the X-ray crystal structure.



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Characterization of the chiral betaine was carried out in the same manner as was done for Reichardt's dye and the dimethyl betaine. To determine the second-order polarizability of this dye, its UV–vis absorption spectrum was obtained in several solvents (Table I), the maximum of the solvatochromic band was determined in each solvent,

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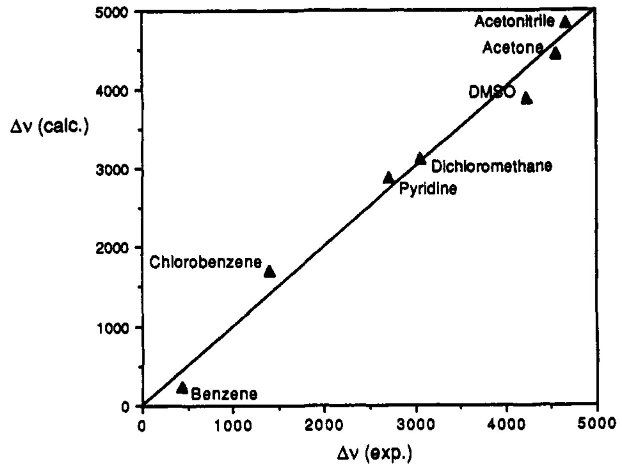
[17] Schweig, A.; Reichardt, C. *Z. Naturforsch.* **1966**, *21a*, 1373.



$$\nu(\text{calc.}) = -15494\left[\frac{n^2-1}{2n^2+1}\right] + 5413\left[\frac{\varepsilon-1}{\varepsilon+2} - \frac{n^2-1}{n^2+2}\right] + 15718\ (\text{cm}^{-1})$$

Figure 3. Solvatochromic data (absorption maxima) for the chiral betaine, **5**, fit to the McRae equation (eq 1, $\Delta\nu$ relative to 12 000 cm^{-1}).

and the data were fit to eq 1 (Figure 3). Interestingly, we observed that the chiral betaine is even more highly solvatochromic than is Reichardt's dye. Again, using the value of the constant B (5413), a cavity radius of 6 Å, and the calculated value (AM1) of 4.56×10^{-29} C-m for the ground-state dipole moment of the chiral betaine,[12] we compute, from eq 2, the excited-state dipole moment of this dye to be 1.72×10^{-29} C-m. The transition dipole moment for the chiral betaine in acetonitrile (λ_{max} at 600 nm) was determined to be 5.00×10^{-29} C-m; from this data the β_{xxx} (in acetonitrile) for this betaine for SHG at 1064 nm is computed, using eq 3, to be 14×10^{-30} esu. Based on this result, and the fact that it must pack in a noncentrosymmetric space group, we conclude that the chiral betaine could be a good crystalline material for SHG.

At present, however, we have not been able to grow crystals of the chiral betaine to determine the X-ray structure and perform SHG experiments. The method used to crystallize other pyridinium-*N*-phenoxide betaines, recrystallization from aqueous ethanol, has been unsuccessful with this dye. The chirality of the betaine may actually inhibit its crystal growth because there are two opposing forces at work. The large ground-state dipole moment of the dye favors the molecules packing in a centrosymmetric crystal so as to cancel their dipole moments and lower the energy, but the chirality of the dye requires that they pack in a noncentrosymmetric crystal. Furthermore, hydrogen bonding between the NH groups may also affect the crystal packing. As a result the chiral betaine is very difficult to crystallize; all attempts have resulted in either an oil or a glassy solid.

It is important to note that even when crystals are successfully grown, there is no guarantee that they will be efficient for SHG. The lack of a center of symmetry does indeed guarantee that the chiral betaine crystals will be capable of SHG, but the packing of the molecules may still be such that the amount (efficiency) of SHG is low (there may be near cancellation of the dipole moments in the crystal). Also it is possible that the crystal may lack sufficient transparency for efficient SHG, i.e., it may absorb strongly at the desired laser frequencies, which, obviously, would interfere with SHG.

Use of the Betaines of Poled Polymer Films. As mentioned earlier, the fact that the pyridinium-*N*-phenoxide betaines studied here crystallize in centrosymmetric space groups (except, of course, the chiral betaine) makes them of no use for SHG as crystalline materials. On the other hand, they may be very useful for SHG in poled polymer films. Clearly the large β of the betaines makes the molecules capable of efficient SHG. Also the large dipole moment in the ground state can enhance alignment of the betaine molecules with the poling field, which increases the efficiency of poled polymer films for SHG.[5] Additionally, the strong solvatochromism of the betaines can be used to advantage. The position of the absorption bands of a nonlinear dye in relation to the laser frequencies (both fundamental and doubled) can have a great effect on its efficiency for SHG (as well as other nonlinear processes). Ideally, the absorption bands of the dye should be close to the laser frequencies in order to take advantage of the so-called *resonant enhancement* of β, which increases SHG (see eq 3).[4] However the bands should not overlap with the laser frequencies and cause absorption of the laser light, because, as mentioned earlier, this interferes with SHG. We know that the absorption bands of a highly solvatochromic compound can shift greatly depending on the solvent in which the compound is placed. As we have shown recently, this applies in solid polymers as well as in liquid solvents.[18] By the appropriate choice of polymer matrix, it should be possible to "tune" (move) the absorption bands of a solvatochromic dye in a poled polymer film to the optimum position for SHG at some desired laser wavelength. Clearly the pyridinium-*N*-phenoxide betaines, whose solvatochromic shifts can span the entire visible (and part of the UV) range of the spectrum, would be ideal for such applications. The only drawback to the use of these betaines for such applications might be that their solvatochromic absorption bands are sometimes broad and thus, in some cases, may overlap with the laser frequencies.

Conclusions. In summary, we have shown that the highly solvatochromic pyridinium-*N*-phenoxide betaines can have large second-order molecular polarizabilities and thus they show promise as dyes for efficient SHG. With the exception of chiral betaines, which must crystallize in noncentrosymmetric space groups, the utility of the betaines for SHG applications is limited to use in poled polymer films because they crystallize in centrosymmetric space groups. We have also demonstrated that the transition intensities and second-order polarizabilities, but not the solvatochromism, of these dyes decrease significantly upon replacement of the phenyl groups on the phenoxide ring by methyl groups. Lastly, we have shown that the potential of the betaines for SHG in poled polymer films is high because of their large ground-state dipole moments and second-order polarizabilities, as well as the ability to shift their solvatochromic absorption bands to permit resonant enhancement of SHG. Future work in this area will concentrate on elucidating further the effects of substituents on the solvatochromic and optical properties of the pyridinium-*N*-phenoxide betaines, conducting poling experiments with the betaines, and attempts to crystallize the chiral betaine and determine its utility as a crystalline material for SHG applications.

Experimental Section

Unless otherwise specified, all reagents were purchased from Aldrich an used without further purification. Reichardt's dye was provided by Dr. Christian Reichardt at Fachbereich Chemie der Philipps-Universität in Marburg, West Germany. All solvents used for the solvatochromic measurements were anhydrous gold label quality. The NMR used was an IBM-Bruker 200-MHz

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Fourier transform spectrometer. Reported NMR spectra were clean and possessed proper integrations, so elemental analyses were obtained only in the case of the new compounds. UV-vis spectra were obtained on a HP 8452A photo diode array spectrometer. Molecular orbital calculations were performed by using the AM1 method in version 2.11 of the AMPAC program, available from QCPE, Department of Chemistry, Indiana University, Bloomington, IN (program no. 506).[12] The supercomputer used was a CRAY X-MP/24, provided by the Alabama Supercomputer Network.

Synthesis of Dimethyl Betaine. Synthesis of (Dimethylamino)phenol.[19] Into a 50-mL one-necked flask flushed thoroughly with nitrogen and equipped with a magnetic stirring bar were placed 2.0 g of 10% palladium on activated carbon, 15 mL of 96–98% formic acid, and 1.0 g of 2,6-dimethyl-4-nitrophenol. The stirred mixture was heated on a water bath at 90–100 °C for about 2 h to carry out the reduction of the nitro group to an amino group. The mixture was then removed from the water bath and 10 mL of concentrated hydrochloric acid was added. The palladium/carbon catalyst was filtered off and washed with 10–15 mL of hot water, and the wash water was combined with the original filtrate. This solution was then rotoevaporated to a volume of about 5–10 mL and 10–15 mL of concentrated hydrochloric acid was again added. The solution was placed overnight in a freezer at around 0 °C to precipitate the aminophenol hydrochloride salt as a white (or tan) solid. The solid was then filtered, washed with 5–10 mL of cold concentrated hydrochloric acid, and dried under vacuum overnight, yielding about 1.0 g of 2,6-dimethyl-4-aminophenol hydrochloride. ^{1}H NMR (d_6-DMSO): 10.14 ppm (s 3 H, NH_3^+), 6.94 ppm (s, 2 H, aromatic), 2.18 ppm (s, 6 H, CH_3).

Coupling of (Dimethylamino)phenol with Pyrylium Salt.[20] To about 0.70 g of the aminophenol hydrochloride salt from the previous step dissolved in 10 mL of 95% aqueous ethanol was added about 12–14 mL of 0.333 N ethanolic KOH (about 4.0–4.4 mmol of KOH). This mixture was then added to a 100-mL one-necked flask equipped with a magnetic stirring bar and a reflux condenser containing 1.4 g of 2,4,6-triphenylpyrylium tetrafluoroborate and 0.8 g of sodium acetate trihydrate, and the mixture was refluxed for about 6 h. The mixture was filtered to remove KCl, and 10 mL of 50–60% aqueous fluoroboric acid was added to the filtrate. The filtrate was then poured into 300–500 mL of water and refrigerated ovenight to "knock" the crude betaine fluoroborate salt out of solution (often as a lump). The crude salt was filtered and dissolved in 10–15 mL of glacial acetic acid (heating may be necessary) and then added dropwise, very slowly at first, into 150 mL of stirring anhydrous diethyl ether to precipitate the betaine salt as a yellow solid. The salt was filtered and washed with 50 mL of ether, and the solution/precipitation was repeated a second time, using methanol as the solvent instead of acetic acid. This procedure was superior to Reichardt's recrystallization from methanol or ethanol.[20] This step was then repeated a third time, and the salt was filtered, washed with ether, and finally dried under vacuum to yield about 1.0 g (50% of theoretical) of the pure 2,6-dimethyl betaine tetrafluoroborate salt. ^{1}H NMR (d_6-acetone): 8.54 ppm (s, 2 H, 3,5-H of pyridine ring), 8.26–8.31 (m, 2 H, aromatic), 7.38–7.79 (m, 13 H, aromatic), 7.13 (s, 2 H, 3,5-H of phenoxide ring), 3.0 ± 0.5 (s, broad, OH and H_2O of crystallization), 2.01 (s, 6 H, CH_3).

Conversion of Dimethyl Betaine Salt into Dye.[20] To 1.0 g of the betaine tetrafluoroborate salt dissolved in 75 mL of methanol was added 10 mL of 15% sodium methoxide in methanol, and the solution was heated for 5–10 min. To this solution was added 200 mL of 10% aqueous NaOH, and the mixture was refrigerated overnight to bring the dye out of solution. The dye was then extracted into 500–600 mL of chloroform (easier than filtering as in ref 20), in 75–100-mL portions (forming a blue solution); the chloroform layers were combined, washed with two or three 100-mL portions of water (until the wash water was neutral to litmus paper), and, finally, dried over anhydrous sodium sulfate. Upon evaporation of the chloroform and drying in vacuum, the pure 2,6-dimethyl betaine dye, **3** was left as a dark violet solid; yield about 0.9 g. To remove traces of water and methanol from the betaine, it was dried overnight at 50 °C in an Abderhalden drying pistol in the presence of P_2O_5. ^{1}H NMR ($CDCl_3$): 8.12ppm (s, 2 H, 3,5-H of pyridine ring), 7.91–7.95 (m, 2 H, aromatic), 7.60–7.63 (m, 4 H, aromatic), 7.28–7.38 (m, 9 H, aromatic), 6.47 (s, 2 H, 3,5-H of phenoxide ring), 3.0 ± 1.0 (s, broad, H_2O fo crystallization), 1.90 (s, 6 h, CH_3).

Synthesis of Chiral Betaine. Synthesis of Bromopyrylium Tetrafluoroborate Salt.[21] Into a three-necked flask equipped with an addition funnel, condenser, thermometer, and a magnetic stirring bar were placed 42.0 g of benzalacetophenone (chalcone), 20.0 g of *p*-bromoacetophenone, and 70 mL of 1,2-dichloroethane. The stirred mixture was heated to 70–75 °C and 25 mL of 85% ethereal fluoroboric acid was added dropwise from the addition funnel over about 30 min. After the addition was complete, the mixture was refluxed for about 2 h and then cooled overnight in a refrigerator to precipitate some of the crude pyrylium salt. The yellow precipitate was filtered, 100–150 mL of diethyl ether was added to the filtrate, and the mixture was again refrigerated overnight to precipitate the rest of the salt, which was then filtered and combined with the first portion. The crude pyrylium salt was purified by dissolution in 100 mL of hot acetonitrile, followed by precipitation with 300–400 mL of ether, refrigeration overnight, and filtering. The yield was about 20–25 g of purified 2-(4-bromophenyl)-4,6-diphenylpyrylium tetrafluoroborate. ^{1}H NMR (CD_3CN): 8.64–8.68 ppm (m, 2 H, 3,5-H of pyrylium ring), 8.24–8.40 (m, 6 H, aromatic), 7.59–7.90 (m, 8 H, aromatic).

Synthesis of Chiral Aminonitrophenol.[22] A solution containing 1.0 g of 5-nitrosalicyaldehyde and 2.0 g of (*R*)-(+)-*sec*-butylamine in 10–15 mL of 95% aqueous ethanol was cooled to around 0 °C in an ice–water bath. About 1.0 g of sodium borohydride was added to the stirring solution in small portions over a period of about 10 min, and the solution was then allowed to warm slowly to room temperature over a couple of hours. Another 0.5 g of sodium borohydride was added, and the mixture was stirred overnight to complete the reduction amination (keeping the flask loosely stoppered). To this mixture was then added 50 mL of water, and the resulting solution was extracted with about 400–500 mL of dichloromethane, in 75–100-mL portions. The dichloromethane solution was then dried over anhydrous sodium sulfate, and the solvent was rotoevaporated to leave behind the aminonitrophenol as a yellow solid (sometimes it comes out as an oil, which solidified upon standing). The solid was dried thoroughly under vacuum, yielding about 1.0–1.2 g of chiral 2-[(*sec*-butylamino)methyl]-4-nitrophenol. ^{1}H NMR (d_6-acetone): 7.96–8.04 (m, 2 H, aromatic), 6.74–6.79 (d, 1 H, aromatic), 5.95 (s, broad, 2 H, NH and OH), 4.17–4.18 (d, 2 H, benzylic CH_2), 1.30–1.70 (m, 3 H, CH and CH_2 of *sec*-butyl group), 1.15–1.19 (d, 3 H, CH_3 of *sec*-butyl group), 0.91–0.99 (t, 3 H, CH_3 of *sec*-butyl group).

Reduction of Aminonitrophenol to Aminophenol.[21] Following the procedure used to reduce the 2,6-dimethyl-4-nitrophenol, 1.0 g of the chiral aminonitrophenol prepared in the previous step was reduced to 2-[(*sec*-butylamino)methyl]-4-aminophenol by using formic acid and palladium/carbon catalyst. The workup of the reaction was slightly different from that used for the 2,6-dimethyl-4-aminophenol. After the palladium/carbon was filtered off and washed with water, the filtrate was rotoevaporated to near dryness, 20–25 mL of 95% aqueous ethanol was added, and the solution was again rotoevaporated to near dryness (to remove acid). This step was repeated a second time, only this time the solution was rotoevaporated to complete dryness, yielding brownish white crystalline flakes of the aminophenol hydrochloride salt. The salt was then immediately placed in a vacuum drying oven and dried thoroughly under vacuum overnight to remove any last traces of water and acid. The salt was extremely hygroscopic; contact with moisture from the air should be minimized by storing the salt under dry nitrogen (it is best to use the salt in the next step as soon as possible after drying). The yield was about 1.0 g of chiral 2-[(*sec*-butylamino)-

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Table II. Solvatochromic Data and Ground (μ_g) and Excited State (μ_e) Dipole Moments for the Pyridinium-*N*-phenoxide Betaines and UV–Vis Absorption Data, Transition Dipole Moments (μ_{eg}), and Second-Order Polarizabilities (β_{xxx}) for These Betaines in Acetonitrile (Dried)

	betaine		
quantity	2	3	5
B (McRae eq, cm^{-1})	5170	3802	5413
μ_g (C-m)[a]	5.67×10^{-29}	5.31×10^{-29}	4.67×10^{-29}
μ_e (C-m)	3.49×10^{-29}	3.60×10^{-29}	1.72×10^{-29}
λ_{max} (nm)	625	635	600
extinction coefficient (mol^{-1} cm^{-1})	4681	1271	1231
half-width at half-maximum (cm^{-1})	2025	2572	2077
μ_{eg} (C-m)	1.01×10^{-29}	5.78×10^{-30}	5.00×10^{-30}
β_{xxx} at 1064 nm (esu)	34×10^{-30}	8.8×10^{-30}	14×10^{-30}

[a] Obtained from AM1 calculations.[12]

methyl]-4-aminophenol hydrochloride.

Coupling of Aminophenol with Bromopyrylium Salt.[22] The coupling was carried out in the same manner as for the 2,6-dimethyl betaine, using 1.0 g of the chiral aminophenol hydrochloride salt and 2.0 g of the bromopyrylium salt. In the workup of the chiral betaine tetrafluoroborate salt, much greater quantities of ether were required in the precipitation steps, and the step with acetic acid was omitted. The crude salt was dissolved in 10–15 mL of methanol, as before, and then precipitated by slow dropwise addition to 900–1000 mL of stirring ether (this large quantity of ether is essential, otherwise the betaine salt will coagulate into a lump). After the second methanol/ether precipitation, the salt was washed with copious quantities of ether (in fact, it is advisable to allow the salt to stand in pure ether for a couple of hours and then complete the washing) and finally dried under vacuum to yield about 2.0 g (50% of theoretical) of the pure chiral (*sec*-butylamino)methyl bromo betaine tetrafluoroborate. ^{1}H NMR (d_6-acetone): 8.59–8.63 ppm (m, 2 H, 3,5-H of pyridine ring), 8.27–8.31 (m, 2 H, aromatic), 7.44–7.71 (m, 14 H, aromatic), 6.89–6.91 (d, 1 H, phenoxide ring), 4.22–4.28 (t, 2 H, benzylic CH_2), 3.0 ± 0.5 (s, broad, OH, NH_2+, and H_2O and CH_3OH of crystallization), 1.5–2.1 (m, 3 H, CH and CH_2 of *sec*-butyl group), 1.35–1.38 (d, 3 H, CH_3 of *sec*-butyl group), 0.95–1.02 (t, 3 H, CH_3 of *sec*-butyl group).

Conversion of Salt to Chiral Betaine Dye.[20] The conversion of the chiral betaine tetrafluoroborate salt into dye was carried out in exactly the same manner as for the dimethyl betaine, using 150 mL of methanol, 25 mL of 15% sodium methoxide in methanol, and 400 mL of 10% aqueous NaOH. Upon evaporation of the chloroform and drying in vacuum, the pure chiral (*sec*-butylamino)methyl bromo betaine dye, **5**, is left as a dark violet solid, yield 1.5 g. Again, to remove traces of methanol and water from the betaine, it was dried overnight at 50 °C in an Abderholden drying pistol in the presence of P_2O_5. The chiral betaine was found to decompose at temperatures above 60 °C. Also some reversible reaction (evident from NMR) apparently occurs in chloroform solutions of this betaine upon standing for periods of several hours. Anal. Calcd (excluding any water or methanol or crystallization): C, 72.46; H, 5.55; N, 4.97; Br, 14.18. Found: C, 69.34; H, 5.50; N, 4.52; Br, 13.79. ^{1}H NMR (CD_3CN): 8.29 ppm (s, 2 H, 3,5-H of pyridine ring), 8.01–8.05 (m, 2 H, aromatic), 7.14–7.70 (m, 12 H, aromatic), 6.72 (s, 1 H, 5-H of phenoxide ring), 6.62–6.66 (d, 1 H, 3-H of phenoxide ring), 6.23–6.27 (d, 1 H, 2-H of phenoxide ring), 4.5 ± 0.5 (s, broad, NH and H_2O or CH_3OH of crystallization), 3.25–3.75 (m, 2 H, benzylic CH_2), 1.15–1.24 (m, 3 H, CH and CH_2 of *sec*-butyl group), 0.69–0.86 (m, 6 H, CH_3 of *sec*-butyl group).

Solvatochromic Measurements. All solvents were dried over 3-Å molecular sieves, except for benzene, which was dried over 4-Å sieves, and water, which of course was not dried.[23] Dilute solutions of the dimethyl betaine and the chiral betaine were prepared in each solvent, and the solutions were dried to remove any water present that may have come from the dyes (such as water of crystallization). UV–vis absorption spectra were obtained on each solution in the range 200–800 nm. The longest wavelength absorption band of each dye was its highly solvatochromic charge-transfer band. The maximum of this band for both dyes was determined in each solvent and the data (excluding water, alcohols, and ethers) were fit to the McRae equation (eq 1) by means of multiple linear regression and the constant B was obtained. Data for Reichardt's dye were obtained from the literature and also fit to the McRae equation.[7] The results are shown in Table I and Figures 1, 2, and 3.

The cavity radius for the betaines (6 Å) was obtained from literature values of bond lengths by using our previously described method.[4] From the constant B, the cavity radius, and the calculated ground-state dipole moment,[13] the excited-state dipole moment was computed for all three betaines using eq 2. The molar extinction coefficient of each dye in acetonitrile was determined by preparing solutions at four concentrations, obtaining UV–vis spectra, and fitting the data to Beer's law. Half-widths at half-maximum were also determined; from this data the transition dipole moments (in acetonitrile) were computed as described previously,[4] treating the bandshape as approximately Gaussian (although the true bandshape for the pyridinium-*N*-phenoxide betaines is neither pure Gaussian nor pure Lorentzian).[24,25] The β_{xxx} (in acetonitrile) of each betaine for SHG at laser wavelength 1064 nm was then computed by using the two-level model, eq 3.[4] The results are shown in Table II.

Acknowledgment. We would like to acknowledge the assistance of Steven Zutaut, who performed the AM1 calculations on the betaines. Also some solvatochromic measurements on the dimethyl betaine were carried out by Nina Souresrafil. Financial support of this work was provided by the National Aeronautics and Space Administration and IBM Research.

Registry No. **2**, 10081-39-7; **3**, 104999-27-1; **5**, 130351-41-6.

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