Determination of the Ground and Excited State Dipole Moments of Free Base Chlorin and Isobacteriochlorin

Amarnauth Singh, Wen-Ying Huang, and Lawrence W. Johnson*

Department of Chemistry, York College of The City University of New York, Jamaica, New York 11451

Received: June 29, 1999; In Final Form: October 5, 1999

The ground state dipole moment of free base chlorin (H_2Ch) was determined by dielectric constant measurements of H_2Ch/benzene solutions ($\mu_g = 2.93 \pm 0.08$ D). This was combined with the previously measured change in dipole moment ($\Delta\mu_{ge} = -0.255 \pm 0.005$ D) associated with the $S_1 \leftarrow S_0$ ($\pi\pi^*$) transition to calculate the excited-state dipole moment ($\mu_e = 2.68 \pm 0.08$ D) of H_2Ch. These values were used with solvatochromic shift data to find the cube of the cavity radius, a^3, for the H_2Ch molecule; the assumption was made that the cis and trans tautomers of free base isobacteriochlorin (H_2iBC) have this same a^3. This number ($(4.49 \pm 0.05) \times 10^{-23}$ cm^3) was combined with the spectral shifts and measured $\Delta\mu_{ge}$ vectors to determine the ground and excited state dipole moments of *cis*-H_2iBC ($\mu_g = 0.35 \pm 0.01$ D; $\mu_e = -0.97 \pm 0.01$ D) and *trans*-H_2iBC ($\mu_g = 2.16 \pm 0.05$ D, $\mu_e = 3.51 \pm 0.05$ D). Our solvatochromic shift data also indicated that when inferring the sign of a Stark effect determined change in dipole moment, only solvents with low polarizabilities (nonaromatic) should be used.

Introduction

Free base isobacteriochlorin (H_2iBC) is an isomer of bacteriochlorin in which the two pyrrole rings with reduced double bonds are adjacent to each other instead of on opposite sides of the molecule. This free base porphyrin exists as an equilibrium mixture of two tautomers, cis and trans (See Figure 1, parts a and b). The isobacteriochlorin ring is of interest because it has the same fundamental structure as siroheme, the prosthetic group of sulfite and nitrite reductases; these enzymes catalyze the six-electron reductions of the sulfite ion to hydrogen sulfide and the nitrite ion to ammonia,[1,2] respectively. It is also important theoretically because it is one of the stable variations of the totally unsaturated porphin structure.[3]

The change in dipole moment ($\Delta\mu_{ge}$) associated with the $S_1 \leftarrow S_0$ ($\pi\pi^*$) transition of each tautomer was measured earlier.[4,5] However, since H_2iBC exists as a mixture of *cis*- and *trans*-H_2iBC, it was not possible to use standard methods (e.g., measuring the dielectric constants of dilute H_2iBC solutions) to experimentally determine the ground-state dipole moment (μ_g) of each of these molecules. The importance of this comes from the fact that if μ_g and $\Delta\mu_{ge}$ are known, then the excited state dipole moment (μ_e) can immediately be determined.

The solvatochromic shift method[6,7] seemed to provide a relatively simple way of circumventing this dilemma and finding the μ_g value for each tautomer. A problem, however, with this technique is the uncertainty associated with the molecular cavity volume term, a^3, where a is usually assumed to be the molecule's radius. Our way of dealing with this approximation was to first study free base chlorin (Figure 1c, H_2Ch). This molecule could be isolated and purified, and thus its ground state dipole moment could be determined. Also, the $\Delta\mu_{ge}$ associated with its Q_y origin band had already been measured;[8,9] so, by determining its solvatochromic shift in a series of solvents with similar refractive indices, and then adding the μ_g and $\Delta\mu_{ge}$ values, we were able to determine a^3 for H_2Ch. We assumed that this was the same value for the isobacteriochlorin tautomers. Then, we combined their previously determined changes in dipole moment values with their solvatochromic shifts, which we had measured, and determined the ground state and excited-state dipole moments for *cis*-H_2iBC and *trans*-H_2iBC. In this paper, we report the ground and excited-state dipole moments of free base chlorin and cis and trans free base isobacteriochlorin.

Experimental Section

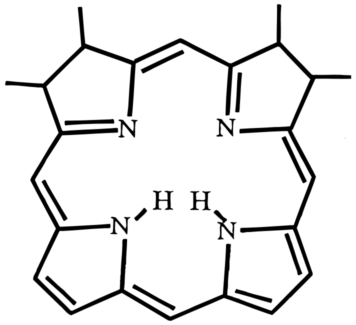
Free base chlorin and isobacteriochlorin were synthesized and purified using the methods of Egorova et al.[10] and Eisner and Linstead.[11] The ground state dipole moment of H_2Ch was determined from the dielectric constants of a series of H_2Ch/benzene solutions and then using Guggenheim's computational method.[12] In this technique, based on the Debye equation, a plot of $\epsilon - n^2$ against C is made, where ϵ is the dielectric constant of the solution, n is it's refractive index, and C is its molar concentration; the value of the slope ($\epsilon - n^2/C$) leads to the ground state dipole moment (μ_g) when inserted into

$$\mu_g^{\,2} = \frac{9kT}{4\pi N}\frac{3}{(\epsilon + 2)(n^2 + 2)}\left(\frac{\epsilon - n^2}{C}\right)$$

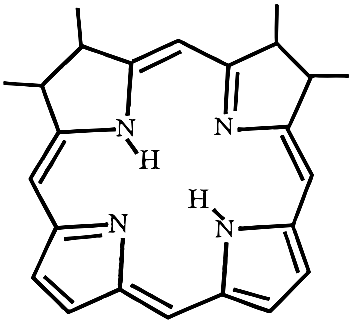
where k is Boltzmann's constant, T is temperature (K), and N is Avogadro's number.

Data for this calculation was collected using a Sargent Chemical Oscillometer. A calibration curve was obtained by plotting the instrument's response verses the dielectric constants for cyclohexane, benzene, toluene, and *o*-xylene. All solvents were spectroscopic or HPLC grade and were left standing over 0.4 Å molecular sieves for more than 1 week to ensure that they were anhydrous. Dilute solutions ranging from 3.5×10^{-5} to 8.6×10^{-5} M of H_2Ch in benzene were prepared, and their relative instrument responses were measured; benzene was used because of the low solubility of H_2Ch in more desirable solvents (e.g., *n*-octane, cyclohexane). The dielectric for each dilute

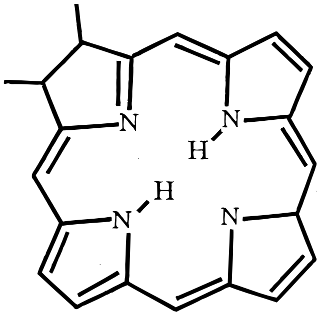
10.1021/jp9922099 CCC: $19.00



(a) *cis*-H_2iBC



(b) *trans*-H_2iBC



(c) H_2Ch

Figure 1. Structures of free base isobacteriochlorin and free base chlorin.

solution was then determined from the calibration curve. Refractive indices and dielectric constants for the pure solvents used were obtained from the *Handbook of Chemistry and Physics* (1997−1998).[13] Standard techniques were used to determine densities and refractive indices of solutions. The molar concentrations and relative dielectrics recorded in Table 1 are average values determined from four separate experiments.

All room-temperature electronic absorption spectra of H_2Ch and *cis*- and *trans*-H_2iBC were recorded using a Perkins-Elmer (Lambda 19) UV/vis/NIR spectrometer. Each absorption maximum reported in Tables 2−5 is an average of 10 absorption scans; the slit band-pass was 1 nm, a data point was taken every 0.05 nm, and the scan speed was 30 nm/min. Fourth-order derivative spectra[14] were made using the Lambda 19 software to precisely determined the absorption maximum associated with each of the H_2Ch, *cis*-H_2iBC, and *trans*-H_2iBC peaks reported in this paper.

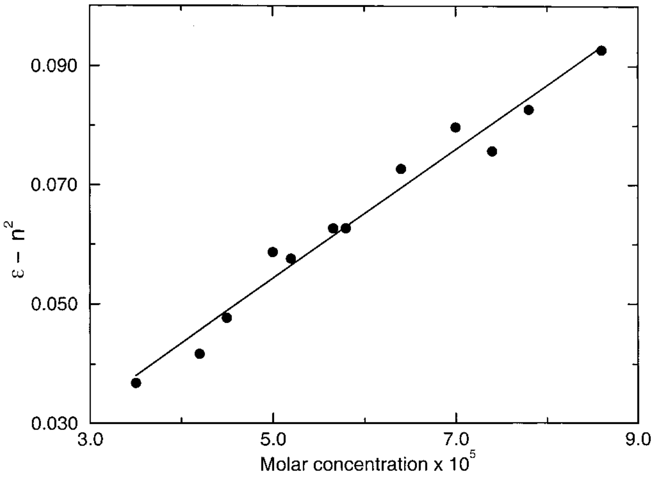


Figure 2. Plot of $\epsilon - n^2$ against molar concentration for H_2Ch/benzene solutions. (The error bars are within the data point circles.)

TABLE 1: Concentrations of H_2Ch/Benzene Solutions and Their Relative Dielectrics; ϵ Is the Dielectric Constant and n the Refractive Index

concentration M [$\times 10^5$]	ϵ	$\epsilon - n^2$
3.5 ± 0.1	2.284 ± 0.001	0.0368
4.2 ± 0.1	2.289 ± 0.001	0.0417
4.5 ± 0.1	2.295 ± 0.001	0.0477
5.0 ± 0.1	2.306 ± 0.001	0.0587
5.2 ± 0.1	2.305 ± 0.001	0.0576
5.7 ± 0.1	2.310 ± 0.001	0.0627
5.8 ± 0.1	2.310 ± 0.001	0.0627
6.4 ± 0.1	2.320 ± 0.001	0.0727
7.0 ± 0.1	2.327 ± 0.001	0.0797
7.4 ± 0.1	2.323 ± 0.001	0.0757
7.8 ± 0.1	2.330 ± 0.001	0.0827
8.6 ± 0.1	2.340 ± 0.001	0.0927

Results and Discussion

The ground-state dipole moment of free base chlorin was determined from the solution dielectric constant data which is summarized in Table 1 and plotted in Figure 2. A linear regression analysis on these data gave a slope of 1083 ± 3 M^{-1} with $r^2 = 0.97$. From this slope, the ground state dipole moment of H_2Ch was calculated to be 2.93 ± 0. 08 D. For comparison, there are a few theoretically determined values for free base chlorin's ground state dipole moment; two of these are 0.84[15] and 1.54 D.[16] (We also did calculations using Biosym/MSI Zindo 95.0/3.0 and Dmol 95.0/3.0 programs; Zindo (Zerner's INDO) gives a semiempirical quantum mechanical approach, and Dmol is a first principles (ab initio) quantum chemistry program. We obtained values of 2.28 and 2.75 D, respectively.)

Earlier Stark effect experiments by two research groups determined the absolute value of the change in dipole moment associated with the molecule's $S_1 \leftarrow S_0$ ($\pi\pi^*$) excitation to be 0.255 ± 0.005 D.[8,9] The sign of this change had been inferred by the shift of the origin band in going between an *n*-hexane solution (636.2 nm) and a neat thin film (647.0 nm). On the basis of this red shift of 262 cm^{-1}, the dipole was assumed to have increased in the excited state.[8] However, in this present work, although we also observed a red shift of free base chlorin's Q_y band in a series of polar aromatic solvents, we found that this band shifts to higher energy, a blue shift, in a series of nonaromatic polar solvents. On the basis of this later observation, we concluded that for H_2Ch $\Delta\mu_{ge} = -0.255 \pm 0.005$ D. (This is discussed more fully later in this section of the paper.) We assumed that H_2Ch retains its C_{2v} symmetry in the excited

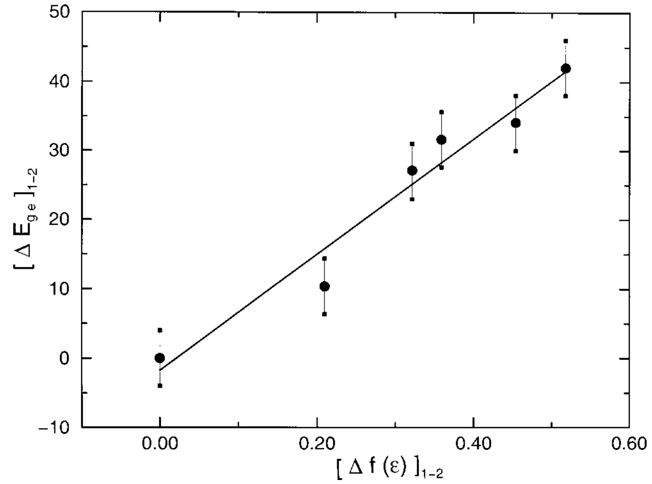


Figure 3. Plot of solvatochromic shifts of absorption maxima (cm^{-1}) against dielectric constant differences for H_2Ch in a series of solvents.

TABLE 2: Refractive Indices (*n*), Dielectric Constant (ϵ), and Absorption Maxima for H_2Ch in a Series of Solvents

solvent	*n*	ϵ	$[\Delta f(\epsilon)]_{1-2}$	abs (cm^{-1})	$[\Delta E_{ge}]_{1-2}$ (cm^{-1})
octane	1.394	1.886	0	15701 ± 2	0
butyl ether	1.398	3.083	0.210	15711 ± 2	10
isobutyl isobutyrate	1.398	4.390	0.322	15728 ± 2	27
isobutyl acetate	1.390	5.068	0.359	15732 ± 2	31
2-chlorobutane	1.396	8.064	0.454	15735 ± 2	34
4-methyl-2-pentanone	1.396	13.11	0.518	15743 ± 2	42

state, so μ_g and $\Delta\mu_{ge}$ should be parallel, and therefore the dipole moment of H_2Ch in its first excited state is 2.68 ± 0.08 D.

Since we now had chlorin's μ_g and $\Delta\mu_{ge}$ values, we proceeded to measure the solvatochromic shift of its Q_y band in a series of solvents of similar refractive indices (*n*) but different dielectric constants (ϵ). These data are summarized in Table 2. To carry out the solvatochromic shift analysis, we used the equation derived by Suppan,[6] $\Delta\nu_{1-2}hc = -\bar{\mu}_g \cdot \Delta\bar{\mu}_{ge} a^{-3} \Delta f(\epsilon)_{1-2}$. Here $f(\epsilon) = 2(\epsilon - 1)/(2\epsilon + 1)$ and $\Delta f(\epsilon)_{1-2}$ is the change in the dielectric constant function between solvents 1 and 2; $\Delta\nu_{1-2}$ is the solvatochromic shift, in wavenumbers, of the absorption band between solvents 1 and 2; $\Delta\mu_{ge}$ is the change in the molecule's dipole moment in going from its ground state to the excited state ($\Delta\mu_{ge} = \mu_e - \mu_g$). The assumptions used by Suppan in deriving this equation were that (1) the dipole moments in the Franck−Condon and relaxed states are the same, (2) the cavity radius, *a*, is the same for both states, and (3) the polarizability (α) of the molecule in a spherical cavity is $\alpha = a^3$. To use Suppan's equation, all shift measurements had to be made in solvents which have essentially the same refractive index; we used solvents with $n = 1.39$.

The solvatochromic shift data for H_2Ch is plotted in Figure 3, $\Delta\nu_{1-2}$ hc = $[\Delta E_{ge}]_{1-2}$. A linear regression analysis on the data gave a line with a slope of 84 ± 2 cm^{-1} and an r^2 value of 0.96. The slope is equal to $\bar{\mu}_g \cdot \Delta\bar{\mu}_{ge} a^{-3}$ which, after inserting the experimentally measured values of μ_g and $\Delta\mu_{ge}$ into the equation, yielded $a^3(H_2Ch) = (4.49 \pm 0.05) \times 10^{-23}$ cm^3. We then made the assumption that $a^3(H_2Ch) \equiv a^3(H_2iBC)$ and proceeded to calculate the ground-state dipole moments of cis and trans free base isobacteriochlorin. This solvatochromic shift data is summarized in Tables 3 and 4 and plotted in Figures 4 and 5, respectively. The slope of the *cis*-H_2iBC data in Figure 4 is 52 ± 1 cm^{-1} with an r^2 value of 0.94; the corresponding $\Delta\mu_{ge}$ value is −1.32 ± 0.08 D.[5] Combining these quantities with a^3 gave a ground state dipole moment of 0.35 ± 0.08 D and subsequently an excited state dipole moment of −0.97 ± 0.08 D.

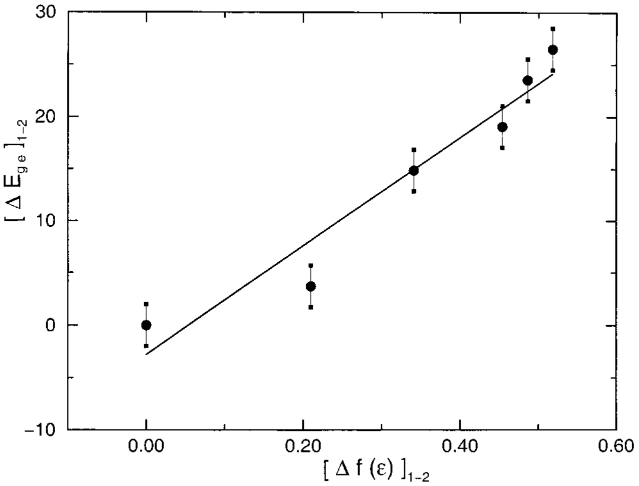


Figure 4. Plot of solvatochromic shifts of absorption maxima (cm^{-1}) against dielectric constant differences for *cis*-H_2iBC in a series of solvents.

TABLE 3: Refractive Indices (*n*), Dielectric Constant (ϵ), and Absorption Maxima for *cis*-H_2iBC in a Series of Solvents

solvent	*n*	ϵ	$[\Delta f(\epsilon)]_{1-2}$	abs (cm^{1})	$[\Delta E_{ge}]_{1-2}$ (cm^{1})
octane	1.394	1.886	0	15726 ± 1	0
butyl ether	1.398	3.083	0.210	15730 ± 1	4
isobutylamine	1.397	4.710	0.341	15741 ± 1	15
2-chlorobutane	1.396	8.064	0.454	15746 ± 1	20
pentanal	1.394	10.00	0.486	15750 ± 1	24
4-methyl-2-pentanone	1.396	13.11	0.518	15753 ± 1	27

TABLE 4: Refractive Indices (*n*), Dielectric Constant (ϵ), and Absorption Maxima for *trans*-H_2iBC in a Series of Solvents

solvent	n	ϵ	$[\Delta f(\epsilon)]_{1-2}$	abs (cm^{-1})	$[\Delta E_{ge}]_{1-2}$ (cm^{-1})
octane	1.394	1.886	0	17463 ± 3	0
butyl ether	1.398	3.083	0.210	17412 ± 3	−51
isobutyl isobutyrate	1.398	4.390	0.322	17379 ± 3	−84
isobutyl acetate	1.390	5.068	0.359	17367 ± 3	−96
2-chlorobutane	1.396	8.064	0.454	17350 ± 3	−113
pentanal	1.394	10.00	0.486	17324 ± 3	−139
4-methyl-2-pentanone	1.396	13.11	0.518	17315 ± 3	−148

The slope of the *trans*-H_2iBC data in Figure 5 is −281 ± 3 cm^{-1} and $r^2 = 0.98$. When this was combined with the previously measured $\Delta\mu_{ge}$ value of 1.64 ± 0.05 D[4] and $a^3 = (4.49 \pm 0.05) \times 10^{-23}$ cm^3, we obtained $\bar{\mu}_g = 1.53 \pm 0.05$ D/cos θ. Where θ is the angle between vectors $\bar{\mu}_g$ and $\Delta\bar{\mu}_{ge}$. Since *trans*-H_2iBC has C_s symmetry, $\bar{\mu}_g$ and $\bar{\mu}_e$ are not necessarily parallel. To help find ϕ, the angle between $\bar{\mu}_g$ and $\bar{\mu}_e$, we examined our Zindo and Dmol calculations on H_2iBC. Both estimated that the *trans*-H_2iBC ground state dipole moment passes almost symmetrically between the two reduced rings. From the Stark effect data from the molecule in an *n*-octane crystal matrix,[4] it had been concluded that, when the inner protons shifted from one set of equivalent nitrogens to the other, the $\Delta\mu_{ge}$ vector rotated 90°; it was surmised that $\Delta\bar{\mu}_{ge}$ was either parallel to the H−H axis of the protonated nitrogens or to the N−N axis of the unprotonated nitrogens, and consequently $\Delta\bar{\mu}_{ge}$ changed direction by 90° in going from one trans tautomer to the other. The angle (θ) between the ground state dipole moment and $\Delta\bar{\mu}_{ge}$ is then 45°. Thus, for *trans*-H_2iBC the ground state dipole moment was found to be 2.16 ± 0.05 D, the excited-

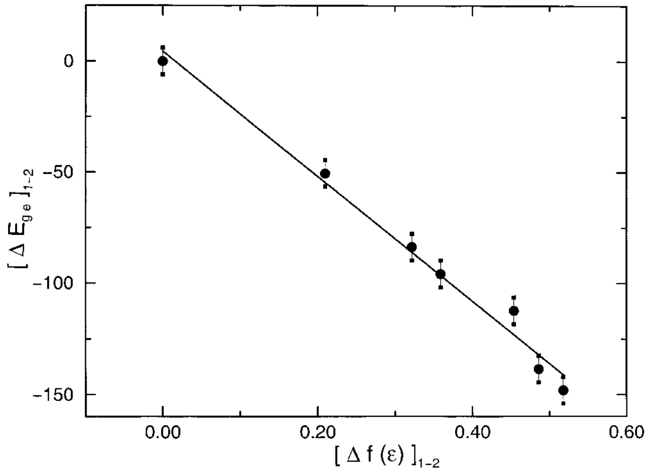


Figure 5. Plot of solvatochromic shifts of absorption maxima (cm^{-1}) against dielectric constant differences for *trans*-H_2iBC in a series of solvents.

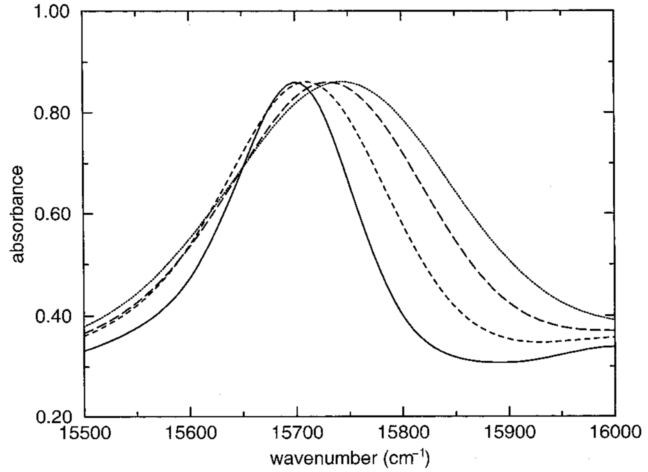


Figure 6. Absorption spectra of H_2Ch in octane (—), butyl ether (- - -), 2-chlorobutane (— — —), and 4-methyl-2-pentanone (• • •).

state dipole moment 3.51 ± 0.05 D, and the angle (ϕ) between them is 19.4° ± 0.5°.

As was mentioned earlier in this paper, in previous Stark effect experiments[8] on H_2Ch, its $\Delta\mu_{ge}$ was given a positive sign based on the red shift of the Q_y origin in going between an *n*-hexane solution and a neat H_2Ch film. In this work, we have used a wider range of solvents and found some diversity in the H_2Ch shift results. In aromatic solvents, the $S_1 \leftarrow S_0$ origin band shifted to the red as the solvent's dielectric was increased; this is consistent with previous observations.[8] However, in nonaromatic polar solvents, a blue shift was observed as the solvent dielectric was increased (Figure 6). Similarly, *cis*-H_2iBC also red-shifted with increasing dielectric of the aromatic solvents, but blue-shifted with increasing dielectric in saturated polar solvents (Figure 7). *trans*-H_2iBC consistently red-shifted as the dielectric of the solvent increased for aromatic and nonaromatic solvents (Figure 8). All of these origin band shifts for aromatic solvents are illustrated in Figure 9 and are listed in Table 5.

The explanation for these results came from work by Bayliss.[17,18] The initial observation in this theory is that the electronic absorption spectra of organic molecules in solution are red shifted with respect to those made in the gas phase. This is due to solvent polarization by the transition dipole of the molecule being excited; the extent of the polarization depends on the solvent's dielectric constant. Bayliss and McRae[16] relate the frequency shift of the absorption band in solution to solvation energies of the solute in its ground and excited states; solvation energies depend on several types of intermolecular interactions (e.g., dipole−dipole, dipole-polarization, dispersion). When the solute molecule is in its electronic ground state and it is in equilibrium with the surrounding solvent cage, the solvation energy depends on the geometry of the solvent and solute molecules and on the degree of mutual orientation interaction, if the solvent and solute molecules are polar. Thus, at the instant of excitation, the solute molecule is

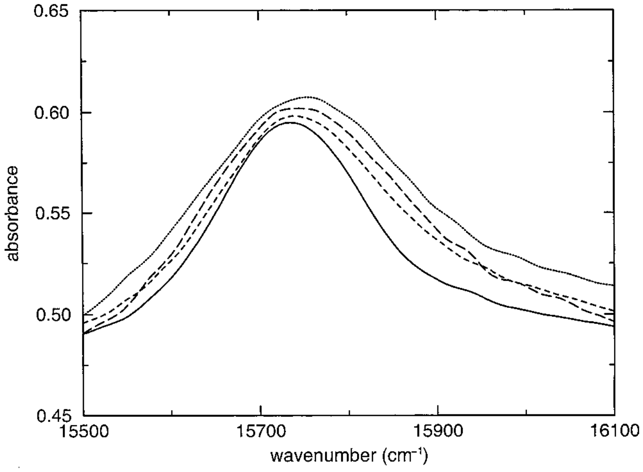


Figure 7. Absorption spectra of *cis*-H_2iBC in octane (—), butyl ether (- - -), 2-chlorobutane (— — —), and 4-methyl-2-pentanone (• • •).

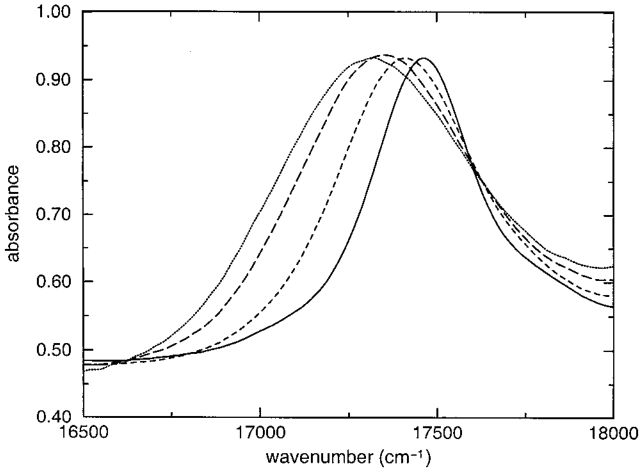


Figure 8. Absorption spectra of *trans*-H_2iBC in octane (—), butyl ether (- - -), 2-chlorobutane (— — —), and 4-methyl-2-pentanone (• • •).

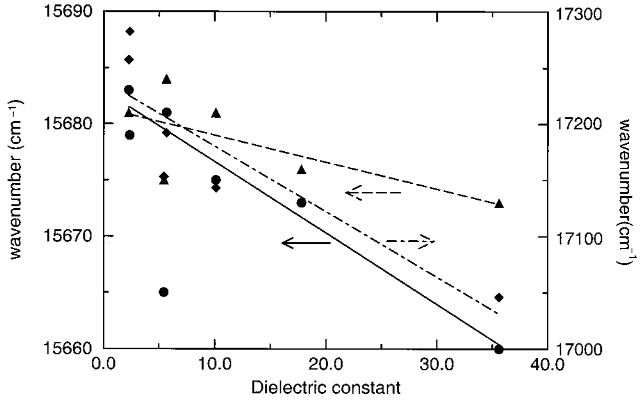


Figure 9. Plot of absorption maxima (cm^{-1}) against dielectric constant for H_2Ch (●), *cis*-H_2iBC (▲), and *trans*-H_2iBC (◆) in a series of aromatic solvents. (The errors associated with these data are minimal and are listed in Table 5.)

TABLE 5: Dielectric Constant (ϵ) and Absorption Maxima (cm^{-1}) for H_2Ch, *cis*-H_2iBC, and *trans*-H_2iBC in a Series of Aromatic Solvents

solvent	ϵ	H_2Ch	cis	trans
benzene	2.28	15683 ± 2	15681 ± 1	17257 ± 3
toluene	2.37	15679 ± 2		17282 ± 3
bromobenzene	5.45	15665 ± 2	15675 ± 1	17153 ± 3
chlorobenzene	5.69	15681 ± 2	15684 ± 1	17193 ± 3
1,2 dichlorobenzene	10.11	15675 ± 2	15681 ± 1	17143 ± 3
benzaldehyde	17.8	15673 ± 2	15676 ± 1	
nitrobenzene	35.6	15660 ± 2	15673 ± 1	17046 ± 3

momentarily surrounded by a solvent cage whose size and structure are those that are suited to the ground-state molecule. This is a strained condition; the two contributions to this are packing strain and orientation strain. Orientation strain is expected when the solvent and solute molecules are polar and when the solute's dipole moment changes during the electronic transition. Packing strain is expected when the solute molecule is larger in the excited state. The example case in Bayliss' work[17] of interest here is the one in which both the solvent and solute are polar and the solute undergoes an electronic transition which is accompanied by a change in the molecule's dipole moment. The ground state solvation energy is largely due to dipole−dipole forces and the solvent cage is oriented around the solute molecule. If upon excitation the dipole decreases, then the dipole−dipole contribution to the solvation energy decreases. The effect on the solution spectrum is that the band shifts to the blue, moves to higher energy. The size of the blue shift depends on a number of factors, e.g., magnitude of the decrease in dipole moment during the transition and the size of the dipole moment of the solvent. Thus, in the case of a $-\Delta\mu$ associated with the electronic transition, there are two opposite shifts, which are superimposed; the general polarization shift moves the spectrum to the red, and the decrease in dipole moment shifts the spectrum to the blue. The overall shift of the band that is experimentally observed depends on the relative sizes of these effects. This was what we have observed for H_2Ch and *cis*-H_2-iBC; in an aromatic environment, a red shift is observed because of the dominance of solvent polarization induced by the transition dipole associated with the excitation. However, in polar nonaromatic solvents, which have smaller polarizabilities, the blue shift due to the decrease in dipole moment was dominant. For molecules in which the dipole moment increases ($+\Delta\mu$) during the electronic transition, the dipole−dipole interactions with the solvent cage increases and the absorption band red shifts; since the polarization shift also produces a red shift, these spectra always go to lower energy. This was the situation for *trans*-H_2iBC. It exhibited a large red shift in aromatic and nonaromatic surroundings.

In this work, we have experimentally determined the ground state dipole moment of H_2Ch (μ_g, 2.93 ± 0.08 D). Since the $\Delta\mu_{ge}$ had already been measured (−0.255 ± 0.005 D),[8,9] we found μ_e (2.68 ± 0.08 D). Then, from the cube of molecular cavity radius determined from the chlorin data, we used the solvatochromic shifts of *cis*- and *trans*-H_2iBC to determine their respective μ_g values (0.35 ± 0.08 and 2.16 ± 0.05 D). From previously measured changes in dipole moments ($\Delta\mu_{ge}$) of their lowest energy $\pi\pi^*$ transitions,[4,5] we were able to determine their respective excited-state dipole moments (−0.97 ± 0.08 and 3.51 ± 0.05 D). Free base chlorin and cis free base isobacteriochlorin have C_{2v} symmetry, so $\bar{\mu}_g$ and $\bar{\mu}_e$ are parallel; however, *trans*-H_2iBC has C_s symmetry and there is an angle of 19.4° ± 0.5° between $\bar{\mu}_g$ and $\bar{\mu}_e$. Also, our solvatochromic shift experiments indicated that only those measurements made in solvents with low polarizability (nonaromatic) should be used to infer the sign of a change in dipole moment derived from a Stark effect experiment.

Acknowledgment. This work was supported by the National Institutes of Health (GM08153).

References and Notes

(1) Moura, I.; LeGall, J.; Lino, A. R.; Peck, H. D., Jr.; Fauque, G.; Xavier, A. V.; Der Vartanian, D. V.; Moura, J. J. G.; Huynh, B. H. *J. Am. Chem. Soc.* **1988**, *110*, 1075.

(2) Ostrowski, J.; Wu, J. Y.; Rueger, D. C.; Miller, B. E.; Siegel, L. M.; Kredich, N. M. *J. Biol. Chem.* **1989**, *264*, 15726.

(3) Gouterman, M. In *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. III, pp 1−165.

(4) Johnson, L. W.; Murphy, M. D.; Pope, C.; Forest, M.; Lombardi, J. R. *J. Chem. Phys.* **1987**, *86*, 4335.

(5) Singh, A.; Huang W.-Y.; Johnson, L. W. *J. Chem. Phys.* **1999**, *111*, 3612.

(6) Suppan, P. *J. Photochem. Photobiol.* **1990**, *50*, 293.

(7) Amos, A. T.; Burrows, B. L. *Adv. Quantum Chem.* **1973**, *7*, 289.

(8) Dicker, A. I. M.; Johnson, L. W.; Noort, M.; van der Waals, J. H. *Chem. Phys. Lett.* **1983**, *94*, 14.

(9) Burkhalter, F. A.; Suter, G. W.; Wild, U. P.; Samoilenko, V. D.; Razumova, W. D.; Personov, R. I. *Chem. Phys. Lett.* **1983**, *94*, 483.

(10) Egorova, G. D.; Solov'ev, K. N.; Shul'ga, A. M. *Zh. Obshch. Khim.* **1967**, *37*, 357.

(11) Eisner, U.; Linstead, R. P. *J. Chem. Soc.* **1955**, 3742.

(12) Guggenheim, E. A. *Trans. Faraday Soc.* **1949**, *45*, 714.

(13) Lide, D. R. *Handbook of Chemistry and Physics*, 78th ed.; CRC Press: Boca Raton, 1997−1998.

(14) Butler, W. L. Fourth derivative spectra. *Methods Enzymol.* **1979**, *56*, 501.

(15) Weiss, C.; Kobayashi, H.; Gouterman, M. **1965**, *16*, 415.

(16) Petke, J. D.; Maggiora, G. M.; Shipman, L. L.; Christoffersen, R. E. *J. Mol. Spectrosc.* **1978**, *73*, 311.

(17) Bayliss, N. S.; McRae, E. G. *J. Phys. Chem.* **1954**, *58*, 1002.

(18) Bayliss, N. S. *J. Chem. Phys.* **1950**, *18*, 292.