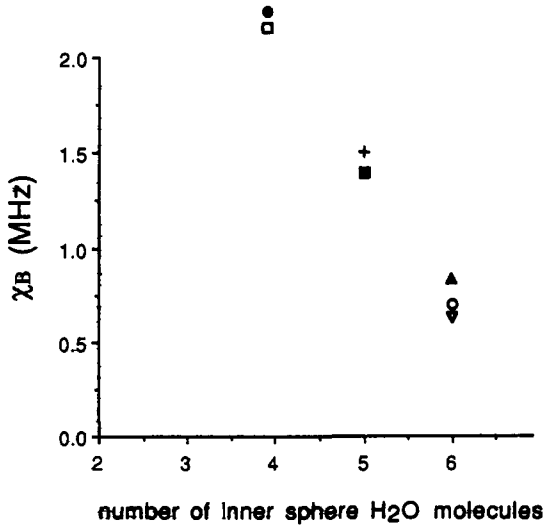


**Figure 2.** Variation of $\chi_B$ with number of $H_2O$ molecules ($6-n$) in the inner coordination sphere of $Mg^{2+}$. Data shown corresponds to $ATP^{4-}$ (●), $ADP^{3-}$ (□), glucose 1-phosphate (+), glucose 6-phosphate (■), $tRNA^{Phe}$ [native (▲) and nonnative (▽) conformations], and 5S rRNA (○). Values for $\chi_B$ (±10%) were determined by line-shape analysis of data determined by systematic titration and variable-temperature experiments, and from relaxation measurements.[8,11,21]

are added to a 0.22 mM solution of *Escherichia coli* 5S rRNA. A resonance was observed after the addition of 1 equiv of magnesium, and so in contrast to most tRNAs, 5S rRNA does not possess strong $Mg^{2+}$ binding sites (i.e., $K_a$ are all $<10^4$ $M^{-1}$).[8,16] The formation of the ribosomal complex from rRNA and protein components would demand a certain flexibility on the part of the RNA and is in keeping with the absence of tight-binding $Mg^{2+}$ domains at intrastrand cross-links, such as those found in tRNA.[16] A total line-shape analysis[17] of the data in Figure 1 for 80 bound ions[5] gave the following binding parameters: $K_a = 236 \pm 20$ $M^{-1}$; $\Delta G^* = (13.1 \pm 0.2) \times 10^3$ kcal; $k_{off} = 1.5 \times 10^3$ $s^{-1}$ ($k_{on} = K_a k_{off} = 3.5 \times 10^5$ $s^{-1}$); $\chi_B = 0.69 \pm 0.1$ MHz. Parameter $\chi_B$ is given by $e^2Qq_{zz}/h$, where $Q$ is the quadrupole moment and $q_{zz}$ is the electric field gradient at the nucleus. The value of $\chi_B$ is dependent on the asymmetry at the metal center[18,19] and should therefore be a probe of the inner coordination sphere of the ion. The plot in Figure 2 displays a systematic variation in $\chi_B$ with substitution of the inner-sphere waters ($n$), reflecting the increasing electric field gradient and the greater asymmetry in the ligand environment of $Mg^{2+}$.[20] Previous determinations of $\chi_B$ for $Mg^{2+}$ binding sites on proteins (troponin c, $\chi_B \sim 1.1$ MHz; calmodulin and tryptic fragments, $\chi_B \sim 1.6$ MHz; phospholipase, $A_2$, $\chi_B \sim 1.4$–2.3 MHz)[19,21,22] reflect a larger asymmetry and coordination number. The small value of $\chi_B$ for RNA complexes indicates retention of the hydration shell and outer-sphere coordination by $Mg(H_2O)_6^{2+}$. For free $Mg^{2+}$ ($\tau_c \sim 0.1$–$0.01$ ns) with a $T_1$ of 173 ms, $\chi$ can be estimated from the relationship $1/T_1 = (3\pi^2/10)\chi^2(2I+3)\tau_c/[I^2(2I-1)]$ to give $\chi = 7.7$–$24$ kHz. The larger value for $Mg(H_2O)_6^{2+}$ bound to RNA suggests multiple hydrogen-bonding interactions between backbone phosphates, base O and N atoms, and sugar hydroxyls. Computer graphics analysis of $Mg(H_2O)_6^{2+}$ binding sites in the major and minor grooves of dsRNA suggests that five to seven H bonds can form for each hexaaquo ion.[23] This also explains the relatively large value of $K_a$,[24,25] which is similar to that determined for $tRNA^{Phe}$ (yeast).[8] An upper limit for the excess energy of each bound $Mg^{2+}$ ion resulting from H-bond formation over direct phosphate coordination (which allows three to four fewer H bonds) can be estimated from the relative $K_a$'s for magnesium binding to phosphodiesters ($\sim 3$ $M^{-1}$) and RNA ($\sim$200–250 $M^{-1}$), using the relationship $\Delta G° = -RT \ln K_a$. We calculate $\Delta\Delta G° \sim 0.75$ kcal/mol per $Mg^{2+}$ ion in favor of maximal H-bond interactions. Stabilization of the hydration sphere can therefore be ascribed to the dominance of hydrogen-bond formation.

In this paper we have demonstrated the absence of "strong" $Mg^{2+}$ binding sites on 5S rRNA. Magnesium–RNA chemistry is likely to be dominated by hexahydrated ions held in the major and minor grooves of dsRNA by hydrogen-bonding. The coordination state of $(Mg^{2+})_{bound}$ may be deduced from $\chi_B$. The rate of $Mg^{2+}$ exchange ($k_{ex} \sim 1.5 \times 10^3$ $s^{-1}$) is rapid enough to support metalloregulatory mechanisms for conformational changes in RNA tertiary structure.[7]

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## Effect of Nonexcitonic Interactions among the Paired Molecules on the $Q_y$ Transition of Bacteriochlorophyll Dimers. Applications to the Primary Electron Donors P-860 and P-960 in Bacterial Reaction Centers

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X-ray diffraction of reaction centers[1] (RCs) from two strains of purple bacteria, *Rhodobacter sphaeroides*[2,3] and *Rhodopseudomonas viridis*,[4] revealed that their primary electron donors, P-860 and P-960, are tight dimers of bacteriochlorophyll (Bchl)

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‡ In partial fulfillment of a M.Sc. Thesis.

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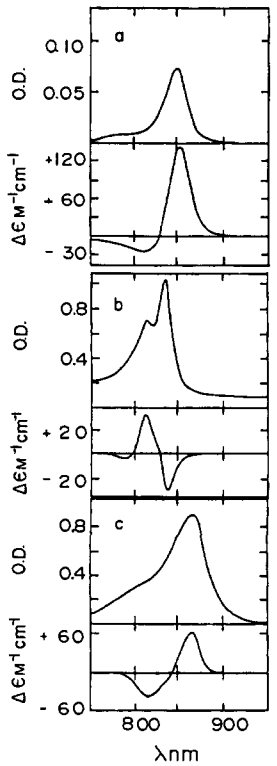


**Figure 1.** Optical absorption (upper curves) and circular dichroism (lower curves) of (a) $6.25 \times 10^{-7}$ M dimers of Bchla in FW; (b) $8.3 \times 10^{-6}$ M dimers of Bchla' in FW; and (c) $7.8 \times 10^{-6}$ M dimers of Bpheida in FW (the same as Bpheida'). Conditions for dimer preparation are given in ref 10. All solutions contain $5.8 \times 10^{-3}$ M Triton X-100.

a and b, respectively. The geometry of the paired molecules is such that their transition monopoles strongly interact, resulting in a bathochromic shift of the $Q_y$ bands.[5-7] Recent calculations based upon interactions among point-charge monopoles (PCM) showed that exciton coupling among the localized $Q_y$ transitions of the paired molecules[5-7] can account for part of the shift. The origin of the remaining nonexcitonic shift is controversial.[5-7] In this communication we show that there is a ratio of 1.2–1.5 between the nonexcitonic shift and the exciton splitting of the $Q_y$ transition in several Bchl dimers in vitro. Application of this ratio when calculating the spectra of Bchl dimers with geometries of the special pair has resulted in wavelengths and intensities for the primary donor's $Q_y$ excitonic transitions comparable to those derived from experimental data. This finding is contradictory to the idea that most of the $Q_y$ shift in the Bchl dimers is caused by admixing with a low-lying charge-transfer (CT) transition.[5a,6,8]

Dimers were prepared as previously described[9,10] from Bchla,[11a] bacteriophenophytin a (Bphea), bacteriopheophorbide a (Bpheida),[11b] and the corresponding epimers:[12] Bchla' and Bpheida'.[13] Each molecule dimerized spontaneously in a 3:1 (v/v) formamide/water solution that contained micelles of the detergent Triton X-100. During dimerization the single $Q_y$ absorption band of each monomer and the associated weak, single-banded CD were replaced by two new bathochromically shifted transitions and two relatively strong CD bands with opposite signs.[14] In each case, the combined oscillator strength of the dimer's lowest energy transitions was more than twice that of the corresponding monomer's transition (the origin of this "hyperchromicity" was recently addressed by using two alternative approaches[5b,15]). The Bchla dimer[10] (termed Bchl-853 for the longest wavelength transition[10a]) has a single absorption band at 853 nm accompanied by a strong, positive CD at 853 nm and a weak negative CD at 810–815 nm that can be observed at very low pigment concentrations (Figure 1a). The Bchla' dimer (Bchla'-835) absorbs at 835 and 808 nm.[14] The accompanying CD bands are equal in magnitude and have opposite signs (Figure 1b). The Bpheida and Bpheida' dimers (Bpheid-860) have similar spectra with maximum absorption at 860 and 805 nm. The CD bands are strong and have opposite signs (Figure 1c). The Bphea dimer, Bphea-855, (not shown) absorbs strongly at 855 nm with accompanying CD bands at 855 nm (positive) and 810 nm (negative). Note that in a mixture of water and acetic acid containing lauryldimethylamine oxide (LDAO) micelles, the absorption band of the Bphe aggregates is seen at 850 nm and the CD signals are seen at 850 nm (positive) and 815 nm (negative).[11a] Besides the $Q_y$ and $Q_x$ excitonic transitions, no other transitions were observed in the vis-near-IR ranges for any of the pigments studied.

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(14) To find the bands' positions we examined their second derivatives (after conversion to wavenumbers) and then deconvoluted the spectra using the CURFIT program (written in Fortran) and the CDMASTER program (written in Turbo-Pascal) of the Weizmann Institute.

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Apparently, the new bands in the spectra (CD and optical absorption) of each dimer are the result of transitions into the $Q_y$ exciton states.[7,10,15] The exciton splittings are 794, 649, 600–620, and 400 $cm^{-1}$ for Bpheida-860 (or Bpheida'-860), Bphea-855, Bchl-853, and Bchla'-835, respectively. The corresponding shifts of the transitions' gravity centers with respect to the monomeric $Q_y$ transitions are 1132, 1137, 786–823, and 644 $cm^{-1}$, respectively. The ratio between the shift of the gravity center and the energy difference between the two excitonic transitions is 1.2–1.5 in the five dimers studied. A similar large shift of the exciton's gravity center was recently observed for Chla and Chlb dimers prepared under the same conditions (Scherz and Rosenbach-Belkin, unpublished data), and this seems to be a general characteristic of the hydroporphyrin dimers.

The intensity of the lower energy $Q_y$ excitonic transition in each of the studied dimers is much higher than the intensity of the higher energy one, yet both are strongly shifted to the near-IR. These observations cannot be explained by a mixing between $Q_y$ and charge-transfer transitions (as recently suggested for the in vivo Bchl dimers P-860 and P-960[5a,8]). Such mixing would preferentially shift the lower energy excitonic transition to the near-IR and significantly reduce its intensity while the higher energy $Q_y$ transition would not be greatly shifted with respect to the monomeric $Q_y$ transition.[5a,d] In fact, for the particular geometries of P-860 and P-960, the expected energy difference between the two excitonic transitions is about 5 times the exciton coupling.[5a,8] These predictions are applicable to any Bchl dimer's geometry in which the transition to the lower energy $Q_y$ exciton is much stronger than the higher energy transition. In contrast, increases in configuration interactions[5b,16] in each of the coupled Bchls, increases in interactions among the paired molecules when one is excited[9c] (the nonresonance "D" term that was originally introduced by Davidov[9c]), and dispersive interactions among their excited states[9a,b] should shift the two $Q^y$ excitonic transitions equally, without introducing a new band. Hence, if the nonexcitonic shift of the $Q_y$ excitonic transitions is related to any of these three mechanisms (or their combinations), their energy difference (exciton splitting) should always be 2 times the exciton coupling[5b,c,7,9a,b] regardless of the dimer's geometry.

The resemblance between the Bchl-853 spectra (CD and absorption) and the spectra of P-860[10a] appears to indicate that, both in vitro and in vivo, the nonexcitonic shifts of the Bchl $Q_y$ transitions are due to similar mechanisms. Simple arithmetic shows that if the ratio between the nonexcitonic shift and the splitting of the $Q_y$ excitonic transitions is 1.5, then the higher energy transition will be halfway (in wavenumbers) between the lower energy excitonic and the monomeric $Q_y$ transitions. The energies of the $Q_y$ transitions of monomeric Bchla and Bchlb in vitro are 12 820[10] and 12 578[17] $cm^{-1}$, respectively; therefore the upper $Q_y$ excitonic transitions in P-860 and P-960 are expected to be at 12 223 (818 nm) and 11 497 $cm^{-1}$ (869 nm), respectively. There is good agreement between these numbers and the values deduced from linear dichroism measurements of RCs[18] (~12 350 and 11 760 $cm^{-1}$). Assuming that the small differences are due to CT admixing, we propose that the CT contribution to the shift of the lower excitonic transition in P-860 and P-960 is ~120 and 300 wavenumbers, respectively.

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## Effects of Added Water on Thermodynamic Aspects of Hydrogen-Bond-Based Molecular Recognition in Chloroform[1]

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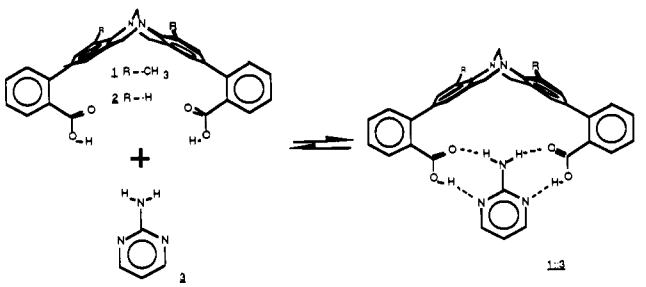
The hydrogen bond is a frequently cited contributor to intermolecular forces.[3,4] Host–guest systems based on hydrogen-bonding interactions in organic solvents are well-known.[5] Pauling recognized that the contribution a hydrogen bond makes to molecular interactions is, in the presence of water, limited to the difference between the hydrogen bond to the substrate and the hydrogen bond to a water molecule.[3] Water is a competitive inhibitor of binding. Here we evaluate the effects of traces of water in chloroform on association constants for a hydrogen-bond-based system. It is shown that the free energy of binding is not very strongly affected by the presence of water in chloroform, but the enthalpy and entropy of binding are significantly altered in a mutually compensating manner.

The binding of host **1** and 2-aminopyrimidine (**3**) was measured in chloroform in the presence and near absence of water and at several different temperatures.[6] "Single-point" variable-temperature binding studies have been used recently with NMR data to evaluate the thermodynamics of host–guest binding.[8,9] If the chemical shifts of the observed proton in the bound and unbound components are *temperature invariant* and if both shifts are known, then an association constant can be calculated on the basis of one spectroscopic observation.[9]

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