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center was recently observed for Chla and Chlb dimers prepared under the same conditions (Scherz and Rosenbach-Belkin, unpublished data), and this seems to be a general characteristic of the hydroporphyrin dimers.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 12820[10] and 12578[17] cm^{-1}, respectively; therefore the upper Q_y excitonic transitions in P-860 and P-960 are expected to be at 12223 (818 nm) and 11497 cm^{-1} (869 nm), respectively. There is good agreement between these numbers and the values deduced from linear dichroism measurements of RCs[18] (~12350 and 11760 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.

Acknowledgment. We are grateful to Dr. D. Tal from the Department of Biochemistry, Weizmann Institute of Science, for his advice on the analytical separation technique. This work was supported by the US–Israel Binational Science Foundation, Grant No. 84-00144.

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(16) Reference 5b considers an additional CI due to interactions of the individual Bchl molecules in P-960 with adjacent aromatic residues. However, since the Bchls are aromatics they may induce this effect on each other.

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

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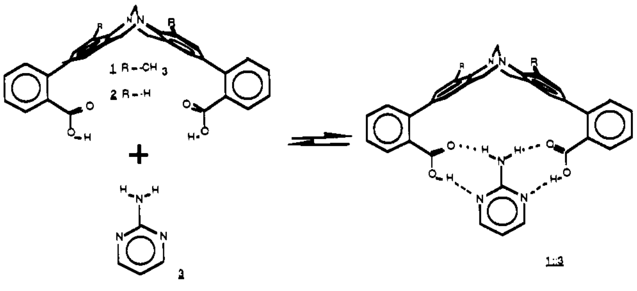
The hydrogen bond is a frequently cited contributor to intermolecular forces.[3,4] Host–guest systems based on hydrogen-bonding interactions in organic solvents are well-known.[5] Pauling recognized that the contribution a hydrogen bond makes to molecular interactions is, in the presence of water, limited 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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(6) Host **1** was prepared from 2-bromobenzoic acid and 2-methyl-4-bromoaniline by a path analogous to that used to prepare host **2**.[7] Spectroscopic data, combustion analysis, and crystallographic data all support the indicated structure and the suggested mode of binding.

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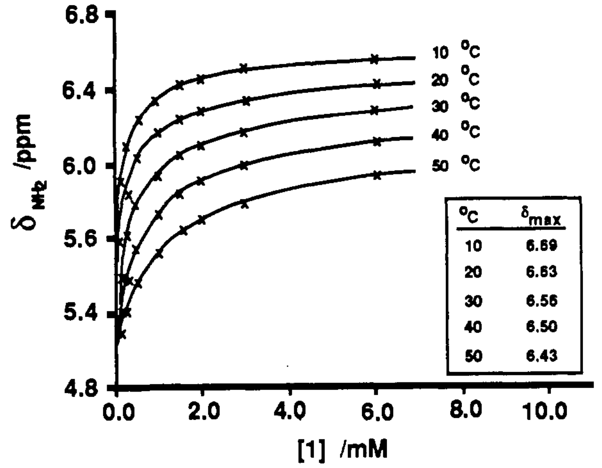

Figure 1. Observed (×) and calculated effects of host **1** on the chemical shift of the NH_2 group of guest **3** as revealed by dilution of a 1:1 mixture of **1** and **3**. δ_{max} is the chemical shift of the NH_2 in the complex. Lines were calculated according to the formula $\delta_{obsd} = \delta_s + \Delta\delta[1 + (K_d/2C_0) - [(K_d/2C_0)^2 + (K_d/C_0)]^{1/2}]$, where δ_s is the chemical shift of unbound guest, K_d is the dissociation constant for the interaction, C_0 = [**1**] = [**3**], and $\Delta\delta = (\delta_{max} - \delta_s)$.[14e]

The protons usually observed in host–guest studies of hydrogen-bond-based systems are the H-bonded protons. The data (Figure 1) demonstrate that *"single-point" variable-temperature binding studies based on H-bonded protons should be eschewed.* Such studies can lead to large errors in enthalpies and entropies of binding because *the chemical shift of a hydrogen-bonded proton will usually be significantly temperature dependent.*[10] Here the chemical shift of the amino group in the complex **1**::**3** is found through extrapolation to be 6.63 ppm at 20 °C but 6.43 ppm at 50 °C. This change (upfield, 0.0066 ppm/°C) is typical of temperature effects previously observed for H-bonded protons and mandates that the variable-temperature study be carried out by observing many different concentrations of host and guest at each temperature.[10,11,13]

In dry $DCCl_3$, association constants (K_a) ranged from 1000 to 24 000 M^{-1}.[15] [For dry chloroform (T, K_a): 283 K, 24 000 M^{-1}; 293 K, 9400 M^{-1}; 303 K, 4800 M^{-1}; 313 K, 2100 M^{-1}; 323 K, 1000 M^{-1}.] Addition of water to this system ($DCCl_3$ was saturated with H_2O prior to preparation of the solutions) lowered the free energy of binding by only about 15%, decreasing binding at 293 °C by only 0.7 kcal/mol. [For wet chloroform (T, K_a): 288 K, 3600 M^{-1}; 293 K, 2800 M^{-1}; 303 K, 1650 M^{-1}; 313 K, 1000 M^{-1}; 323 K, 700 M^{-1}.] This small change is characteristic of other host–guest systems we have observed: at 20–25 °C, small amounts of water in the chloroform (up to 30–40 equiv, relative to the host) diminish association constants by factors of only 2–6 vis-à-vis dry chloroform.

A van't Hoff plot for binding of **1** and **3** in "dry" chloroform and in "wet" chloroform (Figure 2) reveals that in dry $DCCl_3$ $\Delta H = -14.3 \pm 0.6$ kcal/mol and $\Delta S = -30 \pm 1.7$ cal·mol^{-1}·deg^{-1}.[15,16]

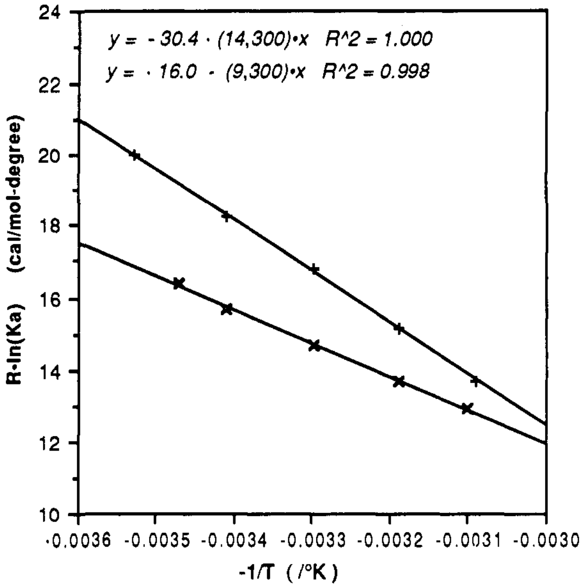

Figure 2. Two van't Hoff plots for binding of 2-aminopyrimidine (**3**) by host **1** under two different conditions. The slope of the plot changes substantially in going from dry chloroform (+) to wet chloroform (×).[15,16]

In wet $DCCl_3$ the ΔH of binding was -9.3 ± 0.6 kcal/mol. This loss of 5 kcal/mol of enthalpy is consistent with the picture of water as a competitive inhibitor. This loss, however, is largely counterbalanced by a substantial change in the entropy of binding, the magnitude of which changes from −30.4 cal·mol^{-1}·deg^{-1} in dry chloroform to -16 ± 2.2 cal·mol^{-1}·deg^{-1} in wet chloroform.

The results suggest a simple model: binding in dry chloroform (eq 1) requires substantial loss of rotational/translational freedom for one solute. The loss is only partially compensated by new vibrational modes in the product, and 30 eu is a reasonable change for the event.[17] In contrast, binding in wet chloroform (eq 2) requires the association of hydrated solutes. The binding event is accompanied by liberation of water molecule(s), and the net entropy change is therefore smaller than in eq 1. The model illustrates an interesting parallel between binding in wet organic solvents and in water: in both cases liberation of water provides a compensating factor that helps to offset the expected entropic disadvantage of host–guest association.

$$\mathrm{H + G = H{::}G} \tag{1}$$

$$\mathrm{H{\cdot}(H_2O)_{\mathit{m}} + G{\cdot}(H_2O)_{\mathit{n}} = H{::}G{\cdot}(H_2O)_{(\mathit{m}+\mathit{n})-\mathit{x}} + (H_2O)_{\mathit{x}}} \tag{2}$$

We conclude that single-point variable-temperature binding studies should be suspected of error *especially if they are based on observations of H-bonded protons.*[10-12,18] Water in the present

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(11) Due to the unusually low frequency of the hydrogen-bond-stretching vibrational mode, several excited states are populated even at low temperatures. Because the stretch is anharmonic, the average bond length increases as the temperature rises. The temperature effect is due to distortion of the H bond rather than dissociation of the complex.[12]

(12) Muller, N.; Reiter, R. C. *J. Chem. Phys.* **1965**, *42*, 3265.

(13) Association constants can be determined by obtaining spectra at a variety of host/guest ratios.[14a-d] An alternative is to hold this ratio constant and obtain spectra at many concentrations.[7] The advantages of the latter method have been discussed.[7,14e]

(14) (a) de Boer, J. A. A.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **1985**, *107*, 5347. (b) Wilcox, C. S.; Cowart, M. D. *Tetrahedron Lett.* **1986**, 5563. (c) Cowart, M. D.; Sucholeiki, I.; Bukownik, R. R.; Wilcox, C. S. *J. Am. Chem. Soc.* **1988**, *110*, 6204. (d) Petti, M. A.; Shepodd, T. J.; Barrans, R. E., Jr.; Dougherty, D. A. *J. Am. Chem. Soc.* **1988**, *110*, 6825. (e) Wilcox, C. S. In *Frontiers of Supramolecular Organic Chemistry and Photochemistry*; Schneider, H.-J., Dürr, H., Eds.; VCH: Weinheim, 1990.

(15) In this paper "dry" $DCCl_3$ means $DCCl_3$ that has been refluxed >2 h over a large excess of $CaCl_2$, distilled, and used within 24 h. All operations were carried out under nitrogen. Solutions were always under nitrogen in oven-dried glassware and nitrogen-filled NMR tubes. These conditions typically afforded samples containing about 0.2–1.0 mM H_2O, as judged by integration of NMR signals. "Wet" $DCCl_3$ was prepared from $DCCl_3$ that was filtered through activated alumina and then saturated with water. The $DCCl_3$ was stirred with excess deionized water for about 1 h and then separated. The concentration of water was estimated by integration of NMR signals to be 30–40 mM.

(16) The uncertainties in ΔH and ΔS (±0.6 kcal/mol and ±2 eu, respectively) are calculated for 95% confidence levels.[19] Curved van't Hoff plots can arise due to heat capacity effects or due to other, less ideal, factors: Leffler, J. E.; Grunwald, E. *Rates and Equilibria of Organic Reactions*; Wiley: New York, 1963. The small uncertainties seen here suggest ΔC_p is insignificant (<30 cal·mol^{-1}·deg^{-1}).

(17) Page, M. I. In *The Chemistry of Enzyme Action*; Page, M. I., Ed.; Elsevier: New York, 1984; pp 18–21.

(18) Low-frequency vibration modes are probable in any molecular complex, and it is important that control studies be carried out before "single-point" variable-temperature studies are accepted.[9] A good approach would be to do a complete binding study at the highest and lowest temperatures of interest, and then, if no change in chemical shift of the complex is noted, the association constants at intermediate temperatures could be filled in by the "single-point" method.

example has no especially large effect on association constants in chloroform, and we expect that this result will be generally true. Water does, however, have a large effect on ΔH and ΔS of association. Therefore future reports concerning the thermodynamics of host-guest binding in organic solvents should carefully stipulate the amount of water present during binding experiments. Attention to this point would help to reduce the uncertainities that arise when binding data from several different laboratories are compared.

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Supplementary Material Available: Purification methods, spectroscopic data (IR, ^{1}H NMR, ^{13}C NMR, MS) and combustion (elemental) analysis for host **1**, complete binding data for all association constants, and plots of calculated and observed chemical shifts for each binding experiment (12 pages). Ordering information is given on any current masthead page.

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Unusual Organic Chemistry on a Metallacarborane Substrate: Formation of a B-Vinyl Ester from Acetyl Chloride

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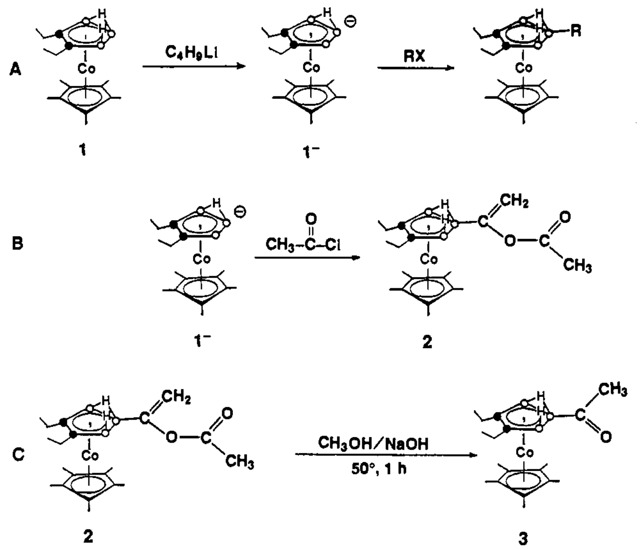
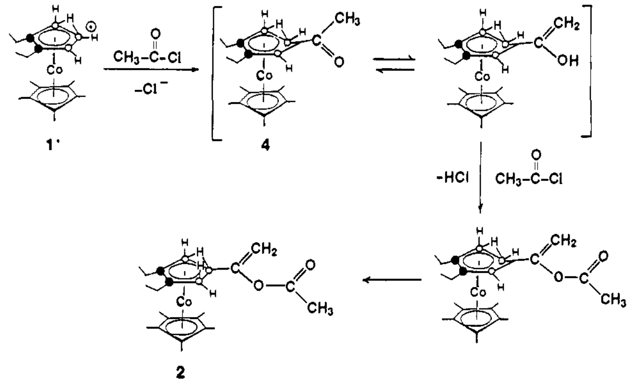
We report an unexpected reaction that has implications for organoborane/organocarborane chemistry, the consequences of which are currently being exploited in our program in transition-metal organometallic synthesis. In developing methods for systematically linking and/or stacking metal-carborane sandwich units such as $(C_5Me_5)Co(Et_2C_2B_3H_5)$ (**1**) as precursors to electron-delocalized oligomers and polymers,[1] we found earlier[1a] that the **1**$^-$ anion (obtained by bridge deprotonation of **1**), when treated with a variety of alkyl and arylalkyl halides, undergoes regiospecific substitution at the middle boron atom [B(5)] to generate the neutral B(5)-alkyl product, as shown in Scheme I (A). (The Fe-arene and Ru-arene analogues of **1** behave similarly[1a]). In the present work, we attempted the analogous synthesis of the B(5)-acetyl derivative via reaction of **1**$^-$ with acetyl chloride in THF at -76 °C, but no acetyl species was detected. Instead, the only identifiable product (55% yield based on **1** consumed) other than the starting material **1** was an air-stable solid (**2**) which has been characterized as the B(5)-(1-vinyl acetate) derivative of **1** [Scheme I (B)].[2] The identity of **2** follows from its 300-MHz ^{1}H, 90-MHz ^{13}C, and 115.8-MHz ^{11}B FT NMR, IR, and mass spectra, supported by X-ray diffraction data. The crystal structure analysis of **2** established the locations of all atoms including hydrogens and confirmed the nature of the vinyl ester (enol acetate) moiety attached to B(5).[3] In a further odd twist of fate, we found that **2** readily undergoes base-catalyzed cleavage to give the B(5)-acetyl derivative **3**, the original target compound, in high yield [Scheme I(C)].[4]

Scheme I[a]



[a](●) C; (O) B, BH.

Scheme II[a]



[a](●) C, (O) B.

[†] Present address: Department of Chemistry, Brandeis University, Waltham, MA 02254.

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(2) A 0.52·5 (1.7 mmol) sample of **1** was deprotonated by treatment with *n*-butyllithium under vacuum in THF at -76 °C as described elsewhere.[1c] To this solution was added, via syringe, 2.1 mmol of acetyl chloride at -76 °C, and the resulting dark orange-brown solution was stirred for 3 days at room temperature, after which the greenish yellow solution was opened to air, the solvent removed by evaporation, and the dark brown solid residue taken up in CH_2Cl_2 and filtered through 2 cm of silica. The filtrate was evaporated, and the dark brown residue was chromatographed on a silica column in 50:50 hexane/CH_2Cl_2, giving two yellow bands, of which the first was **1**, 0.290 g, 0.92 mmol. The second band was yellow-brown **2**, 0.160 g, 0.400 mmol: ^{1}H NMR (δ, ppm, $CDCl_3$) 5.16 (s, $=CH_2$), 5.03 (s, $=CH_2$), 2.14 (s, $COCH_3$), 2.07 (m, CH_2), 1.85 (m, CH_2), 1.70 (s, C_5Me_5), 1.07 (t, CH_3), -4.9 (br s, BHB); ^{13}C NMR (δ, ppm, $CDCl_3$) 169.8 (s, C=O), 160 (br s, CB), 111.8 (t, $=CH_2$), 92.6 (s, C_5 ring), 23.0 (t, CH_2), 21.6 (q, $COCH_3$), 17.6 (q, CH_3), 9.8 (q, C_5Me_5); ^{11}B NMR (δ, ppm, relative to $BF_3{\cdot}OEt_2$, hexane) 11.7 (s, B(5)), -0.8 (d, 125 Hz, B(4,6)); IR (neat, cm^{-1}) 2960 (vs), 2927 (s), 2910 (sh), 2867 (s), 2514 (s), 2358 (w br), 2322 (w br), 1869 (m br), 1750 (vs), 1448 (m), 1379 (vs), 1368 (vs), 1363 (sh), 1237 (vs), 1201 (vs), 1026 (s), 895 (s), 873 (s), 773 (s); exact mass calcd for $^{59}Co^{16}O_2{}^{12}C_{20}{}^{11}B_3{}^1H_{34}{}^+$ 398.2170, found 398.2156.

(3) Crystal data: space group $P2_1/n$; $Z = 4$; $a = 8.368$ (2) Å, $b = 18.757$ (5) Å, $c = 14.234$ (4) Å; $\beta = 97.25$ (2)°; $V = 2216$ (2) Å^3. Data collection parameters: maximum 2θ range 55°, Mo Kα radiation, $\lambda = 0.71069$ Å. The structure was solved by heavy-atom techniques (TEXSAN 5.0) and refined to $R = 0.037$ for 3856 absorption-corrected reflections having $F_o^2 > 3.0\sigma(F_o^2)$. A full report of the structure determination will be given later.

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