by $\Delta G_d = 0.80 \pm 0.05$ eV relative to their energies in polar liquids.[14]

Using the Born dielectric continuum model of the solvent, Weller[15] derived eq 3 to calculate the ion-pair destabilization energy, ΔG_d, in a solvent with a static dielectric constant ϵ_s, if the redox potentials of the donor and acceptor are measured in a medium with a high dielectric constant, ϵ_s':

$$\Delta G_d = e_0^2[(1/2r_1) + (1/2r_2) - (1/r_{12})]/\epsilon_s - e_0^2/[(1/2r_1) + (1/2r_2)\epsilon_s'] \tag{3}$$

where r_1 and r_2 are the radii of the two ions and the remaining parameters are defined above. Since $\epsilon_s = 2.6$ for glassy MTHF at 77 K,[16] $\epsilon_s' = 20$ for butyronitrile at 295 K, $r_{12} = 11 \pm 1$ Å,[12] r_1 for the porphyrin = 5 Å,[12] and r_2 for the quinone = 3 Å,[12] eq 3 predicts that $\Delta G_d = 0.78$ eV. This calculated value agrees remarkably well with the value of $\Delta G_d = 0.8$ eV that we measure directly.

Electron transfer theories beginning with that of Marcus show that the electron transfer rate constant will be greatest when $\Delta G_{cs} + \lambda = 0$, where λ is the total nuclear reorganization energy for the electron-transfer reaction.[17] This reorganization energy comprises terms describing both the solvent reorganization energy, λ_s, and the internal nuclear reorganization of the donor-acceptor molecule, λ_i, where $\lambda = \lambda_s + \lambda_i$. Semiclassical electron-transfer theory[18] is used to fit the data in Figure 2 to a monotonic function with rate constants increasing as free energy of reaction becomes increasingly negative. The plot of ln k_{cs} vs $-\Delta G_{cs}$ in Figure 2 reaches a maximum at $\Delta G_{cs} = -0.6$ eV. Since the dielectric continuum model of the solvent is in reasonable agreement with our experimental results, we can use the expression of Marcus[19] to calculate the solvent reorganization energy, λ_s:

$$\lambda_s = e_0^2[(1/2r_1) + (1/2r_2) - (1/r_{12})][(1/\epsilon_{op}) - (1/\epsilon_s)] \tag{4}$$

where ϵ_{op} is the optical dielectric constant of the solvent and the remaining terms are defined above. Using the parameters given above with $\epsilon_{op} = 2$, eq 4 yields $\lambda_s = 0.3$ eV. Finally, since $\lambda = 0.6$ eV, the internal nuclear reorganization energy of the porphyrin-triptycene-acceptor system is 0.3 eV. This number is similar to values of λ_i determined for other organic π donor-acceptor molecules.[20,21]

Our results show that porphyrin-triptycene-acceptor molecules possess ion-pair states that are destabilized by 0.8 eV in rigid glasses relative to their energies as determined from electrochemical measurements in polar liquids. It is likely that this number will prove to be somewhat dependent on spacer structure. This information can be used to design multistep electron transfer molecules to separate charge efficiently in the solid state. Work along these lines is already proceeding in our laboratory.[22]

Acknowledgment. This work was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy, under Contract W-31-109-Eng-38.

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(14) The temperature dependence of k_{cs} for BC and DB was determined between 10 and 300 K. At 300 K, $k_{cs} > 10^{11}$ s^{-1} for both BC and DB, decreasing gradually to 3×10^{10} s^{-1} just above the 140 K glass transition of MTHF. At the glass transition, k_{cs} falls steeply to 10^9 s^{-1} and 5×10^9 s^{-1} for BC and DB, respectively, and remains constant down to 10 K. The large discontinuity in rate at the glass transition may indicate, as one referee has pointed out, that ΔG_d contains a large entropy term.

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Hydrogen-Bonded Dimers. Direct Study of the Interconversion of Pyridone Dimers and Hydroxypyridine Monomers by Low-Temperature Nuclear Magnetic Resonance Spectroscopy

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The selective formation of duplexes by the pairing of molecules with complementary patterns of hydrogen-bond donors and acceptors helps regulate the storage and replication of genetic information and gives chemists a powerful tool for creating self-assembling structures useful for other purposes.[3] Reversible formation is a fundamental property of these duplexes, but little information about the dynamics of aggregation is available.[4,5] In this communication, we report that the equilibrium of a simple heterocyclic monomer and its tautomeric hydrogen-bonded dimer can be studied directly by low-temperature NMR spectroscopy.

Simple 2-pyridones are slightly less stable than their 2-hydroxypyridine tautomers in the gas phase,[6] but the more polar 2-pyridone form normally predominates in condensed phases.[7,8]

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(8) When a strongly electron withdrawing group is present at C_6, 2-pyridones tend to be less stable than their hydroxypyridine tautomers even in condensed phases.[7a,b] When an amino group is at C_6, variable amounts of 2-pyridone tautomer are present.[9]

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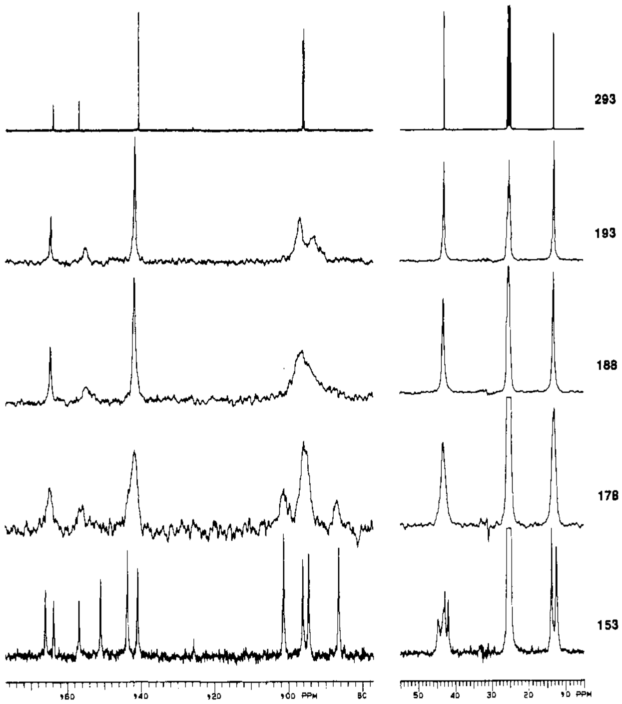
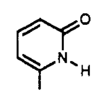
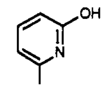


Figure 1. Variable-temperature ^{13}C NMR spectra of a nominally 0.093 M solution of 6-(diethylamino)-2-pyridinol (**2a**) in THF-d_8.

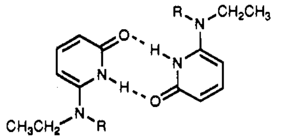
Crystalline 2-pyridones typically exist as hydrogen-bonded dimers,[10] and significant amounts of dimers can also be present in solution.[7a,c] Interconversion of these species is rapid in solution, and only averaged signals for 2-pyridone and its dimer can be observed in ^1H NMR spectra at −120 °C in tetrahydrofuran-d_8 (THF-d_8) at concentrations of 0.1 or 0.06 M. Since the monomer and dimer should have measurably different NH chemical shifts and since both species should be present under the selected conditions of temperature, solvent, and concentration, the equilibrium must simply be too rapid to be studied by low-temperature ^1H NMR spectroscopy. This is consistent with the measured thermodynamic parameters and a diffusion-controlled association.[5]



1a (R = CH_2CH_3)
1b (R = H)



2a (R = CH_2CH_3)
2b (R = H)



3a (R = CH_2CH_3)
3b (R = H)

We reasoned that a substituent at C_6 might retard association or dissociation, so we prepared 6-(diethylamino)-2-pyridone (**1a**)[11] from 6-amino-2-pyridone[12] by a repeated sequence of acetylation (CH_3COCl, pyridine, DMAP) and reduction ($BH_3 \cdot THF$). Its UV spectrum in THF (0.0096 M) contains a strong band at 309 nm, so the compound exists largely as hydroxypyridine **2a** under these conditions.[8] Signals in its ^1H NMR spectrum in THF-d_8 (0.093 M) broaden and split as the temperature is lowered, and at −118 °C two distinct species can be detected. Similar changes occur in the ^{13}C NMR spectra, which are reproduced in Figure 1. One species gives rise to ^1H signals at δ 5.68, 6.00, 7.28, and 9.47, while the other gives rise to signals at δ 5.47 (2 H), 7.28, and 12.7. We propose that the component with the downfield peak at δ 12.7 is a hydrogen-bonded dimer and that the component with the less deshielded peak at δ 9.47 is the solvated hydroxypyridine monomer **2a**. As this hypothesis requires, the relative intensities of the signals assigned to the monomer increase as the concentration decreases.[13] The large ^{13}C chemical shift difference between C_3 (δ 101.3) and C_5 (δ 86.4) in the dimer is highly characteristic of pyridones,[15] so we believe that we are observing the interconversion of a hydroxypyridine monomer and a pyridone dimer, not a hydroxypyridine dimer. Tautomerization may precede dimerization, or it may occur within a hydroxypyridine dimer. Integration indicates that $K = 12 \pm 1$ L/mol at −118 °C in THF for the equilibrium 2 **2a** $\rightleftarrows$ **3a**, so $\Delta G° = -0.77 \pm 0.02$ kcal/mol under these conditions.[16,17a] Furthermore, the downfield ^1H signals coalesce at −87 °C, so $\Delta G^{\ddagger}_{186}$ for the conversion of monomer into dimer is approximately 6.7 ± 0.1 kcal/mol.[17,20] Association and dissociation are therefore not diffusion-controlled.

We doubt that electronic factors make this barrier higher than the one separating 2-pyridone and its dimer, since 2-pyridone and compound **1a** have similar association constants.[16] Evidence that the difference has a steric origin comes from a complementary study of 6-(ethylamino)-2-pyridone (**1b**),[11] prepared as an intermediate during the synthesis of (diethylamino)pyridone **1a**. At −120 °C in THF-d_8 at 0.10 and 0.010 M, ^1H NMR spectra of mixtures of tautomer **2b** and its dimer show only averaged signals. The exocyclic nitrogens of 6-amino-2-pyridones are sp^2-hybridized and fully conjugated with the pyridone ring,[21] so dimers **3a** and **3b** have structures in which all heavy atoms but the methyl carbons lie near a common plane.[22] We argue that ethyl groups directed toward the hydrogen-bonding atoms impede the formation of dimer **3a** and may also inhibit dissociation by blocking the approach of solvent. This implies that dissociation is not a simple separation of hydrogen-bond donor and acceptor, but a more complex process involving prior association of the new acceptor.

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[11] The structure assigned to this new compound is consistent with its IR, NMR, and high-resolution mass spectra. These data are included in the supplementary material.

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[13] Since the equilibrium is sensitive to concentration, it cannot simply involve a slow interconversion of pyridone dimers and hydroxypyridine dimers, or a slow tautomerization of pyridone monomers and hydroxypyridine monomers.[14] Moreover, π-stacking is unlikely to be involved since simple *N*-methylpyridones do not form aggregates in dioxane.[7c]

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[16] A similar association constant has been measured for the dimerization of 2-pyridone in dioxane at 25 °C.[5b,7e] Since $\Delta S°$ in this solvent is small,[5b] the association constant in THF at low temperatures should not be dramatically larger.

[17] (a) Low-temperature ^1H NMR spectra were recorded at 400 MHz in THF-d_8 containing less than 0.04 M water, and probe temperatures were calibrated by using the chemical shifts of methanol. For the calculation of concentrations, the density of THF-d_8 was assumed to vary linearly with temperature.[18] Appropriate pulse delays were used to ensure accurate integrations. (b) Coalescence of the peaks that appear at δ 12.7 and 9.47 in limiting low-temperature spectra of nearly equimolar mixtures of hydroxypyridine **2a** and pyridone dimer **3a** allowed $\Delta G^{\ddagger}$ (kcal/mol) at the coalescence temperature to be estimated by using the equation $\Delta G^{\ddagger} = aT_c[10.319 + \log(T_c[\mathbf{2a}]/k)]$, where T_c is the coalescence temperature (K), $a = 4.575 \times 10^{-3}$, and k is the pseudo-first-order rate constant given by $k = \pi\delta v/2^{1/2}$, where δv is the shift difference (Hz).[19] We assume that the ratio of monomer and dimer at T_c is similar to that measured at 155 K.[16]

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[20] Ultrasonic studies have shown that dissociation of the dimer of 2-pyridone in dioxane is faster ($\Delta G^{\ddagger} = 5.1$ kcal/mol).[5b]

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Evans and Christine Johnson for recording our mass spectra, and we are grateful to Dr. Nga Hoduc for helping us with osmometric measurements. We are also indebted to various reviewers for their perceptive comments.

Supplementary Material Available: Spectroscopic and analytical data for aminopyridones **1a** and **1b** (1 page). Ordering information is given on any current masthead page.

Solution and Solid-State Structure of the "Wittig-Furukawa" Cyclopropanation Reagent[†]

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The Simmons-Smith cyclopropanation of olefins is arguably the most important application of organozinc reagents in organic synthesis.[1] The reaction proceeds under mild conditions[2] and is characterized by broad generality, olefin stereospecificity,[1,2] and a high degree of relative stereoselectivity [with allylic alcohols (ethers),[3-5] acetals,[6] and enol ethers[7]]. Indeed, the strong directing effect of hydroxyl groups was recognized early on[3] and has both preparative[4] and mechanistic significance.[5] Despite the synthetic importance of this reaction, a detailed mechanistic understanding and a structural characterization of the cyclopropanating species are lacking. Early studies by Simmons provided indirect evidence for the existence of a "$ZnCH_2I$" moiety in the active cyclopropanation agent.[1,2] Wittig came to similar conclusions from extensive investigations with the reagents prepared from CH_2N_2/ZnX_2.[8] Since then, much effort has been expended in the development of new synthetic modifications but the structure of the reagents remains unclear.[1,9] Continued current interest in cyclopropanes[10] combined with the burgeoning field of catalytic asymmetric synthesis using organozinc reagents[11] prompted us to study the structure of (halomethyl)zinc compounds. We report herein spectroscopic studies of the bis(halomethyl)zinc cyclopropanation reagents as well as *the first X-ray crystal structure analysis of an (iodomethyl)zinc compound.*

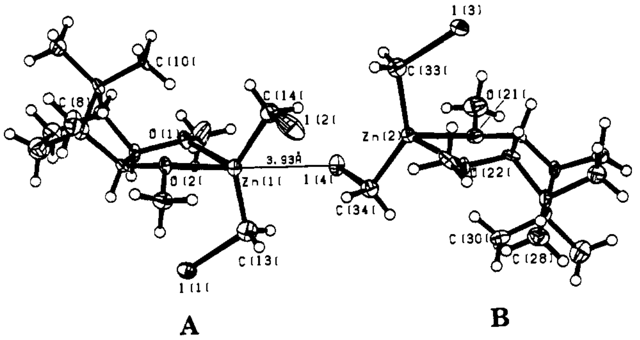

Figure 1. ORTEP view of the two independent molecules of **4** (35% probability ellipsoids).

Scheme I

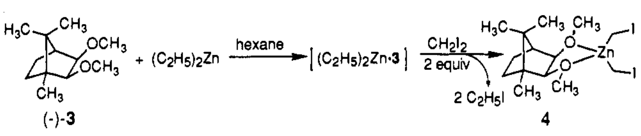

Table I. Selected Bond Lengths and Angles for 4

Bond Lengths, Å

Zn(1)-O(1)	2.103 (10)	Zn(1)-C(13)	1.92 (2)	I(1)-C(13)	2.21 (2)
Zn(1)-O(2)	2.20 (1)	Zn(1)-C(14)	1.98 (2)	I(2)-C(14)	2.16 (2)
Zn(2)-O(21)	2.20 (1)	Zn(2)-C(33)	2.01 (2)	I(3)-C(33)	2.15 (2)
Zn(2)-O(22)	2.231 (10)	Zn(2)-C(34)	2.02 (2)	I(4)-C(34)	2.13 (2)

Bond Angles, deg

O(1)-Zn(1)-C(13)	109.5 (6)	O(21)-Zn(2)-C(33)	106.5 (6)
O(2)-Zn(1)-C(14)	104.3 (5)	O(22)-Zn(2)-C(34)	106.3 (5)
O(1)-Zn(1)-O(2)	72.7 (4)	O(21)-Zn(2)-O(22)	71.7 (4)
O(1)-Zn(1)-C(14)	104.6 (6)	O(21)-Zn(2)-C(34)	107.4 (5)
O(2)-Zn(1)-C(13)	107.9 (6)	O(22)-Zn(2)-C(33)	108.2 (5)
C(13)-Zn(1)-C(14)	138.4 (7)	C(33)-Zn(2)-C(34)	137.5 (6)
I(1)-C(13)-Zn(1)	116.4 (9)	I(3)-C(33)-Zn(2)	115.8 (7)
I(2)-C(14)-Zn(1)	107.9 (8)	I(4)-C(34)-Zn(2)	106.9 (7)

Nonbonded Distances, Å

Zn(1)-I(4)	3.929 (2)	Zn(1)-I(1)	3.513 (2)	Zn(2)-I(3)	3.525 (2)
Zn(2)-I(2)	4.342 (3)	Zn(1)-I(2)	3.350 (3)	Zn(2)-I(4)	3.329 (2)

We chose to study bis(halomethyl)zinc reagents $(ICH_2)_2Zn$ (**1**) and $(ClCH_2)_2Zn$ (**2**) (prepared by the method of Furukawa[12] from Et_2Zn and CH_2I_2 or ICH_2Cl[13]) for three reasons: (1) the reaction mixtures were expected to be homogeneous, (2) the amount of each educt could be precisely controlled, and (3) generation of $(ICH_2)_2Zn$ from Et_2Zn avoids potential "Schlenk-type" equilibria (with ICH_2ZnI and ZnI_2) thought to be important in the reagent derived from Zn(Cu) and CH_2I_2.[1]

[†] Dedicated to Professor Dr. Albert Eschenmoser on the occasion of his 65th birthday.

[‡] Correspondence author for inquiries concerning the X-ray structure determination.

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