

containing both *c*- and *d*<sub>1</sub>-type hemes<sup>28,29</sup> or six *c*-type hemes per molecule.<sup>30</sup> Some reductases react with nitrite in their oxidized form,<sup>31,32</sup> but all, in their reduced state, react with nitrite and form NO-bound heme species. The NO-bound *d*<sub>1</sub>-heme is six-coordinated with histidine as the other axial ligand,<sup>33</sup> while the axial ligand for the siroheme remains undetermined. Most interestingly, the EPR spectrum for the NO-bound heme in the hexaheme nitrite reductase appears to be of the five-coordinate type.<sup>34</sup> Consistent with this observed diversity, our present results make evident that a low-spin state for the initial complex formed between substrate and reductase heme does not have significant other axial ligand requirements.

**Acknowledgment.** We thank the National Institutes of Health (Grant GM-38401 to W.R.S.) and the National Science Foundation (Grant DMB 9001530 to B.H.H.) for support.

**Supplementary Material Available:** Figures S1–S3 depicting a formal diagram of the core, an ORTEP plot of [K(222)]<sup>+</sup> cryptand, and a drawing showing the relative orientation of nitrite ion and Fe–N<sub>p</sub> vectors and Tables SI–SV giving complete crystallographic details, final atomic coordinates, anisotropic thermal parameters, fixed hydrogen atom positions, and a complete listing of bond distances and angles for [K(222)][Fe(NO<sub>2</sub>)-(TpivPP)]·H<sub>2</sub>O·C<sub>6</sub>H<sub>5</sub>Cl (20 pages); listing of observed and calculated structure factor amplitudes (32 pages). Ordering information is given on any current masthead page.

(28) Huynh, B. H.; Liu, M. C.; Moura, J. J. G.; Moura, I.; Ljungdahl, P. O.; Münck, E.; Payne, W. J.; Peck, H. D., Jr.; DeVartanian, D. V.; LeGall, J. *J. Biol. Chem.* **1982**, *257*, 9576.

(29) Timkovich, R.; Cork, M. S.; Taylor, P. V. *J. Biol. Chem.* **1984**, *259*, 1577.

(30) Liu, M. C.; Peck, H. D., Jr. *J. Biol. Chem.* **1981**, *256*, 13159.

(31) Day, E. P.; Peterson, J.; Bonvoisin, J. J.; Young, L. J.; Wilkerson, J. O.; Siegel, L. M. *Biochemistry* **1988**, *27*, 2126.

(32) Muhoberac, B. B.; Wharton, D. C. *J. Biol. Chem.* **1983**, *258*, 3019.

(33) Johnson, M.; Thompson, A. J.; Walsh, T. A.; Barber, D.; Greenwood, C. *Biochem. J.* **1980**, *189*, 285.

(34) Costa, C.; Moura, J. J. G.; Moura, I.; Peck, H. D., Jr.; LeGall, J.; Wang, Y.; Huynh, B. H. *J. Biol. Chem.* **1990**, *265*, 14382.

### Photoinduced Electron Transfer in the Solid State: Rate vs Free Energy Dependence in Fixed-Distance Porphyrin–Acceptor Molecules

George L. Gaines, III,<sup>†</sup> Michael P. O'Neil,<sup>‡</sup> Walter A. Svec,<sup>‡</sup> Mark P. Niemczyk,<sup>‡</sup> and Michael R. Wasielewski<sup>\*†</sup>

Chemistry Division and  
Biological and Medical Research Division  
Argonne National Laboratory, Argonne, Illinois 60439

Received September 17, 1990

Revised Manuscript Received November 28, 1990

Recent interest in the role of the solvent in electron-transfer reactions has focused on ultrafast photoinduced electron transfers,<sup>1</sup> highlighted by investigations into the primary events of bacterial photosynthesis.<sup>2</sup> In contrast to photosynthesis, which exhibits

a quantum yield of primary charge separation near unity at cryogenic temperatures, most photosynthetic model systems based on chlorophyll or porphyrin electron donors exhibit significantly reduced efficiencies of light-initiated, singlet-state electron transfer whenever they are dissolved in rigid glass media.<sup>3</sup> This occurs because solvent dipoles reorient around an ion pair in a polar liquid, decreasing the energy of the ion pair, while solvent dipoles cannot reorient around an ion pair produced within a frozen solvent and, thus, provide little stabilization of the ion pair.<sup>4,5</sup> As a result, the energy level of the ion pair is much higher in the rigid glass than in the liquid. In fact, the ion pair state energy may be so high that it lies above the energy of the excited state, in which case photoinduced electron transfer cannot occur.

We recently reported that the ion-pair states in two porphyrin–tritycene–acceptor molecules are destabilized by as much as 0.9 eV in going from a polar liquid to a rigid glass.<sup>6</sup> To obtain a quantitative picture of the dependence of charge-separation rate on free energy of reaction in the rigid glass, we present electron transfer rate data on 14 porphyrin–tritycene–acceptor molecules, which possess sufficiently large, negative free energies for charge separation to allow electron transfer to compete with excited singlet state decay in glassy 2-methyltetrahydrofuran (MTHF) at 77 K, Figure 1. The compounds in Figure 1 were synthesized by methods described earlier,<sup>6–9</sup> and the details of their preparation will be presented later. Electron transfer rate constants were determined by using picosecond transient absorption and emission techniques along with fluorescence quenching measurements also described earlier.<sup>10</sup>

The free energy of charge separation,  $\Delta G_{cs}$ , in the rigid glass is given by eq 1,

$$\Delta G_{cs} = \Delta G_{ip} - E_s \quad (1)$$

where  $\Delta G_{ip}$  is the free energy of the ion pair in the rigid glass and  $E_s$  is the energy of the lowest excited singlet state of the porphyrin obtained from its fluorescence spectrum. Since ion-pair recombination in porphyrin–acceptor molecules is nonradiative, the value of  $\Delta G_{cs}$  in the rigid glass is difficult to obtain. On the other hand, in polar liquids, the free energies of charge separation in these molecules,  $\Delta G'_{cs}$ , can be estimated by using the one-electron oxidation,  $E_{ox}$ , and reduction,  $E_{red}$ , potentials of the donor and acceptor, respectively, and the coulomb stabilization of the ion pair:

$$\Delta G'_{cs} = E_{ox} - E_{red} - e_0^2/\epsilon r_{12} - E_s \quad (2)$$

where  $e_0$  is the charge of the electron,  $\epsilon$  is the static dielectric constant of the high-polarity medium, and  $r_{12}$  is the center-to-center distance between the ions. We determined  $\Delta G'_{cs}$  for the 14 compounds presented in Figure 2 in butyronitrile at 295 K containing 0.1 M tetra-*n*-butylammonium perchlorate.<sup>11</sup> Since  $r_{12} = 11 \pm 1$  Å for these compounds,<sup>12</sup> the Coulombic term is only 0.065 eV and is neglected. Thus, the plot of  $\ln k_{cs}$  vs  $-\Delta G'_{cs}$  in Figure 2 is based solely on experimentally determined quantities with no corrections applied. Although the plot of  $\ln k_{cs}$  vs  $-\Delta G'_{cs}$  can be used as a predictive tool,  $\Delta G'_{cs}$  obtained from polar solution

(3) Harrison, R. J.; Pearce, B.; Beddard, G. S.; Cowan, J. A.; Sanders, J. K. M. *Chem. Phys.* **1987**, *116*, 429.

(4) (a) Miller, J. R.; Peeples, J. A.; Schmitt, M. J.; Closs, G. L. *J. Am. Chem. Soc.* **1982**, *104*, 6488. (b) Chen, P.; Danielson, E.; Meyer, T. J. *J. Phys. Chem.* **1988**, *92*, 3708.

(5) (a) Kakitani, T.; Mataga, N. *J. Phys. Chem.* **1988**, *92*, 5059. (b) Marcus, R. A. *J. Phys. Chem.* **1990**, *94*, 4963.

(6) Wasielewski, M. R.; Johnson, D. G.; Svec, W. A.; Kersey, K. M.; Minsek, D. W. *J. Am. Chem. Soc.* **1988**, *110*, 7219.

(7) Wasielewski, M. R.; Niemczyk, M. P. *J. Am. Chem. Soc.* **1984**, *106*, 5043.

(8) Wasielewski, M. R.; Niemczyk, M. P.; Svec, W. A.; Pewitt, E. B. *J. Am. Chem. Soc.* **1985**, *107*, 5583.

(9) Wasielewski, M. R.; Niemczyk, M. P.; Johnson, D. G.; Svec, W. A.; Minsek, D. W. *Tetrahedron* **1989**, *45*, 4785.

(10) Wasielewski, M. R.; Johnson, D. G.; Niemczyk, M. P.; Gaines, G. L., III; O'Neil, M. P.; Svec, W. A. *J. Am. Chem. Soc.* **1990**, *112*, 6482.

(11) Wasielewski, M. R.; Smith, R. L.; Kostka, A. G. *J. Am. Chem. Soc.* **1980**, *102*, 6923.

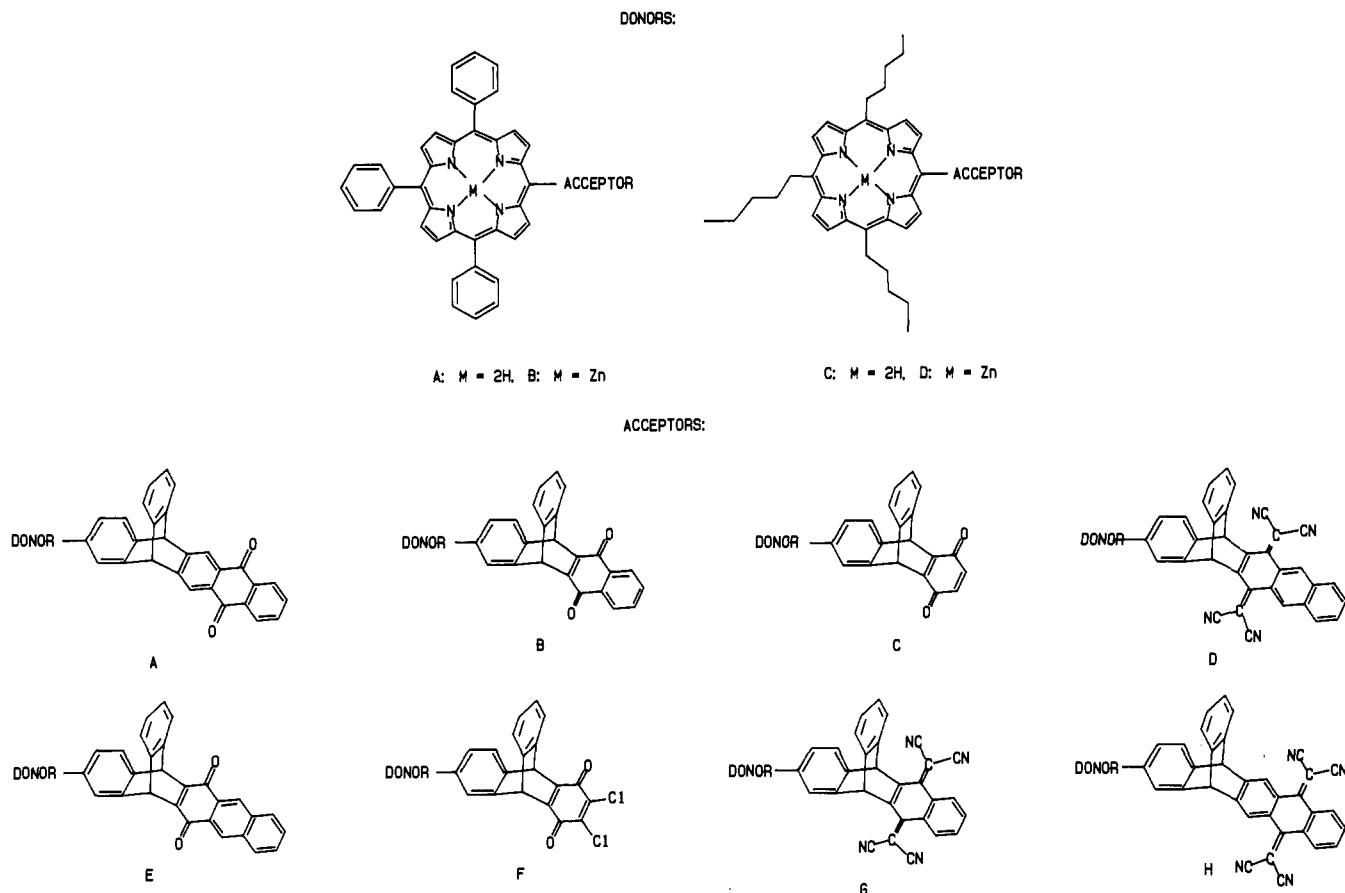
(12) Determined from CPK molecular models.

<sup>†</sup> Biological and Medical Research Division.

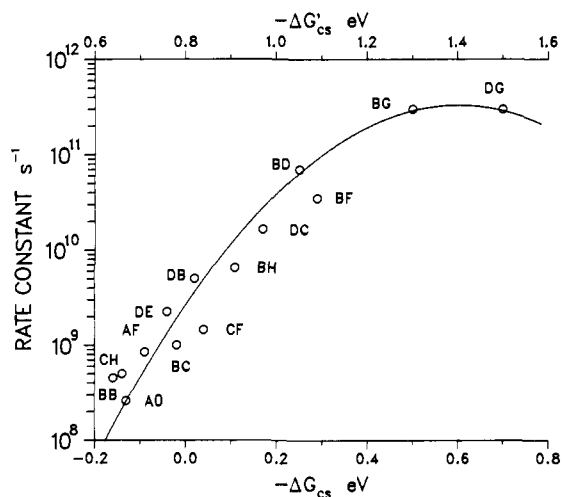
<sup>‡</sup> Chemistry Division.

(1) (a) Brunschwig, B.; Ehrenson, S.; Sutin, N. *J. Phys. Chem.* **1987**, *91*, 4714. (b) Castner, E. W., Jr.; Bagchi, B.; Maroncelli, M.; Webb, S. P.; Ruggiero, A. J.; Fleming, G. R. *Ber. Bunsenges. Phys. Chem.* **1988**, *92*, 363. (c) Maroncelli, M.; Fleming, G. R. *J. Chem. Phys.* **1988**, *89*, 875. (d) Hynes, J. T. *J. Phys. Chem.* **1986**, *90*, 3701. (e) Rips, I.; Klafter, J.; Jortner, J. *J. Chem. Phys.* **1988**, *89*, 4288. (f) Wolynes, P. J. *J. Chem. Phys.* **1987**, *86*, 5133. (g) Sparpaglione, M.; Mukamel, S. *J. Phys. Chem.* **1987**, *91*, 3938. (h) Kahlow, M. A.; Jarzeba, W.; Kang, T. J.; Barbara, P. F. *J. Chem. Phys.* **1988**, *90*, 151. (i) Bashkin, J. S.; McLendon, G.; Mukamel, S.; Marohn, J. *J. Phys. Chem.* **1990**, *94*, 4757. (j) Heitele, H.; Pollinger, F.; Weeren, S.; Michel-Beyerle, M. E. *Chem. Phys.* **1990**, *143*, 325.

(2) Kirmaier, C.; Holten, D. *Photosynth. Res.* **1987**, *13*, 225.

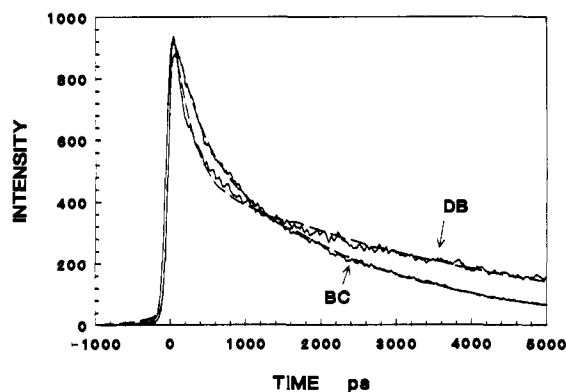


**Figure 1.** Structures of porphyrin–tritycene–acceptor molecules. Each molecule consists of a donor (A–D) covalently attached to an acceptor (A–H) for a total of 32 molecules. Fourteen of these molecules undergo rapid charge separation from the lowest singlet singlet state in glassy MTHF at 77 K.



**Figure 2.** Plot of  $\ln k_{cs}$  vs free energy of reaction. The first letter of each data point label identifies the donor, while the second letter identifies the acceptor as given in Figure 1.  $\Delta G'_{cs}$  and  $\Delta G_{cs}$  are defined in the text. The fit to the data was obtained by using an electronic coupling of  $33 \text{ cm}^{-1}$ , average vibrational frequency of  $500 \text{ cm}^{-1}$ ,  $\lambda = 0.6 \text{ eV}$ , and  $\Delta G_d = 0.8 \text{ eV}$  (ref 18b).

data differs significantly from  $\Delta G_{cs}$  in the rigid glass. Fortunately, we can determine the precise relationship between these two free energy scales. When  $\Delta G_{cs} \approx 0$ , thermal repopulation of the lowest excited singlet state from the ion-pair state may yield biphasic fluorescence decays.<sup>13</sup> Assuming rapid equilibrium between the



**Figure 3.** Fluorescence decay curves for BC and DB in glassy MTHF at 77 K. The fit yields  $k_{cs} = 1 \times 10^9 \text{ s}^{-1}$  and  $k_{rep} = 2 \times 10^9 \text{ s}^{-1}$  for BC;  $k_{cs} = 5 \times 10^9 \text{ s}^{-1}$  and  $k_{rep} = 3 \times 10^9 \text{ s}^{-1}$  for DB.

excited and ion-pair states, these biphasic decays can be fit analytically to a model in which the two equilibrating states decay to ground state with their own respective rate constants. Thus, the data can be used to obtain the rate constants for both the charge separation reaction,  $k_{cs}$ , and the thermal repopulation of the singlet state,  $k_{rep}$ . The value of  $\Delta G_{cs}$  can be obtained directly from the relationship  $\Delta G_{cs} = -RT \ln(k_{cs}/k_{rep})$ . We have observed thermal repopulation of the lowest excited singlet state of the porphyrin in two of these molecules, BC and DB. The decay curves, biexponential fits, and resulting rate constants for BC and DB are given in Figure 3. These data show that  $\Delta G_{cs} < 0.01 \text{ eV}$  for BC and DB. Assuming a linear free energy relationship, the  $\Delta G'_{cs}$  energy scale can be calibrated to yield  $\Delta G_{cs}$  in the rigid glass by using the data for BC and DB, Figure 2. Thus, the energies of the ion-pair states in these molecules are destabilized

(13) Heitele, H.; Finckh, S.; Weeren, S.; Pollinger, F.; Michel-Beyerle, M. E. *J. Phys. Chem.* **1989**, *93*, 5173.

by  $\Delta G_d = 0.80 \pm 0.05$  eV relative to their energies in polar liquids.<sup>14</sup>

Using the Born dielectric continuum model of the solvent, Weller<sup>15</sup> derived eq 3 to calculate the ion-pair destabilization energy,  $\Delta G_d$ , in a solvent with a static dielectric constant  $\epsilon_s$ , if the redox potentials of the donor and acceptor are measured in a medium with a high dielectric constant,  $\epsilon'_s$ :

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

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,<sup>16</sup>  $\epsilon'_s = 20$  for butyronitrile at 295 K,  $r_{12} = 11 \pm 1$  Å,<sup>12</sup>  $r_1$  for the porphyrin = 5 Å,<sup>12</sup> and  $r_2$  for the quinone = 3 Å,<sup>12</sup> 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  $\lambda$  is the total nuclear reorganization energy for the electron-transfer reaction.<sup>17</sup> This reorganization energy comprises terms describing both the solvent reorganization energy,  $\lambda_s$ , and the internal nuclear reorganization of the donor-acceptor molecule,  $\lambda_i$ , where  $\lambda = \lambda_s + \lambda_i$ . Semiclassical electron-transfer theory<sup>18</sup> 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<sup>19</sup> to calculate the solvent reorganization energy,  $\lambda_s$ :

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

where  $\epsilon_{op}$  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  $\lambda_i$  determined for other organic  $\pi$  donor-acceptor molecules.<sup>20,21</sup>

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.<sup>22</sup>

**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.

(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<sup>-1</sup> for both BC and DB, decreasing gradually to  $3 \times 10^{10}$  s<sup>-1</sup> just above the 140 K glass transition of MTHF. At the glass transition,  $k_{cs}$  falls steeply to  $10^9$  s<sup>-1</sup> and  $5 \times 10^9$  s<sup>-1</sup> 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  $\Delta G_d$  contains a large entropy term.

(15) Weller, A. Z. *Phys. Chem. N.F.* **1982**, *133*, 93.

(16) Furutsuka, T.; Imura, T.; Kojima, T.; Kawabe, K. *Technol. Rep. Osaka Univ.* **1974**, *24*, 367.

(17) Marcus, R. A. *J. Chem. Phys.* **1956**, *24*, 966.

(18) (a) Hopfield, J. J. *Proc. Natl. Acad. Sci. U.S.A.* **1974**, *71*, 3640. (b) Jortner, J. *J. Chem. Phys.* **1976**, *64*, 4860.

(19) Marcus, R. J. *J. Chem. Phys.* **1965**, *43*, 679.

(20) Miller, J. R.; Calcaterra, L. T.; Closs, G. L. *J. Am. Chem. Soc.* **1984**, *106*, 3047.

(21) Overing, H.; Paddon-Row, M. N.; Heppener, M.; Oliver, A. M.; Cotsaris, E.; Verhoeven, J. W.; Hush, N. S. *J. Am. Chem. Soc.* **1987**, *109*, 3258.

(22) Wasielewski, M. R.; Gaines, G. L., III; O'Neil, M. P.; Svec, W. A.; Niemczyk, M. P. *J. Am. Chem. Soc.* **1990**, *112*, 4559.

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

Michel Gallant,<sup>1</sup> Minh Tan Phan Viet,<sup>2</sup> and James D. Wuest\*

Département de Chimie, Université de Montréal  
Montréal, Québec, H3C 3J7 Canada

Received June 8, 1990

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.<sup>3</sup> Reversible formation is a fundamental property of these duplexes, but little information about the dynamics of aggregation is available.<sup>4,5</sup> 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,<sup>6</sup> but the more polar 2-pyridone form normally predominates in condensed phases.<sup>7,8</sup>

(1) Fellow of the Natural Sciences and Engineering Research Council of Canada, 1984-1988.

(2) Regional High-Field NMR Laboratory, Département de Chimie, Université de Montréal.

(3) Garcia-Tellado, F.; Goswami, S.; Chang, S.-K.; Geib, S. J.; Hamilton, A. D. *J. Am. Chem. Soc.* **1990**, *112*, 7393-7394. Zhao, X.; Chang, Y.-L.; Fowler, F. W.; Lauher, J. W. *Ibid.* **1990**, *112*, 6627-6634. Seto, C. T.; Whitesides, G. M. *Ibid.* **1990**, *112*, 6409-6411. Hegde, V.; Madhukar, P.; Madura, J. D.; Thummel, R. P. *Ibid.* **1990**, *112*, 4549-4550. Tanaka, Y.; Kato, Y.; Aoyama, Y. *Ibid.* **1990**, *112*, 2807-2808. Tjivikua, T.; Ballester, P.; Rebek, J., Jr. *Ibid.* **1990**, *112*, 1249-1250. Lehn, J.-M.; Mascal, M.; DeCian, A.; Fischer, J. J. *Chem. Soc., Chem. Commun.* **1990**, 479-481. Etter, M. C. *Acc. Chem. Res.* **1990**, *23*, 120-126. Hilger, C.; Stadler, R. *Macromolecules* **1990**, *23*, 2095-2097. Kato, T.; Fujishima, A.; Fréchet, J. M. J. *Chem. Lett.* **1990**, 919-922. Kelly, T. R.; Zhao, C.; Bridger, G. J. *J. Am. Chem. Soc.* **1989**, *111*, 3744-3745. Ducharme, Y.; Wuest, J. D. *J. Org. Chem.* **1988**, *53*, 5787-5789.

(4) For recent references, see: Perrin, C. L.; Dwyer, T. J.; Rebek, J., Jr.; Duff, R. J. *J. Am. Chem. Soc.* **1990**, *112*, 3122-3125. Williams, L. D.; Williams, N. G.; Shaw, B. R. *Ibid.* **1990**, *112*, 829-833. Waltho, J. P.; Williams, D. H. *Ibid.* **1989**, *111*, 2475-2480. Graener, H.; Ye, T. Q.; Laubereau, A. *J. Chem. Phys.* **1989**, *90*, 3413-3416. Gmeiner, W. H.; Poulter, C. D. *J. Am. Chem. Soc.* **1988**, *110*, 7640-7647.

(5) (a) Guillerez, J.; Tiffon, B.; Anclan, B.; Aubard, J.; Dubois, J. E. *J. Phys. Chem.* **1983**, *87*, 3015-3017. (b) Hammes, G. G.; Lillford, P. J. *J. Am. Chem. Soc.* **1970**, *92*, 7578-7585. Hammes, G. G.; Park, A. C. *Ibid.* **1969**, *91*, 956-961. Hammes, G. G.; Park, A. C. *Ibid.* **1968**, *90*, 4151-4157. Hammes, G. G.; Spivey, H. O. *Ibid.* **1966**, *88*, 1621-1625.

(6) For references, see: Karelson, M. M.; Katritzky, A. R.; Szafran, M.; Zerner, M. C. *J. Org. Chem.* **1989**, *54*, 6030-6034. Sygula, A. A. *J. Chem. Res., Synop.* **1989**, 56-57. Cieplak, P.; Bash, P.; Singh, U. C.; Kollman, P. A. *J. Am. Chem. Soc.* **1987**, *109*, 6283-6289. Field, M. J.; Hillier, I. H. *J. Chem. Soc., Perkin Trans. 2* **1987**, 617-622. Schlegel, H. B.; Gund, P.; Fluder, E. M. *J. Am. Chem. Soc.* **1982**, *104*, 5347-5351. Brown, R. S.; Tse, A.; Vederas, J. C. *Ibid.* **1980**, *102*, 1174-1176. Guimon, C.; Garrabe, G.; Pfister-Guillouzo, G. *Tetrahedron Lett.* **1979**, 2585-2588. Beak, P.; Fry, F. S., Jr.; Lee, J.; Steele, F. J. *J. Am. Chem. Soc.* **1976**, *98*, 171-179.

(7) (a) Beak, P.; Covington, J. B.; Smith, S. G.; White, J. M.; Zeigler, J. M. *J. Org. Chem.* **1980**, *45*, 1354-1362. Beak, P. *Acc. Chem. Res.* **1977**, *10*, 186-192. (b) Kuzuya, M.; Noguchi, A.; Okuda, T. *J. Chem. Soc., Perkin Trans. 2* **1985**, 1423-1427. Chevrier, M.; Bensaude, O.; Guillerez, J.; Dubois, J.-E. *Tetrahedron Lett.* **1980**, *21*, 3359-3362. (c) Fujimoto, A.; Inuzuka, K.; Shiba, R. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 2802-2806. Engdahl, K.-Å.; Ahlberg, P. *J. Chem. Res., Synop.* **1977**, 340-341. (d) Elguero, J.; Marzin, C.; Katritzky, A. R.; Linda, P. *Adv. Heterocycl. Chem., Suppl. 1* **1976**, 1-655. (e) Krackov, M. H.; Lee, C. M.; Mautner, H. G. *J. Am. Chem. Soc.* **1965**, *87*, 892-896.

(8) When a strongly electron withdrawing group is present at C<sub>6</sub>, 2-pyridones tend to be less stable than their hydroxypyridine tautomers even in condensed phases.<sup>7a,b</sup> When an amino group is at C<sub>6</sub>, variable amounts of 2-pyridone tautomer are present.<sup>9</sup>

(9) Fujimoto, A.; Inuzuka, K. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 2292-2299. de Kowalewski, D. G.; Contreras, R. H.; de los Santos, C. *J. Mol. Struct.* **1989**, *213*, 201-212. Barlin, G. B.; Pfleiderer, W. *J. Chem. Soc. B* **1971**, 1425-1432. Peresleni, E. M.; Yakhontov, L. N.; Krasnokutskaya, D. M.; Sheinker, Y. N. *Dokl. Akad. Nauk SSSR* **1967**, *177*, 592-595.