

reddish-purple again on exposure to molecular oxygen. Removing solvent under high vacuum produces a green solid, from which the Cu(I) dimer is obtained on recrystallization. Carbon monoxide displaces the bound oxygen cleanly to yield the Cu(I)-carbonyl complex $\text{Cu}(\text{HB}(3,5\text{-Me}_2(\text{pz}))_3)(\text{CO})$.^{9,14} Finally, evaporation of dichloromethane solutions of II with molecular oxygen at room temperature yields the Cu(II) complex $\text{Cu}(\text{HB}(3,5\text{-Me}_2(\text{pz}))_3)\text{Cl}$.¹⁵ The chloride ion must come from the solvent; the oxygen-containing products have not yet been identified.

Two important conclusions on copper-oxygen coordination chemistry emerge from this initial study. First, relatively stable dioxygen adducts can be prepared by adding molecular oxygen to a Cu(I) complex. The stability of II is indeed remarkable in light of the overwhelming tendency of Cu(I) complexes to fully reduce molecular oxygen^{1,2} and may result at least in part from use of the ligand $\text{HB}(3,5\text{-Me}_2(\text{pz}))_3^-$, which imposes a geometry suitable for both the Cu(I) starting material and the Cu(II) product.^{3,7} Second, reacting molecular oxygen with a cuprous complex can produce a superoxide complex. This species has been proposed as an initial reduction product in Cu(I) autoxidations but has not been observed chemically or spectrophotometrically in these reactions.¹ Use of the polypyrazolylborate ligand enables us, at least in part, to isolate this superoxide complex. The methyl substituents minimize molecular aggregation, especially with other Cu(I) species that could lead to further reduction of the bound dioxygen species.¹

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(13) Standard high-vacuum techniques were used to collect and measure gas evolved during these reactions. Mass spectral analysis confirms the presence of molecular oxygen. Both $^{16}\text{O}_2$ and $^{18}\text{O}_2$ samples were analyzed in this way.

(14) Infrared and ^1H NMR data agree with published values. Anal. ($\text{C}_{16}\text{H}_{22}\text{BCuN}_6\text{O}$) C, H, N.

(15) This formulation is based on infrared, visible absorption, and EPR data. Anal. ($\text{C}_{15}\text{H}_{22}\text{BClCuN}_6$) C, H, N.

Proton-Transfer Kinetics in Solids: Tautomerism in Free Base Porphines by ^{15}N CPMAS NMR

H. H. Limbach,*^{1a} J. Hennig,^{1b} R. Kendrick,^{1c} and C. S. Yannoni*^{1c}

IBM Research Laboratory, San Jose, California 95193
Institut für Physikalische Chemie
der Universität Freiburg i.Br.
D-7800 Freiburg, West Germany

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There is considerable interest in studying proton-transfer reactions in the solid state by dynamic NMR spectroscopy, since rate constants may be obtained at low temperatures that are not accessible in solution.^{2,3} The fact that the transfer rate constants in solution and in the solid state may be completely different at a given temperature (kinetic solid state effect—KSSE) does present a complication. Little is known about such effects because it has not been possible so far to obtain rate constants for both phases at the same temperature. KSSE's are inherently very interesting phenomena and may become so large that proton transfer is not observable in the solid state within the NMR time

(1) (a) On leave from the Institut für Physikalische Chemie der Universität Freiburg, i.Br. (b) Institut für Physikalische Chemie der Universität Freiburg, i.Br. (c) IBM Research Laboratory.

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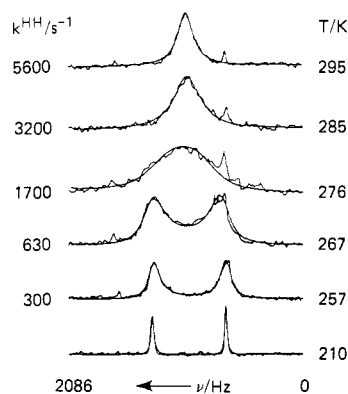
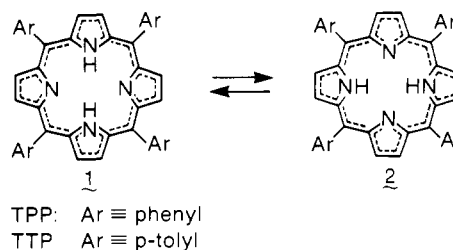


Figure 1. Superposed experimental (6.082 MHz) and calculated ^{15}N CPMAS NMR spectra of 95% ^{15}N -enriched TTP, 10-Hz line broadening, 8000-Hz sweep width, 1.2-s repetition time, 9- μs ^1H - $\pi/2$ pulses, quadrature detection, 25 000 scans on the average; reference, external $^{15}\text{NH}_4\text{NO}_3$. The line width in the absence of exchange was taken from the spectrum at 210 K. The equilibrium constant of the tautomerism was assumed to be unity. k^{HH} is the HH migration rate constant. We attribute the sharp small high-field line to the NH signal of a low-level impurity of nonexchanging tetratolylchlorin, a byproduct of the synthesis.¹⁶

Scheme I



scale, as in the cases of naphthazarin at low temperature^{3,4} and of tropolone.⁵ We present here results of a dynamic ^{15}N CPMAS NMR study of ^{15}N -enriched free-base *meso*-tetraarylporphines which show that a tautomerism known to occur in solution according to Scheme I⁶⁻¹⁰ also takes place in the solid state. We have measured rate constants and kinetic isotope effects in the solid state that are identical with or different from solution data depending on substitution in the aryl groups. These results suggest the resolution of a long-standing paradox involving the problem of proton localization in solid-state porphines.¹¹⁻¹⁴ Finally, our findings suggest how proton-transfer systems may have to be designed to minimize kinetic solid-state effects.

Figure 1 shows the ^{15}N CPMAS NMR spectra of 95% enriched *meso*-tetra-*p*-tolylporphine (TTP) at 6.082 MHz in the solid state at different temperatures.¹⁵ As expected from the solution

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(15) The MAS apparatus used for the experiments has been described previously.^{2,3}

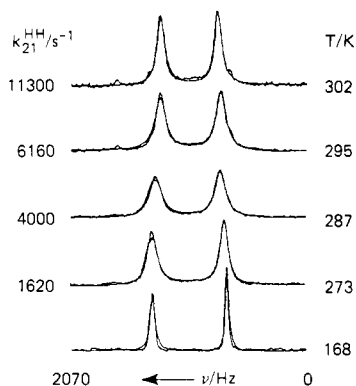


Figure 2. Superposed experimental and calculated ^{15}N CPMAS NMR spectra of 95% ^{15}N -enriched TPP. Experimental conditions as indicated in Figure 1. k_{21}^{HH} is the backward rate constant. The values of the equilibrium constant K are 0.149, 0.136, and 0.124, at 302, 295, and 287 K, respectively. Extrapolated values at 273 and 168 K are 0.111 and 0.015, respectively.

studies,⁷ two singlets are obtained at low temperature which indicates that the proton migration shown in Scheme I is slow on the NMR time scale. At higher temperatures, the lines broaden and coalesce. The line shapes were simulated and the rate constants determined assuming a symmetric rearrangement with two tautomers of equal population. The resulting rate constants are shown in Figure 1. Since the line-shape analysis is not very accurate in the slow-exchange regime, we performed magnetization transfer experiments in the rotating frame on the two ^{15}N lines using a method described previously.⁹ The method was easily adapted to the CPMAS experiment. The protons were decoupled during magnetization transfer. At 204 K, we obtained a value of $k = 4 \text{ s}^{-1}$. A kinetic HH/DD isotope effect of 14 at 295 K was obtained by simulation of the ^{15}N spectra of TTP deuterated in the central proton sites. The rate constants and the kinetic isotope effect that we obtain are, within experimental error, identical with the solution rate constants of *meso*-tetraphenylporphine (TPP)^{8,9} over the entire temperature range. In contrast, the corresponding solid-state spectra of TPP shown in Figure 2 exhibit very different temperature dependence. Although two singlets are observed at low temperature, the two signals do not coalesce at high temperatures. Nevertheless, as the temperature is increased, they do broaden and sharpen again, and the separation between them continuously decreases. The line shape was simulated in terms of two superposed asymmetrical two-site problems with the assumption that the chemical shifts of the NH in tautomer 1 and in tautomer 2 are equal. The same assumption was made for the chemical shifts of the nonprotonated nitrogen atoms. The assumption is justified, because no additional ^{15}N signals are observed in the slow-exchange region at low temperatures.^{17,18} The population of the second tautomer is on the order of 10% at high temperatures where the populations are easily obtained from the line separation by using the assumption that the chemical shifts are independent of the temperature.¹⁹

These results suggest an explanation for the apparent contradiction, stemming from X-ray studies, between a proton disorder in tetragonal free base porphines on the one hand,^{11,12} and proton localization on opposite nitrogen atoms in triclinic TPP on the

other.^{13,14} While X-ray analysis cannot distinguish between fixed protons and a rapid proton migration between two very unequally populated tautomers, the ^{15}N solid-state NMR data clearly show the latter to be the case for triclinic TPP. Although we have not yet studied tetragonal TPP by ^{15}N CPMAS NMR, it is likely that the situation is similar to TPP where the protons move rapidly at room temperature in a symmetric double-minimum potential. This would be consistent with the half hydrogens found in the crystal structure.¹¹

Since TTP and TPP exhibit the same proton dynamics in solution,²⁰ the difference in behavior of the two compounds in the solid state may be due to induction of a more symmetric crystal structure by the methyl groups. Unfortunately, an X-ray analysis has not yet been carried out for TTP. Nonetheless, it appears that appropriate substitution, even at a site that is remote from the migrating protons, can alter the symmetry of the double-minimum potential. For example, preliminary experiments show that proton migration also occurs in phthalocyanine where the degree of asymmetry of the rearrangement is intermediate between that found in TTP and TPP.²¹ We are also studying the influence of asymmetry on the kinetic isotope effect, as well as the effect of adding metal-TPP to TPP in order to make the hydrogen migration symmetric.¹⁴ A complete account of our results will be described in a subsequent paper.

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Perfluorocyclopentadienyl Anion, C_5F_5^-

Gerhard Paprott and Konrad Seppelt*

Institut Für Anorganische und Analytische Chemie
Freie Universität Berlin
1000 Berlin 33, West Germany

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The cyclopentadienyl anion is a classic aromatic ring system with major importance in organometallic chemistry. The pentachloro derivative, C_5Cl_5^- , is known,^{1,2} including some organometallic compounds of it.³ Some effort to achieve C_5F_5^- has become known.⁴⁻⁶ Here we report the synthesis of this novel anion.

Hexachlorocyclopentadiene, C_5Cl_6 , is fluorinated at the saturated carbon atom by heating it to 280 °C with HgF_2 . Products are 10% $\text{C}_5\text{Cl}_5\text{F}$ (bp 80 °C 19 mbar; NMR δ_{F} -131.4) and 20% of its Diels-Alder dimer ($\text{C}_5\text{Cl}_5\text{F}_2$) (mp 170 °C, sublimation 100 °C (10⁻² mbar); NMR δ_{F} -97.3, 102.9). The dimer is monomerized by subliming it in vacuum through a 350 °C hot Pyrex tube. The overall yield of $\text{C}_5\text{Cl}_5\text{F}$ so obtained is close to 30%. This is fluorinated with increasing concentration of elemental fluorine

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(17) It is interesting to note the k_{21} for the asymmetric TPP tautomerism found in the solid (see Figure 2) is close to the symmetric rate constant k found in solution.⁸ Since $K \sim 0.1$ (vide infra), this result is not in agreement with the value of $k_{21} = kK^{1/2}$ predicted by simple Marcus theory.¹⁸

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(19) This assumption was confirmed by measuring ^{15}N spectra of TPP deuterated in the inner-proton sites where the slow-exchange limit is observed at 295 K. A reaction enthalpy of about 6 kJ M⁻¹ was obtained. It is important to note that the rate constants increase continuously with temperature indicating the absence of a phase transition.

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