Figure 1. (a) Framework of ladder silicate ion employed. Junctions represent silicon atoms and pendent oxygen atoms, lines represent bridging oxygen atoms. (b) ORTEP drawing of silicate ion in litiodionite based on the data of Martin Pozas, Rossi, and Tazzoli. Junctions represent silicon atoms; circles represent oxygen atoms.
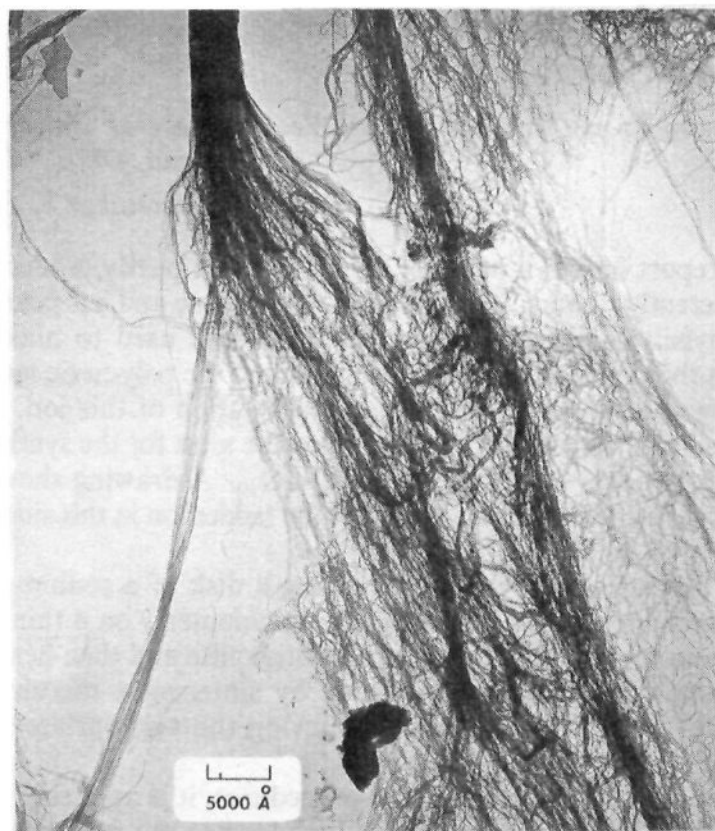

Figure 2. Transmission electron micrograph of the polymer.

The polymer is waxy and is insoluble in a wide range of organic solvents. However, it forms a gellike material with solvents such as dioxane and chloroform. When purified it is a very pale blue. It gives an infrared spectrum showing $Si(CH_3)_3$, SiOH, and SiOSi bands[7] and a Si $2p_{3/2}$ X-ray photoelectron spectrum showing overlapping $SiOC_3$ and SiO_4 peaks. Micrographs of it show fibers that are limp and have very small diameters, Figure 2. Fibers with diameters of 40–60 Å are commonly seen. A few with diameters somewhat above 20 Å are seen.

One sample of the polymer yielded an analysis showing 14.08% C, 3.47% H, and 38.93% Si and gave an Si $2p_{3/2}$ X-ray photoelectron spectrum with $SiOC_3$ and SiO_4 peaks having areas with a ratio 27:73. It yielded K $1s_{1/2}$, Na $1s_{1/2}$, and Cu $2p_{3/2}$ spectra giving evidence for a small amount of potassium but no evidence for sodium or copper. The sample yielded a differential thermal analysis thermogram in air having a very small endotherm at 326 °C and a large exotherm beginning at ~415 °C (decomposition). It gave a differential scanning calorimetry thermogram under helium which showed no transitions between -153 and 267 °C. An X-ray powder pattern of it had a strong broad Bragg angle

peak at 13.5 Å and a weak broad one at 4.86 Å.

On the basis of the procedures used to make the polymer and on the basis of its properties, it appears that some of the fibers in the polymer have a framework consisting of a ladder that is like the one in the parent silicate ion except for the presence of additional internal cross-links and that the rest have frameworks made of ladders of this type which are sparingly joined by oxygen bridges.[8] It further appears that in the sample of the polymer subjected to elemental analysis approximately 37% of the backbone silicon atoms carry silyl groups. In addition it seems probable that the glass transition temperature of the polymer is below -153 °C.

Because fibers are inherent in this polymer and because they are so small, it is of considerable interest.[9,10] Moreover, this polymer is at least in part a ladder polymer (while another organosilicon polymer has been reported to be a ladder polymer,[11] it is now known not to be so[12]). The polymer is also of interest because it is derived from a precursor that is an integral part of a crystalline species and thus one that has very great regularity and very high molecular weight.

(7) Anderson, D. R. In "Analysis of Silicones"; Smith, A. L., Ed.; Wiley: New York, 1974; Chapter 10.

(8) The products of the silylation of silicates generally have frameworks which are the same as, or are similar to, those in the parent silicates. For a review of pertinent data, see: Currell, B. R.; Parsonage, J. R. *J. Macromol. Sci., Chem.* **1981**, *16*, 141.

(9) A group of inherently fibrous organosilicon polymers has been reported earlier, but the structures of these polymers are very different and the fibers are an order of magnitude larger. See, for example: (a) Linsky, J. P.; Paul, T. R.; Kenney, M. E. *J. Polym. Sci., Polym. Phys. Ed.* **1971**, *9*, 143. (b) Zapata, L.; Castelein, J.; Mercier, J. P.; Fripiat, J. *J. Bull. Soc. Chim. Fr.* **1972**, 54.

(10) Litidionite is not fibrous.

(11) Brown, J. F., Jr.; Vogt, L. H., Jr.; Katchman, A.; Eustance, J. W.; Kiser, K. M.; Krantz, K. W. *J. Am. Chem. Soc.* **1960**, *82*, 6194.

(12) Frye, C. L.; Klosowski, J. M. *J. Am. Chem. Soc.* **1971**, *93*, 4599.

Photo-CIDNP Study of Adenosine 5′-Monophosphate. Pair-Substitution Effects due to Cation Radical Deprotonation

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The dye-sensitized generation of nuclear spin polarization in amino acid residues has been very useful in probing the surface structure of proteins.[1–3] Recently we found that nucleic acid bases can be polarized as well by making use of a cyclic reaction scheme similar to that employed in the case of amino acids. These effects are likely to be useful in elucidating structural features of nucleotides and their interactions with other molecules, like nucleotide binding proteins. Photo-CIDNP was observed in 5′-AMP and 5′-GMP in the presence of 3-(carboxymethyl)lumiflavin.[4] Unlike

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(1) Kaptein, R.; Dijkstra, K.; Nicolay, K. *Nature (London)* **1978**, *274*, 293–294.

(2) Kaptein, R. In "Nuclear Magnetic Resonance Spectroscopy in Molecular Biology"; Pullman B., Ed.; Reidel: Dordrecht, The Netherlands, 1978; pp 211–219.

(3) Lenstra, J. A.; Bolscher, B. G. J. M.; Stob, S.; Beintema, J. J.; Kaptein, R. *Eur. J. Biochem.* **1979**, *98*, 385–397.

the case of amino acids, we observed for AMP a strong dependence of the polarization on pH and added buffer salts, for which we would like to present an explanation. In a following paper we shall demonstrate that these effects can be used to study conformational properties of dinucleotides.
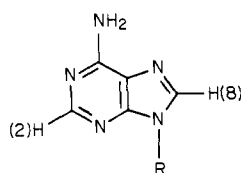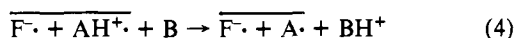
5′-AMP, R = ribose 5′-phosphate

^{1}H laser photo-CIDNP spectra were taken at 360 MHz as described previously.[2] Difference spectra were obtained by an alternating light–dark cycle and subtracting the resulting spectra. To obtain the "light" spectrum the sample was irradiated for 0.6 s by an argon ion laser prior to data acquisition. All pH values represent uncorrected pH meter readings.

Figure 1 shows the behavior of the polarization of the adenine H-8 and H-2 protons of 5′-AMP in the presence of increasing amounts of phosphate at pH 7.0. The positive polarization for H-8 decreases by the addition of phosphate until at high phosphate concentrations a strong emission is observed. By contrast, the CIDNP effect of H-2 decreases without change of sign. This behavior suggests a pair-substitution sequence,[6,7] involving two interconverting radical pairs which give rise to opposite polarizations for H-8.

The polarization reversal only occurs at pH's where appreciable amounts of ^{2}HPO$_4^{2-}$ ions are present, indicating a deprotonation of the primarily formed AMP radical cation on the CIDNP time scale (10^{-9}–10^{-8} s). The amino protons at the 6 position in the adenine ring are possibly acidic in the radical cation, and indeed, the phosphate effect could not be detected in the N$_6$,N$_6$-dimethyladenosine, whereas it was still present in the monomethylated derivative.

These observations can be accounted for by a reaction sequence involving electron transfer from the adening ring in AMP (AH) to triplet excited flavin (^{3}F) followed by a deprotonation of the AMP derived radical cation by a suitable base (B):

$$F \xrightarrow{h\nu} {}^1F \rightarrow {}^3F \tag{1}$$

$$^3F + AH \rightarrow \overline{F^-\cdot + AH^+\cdot} \tag{2}$$

$$\overline{F^-\cdot + AH^+\cdot} \rightarrow F + AH(\uparrow) \tag{3}$$

$$\overline{F^-\cdot + AH^+\cdot} + B \rightarrow \overline{F^-\cdot + A\cdot} + BH^+ \tag{4}$$

$$\overline{F^-\cdot + A\cdot} \xrightarrow{H^+} F + AH(\downarrow) \tag{5}$$

The bar indicates a spin-correlated radical pair. In the absence of a base, positive polarization ($\uparrow$) is generated by reactions 1–3, while in the presence of a high concentration of a base the reactions 1, 2, 4, and 5 lead to the observed emission for the adenine H-8 ($\downarrow$). With the polarization change of H-8 a concomitant reversal of flavin polarization was observed. This implies a change in sign of Δg for the radical pairs involved.[5] For H-2 the hyperfine coupling (hfc) constant must also change sign, whereas for H-8 it remains the same (negative).

In a pair-substitution sequence the magnetic parameters (g values and hfc constants) of the two radical pairs provide a clock to which reaction rates can be related.[6,7] Unfortunately the magnetic parameters of the AMP derived radicals are not known, but some reasonable estimates can be made and further information on Δg's can be obtained from the magnetic field dependence. Therefore we carried out the titration of AMP with
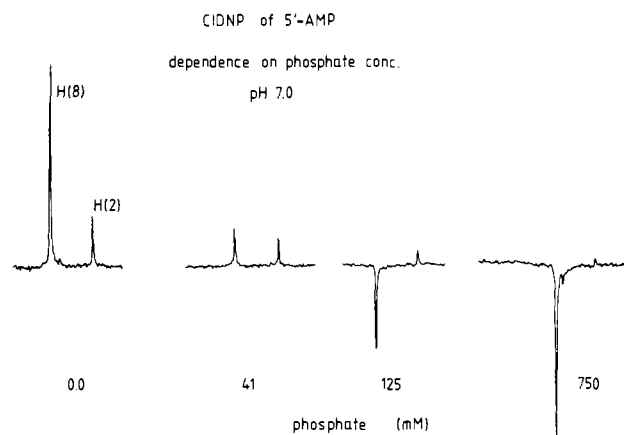

Figure 1. 360-MHz ^{1}H photo-CIDNP difference spectra of the aromatic protons of 5′-AMP in the presence of various concentrations of phosphate at pH 7.0.
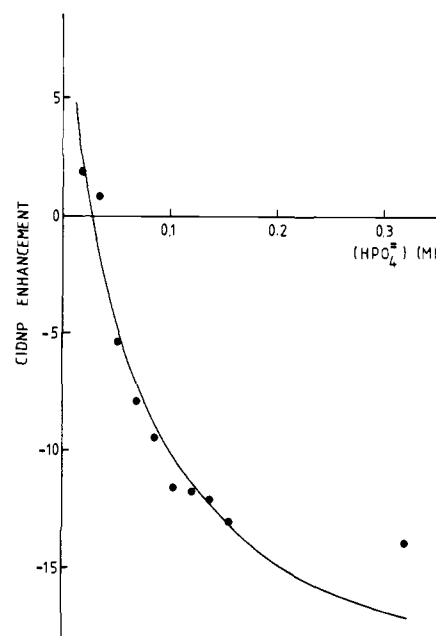

Figure 2. Photo-CIDNP enhancement (ratio of intensities in difference and dark spectra) of H-8 of 5′-AMP vs. phosphate concentration at pH 7.0. The solid line represents the theoretical curve calculated on the basis of the pair substitution theory with the following parameters. AMP radical cation: g = 2.0033, A_{H-8} = –2 G. AMP neutral radical: g = 2.0035, A_{H-8} = –5 G. the g value of the flavin radical anion was taken as 2.0034.[9]

phosphate at 100 MHz on a Varian XL-100 NMR spectrometer and observed a small shift of the titration curve to lower phosphate concentrations when compared with the 360-MHz experiment. We then performed a series of computer simulations of these titrations using a FORTRAN program described by Den Hollander,[8] slightly modified to accommodate our cyclic reaction scheme. Many combinations of magnetic parameters were tested by using the known values for the flavin radical[9,10] and estimated values for the two AMP radicals (the hfc constants were not allowed to exceed 5 G). Only those combinations which led to the observed small influence of the magnetic field were accepted. These simulations yielded values for the second-order rate constant (k_4) of the deprotonation of the AMP radical cation by phosphate ranging from 2–6 × 10^9 M^{-1} s^{-1}, which is close to the diffusion controlled limit, as expected for this type of acid–base reactions.

(4) Kaptein, R.; Nicolay, K.; Dijkstra, K. *J. Chem. Soc., Chem. Commun.* **1979**, 1092–1094.
(5) Kaptein, R. *Chem. Commun.* **1971**, 732–733.
(6) Den Hollander, J. A. *Chem. Phys.* **1975**, *10*, 167–184.
(7) Kaptein, R. In "Chemically Induced Magnetic Polarization"; Muus, L. T., et al., Eds.; Reidel: Dordrecht, The Netherlands, 1977; pp 257–266.

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(9) Ehrenberg, A.; Eriksson, L. E. G.; Müller, F. *Flavins Flavoproteins* **1966**, *8*, 37–48.
(10) Kaptein, R.; Dijkstra, K.; Müller, F.; van Schagen, C. G.; Visser, A. J. W. G. *J. Magn. Res.* **1978**, *31*, 171–176.

Figure 2 shows such a calculated curve for $k_4 = 3 \times 10^9$ M^{-1} s^{-1} together with the experimental data obtained at 360 MHz.

Lower values for the deprotonation rates were found when buffers with lower pK_a values were used (acetate, formate). Since in these cases the reaction rates are also likely to be diffusion controlled, this decrease in deprotonation efficiency can probably be described by the equation due to Eigen et al.,[11] $k = k_0 10^{\Delta pK}(1 + 10^{\Delta pK})^{-1}$, where k_0 is the diffusion controlled rate constant and $\Delta pK = pK_A - pK_D$, the difference in pK_a's of proton acceptor and donor. Under this assumption a value for the pK_a of the AMP derived radical cation (p$K_a = 4.0 \pm 0.2$) was found. Buffers with pK_a values lower than 3 (mono-, di-, and trichloroacetate, the H$_2$PO$_4^-$ ion) were unable to cause sufficiently rapid deprotonation to be observable on the CIDNP time scale, as predicted by the Eigen equation.

In summary the following conclusions can be drawn: (1) The quenching of the flavin triplet by 5'-AMP involves electron transfer from the adenine ring. (2) In the presence of a suitable base catalyst fast deprotonation of the primarily formed AMP radical cation leads to the observation of a radical-pair substitution effect in the CIDNP experiment. (3) Since both radical pairs lead to the same diamagnetic products (ground-state flavin and AMP), this pair substitution modulates the CIDNP signals observed for the aromatic protons in AMP. (4) The deprotonation of the AMP radical cation (p$K_a = 4.0 \pm 0.2$, measured in ^{2}H$_2$O) by phosphate occurs with a rate constant of $(4 \pm 2) \times 10^9$ M^{-1} s^{-1}, which is close to the diffusion controlled limit.

(11) Eigen, M. *Angew. Chem., Int. Ed. Engl.* **1964**, 1–19.

(12) Other cases of electron-transfer reactions followed by protonation–deprotonation reactions have been observed before by photo-CIDNP. See for instance: (a) Hutton, R. S.; Roth, H. D.; Manion Schilling, M. L. *J. Chem. Phys.* **1980**, *72*, 4368. (b) Roth, H. D.; Lamola, A. A. *J. Am. Chem. Soc.* **1974**, *96*, 6270. However, in these cases the CIDNP effect originated from only one radical pair and no pair-substitution effects were observed.

Addition of Diphenylphosphine Oxide to Arenesulfonylhydrazones: Novel Adducts from Tosylhydrazones and a New Synthesis of Alkyldiphenylphosphine Oxides from Trisylhydrazones

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There are precious few high-yield additions to arenesulfonylhydrazones.[1] Such additions have the potential for becoming as important to organic synthesis as the chemistry derived from the discovery of conditions for α-proton removal,[2] which extended the usefulness of arenesulfonylhydrazones from diazoalkane and carbene precursors[3] to invaluable intermediates for regiospecific

alkylation[4] and olefin formation.[5] Secondary phosphine oxides have been reported to add to the C–N double bonds of hydrazones;[6] however, following the literature method, we were unable to prepare adducts of diphenylphosphine oxide (1) and tosylhydrazones 2. Therefore we have developed conditions which give the analytically pure adducts, 3 (Scheme I), in good to excellent yields. The adducts from ketone tosylhydrazones are very delicate; acid, base, and heat decompose them rapidly back to starting material in what appears to be the most facile E$_i$ reaction reported for a phosphine oxide. Conditions also have been found under which sulfinic acid and nitrogen are eliminated to yield alkyldiphenylphosphine oxides in the mildest method extant for these synthetically useful compounds.

No adducts could be isolated when 1 and 2a or 1 and cyclohexanone phenylhydrazone were stirred in methanol or ethanol, either at room temperature or at reflux.[6] In contrast, treatment of some representative aldehyde and ketone tosylhydrazones with 1 in ethereal solvents at 20–25 °C allows the adducts to be isolated by simple filtration in 58–100% yields (see Table I). The ^{13}C NMR spectra all lacked the resonance due to the C doubly bonded to N characteristic of 2 (δ 155–165)[7] and all contained instead a doublet for the carbon bonded to nitrogen and phosphorus (see Table I for spectral parameters). The alternative structure for the adducts in which the oxygen of 1 has bonded to the imino carbon of 2 would give a smaller ^{13}C–^{31}P coupling constant.[8]

Under the same conditions that are successful for 2a, cyclohexanone mesitylenesulfonylhydrazone[9] and cyclohexanone trisylhydrazone are unreactive. The ^{13}C NMR resonances due to the imino carbons of these three hydrazones are δ 162.7, 160.9, and 160.5, respectively.[7] The similarity of these values indicates that steric effects, not electronic ones,[10] are responsible for the lack of reactivity of the trimyl-[9] and trisylhydrazones. The imino resonance of cyclohexanone phenylhydrazone, which also does not give an adduct, is shifted upfield to δ 150.6, so that the lack of reactivity in this case is an electronic effect.[10] The trimyl-hydrazone[9] of cyclohexanecarboxaldehyde does form an adduct, but the yield (55%) is lower than that of the corresponding tosylhydrazone (2f) under the same conditions.

The adducts 3 decompose back to 1 and 2 when exposed to acid, base, or heat. The sensitivity to base explains why basic catalysis is not helpful, as it is for the addition to carbonyl compounds.[11,12] The ketone tosylhydrazone adducts are much less stable toward acid and heat than those derived from aldehyde tosylhydrazones. In solution the former decompose thermally at 35 °C in a matter of hours whereas the latter decompose at a comparable rate at 65 °C. This order of reactivity parallels the order of stability of the corresponding carbenium ions (benzylic > secondary > primary). This correlation explains why no adduct was observed with benzaldehyde tosylhydrazone. The facility of the thermal elimination of 1 from the ketone tosylhydrazone adducts is extraordinary, considering the fact that alkyldiphenylphosphine oxides, even those with γ-carbonyl groups,[13] are remarkably resistant to

(1) Shapiro, R. H.; Gadek, T. *J. Org. Chem.* **1974**, *39*, 3418. Hutchins, R. O.; Milewski, C. A.; Maryanoff, B. E. *J. Am. Chem. Soc.* **1973**, *95*, 3662. Bertz, S. H. *Tetrahedron Lett.* **1980**, *21*, 3151. Vedejs, E.; Dolphin, J. M.; Stolle, W. T. *J. Am. Chem. Soc.* **1979**, *101*, 249. Orere, D. M.; Reese, C. B. *J. Chem. Soc., Chem. Commun.* **1977**, 280.

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(11) Horner, L.; Hoffmann, H.; Wippel, H. G.; Klahre, G. *Chem. Ber.* **1959**, *92*, 2499.

(12) Sasse, K. *Methoden Org. Chem. (Houben-Weyl)*, 4th Ed. **1963**, *12*, 154.