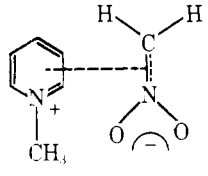
($\sim 10^{-4}$ M) whereas the NMR data were initially obtained on much more concentrated solutions. A direct comparison was made by recording the NMR spectra on the same solutions used for the UV–vis spectroscopy using pulse-Fourier transform techniques to give sufficient S/N enhancement in the ^{1}H NMR spectra. The NMR spectra were identical to those obtained previously, taking into account the change in operating frequency between the two spectrometers, indicating that only the 1,4 isomer was present.

E. Conclusions. The NMR spectra of the adducts clearly indicate that in every case the only compound isolated was the adduct from attack at C_4 in the pyridinium-ion ring. It is possible that a very fast isomerization reaction takes place, although this seems unlikely as no other isomers were found in any of the systems in what would be the equilibrium mixture and also because of the observations made on analogous reactions of nitroaromatics with carbanions referred to in the introduction.

Another possibility is that there is only one isomer formed in the reaction, suggesting a very specific interaction between the two components prior to the attack of the nucleophile on the ring. This is reminiscent of the suggestion of Kosower[9] that specific charge-transfer interaction might influence these reactions. It should be noted that although the example chosen by Kosower[10] is probably a δ complex,[11] this does not invalidate the idea itself of a specific orientation of the two components in the reaction determining the position of attack. The appropriate complex for these components could be **13**,



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where the σ carbon of the nitroalkane anion would be well oriented for the attack to occur at C_4. Independent of the reason, the results do suggest that there can be specific orientation of attack in some cases, contrary to the ideas of Lyle.[12]

For the two nucleophiles studied, two different types of behavior have been found and further investigation of these related systems by stopped flow techniques using UV–vis spectroscopy using the spectral assignments given would be warranted as would also studies of the reactions of other nucleophiles with these substrates where the position(s) of attack is clearly defined by deuterium labeling and NMR spectroscopy. A decision involving the different factors governing the position of nucleophilic attack on these substrates[9,12,13] will more easily be made when the experimental data are unambiguous.

Acknowledgments. The authors would like to thank the National Research Council of Canada for a grant in aid of research (C.A.F.) and the Canadian Government for the award of a Commonwealth Fellowship (S.W.H.D.).

Registry No.—*N*-Methyl-3,5-dinitropyridinium *p*-toluenesulfonate, 68843-50-5; 3,5-dinitropyridine, 940-06-7; methyl *p*-toluenesulfonate, 80-48-8; nitromethane, 75-52-5; nitroethane, 79-24-3; deuterated nitroethane anion, 68843-51-6; 3-cyanopyridinium methiodide, 1004-16-6; 1-ethyl-3-cyanopyridinium, 68843-52-7; 1-propyl-3-cyanopyridinium, 68843-53-8; *N*-benzyl-3-cyanopyridinium chloride, 14535-08-1; nitroethane anion, 25590-58-3; nitromethane anion, 18137-96-7; 3,5-dichloropyridinium methiodide, 23029-86-9; 1-propyl-3,5-dichloropyridinium, 68843-54-9; *N*-benzyl-3,5-dichloropyridinium chloride, 68843-55-0; 3,5-dicyanopyridinium methyl *p*-toluene sulfonate, 15834-67-0; 18-crown-6 ether 1:1 complex with the potassium salt of nitromethane anion, 68844-28-0; 18-crown-6 ether 1:1 complex with the potassium salt of nitroethane anion, 68844-29-1.

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Nitrogen-15 Nuclear Magnetic Resonance Spectroscopy. Effects of Hydrogen Bonding and Protonation on Nitrogen Chemical Shifts of Pyrazoles[1]

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The ^{15}N chemical shifts of pyrazole, *N*-methylpyrazole, 3-methyl- and 3,5-dimethylpyrazoles, and indazole have been measured as a function of solvent and acidity of the medium. Hydrogen bonding and protonation result in upfield shifts of both the pyridine- and pyrrole-type nitrogen resonances of these substances with the effect being larger at the pyridine-type nitrogens. The protonation shifts far exceed those resulting from hydrogen bonding.

The value of ^{15}N NMR spectroscopy in elucidating effects of hydrogen bonding and protonation in diazoles has been clearly demonstrated for imidazoles.[2,3] Because of the proximity of their nitrogens, pyrazoles should be especially interesting in this respect as suggested by the data on the effects of solvents on the ^{14}N shifts[4] of pyrazole, indazole, and their *N*-methyl derivatives.

Several pyrazoles have been studied by ^{13}C NMR.[5,6] How-

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Table I. ^{15}N Chemical Shifts[a] of *N*-Methylpyrazole at 25.0 °C in Hydrogen Bonding and Protonating Media

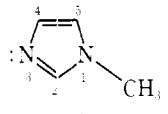
solvent	$\delta^{15}N$ N1	$\delta^{15}N$ N2	$\bar{\delta}^{15}N$[b]	$\delta N1 - \delta N2$[c]
$CHCl_3$	174.6	70.3	122.4	104.3
CF_3CH_2OH	176.0	88.2	132.1	87.8
CH_3CO_2H	175.2	87.4	131.3	87.8
CF_3CO_2H (2 M) in CH_3CO_2H	180.2	140.2	160.2	40.0
Aqueous HCl				
pH 5.96	173.9	83.2	128.6	90.7
pH 2.10	179.4	131.9	155.7	47.5
pH 1.71	180.6	142.7	161.7	37.9
pH 1.04	182.8	162.2	172.5	20.6
pH 0.06	183.7	170.2	177.0	13.5

[a] Of 2 M solutions in ppm upfield from external 1 M $D^{15}NO_3$ in D_2O. [b] Average shifts of nitrogens. [c] Difference between the shifts of N1 and N2.

ever, nitrogen NMR is expected to be more informative because influences on the nucleus directly involved in chemical interactions can be studied in a straightforward manner.

Results and Discussion

Like *N*-methylimidazole **1**, *N*-methylpyrazole **2** shows two ^{15}N NMR resonances: that of the pyrrole-type nitrogen, N1, at high field and the pyridine-type nitrogen, N2, at lower field. The differences in these shifts for **1** and **2** are comparable in



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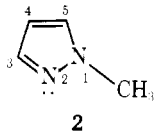

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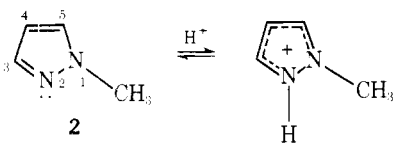
magnitude and range from about 80 to 100 ppm depending on the solvent (see Table I). Probably because of the −I effect of each nitrogen on the other, the shifts of both nitrogens in *N*-methylpyrazole are some 35–40 ppm downfield from their counterpart in *N*-methylimidazole.

It will be seen from the data in Table I that an increase in hydrogen bonding, as brought about by a change of solvent from chloroform to trifluoroethanol, causes the resonance of N2 of **2** to shift upfield by 17.9 ppm with a small concomitant upfield shift of 1.4 ppm for the resonance of N1. The behavior of the N3 resonance of **1** is similar (16.4-ppm upfield shift in going from cyclohexane to methanol), but for **1** the N1 resonance moves 3.2 ppm downfield as hydrogen bonding increases.

Formation of the conjugate acid of *N*-methylpyrazole **3** results in 100 and 4 ppm upfield changes in the chemical shifts of N2 and N1, respectively. The shift difference, $\delta N1 - \delta N2$, for **3** is much smaller than for **2** because the nitrogens are more



2 **3**

nearly equivalent in the *N*-methylpyrazolium ion. In water, the average of the shifts of **3** is 177.8 ppm, which is upfield of the value for **2**, and the shift difference between N1 and N2 is 12.1 ppm. The pH dependences of the ^{15}N shifts of **2** are shown in Figure 1, and these correspond to a pK_a of 2.15, which is quite comparable to the reported value of 2.04[7] when one considers the difference in concentrations involved.

Although **2** has about the same shift in trifluoroethanol and acetic acid, addition of an equivalent of trifluoroacetic acid

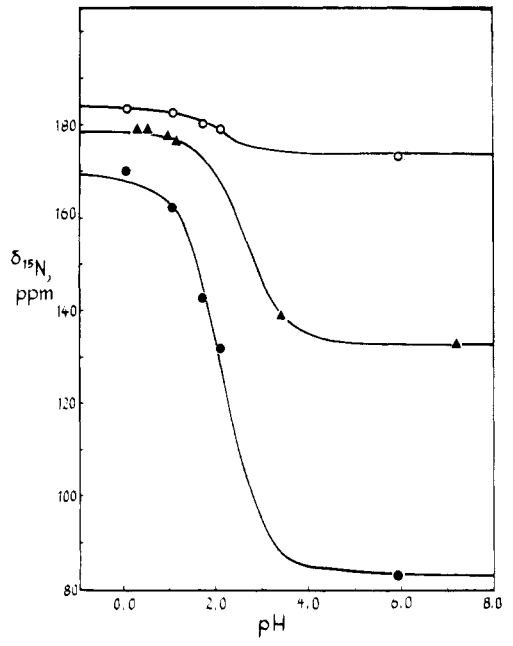
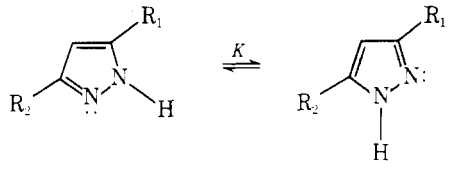


Figure 1. Titration curves of pyrazole (▲) and *N*-methylpyrazole (N1, ○; N2, ●) in aqueous solution. The lines are calculated for pK_a values of 2.63 and 2.15 for pyrazole and *N*-methylpyrazole.

to a 2 M solution of **2** in acetic acid causes the N1, N2 shift difference to decrease from 87.8 to 40.0 ppm and the average of the shifts to move upfield by 28.9 ppm. These changes are surely the result of partial protonation, the extent of which may be estimated to be about 60% from the shifts of **2** and **3** in acetic acid and water, respectively.

Pyrazoles with labile NH bonds exhibit ^{15}N shifts in solution which are usually the weighted average of those of the two rapidly equilibrating tautomers (eq 1). With **4a–4b**, when



(1)

4a, $R_1 = R_2 = H$ **4b**, $R_1 = R_2 = H$
5a, $R_1 = CH_3$; $R_2 = H$ **5b**, $R_1 = CH_3$; $R_2 = H$
6a, $R_1 = R_2 = CH_3$ **6b**, $R_1 = R_2 = CH_3$

equilibration is fast, the equilibrium constant K is unity; the nitrogens are equivalent and give rise to a single ^{15}N resonance. The average of these nitrogen shifts is 5–7 ppm upfield of the average of the N1, N2 shifts of **2** in the same solvents, probably as the consequence of the fact that the hydrogen of N1 of **4** can be a hydrogen-bond donor and this is not possible for N1 of **2**. With **4a** in dimethyl sulfoxide solution, separate (albeit somewhat broadened) resonances for N1 and N2 can be observed, which is in agreement with slow equilibration in this solvent.[6] The average of these resonances (120.4 ppm) is downfield from the averages observed for chloroform or trifluoroethanol solutions as expected for decreases in hydrogen bonding at the >C=N̈– nitrogen arising from either self-association or association with hydrogen-bond donor solvents.[7] Intermediate rates of tautomeric exchange for **5** and **6** in chloroform resulted in ^{15}N resonances so broadened as to cause reduction of signal strength below detectable levels. For these substances, addition of a trace of trifluoroacetic acid sharpened the signals by increasing the exchange rates.

As for **2**, an increase in the hydrogen-bonding power of the solvent leads to an upfield shift of the ^{15}N resonance of **4** and this amounts to 8.7 ppm in going from chloroform to trifluoroethanol (see Table II). The protonation shifts of **4**, like those

Table II. ^{15}N Chemical Shifts [a] of Pyrazole 4, 3-Methylpyrazole 5, and 3,5-Dimethylpyrazole 6 at 25.0 °C in Hydrogen-Bonding and Protonating Media

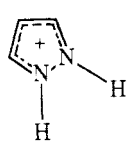
	$\delta^{15}N$			
		5		
solvent	4	N2	N1	6
$CHCl_3$	128.5	128.1	133.8	133.6
$(CH_3)_2SO$	73.9, 166.9[b]			
CF_3CH_2OH	137.2	139.5	142.1	144.0
CH_3CO_2H	138.2	144.9	149.7	159.5
CF_3CO_2H (2 M) in CH_3CO_2H	169.7	177.0	179.5	182.8
CH_3CO_2H[c]	178.7	180.8	183.5	183.5
CH_3OH	175.8, 178.0[d]	177.9	181.2	182.9
H_2O	132.8, 179.5[d]			
aqueous HCl (pH)	179.1 (0.45)	181.1 (0.6)	184.6 (0.6)	185.7 (1.66)
	178.9 (0.45)	179.9 (1.66)	183.4 (1.66)	184.5 (2.39)
	177.7 (0.95)			
	176.7 (1.10)			
	139.3 (3.43)			

[a] For 2–2.4 M solutions in ppm upfield from external 1 M $D^{15}NO_3$ in D_2O. [b] 4 M solution; relatively broad lines. [c] The HCl salt is the solute. [d] The methyl iodide salt 8 at 1.5 M is the solute.

of its *N*-methyl derivative **2**, are much larger than this, with the ^{15}N resonance of the pyrazolium ion **7** being 45.9 ppm upfield of that of **4** (178.8 ppm in water, extrapolated from the titration curve of Figure 1).

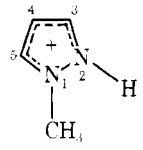
Addition of an equivalent of trifluoroacetic acid to a 2 M solution of **4** in acetic acid causes an upfield shift of the nitrogen resonance of 31.5 ppm, and this is the result of partial protonation as for **2** in the same medium. The extent of protonation is estimated at about 78% and is larger for **4** than for the less basic **2**.[8]

The effect of methylation at nitrogen on the ^{15}N resonance of the pyrazolium ion is small, and there is less than 1-ppm difference in the shifts of **7** and **8** (in water). The ^{15}N reso-



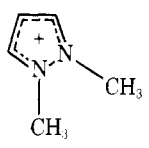
178.8 ppm

7



171.7 ppm, N2
183.8 ppm, N1

3



179.5 ppm

8

nances of the *N*-methylpyrazolium ion **3**, however, differ by as much as 12 ppm, with the *N*-methyl nitrogen, N1, more shielded than the nitrogens of **8** and the shift of the NH nitrogen, N2, of **3** downfield from those of **7**. These differences appear to be the result of an unequal distribution of the positive charge between the two nitrogens of **3**, with less positive charge on N1.

The *C*-methylpyrazoles **5** and **6** have averaged ^{15}N resonances more upfield than those of either **2** or **4**. Thus, the average shift of 3,5-dimethylpyrazole **6** is 11.2 and 5.1 ppm upfield of the average shifts of **2** and **4**, respectively, in chloroform. Similar shift effects are observed for the corresponding pyrazolium ions.

The nitrogens of 3-methylpyrazole **5** and 3-methylpyrazolium ion **9** are not equivalent. In the proton-coupled spectrum of **9**, the high-field resonance is that of a nitrogen coupled to H4 and H5 with coupling constants of 4.6 and 6.6 Hz, respectively. The low-field resonance is that of a nitrogen equally coupled to all five hydrogens (J_{NH} = 3.4 Hz) and is

Table III. ^{15}N Chemical Shifts [a] of Indazole 11 at 25.0 °C in Hydrogen-Bonding and Protonating Media

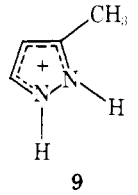
	concn,		$\delta^{15}N$		$\delta N1 -$
solute	M	solvent	N1	N2	$\delta N2$[b]
11	1.5	CH_3COCH_3	194.4	58.9	135.5
11	1.5	CF_3CH_2OH	201.0	84.6	116.4
11	1.5	CH_3CO_2H	198.2	86.9	111.3
11	1.4	CF_3CO_2H (1.4 M) in CH_3CO_2H	201.7	118.1	83.6
11·HCl	1.5	CH_3CO_2H	204.2	170.1	34.1
11·HCl	1.2	H_2O (pH < −0.5)	206.0	174.6	31.4
11·HCl	1.3	CH_3OH	201.1		

[a] In ppm upfield from external 1 M $D^{15}NO_3$ in D_2O. [b] Differences between the shifts of N1 and N2.

probably that of N2 because this nucleus is three bonds removed from each of the hydrogens in the molecule. The coupling assignments were confirmed by selectively decoupling H4, H5, and the methyl hydrogens. In the proton-coupled spectrum of the conjugate base, 3-methylpyrazole **5**, the downfield resonance also corresponds to N2; the upfield one is that of N1 with the coupling constants J_{N1-H4} and J_{N1-H5} approximately 6 and 14 Hz, respectively. Thus, deprotonation results in an increase in the coupling between nitrogen and the α-hydrogen, an effect previously noted in pyridine.[9]

The average shifts of 3-methylpyrazole **5** and its conjugate acid **9** resemble those of **2** in the same solvents (see Tables I and II), except that those of **2** are 10–18 ppm further downfield. From this it is clear that the overall nitrogen shieldings in pyrazoles are more influenced in the upfield direction by a C3 methyl than an *N*-methyl. The reverse is true for 4-methylimidazolium ions.

The protonation shifts of **5** and **6** are large like those of the other pyrazoles with the shifts of the nitrogens of 3-methylpyrazolium ion **9** and those of 3,5-dimethylpyrazolium ion **10**



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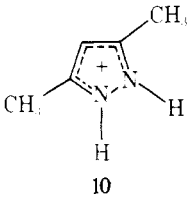
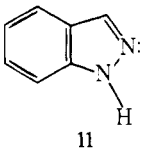


10

in water being approximately 42 ppm upfield of the conjugate bases in trifluoroethanol.

Although indazole **11** has two possible tautomeric forms, the ^{14}N shifts of its nitrogens have been reported to resemble closely those of 1-methylindazole **12** and to be quite different from those of 2-methylindazole **13** (saturated solutions in acetone).[4] Moreover, the ^{13}C shifts of **11**[6b] are more like those of **12** than those of **13**. It is therefore clear that the tautomer of **11** corresponding to **12** is much more stable than that corresponding to **13**. The N2 nitrogen of indazole **11** is therefore



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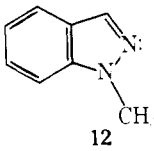

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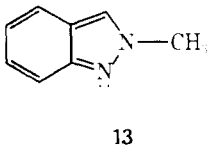

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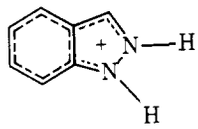
pyridine-like, and its shift is like that of N2 of *N*-methylpyrazole **2** in being more sensitive to hydrogen bonding and protonation than the shift of N1. Thus, solvent changes from acetone to trifluoroethanol to acetic acid cause shifts in the N1 resonance of less than 7 ppm, but 26–28 ppm shifts in the resonance of N2 (see Table III).

Protonation of indazole, which converts both N1 and N2 into amidinium-type nitrogens, **14**, results in upfield shifts of 7.8 and 87.7 ppm of the N1 and N2 resonances, respectively,



14

relative to the shifts of indazole **11** in the same solvent (acetic acid). The 34.2-ppm difference in the shifts of N1 and N2 of **14** is close to 35 ppm, the difference between the N1 shift of **12** and the N2 shift of **13**. One interpretation of this is that 35 ppm corresponds to an intrinsic shift difference resulting from the difference in positions of the nitrogens relative to the benzene ring, and there is a more or less equal positive charge on the two nitrogens of **14**.

Partial protonation of indazole in acetic acid containing an equivalent of trifluoroacetic acid reduces the shift difference between N1 and N2 to 83.5 ppm. From this, the extent of protonation in this solvent can be estimated to be near 38%, which is nearly half the value calculated for the more basic *N*-methylpyrazole **2** under the same conditions.

Experimental Section

The ^{15}N NMR spectra were obtained using a Bruker WH-180 spectrometer operating at 18.25 MHz. The conditions for signal accumulation and solvent purification have been described elsewhere.[2] Commercial samples of the pyrazoles were used without further purification.

Registry No.—**2,** 930-36-9; **4,** 288-13-1; **5,** 1453-58-3; **6,** 67-51-6; **11,** 271-44-3; **11**·HCl, 63725-55-3.

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^{15}N Nuclear Magnetic Resonance of Organophosphorus Compounds. Ring Size and Aziridine Methylation Effects on ^{15}N Shifts and ^{15}N–^{31}P Nuclear Spin Couplings in Heterocyclic Phosphoramidates

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Natural abundance ^{15}N NMR studies have been carried out on a series of cyclic phosphoramidates, including several methylated three-membered ring versions. The three-membered ring aziridine phosphoramidate was observed to have a substantial shielding (34 ppm) with respect to larger ring systems. Large β-substituent effects on the ^{15}N shift were noted along with changes in directly bonded ^{15}N–^{31}P couplings from 9.3 Hz in the nonsubstituted three-membered ring compound to $\leq$1 Hz in the fully substituted 2,2,3,3-tetramethylphosphoramidate. This directly bonded coupling experiences a large increase in going to the larger ring system, reflecting the change from a pyramidal-like (sp^3) nitrogen in the three-membered ring to trigonal (sp^2) in the larger ring compounds and the acyclic (diethylamino)dimethylphosphoramidate, where the observed coupling is 42.2 Hz.

Modern pulsed Fourier transform NMR spectrometers have provided instrumental access to the NMR spectroscopy of increasingly less sensitive nuclei such as ^{15}N (0.36% natural abundance). We have been interested in the systematic study of organosphosphorus compounds using NMR, taking advantage of the doubling of the spectral information via the spin couplings of ^{31}P to such nuclei as ^{13}C, ^{15}N, and ^{17}O. ^{15}N studies in general over the last few years have been more frequent and have concentrated on information obtained through measurements of the ^{15}N chemical shift.[2-4] In this work we analyze, in part, a particular class of organophosphorus compounds containing nitrogen—the aziridine phosphoramidates. There is much interest in the transferability of the substituent effect methodology for ^{13}C analysis to those of ^{15}N. In this class of compounds we were able to systematically test the reliability of such a method and as well explore the sensitivity of directly bonded ^{15}N–^{31}P couplings to those changes in the molecular framework.

Experimental Section

^{15}N spectra were obtained on ~50% solutions in C_6D_6 in 10-mm tubes using a Varian XL-100 WG12/S124 FT NMR spectrometer at 10.138 MHz or FT-80A at 8.059 MHz. Typical conditions were 2500 Hz spectral width, 1–4 s acquisition time, 12–25° pulses, no pulse delay, and 35000–53000 transients. ^{15}N resonance frequencies were directly measured for each compound and compared with the frequency of CH_3NO_2 in a 90% solution in C_6D_6 in a separate experiment for purposes of chemical shift referencing. For the 8.059-MHz studies, 0.05 M $Cr(AcAc)_3$ was used to shorten the long ^{15}N T_1's.

^{13}C spectra were obtained on a Varian FT-80A at 20.0 MHz using ~30% solutions (C_6D_6) in 10-mm tubes. Typical conditions were 2000 Hz spectral width, 2–4 s acquisition times, 45 ° pulses, no pulse delay, collecting 100–200 transients, and transforming without exponential weighting.

Materials. All compounds were prepared by reaction between trimethyl phosphite and the appropriate 2-iodoalkyl azide, according to the published procedure.[5] The iodo azides were synthesized via the method of Fowler et al.[6] For the aziridine phosphoramidates the boiling points are: **1**, bp 79–80 °C (3.0 mm) [lit.[7] bp 107 °C (15 mm)];

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