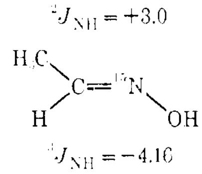
^{15}N Nuclear Magnetic Resonance Spectroscopy. XIII. Pyridine-^{15}N[1]

Robert L. Lichter and John D. Roberts*

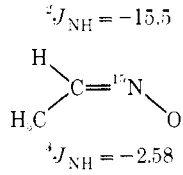
Contribution No. 4196 from the Gates and Crellin Laboratories of Chemistry,
California Institute of Technology, Pasadena, California 91109.
Received January 18, 1971

Abstract: From high-resolution proton, ^{13}C, and ^{15}N nuclear magnetic resonance spectra of ^{15}N-enriched pyridine and its hydrochloride, all of the chemical shifts, ^{15}N–H, and ^{15}N–^{13}C coupling constants have been obtained. Attention is centered on the coupling constants, which are compared with other values and discussed in light of the known inapplicability to pyridine of the average energy approximation. The coupling $^{2}J_{NH}$ exhibits the normal dependence on geometry, and the algebraic increase observed on protonation parallels the behavior exhibited by other acyclic compounds with unsaturated nitrogen. The coupling $^{1}J_{NC}$ in pyridine increases 30-fold on protonation, which accords with qualitative predictions. In contrast to the absence of C–N coupling over more than one bond in saturated systems (glycine, alanine, 1,1-dimethylhydrazine), pyridine and pyridinium ion display substantial C–N couplings over two and three bonds. Because large two-bond C–N couplings are also observed in dimethylnitrosamine as well as in some amides, the presence of a π system is felt to be important for the longer range couplings. Substantial solvent effects are observed on these couplings which may be attributed to increasing hydrogen bonding at nitrogen. On the basis of changes in ^{15}N chemical shifts and ^{15}N–H coupling constants, $^{1}J_{NC}$ is shown to very likely undergo a change in sign when the nitrogen is protonated.

As the availability of ^{15}N-labeled compounds has grown, measurement of spin–spin couplings between nitrogen and other magnetic nuclei has evoked increasing interest, not only for theoretical reasons, but also because of the obvious utility in structure elucidation. The available data permit some generalizations as to the relationships between structure and nitrogen–proton coupling constants. Typically, two-bond couplings in saturated systems are of the order 0–1 Hz,[2,3] while unsaturation at either carbon or nitrogen leads to values with enhanced magnitude.[2,4] Three-bond couplings in saturated systems are generally larger than two-bond couplings,[2,5] and the enhancement on unsaturation is not as great.[2,3b,4b,c,e,f,5c,6] More significantly, in compounds with fixed geometry, both two-bond and three-bond couplings are larger in magnitude than that proton which lies closer in space to the lone-pair electrons on nitrogen;[3c,d] this observation has been exploited extensively in assigning preferred conformations of nitrosamines and related compounds.[7] In particular, the signs of the larger and smaller two-bond ^{15}N–H coupling constants, as in *trans*-acetaldoxime (**1**), were found to be negative and positive, respectively,[4c,d] and both increase algebraically on protonation. The same relative magnitudes hold for the three-bond couplings, but in this case protonation leads to an algebraic decrease.[4d] The proton–nitrogen couplings in quinoline-^{15}N follow the same general pattern.[3d,8]



1 (*trans*)



1 (*cis*)

Much less is known about carbon–nitrogen coupling constants. A relationship between the magnitude of $^{1}J_{NC}$ and the degree of s character in the C–N bonding orbitals has been suggested[2] but there are as yet insufficient data to test its generality.

In Table I are presented selected values of ^{15}N–H and ^{15}N–^{13}C coupling constants illustrating some of the generalizations adduced above. It is apparent from these data that the lone-pair electrons on nitrogen play a decisive role in the relative and absolute magnitudes of the coupling constants. These electrons are also known to have marked effects on chemical shifts, of which the "anomalous" low-field nitrogen shift of pyridine is the classic example.[9] The importance of the lone-pair electrons has also been stressed in discussions of the ^{1}H[9a,10] and ^{13}C[11] resonance line positions in

---

[1] (a) Part XII: R. L. Lichter and J. D. Roberts, *J. Amer. Chem. Soc.*, **93**, 3200 (1971); (b) supported by the Public Health Service, Grant No. GM-11072-07, from the Division of General Medical Sciences.

[2] G. Binsch, J. B. Lambert, B. W. Roberts, and J. D. Roberts, *J. Amer. Chem. Soc.*, **86**, 5564 (1964).

[3] (a) E. W. Randall and D. Shaw, *Spectrochim. Acta, Part A*, **23**, 1235 (1967); (b) W. McFarlane, *J. Chem. Soc. A*, 1660 (1967); (c) F. G. Riddell and J. M. Lehn, *ibid.*, *B*, 1224 (1968); (d) R. L. Lichter and J. D. Roberts, *Spectrochim. Acta, Part A*, **26**, 1813 (1970).

[4] (a) A. J. R. Bourn and E. W. Randall, *J. Mol. Spectrosc.*, **13**, 29 (1964); (b) A. K. Bose and I. Kugajesky, *Tetrahedron*, **23**, 1489 (1967); (c) D. Crépaux and J. M. Lehn, *Mol. Phys.*, **14**, 547 (1968); **16**, 225 (1969); (d) J. P. Kintzinger and J. M. Lehn, *Chem. Commun.*, 660 (1967); (e) M. Ohtsuru, K. Tori, J. M. Lehn, and R. Seher, *J. Amer. Chem. Soc.*, **91**, 1187 (1969); (f) G. A. Olah and T. E. Kiovsky, *ibid.*, **90**, 4666 (1968); (g) G. Binsch and J. D. Roberts, *J. Phys. Chem.*, **72**, 4310 (1968).

[5] (a) P. G. Gassman and D. C. Heckert, *J. Org. Chem.*, **30**, 2859 (1965); (b) Y. Terui, K. Aono, and K. Tori, *J. Amer. Chem. Soc.*, **90**, 1069 (1968); (c) A. A. Bothner-By and R. H. Cox, *J. Phys. Chem.*, **73**, 1830 (1969); (d) R. L. Lichter and J. D. Roberts, *J. Org. Chem.*, **35**, 2806 (1970).

[6] (a) W. McFarlane, *Mol. Phys.*, **10**, 603 (1966); (b) H. Hogeveen, *Recl. Trav. Chim. Pays-Bas*, **86**, 1288 (1967).

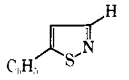
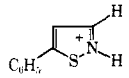
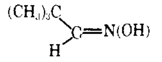
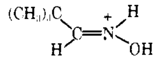
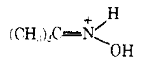
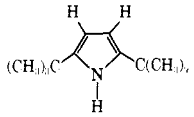
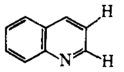
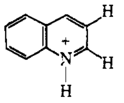
[7] (a) T. Axenrod, P. S. Pregosin, and G. W. A. Milne, *Chem. Commun.*, 702 (1968); (b) T. Axenrod, P. S. Pregosin, and G. W. A. Milne, *Tetrahedron Lett.*, 5293 (1968); (c) T. Axenrod, M. J. Wieder, and G. W. A. Milne, *ibid.*, 401 (1969); (d) T. Axenrod, M. J. Wieder, and G. W. A. Milne, *ibid.*, 1397 (1969).

[8] K. Tori, M. Ohtsuru, K. Aono, Y. Kawazoe, and M. Ohnishi, *J. Amer. Chem. Soc.*, **89**, 2765 (1967).

[9] (a) J. D. Baldeschwieler and E. W. Randall, *Proc. Chem. Soc.*, 303 (1961); (b) H. Saîto, K. Nukada, H. Kato, T. Yonezawa, and K. Fukui, *Tetrahedron Lett.*, 111 (1965); (c) R. Price, Ph.D. Dissertation, University of London, 1969.

[10] (a) J. B. Merry and J. H. Goldstein, *J. Amer. Chem. Soc.*, **88**, 5560 (1966); (b) S. Castellano, C. Sun, and R. Kostelnik, *J. Chem.*

Table I. Representative ^{15}N–H and ^{15}N–^{13}C Coupling Constants[a]

Compd	$^2J_{NH}$	$^3J_{NH}$	$^1J_{NC}$	Ref
CH_3NH_2	1.0		7	2
$CH_3\overset{+}{N}H_3$	0.8		<8	2
$\overset{-}{O}OCCH(CH_3)\overset{+}{N}H_3$	<0.5	3.1	*b*	5d
$(CH_3CH_2)_4\overset{+}{N}$	0.3[c]	2.5[d]	4.0[e]	2b, 5a
$C_6H_5CH{=}NCH_3$	0.6 (CH_3) 3.9 (CH)		<3 (CH_3) 7.1 (CH)	2
$(CH_3)_2NCHO$	+1.1 (CH_3) −15.6 (CH)		13.4[f] (CH)	4a
CH_3CONH_2		1.3	~15[g]	2
$H_2C{=}N(OH)$	−13.8 (H_{anti}) +2.68 (H_{syn})			4c, d
	−14.2			4c, d
	−4.2			
	+3.0			4c, d
	+3.5			4c, d
$(CH_3)_2N^{15}N{=}O$		0.8 (H_{syn}) 2.2 H($_{anti}$)	*b*	7a
$(CH_3)_2C{=}N(OH)$		−4.0 (H_{anti}) −2.2 (H_{syn})		3d
		−4.5 (H_{anti}) −3.2 (H_{syn})		3d
$CH_3CH{=}^{15}NNCH_2CH_3$	(−)14.5 (H_{anti})[h] (+)4.5 (H_{syn})[h]	(−)2.3 (H_{syn})[h] (−5.1) (H_{anti})[h] 2.5 (CH_2)		*i*
$(CH_3)_3\overset{+}{N}CH{=}CH_2$	−4.9	−7.8 (trans) −3.5 (cis)		3e
		5.2		*j*
	−11.0	−1.3		3d, 7
	−2.0	−4.5		3d, 7

[a] In hertz; absolute values unless otherwise indicated. [b] See Table V. [c] Tetramethylammonium hydroxide. [d] Tetramethylammonium chloride. [e] E. Bullock, D. G. Tuck, and E. J. Woodhouse, *J. Chem. Phys.*, **38**, 2318 (1963). [f] J. I. Kroschwitz and J. D. Roberts, unpublished results. [g] $^2J_{NC}$ = 9.5 Hz.[f] [h] The sign is assumed on the basis of the results described in ref 3c and 3d. [i] D. M. Lemal and R. L. Lichter, unpublished results; R. L. Lichter, Ph.D. Dissertation, University of Wisconsin, 1967. [j] D. Gagnaire, R. Ramasseul, and A. Rassat, *Bull. Soc. Chim. Fr.*, 415 (1970).

terms of a large contribution to the paramagnetic parts of the chemical shifts from a low-lying n → π^* transition[12–19] so that the commonly invoked average-energy approximation is thought to no longer hold. This approximation is employed in many calculations of cou-

---

Phys., **46**, 327 (1967); (c) G. Fraenkel, D. G. Adams, and R. R. Dean, *J. Phys. Chem.*, **72**, 944 (1968).

(11) (a) P. C. Lauterbur, *J. Chem. Phys.*, **43**, 360 (1965); (b) R. J. Pugmire and D. M. Grant, *J. Amer. Chem. Soc.*, **90**, 697 (1968); (c) R. J. Pugmire and D. M. Grant, *ibid.*, **90**, 4232 (1968).

(12) D. E. O'Reilly, *Progr. Nucl. Magn. Resonance Spectrosc.*, **2**, 1 (1966).

(13) A. Saika and C. P. Slichter, *J. Chem. Phys.*, **22**, 26 (1954).

(14) M. Karplus and J. A. Pople, *ibid.*, **38**, 2803 (1963).

(15) V. M. S. Gil and J. N. Murrell, *Trans. Faraday Soc.*, **60**, 248 (1964).

(16) (a) J. A. Pople, *J. Chem. Phys.*, **37**, 53, 60 (1962); (b) J. A. Pople, *Mol. Phys.*, **7**, 301 (1964).

(17) T. K. Wu, *J. Chem. Phys.*, **49**, 1139 (1968); **51**, 3622 (1969).

(18) (a) T. Tokuhiro, N. K. Wilson, and G. Fraenkel, *J. Amer. Chem.*

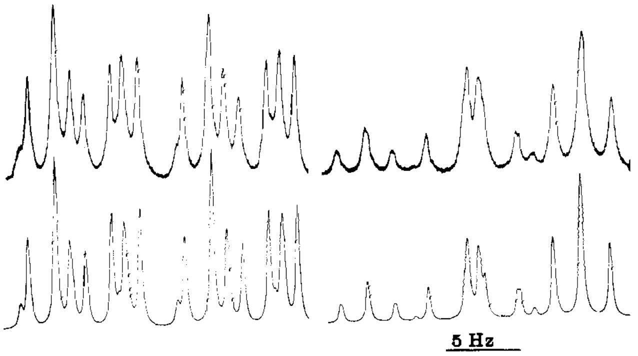


Figure 1. Pmr spectrum of pyridine-^{15}N, H, and H$_3$. The upper trace is the experimental spectrum, while the lower is the calculated spectrum based on the parameters given in Table II.

pling constants,[20] and is implicit in the available relationships of coupling constants to s character. Such expressions[2,21] in fact are known to fail when nitrogen chemical shifts have unusually low values.

In view of the geometrical dependence of nitrogen couplings, and of the relationship between coupling constants and chemical shifts, it was of interest to determine if the $^{15}N-^{1}H$ and $^{15}N-^{13}C$ coupling constants in pyridine followed the same pattern. We have accordingly determined these values in pyridine and in pyridinium ion, the former both as the neat liquid and as a 30% (v/v) methanol solution. To supplement the values given in Table I, we report here also the $^{15}N-^{1}H$ and $^{15}N-^{13}C$ coupling constants of a few nonaromatic compounds. Before this work was completed, we became aware of the parallel studies by Price[9c] on the $^{15}N-^{1}H$ coupling constants; our results agree in essence with his.

Experimental Section

Pyridine-^{15}N (98.9% enriched, Merck Sharp and Dohme of Canada) was used without further purification. The hydrochloride was obtained by passage of dry hydrogen chloride gas through a methanolic solution with external cooling to prevent loss by volatilization. Glycine-^{15}N and alanine-^{15}N, enriched to 95%, were obtained from Bio-Rad Laboratories. *N*-Nitrosodimethylamine-*2*-^{15}N was prepared from dimethylamine and ^{15}N-enriched sodium nitrite (Merck Sharp and Dohme of Canada, 96.0% enrichment) according to the method of Hatt.[22] Reduction of this material with lithium aluminum hydride in ether,[23] followed by aqueous work-up and distillation in a nitrogen atmosphere, afforded 1,1-dimethylhydrazine-*2*-^{15}N.

Proton spectra were taken on a Varian A 56/60 spectrometer, and line positions, measured either with respect to internal cyclopentane (neat pyridine) or internal methanol (pyridine and pyridinium ion[24]) by the audio-sideband calibration technique, are the results of at least three determinations alternating in sweep direction at sweep rates of 0.05 or 0.1 Hz/sec. The amino acids were run as aqueous solutions with water as the internal reference, while

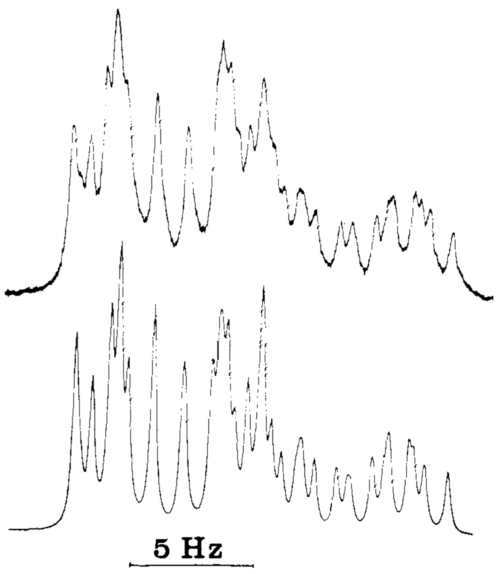


Figure 2. Pmr spectrum of pyridine-^{15}N, H$_4$. As in Figure 1, the upper and lower traces are the experimental and calculated spectra, respectively.

N-nitrosodimethylamine and 1,1-dimethylhydrazine were neat liquids containing a trace of TMS. Carbon-13 and nitrogen-15 spectra were taken on a Varian DFS-60 spectrometer operating at 15.08 (^{13}C) and 6.07 (^{15}N) MHz under conditions of complete proton decoupling.[25,26] At sweep rates of 2–4 Hz/sec, carbon line positions were measured with respect to the carbon resonances of cyclopentane[27] and methanol, as above, while nitrogen shifts were measured with respect to external ^{15}N-enriched nitric acid. Because of long-term field instabilities, it was not possible to obtain high-resolution spectra without proton decoupling.

Results

Proton Spectra. The spectra of neat pyridine and pyridinium ion are shown in Figures 1–4, together with calculated spectra resulting from iterative fitting of the experimental line positions, using the program LAOCN3.[28] The best values of the coupling constants obtained for these systems, as well as those for the 30% (v/v) methanol solution, are given in Table II. At worst, the calculated probable errors were not greater than 0.05 Hz, and most were less than 0.02 Hz. Visual comparisons of calculated and experimental spectra are satisfactory except for the high-field region of the pyridinium ion spectrum (Figure 4). Although calculated line positions agree well with experimental values, line intensities are not always reproduced. The appearance of the calculated spectrum was markedly insensitive to detailed assignments of experimental to calculated frequencies, and to the signs of the N–H coupling constants.[29] The reliability of values obtained from this tightly coupled part of the spectrum is thus questionable;[28b] nevertheless, the proton–proton coupling constants agree well with published values,[10]

Soc., **90**, 3622 (1968); (b) T. Tokuhiro and G. Fraenkel, *J. Amer. Chem. Soc.*, **91**, 5005 (1969).

(19) W. Adam, A. Grimson, and G. Rodriguez, *J. Chem. Phys.*, **50**, 645 (1969).

(20) For a general discussion, see M. Barfield and D. M. Grant, *Advan. Magn. Resonance*, 1, 149 (1965).

(21) (a) A. J. R. Bourn and E. W. Randall, *Mol. Phys.*, **8**, 567 (1964); (b) E. W. Randall and D. G. Gillies, in ref 12, Vol. 6, in press.

(22) H. H. Hatt, "Organic Syntheses," Collect. Vol. II, Wiley, New York, N. Y., 1943, p 211.

(23) D. M. Lemal, F. Menger, and E. Coats, *J. Amer. Chem. Soc.*, **86**, 2395 (1964).

(24) Perdeuteriomethanol (containing some residual protiated material) was used instead of ordinary methanol because the resonance of the exchangeable protons in the latter solvent obscured the lower field region of interest.

(25) (a) F. J. Weigert and J. D. Roberts, *J. Amer. Chem. Soc.*, **89**, 2967 (1967); (b) F. J. Weigert and J. D. Roberts, *ibid.*, **90**, 3543 (1968).

(26) F. J. Weigert, M. Jautelat, and J. D. Roberts, *Proc. Nat. Acad. Sci. U. S.*, 60, 1152 (1968).

(27) External cyclohexane was used as standard for the amino acids.

(28) (a) A. A. Bothner-By and S. M. Castellano in "Computer Programs for Chemistry," Vol. 1, D. F. DeTar, Ed., W. A. Benjamin, New York, N. Y., 1968, p 10; (b) see R. J. Abraham and S. M. Castellano (*J. Chem. Soc. B*, 49 (1970)) for a discussion of uncertainties in spectral analysis.

(29) The signs of the proton–proton couplings were generally kept in accord with those in the literature.[10a] Reversing the sign of J_{26} was found to have no effect on the appearance of the spectrum.

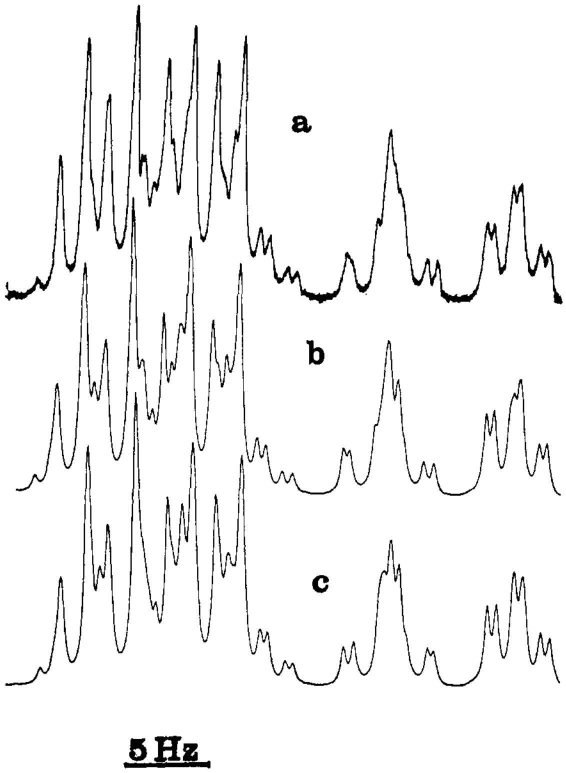
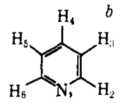
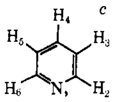
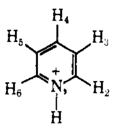


Figure 3. Pmr spectrum of pyridinium-^{15}N hydrochloride in methanol, H_1 and H_3: (a) experimental spectrum; (b) calculated spectrum based on parameters in Table II; (c) calculated spectrum as in b but with J_{26} positive.

and except for J_{14}, the nitrogen–proton couplings are in accord with those observed with trifluoroacetic acid as solvent.[9c] In none of the cases is the iterative analysis capable of unambiguous determination of the signs of the ^{15}N–H coupling constants. These have been assigned in analogy to results of spin-tickling experiments with quinoline-^{15}N.[8,9c]

Table II. Proton–Proton and Proton–Nitrogen Coupling Constants[a] in Pyridine-^{15}N

	 [b]	 [c]	
J_{23}	4.88	4.97	5.94
J_{24}	1.83	1.81	1.51
J_{25}	0.97	0.90	0.67
J_{26}	−0.12	−0.16	−0.55
J_{34}	7.62	7.83	7.93
J_{35}	1.34	1.38	1.64
J_{12}	−10.76	−10.06	−3.01 (−2.2)[d]
J_{13}	−1.53	−1.56	−3.98 (−4.3)[d]
J_{14}	±0.21	±0.18	±0.69 (0.3)[d]

[a] In hertz. [b] Neat. [c] 30% (v/v) solution in methanol. [d] Reference 9c, trifluoroacetic acid solvent.

Carbon Spectra. With the initial exception of that derived from C-2 in neat pyridine, all ^{13}C–^{15}N coupling constants were directly measurable from the proton-decoupled ^{13}C spectra (Figure 5). In the case of C-2, a sweep rate of 1 Hz/sec allowed observation of only a singlet, but application of the sensitivity-enhancement computer program SNARE[30] revealed a doublet separated by $^1J_{NC}$ = 0.45 ± 0.1 Hz. This value was confirmed when the sweep rate was reduced to 0.1 Hz/sec (Figure 6). Table III summarizes the coupling

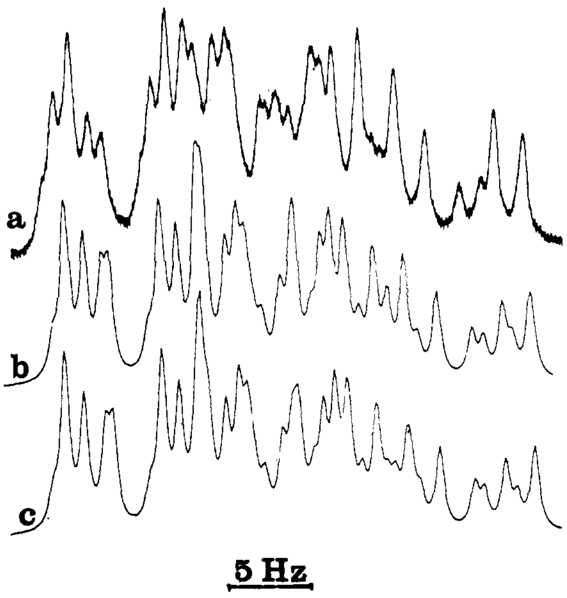


Figure 4. Pmr spectrum of pyridinium-^{15}N hydrochloride in methanol, H_2. The labels have the same significance as in Figure 3.

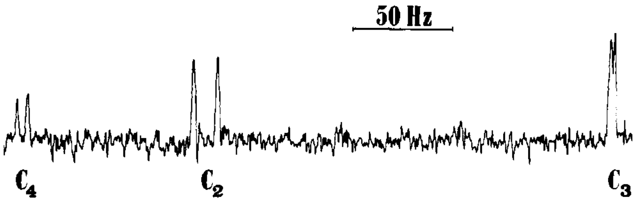


Figure 5. Natural-abundance ^{13}C spectrum of pyridinium-^{15}N hydrochloride in methanol. The spectrum was obtained with complete proton decoupling after 23 scans at a sweep rate of 5 Hz/sec.

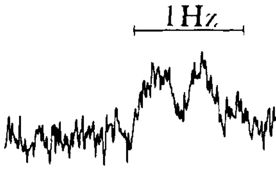
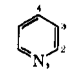
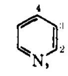
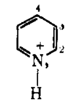


Figure 6. Natural-abundance ^{13}C resonance of C-2 in pyridine-^{15}N. The signal was obtained with complete proton decoupling after a single scan at a sweep rate of 0.1 Hz/sec.

Table III. Carbon–Nitrogen Coupling Constants in Pyridine-^{15}N[a]

	 [b]	 [c]	 [c]
$\|^1J_{12}\|$	0.45	0.7	12.0
$\|^2J_{13}\|$	2.4	2.6	2.1
$\|^3J_{14}\|$	3.6	3.8	5.3

[a] In hertz, ±0.1 Hz. [b] Neat. [c] 30% (v/v) in methanol.

---

(30) (a) G. A. Petersson, Ph.D. Dissertation, California Institute of Technology, 1970; (b) G. A. Petersson, R. L. Lichter, and J. D. Roberts, manuscript in preparation.

constants for all pyridine systems; the chemical shifts agreed with those previously reported,[11] with minor differences attributable to differences in measurement conditions.

^{15}N Spectra. The nitrogen chemical shifts obtained directly from the proton-decoupled ^{15}N spectra (Table IV) agree with published values.[9] The proton-decoupled signals derived from both neat and methanolic pyridine were not inverted. Because the nuclear Overhauser effect on ^{15}N resonances on proton irradiation normally produces inverted ^{15}N signals,[1a] the absence of inversion implies a negligible nuclear Overhauser effect in these systems. Apparently, the exchange lifetime of the hydrogen-bonded proton in the pyridine–methanol complex is too short to provide an effective relaxation pathway for the ^{15}N nucleus.[1a]

Table IV. Nitrogen Chemical Shifts of Pyridine-^{15}N

	δ_N, ppm[a]
Pyridine, neat	56.8
Pyridine–methanol	74.4
Pyridinium hydrochloride	170.1

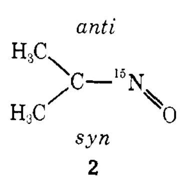
[a] Upfield with respect to external $H^{15}NO_3$; estimated error, 0.2 ppm.

Other ^{15}N–^{13}C Couplings. Table V shows the measured coupling constants for a few nonaromatic ^{15}N-containing compounds. The ^{15}N splittings in *N*-nitrosodimethylamine (**2**) were resolvable although the carbon resonances were broadened, presumably because coupling to the adjacent ^{14}N nucleus is only partially eliminated by quadrupole-induced relaxation. The carbon chemical shifts, assigned on the basis of the proton frequencies required to decouple each carbon separately, follow the same geometrical pattern as the proton shifts,[7a] with the resonance of the syn carbon being at higher field. The larger chemical-shift difference, compared to the ~0.7-ppm difference in the proton shifts, is possibly attributable to the anisotropy of the *N*-nitroso group,[31] but is more likely to arise from electric-field effects, as have been suggested to explain the 5-ppm difference in the methyl carbon chemical shifts of dimethylformamide.[32]

Table V. Carbon–Nitrogen Coupling Constants in Some Nonaromatic Compounds

	$^1J_{NC}$, Hz	$^2J_{NC}$, Hz
$H_3N^+CH_2COO^-$		
pH 6.33	6.2	0
pH 13.68	4.8	0
$H_3N^+C(CH_3)HCOO^-$		
pH 6.37	5.6	0
pH 13.64	4.4	0[a]
N-Nitrosodimethylamine (**2**)[b]		7.5 (anti) 1.4 (syn)
1,1-Dimethylhydrazine-*2*-^{15}N		<1[c]

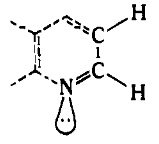
[a] No two-bond coupling was observed to either carbon. [b] $\delta_{^{13}C}$ (CH$_3$, anti) = 153.05 ppm, $\delta_{^{13}C}$ (CH$_3$, syn) = 160.94 ppm, CS$_2$ reference. [c] $^3J_{NH}$ = 3.2 Hz.



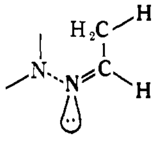
2

Discussion

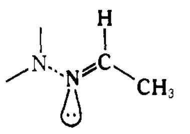
Comparison of the proton–nitrogen coupling constants of pyridine and quinoline with those of the oximes and hydrazones (Table I) shows the same kind of correlation between lone-pair orientation and coupling exists for these types of compounds. The relationships are emphasized by considering structures **3**–**8**. Thus, the coupling pathways in pyridine and quinoline (**3**)



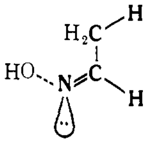
3



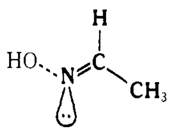
4



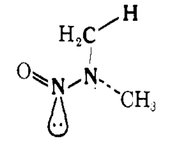
5



6



7



8

bear a formal resemblance to those in *anti*-acetaldehyde ethylhydrazone (**4**), *anti*-acetaldoxime (**6**), and to the syn protons in *N*-nitrosodimethylamine (**8**). Indeed, allowing for possible effects of substituent electronegativity, the corresponding values of $^2J_{NH}$ and $^3J_{NH}$ are the same for **3**, **4**, and **6**.[33] In like manner, the changes on protonation in this series of compounds, while differing in magnitude (probably because of the different degrees of protonation), are in the same direction: $^2J_{NH}$ becomes more positive, while $^3J_{NH}$ decreases algebraically. These variations have been qualitatively correlated[8,9c] with presumed changes in the s character of the N–C and C–C bonding orbitals. The former is assumed to increase in the order $=\overset{|}{N}: < =\overset{|}{N}^{+}\text{–H} < =\overset{|}{N}^{+}\text{–C}$ as the electronegativity of the nitrogen substituent increases. Indeed, taking into account the negative magnetogyric ratio of ^{15}N, the effects of protonation parallel those exhibited by $^2J_{CH}$ and $^3J_{CH}$ in the X^{13}CCH and X^{13}CCCH fragments as the electronegativity of X is increased,[34,35] as well as those shown by $^2J_{PH}$ and $^3J_{PH}$ in PCH and PCCH fragments, respectively.[4c] Nevertheless, other contributions to the coupling cannot be excluded, particularly those involving the π system. However, it is likely that contributions from this source are similar in both free and protonated pyridine, as the similarity of the values of $^3J_{NH}$ in pyridinium ion and 2,5-di-*tert*-butylpyrrole

---

(31) (a) G. J. Karabatsos and R. A. Taller, *J. Amer. Chem. Soc.*, **86**, 4373 (1964); (b) R. K. Harris and R. A. Spragg, *J. Mol. Spectrosc.*, **23**, 158 (1967).

(32) (a) W. McFarlane, *Chem. Commun.*, 418 (1970); (b) *cf.* also P. S. Pregosin and E. W. Randall, *ibid.*, 399 (1971), who report the ^{13}C chemical shifts of nitrosoamines.

(33) It is noteworthy that $^2J_{NH}$ in benzalmethylamine (3.9 Hz) does not accord with this scheme, but agrees with values for *syn*-acetaldehyde ethylhydrazone (**5**) and *syn*-acetaldoxime (**7**) (Table I). Therefore, the trans relationship between the phenyl and methyl groups at the carbon–nitrogen double bond can be inferred.

(34) G. Miyazima, Y. Utsumi, and K. Takahashi, *J. Phys. Chem.*, **73**, 1370 (1969).

(35) G. J. Karabatsos and C. E. Orzech, Jr., *J. Amer. Chem. Soc.*, **87**, 560 (1967), and preceding papers in this series.

(Table I) indicates. As suggested earlier, the most likely contributions appear to arise from changes in the average excitation energy as the lone pair is replaced by an N–H bond.[36] Price[9c] has suggested that a lowering of the average excitation energy can account in part for the large negative value of $^2J_{NH}$ compared to that expected on the basis of the C–H coupling constants in benzene.[37] However, a more meaningful comparison between heterocyclic and carbocyclic systems would be that between pyridine and the isoelectronic phenyl anion. Parallel carbon and nitrogen chemical-shift behavior has been noted in these two systems;[38] thus, the C-1 resonance of phenyl anion lies 40 ppm below that of benzene, which is similar in character to the 113-ppm low-field shift of pyridine with respect to pyridinium ion. Changes in the average excitation energy were proposed as the most promising explanation. Unfortunately, the carbon–hydrogen coupling constants of phenyl anion are not known.

However, accepting for the moment the benzene–pyridinium ion analogy, it is of interest to compare the relative values and signs of the corresponding coupling constants (Table VI). While the values for pyridinium ion do not show the same proportionality as those for benzene, the sign change for the latter case matches that in the former if $^4J_{NH}$ is positive. Because of the small magnitude of $^4J_{NH}$ this conclusion is not demanded but receives some support by extending the progression of sign alternation observed by Crépaux, *et al.*,[4c] who noted that protonation of ^{15}N-containing compounds leads to algebraic decreases, increases, and decreases in $^1J_{NH}$, $^2J_{NH}$, and $^3J_{NH}$, respectively. If this pattern is maintained, then an algebraic increase in $^4J_{NH}$ is expected on protonation. The observed increase in magnitude of $^4J_{NH}$ in the conversion of pyridine to pyridinium ion is thus in accord with a positive sign for this coupling in pyridinium ion, although nothing may be inferred about the sign of $^4J_{NH}$ in pyridine itself.

Table VI. Carbon–Proton and Nitrogen–Proton Coupling Constants in Benzene and Pyridinium Ion

	$X = {}^{13}C^a$	$X = {}^{15}N$
$^2J_{XH}$, Hz	+1.0	−3.01
$^3J_{XH}$, Hz	+7.4	−3.98
$^4J_{XH}$, Hz	−1.1	±0.69

[a] Reference 25a.

In all the compounds discussed so far, the axis of the nitrogen lone-pair orbital is coplanar with the C–H bonds of the protons to which the nitrogen nucleus is coupled, and this might well seem to be a condition for the existence of the "anomalous" coupling constants, especially when the value of $^3J_{NH}$ in 2,5-di-*tert*-butylpyrrole is considered. However, $^2J_{NH}$ values in formamide (−19 Hz)[21a,39] and *N*,*N*-dimethylformamide (Table I), in which the lone pair is also part of a π system, are even larger than the corresponding values in the heterocycles, which is understandable by comparison with $^2J_{HH}$ in formaldehyde where oxygen plays a decisive role.[4a,40] This ambiguity is lessened by considering the carbon–nitrogen coupling constants (Tables I, III, and V). Assuming the dominance of the Fermi contact mechanism, Binsch, *et al.*,[2] have proposed a relationship (eq 1) between the products of the per cent s

$$S_N S_C = 80 J_{NC} \qquad (1)$$

character in each of the orbitals of a C–N bond and the magnitude of $^1J_{NC}$. The values of $^1J_{NC}$ in glycine and alanine (Table V) are in accord with this equation, and indeed, the decrease of the coupling with increasing pH can be attributed to a change in the hybridization (bond angle) at nitrogen resulting from deprotonation, while the hybridization at carbon remains constant. Similarly, the large values of $^1J_{NC}$ in dimethylformamide and acetamide correlate to some degree with anticipations based on eq 1. In view of these results, the remarkably small value of $^1J_{NC}$ in pyridine can only be taken to mean that the assumptions inherent in eq 1 (see introductory statement) do not hold for pyridine, and very likely not for the hydrazones, oximes, and related compounds either.[41]

Discussion of $^2J_{NC}$ and $^3J_{NC}$ is hampered by existence of very few C–N or C–C values for comparison. The very recently reported values of $^1J_{NC}$ and $^2J_{NC}$ in some isocyanides[42] are hard to apply to the systems studied here. However, it is relevant to note that the value of 2.4 Hz for $^2J_{NC}$ is close to the value of 1.4 Hz for the syn two-bond coupling in *N*-nitrosodimethylamine, in which the anti orientations of the nitrogen lone-pair electrons with respect to the carbons of interest are similar (*cf.* **3** and **8**). Considering the absence of two-bond N–C coupling in 1,1-dimethylhydrazine-*2*-^{15}*N*, and in glycine and alanine, it seems likely that a π system is necessary for transmission of spin–spin interaction through two bonds, although there have been no reports of three-bond vicinal N–C couplings in saturated systems.

Solvent Effects. That valuable information about spectral parameters can be obtained by variations in medium is well known. In particular, the direction of changes in coupling constants with solvent has been shown to be related to the signs of the coupling constants.[43] In the case of pyridine, the upfield shifts of the nitrogen resonance position in methanol and water have been attributed to the increasing degree of hydro-

---

[36] Skeletal geometry also can be important, as the two values in trimethylvinylammonium ion indicate (Table I), but in the heterocyclic systems, of course, the geometry remains fixed.

[37] Price's estimation of $^2J_{NH}$ assumes a value of 6 Hz for $^2J_{CH}$. In fact, $^2J_{CH}$ in benzene is 1.0 Hz,[25a] so that the discrepancy between the estimated and observed values of $^2J_{NH}$ in both pyridine and pyridinium ion is even greater than Price has concluded. Nevertheless, the general conclusion that lowering of the average excitation energy can increase the magnitude of the coupling constant is not affected.

[38] A. J. Jones, D. M. Grant, J. G. Russell, and G. Fraenkel, *J. Phys. Chem.*, 73, 1624 (1969).

[39] R. J. Chuck, D. G. Gillies, and E. W. Randall, *Mol. Phys.*, **16**, 121 (1969).

[40] J. A. Pople and A. A. Bothner-By, *J. Chem. Phys.*, **42**, 1339 (1965).

[41] On the basis of these arguments, the low nitrogen chemical shift of benzalmethylamine (48 ppm: J. B. Lambert, G. Binsch, and J. D. Roberts, *Proc. Nat. Acad. Sci. U. S.*, **51**, 735 (1964)) would suggest a small value of $^1J_{NC}$ for this compound, in contrast with the 7.1-Hz value observed. However, here the lone-pair electrons on nitrogen bear an anti orientation to the methine proton attached to the adjacent carbon, while in pyridine and the compounds chosen for comparison the syn orientation obtains. The result for benzalmethylamine, if general, indicates a remarkable dependence of the *one-bond* coupling on geometry.

[42] I. Morishima, A. Mizuno, T. Yonezawa, and K. Goto, *Chem. Commun.*, 1321 (1970).

[43] See, *e.g.*, P. Laszlo, *Progr. Nucl. Magn. Resonance Spectrosc.*, 3, 231 (1968).

gen bonding expected in the hydroxylic media, where the n → π* excitation energy of the lone-pair electrons has been increased, with concomitant reduction of the contribution of its effect on the chemical shift.[9a,b] Pyridinium ion, of course, represents the extreme case of complete proton transfer. The variations in the N–C and N–H coupling constants, particularly in $^1J_{NC}$ and $^2J_{NH}$, can presumably be ascribed largely to the same source. In fact, using both chemical shifts and coupling constants, estimates of the degree of hydrogen bonding can be made, from which it can be inferred that the values of $^1J_{NC}$ in neat pyridine and in pyridinium ion are very likely of opposite sign. The argument follows from the ^{15}N chemical-shift data (Table IV), and assuming only a two-component equilibrium (free pyridine ⇄ hydrogen-bonded pyridine), the extent of hydrogen bonding is estimated to be about 15% in methanol, while from consideration of the values of $^2J_{NH}$, the degree of hydrogen bonding is estimated to be about 9%. That different, parameter-dependent values are obtained is to be expected because of the different degrees to which chemical shifts and coupling constants respond to electronic and environmental changes. From the average value, 12%, $^1J_{NC}$ in pyridinium ion can be predicted, depending on whether a sign change occurs in going from neat liquid to a methanolic solution. In the absence of a sign change, $^1J_{NC}$ is predicted to be 2.5 Hz, while a value of 9 Hz is obtained if such a sign change exists. The closeness of the latter value to that experimentally observed suggests that in fact a change in sign has taken place. To our knowledge this is the first experimental indication of a change in sign of any C–N coupling constant. Absolute signs of such couplings are known only for acetonitrile[6a] ($^1J_{N\equiv C} = -17.5$ Hz) and methyl isocyanide[3b] ($^1J_{NCH_3} = -10.6$ Hz, calculated from the reported ^{14}N value); in both cases the values are considerably lower than those predicted from eq 1. A study of the effects of solvent and protonation on the acetonitrile coupling would be of interest.

Acknowledgment. We are much indebted to Dr. Frank J. Weigert for helpful suggestions and to Drs. E. W. Randall and R. Price for informing us of the results of their experiments before publication.

Absolute Configuration at a Sulfenamide Chiral Axis. Crystal and Molecular Structure of *N*-(1-α-Naphthylethyl)-*N*-(benzenesulfonyl)trichloromethanesulfenamide[1]

Jack Kay, Milton D. Glick, and Morton Raban*

Contribution from the Department of Chemistry, Wayne State University, Detroit, Michigan 48202. *Received September 12, 1970*

Abstract: The crystal structure of *N*-(1-α-naphthylethyl)-*N*-(benzenesulfonyl)trichloromethanesulfenamide has been determined by three-dimensional X-ray diffraction. The molecule crystallizes in space group $P2_1$ with lattice constants $a = 12.233$ (6) Å, $b = 8.546$ (5) Å, $c = 10.440$ (5) Å, $\beta = 110.20$ (1) °, $Z = 2$. Refinement of 1536 diffractometer data yielded a conventional discrepancy factor of 0.075. The structure found, which features a nearly planar trivalent nitrogen atom, has implications concerning torsional isomerism about heteroatom–heteroatom bonds (in this case between trivalent nitrogen and divalent sulfur) and concerning the possible existence of p-d π-bonding in S–N bonds. The incorporation of an asymmetric carbon atom of known configuration allowed the assignment of absolute configuration to the sulfenamide chiral axis.

The structure and conformational analysis of molecules with sulfur–nitrogen bonds has been a topic of recent interest. A number of X-ray crystallographic structure determinations of molecules with different kinds of sulfur nitrogen bonds have appeared.[2–4] In addition, nuclear magnetic resonance (nmr) spectroscopic studies have indicated interesting features in the structure and conformation of sulfenamides, molecules containing divalent sulfur bonded to trivalent nitrogen.[5–7]

The nmr spectra of dialkylsulfenamides[5] (RSNR′R″) and *N*-arenesulfonylsulfenamides[6,7] (RSNR′SO$_2$Ar) exhibit chemical shift nonequivalence of diastereotopic[8] nuclei at low temperature. This nonequivalence has been adduced as evidence for asymmetry in the sulfen-

---

(1) This work was supported in part by grants from the National Science Foundation (No. GP-17092 and GP-15070) and the Edmond de Rothschild Foundation. We thank the Wayne State University Computing and Data Processing Center for the use of their facilities.

(2) (a) R. E. Cook, M. D. Glick, J. J. Rigau, and C. R. Johnson, *J. Amer. Chem. Soc.*, 93, 924 (1971); (b) S. Neidle and D. Rogers, *J. Chem. Soc. B*, 694 (1970); (c) Y. Okaya, *Acta Crystallogr., Sect. B*, 25, 2257 (1969); (d) H. Zacharis and L. M. Trefonas, *J. Heterocycl. Chem.*, 7, 755 (1970); (e) B. Leandri, V. Busetti, G. Valle, and M. Mammi, *Chem. Commun.*, 413 (1970); (f) A. C. Hazell, G. A. Wiegers, and A. Vos, *Acta Crystallogr.*, 20, 186 (1966); (g) G. A. Wiegers and A. Vos, *ibid.*, 20, 192 (1966); (h) E. M. Holt and S. L. Holt, *Chem. Commun.*, 1704 (1970); (i) A. Kálmán, B. Duffin, and A. Kucsman, *Acta Crystallogr., Sect. B*, 27, 586 (1971).

(3) T. Jordan, H. W. Smith, L. L. Lohr, and W. N. Lipscomb, *J. Amer. Chem. Soc.*, 85, 846 (1963).

(4) For other examples, see O. Kennard and D. G. Watson, "Molecular Structures and Dimensions," Vol. 1, Crystallographic Data Centre, Cambridge, U. K., and the International Union of Crystallography, N. V. A. Oosthoek's Uitgevers Mij, Utrecht, pp 49–50, 292–299.

(5) M. Raban, G. W. J. Kenney, Jr., and F. B. Jones, Jr., *J. Amer. Chem. Soc.*, 91, 6677 (1969).

(6) M. Raban and F. B. Jones, Jr., *ibid.*, 91, 2180 (1969).

(7) M. Raban and F. B. Jones, Jr., *ibid.*, 93, 2692 (1971).

(8) K. Mislow and M. Raban in "Topics in Stereochemistry," Vol. I, E. L. Eliel and N. L. Allinger, Ed., Wiley, New York, N. Y., 1967.