The Hydrogen Bond Studied by Nitrogen-14 Nuclear Magnetic Resonance. II. Heteronuclear Magnetic Double Resonance Study of Nitrogen-14 Hydrogen-Bond Shifts of Pyrroles and Indole

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Abstract: The effects of hydrogen bonding on the ^{14}N chemical shifts of pyrroles and indole have been investigated with heteronuclear magnetic double resonance. ^{14}N downfield shifts of 1–15 ppm are observed where the N–H proton acts as a proton donor. In the case of self-association, downfield shifts of ^{14}N signals are also found. These results are interpreted in terms of the electron redistribution effect at the nitrogen atom transferred from the proton acceptor. A calculation employing the Karplus–Pople approximation failed to predict the variation in ^{14}N shifts. The ^{14}N hydrogen-bond shifts in pyrroles and indole correlate with their ^{14}N chemical shifts, both of which are influenced by the electron density of the nitrogen atom. A linear correlation between ^{14}N and proton hydrogen-bond shifts is found. An explanation is made of the origin of the above correlation.

In the study of the hydrogen-bond system X–H···Y by nuclear magnetic resonance spectroscopy, most of the work has been focused on proton resonance studies. Proton chemical shift variations are caused mainly by rather indirect quantities such as the electric-field and the magnetic-anisotropy effects of a proton acceptor Y.[1] Recently there appeared some articles which report elaborate investigations of the chemical shifts of other nuclei in proton donors (X) and acceptors (Y). It is expected that more direct information can be obtained about the nature of the hydrogen bond through these studies. The ^{14}N and ^{13}C chemical shifts of proton acceptors such as pyridine,[2] acetonitrile, and methyl isocyanide[3] are shifted upfield in the presence of a proton donor, indicating a contribution of the charge-transfer structure X^-H-Y^+. The ^{17}O chemical shift was observed to shift upfield in the hydrogen bond for a proton-donating hydroxyl group of methanol-^{17}O.[4] Florin and coworkers have studied ^{17}O shifts of liquid and vapor water[5] and of water–ammonia solutions.[6] Reuben[7] separated the ^{17}O hydrogen-bond shift of water in various solvents into proton-donating and proton-accepting contributions. Similar considerations were carried out in the ^{15}N study[8] of $^{15}NH_3$–solvent systems. In both cases, hydrogen bonds are formed by lone-pair electrons and a proton in the same molecule, and the separation of two kinds of contributions is quite difficult.

In this paper we report the ^{14}N hydrogen-bond shift of a ^{14}N–H···Y system and the correlation between ^{14}N and proton chemical shifts, in the hope of better understanding the nature of ^{14}N chemical shifts and the effect of the magnetic anisotropy.[9] For the detection of a ^{14}N hydrogen-bond shift, the concentration of the solute should be as low as possible because of the equilibrium of hydrogen-bond formation. The direct measurement of the ^{14}N chemical shift in such a system, however, has a serious limitation because of its low sensitivity. The indirect method utilizing the heteronuclear double resonance technique,[10] on the other hand, is of great advantage for observations under conditions of extreme dilution, since the ^{14}N shift can be obtained readily from the proton peak by the irradiation of the ^{14}N nucleus. In this paper ^{14}N shifts of pyrrole, indole, 2-acetylpyrrole, and 2,5-diacetylpyrrole were observed by the indirect method. The accuracy of the ^{14}N shift depends on the amount of spin coupling, quadrupole relaxation time, and the rate of the proton exchange. Relatively accurate measurement of ^{14}N shifts was feasible in the present experiment, as the latter two effects do not seriously influence the magnetic resonance spectra of these compounds.

Downfield shifts of 1–15 ppm for ^{14}N signals are observed when the N–H group acts as a proton donor. The relatively large chemical shift variation cannot be explained by the usual electric-field and magnetic-anisotropy effects of the proton acceptor. The correlation between ^{14}N and proton hydrogen-bond shifts is also discussed.

Experimental Section

A Varian HA-100 spectrometer was used with a probe doubly tuned to accept the 7.22-MHz ^{14}N irradiation frequency as well as the 100-MHz proton frequency used for a monitor. An NMR Specialties HD-60 B heteronuclear spin decoupler equipped with a Hewlett-Packard 200 ABR audiofrequency oscillator was used to drive the 7.22-MHz modulated frequency. All measurements were carried out in the frequency-sweep mode[11] with a small amount of TMS added to samples for field-frequency stabilization.

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[1] (a) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, N. Y., 1959, pp 407–409; (b) J. A. Pople, "Hydrogen Bonding," D. Hadzi, Ed., Pergamon Press, London, 1959, p 71.

[2] H. Saitô, K. Nukada, H. Kato, T. Yonezawa, and K. Fukui, *Tetrahedron Lett.*, 111 (1965).

[3] A. Loewenstein and Y. Margalit, *J. Phys. Chem.*, 69, 4152 (1965).

[4] J. Reuben and D. Samuel, *Israel J. Chem.*, 1, 229 (1963).

[5] A. E. Florin and M. Alei, Jr., *J. Chem. Phys.*, 47, 4268 (1967).

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[7] J. Reuben, *J. Amer. Chem. Soc.*, 91, 5725 (1969).

[8] W. M. Litchman, M. Alei, Jr., and A. E. Florin, *ibid.*, 91, 6574 (1969).

[9] (a) H. Saitô, K. Nukada, T. Kobayashi, and K. Morita, *ibid.*, 89, 6605 (1967); (b) H. Saitô and K. Nukada, *J. Mol. Spectrosc.*, 18, 1 (1965).

[10] (a) J. D. Baldeschwieler and E. W. Randall, *Proc. Chem. Soc., London*, 303 (1961); (b) P. Hampson and A. Mathias, *Mol. Phys.*, 11, 541 (1966); (c) P. Hampson and A. Mathias, *ibid.*, 13, 361 (1967); (d) P. Hampson and A. Mathias, *J. Chem. Soc. B*, 673 (1968).

[11] The resonance condition $\gamma H_0(1-\sigma) = \hbar\nu$ shows that there is the following relation between frequency and field sweep methods: higher field = lower frequency = more shielded, lower field = higher frequency = less shielded, where H_0, σ, and ν denote the external magnetic field, magnetic shielding constant, and radiofrequency, respectively.

Table I. Variation of ^{14}N and Proton Shifts (ppm) of Pyrrole and Indole with Various Solvents (Infinite Dilution)

	Pyrrole				Indole			
			Hydrogen-bond shift[c]				Hydrogen-bond shift[c]	
Solvents	^{14}N shift[a]	Proton shift[b]	^{14}N	^{1}H	^{14}N shift[a]	Proton shift[b]	^{14}N	^{1}H
Carbon tetrachloride	−120.7 ± 0.4	−7.88	0	0	−99.5 ± 1.4	−7.68	0	0
Benzene-d_6	−122.0 ± 0.4	−6.90	−1.3	+0.98	−100.5 ± 0.7	−6.70	−1.0	+0.98
Neat (self-association)	−125.7 ± 0.4	−7.33	−5.0	+0.55	−105.2 ± 1.4[d]		−5.7[d]	
Acetic acid	−125.7 ± 0.4	−9.21	−5.0	−1.33	−105.5 ± 0.7	−9.35	−6.0	−1.67
Dioxane	−126.5 ± 0.4	−9.46	−5.8	−1.58	−105.3 ± 1.0	−9.63	−5.8	−1.95
Acetone	−127.5 ± 0.4	−9.96	−6.8	−2.08	−105.9 ± 0.7	−10.18	−6.4	−2.50
Acetonitrile	−128.6 ± 0.4	−9.10	−7.9	−1.22	−107.0 ± 0.7	−9.24	−7.5	−1.56
DMF-d_7	−131.2 ± 0.4	−10.78	−10.5	−2.90				
Triethylamine	−132.6 ± 0.4	−10.92	−11.9	−3.04	−111.7 ± 1.0	−11.21	−12.2	−3.53
H_2O	−132.8 ± 1.4	−10.42	−12.1	−2.54				
DMSO	−134.8 ± 0.4	−11.02	−14.2	−3.14	−114.9 ± 1.0	−11.35	−15.4	−3.67

[a] Downfield from ammonium ion. [b] Downfield from tetramethylsilane. [c] Values in carbon tetrachloride solution are chosen as the standard. [d] Estimated from the trends in dilution curves.

The ^{14}N shift was determined from a maximum point of the N-H proton signal in the plot of N-H proton peak intensities against the ^{14}N irradiation frequency swept manually (Figure 1). The irradiation frequency was directly monitored with a Takeda-Riken TR-3977 frequency counter. Attention was paid to prevent drift of the base line and to keep the resolution of the spectrometer high enough for accurate observation of the ^{14}N shift. The same measurements were repeated at least three times and the values were averaged.

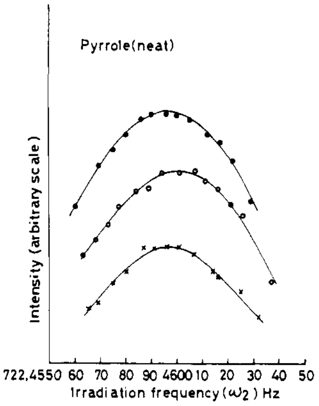

Figure 1. Plots of NH proton intensities against the ^{14}N irradiation frequencies of neat pyrrole. Three experiments were performed under the same conditions.

A sample of 4.5 *M* NH_4NO_3 in 3 *N* aqueous hydrochloric acid was used as a reference for ^{14}N shifts.[10b] All ^{14}N shifts were expressed relative to that of ammonium ion, and the conversion to the values relative to the nitrate peak usually employed as a standard were performed using a factor of 353.5 ± 0.5 ppm. All chemicals except deuterated solvents were distilled after drying with a pertinent drying agent.

Results and Discussion

^{14}N and Proton Hydrogen-Bond Shifts. Resonance frequencies of ^{14}N are plotted against the mole fraction of pyrrole over a range from 0.01 mol fraction to neat liquid in various solvents (Figure 2). Hydrogen-bond shifts, defined as the difference between the completely free and the hydrogen-bonded state,[12] are given in Table I. The free ^{14}N and proton shifts used as a reference are obtained by extrapolating to infinite dilution in carbon tetrachloride solution. The completely hydrogen-bonded shifts are obtained from the values for the neat liquid or infinitely dilute state in the proton acceptors.

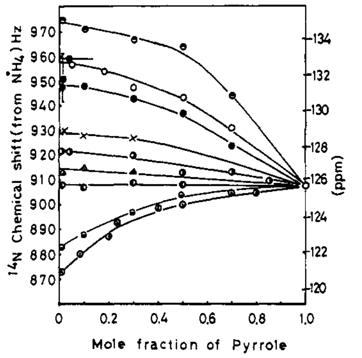

Figure 2. ^{14}N shifts of pyrrole in various solvents: ◓, in DMSO; ⊗, in water; ○, in triethylamine; ●, in DMF-d_7; ×, in acetonitrile; ◑, in acetone; △, in dioxane; ◐, in acetic acid; ◒, in benzene; and ⊙, in carbon tetrachloride.

A. Self-Association of Pyrrole (I). Figure 2 shows that ^{14}N shifts of pyrrole are displaced upfield (lower frequency)[11] on dilution with carbon tetrachloride. This is interpreted in terms of the break-up of the self-association of pyrrole, since carbon tetrachloride has no solvent effect on nmr spectra. As Happe[15] described in a study of proton spectra, the self-association seems to be the N-H···π hydrogen bond, in which the π electrons of pyrrole act as a proton acceptor. The dipole-moment measurement also agrees with Happe's model.[16] In

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(12) This is a limit of the larger equilibrium constant, $K \gg 1$. Strictly speaking, chemical shifts of the completely free and hydrogen-bonded state do not always correspond with the shifts at infinite dilution in carbon tetrachloride (δ_0) and in proton acceptors (δ_D). The correct hydrogen-bond shift δ_{AD} is expressed with the finite equilibrium constant K.[13]

$$\delta_{AD} = [(1 + K)/K](\delta_0 - \delta_D)$$

The difference between the hydrogen-bond shift and the correct one is negligible for larger K (11.0[14a] or 20.8[14b]), as in the case of DMSO solutions. The discrepancy between the true hydrogen-bond shift with consideration of the equilibrium and an apparent one as described in this paper is not serious in the case of a relatively strong proton acceptor ($K \gg 1$). We aim in this paper to investigate the direction and the relative amounts of the variation of ^{14}N shifts on hydrogen bonding and to correlate the mechanism of the electron transfer.

(13) C. M. Huggins, G. C. Pimentel, and J. N. Shoolery, *J. Chem. Phys.*, **23**, 1244 (1955).

(14) (a) M. T. Chenon and N. Lumbroso-Bader, *C. R. Acad. Sci.*, **266**, 293 (1968); (b) D. M. Porter and W. S. Brey, Jr., *J. Phys. Chem.*, **72**, 650 (1968).

(15) J. A. Happe, *ibid.*, **65**, 72 (1961).

(16) (a) H. Lumbroso, *J. Chim. Phys. Physiochim. Biol.*, **51**, 132 (1954); (b) M. Gomel and H. Lumbroso, *Bull. Soc. Chim. Fr.*, 2200 (1962).

Table II. Variation of ^{14}N and Proton Shifts (ppm) of 2-Acetylpyrrole and 2,5-Diacetylpyrrole with Various Solvents (0.01 Mol Fraction)

	2-Acetylpyrrole				2,5-Diacetylpyrrole			
			Hydrogen-bond shift				Hydrogen-bond shift	
Solvents	^{14}N shift[a]	Proton shift[b]	^{14}N	^{1}H	^{14}N shift[a]	Proton shift[b]	^{14}N	^{1}H
$CDCl_3$	−127.5 ± 0.4[c]	−9.76	0[d]	0[d]	−121.3 ± 0.4	−9.93	0[d]	0[d]
Benzene-d_6	−127.6 ± 0.4	−9.98	−0.1	−0.22	−122.0 ± 0.6	−10.00	−0.7	−0.07
Acetonitrile	−130.1 ± 0.4	−9.92	−2.6	−0.16	−124.9 ± 0.4	−10.10	−3.6	−0.17
Dioxane	−131.2 ± 0.4	−10.68	−3.7	−0.92	−128.0 ± 0.4	−11.14	−6.7	−0.21
Acetone	−130.5 ± 0.4	−10.77	−3.0	−1.01	−124.4 ± 0.4	−10.74	−3.1	−0.81
Acetic acid					−125.6 ± 0.4	−10.95	−4.3	−1.02
Triethylamine	−132.8 ± 1.0	−11.30	−5.3	−1.54				
DMF-d_7	−133.4 ± 0.5	−11.71	−5.9	−1.95				
DMSO	−137.9 ± 0.5	−12.04	−10.4	−2.28	−133.0 ± 1.5	−12.44	−11.7	−2.51

[a] Downfield from ammonium ion. [b] Downfield from tetramethylsilane. [c] ^{14}N shift in carbon tetrachloride is found to be −126.8 ± 0.7 ppm. [d] Values in deuteriochloroform are chosen as the standard.

Figure 3 correlations between ^{14}N and NH or CH proton shifts are illustrated. It should be noted that the variations of chemical shift with concentration of the solute molecule are in opposite directions for ^{14}N and proton shifts.

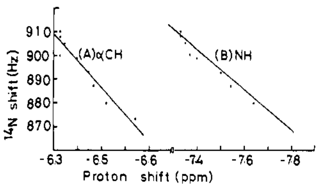

Figure 3. A correlation of ^{14}N shifts with α-CH and NH protons in pyrrole.

In the self-association of pyrrole, the ^{14}N hydrogen-bond shift is −5.0 ± 0.8 ppm, while the corresponding proton shift is +0.55 ppm.[17] Accordingly, the ^{14}N resonance reflects more sensitively weak molecular interactions such as N–H···π hydrogen bonds than does the proton resonance. The local diamagnetic field of pyrrole is too small to explain the variation of the ^{14}N hydrogen-bond shift. The most probable cause of the ^{14}N hydrogen-bond shift is the variation of electron distribution around the nitrogen atom through hydrogen-bond formation. Thus the ^{14}N hydrogen-bond shift gives additional information, which is unobtainable from the study of the proton shift, about the electronic nature of hydrogen-bond formation.

B. The Hydrogen Bond of Pyrrole with Base. The dilution curves in Figure 2 show that in solvents such as DMSO, triethylamine (TEA), DMF-d_7, acetonitrile, acetone, and dioxane the ^{14}N shift is downfield (to higher frequency) compared with the neat state. This is also accompanied by downfield shifts of NH proton signals (Table I). This is caused by the formation of the N–H···base hydrogen bond, since these solvent molecules act as stronger proton acceptors than the solute molecule. The largest ^{14}N hydrogen-bond shift is observed in DMSO, the strongest proton acceptor among the solvents. Downfield shifts are also observed on dilution with protic solvents such as water and acetic acid, and these solvents would also behave as proton acceptors. In fact the nitrogen atom of pyrrole is not expected to act as a proton acceptor, since the lone-pair electrons of the nitrogen atom conjugate with π electron orbitals of the molecule.

C. Indole (II). The ^{14}N and proton shifts of indole extrapolated to infinite dilution are shown in Table I. The ^{14}N hydrogen-bond shift due to self-association is estimated from the dilution curve. Self-association was proposed by Reinecke and his coworkers[18] to be a combination of hydrogen bonding and a local-dipole interaction. The latter seems to be important, since the ^{14}N hydrogen bond shift due to self-association is much larger than that of hydrogen bonding with benzene as a proton acceptor (Table I). It is very difficult, however, to discriminate between the contribution of the hydrogen bond and the local-dipole interaction.

The ^{14}N downfield shift on hydrogen-bond formation is similar for pyrrole and indole in the same solvent. The NH proton-donating power of indole, however, seems to be larger than for pyrrole, since proton hydrogen-bond shifts are definitely larger in indole than in pyrrole. This is explained by the larger polarizing effect of the N–H bond through the larger electron density of the nitrogen atom in indole, as shown later.

D. 2-Acetylpyrrole (III) and 2,5-Diacetylpyrrole (IV). The sparing solubility of III and IV makes an elaborate dilution study difficult. A measurement at 0.01 mol fraction is assumed to indicate the value at infinite dilution, since the effect of the self-association can almost be disregarded in this concentration, as shown in the concentration studies of I and II. The ^{14}N and proton hydrogen-bond shifts of III and IV, shown in Table II, are smaller than those of I and II.

^{14}N Chemical Shifts of Pyrroles and Indoles. ^{14}N shifts of pyrroles and indoles at 0.01 mol fraction are summarized in Table III, together with those of carbazole. Literature values of ^{14}N chemical shifts of pyrrole and indole[19] are also listed for comparison, although the measurements were not performed on dilute solutions. The wide spread of ^{14}N resonances is primarily caused by the delocalization effect of the π electrons at the nitrogen atom. The ^{14}N shift decreases

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(17) For self-association of pyrrole, Happe calculated the N–H proton hydrogen-bond shift to be 1.93 ppm with equilibrium constant $K = 4.3$. A formula to describe this equilibrium is different from the one given in ref 12. By employment of the linear relationship between ^{14}N and proton chemical shifts as shown in Figure 3, the true ^{14}N hydrogen-bond shift for self-association is estimated to be 19 ppm from Happe's results. In this section, however, attention is paid to the ratio of ^{14}N to proton hydrogen-bond shifts.

(18) M. G. Reinecke, H. W. Johnson, Jr., and J. F. Sebastian, *J. Amer. Chem. Soc.*, 91, 3819 (1969).

(19) D. Herbison-Evans and R. E. Richards, *Mol. Phys.*, 8, 19 (1964).

Table III. ^{14}N Chemical Shifts of Pyrrole and Related Compounds (0.01 Mol Fraction, Referred to $^{+}NH_4$)

	^{14}N chemical shift, ppm	Solvent	Lit. value[a] ^{14}N shift	Lit. value[a] Solvent
2-Acetylpyrrole	-126.1 ± 0.4	CCl_4		
2,5-Diacetylpyrrole	-121.3 ± 0.4	$CDCl_3$		
Pyrrole	-120.7 ± 0.4[b]	CCl_4	-123.5 ± 2	Neat
	(-125.7 ± 0.4)[c]	(neat)		
α-Methylindole	-107.0 ± 1.0	Benzene-d_6		
Indole	-99.5 ± 1.4[b]	CCl_4	-102.5 ± 4	Ethyl ether
β-Methylindole	-97.3 ± 1.0	Benzene-d_6		
Carbazole	-89.6 ± 1.0	Acetone		

[a] Reference 10. [b] Values at infinite dilution. [c] Value for neat liquid.

Table IV. Electron-Density and Bond-Order Matrices for Pyrrole and Its Hydrogen-Bonded State by the CNDO Method

		Pyrrole	Pyrrole + H_2O	Pyrrole + NH_3
Electron density (N)	P_{xx}	1.1769	1.1766	1.1710
	P_{yy}	1.0382	1.0616	1.0638
	P_{zz}	1.6859	1.6835	1.6794
		3.9010	3.9217	3.9142
	P_{ss}	1.2095	1.2183	1.2192
		5.1105	5.1400	5.1334
Bond order[a] (C=N)	$P_{x_1x_2}$	−0.3594	−0.3590	−0.3590
	$P_{y_1y_2}$	−0.1504	−0.1540	−0.1551
	$P_{z_1z_2}$	0.4395	0.4408	0.4439
	$P_{y_1z_2}$	−0.3019	−0.3048	−0.3065
	$P_{x_1y_2}$	−0.4376	−0.4376	−0.4381
	$P_{s_1s_2}$	0.2719	0.2706	0.2708
Electron density (H)	P_{ss}	0.8927	0.8667	0.8670

[a] Suffixes 1 and 2 correspond to the nitrogen and adjacent carbon atoms, respectively.

in the following order: indole > pyrrole > 2,5-diacetylpyrrole > 2-acetylpyrrole. This correlates well with the ^{14}N and proton hydrogen-bond shifts in the stronger proton acceptors such as DMSO studied in the previous section (Table I and II). The above correlation is reasonable, because ^{14}N shifts and proton-donating ability are both strongly influenced by π-electron densities at the nitrogen atom.

Charge-Transfer Effects of the Hydrogen Bond. A hydrogen bond expressed as X–H···Y consists of the following contributions, according to Coulson and Danielson,[20] where X–H and Y stand for proton donor and acceptor, respectively

$$X\text{—}H\cdots Y$$
1, pure covalent

$$X^{-}H^{+}\ \ Y$$
2, ionic

$$X^{-}\text{-}H\text{-}Y^{+}$$
3, charge transfer

The electron density of X is increased by contributions of **2** and **3**. It is expected that the upfield chemical shift of X is caused by the increased electron density at X. X ($= {}^{14}N$) hydrogen-bond shifts of pyrrole and related compounds are downfield. This discrepancy prompts us to consider the redistribution[21] of electrons transferred from the proton acceptor toward the moiety other than X–H···Y. To clarify this point, we tried to calculate the electronic structures of pyrrole and its hydrogen-bonding system (pyrrole + water and pyrrole + ammonia) by the CNDO/2 method.[22] Ammonia is employed as a model compound of a proton acceptor, corresponding to triethylamine. The distances N···N and N···O are assumed to be 2.9 Å, along with the coordinate system illustrated in Figure 4.

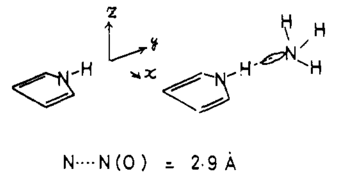

Figure 4. Coordinate systems used for the calculations.

The electron-density and bond-order matrices for the nitrogen atom are shown in Table IV. Suffixes *x*, *y*, *z*, and s denote $2p_x$, $2p_y$, $2p_z$, and 2s orbitals, respectively. All bond orders except those cited in Table IV are zero considering the molecular geometry. On hydrogen-bond formation, P_{yy} and P_{ss} composing the N–H σ bond increase due to the charge transfer from the proton acceptor, as shown in the third and fourth columns of Table IV. An increase of P_{yy} and P_{ss} is partially compensated by a decrease of P_{xx} and P_{zz}.[23] This result shows that the electron density of the nitrogen atom, especially 2p electron density corresponding with the paramagnetic term of the ^{14}N shift, increases with hydrogen-bond formation.[24] Employing the paramagnetic contribution formulated by Karplus and Pople[25] with the mean excitation energy 10 eV, we calculated the ^{14}N shielding constants shown in Table V. Thus the theoretical expectation is the reverse of the experimental results in the present study. The calculation of the ^{14}N shift is successful, however, for

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(20) C. A. Coulson and U. Danielsson, *Ark. Fys.*, **8**, 239, 245 (1954).

(21) In the case of the water molecule this effect is calculated employing the LCAO-MO-SCF method of Gaussian orbitals: K. Morokuma and L. Pedersen, *J. Chem. Phys.*, **48**, 3275 (1968).

(22) (a) J. A. Pople, D. P. Santry, and G. A. Segal, *ibid.*, **43**, 5129 (1965); (b) J. A. Pople and G. A. Segal, *ibid.*, **43**, 5136 (1965); (c) *ibid.*, **44**, 3289 (1966).

(23) This is in good agreement with a similar calculation for the glycine–water hydrogen-bond system: A. Imamura, H. Fujita, and C. Nagata, *Bull. Chem. Soc. Jap.*, **42**, 3118 (1969).

(24) This result leads to the conclusion that the mean inverse cube distance from the nitrogen nucleus to electrons of the 2p orbital, $\langle r^{-3}\rangle_{2p}$, decreases according to the formula[25]

$$\langle r^{-3}\rangle_{2p} = {}^{1}/_{24}\{[0.393 - 0.35(\sigma - 4)]/a_0\}^3$$

where σ and a_0 denote the electron density and Bohr radius, respectively. This trend is in contrast to the interpretation of the similar downfield shift of ^{13}C hydrogen-bond shift in chloroform,[26] in which Lichter and Roberts suggest the increase of the $\langle r^{-3}\rangle$ term on hydrogen-bond formation.

(25) M. Karplus and J. A. Pople, *J. Chem. Phys.*, **38**, 2803 (1963).

(26) R. L. Lichter and J. D. Roberts, *J. Phys. Chem.*, **74**, 912 (1970).

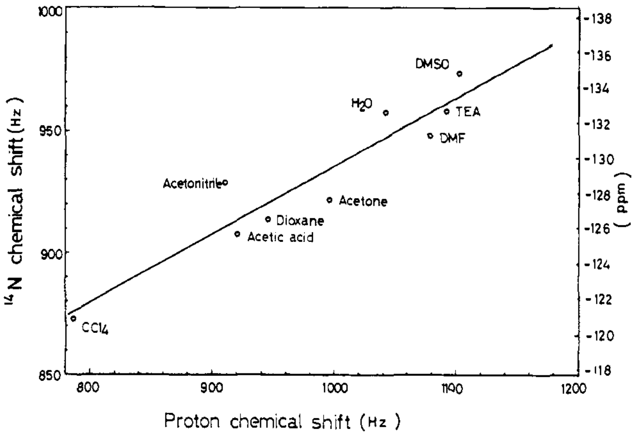

Figure 5. A correlation between ^{14}N and proton shifts of pyrrole in various solvents.

the difference between pyridine and pyridinium ion,[27] heteroaromatic compounds,[28] and nitro compounds.[29] A similar treatment for ^{13}C chemical shifts[30] well interpreted the variation of the shifts with solvents or substituents. ^{14}N hydrogen-bond shifts of amides with proton donors were explained as due to the changes of electron density at the nitrogen atom.[31] It is not clear at present what stage of the above approximation is inadequate in the treatment of hydrogen-bond shifts.

Table V. Calculation of the Paramagnetic Term of the ^{14}N Chemical Shift (ppm)

	σ_p	Hydrogen-bond shift	Exptl value
Pyrrole	−422.7	0	0
Pyrrole + H_2O	−418.3	+4.4	−12.1
Pyrrole + NH_3	−395.7	+27.0	−11.9 (triethylamine)

A Linear Correlation of ^{14}N and Proton Shifts. In Figure 5 is illustrated a correlation between the ^{14}N and proton shifts at infinite dilution[32] in various solvents. Acetonitrile and DMSO occupy a position above the line obtained by the least-squares method, and triethylamine, DMF, and acetone lie under it;[33] the same trend is observed in the other compounds (see Tables I and II). The gradients[34] of the least-squares lines are given in Table VI. A similar linear correlation of ^{14}N and proton shifts is found for formamide and *N*-methylacetamide[35] for various cases of molecular interactions, as shown in Table VI. The proton hydrogen-bond shift is generally interpreted in terms of an electric-field effect and a magnetic-anisotropy effect caused by a proton acceptor. The latter effect is predominant in aromatic compounds and it is excluded in the discussion of the nonaromatic solvents. The downfield shift of the proton signal for a hydrogen bond is theoretically formulated by Marshall and Pople[36] and by Buckingham,[37] who evaluated the effect of the electrostatic field *E* caused by the proton acceptor as

Table VI. The Gradients of the Linear Curves

	$\frac{\partial\delta^{14}\mathrm{N}}{\partial\delta^{1}\mathrm{H}}$	Lit.
Pyrroles		
Indole	4.1	*a*
Pyrrole	3.9	*a*
2-Acetylpyrrole	3.4	*a*
2,5-Diacetylpyrrole	4.1	*a*
	Av 3.9 ± 0.5	
Formamide[c]	5.6	*b*
N-Methylacetamide[c]	5.2	*b*

[a] This paper. [b] Reference 35. [c] Self-association.

$$\sigma_{\mathrm{E}} = -\frac{881}{216}\frac{a_0^3}{mc^2}E^2 \tag{1}$$

$$\sigma_{\mathrm{E}} = -2 \times 10^{-12}E_z - 10^{-18}E^2 \tag{2}$$

In addition, the electron density around the N–H proton decreases on hydrogen-bond formation, as shown in Table IV. The contribution to the proton hydrogen-bond shift arises from a diamagnetic shielding effect[38]

$$\Delta\sigma_{\mathrm{dia}} = 17.8Z\Delta q_{\mathrm{H}} \tag{3}$$

where Δq_{H} and Z denote the difference in electron density before and after hydrogen bonding at the hydrogen atom and the effective nuclear charge (usually taken as 1.2), respectively. The downfield shift based on eq 3 is calculated as 0.5 ppm in the case of the pyrrole–ammonia system. The contribution of the diamagnetic term is 16% of the total downfield shift, 3 ppm, in pyrrole (Table I).

The downfield shift is then composed of the following two terms.

$$\Delta\delta^{1}\mathrm{H} = \Delta\sigma_{\mathrm{dia}} + \sigma_{\mathrm{E}} \tag{4}$$

Experimental correlations between ^{14}N and proton shifts show that

$$\Delta\delta^{1}\mathrm{H} \propto \Delta\delta^{14}\mathrm{N} \tag{5}$$

If we assume that

$$\Delta\sigma_{\mathrm{dia}} \propto \sigma_{\mathrm{E}} \tag{6}$$

the following relation is obtained.

$$\Delta\delta^{14}\mathrm{N} \propto \Delta\sigma_{\mathrm{dia}} \tag{7}$$

The above relation is not so unreasonable for a hydrogen-bond system in which an electron-transfer process occurs, even though the calculation in the preceding section failed to give the correct sign. An alternative method for evaluation of the diamagnetic term will be described in the subsequent paper.[35]

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(33) This trend is explained as due to a difference of relative contributions of diamagnetic-shielding and electric-field effects (see eq 4).

(34) Calculated after ^{14}N and proton chemical shifts are expressed in parts per million.

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