Relationships of the ^{15}N Nuclear Magnetic Resonance Chemical Shift and the ^{15}N–^{1}H Spin Coupling Constant to the Infrared Stretching Frequency of the Amino Group in Saturated Primary Amines and Anilines

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The amino group stretching frequency (ν_{NH}) and the ^{15}N chemical shift (δ^{15}N) were measured for saturated primary amines. A good linear relationship was found between them, with the slope being the opposite of that found in substituted anilines. A linear relationship was also found for substituted anilines between ν_{NH} and the ^{15}N–^{1}H spin coupling constant ($^{1}J_{^{15}N,^{1}H}$). CNDO/2 calculations were done for representative molecules to obtain the NH stretching frequency, the local paramagnetic term of ^{15}N, and the nitrogen 2*s*–hydrogen 1*s* bond order, on the basis of which the characteristic behaviour found for the i.r. and n.m.r. parameters was interpreted.

The ^{15}N chemical shift of the amino group in saturated primary amines (RNH_2) gives very useful information on the structure of the substituent.[1,2] It has been reported[2] that the substitution of a methyl group for a hydrogen on the α-carbon (α-H) of R-NH_2 changes the ^{15}N chemical shift to lower magnetic field, whereas, in the case of the substitution of β-H, the shift is to higher magnetic field. This behaviour is similar to that of the ^{17}O chemical shift (δ^{17}O) found in saturated alcohols (ROH).[3] Previously we have reported[4] that a linear relationship exists between the OH stretching frequency (ν_{OH}) and δ^{17}O of ROH. Our continued interest in studying the relationship between the i.r. stretching frequency and the n.m.r. chemical shift led us to measure the NH stretching frequency (ν_{NH}) and the ^{15}N chemical shift (δ^{15}N) of the amino group in RNH_2. The ν_{NH} value shifts to lower wavenumber when the α-H is substituted by a methyl group, but to a higher one in the case of substitution for β-H.[5] This behaviour is like that of ν_{OH} found in ROH.[6] Therefore, regression analysis was done for the relationship between ν_{NH} and δ^{15}N observed for nine saturated primary amines. To explain the experimental result theoretically, we have performed the CNDO/2 calculation[7] for a series of methyl-substituted methylamines and obtained the approximate values of ν_{NH} and the ^{15}N local paramagnetic term.[8] In order to compare the important factors influencing the NH stretching frequency and the local paramagnetic term in RNH_2 with those in amino compounds having the π-electron system, we also studied the relationships among the n.m.r. parameters (δ^{15}N and $^{1}J_{^{15}N,^{1}H}$) and the NH stretching frequency in *para*- and *meta*-substituted anilines.

Experimental

All the compounds used were available commercially. I.r. spectra were recorded on a JASCO A-702 i.r. spectrophotometer calibrated for the rotational bands of ammonia gas. Samples were dissolved in chloroform at a concentration of *ca.* 0.1 mol dm^{-3} (cell length 0.5 cm). Nitrogen-15 n.m.r. spectra were recorded with a Varian XL-200 Fourier transform spectrometer. Calculations were performed on a FACOM M-150F computer.

Results and Discussion

NH Stretching Frequency–^{15}N Chemical Shift Relationship.—The ν_{NH} and the δ^{15}N values observed for the saturated primary amines are listed in Table 1, together with the δ^{15}N values reported for the corresponding amines.[2a] Because the primary amines have an antisymmetric stretching frequency ($\nu_{NH}{}^{as}$) and a symmetric one ($\nu_{NH}{}^{s}$), the values estimated using equation (1) were approximately adopted as the ν_{NH} value of

$$\nu_{NH} = \{[(\nu_{NH}{}^{as})^2 + (\nu_{NH}{}^{s})^2]/2\}^{\frac{1}{2}} \qquad (1)$$

primary amines.[9] The values of ν_{NH} and δ^{15}N are shifted to lower wavenumber and lower magnetic field, respectively, by the β-methyl effect (*i.e.*, the effect of substitution of the methyl group for the α-H) on going from CH_3NH_2 (1) through $CH_3CH_2NH_2$ (5) and $(CH_3)_2CHNH_2$ (7) to $(CH_3)_3CNH_2$ (9), but to higher values with an increasing γ-effect (*i.e.*, the effect of substitution for the β-H) as seen on going from (3) to (2).

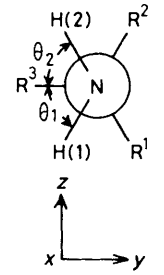
Table 1. Amino stretching frequencies in chloroform and ^{15}N chemical shifts.

No.	Compound	$\nu_{NH}{}^{as}$/cm^{-1}	$\nu_{NH}{}^{s}$/cm^{-1}	ν_{NH}/cm$^{-1\,a}$	δ^{15}N (p.p.m.) Neat[b] (CH_3OH)[c]
(1)	CH_3NH_2	3 394	3 328	3 361	6.3[d] (2.9)
(2)	$(CH_3)_2CHCH_2NH_2$	3 390	3 326	3 358	17.5 (17.5)
(3)	$CH_3(CH_2)_2NH_2$	3 386	3 318	3 352	20.9 (20.6)
(4)	$CH_3(CH_2)_3NH_2$	3 385	3 317	3 351	23.5 (20.8)
(5)	$CH_3CH_2NH_2$	3 384	3 317	3 350	27.7[d] (24.8)
(6)	$CH_3CH_2(CH_3)CHNH_2$	3 378	3 310	3 344	39.4 (38.0)
(7)	$(CH_3)_2CHNH_2$	3 375	3 308	3 342	44.4 (42.1)
(8)	cyclo-$C_6H_{11}NH_2$	3 372	3 307	3 340	41.2 (39.8)
(9)	$(CH_3)_3CNH_2$	3 363	3 300	3 332	59.6 (55.9)

[a] $\nu_{NH} = \{[(\nu_{NH}{}^{as})^2 + (\nu_{NH}{}^{s})^2]/2\}^{\frac{1}{2}}$. [b] Reference signal; external {$HCONH_2$–$(CD_3)_2SO$ (vol/mol 1:1)}. δ value; calculated by assuming δ(ref.) = 112.2 p.p.m. [c] Ref. 2a; measured with respect to 1M-HNO_3, conversion constant = 374.0 p.p.m., in CH_3OH. [d] Compounds (1) and (5) are 40 and 70% H_2O solutions, respectively.

Table 2. Bond lengths (Å), angles (°),[10] and co-ordinates[a] of methyl-substituted methylamines

R_{C-C}	1.54	$C\hat{N}H$	112.2
R_{C-N}	1.47	$H\hat{N}H$	105.8
R_{N-H}	1.01	$C\hat{C}N = C\hat{C}C$	109.47
R_{C-H}	1.09	$C\hat{C}H = H\hat{C}H$	
		$\theta_1 = \theta_2$	



	R^1	R^2	R^3
(1)	H	H	H
(5a)	CH_3	H	H
(5b)	H	H	CH_3
(7a)	CH_3	CH_3	H
(7b)	CH_3	H	CH_3
(9)	CH_3	CH_3	CH_3

[a] The geometry of the β-methyl group was assumed to be exactly staggered.

The plot of $\delta^{15}N$ against ν_{NH} observed gives a good linear relationship which can be expressed as equation (2), where *n* is the number of data points and *r* the correlation coefficient. Equation (2) may prove useful for estimating the $\delta^{15}N$ value for

$$\delta^{15}N = -1.7601\nu_{NH} + 5923.5 \qquad (2)$$
$$(n = 9, r = 0.986)$$

RNH_2 from the ν_{NH} value which is much easier to observe than the $\delta^{15}N$ value. The relationship found is discussed below on the basis of the CNDO/2 calculations.[7]

CNDO/2 Calculations.—On the basis of available data[10] for analogous compounds, we adopted the geometries and co-ordinates of the model compounds (1), (5), (7), and (9) shown in Table 2. With compounds (5) and (7) which have two conformers, the NH stretching frequencies and the ^{15}N local paramagnetic terms for both conformations (5a) and (5b) and (7a) and (7b) were calculated.

(a) NH *Stretching frequency.* The amino stretching bands are known to correspond virtually only to the NH_2 stretching modes. For example, the potential energy distributions of $\nu_{NH}{}^{as}$ and $\nu_{NH}{}^{s}$ in methylamine have been evaluated to be 100%, respectively, by normal co-ordinate analysis.[11] Therefore, the ν_{NH} value obtained by equation (1) can be assumed to be approximately equal to a pure NH stretching frequency in the NH_2 group. Because the amine has two N–H bonds [NH(1) and NH(2)], which have environmental differences in conformations (5a) and (7b), both of the NH(1) and NH(2) stretching frequencies were calculated for (5a) and (7b).

Based on a harmonic oscillator model, the force constant (*K*) of the NH stretching band was calculated from the second derivative of change in total energy (*E*) with the variation in the NH bond length (R_{NH}) near the optimum NH bond length (R_{NH}). The assumption gave equation (3),[7,12] where $K =$

$$E = Kq^2/2 \qquad (3)$$

$\partial^2E/\partial q^2$ and $q = R_{NH} - R_{NH}$. The proton potential function in the direction of the NH axis was obtained by five-point calculations at 0.01 Å intervals of R_{NH} around the energy minimum, retaining another NH bond length at 1.07 Å because the R_{NH} value of an NH_2 group was calculated to be *ca.* 1.07 Å. The *K* value was calculated from the potential function and the NH stretching frequency (ν_{NH}) was obtained from the *K* value by the usual method.[12] The ν_{NH} value thus calculated corresponds to the ν_{NH} value given by equation (1).

The R_{NH}, *K*, and ν_{NH} values obtained from the CNDO/2 calculations are given in Table 3. Although the CNDO/2 calculations, in general, overestimate the values,[4,7,13] the tendency was for the ν_{NH} value to decrease as the R_{NH} value increased. The calculated ν_{NH} values ran closely parallel to the experimental ones which shifted to lower wavenumbers with an increasing number of β-methyl groups, as for compounds (1), (5), (7), and (9).

(b) ^{15}N *Local paramagnetic term.* Because the diamagnetic term is considered to be effectively constant for a nitrogen atom,[14] the ^{15}N chemical shift is assumed to be mainly governed by the local paramagnetic term (σ_p). According to Pople–Karplus theory,[8] the *ii*-component of the local paramagnetic contribution of atom A bound to atom B is given by equation (4), where ΔE is the average electronic excitation

$$(\sigma_p{}^{AA})_{ii} = -\frac{e^2\hbar^2}{2m^2c^2(\Delta E)}\langle r^{-3}\rangle_{2p}\,[(Q_{AA})_{ii} + \sum_{B\neq A}(Q_{AB})_{ii}] \qquad (4)$$

energy, $[(Q_{AA})_{ii} + \sum_{B\neq A}(Q_{AB})_{ii}]$ is the orbital term which is obtained from the charge density–bond order matrix, and $\langle r^{-3}\rangle_{2p}$ is the mean inverse cube radius for the nitrogen *2p* orbitals. The $\langle r^{-3}\rangle_{2p}$ value was evaluated from equation (5). The Z_{2p} value of the nitrogen atom is given by equation (6)

$$\langle r^{-3}\rangle_{2p} = \frac{1}{24}(Z_{2p}/a_0)^3 \qquad (5)$$

$$Z_{2p} = 3.90 - 0.35\,(P_{AA} - 5) \qquad (6)$$

in accord with Slater's rules,[15] where P_{AA} is the charge density on the nitrogen atom. The values of $\langle r^{-3}\rangle_{2p}$ and $[(Q_{AA})_{ii} + \sum_{B\neq A}(Q_{AB})_{ii}]$ obtained from the CNDO/2 calculation are listed in Table 3. If those values are the main factors determining σ_p, the $\delta^{15}N$ values should shift to higher magnetic field on going from compound (1) through (5) and (7) to (9). But the $\delta^{15}N$ values shown in Table 1 exhibit a shift to lower magnetic field. The result clearly suggests that σ_p is not governed primarily by $\langle r^{-3}\rangle_{2p}$ and $[(Q_{AA})_{ii} + \sum_{B\neq A}(Q_{AB})_{ii}]$ in this case.

The downfield shifts of $\delta^{15}N$ due to β-methyl groups found for compounds (1), (5), (7), and (9) are in parallel with the decrease in the ionization potentials.[16] Therefore, it is assumed that, as an approximation, we can substitute the ionization potential for ΔE in equation (4), as assumed in the study on the $\delta^{17}O$ value of ROH.[4] Applying Koopmans' theorem,[17] the ΔE value is assumed to be the negative of the highest occupied orbital energy (ε_{HOMO}). The calculated σ_p values are given in Table 3. The increase in the absolute value of σ_p due to the β-methyl effect in the model compounds is consistent with the increase in the downfield shift of $\delta^{15}N$. This result indicates that σ_p is primarily governed by ΔE in this case.

Ebraheem and Webb[18] have calculated the nitrogen nuclear screening constants using Pople's theory,[19] within the CNDO/S framework;[20] the excitation energy ($E_k - E_j$) is given by equation (7), where ε_k and ε_j are eigenvalues of the unperturbed

$$E_k - E_j = \varepsilon_k - \varepsilon_j - J_{jk} + 2K_{jk} \qquad (7)$$

molecule, and J_{jk} and K_{jk} are the Coulomb and exchange integrals, respectively. They have reported[18] that this approach provides a satisfactory account of the ^{15}N nuclear screening tensors of some simple molecules. Therefore, we also did the calculations

Table 3. Optimum NH bond lengths, NH stretching frequencies,[a] and ^{15}N local paramagentic terms[b] for methyl-substituted methylamines by CNDO/2 calculation

Compound	No.	R_{NH}/Å	K/mdyn Å^{-1}	ν_{NH}/cm^{-1}	P_{AA}	$10^{-24}<r^{-3}>_{2p}$/cm^{-3}	ε_{HOMO}/a.u.	ii	$(Q_{AA})_{ii} + \sum_{B \neq A}(Q_{AB})_{ii}$	$(\sigma_p^{AA})_{ii}$ (p.p.m.)	σ_p(p.p.m.)[c] [σ_p(p.p.m.)][d]
CH_3NH_2	(1)	1.0675	14.1914	5 061.1	5.2027	15.7856	−0.523 32	xx	1.875 64	−223.2	−246.2
								yy	2.211 97	−263.3	(−198.9)
								zz	2.118 50	−252.1	
$CH_3CH_2NH_2$	(5a)	1.0679[e]	14.1830[e]	5 059.6[e]	5.2080	15.7627	−0.513 25	xx	1.883 91	−228.3	−249.7
								yy	2.190 00	−265.4	(−189.4)
								zz	2.107 81	−255.4	
	(5b)	1.0677	14.1789	5 058.9	5.2126	15.7428	−0.506 99	xx	1.888 31	−231.3	−251.6
								yy	2.206 08	−270.3	(−193.2)
								zz	2.065 93	−253.1	
$(CH_3)_2CHNH_2$	(7a)	1.0684	14.1708	5 057.4	5.2124	15.7436	−0.503 50	xx	1.890 46	−233.2	−253.3
								yy	2.171 37	−267.9	(−185.0)
								zz	2.098 46	−258.9	
	(7b)	1.0682[e]	14.1718[e]	5 057.6[e]	5.2164	15.7264	−0.497 39	xx	1.894 47	−236.3	−255.4
								yy	2.186 02	−272.7	(−185.6)
								zz	2.060 89	−257.1	
$(CH_3)_3CNH_2$	(9)	1.0687	14.1652	5 056.4	5.2197	15.7121	−0.488 41	xx	1.899 58	−241.1	−259.1
								yy	2.168 82	−275.3	(−182.2)
								zz	2.056 14	−261.0	

[a] Calculated by applying least-squares quadratic fit using five points (see text). [b] σ_p was calculated using the bond length listed in Table 2 (R_{NH} 1.01 Å). [c] $\sigma_p = 1/3[(\sigma_p^{AA})_{xx} + (\sigma_p^{AA})_{yy} + (\sigma_p^{AA})_{zz}]$. [d] Calculated by the CNDO/S method (see text). [e] Mean values for NH(1) and NH(2) in the amino group (see text).

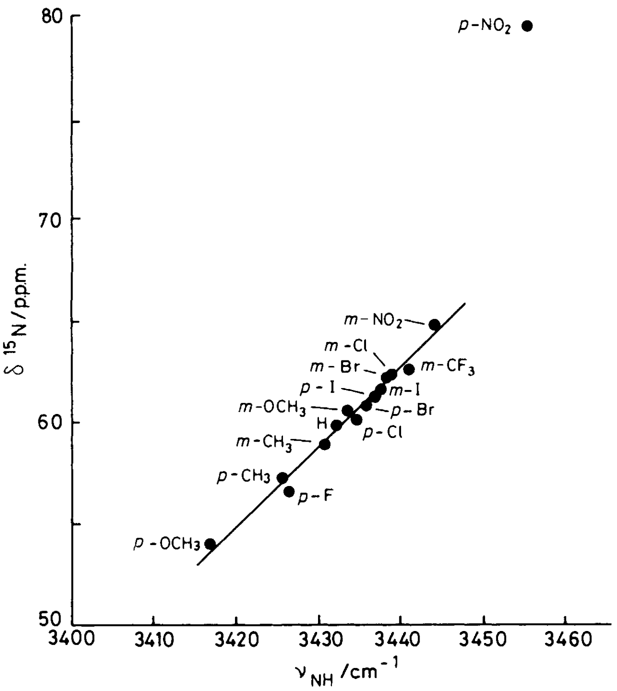


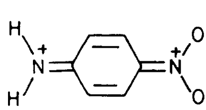
Figure 1. Plots of ^{15}N chemical shifts[a] against NH stretching frequencies[b] in *para*- and *meta*-substituted anilines.[c] [a] Ref. 22; conversion factor = 380.4 p.p.m., in $(CD_3)_2SO$. [b] Ref. 9; $\nu_{NH} = \{[(\nu_{NH}^{as})^2 + (\nu_{NH}^{s})^2]/2\}^{\frac{1}{2}}$, in CS_2. [c] Regression analysis gave the equation $\delta^{15}N = 0.3855\,\nu_{NH} - 1263.7$ ($n = 14, r = 0.990$)

applying the CNDO/S method for a series of methyl-substituted methylamines and obtained values for σ_p (see σ_p values in parentheses in Table 3). However, the result differed from the experimental one. The CNDO/S calculation was not efficient enough to explain the β-methyl effect on σ_p of ^{15}N in the compounds examined.

(c) *Calculated* ν_{NH}–σ_p *relationship.* We obtained equation (2) for the empirical relationship between the ν_{NH} and the $\delta^{15}N$ values. Although the existence of a certain relationship between the ν_{NH} and the $\delta^{15}N$ values can be expected, there had been no straightforward proof of the linearity of this relationship. A linear relationship ($n = 6$, $r = 0.970$) was also found between the calculated ν_{NH} and σ_p values for the model compounds, thus providing theoretical support for the empirical relationship.

Comparison of ν_{NH}–$\delta^{15}N$ *Relationships Found in Saturated Primary Amines and Substituted Anilines.*—A rough linear relationship ($n = 10$, $r = 0.922$) has been reported between ν_{NH} and $\delta^{15}N$ for *para*- and *meta*-substituted anilines ($XC_6H_4NH_2$) including *p*-nitroaniline.[21] As shown in Figure 1, we obtained a good linear relationship ($n = 14$, $r = 0.990$) between ν_{NH} and $\delta^{15}N$ reported for $XC_6H_4NH_2$,[9,22] excluding *p*-nitroaniline. Interestingly, the slope observed for $XC_6H_4NH_2$ was in just the opposite direction to that of RNH_2. It has been reported[5,9,23] that the amino stretching frequencies in RNH_2 and $XC_6H_4NH_2$ are proportional to Taft σ* of R and the substituent constants of X, respectively, and that the shift to lower wavenumber occurs when R or X is an electron-donating substituent. With the substituent effects on the amino stretching frequencies, RNH_2 and $XC_6H_4NH_2$ resemble each other in appearance.

On the other hand, the $\delta^{15}N$ values in $XC_6H_4NH_2$ have been reported to shift to lower magnetic field upon introduction of an electron-withdrawing substituent in the phenyl group and to be proportional to the π-electron densities at the nitrogen atom of the amino group calculated by Hückel LCAO.[22] If we accept that the $\delta^{15}N$ value is approximately governed by $(\sigma_p^{AA})_{ii}$[14] which is given by equation (4), the above fact indicates that the $\delta^{15}N$ value is primarily governed by the $<r^{3}>_{2p}$ and/or the $[(Q_{AA})_{ii} + \sum_{B\neq A}(Q_{AB})_{ii}]$ terms in this case, as pointed out by Kato *et al.*[24] to explain the $\delta^{17}O$ behaviour in $XC_6H_4OCH_3$. In the case of RNH_2, the shift to lower magnetic field is caused by electron-donating substituents. These facts support the idea that the $\delta^{15}N$ value of RNH_2 is primarily governed by the ΔE term, as mentioned in the previous paragraph. Thus, we can understand the opposite slopes of the ν_{NH}–$\delta^{15}N$ relationships found for RNH_2 and $XC_6H_4NH_2$.



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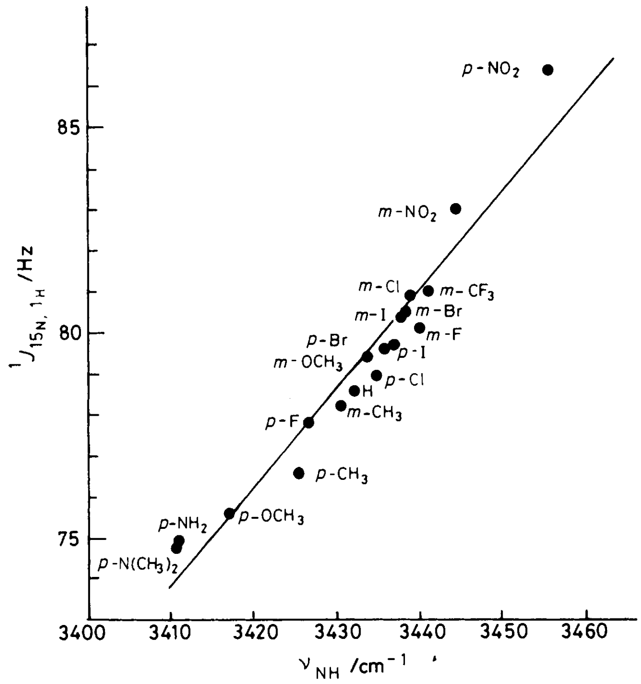


Figure 2. Plots of ^{15}N–^{1}H spin coupling constants[a] against NH stretching frequencies[b] in *para*- and *meta*-substituted anilines.[c] [a] Ref. 22; in $CDCl_3$. [b] Ref. 9; $\nu_{NH} = \{[(\nu_{NH}^{as})^2 + (\nu_{NH}^{s})^2]/2\}^{\frac{1}{2}}$, in CS_2. [c] Regression analysis gave the equation $^{1}J_{^{15}N,^{1}H} = 0.2421\,\nu_{NH} - 751.8$ ($n = 18, r = 0.967$)

As seen from Figure 1, the point for the *p*-nitroaniline greatly deviated from the line. The reason may be an abnormally strong 'through resonance interaction' between the NH_2 and NO_2 groups as in (A) by which not only the π-electron density but also the other terms controlling $\delta^{15}N$ are influenced to deviate to lower magnetic field. The through-resonance interaction promotes N–H bond polarization which suppresses the shift to higher wavenumber induced by the electron-withdrawal factor; this effect may also contribute to the deviation from the linear relationship. The important factors controlling the ν_{NH} value are discussed in the next paragraph using the information obtained from the behaviour of the n.m.r. ^{15}N–^{1}H spin coupling constants.

NH *Stretching Frequency*–^{15}N–^{1}H *Spin Coupling Constant Relationship in* p- *and* m-*Substituted Anilines.*—For a series of

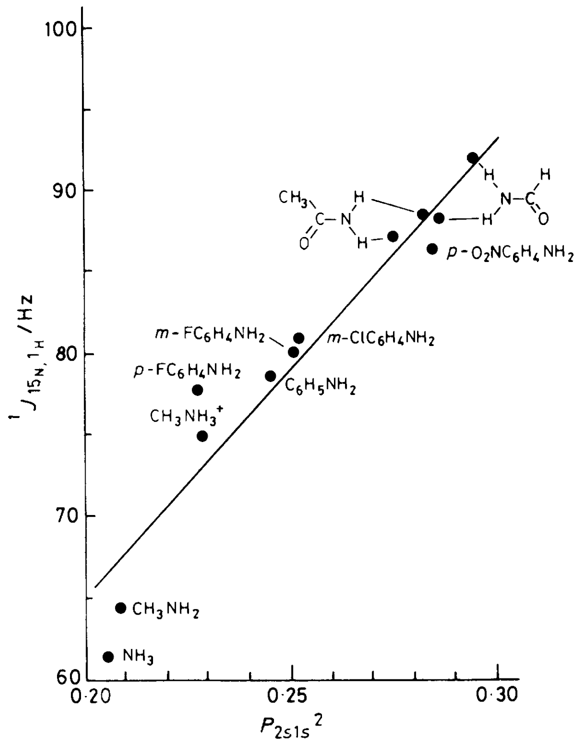
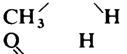
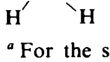


Figure 3. Plots of ^{15}N–^{1}H coupling constants against P_{2s1s} in YNH$_2$.[a]
[a] Regression analysis gave the equation ${}^{1}J_{^{15}N,^{1}H} = 294.8\,P_{2s1s}{}^{2} + 5.2$ ($n = 12, r = 0.962$).

anilines, $XC_6H_4NH_2$, a good linear relationship was found between ν_{NH} and the ^{15}N–^{1}H spin coupling constant[22] (${}^{1}J_{^{15}N,^{1}H}$) as shown in Figure 2. Theoretical[25] and experimental[26] proof exists that ${}^{1}J_{A,H}$ is linearly related to the (s%) character of the hybrid orbitals forming the A–H bond. In order to interpret the ν_{NH}–${}^{1}J_{^{15}N,^{1}H}$ relationship obtained, we inspected the available geometries for the compounds having an amino group (YNH$_2$) and did the CNDO/2 calculations. Table 4 lists the values of θ and $P_{2s1s}{}^{2}$ for the amino compounds, YNH$_2$, together with the available ${}^{1}J_{^{15}N,^{1}H}$ values, where θ is the out-of-plane angle of the N–Y bond from the HNH plane and $P_{2s1s}{}^{2}$ is the square of the bond order between the nitrogen 2s and the hydrogen 1s calculated by the CNDO/2 method on the basis of its geometry. The θ values of RNH$_2$ are nearly constant in the range 52.9—51.3° and are close to the 54.7° of sp^3-hybridization, but those of $XC_6H_4NH_2$ vary greatly from 46.4° to 10.6° depending upon X and are intermediate between the 54.7° of sp^3-hybridization and the 0° of sp^2. The ${}^{1}J_{^{15}N,^{1}H}$ values were plotted against the calculated $P_{2s1s}{}^{2}$ values and a good linear relationship (Figure 3) was found. The plotted points for the reference compounds, ammonia or methylamine (sp^3) and formamide (sp^2), are located at both terminals of the line, and the points for $XC_6H_4NH_2$ are located in between depending on the $P_{2s1s}{}^{2}$ value. This result indicates that in YNH$_2$, the ${}^{1}J_{^{15}N,^{1}H}$ value is proportional to the (s%) character of the NH bond. Accordingly, the ν_{NH}–${}^{1}J_{^{15}N,^{1}N}$ relationship suggests that the ν_{NH} value in $XC_6H_4NH_2$ is also governed primarily by the (s%) character of the NH bond.

Unfortunately, the ${}^{1}J_{^{15}N,^{1}H}$ value for most of the saturated primary amines examined, which are liquid over a wide temperature range, was not observable even at low temperature because of the rapid proton exchange. However, the ${}^{1}J_{^{15}N,^{1}H}$ values for those compounds, if observable without an influence of the proton exchange, are predicted not to differ much from that of methylamine, since small differences in the (s%) character of those amines are indicated from the θ values. The important factor causing the considerable differences in the ν_{NH} value of RNH$_2$ depending upon R is not simply assignable. Assuming that the ν_{NH} values of RNH$_2$ are also influenced mainly by their (s%) character, the ν_{NH} values with small differences should be observed for RNH$_2$. In spite of the small differences in the θ and the $P_{2s1s}{}^{2}$ values, however, considerably large differences were observed for the ν_{NH} values of RNH$_2$; compared with the ν_{NH} value of methylamine, for example, those of ethylamine and isopropylamine shift to lower wavenumber by 11 and 19 cm^{-1}, respectively. This finding implies that the factors important in controlling ν_{NH} of the RNH$_2$ and $XC_6H_4NH_2$ systems also differ, as mentioned for the δ^{15}N behaviour. Presumably, the effect of non-bonding interactions, which has been described for the ν_{OH} value of ROH,[4] is an important factor causing clear differences in the ν_{NH} value of the RNH$_2$ system.

Table 4. Out-of-plane angle (θ) of N–Y bond from the HNH plane, the square of the bond order ($P_{2s1s}{}^{2}$) of the N–H bond calculated by the CNDO/2 method, and ^{15}N–^{1}H spin coupling constant (${}^{1}J_{^{15}N,^{1}H}$) in YNH$_2$

Compound	θ(°)	$P_{2s1s}{}^{2}$ [a]	${}^{1}J_{^{15}N,^{1}H}$/Hz
NH$_3$	53.8[b]	0.205 73	61.2[p]
CH$_3$NH$_2$	52.2[c]	0.209 03	64.5[p]
CH$_3$CH$_2$NH$_2$	51.3[d]	0.207 00[n]	(n.o.)[q]
(CH$_3$)$_2$CHNH$_2$	52.9[e]	0.218 40[n]	(n.o.)[q]
CH$_3$NH$_3^+$	54.2[f]	0.228 94	74.92[f]
p-FC$_6$H$_4$NH$_2$	46.4[g]	0.227 88	77.8[r]
C$_6$H$_5$NH$_2$	37.5[h]	0.245 36	78.6[r]
m-FC$_6$H$_4$NH$_2$	36.2[i]	0.251 87[o]	80.1[r]
m-ClC$_6$H$_4$NH$_4$	34.6[j]	0.252 42[o]	80.9[r]
p-O$_2$NC$_6$H$_4$NH$_2$	10.6[k]	0.284 80	86.4[r]
	0[l]	0.275 29	87.2[s]
		0.282 26	88.5[s]
	0[m]	0.286 35	88.0[t]
		0.294 63	92.0[t]

[a] For the sake of simplicity, the bond lengths C----C (1.395 Å), C——H (1.09 Å) and bond angles (120°) for the benzene ring were used. [b] K. Kuchitsu, J. P. Gullory, and L. S. Bartell, *J. Chem. Phys.*, 1968, **49**, 2488. [c] T. Nishikawa, T. Itoh, and K. Shimoda, *ibid.*, 1955, **23**, 1735. [d] M. Tsuboi, K. Tamagake, A. Y. Hirakawa, J. Yamaguchi, H. Nakagawa, A. S. Manocha, E. C. Tuazon, and W. G. Fately, *ibid.*, 1975, **63**, 5177. [e] S. C. Mehrotra, L. L. Griffin, C. O. Britt, and J. E. Boggs, *J. Mol. Spectrosc.*, 1977, **64**, 244. [f] L. W. Reeves and A. S. Tracey, *J. Am. Chem. Soc.*, 1974, **96**, 1198. [g] A. Hastie, D. G. Lister, R. L. McNell, and J. K. Tyler, *Chem. Commun.*, 1970, 108. [h] D. G. Lister and J. K. Tyler, *J. Mol. Struct.*, 1974, **23**, 253. [i] G. Cazzoli, D. Damiani, and D. G. Lister, *J. Chem. Soc., Faraday Trans. 2*, 1973, **69**, 119. [j] A. Nonat, A. Bouchy, and G. Roussy, *J. Mol. Struct.*, 1983, **97**, 83. [k] M. Colapietro, A. Domenicano, C. Marciante, and G. Portalone, *Acta Crystallogr.*, 1981, **A37**, C199. [l] G. A. Jeffrey, J. R. Ruble, R. K. McMullan, D. J. DeFrees, J. S. Blinkley, and J. A. Pople, *ibid.*, 1980, **B36**, 2292. [m] M. Kitano and K. Kichitsu, *Bull. Chem. Soc. Jpn.*, 1974, **47**, 67. [n] Mean value of $P_{2s1s}{}^{2}$ calculated for amino group in *trans*- and *gauche*-forms. [o] Mean value of $P_{2s1s}{}^{2}$ calculated for two N–H bonds in amino group. [p] M. Alei, Jr., A. E. Florin, W. M. Litchman, and J. F. O'Brien, *J. Phys. Chem.*, 1971, **75**, 932. [q] Not observed (see text). [r] T. Axenrod, P. S. Pregosin, M. J. Wieder, and G. W. A. Milne, *J. Am. Chem. Soc.*, 1969, **91**, 3681. [s] A. D. Marco and M. Llinás, *Org. Magn. Reson.*, 1979, **12**, 454. [t] B. Sunners, L. H. Piette, and W. G. Schneider, *Can. J. Chem.*, 1960, **38**, 681.

In conclusion, the empirical linear relationships found among the i.r. stretching frequency and the n.m.r. parameters of amino compounds and the substituent effects on ν_{NH}, δ^{15}N, and ${}^{1}J_{^{15}N,^{1}H}$ in amino compounds were interpreted by the theoretical treatment using the CNDO/2 method. The information obtained in the present study should be useful for understanding the i.r. and n.m.r. behaviour found in analogous compounds.

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