dihedral angles. If this is the case, the large difference in the $^3J_{PCCH}$ couplings suggests that this kind of coupling in three-coordinate phosphorus compounds may have an angular dependence which is rather more complicated than a simple Karplus-type relationship, because account will have to be taken of the orientation about the P–C bond as has already been proposed for $^2J_{PCH}$ couplings,[16] and is well known for nitrogen compounds.[17]

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[16] (a) D. Gagnaire, J. B. Robert, and J. Verrier, *Chem. Commun.*, 819 (1967); (b) J. P. Albrand, D. Gagnaire, J. M. Martin, and J. B. Robert, *Bull. Soc. Chim. Fr.*, 40 (1969).

[17] *Cf.* R. L. Lichter and J. D. Roberts, *J. Amer. Chem. Soc.*, **93**, 5218 (1971), and references cited therein.

Nitrogen-15 Magnetic Resonance Spectroscopy. XV. Natural-Abundance Spectra. Chemical Shifts of Hydrazines[1]

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Abstract: The ^{15}N resonances of the methylhydrazines and some phenylhydrazines have been determined at the natural-abundance level of ^{15}N. The chemical shifts for the methyl compounds were interpretable in terms of deshielding α and β effects. The β shift, -24.4 ppm, is substantially larger than that found for amine ^{15}N (-18.2 ppm) or hydrocarbon cmr resonances (-9.7 ppm), and an explanation is offered in terms of possible steric influences. Although the ^{15}N shifts of the phenylhydrazines also change with structure, the data are so far insufficient to allow derivation of substituent parameters. Nonetheless, the effects of substitution appear to be less systematic than for the alkylhydrazines. The cmr chemical shifts of the methylhydrazines have been measured. While the shifts do not correlate with the ^{15}N shifts, they can be expressed in terms of deshielding β and shielding γ effects comparable to those found for hydrocarbons and alcohols.

A number of ^{15}N chemical shifts of amines at the natural-abundance level have recently been reported[2] and were shown to be subject to structural influences which parallel to a substantial degree those which determine carbon chemical shifts. Hydrogen bonding was also suggested as a possible contributing factor to the shifts, although no explicit isolation of its effect could be adduced. As an adjunct to that work, we have measured the chemical shifts of the methylhydrazines and a few phenylhydrazines, and report here the effect of substituents on the nitrogen chemical shifts of this type of molecule.

Results

The ^{15}N chemical shifts of the methylhydrazines, obtained with complete proton noise decoupling,[3] are given in Table I. The resonances of the unsymmetrical hydrazines were assigned in part on the basis of the upright or inverted disposition of the signal, which may be taken as an indication of the presence or absence of a nuclear Overhauser effect (NOE).[4] Consistent with the assignments is the observation that those nitrogen atoms bearing protons were in general detectable after many fewer scans than the fully substituted atoms. Correlating with the difficulty experienced in detecting resonances of tertiary amines in natural abundance,[2,5] this result is very likely attributable to longer relaxation times for these nuclei.[6] Because neither of these criteria is definitive, it is of interest to consider briefly other possible bases for assignment. The early successful identification of carbon resonances derives in large part from analysis of spectral patterns arising from spin–spin coupling to directly bonded protons.[7] Subsequent derivation of substituent parameters then allowed characterization of resonances of more com-

Table I. ^{15}N Chemical Shifts of Hydrazine and Its Methyl Derivatives[a]

	$\delta_{N\text{-}1}$, ppm		$\delta_{N\text{-}2}$, ppm
H_2NNH_2		328.7[b]	
CH_3NHNH_2	321.9[b]		299.4[b]
$(CH_3)_2NNH_2$	316.6[c]		275.3[b]
$CH_3NHNHCH_3$		300.5[c]	
$(CH_3)_2NNHCH_3$	301.6[c]		279.2[b]
$(CH_3)_2NN(CH_3)_2$[d]		271.5[b]	

[a] With respect to external $H^{15}NO_3$, error ~0.3 ppm. [b] Inverted signal. [c] Upright signal. [d] Contaminated with about 30% 1,1,2-trimethylhydrazine, for which the N-2 chemical shift was 279.9 ppm.

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[1] Supported by the Public Health Service, Research Grant No. GM-11072, from the Division of General Medical Sciences, and the National Science Foundation.

[2] Part XIV: R. L. Lichter and J. D. Roberts, *J. Amer. Chem. Soc.*, **94**, 2495 (1972).

[3] (a) F. J. Weigert, M. Jautelat, and J. D. Roberts, *Proc. Nat. Acad. Sci. U. S.*, 60, 1152 (1968); (b) L. F. Johnson and M. E. Tate, *Can. J. Chem.*, 47, 63 (1969).

[4] (a) R. L. Lichter and J. D. Roberts, *J. Amer. Chem. Soc.*, **93**, 3200 (1971); (b) R. A. Cooper, R. L. Lichter, and J. D. Roberts, paper in preparation.

[5] J. P. Warren and J. D. Roberts, unpublished results.

[6] W. M. Litchman, Abstracts, 161st National Meeting of the American Chemical Society, Los Angeles, Calif., March 29, 1971, No. PHYS-010.

[7] (a) See, *e.g.*, D. M. Grant and E. G. Paul, *J. Amer. Chem. Soc.*, **86**, 2984 (1964); (b) J. D. Roberts, F. J. Weigert, J. I. Kroschwitz, and H. J. Reich, *ibid.*, **92**, 1338 (1970).

plicated molecules. Application of the former technique, as well as its extension to off-resonance decoupling,[7b] is in general not possible in nitrogen spectroscopy because, in the absence of proton irradiation, prototropic exchange renders the nitrogen resonances undetectable.[4] Conceivably, assignments might have been made on the basis of substituent effects anticipated from carbon spectroscopy, where α and β shifts are comparable in magnitude.[7a] Indeed, before the amine results were complete, the best hydrazine assignments were thought to be the reverse of those shown in Table I, because larger α than β shifts seemed intuitively more reasonable. However, the alkyl-substituent parameters obtained from the amines ($\alpha = -8.7$ ppm, $\beta = -18.2$ ppm) cast doubt on this assumption. In fact, if the hydrazines are viewed as successively substituted derivatives of ammonia, methylamine, and dimethylamine, the corresponding changes induced by substitution of hydrogen by the amino, methylamino, and dimethylamino groups to yield the respective hydrazines are approximately independent of the structures of the parent compounds. Thus, with the assignments in Table I, ammonia[8] and hydrazine, methylamine[8] and methylhydrazine,[7] and dimethylamine[8] and dimethylhydrazine all differ in chemical shift by about the same value (56 ppm), while the reversal of these assignments leads to increases in the chemical-shift differences. The former result is more nearly in accord with expectations of substituent effects on resonance line positions.

Nevertheless, although all these arguments are attractive, they are hardly compelling, especially because the resonance of tetramethylhydrazine, which has no directly bonded protons, was inverted. For this reason, the lines were assigned unambiguously by determination of the resonance of N-2 of 1,1-dimethylhydrazine enriched at that position to 95%. Under the measurement conditions (see Experimental Section) the enriched-atom resonance came at ~271 ppm, confirming, and indeed demanding, the assignments given in Table I.

One further observation warrants discussion. The resonance lines of all the hydrazines were narrow, which indicates that the quadrupole moment of the adjacent ^{14}N nucleus ($I = 1$) has little effect on the ^{15}N relaxation rate. A qualitative consideration of this relaxation mechanism suggests that only a minor contribution is to be expected. The argument is that the line width of a resonance broadened by quadrupole-induced relaxation will be proportional to the coupling constant between the nuclei and the T_1 of the quadrupolar nucleus.[9] Thus, in the absence of other relaxation mechanisms, the ratio of the line widths of two nuclei coupled to the same ^{14}N is proportional to the ratios of the respective ^{14}N coupling constants. Here, we can use the N–H proton resonances for comparison. Although no data exist for one-bond N–N coupling constants in molecules saturated at nitrogen, to a first approximation, the ratio of these values to N–H coupling constants can be assumed proportional to the ratio of the magnetogyric ratios. Consequently, the ^{15}N line widths are expected to be about one-tenth those of the protons directly bonded to the adjacent ^{14}N atoms. The N-2 proton line width of 1,1-dimethylhydrazine, for example, is about 5 Hz; hence the ^{15}N line width is expected to be about 0.5 Hz, far smaller than actually realized. The same conclusion holds for the N-2 signal when one takes into account the methyl proton line width (~1 Hz) together with the small (~0.5 Hz)[10] ^{14}N–C–H coupling constants.[11,12] The observed line widths were clearly sweep and inhomogeneity broadened.

The ^{15}N chemical shifts for three phenylhydrazines are given in Table II. The assignments for phenylhydrazine are based on the fact that, with the proton-decoupling frequency centered at a value appropriate for a high-field N–H proton resonance, a noise band width of 200 Hz produced a sharp signal for the higher field nitrogen resonance, and a broad signal for the one at low field. Increasing the band width to 600 Hz produced a sharper lower field nitrogen resonance. Clearly, the increased band width served to remove the coupling of N-1 to the aromatic protons.[13] Only a single, inverted, broad resonance, tentatively assigned to N-2 on the basis of the expected NOE, was observed for 1,1-diphenylhydrazine.

Table II. ^{15}N Chemical Shifts of Some Phenylhydrazines[a]

	$\delta_{N\text{-}1}$, ppm		$\delta_{N\text{-}2}$, ppm
$C_6H_5NHNH_2$	288.1		313.4
$C_6H_5NHNHC_6H_5$		281.5[b]	
$(C_6H_5)_2NNH_2$	*c*		287.1[d]

[a] Upfield with respect to external $H^{15}NO_3$. [b] Supersaturated solution in dioxane. [c] Not observed. [d] Broad resonance.

Table III shows the ^{13}C chemical shifts of the methylhydrazines as neat liquids. The assignment for 1,1,2-trimethylhydrazine rests on the relative intensities of the ^{13}C resonances.

Table III. ^{13}C Chemical Shifts of Methylhydrazines[a]

	δ_C, ppm
CH_3NHNH_2	150.46
$(CH_3)_2NNH_2$	142.00
$CH_3NHNHCH_3$	156.25
$(CH_3)_2NNHCH_3$	146.67 (C-1) 158.17 (C-2)
$(CH_3)_2NN(CH_3)_2$[b]	155.21

[a] Measured with respect to internal dioxane, converted to CS_2 scale by the relationship $\delta_{CS_2} = \delta_{\text{dioxane}} + 126.24$. [b] Sample contaminated with ~30% 1,1,2-trimethylhydrazine; $\delta_{C\text{-}1} = 146.76$, $\delta_{C\text{-}2} = 158.20$.

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(8) M. Witanowski and H. Januszewski, *Can. J. Chem.*, **47**, 1321 (1969).

(9) J. A. Pople, *Mol. Phys.*, **1**, 168 (1958).

(10) This value is based on ^{15}N–C–H coupling constants observed by R. Lichter and J. D. Roberts, *Spectrochim. Acta, Part A*, **26**, 1813 (1970).

(11) That proton exchange may contribute to the N-2 proton line width does not affect the argument, because the observed values set an upper limit on the quadrupole-induced relaxation rates.

(12) An alternative approach is to use the relationship $J_{^{14}N-^{15}N}/J_{^{14}N-H} \sim J_{^{13}C-^{15}N}/J_{^{13}C-H}$. With $J_{^{13}C-^{15}N} = 7$ Hz (G. Binsch, J. B. Lambert, B. W. Roberts, and J. D. Roberts, *J. Amer. Chem. Soc.*, **86**, 5564 (1964)) and $J_{^{13}C-H} = 125$ Hz, the ratio $J_{^{14}N-^{15}N}/J_{^{14}N-H}$ (and hence the corresponding line-width ratio) is about 0.07.

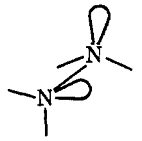
(13) These assignments are the reverse of those very recently reported by Randall and coworkers, who have obtained natural-abundance ^{15}N resonances using Fourier transform techniques: J. M. Briggs, L. F. Farnell, and E. W. Randall, *J. Chem. Soc. D*, 680 (1971).

Discussion

Examination of the ^{15}N shifts in Table I reveals distinct methyl substituent effects. If we assume that this effect arises only from the number and position of the methyl groups, regression analysis yields the parameters $\alpha = -3.6$ ppm/methyl, $\beta = -24.8$ ppm/methyl, $r = 0.986$, standard deviation = 3.7 ppm. While the results are mathematically reasonable, it is clear that, as with amines, the shifts might also be affected by changes in the degree of hydrogen bonding. There is considerable difficulty, however, in attempting to assess the influence of hydrogen bonding because one should take into account the change in shift associated with nitrogen acting as a donor, $^{15}\mathrm{N}\cdots\mathrm{H{-}R}$, and as an acceptor, $^{15}\mathrm{N{-}H}\cdots\mathrm{:R}$, and the change in ability to act in each of these ways with progressive substitution. The only hydrazine studied, which was incapable of hydrogen bonding, was tetramethylhydrazine; this, however, was contaminated with some trimethylhydrazine which can hydrogen bond. Several regression analyses based on somewhat unrealistic assumptions about the importance of hydrogen bonding as a function of substitution indicated that a downfield shift of several parts per million may be associated with hydrogen bonding, consistent with earlier observations.[2,14] Further work is needed to determine whether the effect is real or not.

Of special interest is the relative magnitude of the β shift with hydrazines compared to carbon and other nitrogen compounds. The β shift markedly increases for methyl substitution in the change from alkanes (-9.7 ppm[7]) to amines (-18.2 ppm[2]) to hydrazines (-24.4 ppm). The nature of the β effect is not too well understood.[7b,15] While α shifts in cmr spectra decrease rather smoothly with increasing substitution, the β shifts seem to reach saturation values beyond which further replacement of hydrogen by a substituent has no sizable effect. These observations have been tentatively interpreted in terms of the imposition of steric constraints by substituents at the α and β carbons on the influence of a β substituent, and receive some support by the apparent insensitivity to the electronic nature of the substituent; thus, $\beta_{\mathrm{CH_3}} = -9.7$ ppm, $\beta_{\mathrm{OH}} = -11.6$ ppm.[15,16] If the steric argument is also important for hydrazines, replacing a hydrogen by methyl must give a larger negative β effect than for carbon compounds through having a smaller elongation of the N–N bond when methyl is added.[7b] This seems reasonable in view of the prevalent opinion[17] that the steric requirements of lone pairs are less than those of hydrogen. That the β effect is larger in the change from amine to hydrazine is also in accord with expectations based on steric effects. However, additional experimental work is needed to corroborate the parallelisms so far found.

It is interesting that, while the ^{13}C chemical shifts of the methylhydrazines (Table III) do not seem to correlate in any special way with the ^{15}N shifts, it is possible to derive β- and γ-methyl substituent effects as for hydrocarbons. The observed β shift of -7.8 ppm and γ shift of $+5.3$ ppm are both quite in accord with the results for hydrocarbons and alcohols,[7] so that it is clear that intervention of a nitrogen atom has little influence on the magnitude of the carbon β and γ shifts. That the γ effect is relatively large can be understood in terms of the recently adduced, preferred conformations of hydrazine and, probably, substituted hydrazines,[18] in which the dihedral angle between the lone-pair orbitals is thought to be about 90° (**1**). In such a conformation, there should be significant methyl–methyl interactions.



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The small collection of data of phenylhydrazines prevents much in the way of definite conclusions about the factors which influence the shifts for these compounds. For phenylhydrazine itself, the α shift is greater than the β shift, presumably because of delocalization of the nitrogen electrons,[13] which has analogy in the 64-ppm difference in ^{15}N shift between ammonia and aniline.[2] For the β shift, we can conclude only that the influence of aryl substitution does not appear to be as additive as for methyl substitution.

Experimental Section

Spectra were determined with a Varian DFS-60 spectrometer operating at 6.07 and 15.08 MHz for ^{15}N and ^{13}C, respectively; samples were distilled from potassium hydroxide as previously described.[2] 1,1,2-Trimethyl- and 1,1,2,2-tetramethylhydrazine were synthesized by the method of Beltrami and Bissell;[19] the pmr spectrum of tetramethylhydrazine showed about 30% contamination with trimethylhydrazine, from which it could not be separated. All of the other compounds were commercial materials.

1,1-Dimethylhydrazine-2-^{15}N was synthesized in 60% overall yield (based on enriched sodium nitrite) as previously described.[20] Because of the small amount of material available, the usual procedure for obtaining spectra was reversed, and the sample was contained in a 5-mm o.d. sample tube fixed in a 10-mm tube by concentric rings. No external reference was used for simultaneous measurement, and the chemical shift was estimated by reading the resonance frequency directly from the instrument digital programmer. Because of the stability of the frequency synthesizer, this procedure is accurate at least to 1–2 ppm, enough to positively distinguish between the two nitrogen nuclei. Under these conditions, the resonance of N-1 in natural abundance could not be observed.

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(14) W. M. Litchman, M. Alei, Jr., and A. E. Florin, *J. Amer. Chem. Soc.*, **91**, 6574 (1969).

(15) J. B. Grutzner, M. Jautelat, J. B. Dence, R. A. Smith, and J. D. Roberts, *ibid.*, **92**, 7107 (1970).

(16) In unpublished work by C. Marzin and D. E. Dorman, an electrical component has been found to the β effect in *n*-butyl derivatives which is generally *upfield* as the substituent becomes more electron attracting; *cf.* J. D. Roberts *Pure Appl. Chem., Suppl.*, in press. This kind of electrical effect has also been observed for amines[2] and is quite obvious in the upfield change in the 3,5-carbon resonance on going from piperidines to piperidinium ions by addition of a proton; see W. O. Crain, Jr., W. C. Wildman, and J. D. Roberts, *J. Amer. Chem. Soc.*, **93**, 990 (1971).

(17) (a) J. B. Lambert and R. G. Keske, *ibid.*, **88**, 621 (1966); (b) J. B. Lambert, R. G. Keske, R. E. Carhart, and A. P. Jovanovich, *ibid.*, **89**, 3761 (1967); (c) J. B. Lambert, D. S. Bailey, and B. F. Michel, *Tetrahedron Lett.*, 691 (1970).

(18) (a) J. E. Anderson, D. L. Griffith, and J. D. Roberts, *J. Amer. Chem. Soc.*, **91**, 637 (1969), and references contained therein; (b) M. J. S. Dewar and W. B. Jennings, *Tetrahedron Lett.*, 339 (1970).

(19) R. T. Beltrami and E. R. Bissell, *J. Amer. Chem. Soc.*, **78**, 2467 (1956).

(20) R. L. Lichter and J. D. Roberts, *ibid.*, **93**, 5218 (1971).