# $^{14}$N NMR Studies on Cyclic Nitramines. Correlations of Chemical Shifts with Nitrogen Partial Atomic Charge and π-Orbital Overlap

Michael Kony,* Ian J. Dagley, and D. Ralph Leslie

*Aeronautical and Maritime Research Laboratory (AMRL)-DSTO, P. O. Box 4331, Melbourne, Victoria 3001, Australia*

*Received March 4, 1994*[®]

The $^{14}$N chemical shifts of nitro groups in the NMR spectra of cyclic nitramines have been correlated with their electronic environment in the minimum energy conformers determined using AM1 semiempirical molecular orbital calculations. Both the Mulliken population-derived atomic charge at the nitro nitrogen and the extent of π-orbital overlap influence the observed shifts. Equations useful for predicting the shifts of nitro groups bonded to either the imino group of cyclic guanidines or secondary amines and ureas in heterocycles have been derived and are discussed.

New high nitrogen heterocycles containing nitro groups bonded to nitrogen (nitramines) are of continuing interest as energetic compounds.[1-3] The $^{14}$N NMR spectra of nitramines show comparatively narrow signals for the nitro groups since these possess a high molecular point group symmetry and consequently have small electric field gradients.[4,5] Although these spectra are a readily acquired and potentially useful source of additional structural information, they have seldom been recorded or used in structural assignments. This is principally because the relationship between shift and structure of cyclic nitramines is not well defined,[5] with an earlier investigation only establishing that chemical shifts are influenced, in a qualitative way, by changes in the electronegativity of neighboring groups.[6]

The nitrogen chemical shifts of compounds are largely determined by the paramagnetic term of Ramsey's expression[7] for the screening constant,[8] but its direct calculation is problematic because of the large number of assumptions that must be made.[9] Consequently empirical correlations of shifts with a range of parameters (including substituent effects and calculated π-electron density at the nitrogen) that affect this expression have been established.[10] For classes of compounds with nitro groups bonded to carbon, shifts have been correlated with Taft inductive constants[11,12] and energy absorptions in IR spectra[13] or predicted using simple empirical rules where contributions to shifts from groups are additive.[14]

In this study we have investigated correlations between $^{14}$N chemical shifts and structure for a wide range of cyclic nitramines; compounds containing nitro groups attached to secondary amines (secondary nitramines), ureas (nitroureas) and the imino group of guanidines (nitroguanidines) in cyclic structures have been examined. Since the electronic environment around the nitrogen of the nitro group was expected to influence the observed chemical shifts,[8] correlations using related parameters for the minimum energy conformers determined using Austin Model 1 (AM1)[15] semiempirical molecular orbital calculations were examined.

The $^{14}$N NMR spectral data (chemical shift, line width) recorded for the cyclic nitramines **1**–**19** (Figure 1) in DMSO are included in Tables 1 and 2. The observed chemical shifts are shielded relative to nitromethane, which was the external reference, and have defined ranges of resonances for the different types of nitramine groups: −2 to −11 ppm for nitroguanidines, −24 to −34 ppm for secondary nitramines, and −40 to −48 ppm for nitroureas. The observed line widths vary from 29 to 468 Hz with broadening attributable to increases in rotational correlation times as a result of molecular volume increases[27] and/or increases in the electric field gradient as the positive charge on the nitrogen of the nitro group decreases.[5]

The previously observed trend for nitro resonances to shift to higher field as the electronegativity of adjacent groups increases[6] is evident when some of the chemical

---

[®] Abstract published in *Advance ACS Abstracts,* August 15, 1994.

[1] Archibald, T. G.; Gilardi, R.; Baum, K; George, C. *J. Org Chem.* **1990**, *55*, 2920.

[2] Vedachalam, M.; Ramakrishnan, V. T.; Boyer, J. H.; Dagley, I. J.; Nelson, K. A.; Adolph, H. G.; Gilardi, R.; George, C.; Flippen-Anderson, J. L. *J. Org. Chem.* **1991**, *56*, 3413.

[3] Baum, K.; Nguyen, N. V. *J. Org. Chem.* **1992**, *57*, 3026.

[4] Kintzinger, J. P.; Lehn, J. M.; Williams, R. L. *Mol. Phys.* **1969**, *17*,135.

[5] *Nitrogen NMR*; Witanowski, M., Webb, G. A., Eds.; Plenum Press: London, 1973; Chapters 3 and/or 4.

[6] Bulusu, S.; Axenrod, T.; Autera, J. R. *Org. Magn. Reson.* **1981**, *16*, 52.

[7] Ramsey, N. F. *Phys. Rev.* **1952**, *86*, 243.

[8] Mooney, E. F.; Winson, P. H. In *Annual Review of NMR Spectroscopy*; Mooney, E. F., Ed.; Academic Press: London, 1969; Vol. 2, p 125.

[9] Witanowski, M.; Webb, G. A. In *Annual Review of NMR Spectroscopy*; Mooney, E. F., Ed.; Academic Press: London, 1972; Vol. 5, p 395.

[10] Martin, G. J.; Martin, M. L.; Gouesnard, J. *$^{15}$N-NMR Spectroscopy*; Springer-Verlag: Berlin,1981; pp 83–107.

[11] Eremenko, L. T.; Borisenko, A. A.; Petrov, S. I.; Andronov, V. F. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1968**, *2*, 428.

[12] Magi, M. Y.; Erashko, V. I.; Shevelev, S. A.; Fainzilberg, A. A. *Eesti NSV Tead. Akad. Toim., Keem.-Geol.* **1971**, *20*, 297.

[13] Eremenko, L. T.; Borisenko, A. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1968**, *3*, 675.

[14] Witanowski, M.; Stefaniak, L. *J. Chem. Soc. B* **1967**, 1061.

[15] Dewar, M. J. S., Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

[16] Goodman, L. *J. Am. Chem. Soc.* **1953**, *75*, 3019.

[17] Urbanski, T. *Chemistry and Technology of Explosives*; Pergamon: New York, 1967; Vol. 3, p 19.

[18] Bergman, H.; Ostmaark, H.; Langlet, A. *Paper Summaries Tenth Symposium (International) on Detonation,* NSWCDD/MP-92/456, Naval Surface Warfare Center, Silver Spring, MD, 1993; p 302.

[19] Huang, D.; Rindone, R. R. U.S. Patent 4 937 340, 1990.

[20] Dagley, I. J.; Flippen-Anderson, J. L. Unpublished results.

[21] Ramakrishnan, V. T.; Vedachalam, M.; Boyer, J. H. *Heteroatom Chem.* **1991**, *2*, 669.

[22] Li, W.; Hua, G.; Chen, M. *Proceedings of the Symposium on Pyrotechnics and Explosives*; October 1987, Beijing, China; China Academic Publishers: Beijing, 1987.

[23] Stinecipher, M. M.; Stretz, L. A. *Eighth Symposium (International) on Detonation,* NSWC MP 86–194, Naval Surface Warfare Center, Silver Spring, MD, 1986; p 351.

[24] Dinwoodie, A. H.; Cormack, J. M. Brit. Patent 1 103 285, 1968.

[25] McKay, A. F.; Wright, G. F. *J. Am. Chem. Soc.* **1948**, *70*, 430.

[26] Kony, M.; Dagley, I. J. *Heterocycles* **1994**, *38*, 595.

[27] Boere, R. T.; Kidd, R. G. *Annu. Rep. NMR Spectrosc.* **1983**, *13*, 319.

0022-3263/94/1959-5623$04.50/0

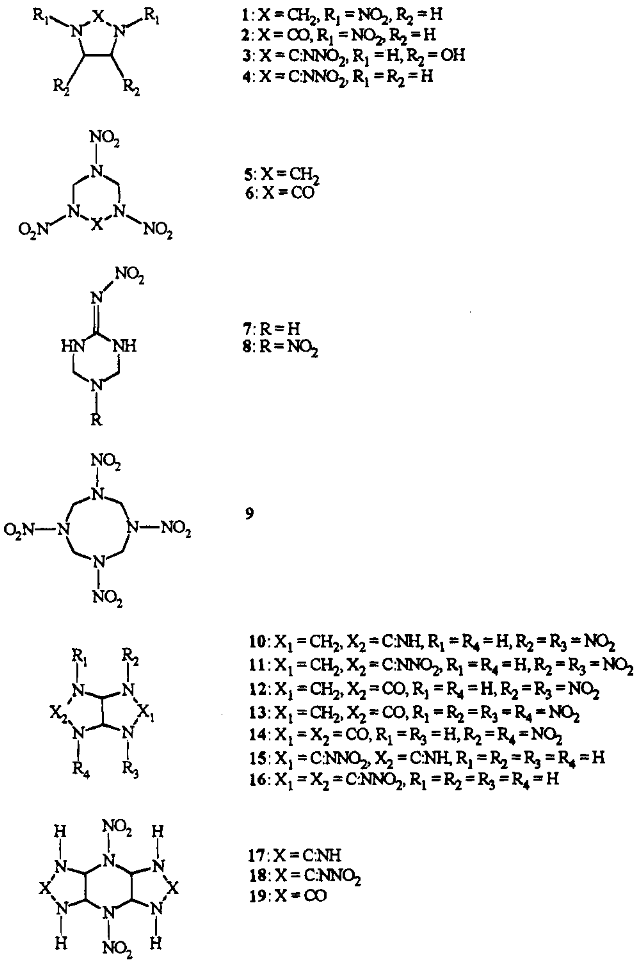


**Figure 1.** Structures of the cyclic nitramines examined in this study.

shifts for the monocyclic compounds containing secondary nitramines and nitroureas are compared (Table 1). Thus substitution of the methylene group (X = $CH_2$) in **1** and **5** with the more electron-withdrawing carbonyl group (**2** and **6**) induces an upfield shift of 14.2 and 22.0 ppm, respectively. Differences in the electronegativity of the adjacent groups affect the charge at the nitrogen of the nitro group. The Mulliken population-derived atomic charge ($Q_N$) at each of these sites were determined for the geometry-optimized (minimum energy, minimal atomic force) conformers of the cyclic nitramines **1–19** using AM1 calculations and are shown in Tables 1 and 2. A simple linear correlation between chemical shift and $Q_N$ was computed for the combined secondary nitramine and nitrourea data; however, the coefficient of correlation between the experimental and calculated chemical shifts was only fair (0.86).

**Table 1. Comparison of the Calculated and Observed Chemical Shifts for Secondary Nitramine and Nitrourea Groups in Various Cyclic Nitramines**[a]

| compound | $Q_N$[b] | $\theta$[b] | $\delta_{exp}$ | $\Delta$ ($\delta_{exp} - \delta_{cal}$) | ref[c] |
|---|---|---|---|---|---|
| **1** | 0.589 | 47.15 | −26.8 (29) | −1.3 | 16 |
| **2** | 0.681 | 0.08 | −41.0 (44) | −0.7 | 17 |
| **5** | 0.609 | 36.23 | −24.0 (48) | 1.0 | |
| **6**[d] | 0.601 | 41.80 | −30.6 (87) | −4.4 | 18 |
| **6**[d,e] | 0.671 | 7.00 | −46.0 (66) | −9.6 | |
| **8**[d] | 0.596 | 45.20 | −23.1 (164) | 3.9 | 19 |
| **9** | 0.640 | 20.80 | −26.9 (85) | 0.8 | |
| **10**·$HNO_3$ | 0.616 | 37.95 | −28.8 (317) | 1.0 | 20 |
| **11** | 0.610 | 39.38 | −29.0 (349)[f] | −0.7 | 20 |
| **12** | 0.608 | 39.94 | −29.1 (190) | −1.3 | 21 |
| **13** | 0.612 | 40.42 | −32.3 (240)[f] | −2.2 | 22 |
| **13**[e] | 0.680 | 23.25 | −48.3 (204)[f] | −0.2 | |
| **14** | 0.679 | 2.93 | −39.7 (273) | −0.2 | 23 |
| **17**[g] | 0.620[h] | 41.41[h] | −34.0[i] | 0.8 | 20 |
| **18**[g] | 0.619 | 39.63 | −31.6 (220)[f] | 1.1 | 20 |
| **19**[g] | 0.615 | 41.01 | −30.2 (202) | 1.9 | 2 |

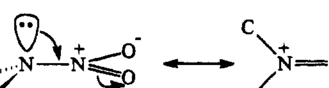
[a] Spectra were recorded using DMSO solutions (0.2 M) at 25 °C; chemical shifts are given in ppm relative to external nitromethane; line widths at half-height are given in parentheses (Hz); calculations were performed using eq 1. [b] Where two or more nitramine groups of the same type are in a molecule, these values represent an average. [c] Methods used to prepare compounds. [d] The calculated parameters ($Q_N$ and $\theta$) and experimental data for these groups were excluded in deriving eq 1. [e] Nitrourea group. [f] Line widths have been estimated. [g] These compounds all have *cis-syn-cis* stereochemistry (i.e. all have methine protons on the same face of the molecule). [h] Two low-energy conformers with a small energy difference (0.367 kcal/mol) exist. In both cases the piperazine ring is in the boat conformation with equatorial CN bonds; the higher energy conformer ($Q_N$ = 0.608, $\theta$ = 39.91) has both nitro groups in axial positions and the other ($Q_N$ = 0.626, $\theta$ = 42.22) has one axial and one equatorial nitro group. The calculated ratio of the conformers (0.35:0.65) was used to determine the weighted values for $Q_N$ and $\theta$ that are quoted in the table. [i] The chemical shift has been averaged from the following: **17**·2HCl, −34.4 ppm (468 Hz); **17**·2$HNO_3$, −33.6 ppm (380 Hz).

**Table 2. Comparison of the Calculated and Observed Chemical Shifts for Nitrimine Groups in Various Cyclic Nitramines**[a]

| compound | $Q_N$ | $\phi$ | α | $\delta_{exp}$ | $\Delta$ ($\delta_{exp} - \delta_{cal}$) | ref[b] |
|---|---|---|---|---|---|---|
| **3** | 0.600 | 15.05 | 11.19 | −2.1 (173) | 0.3 | 24 |
| **4** | 0.601 | 12.40 | 10.91 | −7.4 (85) | −0.7 | 25 |
| **7**·HCl | 0.603 | 8.20 | 5.31 | −8.1 (232) | 0.2 | 19 |
| **8**[c] | 0.607 | 1.47 | 3.76 | −8.9 (134) | 4.7 | 19 |
| **11** | 0.600 | 7.92 | 6.15 | −8.8 (230)[d] | −1.4 | 20 |
| **15** | 0.599 | 12.14 | 7.75 | −2.7[e] | 0.4 | 26 |
| **16** | 0.600[f] | 8.22[f] | 7.85 | −7.5 (307) | 0.7 | 26 |
| **18** | 0.601[f] | 3.53[f] | 7.63 | −11.3 (270)[d] | 0.4 | 20 |

[a] Spectra were recorded using DMSO solutions (0.2 M) at 25 °C; chemical shifts are given in ppm relative to external nitromethane; line widths at half-height are given in parentheses (Hz); calculations were performed using eq 2. [b] Methods used to prepare compounds. [c] The calculated parameters ($Q_N$, α, and $\theta$) and experimental data for this group were excluded in deriving eq 2. [d] Line widths have been estimated. [e] The chemical shift has been averaged from the following: **15**·HCl, −2.0 ppm (346 Hz); **15**·$HNO_3$, −3.3 ppm (200 Hz). [f] These are averaged values for the two nitroguanidine groups.

The nitrogen NMR chemical shifts in amides are determined in part by the π-bond order between the nitrogen and the adjacent $sp^2$ hybridized carbon.[28] A feature of the structure of nitramines is the large range (0–60°) of out-of-plane bending angles ($\theta$) for the amino group (angle between the C–N–C plane and the N–N bond) observed in crystallographic studies.[29] This angle can be viewed as a measure of the extent that hybridization at the amine nitrogen varies between $sp^2$ (0°) and $sp^3$,[2] with smaller angles indicating a greater potential for overlap of π-orbitals on the adjacent nitrogens.



---

(28) Martin, G. J.; Gouesnard, J. P.; Dorie, J.; Rabiller, C.; Martin, M. L. *J. Am. Chem. Soc.* **1977**, *99*, 1381.

Using $\cos^2\theta$ as a measure of the extent of $\pi$-orbital overlap, a multiple regression analysis was performed to give the relationship (eq 1) between the combined experimental chemical shift data for the secondary nitramines and nitroureas, except for those in compounds **6** and **8** (which are discussed separately below), and the calculated $Q_N$ and $\cos^2\theta$ values for the lowest energy conformers.

$$\delta^{14}\mathrm{N} = 226.86 - 470.19\,Q_\mathrm{N} + 53.06\cos^2\theta \quad (1)$$

The coefficient of correlation between these experimental chemical shifts and those calculated using eq 1 is 0.98, and the root mean square (RMS) of the difference between calculated and experimental values (1.2 ppm) compares favorably with the experimental error (±1 ppm). The magnitude of the coefficients for the $Q_N$ and $\cos^2\theta$ terms in eq 1, and the observed range of values for these parameters, indicate that both charge and the extent of $\pi$-orbital overlap contribute significantly to chemical shift.[30]

The chemical shifts calculated for compounds **6** and **8**, obtained by substituting their calculated values for $Q_N$ and $\theta$ into eq 1, are in poor agreement with the experimental data (Table 1). These compounds have a common structural feature not present in any of the other nitramines of this study, a six-membered ring that contains an exocyclic double bond opposite to a secondary nitramine. There is some indication that for compounds of this type AM1 calculations do not identify the lowest energy conformer. The crystal structure of **6** provides larger values of $\theta$ for the secondary nitramine (44.6°) and nitrourea (25.1°).[31] Substitution of these values into eq 1 gives much better predictions of chemical shifts with differences ($\delta_\mathrm{exp} - \delta_\mathrm{cal}$) of $-1.8$ and $-0.9$ ppm for the secondary nitramine and nitrourea, respectively.

For some compounds additional interactions not considered in this correlation may contribute to the experimental chemical shift. The comparatively large chemical shift difference ($\delta_\mathrm{exp} - \delta_\mathrm{cal} = -2.2$ ppm) observed for the secondary nitramines of the bicyclic compound **13** may arise because of the strong steric interactions with the *peri* nitros of the nitrourea group, which further reduce the extent of $\pi$-orbital overlap in the secondary nitramine groups. The AM1 calculations show that, of the all the nitramine groups considered, these have the largest out-of-plane bending angle ($\beta = 6.8°$) for the nitro group (angle between the O−N−O plane and the N−N bond) and nitro twist (dihedral angle between the amine $\pi$-orbitals, or lone pair, and the $\pi$-orbitals at the nitrogen of the nitro group, 15.5°). In this case, by only considering $\theta$, the extent of $\pi$-orbital overlap is overestimated and the calculated chemical shift is therefore too positive.

The nitroguanidines resonate at lower fields than the secondary amines. This is a result of decreased $NO_2$ shielding caused by the presence of $\pi$-conjugation between the *N*-nitro group and the rest of the molecule.[32] As is the case with secondary nitramines and nitroureas, the chemical shift will also be influenced by the extent of $\pi$-orbital overlap in the N−N bond. This is reduced by rotation about the bond (nitro twist) between the nitro and this sp$^2$ hybridized amine. The dihedral angles between the $\pi$-orbitals of the C=N bond ($\alpha$) and the N−N bond ($\phi$) were calculated from the two NC=NN and two C=N−NO torsion angles in the lowest energy conformer for each cyclic nitroguanidine; $\cos^2\alpha$ and $\cos^2\phi$ were then used to indicate the extent of $\pi$-orbital overlap in these bonds.

A multiple regression analysis was performed for data on all the nitroguanidines groups (Table 2), except for **8**, to give the relationship (eq 2) between $\cos^2\alpha$, $\cos^2\phi$, $Q_N$, and the experimental chemical shift data. This equation provides a way of predicting chemical shifts of cyclic nitroguanidines in DMSO; the coefficient of correlation between the predicted and observed chemical shifts is 0.97 (RMS = 0.7 ppm), with the data for **8** being excluded for the reasons discussed previously in this paper. Again both the charge on the nitrogen atom and the extent of $\pi$-orbital overlap are significant in determining chemical shift.[33]

$$\delta^{14}\mathrm{N} = 356.18 - 557.10\,Q_\mathrm{N} + 156.38\cos^2\alpha - 187.45\cos^2\phi \quad (2)$$

Equations 1 and 2 can generally predict the $^{14}$N chemical shifts for cyclic nitramines in DMSO with sufficient accuracy to be used as tools to aid structural assignment. In both equations, the shielding of the $^{14}$N nucleus increases as electron-withdrawing inductive effects increase (i.e. chemical shifts become more negative). The same trend has been previously noted for $^{14}$N chemical shifts of nitroalkanes.[11,34,35] The empirical dependence of chemical shift on charge opposes that predicted by Ramsey's expression[7] and has been attributed to the domination of the direct effect of charge by concomitant changes in either the electronic excitation energy[35] or orbital asymmetry terms of the expression.[34,36]

## Experimental Section

**CAUTION!** Compounds **1−19** are known or potential explosives and should be handled with the appropriate precautions.

Compounds **5** and **9** were obtained from commercial sources. The other cyclic nitramines were prepared by literature methods which are cited in Tables 1 and 2. $^{14}$N NMR spectra were recorded at 21.689 MHz using a Bruker AM 300 spectrometer. The compounds were examined as 0.2 M solutions in DMSO (AR grade) contained in 5 mm sample tubes maintained at 25 °C. Spectral data were collected in the unlocked mode. Chemical shifts were referenced to external nitromethane and were recorded using a spectral width of 20 kHz with a digital resolution of 2.5 Hz. To minimize acoustic ringing a $\pi/2$-$\tau$-$\pi$-$2\tau$-acquire pulse sequence was used with $\tau$ equal to 50 ms. The number of transients required to obtain a good signal to noise ratio changed with line width and varied

---

[29] Gilardi, R. D.; Karle, J. In *Chemistry of Energetic Compounds;* Olah, G. A., Squire, D. R., Eds.; Academic Press: San Diego, 1991; pp 6−10.

[30] A correlation using $Q_N$ and bond order (reviewer's suggestion) was also examined. The N−$NO_2$ bond orders cannot be obtained from HyperChem but were calculated from the internal coordinates of the minimum energy structures using MOPAC, version 6.00. In this case a multiple regression analysis gave a poorer coefficient of correlation (0.92) between the calculated and experimental chemical shifts.

[31] Gilardi, R.; Flippen-Anderson, J. L.; George, C. *Acta Crystallogr.* **1990**, *C46*, 706.

[32] Witanowski, M.; Stefaniak, L.; Webb, G. A. *Annu. Rep. NMR Spectrosc.* **1986**, *18*, 164.

[33] A correlation using $Q_N$ and both N−$NO_2$ and C=N bond orders (reviewer's suggestion) gave a comparatively poor coefficient of correlation (0.82).

[34] Witanowski, M.; Stefaniak, L.; Webb, G. A. *J. Chem. Soc. B* **1967**, 1065.

[35] Mason, J. B.; van Bronswijk, W. *J. Chem. Soc. A* **1970**, 1763.

[36] Witanowski, M. *J. Am. Chem. Soc.* **1968**, *90*, 5683.

from 2000 to 30000. The estimated error in chemical shifts for compounds with narrow (<200 Hz) and broad (>200 Hz) line widths are to 0.5 and 1.0 ppm, respectively. Linewidths reported here are accurate to ±5 Hz and were typically halved when the solutions were heated to 60 °C . Where resonances partially overlap, the line widths were estimated from spectral data obtained at 60 °C.

The HyperChem (release 2) computer program from Autodesk, Inc., was used to perform AM1 calculations to determine the geometry-optimized conformer in vacuo and the Mulliken atomic charge on the nitrogen atoms in the nitro groups in each cyclic nitramine. Calculations used the unrestricted Hartree–Fock method and geometry optimizations were performed using the Polak–Ribiere algorithm.[37]

**Supplementary Material Available:** Total energy, the total energy gradient calculated as a root mean square value, and the binding energy for each of the energy minimized structures (1 page). This information is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

---

[37] Polak, E. *Computational Methods in Optimization*; Academic Press: New York, 1971.