Structure of Nitroguanidine: Nitroamine or Nitroimine? New NMR Evidence from ^{15}N-Labeled Sample and ^{15}N Spin Coupling Constants

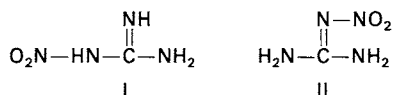S. Bulusu,* R. L. Dudley and J. R. Autera

Energetics and Warheads Division, Armament Engineering Directorate, US Army Armament Research Development and Engineering Center, Dover, New Jersey 07801-5001, USA

The structure of nitroguanidine was investigated by the application of ^{15}N, ^{1}H and ^{13}C NMR spectroscopy of a fully ^{15}N-labeled sample in DMSO-d_6 and DMF solutions and by ^{15}N CP/MAS NMR in the solid state. These spectra confirm the nitroimine structure which has been suggested by other investigations in recent years, and do not lend any support to the commonly used nitroamine structure or for a tautomeric equilibrium with the nitroamine. Useful ^{15}N spin coupling constants to the ^{1}H and ^{13}C nuclei in the assigned structure are reported.

INTRODUCTION

Nitroguanidine is a secondary high explosive used in triple-base gun propellants and in slow-burning rocket propellants.[1] It is commonly represented[1,2] by the structure I, in spite of overwhelming evidence in favor of structure II gathered by a variety of techniques. Thiele[3] proposed structure I originally on the basis of chemical properties, but Barton et al.[4] and Kirkwood and Wright[5] decided in favor of the symmetrical nitrimino structure II from potentiometric titrations and other chemical evidence. Much of this early work has been reviewed in the literature.[6,7] Since then, the structure of nitroguanidine has attracted other investigations by a number of techniques: x-ray crystallography,[8] neutron powder diffraction,[9] infrared,[10] ultraviolet,[12] x-ray photoelectron[13] and proton magnetic resonance spectroscopy,[14] polarographic studies[12,15] and dipole moment measurements.[12] Most of these techniques dealt with the structure in the crystalline state and all of them supported the correctness of structure II. There has been an implicit assumption that in solution both structures are in equilibrium.[16] While this may be true in acidic or basic aqueous solutions, it is not clear whether it is the case in neutral organic solutions. Nitroguanidine is insoluble in most organic solvents except dimethyl sulfoxide (DMSO) and N,N-dimethylformamide (DMF), in which it is sparingly soluble.

The purpose of the work described here was primarily to use ^{15}N NMR of fully ^{15}N-enriched nitroguanidine, both in the solid state and in solution, to distinguish between the two proposed structures. In addition, the ^{1}H and ^{13}C spectra in solution, which are consistent with

the conclusions from the ^{15}N spectra, are presented. It is of obvious importance to distinguish between the two alternative structures of nitroguanidine and other guanidine derivatives in order to rationalize their reactivity and physico-chemical properties such as low acidity, dissociation constants, dipole moments and infrared absorption spectra.

EXPERIMENTAL

Synthesis of [^{15}N$_4$] Nitroguanidine

An intimate mixture of ^{15}NH$_4$^{15}NO$_3$ (5.2 g) and urea (^{15}NH$_2$CO^{15}NH$_2$) (4.04 g) was heated to 190 °C with stirring and to the melt were added 3.3 g of microporous silica bead catalyst (Product HSC-534, Air Products and Chemicals, Marcus Hook, PA, USA) which had been previously dried in an oven for 2 h at 200 °C. The heating was continued for a further 1.25 h at 190 ± 5 °C. After cooling, the mixture was taken up in approximately 300 ml of water and the aqueous extract was filtered and evaporated to yield 6.68 g of guanidine nitrate.

The above guanidine nitrate was then added with stirring over a 30-min period to 5 ml of 98% sulfuric acid maintained at 10 ± 1 °C. The stirring was continued for an additional 30 min at 10 °C, following which the mixture was poured over crushed ice. The precipitate of nitroguanidine obtained was collected, washed with approximately 30 ml of ice–water and dried (1.43 g). Recrystallization from water gave 1.21 g of sample of m.p. 233 °C (lit. m.p., 232 °C). Mass spectrometric analysis showed the molecular ion at m/e 108 was greater than 95%.

NMR spectra

All the NMR spectra were obtained on a Varian XL-200 FT-NMR spectrometer system, equipped with separate

---

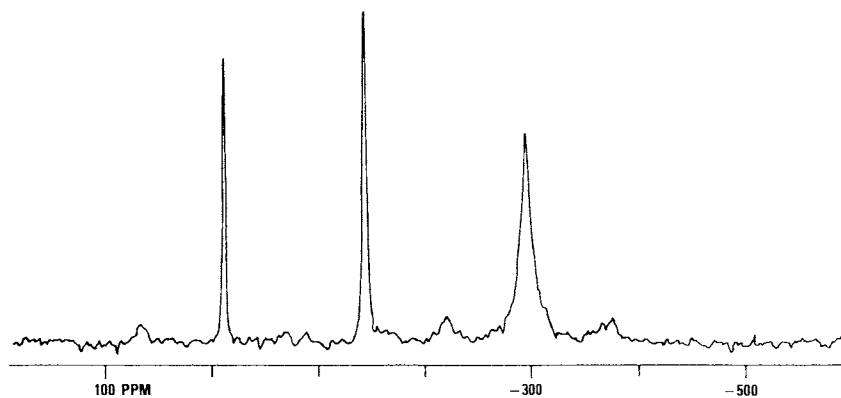* Author to whom correspondence should be addressed.

Figure 1. Nitrogen-15 CP/MAS NMR spectrum of crystalline [^{15}N$_4$]nitroguanidine. Contact time, 4 ms; pulse repetition rate, 5 s; sample spinning speed, 1.6 Hz; 10 000 transients. $\delta[^{15}N(O_2)] = -7$, $\delta(^{15}N) = -140$, and $\delta[^{15}N(H_2)] = -290$ ppm, respectively, measured from $^{15}NO_3^-$ ($\delta = 0$ ppm).

broad band and proton probes for solution spectra and an independent ^{15}N CP/MAS probe for solid sample work. The ^{1}H decoupling power used for obtaining the CP/MAS NMR spectrum was approximately 100 W. The solution spectra (^{15}N and ^{13}C) were run with approximately 15 W decoupling power. The ^{15}N CP/MAS spectrum (Fig. 1) of nitroguanidine was referenced with a ^{15}NH$_4$^{15}NO$_3$ spectrum obtained under identical conditions. The ^{15}N spectrum in solution (DMSO-d_6) was referenced by prior acquisition of a spectrum of ^{15}NH$_4$^{15}NO$_3$ in aqueous solution with a D$_2$O lock. In both cases the chemical shifts were measured from ^{15}NO$_3^-$ (= 0 ppm). Other pertinent acquisition parameters are indicated in the captions of Figs 1–4.

RESULTS AND DISCUSSION

Figure 1 is the ^{15}N CP/MAS spectrum of crystalline [^{15}N$_4$]nitroguanidine, showing three lines. If the unsymmetrical structure I were to be the only possible structure of nitroguanidine, one would expect a four-line ^{15}N spectrum. The symmetrical structure II, on the other hand, should give a three-line spectrum as indeed is seen in Fig. 1. The line widths in this spectrum obscure any ^{15}N–^{15}N couplings, which are generally small.

The ^{15}N spectra of [^{15}N$_4$]nitroguanidine in DMSO-d_6 solution are shown in Fig. 2. Figure 2a and b represent the ^{1}H coupled and the ^{1}H noise decoupled spectra,
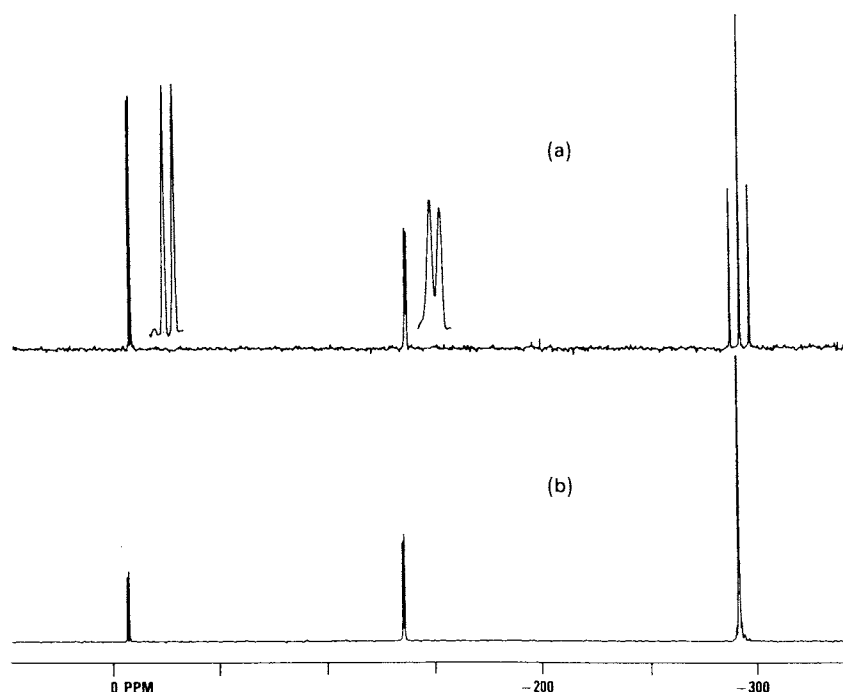

Figure 2. ^{15}N NMR (20.272 MHz) spectra of [^{15}N$_4$]nitroguanidine in DMSO-d_6 solution. Pulse width, 10 μs; delay time, 60 s; 100 scans. (a) ^{1}H coupled spectrum; (b) ^{1}H noise decoupled spectrum. $\delta[^{15}N(O_2)] = -6$, $\delta(^{15}N=) = -135$ and $\delta[^{15}N(H_2)] = -293$, ppm respectively, from $^{15}NO_3^-$. $^1J(^{15}N^{15}N) = 15.4$ Hz, $^1J(^{15}N^1H) = 91.8$ Hz.

Figure 3. ^{1}H NMR spectrum at 200.068 M Hz of [^{15}N$_4$]nitroguanidine in DMSO-d_6 solution. $^1J(^{15}$N^{1}H)$=91.8$ Hz. $\delta(^1$H)$=7.44$ ppm.

either structure I was invalid or that it was in tautomeric equilibrium with structure II, as shown below.

respectively. These spectra are analogous to the solid-state spectrum showing three different ^{15}N absorptions, as required by the symmetrical structure II. The nitroimino nitrogens exhibit spin coupling between each other in both Fig. 2a and b, whereas the amine nitrogen coupling to the hydrogens is evident in Fig. 2a. The same coupling can also be seen in the ^{1}H spectrum (Fig. 3), which again suggests the presence of a single set of protons in the structure as required by structure II. Structure I, on the other hand, would have resulted in a complicated spectrum showing three non-equivalent protons, each coupled to a ^{15}N nucleus. Hence the ^{15}N and ^{1}H spectra in Figs 1, 2 and 3, taken together, clearly favor the symmetrical structure II for nitroguanidine, as previously suggested by a variety of other techniques and in particular by x-ray and neutron diffraction studies.

Possible role of tautomeric exchange between structures I and II

The fact that a three-line ^{15}N spectrum was obtained for nitroguanidine in DMSO solution at room temperature (or slightly above owing to the r.f. heating from the ^{1}H decoupler used for the spectrum in Fig. 2b) meant that

Controlling the temperature of the DMSO solution at 18 °C during the spectral acquisition made no difference. When the spectrum was re-run in a more dilute solution in DMF at −47 °C the same three-line spectrum was obtained, except for the solvent effect on the chemical shifts: $\delta[^{15}$N(O$_2$)]$=-7$, $\delta[^{15}$N(NO$_2$)]$=-137$ and $\delta[^{15}$N(H$_2$)]$=-297$ ppm. Further, the line width of the upfield ^{15}N(H$_2$) peak remained unchanged (7 Hz) between room temperature and −47 °C. It must be concluded from these observations that the tautomeric exchange was too rapid even at −47 °C for the two structures to be resolvable by NMR or, more likely, that the true structure of nitroguanidine is predominantly II. The latter possibility was also strengthened by the observation of only three lines in the CP/MAS solid-state spectrum (^{15}N). The line broadening of the ^{15}NH$_2$ absorption in this spectrum was probably due to a $T_{1\rho}$ or T_2 effect. The proton coupled ^{15}N spectrum (Fig. 2a) and the ^{1}H spectrum (Fig. 3) of [^{15}N$_4$]nitroguanidine also correspond exactly to structure II, and exhibit identical coupling constants, $^1J(^{15}$N^{1}H)$=91.8$ Hz. Hence the possible existence of a tautomeric exchange of structure II with the alternative structure I was not supported by experimental evidence even at the low temperature tried.

Structure II, which may be expected to exhibit asymmetry of the two NH$_2$ groups, probably retains some
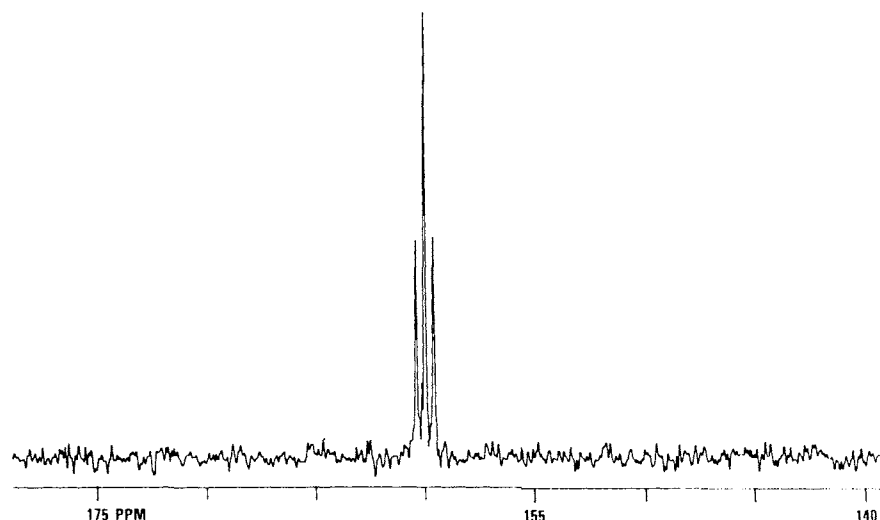

Figure 4. ^{13}C NMR (50.311 M Hz) spectrum of [^{15}N$_4$]nitroguanidine in DMSO-d_6 solution. Pulse width, 6 μs; pulse repetition rate, 2 s; 5000 scans. $^1J(^{15}$N^{13}C)$=19$ Hz. $\delta(^{13}$C)$=160$ ppm from TMS.

Table 1. ^{15}N spin coupling constants from the NMR spectra of ^{15}N-labeled nitroguanidine based on structure II

Coupled spins	Magnitudes of coupling constants	Analogy with literature		
		structure	^1J (Hz)	Ref.
$^1J(^{15}N^{15}N)$	15.4 Hz (Fig. 2)	H_5C_2O \ $C{=}^{15}N{-}^{15}NO_2$ / $(CH_3)_3SiO$	14 ± 1.2	17 (p. 300)
$^1J(^{15}N^1H)$	91.8 Hz (Figs 2a and 3)	$^{15}NH_2{-}\overset{\overset{O}{\|\|}}{C}{-}^{15}NH_2$ (in DMSO)	89 ± 1.0	17 (p. 238)
		$HCO^{15}NH_2$	92	22
$^1J[^{13}C^{15}N(H_2)]$	19.0 Hz (Fig. 4)	$^{15}HN_2{-}\overset{\overset{O}{\|\|}}{C}{-}^{15}NH_2$	20.2	17 (p. 293)
$^1J(^{13}C^{15}N)$	0 Hz (Fig. 4)	$CH_2{=}^{15}N{-}OH$	-2.96	18 (p. 122)
		C_2H_5O \ $C{=}^{15}N{-}^{15}NO_2$ / $(CH_3)_3SiO$	4.4 ± 0.2	17 (p. 290)
		$CH_3CH{=}^{15}N{-}OH$, cis	2.3	18 (p. 124)
$^2J(^{13}C^{15}N)$	0 Hz (Fig. 4)	None		

freedom of rotation around the C=N bond owing to the significant contribution of other resonance forms. This would account for a single ^{15}N chemical shift (Fig. 2) for the NH$_2$ group in solution. The partial π-bond character of this nitrogen should also enhance its chemical shift anisotropy, explaining the appearance of the spinning side-bands (Fig. 1) which are unknown for a strictly sp^3 nitrogen.

^{15}N Coupling constants

The NMR spectra of the fully ^{15}N-labeled nitroguanidine afford the four ^{15}N spin coupling constants on the basis of structure II summarized in Table 1. No attempts were made to determine the signs of the coupling constants. The couplings to ^{13}C were obtained from the ^{13}C spectrum in DMSO solution shown in Fig. 4. It is apparent from Fig. 4 that the coupling constants between the ^{13}C nucleus and the nitrimino nitrogens (^{15}N) are less than the resolving power of the spectrometer parameters used; that is, they are nearly zero.

The ^{15}N coupling constants determined in this work seem to be in line with those observed previously[17-19] for the same nuclei under similar bond hybridizations. Considerable theoretical work[20,21] has been carried out in recent years to calculate the magnitudes and the signs of carbon–nitrogen, nitrogen–nitrogen and nitrogen–

proton spin coupling constants. The same papers also described attempts to obtain experimental correlations to the bond hybridizations and other structural factors, such as the orbital orientation of the lone pair of electrons on nitrogen. Extensive data have already been compiled[17-19] on the ^{15}N-^{13}C and ^{15}N-^{1}H couplings, but data on ^{15}N-^{15}N couplings are still limited[18] owing, presumably, to the requirement of ^{15}N enrichment in the compounds under study. The nearest structural analogies have been selected from the above literature and included in Table 1 for comparison, for each of the coupling constants measured. The general agreement between them, apparent in Table 1, also further substantiates structure II for nitroguanidine.

CONCLUSIONS

Detailed NMR spectroscopic evidence clearly supports structure II for nitroguanidine as against the traditionally written structure I in both the crystalline state and in solution. This study suggests that the symmetrical structure II should be used routinely rather than the structure I to represent nitroguanidine. New data on ^{15}N spin coupling constants to ^{13}C and ^{1}H have been presented and shown to be in line with previously known data on analogous structures.

REFERENCES

1. R. Meyer, *Explosives*, 2nd rev. ed. p. 240. Verlag Chemie, Weinheim (1981).
2. (a) R. C. Weast (Ed.) *Handbook of Chemistry and Physics*, 58th ed. CRC Press, Cleveland, OH (1977–78); (b) J. H. Beynon, J. A. Hopkinson and A. E. Williams, *Org. Mass. Spectrom.* **1**, 179 (1968).
3. J. Thiele, *Justus Liebigs Ann. Chem.* **270**, 16 (1892).
4. S. S. Barton, R. H. Hall and G. F. Wright, *J. Am. Chem. Soc.* **73**, 2201 (1951).
5. M. W. Kirkwood and G. F. Wright, *J. Org. Chem.* **18**, 629 (1953).
6. A. H. Lamberton, *Q. Rev. Chem. Soc.* **5**, 75 (1951).
7. (a) A. F. McKay, *Chem. Rev.* **51**, 301 (1952); (b) J. Stals and M. G. Pitt, *Aust. J. Chem.* **28**, 2629 (1975).
8. J. H. Bryden, *et al.*, *Acta Crystallogr.* **9**, 573 (1956).

9. C. S. Choi, *Acta Crystallogr., Sect. B.* **37,** 1955 (1981).
10. W. D. Kumler, *J. Am. Chem. Soc.* **76,** 814 (1954).
11. N. S. Morozova, *et al.,* Zh. Org. Khim. **19,** 1228 (1983); Engl. Transl., p. 1096.
12. W. D. Kumler and P. P. T. Sah, *J. Org. Chem.* **18,** 669 (1953).
13. T. H. Lee and J. W. Rabalais, *J. Electron Spectrosc. Relat. Phenom.* **11,** 123 (1977).
14. R. E. Richards and R. W. Yorke, *Trans. Faraday Soc.* **54,** 321 (1958).
15. E. Laviron, P. Fournari and G. Refalc, *Bull. Soc. Chim. Fr.* 1024 (1969).
16. T. Urbanski, *Chemistry and Technology of Explosives,* Vol. 4, p. 365. Pergamon Press, Oxford (1984).
17. G. J. Martin, M. L. Martin and J. P. Gouesnard, in *NMR Basic Principles and Progress,* edited by P. Diehl, E. Fluck and R. Kosfeld, Vol. 18. Springer–Verlag, New York (1981).
18. G. Levy and R. L. Litchter, *Nitrogen-15 Nuclear Magnetic Resonance Spectroscopy,* pp. 122–124. Wiley, New York (1979).
19. T. Axenrod, in *Nitrogen NMR,* edited by M. Witanowski and G. A. Webb. Plenum Press, New York (1973).
20. (a) J. M. Schulman and T. Venanzi, *J. Am. Chem. Soc.* **98,** 701 (1976); (b) J. M. Schulman and T. J. Venanzi, *J. Am. Chem. Soc.* **98,** 6739 (1976); (c) J. M. Schulman, J. Ruggio and T. J. Venanzi, *J. Am. Chem. Soc.* **99,** 2045 (1977).
21. T. Khin and G. A. Webb, *Org. Magn. Reson.* **11,** 487 (1978).
22. B. Sunners, L. H. Piette and W. G. Schneider, *Can. J. Chem.* **38,** 681 (1960).