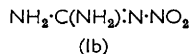
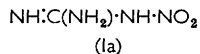


784. *The Denitration of Nitroguanidines in Strong Acids. Part II.**
Absorption Spectra and pK_a Values of Certain Nitroguanidines.

By T. G. BONNER and J. C. LOCKHART.

The structure of certain nitroguanidines and their conjugate acids is discussed and ultraviolet absorption spectra data are adduced to support the nitrimino-form of the free base and the nitramino-form for the ion. Differences in absorption spectra and basicity of the nitroguanidines investigated are interpreted in terms of the resonance structures of the free bases and their conjugate acids.

SOME controversy has existed over the structure of nitroguanidine, the choice being between two tautomers, the nitramino-form (Ia) and the nitrimino-form (Ib).



Wright¹ favoured structure (Ib) since no reaction occurs between nitroguanidine and diazomethane or acetyl chloride, both of which react readily with nitramines; the same is true of 2-nitrimino-1:3-diazacyclopentane. Other evidence for the nitrimino-structure comes from dipole-moment measurements² but absorption spectra have been interpreted as evidence for both forms.^{2,3}

An X-ray study⁴ of nitroguanidine showed the molecule to be almost planar with the carbon atom practically equidistant from the three nitrogen atoms to which it is directly attached. This implies that all three carbon-nitrogen bonds have the same bond order,

* Part I, preceding paper.

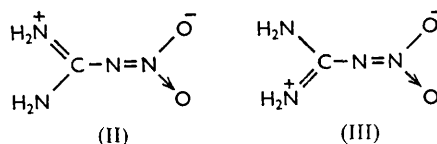
¹ Kirkwood and Wright, *J. Org. Chem.*, 1953, **18**, 629.

² Kumler and Sah, *ibid.*, p. 669.

³ McKay, Picard, and Brunet, *Canad. J. Chem.*, 1951, **29**, 746.

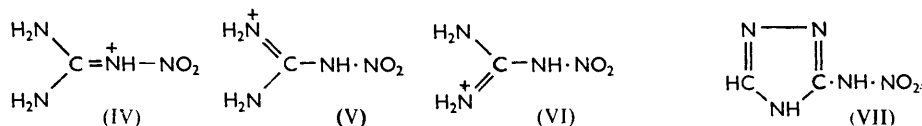
⁴ Bryden, Burkardt, Hughes, and Donohue, *Acta Cryst.*, 1956, **9**, 573.

which is not consistent with either form (Ia) or (Ib). The authors have represented the molecule by eight resonance structures of which the positions of the nuclei are those of the nitrimino-form (Ib), and an attempt was made to weight these structures so that a symmetrical electron distribution exists around the carbon atom. However, equal contributions from the covalent structure (Ib) and the ionic structures (II) and (III) would produce the symmetry found.



Recent evidence for the nitramino-structure has been provided by an investigation by proton magnetic resonance of nitroguanidine.⁵ The curve obtained does not give any indication of the two single protons present in structure (Ia) and is characteristic of proton pairs only, in accordance with structure (Ib).

This conclusion is now confirmed by the ultraviolet absorption spectra of nitroguanidine and its conjugate acid which, although previously investigated, have now been more extensively studied together with several derivatives. In all these nitroguanidines the existence of a strong absorption band at 2600—2700 Å has been observed, the exact position and intensity of which depends on the substituent groups. The absorption spectrum of nitramide⁶ is quite different with a broad band at 2250 Å (ϵ 5900; in water), which suggests that nitroguanidines do not exist in the nitramino-form (Ia). The absorption band characteristic of nitramide appears in the spectra of nitroguanidines in strongly acid solution and reaches maximum intensity in 40—50% sulphuric acid corresponding to complete conversion of the nitroguanidine into its conjugate acid. The change is accompanied by the disappearance of the absorption band characteristic of the free base. A typical example of this change is that of 2-nitrimino-1 : 3-diazacyclopentane shown in Fig. 1. A nitramino-structure would be readily acquired by the conjugate acid by proton uptake on the nitrimino-nitrogen atom. Three principal resonance structures (IV)—(VI) can represent the nitroguanidinium ion thus formed.



As shown in the Table, the majority of nitroguanidine derivatives undergo this characteristic change of spectrum on conversion into their conjugate acids in sulphuric acid. The only exception is 2-nitramino-1 : 3 : 4-triazole, which shows the same hypsochromic shift but to a lesser extent. Evidently the triazole has structural features which modify its absorption characteristics. An aromatic structure for the triazole ring requires the nitramino-form (VII) and the characteristic spectrum of nitramine will be modified by conjugation of the nitramino-group with the ring. Protonation in strongly acid solution will occur at one of the nitrogen atoms, probably at either of the tertiary atoms, and this will reduce conjugation of the nitramino-group with the ring but not sufficiently to produce the spectrum of nitramine.

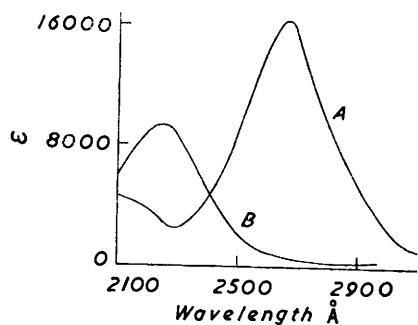
The lower extinction coefficient of *NN*-dimethyl-*N'*-nitroguanidine is clearly an example of steric inhibition of conjugation. If the transition corresponding to the intense absorption of nitroguanidine bases at 2600—2700 Å is from the homopolar ground state (Ib) to the predominantly dipolar excited state (II), the presence of two methyl groups

⁵ Richards and Yorke, *Trans. Faraday Soc.*, 1958, **54**, 321

⁶ Jones and Thorn, *Canad. J. Res.*, 1949, **B27**, 828.

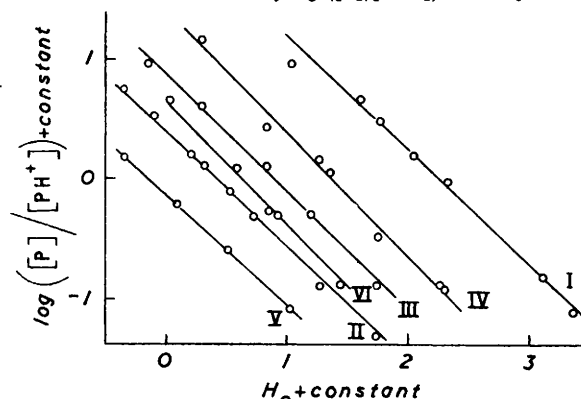
on one amino-nitrogen atom will restrict rotation about the bond linking this nitrogen atom to the central carbon atom and hinder the molecule's attaining the planar configuration necessary for maximum resonance. As the intensity of absorption only is reduced, λ_{max} remaining unchanged, the steric hindrance is relatively weak and is possibly associated with transitions between non-planar ground state and near-planar excited states.⁷ The relatively smaller fall in intensity of the symmetrical *NN'*-dimethyl-*N''*-nitroguanidine may be the result of a weaker operation of this effect. The greatest intensity of absorption occurs in the diazacyclopentane and diazacyclohexane derivatives, and this can be attributed to the rigidity of these ring systems facilitating the formation of the planar configuration of the dipolar excited state.

FIG. 1. Spectrum of 2-nitrimino-1 : 3-diazacyclopentane in sulphuric acid.



A, in 0.1N-acid; B, in 69% acid.

FIG. 2. Variation of $\log ([P]/[PH^+])$ with H_0 .



I, 2-Nitramino-1 : 3 : 4-triazole (0.97); II, 2-Nitrimino-1 : 3-diazacyclohexane (0.96); III, *NN*-Dimethyl-*N''*-nitroguanidine (1.00); IV, 2-Nitrimino-1 : 3-diazacyclopentane (1.01); V, *N*-Methyl-*N''*-nitroguanidine (0.93); VI, Nitroguanidine (1.02).

Values in parentheses are of $\log ([P]/[PH^+])/H_0$.

pK_a Values of Nitroguanidines.— pK_a values are given in the Table. As the absorption spectra of the nitroguanidium ions (except the triazole derivative) indicate a nitramino-structure (IV) corresponding to proton uptake on the nitrimino-nitrogen atom, the relative basicities will depend on the resonance stabilisation achieved by contributions from structures (V) and (VI). The slight increase in basicity (pK_a increases from -0.93 to -0.86) produced by the introduction of a single methyl group on the amino-nitrogen atom is in accord with the inductive effect of this group but the considerable decrease in basicity which follows the substitution of a second methyl group on the same nitrogen atom ($pK_a = -1.20$) is evidence of the greater strain involved in attaining the planar configuration necessary for appreciable contributions in the ground state from the resonance structures of the type (V).

The markedly higher basicity of the diazacyclohexane ($pK_a = -0.71$) than of the diazacyclopentane ($pK_a = -1.36$) can be related to the relative stability of these ring systems with respect to the exocyclic double bond. Since a double bond which is exocyclic to a five-membered ring is more stable than one which is exocyclic to a six-membered ring,⁸ it is possible that greater contributions to the resonance stabilisation from the equivalent structures corresponding to (V) and (VI) will be made in the case of the conjugate acid of the diazacyclohexane than in that of the diazacyclopentane.

The notably weak basic character of 2-nitramino-1 : 3 : 4-triazole is characteristic

⁷ Braude and Waight, "Progress in Stereochemistry," ed. Klyne, Butterworths, London, 1954, p. 126; Baddeley, *Ann. Reports*, 1955, **52**, 131.

⁸ Fleck, *J. Org. Chem.*, 1957, **22**, 439; Brown, *ibid.*, p. 439.

Absorption spectra data, pK_a values, and relative rates (RR) of denitration, in aqueous sulphuric acid.

Compound	Free base		Conjugate acid		pK_a	RR
	ϵ_{\max}	λ_{\max}	ϵ_{\max}	λ_{\max}		
2-Nitramino-1 : 3 : 4-triazole	12,400	2820	6700	2470	-2.5	16.6
2-Nitrimino-1 : 3-diazacyclohexane	15,450	2680	9700	2315	-0.71	8.5
NN-Dimethyl-N'-nitroguanidine	11,350	2710	8010	2250	-1.30	6.6
NN'-Dimethyl-N''-nitroguanidine	13,200	2675	—	—	—	6.3 ^a
N-Methyl-N'-nitroguanidine	14,040	2670	8700	2260	-0.86	3.8 ^a
Nitroguanidine	14,400	2640	9940	2250	-0.93 ^b	1 ^c
4-Methyl-2-nitrimino-1 : 3-diazacyclopentane ...	17,140	2660	—	—	—	0.41
2-Nitrimino-1 : 3-diazacyclopentane	16,170	2655	9440	2260	-1.36	0.33

^a Ref. 9. ^b The pK_a obtained for nitroguanidine above agrees with that obtained in dilute hydrochloric acid,¹¹ recalculated on an H_0 basis. ^c Ref. 10.

of aromatic bases (cf. aniline, pyridine) and originates in the decrease in resonance which results from proton addition to a nitrogen atom.

A significant feature of the ionisation of each nitroguanidine is that a plot of $\log ([P]/[PH^+])$ (where P represents the uncharged nitroguanidine and PH^+ its conjugate acid) against H_0 is a straight line of slope 1, as shown in Fig. 2. These compounds are therefore indistinguishable in their ionisation behaviour from the aromatic bases used by Hammett in the evaluation of the H_0 scale.

Relative Rates of Denitration.—The mechanism of denitration of nitroguanidines in strong acids (previous paper) envisages the expulsion of a nitronium ion from the diprotonated base accompanied by proton transfer involving acid and base species present in the medium. An important factor in this process is the ease of proton uptake, with the second protonation more important than the first. Thus although the triazole is the weakest base, its conjugate acid has the largest number of basic centres for the second protonation, and if this second protonation occurs more readily than with the other nitroguanidinium ions, the relatively high rate of nitration found experimentally would be expected. The order of denitration rates for nitroguanidine and its monomethyl and dimethyl derivatives is also in accord with the expected basicity of their conjugate acids, if this is assumed to depend mainly on the inductive effect on the methyl group. The difference in rates of denitration of the diazacyclohexane derivative and its cyclopentane analogue may be attributed to differences in ring stability, the faster rate for the former corresponding to a greater flexibility of the six-membered ring compared with the five-membered ring in the diprotonated derivatives (the second proton being assumed to add to a ring nitrogen atom).

EXPERIMENTAL

Materials.—These were as in the preceding paper.

Absorption Spectra.—These were measured on a Hilger Uvispek spectrophotometer calibrated with potassium chromate.¹²

Measurement of Ionisation Ratios.—The method developed by Flexser, Hammett, and Dingwall¹³ was used. Indicator ionisation ratios were obtained from the equation $[B]/[BH^+] = (\epsilon_{BH^+} - \epsilon)/(\epsilon - \epsilon_B)$, where ϵ_B and ϵ_{BH^+} are the extinction coefficients of the un-ionised base B and its conjugate acid BH^+ at any selected wavelength and ϵ is that of the mixture of the same wavelength. pK_a values were obtained from the relation $pK_a = H_0 - \log([B]/[BH^+])$, where [B] and $[BH^+]$ are the concentrations of the base and its conjugate acid in a medium of acidity H_0 . The results recorded in the Table are the mean of several values obtained at different H_0 values and different wavelengths.

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⁹ Hardy-Klein, J., 1957, 70.

¹⁰ Simkins and Williams, J., 1952, 3086.

¹¹ Hall, de Vries, and St. Clair Gantz, J. Amer. Chem. Soc., 1955, 77, 6507.

¹² Hogness, Zscheile, and Sidwell, J. Phys. Chem., 1937, 41, 379.

¹³ Flexser, Hammett, and Dingwall, J. Amer. Chem. Soc., 1935, 57, 2103.