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THE TAUTOMERISM OF NITRAMINOPYRIDINES

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^{1}H, ^{13}C and ^{15}N NMR data for nitraminopyridines are discussed in terms of tautomeric equilibria in these compounds. The favoured tautomer is determined mainly from ^{15}N NMR spectroscopy. The chemical shift of the nitrogen atom of the nitro group in nitraminopyridines and *N*-nitroanilines which cannot tautomerize vary from 28·0 to 35·4 ppm in DMSO solution. 3-Nitraminopyridine and 2-nitramino-3- and -5-nitropyridines behave similarly. In the ^{15}N NMR spectra of nitrimino-1-methyldihydropyridines, used as models, an upfield shift of that atom, different from that observed for 2-nitraminopyridine, indicates the significance of the nitrimino tautomer. In contrast, a downfield shift of the ring nitrogen atom of some other compounds shows an increased weight of the nitramino tautomer. 3-Nitraminopyridine, when dissolved in DMSO, does not have the zwitterionic structure. Changes in the chemical shift of the amino nitrogen atom are not readily interpreted. Some proton and carbon chemical shifts and hydrogen–hydrogen and carbon–hydrogen spin–spin coupling constants can also be used to determine the predominant tautomer of 2- and 4-nitraminopyridines.

INTRODUCTION

Tautomeric equilibria in heterocyclic compounds have been extensively studied for many years.[1] Various substituted pyridines are mixtures of tautomeric isomers. Well known examples are hydroxy- and mercaptopyridines.[2,3] Tautomerism is also observed when the pyridine substituents are NHR and CHR_2, where R = COAlk(Ar), CO_2Alk, CN, NO_2 or SO_2Alk(Ar).[1,4]

Data on tautomerism are necessary for interpreting the reactivity, spectral behaviour and other physical properties of compounds. The general method for establishing the relative population of tautomers is to compare the spectroscopic properties of the prototropic species with those of fixed tautomeric models obtained by substitution of hydrogen by an alkyl group (frequently methyl).

Multinuclear magnetic resonance spectroscopy has been widely used to investigate tautomeric equilibria quantitatively.[1d,2,3,5] Because both the ring and amino nitrogen atoms in aminopyridines can be protonated and because the protonation shifts in aniline and pyridine are very large,[6,7] NMR spectroscopy of nitrogen can provide valuable information on their tautomerism.[7] Owing to the presence of three different nitrogen atoms, nitraminopyridines are interesting. Since previous results were not interpreted unambigously,[8–20] we have investigated the spectra of compounds **1–16** (Scheme 1) in order to obtain data on their tautomeric equilibria.

To avoid confusion when comparing the NMR spectra of nitraminobenzenes and nitraminopyridines, special numbering of positions in pyridine der vatives

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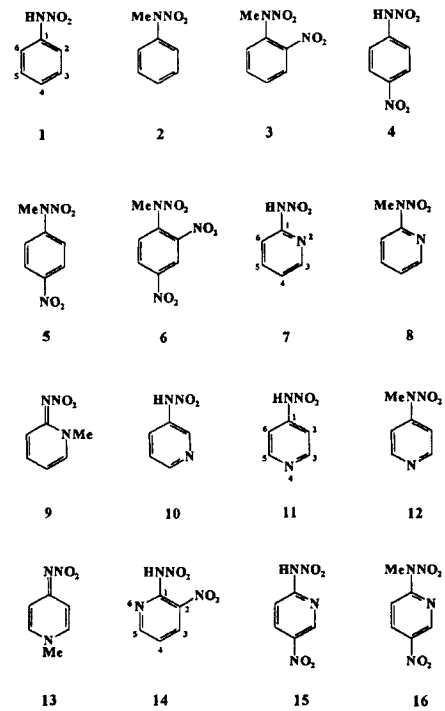


Scheme 1

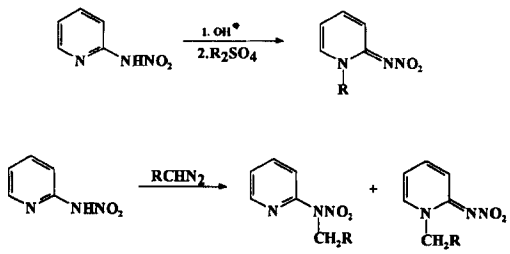
was used; it starts from the carbon atom attached directly to the nitramino group. The numbering is exemplified for some compounds in Scheme 1.

EXPERIMENTAL

Compounds **1–16** have been synthesized previously.[21] Their ^{1}H, ^{13}C and ^{15}N NMR spectra were recorded as described in our earlier papers.[21,22]

RESULTS AND DISCUSSION

Nitraminoarenes with marked acidic properties can react with sodium hydroxide to give the corresponding salts.[23] Alkylation of 2-nitraminopyridine by either alkyl sulphates or diazoalkanes[12,24] leads to the *endo*-alkylated product or to its mixture with 2-(*N*-methyl,*N*-nitroamino)pyridine (see Scheme 2). 4-Nitraminopyridine behaves similarly, i.e. 1,4-dihydro-1-methyl-4-nitriminopyridine or its mixture with 4-(*N*-methyl-*N*-nitroamino)pyridine is obtained by treatment with dimethyl sulphate or diazomethane.[20,25]

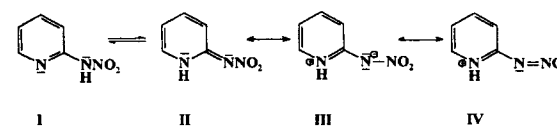


Scheme 2

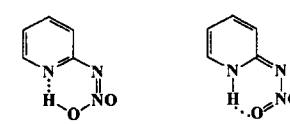
As postulated,[26,27] the isonitramine form is present at small extent at equilibrium R—NH—NO_2 ⇌ R—N=N(O)—OH. Owing to the presence of the ring nitrogen atom in 2-nitraminopyridine, **7**, it can tautomerize to produce the nitrimino form **II**[24] (see Scheme 3). Moreover, *s-cis* conformations of both isonitramino and nitrimino forms would benefit from stabilization due to intramolecular hydrogen bonding[18] (Scheme 4). However,[27] it was found that the nitro group in the nitramino moiety has a low ability to be involved in the formation of hydrogen bonds.

Analysis of the IR spectra of 2-nitraminopyridine in the solid state has led to contradictions. Sheinker *et al.*[14] reported that it takes form **I** exclusively. On the other hand, Taurins[10] has interpreted this spectrum as a superposition of spectra belonging to **II** and **IV**. The contribution of **I** in solution varies from 0 through 38·4 to 85·4% in water, absolute ethanol and dioxane, respectively.[14] ^{1}H NMR[17] and UV spectra[18] have shown that **II** prevails in DMSO and in cyclohexane. Aqueous and dioxane solutions of 4-nitraminopyridine contain about 1 and 94% of **V**, respectively (Scheme 5).[20]

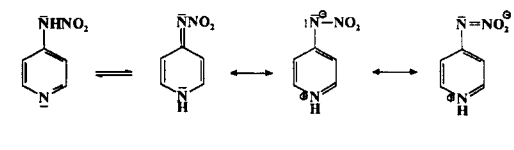
In the crystal of 3-nitro-2-nitraminopyridine, the C—N bond (1·400 Å) in the $CNHNO_2$ moiety is really



Scheme 3



Scheme 4



Scheme 5

a single bond.[21] X-ray studies[21] proved that there is no hydrogen bound to the ring nitrogen. Thus, at least in crystalline state, structures **II–IV** can be excluded.

NMR spectroscopy is very helpful in determining the dominant tautomer.[1–3,5,28,29] Individual tautomers can be distinguished only when the rate of proton exchange is slow on the NMR time-scale. Otherwise, only one statistical signal appears. Sometimes the considerable line broadening[2] can prevent reliable spectral detection. This happens for the signal of the amino hydrogen in the spectra of some of the nitraminoarenes studied.

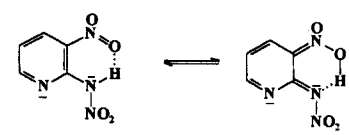
The chemical shift of a 'jumping' hydrogen atom is very sensitive to tautomeric equilibrium. That of the amino hydrogen in the spectra of 2- and 4-nitraminopyridines was found to be 3·4 and 3·3 ppm, respectively. In contrast, for *N*-nitroaniline and 2-nitramino-3-nitropyridine it is 13·86 and 13·56 ppm, respectively (see Table 1 and Refs 22, 30 and 31). This suggests that the amino hydrogen in those compounds is very acidic.

Nitramines ($RNHNO_2$) are known to be weaker acids than the carboxylic derivatives (RCO_2H).[26] The acidity constant of 2- and 4-nitraminopyridines in water was found to be 5·90 and 6·87, respectively.[20,23a] Since the pK_a value for the *aci* form of nitroethane is 4·4, it rules out the presence of any significant amount of the isonitramine form, PyN=N(O)OH.[20] However, it was not observed for 2-nitramino-3-nitropyridine in the crystalline state,[21] and intramolecular hydrogen bonding may appear in compounds carrying the NO_2 and $NHNO_2$ groups in neighbouring positions (Scheme 6).

Table 1. ^{1}H NMR chemical shifts of compounds **1–13**, **15** and **16** (δ in ppm from TMS, in DMSO-d_6)

Compound	Position						
	H-2	H-3	H-4	H-5	H-6	CH_3	N*H*
1	7·50	7·50	7·31	7·50	7·50	–	13·86
2	[a]	[a]	[a]	[a]	[a]	3·68	–
3	–	8·28	7·80	7·97	7·84	3·66	–
4	7·68	8·29	–	8·29	7·86	–	[b]
5	8·36	7·82	–	7·82	8·36	3·75	–
6	–	8·91	–	8·75	8·14	3·78	–
7	–	8·22	7·22	8·08	7·65	–	3·4[c]
8	–	8·72	7·47	8·02	7·70	3·69	–
9	–	8·36	7·05	8·02	8·18	3·80	–
10	8·65	–	8·50	7·53	7·92	–	[b]
11	7·47	8·23	–	8·23	7·47	–	3·3[c]
12	7·55	8·72	–	8·72	7·55	3·71	–
13	8·23	7·49	–	7·49	8·23	3·96	–
15	–	9·19	–	8·70	7·98	–	[b]
16	–	9·34	–	8·77	8·08	3·81	–

[a] Signals of aromatic protons in the range 7·44–7·56 ppm.
[b] No N*H* signals were detected.
[c] Broad singlet.



IX **X**

Scheme 6

Isolation of pure tautomeric forms is not possible when their interconversion is a fast process. In such a case the use of the corresponding methyl derivatives is a reasonable solution. Replacements of the hydrogen by methyl is often assumed to have a minor influence on the NMR spectra. However, the methyl group and other parts of the molecule can interact by steric and electronic, i.e. hyperconjugative and field/inductive, effects, which gives an additional non-tautomeric contribution to the spectrum. Thus, the spectral parameters of the tautomeric form do not have to be properly represented by those of its methyl derivative and suitable corrections should be included.

Both ^{1}H and ^{13}C NMR spectroscopy have been applied to studies of tautomeric equilibria of heterocyclic compounds. As found,[32] the tautomer and rotamer populations can be estimated not only from chemical shifts and coupling constants, but also from the proton relaxation rates and NOE effects.

Unfortunately, the ^{1}H NMR spectra of nitraminobenzenes **1** and **2** at 270 MHz are not resolved, so their usefulness in the estimation of the effect of *N*-methylation is limited. It can be only seen that the signal of H-4 was shifted by +0·13 ppm in the spectrum of **2** (see Table 1). On the other hand, this effect in the *p*-nitro derivatives **4** and **5** is +0·68 and −0·47 ppm for H-2 and H-3, respectively. Of course, this information has limited significance for predicting the tautomeric equilibria in solutions of nitraminopyridines.

The chemical shifts of H-5 and H-6 in the spectra of 2-nitraminopyridine (**7**) and of its fixed tautomeric models **8** and **9** (see Table 1) cannot be used to study the tautomerism of **7**. Other δ values are more sensitive to structural changes in the molecule. The chemical shift of H-4, i.e. *para* to the $NHNO_2$ group, seems to be especially helpful in differentiating between the nitramino and nitrimino forms represented by methyl derivatives **8** and **9**, respectively: δ (**9**) < δ (**7**) < δ (**8**).

There are no hydrogens in the position *para* to the nitramine or nitrimine group in 4-nitraminopyridine (**11**) and its methyl derivatives **12** and **13**. The values of $\delta_{H\text{-}3}$(5) change in the order δ (**13**) < δ (**11**) < δ (**12**).

Although the coupling constants for compounds **1** and **2** are not available, it is seen in Table 2 for compounds **4** and **5** that replacement of the amino hydrogen atom by methyl in **4** diminishes all vicinal J(H,H)

Table 2. Hydrogen–hydrogen spin–spin coupling constants for compounds **1–13**, **15** and **16** [^nJ(H-*k*,H-*l*) in Hz] in DMSO-d_6[a]

	k,l								
Compound	2,3	2,5	2,6	3,4	3,5	3,6	4,5	4,6	5,6
3				8·20	1·46		8·09	1·35	7·68
				8·09			7·68		6·80
4	9·34								9·34
	9·34								9·34
5	9·03								9·03
	9·02								9·02
6					2·61	0·31			8·73
					2·62	0·35			8·81
7				5·94	1·91	0·88	7·26	1·11	8·79
					1·76	0·73	7·11		8·94
8				4·88	1·98		7·79	1·03	8·09
							7·48		7·79
9				6·79	1·68		7·10	1·37	9·00
					1·37		6·79		8·93
10			2·44				4·81	1·52	8·40
			2·60					1·38	8·32
11	7·48	1·90				1·90			7·48
	7·48	1·90				1·90			7·48
12	4·51	1·60	1·60			1·60			4·51
	4·51	1·60							4·51
13	7·02								7·02
	7·02								7·02
15					2·49				9·28
					2·72				9·39
16					2·74	0·66			8·99
					2·80	0·66			9·04

[a] Other coupling constants: **7**, 5·86 [J(H-4,N*H*)]; **10**, 4·73 [J(H-5,N*H*)]; **11**, 1·90 [J(H-2,N*H*)], 1·90 [J(H-3,N*H*)], 1·90 [J(H-5,N*H*)], 1·90 [J(H-6,N*H*)]; **15**, 0·79 [J(H-3,N*H*].

constants by about 0·3 Hz. Owing to tautomerism no such comparison can be made for **7** and its methyl derivative. It seems worthwhile, however, finding all J(H,H) coupling constants following the **8**<**7**<**9** sequence. They are ^3J for H-3–H-4, H-4–H-5 and H-5–H-6 and ^4J for H-3–H-5 and H-4–H-6. The value of ^3J(H-3,H-4) in the spectrum of 2-nitraminopyridine is about 1 Hz higher than those for *N*-methyl-*N*-nitraminopyridines, where tautomerism is not possible.[21] In contrast, all J(H,H) values for compounds **11–13** in Table 2 do not follow the order **13**<**11**<**12** or **12**<**11**<**13**. The values of ^3J(H-3,H-4) for compounds **7** and **9** and of ^3J(H-2,H-3) for compounds **11** and **13** are higher than those for **8** and **12**, respectively (see Table 2). Hence those coupling constants also seem to determine the predominant tautomer.

Of the ^{13}C chemical shifts in the spectrum of 2-nitraminopyridine (**7**) only those of C-1, C-4 and C-6 are average values for individual tautomers represented by the respective methyl derivatives **8** and **9**.[22] However, no similar dependence was found for the carbon chemical shifts in the spectra of compounds **11–13**.

The effect of replacement of the amine hydrogen atom by methyl on the chemical shift of carbon atoms in the compounds studied is shown in Table 3.

In the spectrum of 2-nitraminopyridine (**7**), the coupling constants ^1J(C-*n*,H) for n = 3–6 are average values for individual tautomers represented by the respective methyl derivatives **8** and **9**.[22] Unfortunately, neither δ_C nor J(C,H) values for 4-nitraminopyridine (**11**) are intermediate between such values for compounds **12** and **13**.[22] The effect of replacement of the amino hydrogen atom by methyl on the one-bond C–H

Table 3. Effect of *N*-methylation of nitraminoarenes on carbon chemical shifts in their ^{13}C NMR spectra ($\Delta\delta_{^{13}C}$ in ppm)

Compounds	C-1	C-2	C-3	C-4	C-5	C-6
2 – 1	+4·8	+4·3	+0·2	+2·1	+0·2	+4·3
5 – 4	+3·7	+7·7	−0·4	+2·5	−0·4	+7·7
8 – 7	−1·4	–	+9·2	+6·3	−4·1	+3·9
12 – 11	+23·3	+5·9	+11·1	–	+11·1	+5·9
16 – 15	+1·1	–	+0·7	+2·1	−0·9	+6·7

Table 4. Effect of *N*-methylation of nitraminoarenes on one bond C–H coupling constants in their ^{13}C NMR spectra [Δ^1J(C,H) in Hz]

Compounds	C-2	C-3	C-4	C-5	C-6
2 – 1	−0·1	+0·2	−0·7	+0·2	−0·1
5 – 4	−0·2	+0·8	–	+0·8	−0·2
8 – 7	–	−5·0	−4·9	−1·0	−4·6
12 – 11	−3·5	−5·0	–	−5·0	−3·5
16 – 15	–	+0·9	–	+1·2	−0·1

coupling constants in the compounds studied is shown in Table 4.

Both ^{14}N and ^{15}N NMR spectroscopy have been widely used to study tautomeric equilibria.[3,7a,29] The range of shift changes also favours this method: for ^{14}N it is one and two orders of magnitude greater than those of ^{13}C and ^{1}H, respectively.[2] Because different types of nitrogen in nitraminopyridines exhibit clearly separated ^{15}N NMR shift ranges,[22] this method is especially powerful in the studies concerned. Moreover, since some of those nitrogens can be the reaction sites of tautomeric processes, ^{15}N NMR spectroscopy provides direct access to these equilibria.[2]

The ^{15}N NMR chemical shift of the nitro groups in *N*-methyl-*N*-nitroaminobenzenes and corresponding pyridines and also *N*-nitroanilines (none of them can tautomerize to the nitrimine form) varies from 28·0 to 35·4 ppm in DMSO solution.[21,22] It is 31·3 ppm for 3-nitraminopyridine (**10**), 31·0 ppm for 2-nitramino-3-nitropyridine (**14**) and 33·8 ppm for 2-nitramino-5-nitropyridine (**15**),[21,22] and for the nitrimino-1-methyldihydropyridines **9** and **13** used as the model compounds it is 14·9 and 9·0 ppm, respectively. The distinct upfield shift of the nitro nitrogen atom in 2-nitraminopyridine (**7**) (18·6 ppm) indicates the prevalence of the nitrimino form (see Figure 1).

Unfortunately, the solubility of 4-nitraminopyridine in DMSO was too low for recording its ^{15}N NMR spectrum.[22] Further, the downfield shift of the pyridine nitrogen[22] observed in some compounds (see Figure 2) proves the increased weight of the nitramino tautomer. The effect of tautomeric equilibrium on the chemical shift of amino nitrogen atom is not clear.

The mutual relationships of the ^{15}N NMR chemical shifts of different nitrogen atoms are shown in Figures 3–5. Two different groups of compounds can be distinguished. In most of them the nitramine form is predominant, but compound **7** resembles the nitrimine model **9**. Intramolecular and/or intermolecular hydrogen bonding may be an explanation for the exceptional behaviour observed in the spectrum of 2-nitraminopyridine (**7**). The form **IA** was proposed by Kraus *et al.*[18] to explain the anomalies in the IR spectrum of 2-nitraminopyridine.

The ^{15}N NMR chemical shifts of the corresponding nitrogen atoms in the spectra of 2-nitramino-5-nitropyridine (**15**) and *N*-nitro-*p*-nitroaniline (**4**) are comparable.[22] The results indicate that the structure **XI** (Scheme 7) may be neglected, as was also found in the analysis of the effect of *N*-methylation on the carbon

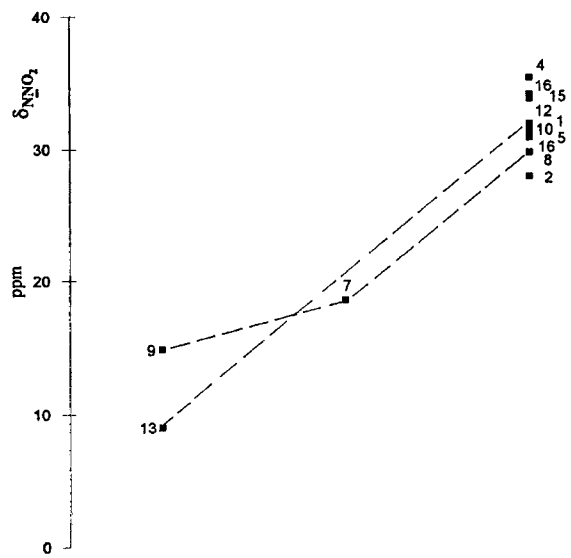


Figure 1. Effect of the molecular structure on ^{15}N chemical shifts of the nitro nitrogen atom of the $NRNO_2$ group in nitraminoarenes **1**, **2**, **4**, **5**, **7**–**10**, **12**, **13**, **15** and **16** in DMSO

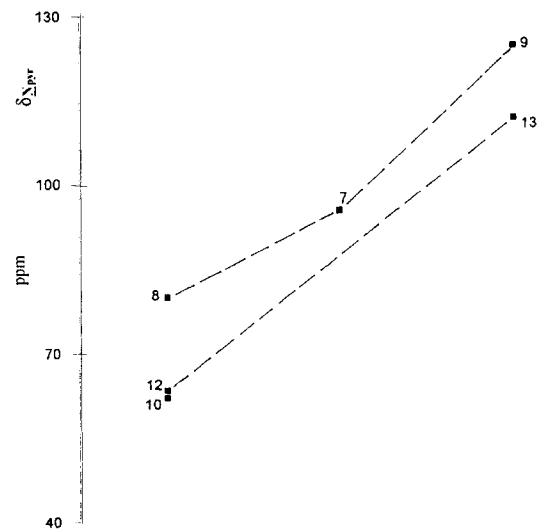


Figure 2. Effect of the molecular structure on ^{15}N chemical shifts of the ring nitrogen atom in nitraminopyridines **7**–**10**, **12** and **13** in DMSO

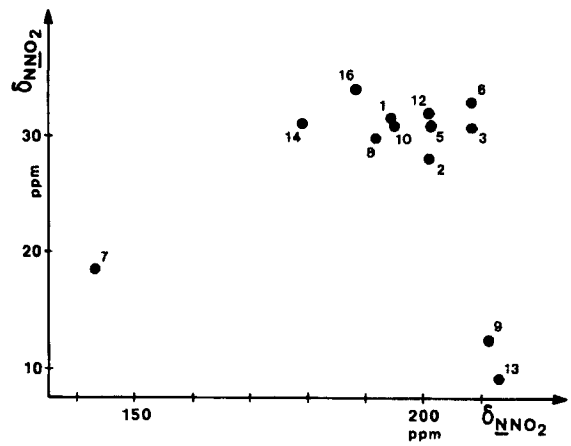


Figure 3. Interrelationship $\delta_{N^{15}NO_2}$ vs $\delta^{15}{}_{NNO_2}$ for compounds **1–16**

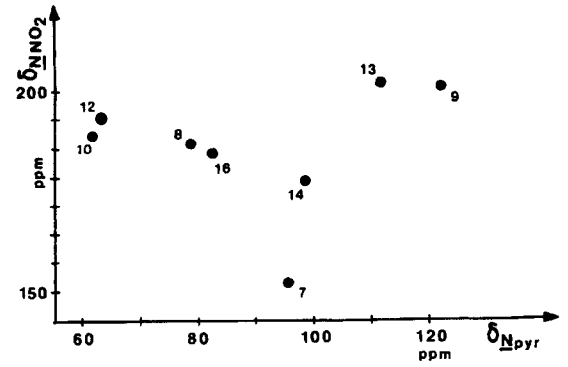


Figure 4. Interrelationship $\delta^{15}{}_{NNO_2}$ vs $\delta^{15}{}_{Npyr}$ for compounds **1–16**

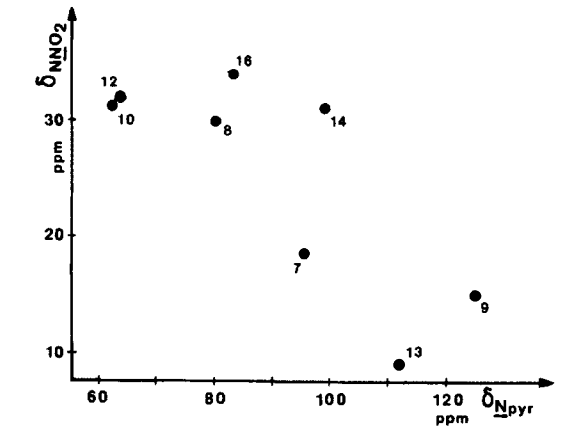
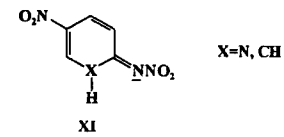
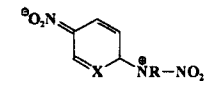


Figure 5. Interrelationship $\delta_{N^{15}NO_2}$ vs $\delta^{15}{}_{Npyr}$ for compounds **1–16**



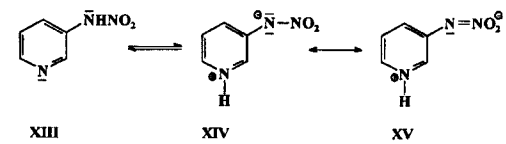
XI

Scheme 7



XII

Scheme 8



XIII XIV XV

Scheme 9

chemical shifts and C–H coupling constants in the spectra of *N*-nitroaminoarenes.

Although x-ray diffraction studies of *N*-methyl-*p*,*N*-dinitroaniline (**5**)[33] show the weight of structure **XII** (X = CH, R = H) to be low, it cannot be totally excluded for X = N (Scheme 8).

The similarity of the ^{15}N NMR spectra of *N*-nitroaniline (**1**) and 3-nitraminopyridine (**10**)[22] proves that the latter compound has the structure **XIII** (Scheme 9) at least in DMSO solution.

Unfortunately, we could not use the respective methylated model compounds. Only one of them, 3-(*N*-methyl-*N*-nitro)aminopyridine, has been described[34] and we found some experimental difficulties in repeating the procedure.

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