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Tautomerism in Nitrotriazoles: Structure Investigation by Combined ^{1}H, ^{13}C and ^{15}N NMR Spectroscopy

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ABSTRACT: The tautomerism and isomerism of triazoles make the structure analysis of such compounds a difficult problem, and in the case of several nitrotriazoles a detailed structure assignment had been lacking up to now. Supported by selected compounds, a definite structure determination of ten nitrotriazoles was achieved by combined application of ^{15}N NMR spectroscopy and increment calculations. This method also succeeded in cases where equilibria of tautomers were present. An evaluation of the shift data and coupling modes gave systematic references to structure and substituent influences. © 1998 John Wiley & Sons, Ltd.

KEYWORDS: NMR; ^{1}H NMR; ^{13}C NMR; ^{15}N NMR; nitrotriazoles; structure; tautomeric equilibria; substituent effects

INTRODUCTION

1,2,3- and 1,2,4-triazoles are heteroaromatic compounds stabilized by mesomeric structures. Their N atoms are either present in a double bond system (pyridine-type N) or with single bonds (pyrrole-type N). The introduction of even one nitro group into triazoles results in a pronounced acidity and in explosive properties.

The mobile protons at the ring nitrogen atoms are responsible for tautomerism, after substitution isomerism has to be taken into account. The distinction of such forms can only be realized with appropriate spectroscopic efforts. As some structural problems with nitro derivatives of triazoles prepared by us had not yet been solved, this prompted us to investigate the tautomerism, isomerism and equilibria existing in certain cases for these and other triazoles.

EXPERIMENTAL

Compounds

Synthesis of nitrated triazoles and bitriazoles. 3-Nitro-1,2,4-triazole (**2**) is prepared from 3-amino-1,2,4-triazole (**1**) by a Sandmeyer reaction[1] and 4-nitro-1,2,3-triazole (**3**) is obtained by cycloaddition of tosyl azide to a nitroethene derivative,[2] as direct *C*-nitration of triazoles is unknown. 5-Amino-3-nitro-1,2,4-triazole (**4**) is accessible by selective reduction of 3,5-dinitro-1,2,4-triazole[3] and 3-nitro-1,2,4-triazol-5-one (**5**) by nitration of 1,2,4-triazol-5-one.[4] The coupling of diazonium compounds with methazonic acid and subsequent cyclization represent a versatile 4-nitro-1,2,3-triazole synthesis[5] yielding exclusively 2-substituted triazoles. Thus 3-(4-nitro-1,2,3-triazol-2-yl)-1,2,4-triazole[6] (**6**) is accessible from 3-amino-1,2,4-triazole (**1**) (see Scheme 1). In the same way we obtained from 2,4-dinitroaniline 2-(2,4-dinitrophenyl)-4-nitro-1,2,3-triazole (**7**) (m.p. 118 °C) and from 5-amino-3-nitro-1,2,4-triazole (**4**) 3-(4-nitro-1,2,3-triazol-2-yl)-5-nitro-1,2,4-triazole[7] (**8**). We were able to convert the mononitro compound **6** into the *N*-nitro derivative[8] **9** by nitration with N_2O_5. As ambident reactivity of nitrotriazoles can be expected, the formation of a mixture of dinitrophenylnitrotriazole **7** and a second compound is not surprising when 2,4-dinitrochlorobenzene is reacted with 4-nitro-1,2,3-triazole (**3**). The second product was identified as 1-(2,4-dinitrophenyl)-4-nitro-1,2,3-triazole[9] (**10**). Also, nitrobitriazole **6** reacts with 2,4-dinitrochlorobenzene to give 1-(2,4-dinitrophenyl)-3-(4-nitro-1,2,3-triazol-2-yl)-1,2,4-triazole (**11**) (m.p. 194 °C).

Spectra

The structure assignment of the tautomeric and isomeric forms in question is based on broadband decoupled, selective decoupled and ^{1}H-coupled ^{13}C and ^{15}N NMR spectra, heteronuclear correlation experiments and gated-decoupling ^{15}N spectra. Gated-decoupling ^{15}N spectra proved to be a very valuable method for structure elucidation, as in such experiments the strong one-bond NOE (nuclear Overhauser effect) leads to ^{15}N signals of H carrying nitrogen atoms with opposite phase, while one-bond and long-range coupling information is retained.

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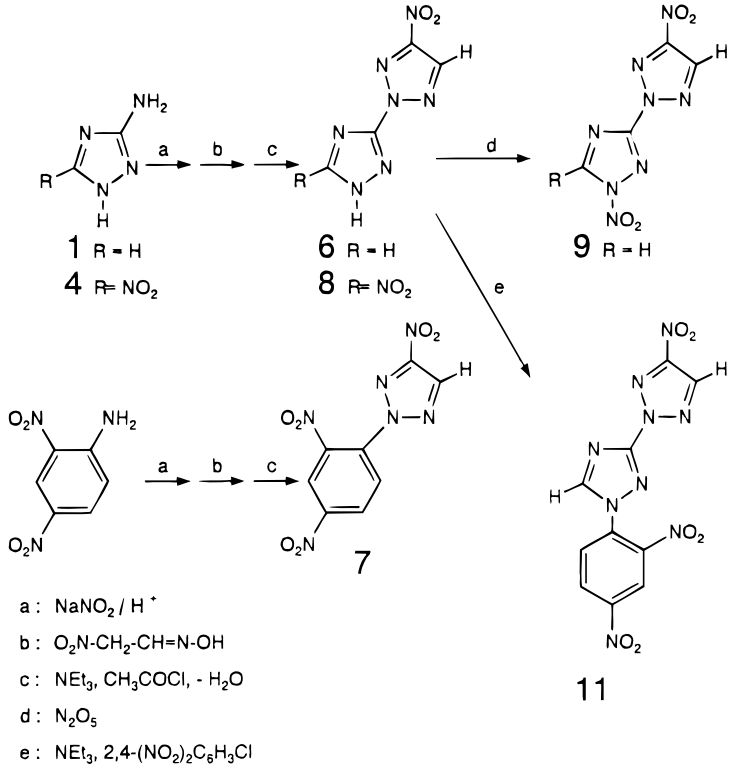

Scheme 1

NMR spectra were recorded on a Varian Gemini 2000 and a Bruker DRX 500 spectrometer at 21 ± 1 °C in DMSO-d_6. The ^{1}H and ^{13}C chemical shifts refer to the solvent signal; the ^{15}N shifts were measured with respect to external CH_3NO_2 defined as 0 ppm.

Since the measured chemical shifts and coupling constants are not always sufficient to assign unambiguously the structure of the triazoles and bitriazoles **2**–**11**, ^{15}N chemical shifts had to be estimated from supplementary increment calculations, a strategy already applied in similar cases.

Increments

Comparison of the ^{15}N data of substituted and unsubstituted compounds permits one to define additive ^{15}N increments Δ for amino, methyl, nitro and nitrotriazolyl groups.

From published ^{15}N chemical shifts of aminomethyl-1,2,4-triazoles **12**–**14**[10] and methyl-1,2,4-triazoles **15** and **16**,[11] a series of increments Δ_{AMINO} can be derived when aminated and nonaminated forms are compared (Fig. 1). Methyl increments Δ_{METHYL} had been calculated by

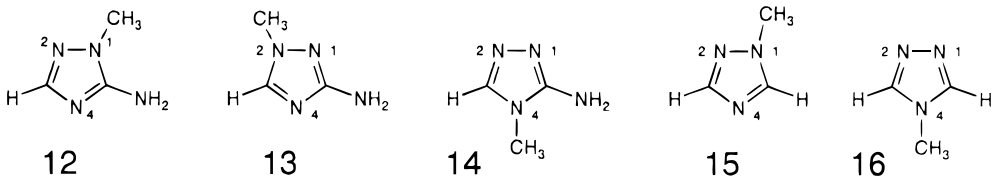

Figure 1. Structures of aminomethyl- and methyl-1,2,4-triazoles.

Table 1. ^{15}N chemical shifts of aminomethyl-1,2,4-triazoles **12**, **13** and **14** and methyl-1,2,4-triazoles **15** and **16**

Atom	**12**	**15**	Δ_{AMINO}	**13**	**15***	Δ_{AMINO}
N-1	−210.6	−171.3	−39.3 (β)	−130.4	−82.2	−48.2 (β)
N-2	−98.0	−82.2	−15.8 (γ)	−187.4	−171.3	−16.1 (γ)
N-4	−166.3	−128.1	−38.2 (β′)	−156.6	−128.1	−28.5 (β′)
	14	**16**	Δ_{AMINO}	Δ_{METHYL}	Δ_{NITRO}	$\Delta_{NTRIAZO}$
N-1	−112.0	−60.3	−51.7 (β)	−5.5 (α)	+5.1 (γ)	−0.1 (γ)
N-2	−75.4	−60.3	−15.1 (γ)	+8.2 (β)	−2.2 (β)	−18.3 (β)
N-4	−241.6	−217.1	−24.5 (β′)	0 (γ)	−10.5 (β′)	−17.1 (β′)

Fritz *et al.*[12] from ^{15}N data for 3-methyl-1,3,4,-thiadiazolone and its non-methylated analogue for the α- and β-positions of the substituent, while the influence of the γ-position was considered to be negligible. When ^{15}N chemical shifts of 3-nitro-1,2,4-triazole (**2**) and nitrobitriazole (**6**) were compared with the data of the basic structure **B1** (see below), we obtained further increments for 3-nitro- and 3-nitrotriazolyl substituents Δ_{NITRO} and $\Delta_{NTRIAZO}$ in the 1,2,4-triazole ring (Table 1).

As the influence of a substituent R on the signals of the various N atoms in a triazole molecule is dependent on distance, the position of any atom in the ring with respect to the substituent position has to be fixed: the atom bearing the substituent is denoted α, its neighbouring atoms β and β' and their neighbouring atoms γ and γ'. The substituent increments Δ are defined unambiguously for different triazole ring positions when two adjacent N-atoms exist in the series α, β and γ.

RESULTS AND DISCUSSION

Identification of tautomeric structures

For 3-nitro-1,2,4-triazole (**2**), three tautomeric forms, **2a**, **2b** and **2c**, can be postulated (Fig. 2). The NMR data (Table 2) allow one to exclude tautomer **2b**: the two ^{15}N signals at 138.6 and 160.7 ppm show a $^{2}J_{N,H\text{-}5}$ coupling with atom H-5 with coupling constants $J = 12$ and 8 Hz, respectively, indicating the presence of a pyridine-like and a pyrrole-like nitrogen atom adjacent to C-5.[10] In order to distinguish between **2a** and **2c**, we apply an increment calculation of the ^{15}N chemical shifts of the basic structures **B1**, **B1***, and **B2** using the data for aminomethylpyridines and the amino and methyl increments Δ_{AMINO} and Δ_{METHYL}. The good agreement of the chemical shifts calculated for **B1** with the experimental values confirms the tautomeric form **2a** [the slight nitro group effect (Table 1) is neglected], i.e. the structure of 3-nitro-1*H*-1,2,4-triazole. The present tautomeric form is delineated by a broken frame in the structures illustrated.

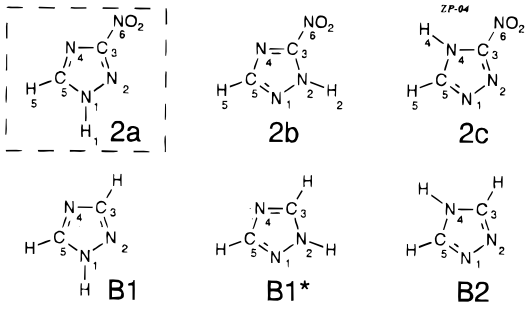

Figure 2. Structures of tautomeric forms **2a**, **2b** and **2c** and 1,2,4-triazole basic structures **B1**, **B1*** and **B2**.

4-Nitro-1,2,3-triazole (**3**) can exist in the tautomeric forms **3a**, **3b** and **3c** (Fig. 3). The ^{15}N signal at -106.7 ppm shows an NOE and a coupling with H-5. This is only consistent with structure **3a**. A second NOE on N-2 or N-3 indicates the presence of a tautomeric equilibrium between **3a** and **3b** or **3a** and **3c**. In order to specify the shift range of the nitrogen signals for an equilibrium between **3a** and **3b** and **3a** and **3c**, we apply an increment calculation with the non-nitrated basic structures **C1** and **C2**, obtained from the NMR data[11] for 1-methyl-1,2,3-triazole (**17**) and 2-methyl-1,2,3-triazole (**18**) and methyl increments Δ_{METHYL} (Table 3). A satisfactory agreement is found only for **3a**/**3b**. The influence of N-2 is decisive, indicating the predominant tautomer **3a** (Table 4).

The three tautomeric forms **4a**, **4b** and **4c** can be expected for 5-amino-3-nitro-1,2,4-triazole (**4**) (Fig. 4). The NMR data (Table 5) do not allow the exclusion of one of the tautomeric forms. An increment correction of the ^{15}N NMR data for aminomethyltriazoles **12**–**14** by methyl and nitro increments Δ_{METHYL} and Δ_{NITRO} gives calculated chemical shifts for the tautomeric forms **4a**, **4b** and **4c**. Comparison with the ^{15}N chemical shift data in Table 5 makes it evident that 5-amino-3-nitro-1,2,4-triazole exists, in DMSO, in the tautomeric form **4a**.

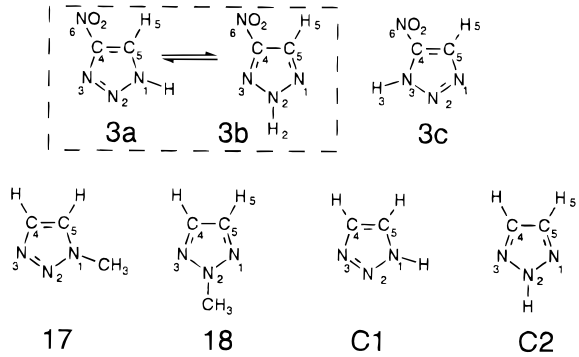

Figure 3. Structures of tautomeric forms **3a**, **3b** and **3c**, 1-methyl-1,2,3-triazole (**17**) and 2-methyl-1,2,3-triazole (**18**) and 1,2,3-triazole basic structures **C1** and **C2**.

Table 2. Chemical shifts δ and coupling constants J of 3-nitro-1,2,4-triazole (**2**) in DMSO-d_6 and of triazole basic structures **B1** and **B2**

Atom	δ (ppm)	Coupling	J (Hz)	Atom	δ (ppm)	Coupling	J (Hz)	NOE	**B1**	**B2**
H-5	8.88	...		N-6	-25.7	...				
H-1	14.06	...		N-2	-92.6	...			-90.4	-60.3
C-5	146.32	$^{1}J_{C\text{-}5,H\text{-}5}$	217.8	N-4	-138.6	$^{2}J_{N\text{-}4,H\text{-}5}$	12		-128.1	-211.6
C-3	163.34	$^{3}J_{C\text{-}3,H\text{-}5}$	14.1	N-1	-160.7	$^{2}J_{N\text{-}1,H\text{-}5}$	8	Found	-165.8	-60.3

Table 3. Chemical shifts δ and coupling constants J of 4-nitro-1,2,3-triazole (**3**) in DMSO-d_6

Atom	δ (ppm)	Coupling	J (Hz)	Atom	δ (ppm)	Coupling	NOE
H-5	9.00	...		N-6	−24.46		
H-1/2	16.1	...		N-3	−44.23		
C-5	125.57	$^1J_{\text{C-5, H-5}}$	205.8	N-2	−52.19		Found
C-4	153.66	$^2J_{\text{C-4, H-5}}$	9.05	N-1	−106.22	$^2J_{\text{N-1, H-5}}$	Found

For 3-nitro-1,2,4-triazolin-5-one (**5**), the two tautomeric hydroxy structures **5a** and **5c** have to be considered in addition to the triazolinone structure **5b** (Fig. 5). Two signals in the ^{15}N spectrum exhibiting NOE identify **5b** as the only existing structure. The two protons show different exchange behaviours owing to their different chemical environments. Whereas N-4 has a mobile proton, the other one at N-1 seems fixed since a ^1J(N, H) is observed. Because of its dihydrotriazole structure, **5b** exhibits spectral deviations from the other nitrated triazoles considered here (Table 6).

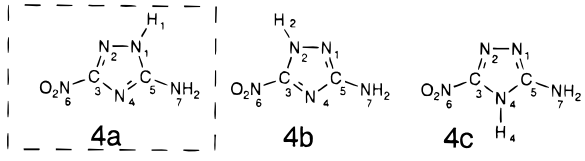

Figure 4. Structures of tautomeric forms **4a, 4b** and **4c** of 5-amino-3-nitro-1,2,4-triazole (**4**).

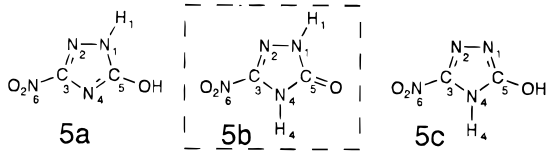

Figure 5. Structures of tautomers **5a, 5b** and **5c** of 3-nitro-1,2,4-triazolin-5-one (**5**).

Three tautomeric forms **6a, 6b** and **6c**, can be postulated for 3-(4-nitro-1,2,3-triazol-2-yl)-1,2,4-triazole (**6**) (Fig. 6). The assignment of the 1,2,4-triazole ^{15}N data (Table 7) is based on the data for compound **2** (Table 2) and allows one to exclude the tautomeric form **6b**, which has no proton on either N-1 or N-4. Comparison with the ^{15}N data for the 1,2,3-triazole basic structure **C2**, without a nitro group correction, enables one to assign the 1,2,3-triazole ring signals of nitrobitriazole (**6**) as well as in the case of the other 4-nitro-1,2,3-triazole derivatives **7**–**11**. To distinguish between **6a** and **6c**, we applied the increment data for **B1** and **B2** (see above), which give for **B1**, corresponding to **6a**, better agreement.

The *C,C*-dinitrobitriazole **8** can exist in three tautomeric forms, **8a**, **8b** and **8c**, with different 1,2,4-triazole ring structures (Fig. 7). The signals of the 1,2,3-triazole ring are easily recognized when the NMR data in Table

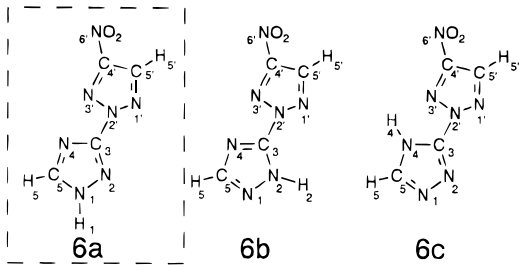

Figure 6. Structures of tautomers **6a, 6b** and **6c** of 3-(4-nitro-1,2,3-triazol-2-yl)-1,2,4-triazole (**6**).

Table 4. Calculated chemical shifts δ (ppm) of 1,2,3-triazole basic structures **C1** and **C2** and shift ranges δ (ppm) for tautomeric equilibria between **3a** and **3b** and **3a** and **3c**

Atom	**C1**	**C2**	**3a–3b**	**3a–3c**
N-1	−137.5	−58.3	−137.5 to −58.3	−137.5 to 29.2
N-2	−24.4	−125.9	−24.4 to 125.9	−24.4
N-3	−29.2	−58.3	−29.2 to −58.3	−29.2 to −137.5

Table 5. Chemical shifts δ of 5-amino-3-nitro-1,2,4-triazole (**4**) in DMSO-d_6 and calculated chemical shifts δ for tautomeric structures **4a, 4b** and **4c**

Atom	δ (ppm)	Atom	δ (ppm)	NOE	**4a**	**4b**	**4c**
H-5	6.89	N-6	−23.75				
H-1	13.2	N-2	−107.49		−108.4	−184.1	−77.6
C-5	157.66	N-4	−179.30		−176.8	−167.1	−246.6
C-3	161.09	N-1	−200.18	Found	−200.0	−133.5	−106.9
		N-7	−327.13	Found			

Table 6. Chemical shifts δ and coupling constants J of 3-nitro-1,2,4-triazolin-5-one (**5**) in DMSO-d_6

Atom	δ (ppm)	Atom	δ (ppm)	Coupling	J (Hz)	NOE
H-1	12.79	N-6	−34.51			
H-4	12.16	N-2	−112.87			
C-3	148.18	N-1	−206.41	$^1J_{\text{N-1, H-1}}$	102.2	Found
C-5	154.97	N-4	−243.89			Found

Table 7. Chemical shifts δ and coupling constants J of 3-(4-nitro-1,2,3-triazol-2-yl)-1,2,4-triazole (**6**) in DMSO-d_6

Atom	δ (ppm)	Coupling	J (Hz)	Atom	δ (ppm)	Coupling	J (Hz)	NOE
H-5′	9.04	...		N-6′	−27.31	...		
C-5′	133.46	$^1J_{\text{C-5′, H-5′}}$	207.9	N-1′	−44.21	$^2J_{\text{N-1′, H-5′}}$	12.5	
C-4′	154.85	$^2J_{\text{C-4′, H-5′}}$	9.0	N-3′	−58.98	...		
				N-2′	−133.84	$^3J_{\text{N-2′, H-5′}}$	10.7	
H-5	8.90	...		N-2	−108.67			
H-1	14.87	...		N-4	−145.19	$^2J_{\text{N-4, H-5}}$	11.0	
C-5	145.95	$^1J_{\text{C-5, H-5}}$	215.2	N-1	−165.91	$^1J_{\text{N-1, H-1}}$	102	Found
C-3	156.55	$^3J_{\text{C-3, H-5}}$	12.9					

Table 8. Chemical shifts δ and coupling constants J of 3-(4-nitro-1,2,3-triazol-2-yl)-5-nitro-1,2,4-triazole (**8**) in DMSO-d_6

Atom	δ (ppm)	Coupling	J (Hz)	Atom	δ (ppm)	Coupling	J (Hz)	NOE
H-5′	9.00	...		N-6′	−28.28	...		
				N-1′	−45.03	$^2J_{\text{N-1′, H-5′}}$	12	
C-5′	134.49	$^1J_{\text{C-5′, H-5′}}$	209.5	N-3′	−60.05			
C-4′	155.36	$^2J_{\text{C-4′, H-5′}}$	9.0	N-2′	−138.3	$^3J_{\text{N-2′, H-5′}}$	10.5	
H-1/2	15.2	...		N-6	−28.28	...		
C-3	150.80	...		N-1	−101.48			Found
C-5	160.09	...		N-2	−138.18			Found
				N-4	−155.63			

8 are compared with the calculated data for structure **C2** and the 1,2,3-triazole compound **3**.

Two NOEs on the N signals of the 1,2,4-triazole point to the existence of a tautomeric equilibrium. In order to determine the existing forms, we calculated for the three tautomers **8a**, **8b** and **8c** the ^{15}N data for the 1,2,4-triazole unit using the basic structures **B1**, **B1*** and **B2** (see above) and nitro and nitrotriazolyl increments Δ_{NITRO} and Δ_{NTRIAZO}. While the measured ^{15}N NMR values argue against the existence of the tautomeric structure **8c**, they are consistent with an equilibrium between **8a** and **8b** (Table 9).

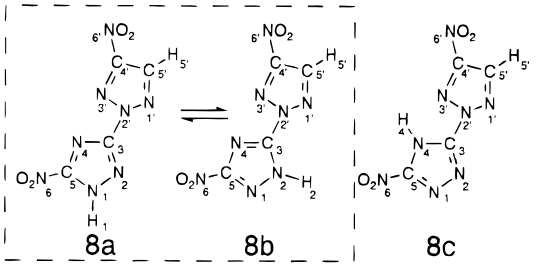

Figure 7. Structures of tautomers **8a**, **8b** and **8c** of 3-(4-nitro-1,2,3-triazol-2-yl)-5-nitro-1,2,4-triazole (**8**).

Identification of isomeric structures

The synthetic pathway of 2-(2,4-dinitro-phenyl)-4-nitro-1,2,3-triazole (**7**) (see Scheme 1) proves its structure and the 2-substitution position of the 1,2,3-triazole ring.

Table 9. Calculated chemical shifts δ (ppm) of basic structure **C2** of 1,2,3-triazole and of 1,2,4-triazole nitrogen atoms in tautomeric structures **8a**, **8b** and **8c**

Atom	C-2	Atom	**8a**	**8b**	**8c**
N-1′	−58.3	N-1	−168.1	−92.7	−62.6
N-2′	−125.9	N-2	−103.6	−179.0	−73.5
N-3′	−58.3	N-4	−155.7	−155.7	−238.5

However, for the isomeric product that we obtained besides **7**, when 4-nitro-1,2,3-triazole was reacted with 2,4-dinitrochlorobenzene, two structures, **10** and **10***, are possible (Fig. 8). As 3-substituted 4-nitro-1,2,3-triazoles are unknown (their formation may be prevented because of steric and electronic reasons), we considered the second isomer to be 1-(2,4-dinitrophenyl)-4-nitro-1,2,3-triazole[9] (**10**).

This is confirmed by the NMR data for the 1,2,3-triazole unit of the dinitrophenyl-substituted 4-nitro-1,2,3-triazoles **7** and **10** (Table 10). The displacement of the dinitrophenyl group from N-2 to N-3 should result in a pronounced signal shift of carbon C-4 in **10***. We find nearly identical C-4 chemical shifts, but a distinct shift of the H-5 signal (1 ppm) and of the C-5 signal (5 ppm). On the other hand, the dinitrophenyl substitution gives ^{15}N signals of unsubstituted and dinitrophenyl substituted nitrogen atoms in **7** and **10** with similar chemical shifts.

Three compounds, **9a**, **9b** and **9c**, can result from the *N*-nitration of mononitrobitriazole **6** (Fig. 9). The preceding tables allow us to assign the NMR signals (Table 11) except for N-2′ and N-4, which are distinguished by 2D N,H long-range correlation. A strong low-field shift is observed for N-1 compared with N-1 in **6a**, the obvious position of the nitro substituent, and for its neighbouring hydrogen atom H-5. Hence it is concluded that the present structure is **9a**.

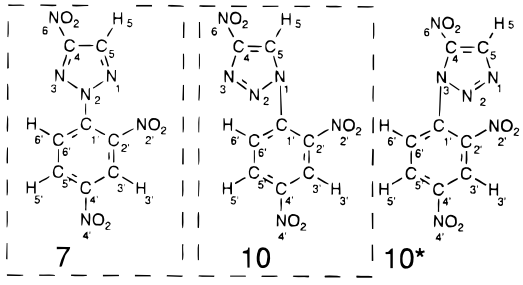

Figure 8. Structures of 2-(2,4-dinitrophenyl)-4-nitro-1,2,3-triazole (**7**), 1-(2,4-dinitrophenyl)-4-nitro-1,2,3-triazole (**10**) and 3-(2,4-dinitrophenyl)-4-nitro-1,2,3-triazole (**10***).

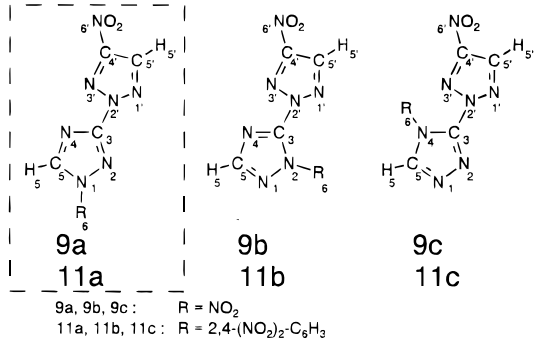

Figure 9. Structures of isomeric substituted bitriazoles **9a–c** and **11a–c**.

Table 10. Chemical shifts δ and coupling constants J of the 1,2,3-triazole ring of 2-(2,4-dinitrophenyl)-4-nitro-1,2,3-triazole (**7**) and 1-(2,4-dinitrophenyl)-4-nitro-1,2,3-triazole (**10**) in DMSO-d_6

7				**10**			
Atom	δ (ppm)	Coupling	J (Hz)	Atom	δ (ppm)	Coupling	J (Hz)
H-5	9.22			H-5	10.18		
C-5	134.66	$^1J_{\text{C-5, H-5}}$		C-5	127.33	$^1J_{\text{C-5, H-5}}$	
C-4	156.29	$^2J_{\text{C-4, H-5}}$		C-4	156.53	$^2J_{\text{C-4, H-5}}$	
N-6	−30.34			N-6	−18.90		
N-1	−44.00	$^2J_{\text{N-1, H-5}}$	13	N-3	−26.44		
N-3	−59.10			N-2	−32.77		
N-2	−138.50	$^3J_{\text{N-2, H-5}}$	11	N-1	−134.58		
		$^3J_{\text{N-2, H-6′}}$	2				

Table 11. Chemical shifts δ and coupling constants J of 3-(4-nitro-1,2,3-triazol-2-yl)-1-nitro-1,2,4-triazole (**9**) in DMSO-d_6

Atom	δ (ppm)	Coupling	J (Hz)	Atom	δ (ppm)	Coupling	J (Hz)
H-5′	9.22	...		N-6′	−28.37	...	
C-5′	134.96	$^1J_{\text{C-5′, H-5′}}$	209.8	N-1′	−43.68	$^2J_{\text{N-1′, H-5′}}$	12.9
C-4′	155.80	$^2J_{\text{C-4′, H-5′}}$	9.1	N-3′	−58.64		
				N-2′	−139.35	$^3J_{\text{N-2′, H-5′}}$	11.1
H-5	10.12	...		N-6	−65.82	...	
C-5	143.79	$^1J_{\text{C-5, H-5}}$	233.9	N-1	−105.63	$^2J_{\text{N-1, H-5}}$	6.9
C-3	152.39	$^3J_{\text{C-3, H-5}}$	15.6	N-2	−118.59		
				N-4	−140.44	$^2J_{\text{N-4, H-5}}$	12.0

Table 12. Chemical shifts δ and coupling constants J of 1-(2,4-dinitrophenyl)-3-(4-nitro-1,2,3-triazol-2-yl)-1,2,4-triazole (**11**) DMSO-d_6

Atom	δ (ppm)	Coupling	J (Hz)	Atom	δ (ppm)	Coupling	J (Hz)
H-5′	9.18	...		N-6′	−27.39	...	
C-5′	137.26	$^1J_{\text{C-5′, H-5′}}$	210	N-1′	−43.38	$^2J_{\text{N-1′, H-5′}}$	13.1
C-4′	158.33	$^2J_{\text{C-4′, H-5′}}$	8.6	N-3′	−58.33		
				N-2′	−139.71	$^3J_{\text{N-2′, H-5′}}$	12.2
H-5	9.66			N-2	−104.93		
C-5	151.25	$^1J_{\text{C-5, H-5}}$	224	N-4	−136.96	$^2J_{\text{N-4, H-5}}$	10.7
C-3	160.22	$^3J_{\text{C-3, H-5}}$	13.4	N-1	−169.49	$^2J_{\text{N-1, H-5}}$	8.0
						$^3J_{\text{N-1, H-6″}}$	1.5

As in the case of the preceding dinitrobitriazole, the substitution position of the 1,2,4-triazole ring in the dinitrophenyl-substituted nitrobitriazole **11** has to be determined because three isomers, **11a**, **11b** and **11c** (Fig. 9), must be considered. Triazole and phenyl ^{13}C NMR signals of the three different rings are easy to distinguish as the $^1J_{C,H}$ coupling constants clearly differ (dinitrophenyl < 200 Hz < 1,2,3-triazole < 1,2,4-triazole; Table 12). Structure **11b** can be excluded because of the occurrence of a weak 1H{1H} NOE between H-5 of the 1,2,4-triazole ring and H-6 of the 2,4-dinitrophenyl group. This interaction is only possible with isomers **11a** and **11c**.

Table 13. Calculated chemical shifts δ (ppm) of 1,2,4-triazole atoms in isomeric structures **11a–c**

Atom	**11a**	**11b**	**11c**
N-1	−165.9	−90.5	−60.4
N-2	−108.7	−184.1	−78.6
N-4	−145.2	−145.2	−228.7

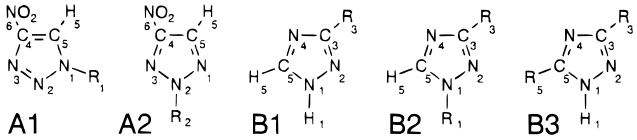

Figure 10. Structures of nitrotriazole structures **A1, A2, B1, B2** and **B3.**

The ^{15}N data for the 1,2,4-triazole ring of the isomers **11a–c** (see Table 11) are calculated from the basic structures **B1**, **B1*** and **B2** and the nitrotriazolyl increments Δ_{NTRIAZO} (Table 13). Good agreement between the measured data and the ^{15}N chemical shifts calculated for isomer **11a** is established. The pronounced substitution effect on the chemical shift of the substitution position N-1 found for **9** is not observed here.

CONCLUSIONS

In Tables 14 and 15 the NMR signal shifts are arranged in order to combine data evidently belonging together.

Table 14. Chemical shift δ (in ppm) of 1,2,3-triazole structures **A1** and **A2**

H-5	C-4	C-5	N-1	N-2	N-3	N-6	Compound	Structure	Substituent
9.1	154	126	−106	−52	−44	−25	**3**	**A1**	R_1 = H
10.2	157	127	−135	−33	−26	−19	**10**	**A1**	R_1 = dinitrophenyl
9.2	156	135	−44	−139	−59	−30	**7**	**A2**	R_2 = dinitrophenyl
9.0	155	134	−44	−134	−59	−27	**6**	**A2**	R_2 = triazolyl
9.0	156	135	−45	−138	−60	−28	**8**	**A2**	R_2 = *C*-nitrotriazolyl
9.2	156	135	−44	−139	−59	−28	**9**	**A2**	R_2 = *N*-nitrotriazolyl
9.2	158	137	−43	−140	−58	−27	**11**	**A2**	R_2 = dinitrophenyltriazolyl

Table 15. Chemical shift δ (ppm) of 1,2,4-triazole structures **B1, B2** and **B3**

H-1	H-5	C-3	C-5	N-1	N-2	N-4	N-3	Compound	Structure	Substituents
14.1	8.9	163	146	−161	−93	−139	−26	**2**	**B1**	$R_3 = NO_2$
14.8	8.8	157	146	−166	−109	−145		**6**	**B1**	R_3 = nitrotriazolyl
...	10.1	153	144	−106	−119	−140		**9**	**B2**	$R_1 = NO_2$, R_3 = nitrotriazolyl
...	9.6	160	151	−170	−105	−137		**11**	**B2**	R_1 = dinitrophenyl, R_3 = nitrotriazolyl
13.2	6.9	161	158	−200	−108	−179	−24	**4**	**B3**	$R_3 = NO_2$, $R_5 = NH_2$
15.2	...	151	160	−101	−138	−156		**8**	**B3**	R_3 = nitrotriazolyl, $R_5 = NO_2$

When two 1,2,3-triazoles (**A1** and **A2**) and three 1,2,4-triazoles (**B1**–**B3**) are distinguished, certain connections and influences become clear and the previous assignments are confirmed. Certain deviations can be explained by tautomeric equilibria and substituent effects. Whereas for the ^{1}H and ^{13}C shifts the type of the substituent at the triazole ring seems to be decisive, the chemical shift of the ^{15}N signals is controlled by the pyridine or pyrrole character of the nitrogen atoms. Distinct substituent-induced effects are observed, however, for structures **B2** and **B3**.

Essential information is obtained from the coupling behaviour of triazoles: C–H coupling constants of the 1,2,3-triazole structures ($^{1}J_{C\text{-}5,\,H\text{-}5} = 206$–$210$ Hz and $^{2}J_{C\text{-}4,\,H\text{-}5} = 8.1$–$9.1$ Hz) are found to be smaller than the 1,2,4-triazole coupling constants ($^{1}J_{C\text{-}3,\,H\text{-}3} = 215$–$234$ Hz and $^{3}J_{C\text{-}5,\,H\text{-}3} = 12.9$–$15.6$ Hz). $^{1}J_{N,\,H}$ coupling (102 Hz) was only measured for **5** and **6**, as tautomeric equilibria and exchange reactions with the solvent prevented the coupling in the case of the other triazoles.

For protons attached to carbon we find $^{2}J_{N,\,H}$ coupling constants of 6.9–8 Hz for pyrrole-like nitrogen atoms and of 10.5–13 Hz for pyridine-like nitrogen atoms. $^{3}J_{N,\,H}$ coupling is observed only in the 1,2,3-triazole ring with 11–12 Hz ($^{3}J_{N\text{-}2,\,H\text{-}5}$), although the same atom sequence (*N*—N—C—*H*) exists in 1,2,4-triazoles.

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