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NMR Studies of the Equilibria Produced by 6- and 8-Substituted Tetrazolo[1,5-*a*]pyridines

Piotr Cmoch,[1] Lech Stefaniak[1]* and Graham A. Webb[2]
[1] Institute of Organic Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, P.O. Box 58, 01-224 Warsaw, Poland
[2] Department of Chemistry, University of Surrey, Guildford, Surrey GU2 5XH, UK

^{1}H, ^{13}C and ^{15}N NMR data are reported for nine tetrazoles. Five of these compounds are found to exhibit valence tautomeric equilibrium between the tetrazole and azide forms. The position of this equilibrium at 298 K is found to be dependent on the solvent and the position and nature of the substituent. More polar solvents favour the tetrazole form. Protonation studies on the two forms using TFA as a solvent are reported. The favoured site of protonation is found to be N-4 for the azide form and N-1 for the tetrazole form.

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INTRODUCTION

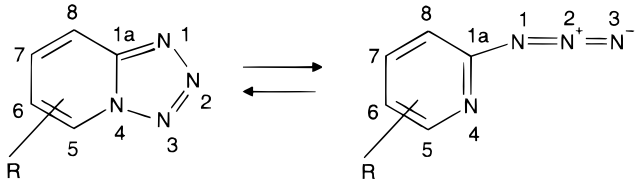
Tetrazoles are known to be important molecules in many areas of commerce, including photography, medicine, agriculture and explosives.[1] We have previously reported preliminary multinuclear magnetic resonance data on compounds from this class.[2] In this paper, we present and discuss our more extensive compilation of multinuclear magnetic resonance data to include a study of valence tautomeric equilibria of the type shown in Fig. 1. The effects on the position of equilibria of this type of variations in the solvent and in the nature and position of the substituent R are reported.

RESULTS AND DISCUSSION

The ^{1}H, ^{13}C and ^{15}N NMR data obtained for nine tetrazoles are given in Tables 1, 2 and 3, respectively.

The multi-nuclear magnetic resonance data for the unsubstituted tetrazolo[1,5-*a*]pyridine derivative have been reported elsewhere[3,4] and are reproduced here (compound **1**) for the purpose of comparison with the results obtained for the substituted compounds **2**–**9**. We also note an earlier report[5] in which ^{1}H and ^{13}C NMR results were given for compounds **2** and **7** taken in acetone solution. However, this is the first time that nitrogen NMR results have become available for these two compounds and multinuclear NMR results for the other compounds listed in Tables 1–3 in a variety of solvents. Concerning this type of valence tautomerism, some additional ^{1}H, ^{13}C NMR[6–9] and ^{15}N NMR[10–12] data are available in the literature.

The ^{1}H and ^{13}C NMR assignments reported in Tables 1 and 2 are made on the basis of comparison with those reported previously[2,3,5–7] for compounds **1**, **2**, **4** and **7** and from the observation of signal multiplicities, relative spin–spin couplings and decoupled spectra. For the ^{13}C assignments, additional information is obtained from proton–carbon correlations, ^{1}H coupled ^{13}C spectra and INADEQUATE measurements. The ^{15}N NMR assignments given in Table 3 are based on those given previously[2–4,10–12] for compound **1**, which exists in the tetrazole form only, and the use of the samples of compounds **3**, **4** and **5**, which are selectively ^{15}N labelled in positions 1 and 3, and compound **6**, which is labelled in position 3 (Fig. 1). It is interesting that the reaction between 2-chloro-6-methyl-5-nitropyridine and labelled potassium azide (KN*NN*), as



Tetrazole form (T) Azide form (A)

1,	R = H	6,	R = 6-Cl, 8-Cl
2,	R = 6-NO_2	7,	R = 8-NO_2
3,	R = 5-CH_3, 6-NO_2	8,	R = 8-COOH
4,	R = 6-Br	9,	R = 8-Cl
5,	R = 6-COOH		

Figure 1. Equilibrium between tetrazole (T) and azide (A) forms of the compounds studied.

* *Correspondence to*: L. Stefaniak.
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Table 1. ^{1}H chemical shifts (ppm) for the azide (A) and tetrazole (T) forms of the compounds investigated

Compound	R	Solvent	H-5		H-6	H-7[a]		H-8[a]	
			A	T	T	A	T	A	T
1[b]	H	DMSO		9.30	7.43		7.84		8.20
		TFA		9.10	7.74		8.32		8.24
2	6-NO_2	$CDCl_3$	9.21	9.88		8.41	8.47	6.93	8.21
						(8.90)	(9.70)	(8.90)	(9.70)
		Acetone[e]	9.20	10.32		8.57	8.60	7.14	8.36
		DMSO		10.62			8.53		8.41
		TFA	9.22	9.86		8.98	8.57	7.80	8.29
						(9.30)	(9.80)	(9.30)	(9.80)
3[c]	5-CH_3, 6-NO_2	$CDCl_3$				8.30	8.35	6.78	8.03
						(8.70)	(9.70)	(8.70)	(9.70)
		Acetone					8.46		8.17
		DMSO					8.43		8.26
		TFA				8.92	8.47	7.65	8.10
						(9.30)	(9.70)	(9.30)	(9.70)
4	6-Br	$CDCl_3$	8.40	9.03		7.73	7.77	6.72	7.99
						(8.55)	(9.40)	(8.55)	(9.40)
		Acetone		9.49			7.98		8.13
		DMSO		9.80			8.01		8.22
		TFA	8.29	9.06		8.36	8.10	7.48	8.02
						(9.10)	(9.40)	(9.10)	(9.40)
5[d]	6-COOH	DMSO		9.78			8.21		8.28
		TFA	8.91	9.63		8.87	8.52	7.73	8.20
						(8.95)	(9.40)	(8.95)	(9.40)
6	6-Cl, 8-Cl	$CDCl_3$	8.21	8.84		7.68	7.73		
		DMSO		9.80			8.35		
		TFA	8.27	8.84		8.25	7.86		
7	8-NO_2	Acetone[e]		9.61	7.77		8.90		
		DMSO		9.77	7.70		8.90		
		TFA		9.30	7.71		8.93		
8	8-COOH	DMSO		9.56	7.58		8.44		
		TFA		9.30	7.86		8.96		
9	8-Cl	$CDCl_3$		8.78	7.21		7.72		
		DMSO		9.35	7.47		8.07		
		TFA		8.85	7.44		7.97		

[a] ^3J(H-7, H-8) coupling constants (Hz) in parentheses.
[b] Data taken from Ref. 3.
[c] Chemical shifts for protons of the 5-CH_3 group: in $CDCl_3$, A 2.85 ppm, T 3.41 ppm; in acetone, T 3.34 ppm; in DMSO, T 3.22 ppm; in TFA, A 2.92 ppm, T 3.25 ppm.
[d] Proton signals of the group COOH are very broad at about 5 ppm.
[e] Data taken from ref. 5.

revealed from the ^{15}N spectrum, can proceed in two different ways (Fig. 2): $Cl^- \rightarrow N_3^-$ nucleophilic substitution and (which is in agreement with earlier studies[13–15]) the ANRORC type, for which a scheme is presented in Fig. 2.

As a result of the synthesis, we obtained two compounds of type **3** with the label in positions N-1, N-3 and N-2, N-4, respectively (see Fig. 2). On the basis of integration, from the ^{15}N spectrum, we can assume that reaction of 2-chloro-6-methyl-5-nitropyridine and the labelled azide took place to *ca.* 80% by the first route and *ca.* 20% by the second route. Owing to labelling, the assignments of all ^{15}N signals became simple. As noted in footnote b in Table 3, there remain a few cases in which it has not been possible to make unambiguous ^{15}N signal assignments owing to the close proximity in which some signals are observed. However, this does not impair our investigation of the valence tautomeric equilibrium given in Fig. 1 since our quantitative estimates of the equilibrium mixture are based on integrated ^{1}H measurements. In distinguishing between the NMR signals arising from each of the two forms, in the equilibrium given in Fig. 1 good use is made of the shielding differences found for the given proton, carbon and nitrogen nuclei in the two forms.

In the ^{1}H NMR spectra we observe small differences between the azide (A) and tetrazole (T) chemical shifts but in the ^{13}C spectra the differences between both forms are much larger and especially big differences are observed in the case of ^{15}N NMR. Other differences are observed in the values of the coupling constants ^3J(H-7, H-8), $^1J(^{13}$C-5, H-5) and $^1J(^{13}$C-8, H-8), which are larger for the tetrazole than for the corresponding azide form. The latter fact is in good agreement with the calculations made by Denisov *et al.*[7] As shown in Tables 1–3, slow exchange occurs on the NMR time-scale between the T and A forms for many of the compounds studied, such that separate NMR signals are observable for the two forms. In these cases it is possible to estimate equilibrium constants for the equilibrium given in Fig. 1. We carried out an experiment (for compound **2**) in which we observed the intensity of an absorption

Table 2. ^{13}C chemical shifts (ppm) for the azide (A) and tetrazole (T) forms of the compounds investigated

			C-1a		C-5[a]		C-6		C-7[a]		C-8[a]	
Compound	R	Solvent	A	T	A	T	A	T	A	T	A	T
1[b]	H	DMSO		148.1		126.4		117.3		133.1		115.2
		TFA		140.2		129.9		120.3		140.6		110.9
2	6-NO_2	$CDCl_3$	160.0	149.1	145.5	125.1	141.0	139.8	134.0	126.5	113.8	116.3
					(190.3)	(196.9)			(171.4)	(175.3)	(175.1)	(178.6)
		Acetone[f]	160.5	150.3	146.1	127.3	143.2	141.3	135.4	127.8	115.0	116.5
		DMSO		149.9		127.7		140.8		128.3		116.2
		TFA	156.6	147.2	137.7	125.0	140.7	140.4	140.4	128.8	116.8	114.4
					(198.2)	(202.0)			(178.3)	(177.7)	(178.7)	(183.0)
3[c]	5-CH_3, 6-NO_2	$CDCl_3$	157.3	148.3	155.1	138.3	141.2	139.3	135.8	128.1	111.8	113.1
									(169.5)	(173.1)	(172.5)	(179.2)
		Acetone		149.5		139.4		140.6		129.4		113.6
		DMSO		148.2		138.4		139.5		128.9		112.6
		TFA	155.3	145.8	151.6	139.2	140.9	140.0	142.5	131.2	113.9	110.7
									(176.9)	(176.2)	(178.3)	(184.2)
4	6-Br	$CDCl_3$ [g]		147.4		125.6		111.7		135.7		116.3
		Acetone		148.5		127.4		112.1		136.8		117.0
		DMSO		147.2		126.8		111.4		136.2		115.9
		TFA	150.3	141.6	139.5	126.4	115.1	115.1	150.5	142.1	116.9	112.2
					(197.2)	(202.0)			(176.3)	(177.4)	(176.5)	(184.9)
5[d]	6-COOH	DMSO		149.0		129.4		121.9		132.6		114.9
		TFA	155.0	145.4	141.9	129.9	123.0	122.2	147.5	136.3	116.3	112.9
					(195.5)	(200.2)			(175.1)	(174.6)	(177.1)	(182.6)
6	6-Cl, 8-Cl	$CDCl_3$	150.0	146.8	145.3	122.2	123.2	121.1	138.1	132.3	127.5	124.9
					(189.2)	(198.2)			(171.9)	(175.6)		
		DMSO		146.6		124.2		120.7		133.1		124.0
		TFA[g]		144.7		121.9		121.2		135.1		127.3
7	8-NO_2	Acetone[f]		144.7		133.2		116.7		132.1		137.6
		DMSO		143.2		132.9		116.2		132.0		135.7
		TFA		140.5		131.6		117.2		133.4		134.4
8	8-COOH	DMSO		146.8		130.3		116.8		136.6		119.4
		TFA		140.0		131.2		120.0		143.2		115.5
9	8-Cl	$CDCl_3$		147.3		124.0		116.5		130.8		123.0
		DMSO		147.1		125.6		117.5		132.3		120.1
		TFA		143.8		124.3		118.9		135.5		120.3

[a] Coupling constants $^1J(^{13}C, H)$ in parentheses.
[b] Data from Ref. 3.
[c] Chemical shifts for ^{13}C nuclei of the CH_3 group: in $CDCl_3$, A 24.2 ppm, T 15.8 ppm; in acetone, T 15.9 ppm; in DMSO, T 15.5 ppm; in TFA, A 17.7 ppm, T 13.2 ppm.
[d] Chemical shifts for ^{13}C nuclei of the COOH group: in DMSO, T 164.6 ppm; in TFA, A 164.8 ppm, T 166.0 ppm.
[e] Chemical shifts for ^{13}C of the COOH group: in DMSO, T 163.5 ppm; in TFA, T 163.6 ppm.
[f] Chemical shifts taken from Ref. 5.
[g] No data for A owing to the low concentration of this form.

signal for a proton undergoing exchange when another proton site is saturated by irradiation with a second r.f. field. When we irradiated, for example, signal H-5 in the tetrazole form we found a response for H-5 of the azide form. This provides proof of saturation transfer and that the system is in equilibrium. In order to obtain additional confirmation of equilibrium we also performed experiments at different temperatures. At higher temperatures, we found larger values for the equilibrium constants. For example (for compound **2**) $T = 253$ K, $K_{A/T} = 0.80$; $T = 298$ K, $K_{A/T} = 1.05$; $T = 323$ K, $K_{A/T} = 1.63$.

Table 4 shows the results obtained for these equilibrium constants, which are found to depend sensitively upon the position and nature of the substituent and on the solvent used.

Compounds **7–9** exist only in the T form in the solvents used here at 298 K, but compounds **2–6** can exist in both forms in $CDCl_3$ and TFA solutions.

It is apparent from Table 4 that only those compounds with an electron-withdrawing substituent at position 6 exhibit equilibrium. This is supported by earlier studies, not involving NMR.[16,17] The strongest electron-withdrawing effect is shown by the NO_2 group in position 6 of the tetrazolopyridine ring. Compounds **7–9** with the same substituents in position 8 do not exhibit this equilibrium behaviour, regardless of the solvent used, but the position of the equilibrium for compounds **2–6** is shifted towards the A form as the polarity of the solvent used decreases.[16]

Messmer and Hajós[8] stated that (a) in aprotic solvents the chemical shifts of all the protons in tetrazoles have higher δ values relative to those in the corresponding azides due to the presence of a ring current in tetrazoles and (b) the electron-releasing methyl group enhances the stability of the tetrazole form. Our observations confirm these facts. In TFA solutions we observe rather the opposite situation because the values of the

Table 3. ^{15}N chemical shifts (ppm) for the azide (A) and tetrazole (T) forms of the compounds investigated

			N-1		N-2		N-3		N-4		NO_2	
Compound	R	Solvent	A	T	A	T	A	T	A	T	A	T
1[a]	H	DMSO		−67.8		−18.3		−31.8		−128.3		
		TFA		−161.3		−13.5		−34.9		−131.3		
2	6-NO_2	$CDCl_3$	−275.1	−66.2	−144.6	28.6	−140.7	−31.8	−96.3	−133.8	−23.4[b]	−17.1[b]
		DMSO		−66.8		26.2		−26.2		−130.7		−17.6
		TFA	−267.1	−94.8	−152.8	7.8	−130.3	−28.8	−191.8	−133.8	−26.0[b]	−24.1[b]
3	5-CH_3, 6-NO_2	$CDCl_3$	−270.0	−65.9	−144.0	25.8	−141.9	−28.5	−91.5	−128.7	−12.3	−18.3
		DMSO		−65.9		23.8		−28.3		−126.7		−14.2
		TFA	−267.9	−106.0	−153.2	1.3	−129.8	−30.5	−198.0	−129.0	−23.6	−19.7
4	6-Br	DMSO		−67.0		18.8		−31.4		−126.1		
		TFA	−275.0	−135.8	−152.1	−9.5	−131.8	−35.3	−201.4	−129.0		
5	6-COOH	DMSO		−68.5		21.7		−29.1		−129.2		
		TFA	−269.3	−119.1	−153.1	−1.8	−130.3	−31.8	−203.8	−131.8		
6	6-Cl, 8-Cl	$CDCl_3$	−276.1	−66.3	−143.3	20.8	−141.4	−28.0	−90.8	−129.8		
		DMSO		−67.1		18.9		−27.3		−126.8		
		TFA		−95.8		−8.4		−30.5		−129.9		
7	8-NO_2	DMSO		−67.3		20.7		−30.0		−122.9		−19.9
		TFA		−106.5		1.1		−31.8		−126.0		−26.4
8	8-COOH	DMSO		−65.3		19.1		−31.7		−125.9		
		TFA		−151.2		−9.7		−33.6		−129.0		
9	8-Cl	DMSO		−67.9		18.2		−27.8		−126.6		
		TFA		−115.0		−6.5		−31.3		−129.7		

[a] Chemical shifts taken from Ref. 3.
[b] Assignments may be reversed.

equilibrium constants found are different from those in $CDCl_3$ solution. It seems difficult to explain such a behaviour, but it is obvious that two competitive reactions exist. TFA can cause opening of the tetrazole ring and protonation of the compound, or first protonation and subsequently opening of the ring. Which mechanism is more probable depends on the nature and the position of the substituents.

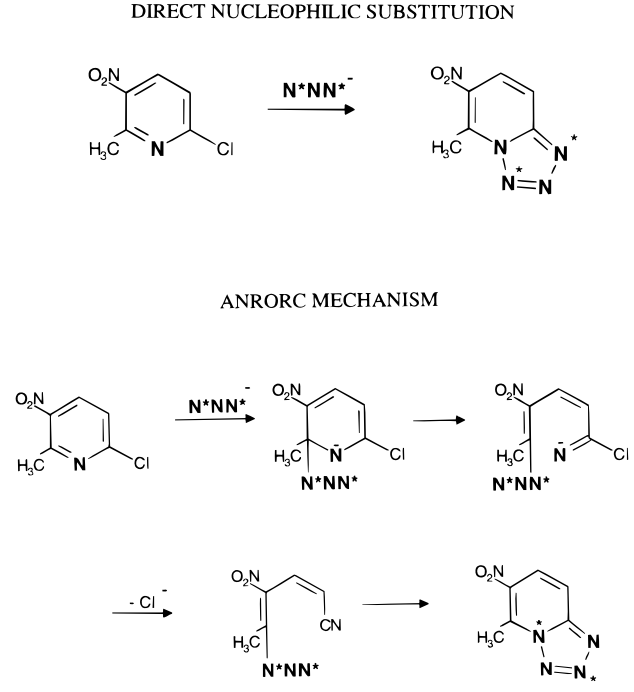

Figure 2. Two possible mechanisms for the reaction between 2-chloro-6-methyl-5-nitropyridine and labelled azide.

The use of TFA as a solvent also gives rise to protonation of the nitrogenous sites. Naumenko *et al.*[18] carried out experiments for 1,5- and 2,5-disubstituted tetrazoles and they came to the conclusion that N-4 in such compounds is protonated. In our experiments with labelled compounds, we ascertained that the protonation site for the tetrazole forms of the compounds studied is N-1, as revealed by the ^{15}N NMR data in Table 3. The N-1 signal of the tetrazoles in TFA as a solvent shows an increase in shielding which varies from 30 to 90 ppm when compared with its value in the other solvents used. The observed increases in nitrogen shielding for N-1 in the T form indicate that protonation occurs for all of the compounds studied and depends on the nature of the substituent in the tetrazolopyridine ring. In compounds with a strong electron-withdrawing substituent, such as a nitro group, the shielding difference between the protonated and non-protonated forms of N-1 is only 30–40 ppm, whereas in the case of other groups it is larger (50–80 ppm). Only for compound **8** is the difference about 90 ppm, indicating that this compound is strongly protonated. For those compounds for which we are able to observe ^{15}N NMR signals for the

Table 4. Azide–tetrazole equilibrium constants (298 K) for some of the compound in different solvents

Compound	R	$CDCl_3$	Acetone	DMSO	TFA
2	6-NO_2	1.05	0.10	0.00	0.28
3	5-CH_3, 6-NO_2	0.08	0.00	0.00	0.18
4	6-Br	0.02	0.00	0.00	0.29
5	6-COOH	0.00	0.00	0.00	0.70
6	6-Cl, 8-Cl	0.31	0.07	0.00	0.02

A form, protonation in TFA occurs preferentially on the ring atom N-4. The differences between the non-protonated and protonated forms ($CDCl_3$/TFA) are −96 and −107 ppm for compounds **2** and **3**, respectively.

CONCLUSION

We conclude that a combination of ^1H, ^{13}C and particularly ^{15}N NMR data provide a very satisfactory method of obtaining quantitative estimates of the position of equilibrium between the tetrazole and azide forms of the compounds studied. The tetrazole an azide tautomers are readily distinguished by their NMR spectra. The positions of the aromatic protons of the A form in chloroform solution are shielded with respect to their corresponding positions in the T form. In particular this applies to H-8, where the shielding difference is about −1.3 ppm. In TFA solution a similar difference in ^1H NMR signals of the two forms is noted, with the exception of that for H-7, which is deshielded upon protonation by 0.5 ppm. In $CDCl_3$ solution the ^{13}C signals of the A form are deshielded with respect to the corresponding T nuclei. This is especially noteworthy for C-5 where the shielding difference between the T and A forms is about 20 ppm. In general, the differences in the positions of the signals of given carbon nuclei for the two forms in $CDCl_3$ are maintained in TFA. In both $CDCl_3$ and TFA very large ^{15}N shielding differences are observed for the two forms. In $CDCl_3$ the N-1, N-2 and N-3 signals are more highly shielded in the A form than are those for the corresponding nuclei in the T form, by *ca.* −210, −160 and −115 ppm, respectively, whereas the opposite situation applies to N-4, where the difference is about +35 ppm. The same situation occurs in the case of TFA solutions but here all of the ^{15}N nuclei of the A form are much more shielded than are the corresponding nuclei in the T form and the differences are N-1 *ca.* −120 ppm, N-2 *ca.* −130 ppm, N-3 *ca.* −100 ppm and N-4 *ca.* −85 ppm.

EXPERIMENTAL

Compounds

The compounds studied were prepared by previously published procedures: compounds **1**, **2**, **3**, **5**, **7** and **8**[5] and compounds **4**, **6** and **9**[19]. Melting points were determined in capillary tubes on a Buchi SMP-20 melting point apparatus. Mass spectra were determined using an AMD-604 spectrometer.

Data for unknown compounds are as follows:

5-Methyl-6-nitrotetrazolo[1,5-*a*]pyridine (**3**). MS: *m/z*; 179 (parent ion), 151, 134, 109, 105, 94, 78, 64, 51. M.p.: 128–129 °C. Analysis: calculated for $C_6H_5N_5O_2$, H 2.79, C 39.11, N 40.22; found, H 2.70, C 39.13, N 40.30%.

6-Carboxytetrazolo[1,5-*a*]pyridine (**5**). MS: *m/z* 164 (parent ion), 136, 119, 109, 80, 64, 53. M.p.: 220–221 °C (decomp). Analysis: calculated for $C_6H_4N_4O_2$, H 2.44, C 43.90, N 34.15; found, H 2.38, C 44.00, N 34.12%.

6,8-Dichlorotetrazolo[1,5-*a*]pyridine (**6**). MS: *m/z* 190, 188, 162, 160, 135, 133, 101, 98, 73. M.p.: 80–81 °C. Analysis: calculated for $C_5H_2Cl_2N_4$, H 1.06, C 31.75, N 29.63; found, H 1.12, C 31.83, N 29.55%.

8-Carboxytetrazolo[1,5-*a*]pyridine (**8**). MS: *m/z* 164 (parent ion), 149, 136, 106, 94, 78, 65. M.p.: 240–241 °C (decomp). Analysis: calculated for $C_6H_4N_4O_2$, H 2.44, C 43.90, N 34.15; found, H 2.30, C 43.79, N 34.21%.

8-Chlorotetrazolo[1,5-*a*]pyridine (**9**). MS: *m/z* 156, 154, 128, 126, 101, 99, 91, 64. M.p.: 192–193 °C (decomp). Analysis: Calculated for $C_5H_3ClN_4$, H 1.94, C 38.83, N 36.25; found, H 2.00, C 38.94, N 36.15%.

Spectra

All the spectra were measured with a Bruker AM 500 spectrometer operating at 500.138, 125.759 and 50.684 MHz for ^1H, ^{13}C and ^{15}N, respectively. Other parameters were as follows: ^{13}C, pulse width 9 μs, acquisition time 1.2 s and relaxation delay 2 s; ^{15}N, pulse width 6 μs, acquisition time 1.4 s and relaxation delay 8 s (INVGATE). Standard experimental conditions and standard Bruker programs for XHCORRD optimized for 170–180 Hz for $^1J(^1H, ^{13}C)$, INEPT optimized for 10–12 Hz for $^2J(^1H, ^{15}N)$, INADEQUATE optimized for 60 Hz for $^1J(^{13}C, ^{13}C)$ and SFDEC measurements were used. For ^1H and ^{13}C spectra in $CDCl_3$, acetone and DMSO solution data are given relative to the TMS signal at 0.0 ppm. In trifluoroacetic acid (TFA), external DMSO was used as a standard, the signal of which appeared at 2.49 ppm. For ^{15}N spectra, in all solvents used an external nitromethane standard was applied, the signal of which is at 0.0 ppm. The temperature of all measurements was 298 K and the concentrations of solutions were between 0.1 and 0.3 mol dm^{-3}.

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REFERENCES

1. R. N. Butler, in *Comprehensive Heterocyclic Chemistry*, edited by A. Katritzky and C. Rees, Vol. 5, p. 834. Pergamon Press, Oxford (1984).
2. P. Cmoch and L. Stefaniak, *Report No. 1695*, p. 272. Institute of Molecular Physics, Cracow, (1995).
3. J. Wiench and L. Stefaniak and G. A. Webb, *Magn. Reson. Chem.* **32**, 373 (1994).
4. M. Witanowski, L. Stefaniak and G. A. Webb (Eds), *Annual Report on NMR Spectroscopy*, Vols 18 and 25. Academic Press, London (1986 and 1993).
5. C. K. Lowe-Ma, R. A. Nissan and W. S. Wilson, *J. Org. Chem.* **55**, 3755 (1990).
6. T. Sasaki, K. Kanematsu and M. Murata, *Tetrahedron* **27**, 5121 (1971).

7. A. Y. Denisov, V. P. Krivopalov, V. I. Mamatyuk and V. P. Mamaev, *Magn. Reson. Chem.* **26**, 43 (1988).
8. A. Messmer and G. Hajós, *J. Org. Chem.* **46**, 843 (1981).
9. A. Messmer, G. Hajós, J. Tamás and A. Neszmélyi, *J. Org. Chem.* **44**, 1823 (1979).
10. C. Thetaz, F. W. Wehrli and C. Wentrup, *Helv. Chim. Acta* **59**, 259 (1976).
11. W. E. Hull, M. Künstlinger and E. Breitmaier, *Angew. Chem.* **92**, 957 (1980).
12. J. A. Cano Gorini, J. Farras, M. Feliz, S. Olivella, A. Sole and J. Vilarrasa, *J. Chem. Soc., Chem. Commun.* 959 (1986).
13. H. van der Plas, *Acc. Chem. Res.* **11**, 462 (1978).
14. J. D. Reinheimer, L. L. Mayle, G. G. Dolnikowski and J. T. Gerig, *J. Org. Chem.* **45**, 3097 (1980).
15. D. A. de Bie, B. Geursten and H. C. van der Plas, *J. Org. Chem.* **50**, 484 (1985).
16. M. Tisler, *Synthesis* 123 (1973).
17. J. H. Boyer and J. Miller, *J. Am. Chem. Soc.* **81**, 4671 (1959).
18. V. Naumenko, A. O. Koren and P. N. Gaponik, *Magn. Reson. Chem.* **30**, 558 (1992).
19. H. Reimlinger, *Chem. Ber.* **103**, 1900 (1970).

