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^{1}H-NMR Spectra of Some Ditriazolyls and Ditriazolylalkanes

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Summary. The proton magnetic resonance spectra of 12 azoles were measured in neutral and acidic solvents. The protonation shifts observed by comparison of the spectra in *DMSO-d_6* and *TFA* were attributed to an amidinium type resonance of the resulting cations. The synthesis and characterization of the azoles are also discussed.

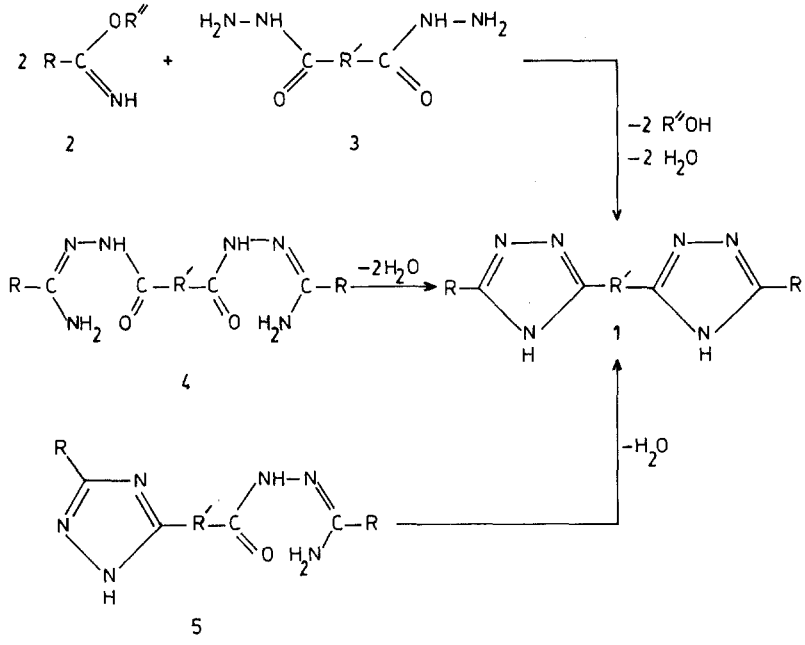
Keywords. ^{1}H-NMR spectra; 1,2,4-Triazoles; Alkanes.

^{1}H-NMR-Spektren einiger Ditriazolyle und Ditriazolylalkane

Zusammenfassung. Es wurden die ^{1}H-NMR-Spektren von 12 Azol-Verbindungen in neutralem (*DMSO-d_6*) und azidischem (*TFA*) Lösungsmittel gemessen und die chemischen Verschiebungswerte verglichen. Der Unterschied beider Werte beruht höchstwahrscheinlich auf einer Amidinium-Typ Resonanz der im azidischen Bereich entstandenen Kationen. Im Rahmen dieser Arbeit wurden 12 Azol-Verbindungen synthetisiert und beschrieben.

Introduction

In recent years, the proton nuclear magnetic resonance spectra of 1,2,4-triazole and some 1,2,4-triazole derivatives have been described [1–8]. Other studies involving the ^{1}H-NMR data of various 1,2,4-triazoles have also been reported [9–19]. In the present study, the ^{1}H-NMR spectra of several di-1,2,4-triazolyls and a number of di-1,2,4-triazolylalkanes measured in hexadeuteriodimethylsulphoxide (*DMSO-d_6*) and trifluoroacetic acid (*TFA*) were examined and the observed protonation shifts were interpreted. Twelve 1,2,4-triazole derivatives (**1**) necessary for the study were obtained by the methods described below (Scheme 1). Thus, di-3-ethyl-,di-3-*n*-propyl- and di-3-*p*-tolyl-1,2,4-triazol-5-yls (compounds **1 a–c**), di-3-*n*-propyl-1,2,4-triazol-5-yl-methane (**1 d**), 1,4-di-3-phenyl-, 1,4-di-3-*p*-tolyl-, 1,4-di-3-*m*-nitrophenyl-, 1,4-di-3-benzyl-, 1,4-di-3-*p*-tolylmethyl-, 1,4-di-3-*p*-nitrophenylmethyl-, 1,4-di-3-*p*-chlorophenylmethyl- and 1,4-di-3-β-naphthyl-1,2,4-triazol-5-yl-*n*-butanes (**1 e–1 l**) were synthesized (Table 1).



Scheme 1

Experimental

Melting points were determined with a Büchi oil heated melting point apparatus and are uncorrected. The ^{1}H-NMR spectra were recorded in *DMSO-d_6* and *TFA* with *TMS* as internal standard, using a Varian 60 A spectrometer. The IR spectra were run as potassium bromide pellets on a Perkin-Elmer spectrometer.

Compounds **1** were synthesized by methods A, B or C.

Method A: A modified method of the route described earlier [20]. The corresponding alkyl imidate hydrochloride (**2** · HCl) (0.02 mol) was dissolved in 50 ml of absolute ethanol and was treated with an ethanolic sodium ethoxide solution obtained by dissolving sodium (0.02 mol) in 40 ml of absolute ethanol. After stirring 15 min at room temperature, the precipitate was filtered. A solution of oxalodihydrazide (or malonodihydrazide) (**3**) (0.01 mol) in appropriate amount of ethanol (90%) was added to the filtrate. After the addition, the mixture was refluxed for 5 h and evaporated at 30–35° under reduced pressure. The crude product was recrystallized from ethanol or another appropriate solvent.

Method B: The corresponding adipoyl-bis-arylamidrazone (**4**) (0.01 mol) [21] was heated at 190–200°C for 1 h and after cooling, the product was recrystallized from *DMSO*-water (1 : 3).

Method C: The corresponding 5-(3-aryl-1,2,4-triazol-5-yl)-N_β-arylimidoyl-*n*-valerohydrazide (**5**) (0.01 mol) [21] was heated at 190–200°C for 1 h. The crystals formed on cooling were recrystallized from *DMSO* – water (1 : 3).

Results and Discussion

Data about the reactions and compounds obtained in the study are compiled in Table 1. IR and ^{1}H-NMR spectral data of the compounds are presented in Tables 2–4.

Table 1. Experimental data for compounds **1**

Compd.	*R*	*R'*	Method	Yield (%)	M.p. (°C)	Molecular[a] formula (*M*)
1a	CH_2CH_3	–	A	50	326 (dec)	$C_8H_{12}N_6$ (192.22)
1b	$CH_2CH_2CH_3$	–	A	43	295	$C_{10}H_{16}N_6$ (220.28)
1c	$C_6H_4 \cdot CH_3(-p)$	–	A	57	>350	$C_{18}H_{16}N_6$ (316.36)
1d	$CH_2CH_2CH_3$	CH_2	A	57	172	$C_{11}H_8N_6$ (234.30)
1e	C_6H_5	$(CH_2)_4$	B–C	95	267[b]	$C_{20}H_{20}N_6$ (344.41)
1f	$C_6H_4 \cdot CH_3(-p)$	$(CH_2)_4$	B	92	251	$C_{22}H_{24}N_6$ (372.46)
1g	$C_6H_4 \cdot NO_2(-m)$	$(CH_2)_4$	B	93	276 (dec)	$C_{20}H_{18}N_8O_4$ (434.41)
1h	$CH_2C_6H_5$	$(CH_2)_4$	C	88	190	$C_{22}H_{24}N_6$ (372.46)
1i	$CH_2C_6H_4 \cdot CH_3(-p)$	$(CH_2)_4$	B	90	185	$C_{24}H_{28}N_6$ (400.51)
1j	$CH_2C_6H_4 \cdot NO_2(-p)$	$(CH_2)_4$	B	87	>350	$C_{22}H_{22}N_8O_4$ (462.45)
1k	$CH_2C_6H_4 \cdot Cl(-p)$	$(CH_2)_4$	B	96	170	$C_{22}H_{22}Cl_2N_6$ (441.35)
1l	β-naphthyl	$(CH_2)_4$	B	89	228	$C_{28}H_{24}N_6$ (444.54)

[a] All elemental analyses (C, H, N) are in accordance with calculated values
[b] Ref. [22] 268–269°

Table 2. IR data for compounds **1** (KBr, cm^{-1})

Compd.	NH	C=N	monosubstituted aromatic ring	disubstituted aromatic ring
1a	3100, 3020	1535	–	–
1b	3130, 3030	1555	–	–
1c	3075, 3045	1550	–	820
1d	3115, 3000	1550	–	–
1e	3110, 3005	1540	725	–
1f	3150, 3030	1560	–	820
1g	3140, 3040	1525	–	808, 720
1h	3120, 3005	1560	720	–
1i	3115, 3010	1550	–	810
1j	3130, 3020	1540	–	815
1k	3115, 3000	1560	–	800
1l	3120, 3010	1540	845, 810, 750	–

The ^{1}H-NMR spectra of the compounds were recorded in *DMSO-d_6* and *TFA*, as a neutral and an acidic solvent, respectively. By comparison of the spectral data given in Tables 3 and 4, it was clearly seen that the signals from the groups attached to C-3 and C-5 positions of the triazole rings were shifted downfield in *TFA* (compare Table 5).

Because of the amphoteric character of the 1,2,4-triazole system [20], it was obvious that compounds **1** form cationic species in *TFA*. Indeed, protonation shifts, obtained by comparison of spectra run in *DMSO-d_6* and *TFA*, observed for type **1** compounds are in agreement with stabilization of the cations such as a, b, c or d in the acidic medium by an amidinium type resonance (Scheme 2) [3, 23]. This

Table 3. ^{1}H-NMR data for compounds **1** (δ/ppm in *DMSO-d_6*)

Compd.	*R*	*R'*	NH
1a	1.27 (t, 6H) 2.74 (q, 4H)	–	14.20 (s, 2H)
1b	1.05 (t, 6H) 1.88 (sext., 4H) 2.83 (t, 4H)	–	14.40 (s, 2H)
1c	2.39 (s, 6H) 7.36 (d, 4H) 7.99 (d, 4H)	–	14.39 (s, 2H)
1d	0.88 (t, 6H) 1.64 (sext., 4H) 2.50 (t, 4H)	3.98 (s, 2H)	13.37 (s, 2H)
1e	7.43 (m, 6H) 7.90 (m, 4H)	1.80 (s, 4H) 2.79 (s, 4H)	13.68 (s, 2H)
1f	2.20 (s, 6H) 7.35 (d, 4H) 7.95 (d, 4H)	1.85 (s, 4H) 2.85 (s, 4H)	13.80 (s, 2H)
1g	7.74 (t, 2H) 8.24 (d, 2H) 8.39 (d, 2H) 8.70 (d, 2H)	1.82 (s, 4H) 2.85 (s, 4H)	13.81 (s, 2H)
1h	3.95 (s, 4H) 7.24 (m, 10H)	1.64 (s, 4H) 2.65 (s, 4H)	13.38 (s, 2H)
1i	2.26 (s, 6H) 3.97 (s, 4H) 7.10 (m, 8H)	1.68 (s, 4H) 2.80 (s, 4H)	13.40 (s, 2H)
1j	4.10 (s, 4H) 7.46 (d, 4H) 8.16 (d, 4H)	1.70 (s, 4H) 2.80 (s, 4H)	13.55 (s, 2H)
1k	3.95 (s, 4H) 7.37 (m, 8H)	1.64 (s, 4H) 2.65 (s, 4H)	13.50 (s, 2H)
1l	7.54 (m, 4H) 7.90–8.15 (m, 8H) 8.54 (s, 2H)	1.86 (2, 4H) 2.86 (s, 4H)	13.76 (s, 2H)

Table 4. ^{1}H-NMR data for compounds **1** (δ/ppm in *TFA*)

Compd.	*R*	*R'*
1a	1,75 (t, 6H) 3.42 (q, 4H)	–
1b	1.24 (t, 6H) 2.39 (sext., 4H) 3.50 (t, 4H)	–
1c	2.61 (s, 6H) 7.77 (d, 4H) 8.27 (d, 4H)	–
1d	1.11 (t, 6H) 2.08 (sext., 4H) 3.19 (t, 4H)	5.00 (s, 2H)
1e	7.85 (m, 6H) 8.25 (m, 4H)	2.24 (s, 4H) 3.38 (s, 4H)
1f	2.40 (s, 6H) 7.75 (d, 4H) 8.21 (d, 4H)	2.33 (s, 4H) 3.43 (s, 4H)
1g	8.17 (t, 2H) 8.47 (d, 2H) 8.67 (d, 2H) 9.14 (d, 2H)	2.31 (s, 4H) 3.48 (s, 4H)
1h	4.49 (s, 4H) 7.57 (m, 10H)	2.07 (s, 4H) 3.20 (s, 4H)
1i	2.43 (s, 6H) 4.47 (s, 4H) 7.38 (m, 8H)	2.10 (s, 4H) 3.35 (s, 4H)
1j	4.62 (s, 4H) 7.62 (d, 4H) 8.40 (d, 4H)	2.10 (s,. 4H) 3.32 (s, 4H)
1k	4.50 (s, 4H) 7.57 (m, 8H)	2.06 (s, 4H) 3.22 (s, 4H)
1l	7.62–8.22 (m, 12H) 8.72 (s, 2H)	2.30 (s, 4H) 3.42 (s, 4H)

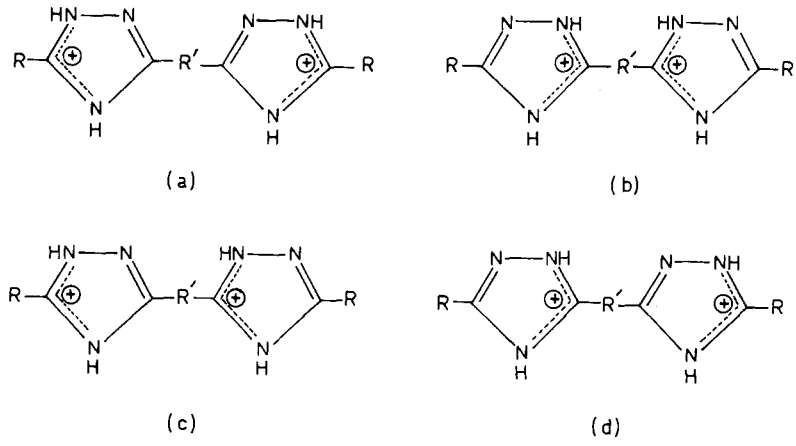
Table 5. Protonation shifts ($\Delta\delta TFA - DMSO\text{-}d_6$) for compounds **1** (ppm)

Compd.	C-3 and C-3′[a] positions	C-5 and C-5′[b] positions
1a	$2CH_3$: 0.48 $2CH_2$: 0.68	–
1b	$2CH_3$: 0.21 $2CH_2$: 0.51 $2CH_2$: 0.67	– – –
1c	$2CH_3$: 0.22 4 arom. H: 0.41 4 arom. H: 0.28	– – –
1d	$2CH_3$: 0.23 $2CH_2$: 0.44 $2CH_2$: 0.69	CH_2: 1.02
1e	6 arom. H: 0.42 4 arom. H: 0.35	$2CH_2$: 0.44 $2CH_2$: 0.59
1f	$2CH_3$: 0.20 4 arom. H: 0.40 4 arom. H: 0.26	$2CH_2$: 0.48 $2CH_2$: 0.58
1g	2 arom. H: 0.43 2 arom. H: 0.23 2 arom. H: 0.28 2 arom. H: 0.44	$2CH_2$: 0.49 $2CH_2$: 0.63
1h	$2CH_2$: 0.54 10 arom. H: 0.33	$2CH_2$: 0.43 $2CH_2$: 0.55
1i	$2CH_3$: 0.17 $2CH_2$: 0.50 8 arom. H: 0.28	$2CH_2$: 0.42 $2CH_2$: 0.55
1j	$2CH_2$: 0.52 4 arom. H: 0.16 4 arom. H: 0.24	$2CH_2$: 0.40 $2CH_2$: 0.52
1k	$2CH_2$: 0.55 8 arom. H: 0.20	$2CH_2$: 0.42 $2CH_2$: 0.57
1l	2 arom. H: 0.18	$2CH_2$: 0.44 $2CH_2$: 0.56

[a] For the signals from *R* groups
[b] For the signals from *R′* groups

situation is in accordance with the reported results for several N-methyl-imidazoles and N-methyl-1,2,4-triazoles [3].

Due to the existence of tautomerism in the 1,2,4-triazole ring [6], the formation of protonated species shown in Scheme 2 might be plausible.



Scheme 2

It was evident that the protonation shift values obtained for β-hydrogens of *R* and *R'* groups were lower than those of the α-hydrogens of the same groups. As a result of the effect of two protonated rings, the protonation shift value for the methylene group (*R'*) of compound **1 d** was higher than the others.

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