A Multinuclear NMR Study of Some Mesoionic 1,3-Dimethyltetrazoles, 1- and 2-Methyltetrazoles and Related Compounds

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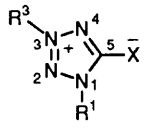
Mesoionic 1,3-dimethyltetrazoles of the type A with sulfur, oxygen and nitrogen exocyclic groups, and related mono- and di-methylated tetrazoles have been investigated by means ^{1}H, ^{13}C, ^{14}N and ^{15}N NMR spectroscopy. The measurements were carried out in Me_2SO and/or CF_3CO_2H solutions. The location of the protonation sites of the tetrazoles has been determined. The hydrogen atom is located on the exocyclic group of the mesoionic aminotetrazole **1**, whereas the monomethylated and unsubstituted tetrazoles are protonated at the N-4 position (compounds **4**, **6**, **8**, **11**–**13**). The monomethylated and non-ring substituted tetrazoles (compounds **4**–**8**, **11**–**14** and **16**) exist as non-mesoionic compounds, but compounds **1**, **2**, **9**, **10** and **15** have a mesoionic structure.

Mesoionic compounds attract attention due to interest in their atypical structures, pharmacological properties,[1] ring–chain tautomerism, protonation and applications in organic synthesis.[1,2] Previously, the structures of some mesoionic compounds were investigated by multinuclear NMR methods. It was shown that the ^{14}N and ^{15}N NMR techniques were especially useful tools for studying the examples presented here for the class of compounds chosen. Thus, ^{15}N NMR is applied to the investigation of structure and site of protonation of some five-membered ring.[3–9] Previously ^{13}C, ^{14}N, ^{15}N and ^{17}O NMR spectroscopy were used to study the mesoionic 1-thia-2,3,4-triazoles. 1-oxa-2,3,4-triazoles,[10,11] type B mesoionic diazoles[12] and type B mesoionic 2,3-diphenyltetrazoles,[13] where type A tetrazoles were disubstituted in positions 1 and 3 and type B ones were disubstituted in positions 2 and 3. However, type A mesoionic tetrazoles had not been investigated previously by multinuclear NMR methods. As a part of our ongoing study of mesoionic structures, we have chosen to examine some mesoionic 1,3-dimethyltetrazoles with various exocyclic groups, and related compounds.



	R^1	R^3	X
1	Me	Me	NH
2	Me	Me	NH_2 Cl
4a	Me	H	NH
5a	Me	H	NAc
6a	H	Me	NH
6c	H	Me	NH_2 CF_3CO_2
7a	H	Me	NAc
9	Me	Me	S
10	Me	Me	SMe Cl
12c	H	Me	SMe CF_3CO_2
15	Me	Me	O

Fig. 1 Mesoionic or potential mesoionic trisubstituted (N-1, N-3, C-5) tetrazoles

Results and Discussion

The ^{14}N and ^{15}N NMR data are presented in Table 1. The compounds studied were characterized by means of mass spectral data as reported in the experimental section.

The assignments of the ^{15}N peaks for the tetrazoles were made on the basis of relations observed for azoles.[14] Thus, the pyrrole-type nitrogen atom (NMe) is expected to resonate within the range δ −270 to −100, whereas the signal of the pyridine-type nitrogen atom =N– should appear in the range δ −140 to 75. The close vicinity of two nitrogen atoms can result in a change in the chemical shift by *ca.* 50 ppm to high frequency.

Mesoionic Tetrazoles (*Compounds* **1**, **2**, **9**, **10**, **15**; *Fig.* 1).—Five nitrogen peaks are observed in the spectrum of the mesoionic 1,3-dimethyltetrazole **1**. The low frequency peak of the exocyclic nitrogen atom is easily identified due to its high shielding. The 2D ^{1}H–^{15}N correlation technique (COLOC) is applied to the identification of the ring nitrogen atoms. The methyl group signal at δ 3.44 is found to be correlated with two nitrogen peaks at δ −178.5 and −43.3. Thus, these signals are assigned to N-1 (pyrrole-type nitrogen atom) and N-2 (pyridine-type nitrogen), respectively.

The ^{1}H signal of the methyl group at δ 3.95 is correlated with three nitrogen peaks: at δ −43.3 (N-2 atom), −116.5 and −117.6. Thus the two low frequency peaks are assigned to the N-3 (N-4) atoms.

Using the COLOC technique (Fig. 2), the nitrogen signal assignments of the mesoionic compounds **2**, **9**, **10** and **15** has been made by analogy with **1**. We assume that the N-3 nitrogen peak should appear at a higher frequency than that of N-4, due to the vicinity of the two nitrogen atoms. However, an unambiguous assignment for **1** and **2** proved impossible because of the similar chemical shifts of the N-3 and N-4 atoms. In some cases, ^{14}N NMR measurements were helpful. As previously demonstrated for type A mesoionic compounds the ^{14}N peak of a nitrogen atom bearing a formal positive charge, is relatively narrow.[10,11] Thus, the peak at δ −117.6 of **1** is assigned to the N-3 atom (half-line width of ^{14}N peak 350 Hz) and the peak at δ −116.5 to the N-4 atom (^{14}N peak too broad to be observed).

Mesoionic Tetrazoles.—Protonation. The mesoionic tetrazole **1**, forms a hydrochloride salt, **2**. The additional hydrogen atom of which can be located either on the exocyclic nitrogen atom, or on a ring nitrogen atom. Protonation of the nitrogen atom should result in a low frequency shift, *ca.* −60 ppm.[14] The expected shielding effect is observed to occur for the exocyclic nitrogen atom. Moreover, the exocyclic signal appears as a

Table 1 ^{14}N and ^{15}N NMR data of some tetrazoles[a]

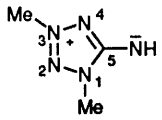
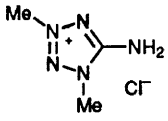
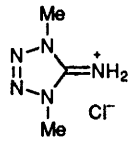
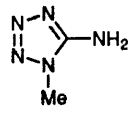
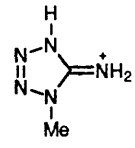
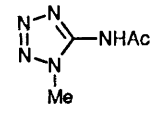
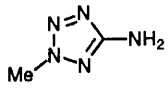
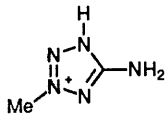
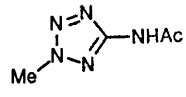
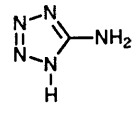
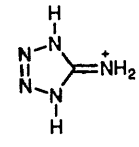
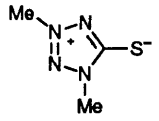
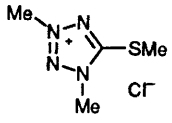
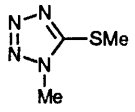
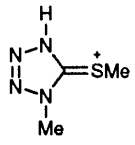
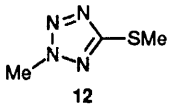
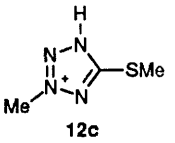
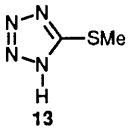
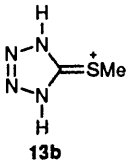
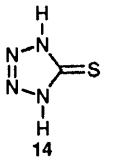
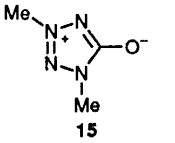
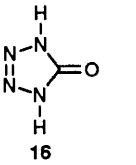
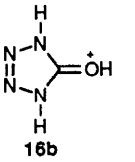
Compound	Solvent	N-1	N-2	N-3	N-4	*exo*-Group
 **1**	Me_2SO	−178.5	−43.3	−117.6 (350)	−116.5	−271.2 (660)
 **2**	Me_2SO	−179.1	−30.6	−109.0 (1100)	−107.4	−320.9 [89.6 t]
 **3**	Me_2SO	−182.0 (2800)	−27.7			−312.6 [89.5 t] (2100)
 **4**	Me_2SO	−183.7 (725)	−21.7	4.7	−90.8	−337.1 [86.8 t] (1200)
 **4b**	CF_3CO_2H	−183.9	−21.9	−31.9	−182.6	−329.4
 **5**	Me_2SO	−160.5 (1000)	−10.1	8.7	−65.6	−268.8
 **6**	Me_2SO	−114.5[b]	−114.7[b] (570)	−5.1	−81.5	−338.2 [84.7 t]
 **6c**	CF_3CO_2H	−178.9 (860)	−30.3	−105.7 (370)	−108.4	−333.5
 **7**	Me_2SO	−93.6	−107.6 (630)	3.4	−66.8	−261.9 [92.6 d] (2400)
 **8**	Me_2SO	−145[c] (2500)	−28[c]			−338.1 [86.6 t] (1800)
 **8b**	CF_3CO_2H	−184.4 (2100)	−29.2			−329.2

Table 1 (*continued*)

Compound	Solvent	N-1	N-2	N-3	N-4
 **9**	Me_2SO	−148.2	−26.6	−107.9	−74.8
 **10**	Me_2SO	−148.6	−16.5	−100.9	−71.1
 **11**	Me_2SO	−157.7 (430)	−7.0	11.2	−55.3
 **11b**	CF_3CO_2H	−157.1 (940)	−10.9	−17.2	−119.4
 **12**	Me_2SO	−81.5	−101.2 (230)	2.3 (920)	−53.3
 **12c**	CF_3CO_2H	−111[c]	−11.6	−101.1 (660)	−79.5
 **13**	Me_2SO	−102[c] (1300)	−6.0 (1750)		
 **13b**	CF_3CO_2H	−139.5 (2600)	−16.4		
 **14**	Me_2SO	−148[c] (730)	−17[c] (2500)		
 **15**	Me_2SO	−178.4 (814)	−39.3 (1100)	−117.7 (260)	−113.5
 **16**	Me_2SO	−180.2 (2100)	−29.9		
 **16b**	CF_3CO_2H	−187[c] (1100)	−35[c] (2500)		

[a] ^{15}N NMR chemical shifts (ppm) from neat nitromethane as an external standard; ^{14}N NMR signal half-width in brackets, if the signal was detectable (Hz); ^{1}H–^{15}N coupling constant (Hz) in square brackets, if it was observed; t = triplet, d = doublet. [b] The assignment can be reverse. [c] Data from ^{14}N NMR measurement.

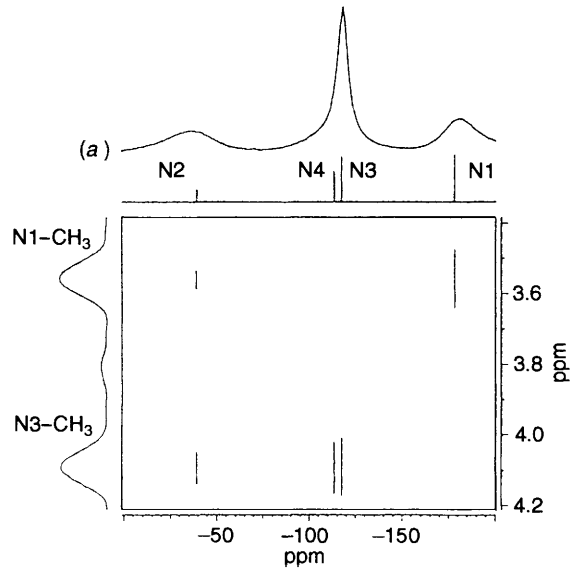


Fig. 2 ^{1}H–^{15}N COLOC spectrum of **15**; trace (*a*) ^{14}N NMR spectrum given for comparison purposes

triplet (coupling constant 89.6 Hz). Consequently, the data suggest unambiguously the position of protonation.

Mesoionic Tetrazoles.—Valence tautomerism. It has been claimed[1,2] that the mesoionic type A tetrazoles can exist as a linear valence tautomer MeN=N–N(Me)–N=C=X (X = NH, O, S). In which case the signals of the nitrogen atoms of the structural element MeN=N– should appear at *ca.* δ 100, as observed for this type of functional group.[12] The values of the ^{15}N chemical shifts observed for the tetrazoles described in the present work suggest the presence of the cyclic form of mesoionic structures. The similarity of the ^{15}N data of compounds which are expected to be cyclic (**2**, **10**) is an additional proof of the cyclic mesoionic structure. We have not seen any evidence of minor component in the ^{15}N, ^{13}C and ^{1}H spectra.

Monomethylated Tetrazoles (*Compounds* **4**, **5**, **6**, **7**, **11** *and* **12**).—The INEPT technique, optimized for a coupling constant of 2 Hz, permits us to detect the peak of the nitrogen atoms connected to the methyl groups and the peaks of vicinal nitrogen atoms. Thus, two ^{15}N peaks are observed in the INEPT spectra of 1-methylated tetrazoles (**4**, **5**, **11**) and three nitrogen peaks are observed for the 2-methylated compounds (**6**, **7**, **12**).

The ^{15}N NMR spectrum of the 1-methylated aminotetrazole, **4**, (Me_2SO solution) consists of five peaks. Two nitrogen signals (δ −183.7, −21.7) are present in the corresponding INEPT spectrum. The signals detected by the INEPT technique are assigned as follows: the peak at δ −183.7 to the NMe atom (pyrrole-type nitrogen atom) and the peak at δ −21.7 to the N-2 atom (pyridine-type nitrogen). The remaining signals are assigned to the N-3 atom (δ 4.7, pyridine-type nitrogen atom attached to two other nitrogens), and to the N-4 atom (δ −90.8). The signal (δ −337.1) is assigned to the exocyclic group. Generally, the signals of the exocyclic nitrogen atoms are easily identified for all of the tetrazoles **1**–**8**, because of their typical chemical shifts they range from −340 to −270 ppm and coupling constants ^{15}N–^{1}H (*ca.* 90 Hz).

Three ^{15}N signals are detected by the INEPT technique applied to **6** (Me_2SO solution). The high frequency peak, δ −5.1, is assigned to the N-3 atom (pyridine-type nitrogen atom attached to two other nitrogen atoms). The two peaks at δ −114.5 and −114.7 are assigned to the N-1 and N-2 atoms respectively. However, an unambiguous assignment is impossible because of the similarity of the chemical shifts.

The remaining two signals (detected by the standard ^{15}N NMR experiment) are assigned to the N-4 atom (δ −81.5) and to the *exo*-nitrogen atom (δ −338.2), respectively.

The assignments of the signals of **5**, **11** and **7**, **12** are made on the basis of similar arguments.

Monomethylated tetrazoles, with an SMe exocyclic group have been measured previously in Me_2SO solution.[4–7] We have repeated this experiment in order to collect data taken under the same experimental conditions. The results obtained are consistent with the published data.

Protonation of Monomethylated Tetrazoles (*Compounds* **4b**, **6c**, **11b** *and* **12c**).—We have measured the ^{15}N NMR spectra of the tetrazoles **4**, **6**, **11** and **12** in CF_3CO_2H solution in order to determine the position of protonation. A strong shielding effect for **4** and **11**, *ca.* −70 ppm is observed for the signals of the N-4 and *ca.* −30 ppm for the signals of N-3 atoms, whereas the remaining peaks are practically unchanged. Although the protonated compounds may exist in several possible forms, the data suggest that the major structure is that protonated on the N-4 atom, in contrast to the mesoionic aminotetrazole, **1**, which is protonated on the exocyclic nitrogen. Following the protonation of compounds substituted with methyl groups in position **2**, (**6** and **12**) we obtained mesoionic cations (**6c** and **12c**) with nitrogen chemical shifts very similar to those of the salts of type A mesoionic compounds (**2** and **10**). The alkylation of monosubstituted compounds occurs in a similar way. The methylation of 1-substituted tetrazoles results in 1,4-disubstituted derivatives, whereas 2-substituted compounds yield the 2,4-dimethylated species. Thus, the methyl group is deduced to be located in both cases on the N-4 atom.

Recently[9] a study has been made of the protonation of 5-alkyltetrazoles, substituted on the N-1 or on the N-2 atom. The authors conclude, on the basis of ^{15}N NMR data, that the proton is located at the N-4 position. Our results lead to the conclusion that the mono-methylated tetrazoles, with the $-NH_2$ or –SMe group at the C-5 position, behave in the same way.

The tetrazoles **4**–**7** (in Me_2SO solution) can potentially exist in the mesoionic forms **4a**–**7a** (Fig. 1), depending on the hydrogen atom location. We have considered both structures: mesoionic and non-mesoionic. The ^{15}N peaks of the exocyclic atoms should appear as a triplet (**4**, **6**) or doublet (**5**, **7**) in the coupled ^{15}N NMR spectra. In contrast to the mesoionic species (Fig. 1), in which the appropriate signals should be a doublet (for **4a** and **6a**) or a singlet (**5a**, **7a**). Our ^{15}N NMR data unambiguously suggest the presence of the non-mesoionic structures for the compounds studied. The appropriate coupling constant is not observed for **5**. However, the chemical shifts of the ring nitrogen atoms are different from those observed for **1**, thus the observed data exclude the mesoionic structure. It is interesting that the ^{15}N chemical shifts of the protonated 2-methyltetrazole, **6**, (spectrum taken in CF_3CO_2H) are quite similar to those of the mesoionic salt compound **2**.

Unsubstituted Tetrazoles (*Compounds* **8**, **13**, **14** *and* **16**).—The ^{15}N NMR spectra of the remaining tetrazoles consist of two averaged signals from the ring nitrogen atoms. The high frequency signals in the region from *ca.* δ −30 to −6, are assigned to the N-2 (N-3) atom (pyridine-type nitrogen atom) and the signals in the region δ −180 to −100 are assigned to the N-1 (N-4) atoms.

Comparison of the ^{15}N NMR spectra taken in Me_2SO and CF_3CO_2H lead us to the conclusion that the second additional hydrogen atom of the protonated tetrazoles (**8**, **13**) is located on the N-4 atom, the corresponding shielding effect is *ca.* −40 ppm.

We were thinking[7] that the ^{15}N NMR spectrum of **14** might

Table 2 ^{13}C and ^{1}H NMR data of some tetrazoles and related compounds[a]

	Solvent	C-5	1-Me	2-Me	3-Me	*exo*-Groups
1	Me_2SO	162.5	30.7 (3.44)		41.2 (3.95)	
2	Me_2SO	158.1 [2.34]	34.4 (3.99)		45.5 (4.34)	NH_2 (8.25)
3	Me_2SO	148.5	34.5 (3.95)			N*H* (0.84)
4	Me_2SO	155.8 [1.85]	31.5 (3.69)			NH_2 (6.6)
4b	CF_3CO_2H	151.9 [2.5]	35.5 (3.18)			NH_2 (6.7)
5	Me_2SO	149.9 [2.54]	34.1 (3.85)			NH_2 (11.0) Me 22.7 (2.14) CO 169.5 [6.4]
6	Me_2SO	167.2		38.8 (4.06)		NH_2 (5.96)
6c	CF_3CO_2H	160.6			43.5 (3.76)	
7	Me_2SO	159.6		39.7 (4.27)		N*H* (10.9) Me 23.1 (2.07) CO 168.0
8	Me_2SO	156.9				NH_2 (6.84) ring 1-N*H* (14.3)
8b	CF_3CO_2H	152.2				
9	Me_2SO	173.9	34.2 (3.86)		41.8 (4.26)	
10	Me_2SO	162.4	36.7 (4.15)		43.4 (4.59)	Me 15.7 (2.87)
11	Me_2SO	154.7	33.4 (3.91)			Me 15.0 (2.72)
11b	CF_3CO_2H	160.0	36.7 (3.44)			Me 16.4 (2.29)
12	Me_2SO	163.9		39.8 (4.32)		Me 14.0 (2.62)
12c	CF_3CO_2H	167.6			43.8 (3.89)	Me 15.7 (2.13)
13	Me_2SO	155.2				Me 14.4 (2.68)
13b	CF_3CO_2H	160.8				Me 16.5 (2.16)
14	Me_2SO	158.2				
15	Me_2SO	161.1 [1.9]	30.3 (3.55)		42.1 (4.08)	
16	Me_2SO	154.3				ring N1, N2 (19.97)

[a] The ^{13}C NMR chemical shifts (ppm) from TMS; the ^{1}H NMR chemical shifts (ppm) from TMS in brackets; ^{1}H–^{13}C coupling constant (Hz) in square brackets.

consist of four signals, and the hydrogen atoms would be located on N-1 and N-2. During the present work it was impossible to detect any ^{15}N signals in spite of using long acquisition times. This is probably because of the presence of proton dynamic effects. Only two averaged signals (δ −148, −17) are detected by the ^{14}N NMR technique. We suppose that the most likely structure is the one with the protons located on the N-1 and N-4 nitrogen atoms, by analogy with the remaining unsubstituted tetrazoles. However, an unambiguous conclusion is not possible at the present time.

The ^{1}H and ^{13}C data are presented in Table 2. The results are less useful for structural investigations, but they can be used for a simple and rapid identification of these compounds. Especially, the typical signal for C-5, seems to be very useful for this purpose.

Conclusions

In general, ^{15}N NMR seems to be the best means of studying tetrazole structures. The data obtained suggest, that unsubstituted and monosubstituted tetrazoles in CF_3CO_2H solution are protonated at the N-4 position, whereas the exocyclic nitrogen atom is protonated for the mesoionic 1,3-dimethyl-5-aminotetrazole. The ^{14}N NMR technique yields additional information, for example it permits us to conclude that the positive charge is located on the N-3 atom. The ^{1}H and ^{13}C NMR methods are less useful in this regard, however they can be used for identification purposes.

Experimental

All of the NMR measurements were recorded on a Bruker AM 500 machine. The dedicated ^{15}N Bruker probe (10 mm tube) was employed for all ^{15}N NMR experiments. The solution concentrations used were *ca.* 0.1–1 mol dm $^{-3}$. Either the deuterium signal of the solvent ([$^{2}H_6$]Me_2SO) or the signal of an external reference (CD_3NO_2, CD_3COCD_3) were used as a lock. The flip angle of *ca.* 45° was applied for all measurements. The solvent peaks were used as a reference for ^{1}H and ^{13}C measurements in Me_2SO solution (δ_H = 2.49; δ_C = 39). The signals of [$^{2}H_6$]acetone were used for the measurements in CF_3CO_2H solution (δ 2.15; 38.5, respectively). The [$^{2}H_3$]nitromethane peak was applied as a ^{14}N and ^{15}N reference (δ_N = 0.0).

Generally, the ^{15}N chemical shifts were obtained from the standard proton decoupled NMR experiment. The more effective INEPT techniques were used in order to obtain the coupled spectra. Thus, the ^{1}H–^{15}N coupling constants of the exocyclic nitrogen atoms were determinated just by the INEPT experiment, optimized for the coupling value of 90 Hz.

However, in some cases we could not detect any signals by this technique, in spite of our expectation to the contrary. Probably, fast proton exchange results in the INEPT technique becoming ineffective.

^{13}C NMR measurements. The spectra were recorded at 125.76 MHz, with a relaxation delay of 2 s and an acquisition time of 1.5 s. About 1000–5000 scans were acquired in order to obtain good quality spectra.

^{14}N NMR measurements. The spectra were recorded at 36.118 MHz, with a relaxation delay of 0 s and an acquisition time of 0.2 s; *ca.* 10 000 scans were acquired.

^{15}N NMR measurements. The frequency of 50.698 MHz was applied, with a relaxation delay of 4–6 s, and an acquisition time of *ca.* 1 s; *ca.* 1000–10 000 scans were collected.

INEPT experiments. The standard Bruker software was applied in order to detect the peaks of the exocyclic groups. The value of 90 Hz was used for the experiment. The modified INEPT program (optimized to the value of 2 Hz) was used for the identification of the ring nitrogen atoms.[15] A relaxation delay of 2 s was used.

^{1}H–^{15}N 2D correlation experiments. The standard Bruker routine COLOC, optimized to the value of 2.5 Hz, was applied. A matrix of 1024 × 32 was used for the data acquisition, and of 1024 × 64 matrix for the transformed spectrum. A relaxation delay of 2 s was used, *ca.* 1000 scans for each FID were collected.

The mass spectra were obtained on a AMD–INTECTRA model AMD-604 spectrometer (direct inlet; temperature of the IS 220°, 70 eV; accelerating voltage 8 kV).

1,3-*Dimethyltetrazolium-5-thiolate* (**9**). The mixture of **12** (0.7 g, 5.4 mmol) and dimethylsulfate (0.7 g, 5.6 mmol) was heated at 90 °C for 1 h, then the powdered anhydrous sodium sulfide (1.5 g, 20 mmol) was added. The mixture was heated for 1 h, then the product was separated by extraction with CH_2Cl_2 and evaporation of solvent *in vacuo*. Yield: 0.29 g (2.2 mmol) 40%; MS *m/z* 130 (M^+, parent peak).

1,3-*Dimethyl-5-methylmercaptotetrazolium hydrochloride* (**10**). The mixture of **12** (0.7 g, 5.4 mmol) and dimethylsulfate (0.7 g, 5.6 mmol) was heated at 90 °C for 1 h, then ethanol (10 cm^3) and concentrated hydrochloric acid (1 cm^3) were added. The mixture were cooled overnight, the salt was filtrated off and dried *in vacuo*. Yield: 0.71 g (3.9 mmol) 70%.

1,3-*Dimethyltetrazolium-5-olate* (**15**). Although tetrazole **9** was obtained for the first time by methylation of 5-hydroxy-2-methylotetrazole with diazomethane,[16] we used a modified method. Thus, the mixture of 12 (0.7 g, 5.4 mmol) and dimethylsulfate (0.7 g, 5.6 mmol) was heated at 90 °C for 1 h, then the solution of KOH (1 g, 18 mmol) in 10 cm^3 was added. The mixture was heated for 0.5 h, the product was separated by extraction with CH_2Cl_2 and evaporation of solvent *in vacuo*. Yield: 0.37 g (3.24 mmol) 60%; MS: *m/z* 114 (M^+, parent peak).

Tetrazole **8** is commercially available. The other compounds were obtained according with published procedures: **1–3**,[17] **4–7**,[18] **8**-commercial, **11**, **12**,[6] **13**,[19,20] **14**,[21] **16**.[16]

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