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TETRAZOLIUM *N*-AMINIDES

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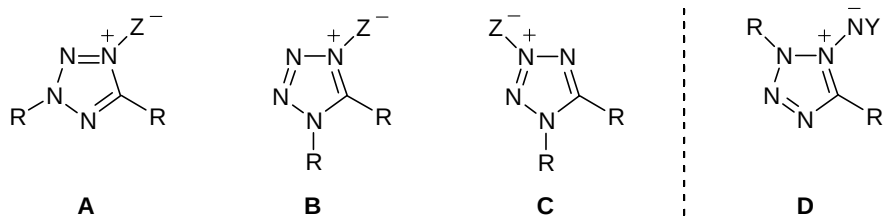
Abstract – Tetrazolium *N*-aminides (**8**–**10**), *i.e.* the first derivatives of the types (**A**–**C**; Z = NY), have been prepared *via* the tetrazolium salts (**5**–**7**) and fully characterized. The preferred geometries of **8c**–**10c** have been determined by a Hartree-Fock and Density Functional Theory calculation [HF/6-31G(d), B3LYP/6-31G(d)].

INTRODUCTION

Azolium *N*-aminides [1] have been a field of proper attention since Timpe [2] and Tamura *et al.*,[3] in a wider context, have surveyed this class of compounds some decades ago. A recent review [4a] demonstrates that much effort has been spent on diazolium, triazolium, and thiazolium *N*-aminides, whereas examples of the tetrazole series have not been studied until now. This led us to prepare representatives of the types (**A**–**C**; Z = NY), *i.e.* congeners of the earlier described tetrazolium *N*-oxides [5] and *N*-ylides.[6] Approaches towards the model (**D**) [4b] were not intended since a 1,2-substitution pattern does not match established tetrazolium structures.[7]

Scheme 1



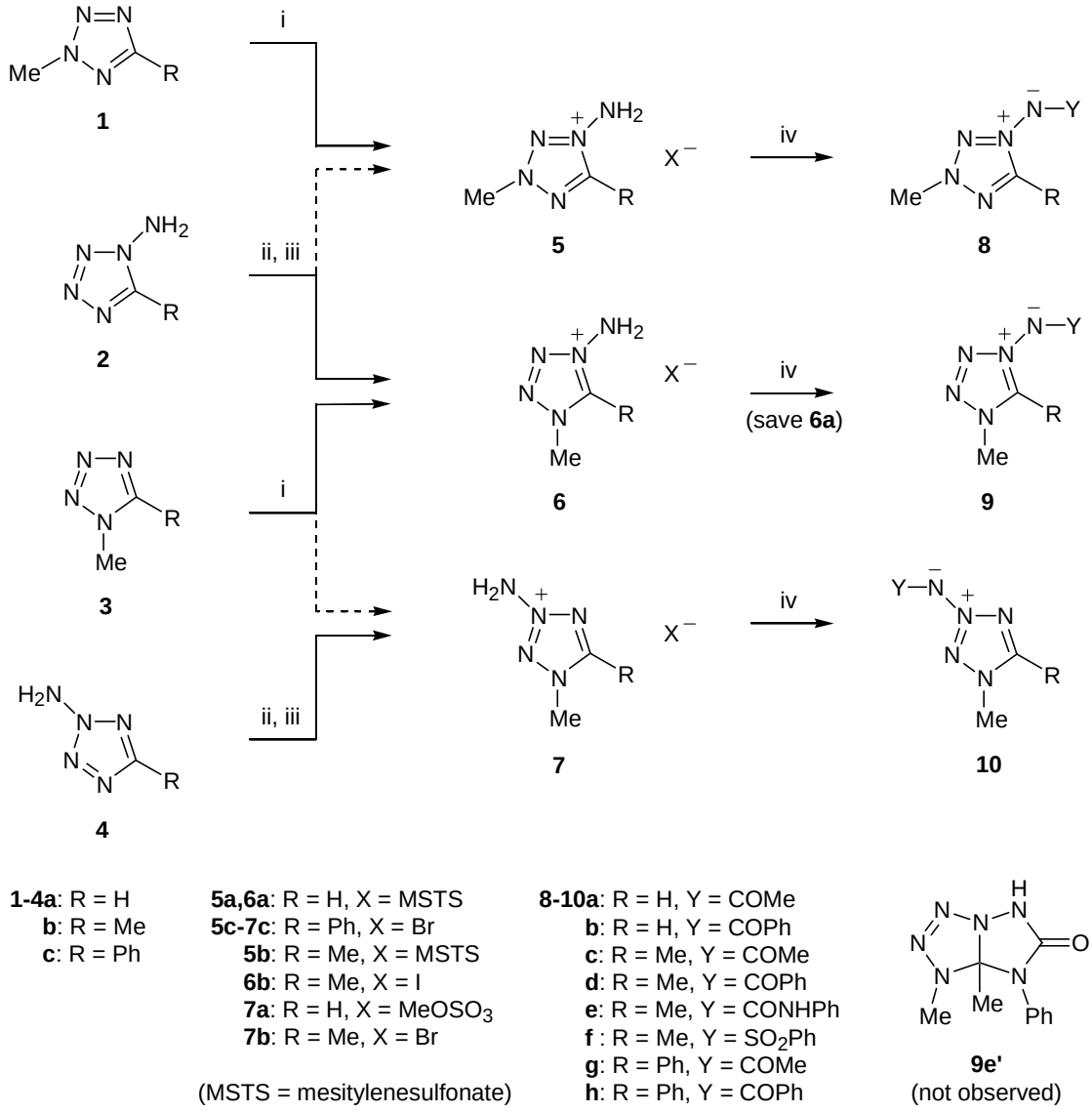
A: Z = NY; Z = O [refs.[5a,c,d]]; Z = CHY, CY_2 [ref.[6b]]
B: Z = NY; Z = O [ref.[5b,c]]; Z = CHY [ref.[6c]], CY_2 [refs.[6a,c,d]]
C: Z = NY; Z = CHY [ref.[6b]], CY_2 [refs.[6a,b,d]]

(Y = EWG)

RESULTS AND DISCUSSION

The route to the title class we followed was the general one *via* aminoazolium salts.[2–4] As candidates we chose the tetrazolium salts (**5**–**7**) (Scheme 2). These compounds were expected to result from amination of the tetrazoles (**1**) and (**3**) or from methylation of **2** and **4**. The precursors (**2**) and (**3**), like all 1*H*-tetrazoles, should react as ambident nucleophiles and hence afford mixtures of isomers, whereas with ring types such as **1** and **4** quaternization occurs regiospecifically (*cf.* ref.[7]).

Scheme 2



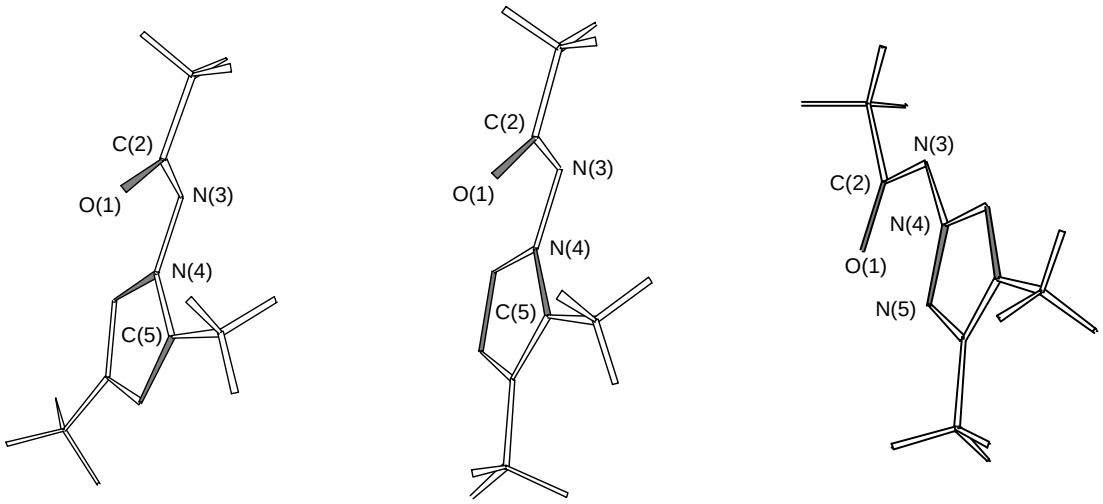
Reagents and conditions: i, MSH, 20 °C, 24 h; ii, $(MeO)_2SO_2$, 20 °C, 24 h (5 d with **2c**, **4c**); iii, anion exchange resin / NaBr, KI (save **7a**); iv; MeCOCl, PhNCO / Et_3N or PhCOCl, $PhSO_2Cl$ / K_2CO_3, 20 °C, 1 h (4 h for **9f**)

Starting with the isomer-pure approaches to the two series of salts (**5**) and (**7**), we found that methylation of the tetrazoles (**4a–c**) with dimethyl sulfate proceeded satisfactorily to give, after anion exchange, the

derivatives (**7a–c**) in reasonable yield (Table 1). Amination of **1** was more sluggish (also in comparison with the analogous reaction of **3**, see below): On treatment of **1a–c** with *O*-mesitylsulfonylhydroxylamine (MSH) we achieved a mere 15 (**1a**), 43 (**1b**),[8] and 13% of conversion (**1c**) and thus could isolate **5b** only. In order to provide the remaining salts of type (**5**), the tetrazolamines (**2a**) and (**2c**) were treated with dimethyl sulfate to afford 1 : 4 and 3 : 4 mixtures of **5** and **6**, respectively. The first of these proved to be inseparable (see later), whereas the more expedient proportions resulting from the second reaction allowed isolation of both **5c** and **6c**. Regarding the entry to the other salts of series (**6**), treatment of the tetrazoles (**3a**) and (**3b**) with MSH produced 13 : 2 and 12 : 1 mixtures of **6** and **7**, from which **6a** and **6b** (X = MSTS in place of I) could be isolated in moderate yield.[9] Again amination did not attain completion, but here, because of the higher nucleophilicity of 1*H*-tetrazoles (*cf.* ref.[6b]), the extent of conversion surpassed that observed above with **1a,b** by reaching 30 and 66%, respectively. Since the amount of the 5-methyl salt (**6**) appeared insufficient, an improvement was attempted by methylation of the tetrazolamine (**2b**); indeed, from the resultant 5 : 1 mixture of **6** and **5** we obtained, after anion exchange, the major component in 60% yield.

Conversions of aminoazolium salts into acceptor-stabilized *N*-aminides are advantageously carried out by base-mediated generation of the (labile) parent aminide and *in situ* substitution of the latter.[2–4] We applied this protocol to all of the salts (**5**–**7**) and obtained the desired products (**8–10**) in straightforward manner. The sole exception concerns aminides of type (**9**) with R = H: The salt (**6a**), in line with other 1,4-disubstituted tetrazolium compounds having hydrogen at C(5),[10] evolved gaseous nitrogen when submitted to the above procedure. This decomposition even interferes with anion exchange (X = $MeOSO_3 \rightarrow Br$) when attempted with **6** (R = H) which was formed by methylation of **2a** as the predominant isomer (80%). These observations recall our earlier findings with 5-unsubstituted ylides of type (**B**; Z = CHCOPh).[6b] Nonetheless, this base-sensitivity of salts (**6**; R = H) provides an entry to aminides (**8**) having R = H: Since, as shown, compound (**5a**) had proved to be unisolable because of the low yield, we recurred to the above mentioned (inseparable) 1 : 4 mixture of **5** and **6** obtained from **2a** and treated the material directly with base and the acyl chloride. By this procedure, which removed the undesired component (**6**), the aminide (**8b**) could be secured. Efforts to isolate also the congener (**8a**) remained unrewarded, although the NMR spectrum gave indications that some was formed.[11]

Two modifications of the above sequence **2** $\rightarrow$ **6** $\rightarrow$ **9** were attempted in view of reports from the 1,2,4-triazole series: (i) 4-Aminotriazolium salts have been acylated *prior to* deprotonation to give the corresponding amido salts which were in part isolated.[12a,13] We applied this variant to **6b** by heating the compound with acetic anhydride in acetic acid (*cf.* ref.[12a]), but hereby we caused decomposition.[14] (ii) A variety of triazolium 4-aminides have been made by quaternization of *N*-(triazol-4-yl)amides, -ureas, and -sul-



O(1)-C(2)-N(3)-N(4) -2.9	O(1)-C(2)-N(3)-N(4) 0.1	O(1)-C(2)-N(3)-N(4) 0.2
C(2)-N(3)-N(4)-C(5) -57.0	C(2)-N(3)-N(4)-C(5) -54.0	C(2)-N(3)-N(4)-N(5) -0.9
0.00	1.61	4.25
8c	**9c**	**10c**

Figure 1. Structures of the acetylaminides (**8c**), (**9c**), and (**10c**), calculated at the B3LYP/6-31G(d) level of theory (gas phase); dihedral angles (°) and relative energies (kcal/mol) shown [17a]

fonamides followed by deprotonation.[12a-c] We tried to convert the acetyl [15a] and the phenylcarbamoyl [15b] derivatives of **2b** into the aminides (**9c**) and (**9e**): Treatment of these substrates with methyl iodide (*cf.* ref.[12]) had no appreciable effect, but dimethyl sulfate gave mixtures of quaternary products analogous to **5** and **6** (ratio 15 : 85) which, after addition of base, afforded **9c** and **9e** in 36 and 65% yield.

The aminides (**8**–**10**) are reasonably stable solids. Their spectral data match those of congeners [2–4] in that IR carbonyl and sulfonyl absorptions appear at lowered frequencies and UV long-wavelength maxima (charge-transfer bands) exhibit a negative solvatochromism (Table 2; for the latter phenomenon, see **8b,c**, **9d,e**, and **10a,b,e,f**). Ring closure of **9e** into **9e′** was not observed, a process of this kind might be expected since cyclizations have been reported for imidazolium *N*-carbamoylaminides [1b] and „vinylogous“ tetrazolium *N*-aminides.[16] Finally, lowest energy geometries of the derivatives (**8c**), (**9c**), and (**10c**) were of interest. Structures optimized at the B3LYP/6-31G(d) level are shown in Figure 1: The aminide group is *Z* configurated throughout [17b] and, in the case of **10c**, also coplanar with the heterocyclic ring.[17c] Calculations at the HF/6-31G(d) level gave similar structures for **8c** and **9c**, but in the case of **10c**, the functional group is perpendicular to the ring [O(1)-C(2)-N(3)-N(4) –1.4°; C(2)-N(3)-N(4)-N(5) 91.9°]; this conformer was found more stable (by 1.24 kcal/mol) than the coplanar one showing O(1)-C(2)-N(3)-N(4) 0.0° and C(2)-N(3)-N(4)-N(5) 0.0°.

EXPERIMENTAL

Mp: Linström apparatus; elemental analysis: CHN Analyzer 1106 Carlo Erba; IR: Philips PU-9800 FTIR; NMR: Bruker DRX-400 (400.1 and 100.6 MHz for ^{1}H and ^{13}C, respectively; TMS as internal standard); UV/Vis: Philips PU-8730. Theoretical calculations: Program package Gaussian 98, revision A.9.[18]

Table 1. Yields, Melting Points, and Elemental Analyses (Calcd / Found) of Tetrazolium Salts (**5**–**7**) and Aminides (**8**–**10**)

Compd	Yield	From	mp (°C)	Recryst. from	Formula	C	H	N
5b	24	**1b**	167−168	EtOH/Et_2O	$C_{12}H_{19}N_5O_3S$	45.99 / 46.08	6.11 / 6.17	22.35 / 21.93
5c	28	**2c**	166−169 [c]	EtOH	$C_8H_{10}N_5Br$	37.52 / 37.35	3.94 / 3.82	27.35 / 27.42
6a	20	**3a**	142	EtOH	$C_{11}H_{17}N_5O_3S$	44.14 / 44.27	5.72 / 5.82	23.40 / 23.42
6b	60	**2b**	122	EtOH/Et_2O	$C_3H_8N_5I$	14.95 / 15.00	3.35 / 3.29	29.06 / 29.20
6b [a]	54	**2b**	85−86 [d]	EtOH/Et_2O	$C_3H_8N_5Br$	18.57 / 18.80	4.16 / 4.38	36.09 / 35.48
6b [b]	24	**3b**	143	EtOH	$C_{12}H_{19}N_5O_3S$	45.99 / 46.06	6.11 / 6.14	22.35 / 22.32
6c	29	**2c**	112−113	EtOH/Et_2O	$C_8H_{10}N_5Br$	37.52 / 37.64	3.94 / 3.93	27.35 / 27.52
7a	93	**4a**	96−97	EtOH	$C_3H_9N_5O_4S$	17.06 / 17.11	4.30 / 4.27	33.16 / 33.25
7b	69	**4b**	150−153 [c]	EtOH/Et_2O	$C_3H_8N_5Br$	18.57 / 18.51	4.16 / 4.18	36.09 / 35.69
7c	43	**4c**	164	EtOH	$C_8H_{10}N_5Br$	37.52 / 37.22	3.94 / 3.81	27.35 / 27.16
8b	11	**2a**	170−171	EtOH	$C_9H_9N_5O$	53.20 / 53.19	4.46 / 4.56	34.47 / 34.35
8c	43	**5b**	130 [e]	EtOH/Et_2O	$C_{11}H_{12}N_8O_8$ [f]	34.38 / 34.20	3.15 / 3.10	29.16 / 28.91
8d	72	**5b**	151	EtOH	$C_{10}H_{11}N_5O$	55.29 / 55.10	5.10 / 5.12	32.24 / 32.40
8e	69	**5b**	165−167	EtOH	$C_{10}H_{12}N_6O \cdot H_2O$	47.99 / 48.18	5.64 / 5.69	33.58 / 33.26
8f	71	**5b**	122−124	EtOH	$C_9H_{11}N_5O_2S$	42.68 / 42.65	4.38 / 4.39	27.65 / 27.62
8g	60	**5c**	149−150 [e]	EtOH/Et_2O	$C_{16}H_{14}N_8O_8$ [g]	43.06 / 43.16	3.16 / 3.23	25.11 / 24.87
8h	68	**5c**	161−162	EtOH/Q [h]	$C_{15}H_{13}N_5O$	64.51 / 64.29	4.69 / 4.69	25.07 / 25.43
9c	65	**6b**	134 [e]	EtOH	$C_{11}H_{12}N_8O_8$ [i]	34.38 / 34.55	3.15 / 3.20	29.16 / 28.81
9d	83	**6b**	166	EtOH	$C_{10}H_{11}N_5O$	55.29 / 55.24	5.10 / 5.12	32.24 / 32.19
9e	68	**6b**	130−131	EtOH	$C_{10}H_{12}N_6O \cdot H_2O$	47.99 / 48.00	5.64 / 5.71	33.58 / 33.63
9f	63	**6b**	131−132	EtOH	$C_9H_{11}N_5O_2S$	42.68 / 42.43	4.38 / 4.36	27.65 / 27.80
9g	60	**6c**	146−147	EtOH/Et_2O	$C_{10}H_{11}N_5O$	55.29 / 55.13	5.10 / 5.15	32.24 / 32.14
9h	72	**6c**	149	EtOH	$C_{15}H_{13}N_5O$	64.51 / 64.05	4.69 / 4.76	25.07 / 25.09
10a	67	**7a**	128−129	EtOH/Et_2O	$C_4H_7N_5O$	34.04 / 33.81	5.00 / 4.92	49.62 / 49.27
10b	74	**7a**	149−150	EtOH	$C_9H_9N_5O$	53.20 / 53.35	4.46 / 4.52	34.47 / 34.70
10c	64	**7b**	97−98 [e]	EtOH/Et_2O	$C_{11}H_{12}N_8O_8$ [j]	34.38 / 34.37	3.15 / 3.14	29.16 / 29.09
10d	89	**7b**	189−190	EtOH	$C_{10}H_{11}N_5O$	55.29 / 55.29	5.10 / 5.32	32.24 / 32.33
10e	78	**7b**	227−228	EtOH	$C_{10}H_{12}N_6O$	51.72 / 51.72	5.21 / 5.21	36.19 / 36.40
10f	87	**7b**	161−162	EtOH/Et_2O	$C_9H_{11}N_5O_2S$	42.68 / 42.47	4.38 / 4.29	27.65 / 27.69
10g	55	**7c**	138−139	EtOH/Et_2O	$C_{10}H_{11}N_5O$	55.29 / 55.10	5.10 / 5.26	32.24 / 32.27
10h	73	**7c**	125−126	EtOH	$C_{15}H_{13}N_5O$	64.51 / 64.32	4.69 / 4.73	25.07 / 25.25

[a] X=Br in place of I. [b] X = MSTS in place of I. [c] Decomp. [d] Hygroscopic. [e] Hygroscopic (*cf.* also ref.[26]). [f] Picrate, mp 124−125 °C (EtOH). [g] Picrate, mp 165−166 °C (EtOH). [h] Q = light petroleum. [i] Picrate, mp 164−165 °C (EtOH). [j] Picrate, mp 198−199 °C (EtOH).

Table 2. Spectral Data of Tetrazolium Salts (**5**–**7**) and Aminides (**8**–**10**)

Compd	IR (ν, cm^{-1}; KBr // ^1H / ^{13}C NMR (δ, ppm; $CDCl_3$ or * DMSO-d_6) // UV (λ_{max}, nm; solvents specified below) [a]
5b	3232 // * 2.17 (s, 3H), 2.48 (s, 6H), 2.64 (s, 3H), 4.50 (s, 3H), 6.75 (s, 2H), 8.00 (br s, 2H) / 8.5 (q), 20.2 (q), 22.6 (q, 2C), 43.1 (q), 129.9 (d, 2C), 135.9 (s, 2C), 136.5 (s), 142.3 (s), 156.3 (s)
5c	3250−2750 (br), 3113, 3013, 1623 // 4.69 (s, 3H), 7.67−7.85 (m, 3H), 8.14−8.26 (m, 2H), 8.47 (s, 2H) / 43.7 (q), 119.8 (s), 129.32 (d, 2C), 129.34 (d, 2C), 133.5 (d), 154.6 (s)
6a	3192, 3045 // * 2.17 (s, 3H), 2.49 (s, 6H), 4.26 (s, 3H), 6.76 (s, 2H), 8.06 (br s, 2H), 11.08 (s, 1H) / 20.2 (q), 22.7 (q, 2C), 37.6 (q), 129.9 (d, 2C), 135.9 (s, 2C), 136.6 (s), 141.2 (d), 142.1 (s)
6b	3240, 1625 // * 2.79 (s, 3H), 4.23 (s, 3H), 7.73 (s, 2H) / 8.7 (q), 37.0 (q), 151.2 (s)
6c	3250−2800 (br), 3349, 3130, 3050, 1630 // * 4.27 (s, 3H), 7.75−7.80 (m, 2H), 7.84−7.89 (m, 1H), 8.01−8.04 (m, 2H), 8.08 (s, 2H) / 38.0 (q), 116.1 (s), 129.1 (d, 2C), 131.0 (d, 2C), 133.9 (d), 148.7 (s)
7a	3075, 2963, 1254, 1222 // * 3.38 (s, 3H), 4.21 (s, 3H), 9.96 (s, 1H), 10.04 (br s, 2H) / 37.3 (q), 52.8 (q), 147.8 (d)
7b	3142, 2990 // * 2.68 (s, 3H), 4.13 (s, 3H), 9.94 (s, 2H) / 9.2 (q), 35.8 (q), 157.3 (s)
7c	3250−2750 (br), 3142 // * 4.28 (s, 3H), 7.72−7.76 (m, 2H), 7.78−7.83 (m, 1H), 7.92−7.96 (m, 2H), 10.23 (s, 2H) / 37.6 (q), 120.0 (s), 129.533 (d, 2C), 129.537 (d, 2C), 133.2 (d), 156.5 (s)
8b	3151, 1596, 1552 // * 4.48 (s, 3H), 7.35−7.45 (m, 3H), 7.97−8.06 (m, 2H), 10.63 (s, 1H) / 40.3 (q), 127.6 (d, 2C), 127.8 (d, 2C), 130.2 (d), 136.8 (s), 143.8 (d), 168.3 (s) // 291 /303 /307 /310 /315 /324 /324 /324 [b]
8c	1585 // 2.11 (s, 3H), 2.59 (s, 3H), 4.44 (s, 3H) / 9.4 (q), 22.2 (q), 42.3 (q), 155.7 (s), 175.8 (s) // 254 /263 /283 /291 / 297 /293 [c]
8d	1606, 1571 // 2.60 (s, 3H), 4.37 (s, 3H), 7.38−7.46 (m, 3H), 8.14−8.17 (m, 2H) / 9.0 (q), 41.6 (q), 127.4 (d, 2C), 127.8 (d, 2C), 130.0 (d), 135.6 (s), 154.8 (s), 171.2 (s)
8e	3411, 3269, 1626 // * 2.49 (s, 3H), 3.45 (s, *ca.* 2H), 4.44 (s, 3H), 6.76−6.82 (m, 1H), 7.07−7.18 (m, 2H), 7.48−7.55 (m, 2H), 8.53 (s, 1H) / 9.1 (q), 42.2 (q), 117.4 (d, 2C), 119.6 (d), 128.3 (d, 2C), 142.3 (s), 154.7 (s), 161.4 (s)
8f	1297, 1140 // 2.55 (s, 3H), 4.33 (s, 3H), 7.38−7.52 (m, 3H), 7.81−7.89 (m, 2H) / 9.3 (q), 42.7 (q), 127.0 (d, 2C), 128.6 (d, 2C), 131.3 (d), 142.9 (s), 155.9 (s)
8g	3425, 1606, 1592 // 2.12 (s, 3H), 2.93 (s, *ca.* 2H), 4.51 (s, 3H), 7.48−7.64 (m, 3H), 8.17−8.27 (m, 2H) / 22.4 (q), 42.5 (q), 121.1 (s), 128.4 (d, 2C), 128.9 (d, 2C), 132.6 (d), 153.6 (s), 176.6 (s)
8h	1602, 1566 // 4.45 (s, 3H), 7.35−7.60 (m, 6H), 8.18−8.26 (m, 2H), 8.28−8.36 (m, 2H) / 42.5 (q), 121.5 (s), 127.9 (d, 2C), 128.4 (d, 2C), 128.6 (d, 2C), 129.0 (d, 2C), 130.6 (d), 132.7 (d), 136.4 (s), 153.6 (s), 171.9 (s)
9c	1578 // 2.06 (s, 3H), 2.62 (s, 3H), 4.18 (s, 3H) / 8.7 (q), 22.3 (q), 36.2 (q), 146.3 (s), 176.2 (s)
9d	1601, 1568 // 2.63 (s, 3H), 4.15 (s, 3H), 7.37−7.48 (m, 3H), 8.10−8.14 (m, 2H) / 8.7 (q), 36.2 (q), 127.8 (d, 2C), 128.1 (d, 2C), 130.5 (d), 136.0 (s), 146.5 (s), 171.7 (s) // 250 /261 /262 /268 /269 [d]
9e	3269, 1629 // * 2.55 (s, 3H), 4.18 (s, 3H), 6.72−6.77 (m, 1H), 7.08−7.13 (m, 2H), 7.49−7.52 (m, 2H), 8.42 (s, 1H) / 8.3 (q), 36.4 (q), 117.2 (d, 2C), 119.4 (d), 128.2 (d, 2C), 142.5 (s), 147.5 (s), 162.3 (s) // 271 /276 /279 /282 [e]
9f	1284, 1144 // * 2.59 (s, 3H), 4.13 (s, 3H), 7.41−7.54 (m, 3H), 7.61−7.68 (m, 2H) / 8.5 (q), 36.6 (q), 126.4 (d, 2C), 128.5 (d, 2C), 130.8 (d), 143.8 (s), 149.6 (s)
9g	1588 // 1.97 (s, 3H), 4.23 (s, 3H), 7.61−7.66 (m, 2H), 7.68−7.76 (m, 3H) / 22.2 (q), 37.4 (q), 117.5 (s), 129.2 (d, 2C), 129.6 (d, 2C), 133.5 (d), 146.3 (s), 177.7 (s)
9h	1596, 1562 // 4.20 (s, 3H), 7.31−7.40 (m, 3H), 7.50−7.55 (m, 2H), 7.58−7.63 (m, 1H), 7.76−7.79 (m, 2H), 8.01−8.04 (m, 2H) / 37.4 (q), 146.1 (s), 173.5 (s) [f]
10a	3079, 1595 // * 1.85 (s, 3H), 4.20 (s, 3H), 9.81 (s, 1H) / 22.7 (q), 36.9 (q), 146.5 (d), 174.0 (s) // 273 /280 /284 /285 / 298 /304 /303 /304 [b]
10b	3075, 1599, 1572 // * 4.24 (s, 3H), 7.37−7.50 (m, 3H), 8.02−8.08 (m, 2H), 9.87 (s, 1H) / 36.9 (q), 127.77 (d, 2C), 127.82 (d, 2C), 130.3 (d), 136.7 (s), 146.5 (d), 169.7 (s) // 281 /297 /300 /302 /310 /318 /318 /318 [b]
10c	3431 (br), 1595 // 2.08 (s, 3H), 2.43 (s, *ca.* 2H), 2.68 (s, 3H), 4.12 (s, 3H) / 9.3 (q), 23.2 (q), 35.3 (q), 154.3 (s), 176.3 (s)
10d	1607, 1571 (w) // 2.58 (s, 3H), 4.03 (s, 3H), 7.37−7.47 (m, 3H), 8.12−8.17 (m, 2H) / 9.4 (q), 35.4 (q), 128.1 (d, 2C), 128.5 (d, 2C), 130.9 (d), 136.6 (s), 154.5 (s), 171.3 (s)
10e	3299, 1623 // * 2.58 (s, 3H), 4.02 (s, 3H), 6.77−6.82 (m, 1H), 7.13−7.18 (m, 2H), 7.52−7.56 (m, 2H), 8.64 (s, 1H) / 8.8 (q), 34.8 (q), 154.3 (s), 160.1 (s) [f] // 302 /313 /315 /316 /318 /323 /325 /326 [b]
10f	1300, 1142 // * 2.50 (s, 3H), 3.95 (s, 3H), 7.46−7.54 (m, 3H), 7.79−7.83 (m, 2H) / 8.9 (q), 35.1 (q), 126.9 (d, 2C), 128.5 (d, 2C), 131.3 (d), 143.0 (s), 155.3 (s) // 272 /279 /280 /282 /283 /289 /288 /290 [b]
10g	1600, 1546 (w) // 2.10 (s, 3H), 4.31 (s, 3H), 7.58−7.73 (m, 3H), 7.77−7.89 (m, 2H) / 22.3 (q), 36.0 (q), 119.0 (s), 128.0 (d, 2C), 128.8 (d, 2C), 132.0 (d), 154.3 (s), 174.7 (s)
10h	1599, 1567 // 4.25 (s, 3H), 7.35−7.46 (m, 3H), 7.52−7.57 (m, 2H), 7.59−7.64 (m, 1H), 7.75−7.78 (m, 2H), 8.16−8.19 (m, 2H) / 36.8 (q), 155.1 (s), 170.9 (s) [f]

[a] Charge-transfer absorptions for **8b,c**, **9d,e**, and **10a,b,e,f**. [b] H_2O /MeOH /EtOH /*i*-PrOH /MeCN /$CHCl_3$ /CH_2Cl_2 /dioxane. [c] EtOH /*i*-PrOH /MeCN /$CHCl_3$ /CH_2Cl_2 /dioxane. [d] *i*-PrOH /MeCN /$CHCl_3$ /CH_2Cl_2 /dioxane. [e] MeCN /$CHCl_3$ / CH_2Cl_2 /dioxane. [f] Carbon signals of Ph omitted.

The following compounds were prepared by reported procedures: (i) *O*-mesitylsulfonylhydroxylamine (MSH);[19] (ii) 5-methyltetrazole;[20] (iii) 2-methyltetrazoles (**1a**),[21] (**1b**),[22] and (**1c**);[23] (iv) tetrazol-1-amines (**2a**) [24] and (**2c**);[24] (v) 1-methyltetrazoles (**3a**),[6b] (**3b**),[22] and (**3c**);[23] (vi) tetrazol-2-amines (**4a**) [24] and (**4c**).[24]

Amination of 5-methyltetrazole. Adopting the method of ref.,[24] a solution of hydroxylamine-*O*-sulfonic acid (27.1 g, 240 mmol) in water (50 mL) was added dropwise with stirring at 75 °C to 5-methyltetrazole (8.40 g, 100 mmol) and Na_2CO_3 (23.3 g, 220 mmol) dissolved in water (125 mL). After the hot mixture has been stirred for 1 h, it was cooled and extracted with ethyl acetate for 20 h. The organic extract was concentrated *in vacuo* and chromatographed on silica gel using dichloromethane–ethyl acetate (2 : 1) as eluant to afford, successively, 5-methyltetrazol-2-amine (**4b**) and 5-methyltetrazol-1-amine (**2b**).
2b: 4.00 g (41%), mp 44 °C (ethanol–light petroleum; lit.,[25] mp 44–45 °C); IR (KBr): 3600–3100, 1636 cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.54 (s, 3H), 5.65 (s, 2H); ^{13}C NMR ($CDCl_3$): δ 8.3 (q), 151.7 (s).
4b: 2.65 g (27%), colorless oil; IR (neat): 3306, 3179, 1622 cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.46 (s, 3H), 6.57 (br s, 2H); ^{13}C NMR ($CDCl_3$): δ 11.0 (q), 161.6 (s). – *N*-Benzylidene-5-methyltetrazol-2-amine (prepared after ref.[24]): mp 70 °C (ethanol); ^1H NMR ($CDCl_3$) δ 2.61 (s, 3H), 7.48–7.53 (m, 2H), 7.56–7.61 (m, 1H), 7.93–7.97 (m, 2H), 9.26 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 10.9 (q), 128.8 (d, 2C), 129.2 (d, 2C), 130.8 (s), 132.9 (d), 157.4 (d), 161.1 (s). Anal. Calcd for $C_9H_9N_5$: C 57.74, H 4.85, N 37.41. Found C 57.87, H 5.16, N 37.33.

Amination of 2-methyltetrazole (1a), 2,5-dimethyltetrazole (1b), 2-methyl-5-phenyltetrazole (1c), and 1-methyltetrazole (3a). General procedure: A solution of the appropriate tetrazole (6 mmol) and MSH (1.28 g, 6 mmol) in dichloromethane (50 mL) was allowed to stand at 20 °C for 24 h. The mixture was extracted with water (1 x 20 mL, 2 x 10 mL) and the combined aqueous layers were concentrated to dryness *in vacuo*. The residue was washed with ether and recrystallized to give the substituted aminotetrazolium mesitylenesulfonates (**5b**) and (**6a**), respectively; for data, see Tables 1 and 2. – In the case of **1a** and **1c**, the reaction mixture contained a small amount of **5** that could not be isolated: ^1H NMR ($CDCl_3$): δ (s) 4.58 / 4.38 and 10.20 / 8.94 (**5a** / **1a**), intensity 1 / 6; δ (s) 4.65 / 4.43 (**5c**, X = MSTS in place of Br) / **1c**), intensity 1 / 7.

Methylation of 5-methyltetrazol-1-amine (2b), 5-phenyltetrazol-1-amine (2c), tetrazol-2-amine (4a), 5-methyltetrazol-2-amine (4b), and 5-phenyltetrazol-2-amine (4c). General procedure: A solution or suspension of the respective tetrazole (2 mmol) in dimethyl sulfate (2 mL, *ca.* 20 mmol) was kept at 20 °C for 24 h (5 d in the case of **2c** and **4c**). Then ether (10 mL) was added whereupon the aminotetrazolium methylsulfate (**7a**) crystallized. In the other cases, the ethereal phase was extracted with water (3 x 5 mL),

the aqueous layers were concentrated *in vacuo* to one half and allowed to pass a column packed with anion exchange resin containing bromide or iodide ion. The resultant solution was concentrated and the residue recrystallized from the appropriate solvent (Table 1) to afford the aminotetrazolium halides (**6b**), (**7b**), and (**7c**), respectively. For separation of the aminotetrazolium bromides (**5c**) and (**6c**), the material obtained by anion exchange was dissolved in ethanol and kept at 0 °C to allow crystallization of **5c**; the mother liquor was concentrated and, after addition of ether, the product (**6c**) crystallized. For data, see Tables 1 and 2.

Substituted tetrazolium *N*-aminides (8–10). (i) **8c,g**, **9c,g**, and **10a,c,g**: General procedure: To a stirred suspension of the appropriate tetrazolium salt (2 mmol) in dichloromethane (10 mL) was added at 20 °C triethylamine (0.40 g, 4 mmol) followed by a solution of acetyl chloride (0.16 g, 2 mmol) in the same solvent (5 mL). 1 h later the mixture was concentrated to dryness and aqueous K_2CO_3 (0.35 g, *ca.* 2.5 mmol; 10 mL) was added. Evaporation *in vacuo* left a residue from which the product was extracted with dichloromethane. – (ii) **8e**, **9e**, and **10e**: As method (i) except that only half the amount of triethylamine (0.20 g, 2 mmol) and phenyl isocyanate (0.24 g, 2 mmol) were employed. – (iii) **8b,d,f,h**, **9b,d,f,h**, and **10b,d,f,h**: General procedure: To the appropriate tetrazolium salt (2 mmol), dissolved in water (10 mL), was added with vigorous stirring at 20 °C K_2CO_3 (0.35 g, *ca.* 2.5 mmol) followed by a solution of benzoyl chloride (0.28 g, 2 mmol) or benzenesulfonyl chloride (0.35 g, 2 mmol) in dichloromethane (15 mL). After 1 h the aqueous phase was extracted with dichloromethane (3 x 10 mL); the combined organic layers were dried over Na_2SO_4 and concentrated to give the product. – (iv) **8b**: A mixture of tetrazol-1-amine (**2a**) (0.77 g, 9 mmol) and dimethyl sulfate (9 mL) was kept at 20 °C for 24 h. Then ether was added to precipitate an oil that was dissolved in water. Treatment with K_2CO_3 and benzoyl chloride and work-up according to (iii) afforded the product. – For data, see Tables 1 and 2.

REFERENCES AND NOTES

1. a) For the term "aminide" (instead of the widely used "imide"), see: Revised Nomenclature for Radicals, Ions, Radical Ions and Related Species (IUPAC recommendations 1993), *Pure Appl. Chem.*, 1993, **65**, 1357; *cf.* also ref.[1b]; b) J. Valenciano, E. Sánchez-Pavón, A. M. Cuadro, J. J. Vaquero, and J. Alvarez-Builla, *J. Org. Chem.*, 2001, **66**, 8528.
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14. A detailed study is in progress.
15. a) *N*-(5-Methyltetrazol-1-yl)acetamide, mp 101 °C (ethanol); IR (KBr): ν 3183, 1711, 1531 cm^{-1}; ^{1}H NMR (DMSO-d_6): δ 2.15 (s, 3H), 2.39 (s, 3H), 12.26 (s, 1H); b) *N*-(5-methyltetrazol-1-yl)-*N*′-phenylurea, mp 202 °C (ethanol); IR (KBr): ν 3333, 3195, 1676 cm^{-1}; ^{1}H NMR (DMSO-d_6): δ 2.44 (s, 3H), 7.03–7.08 (m, 1H), 7.31–7.36 (m, 2H), 7.48–7.51 (m, 2H), 9.77 (s, 1H), 10.54 (s, 1H).
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17. a) Total energies of **8c**, **9c**, and **10c** (absolute minima): –544.84346, –544.84089, and –544.83669 a.u. b) *E* configuration resulted in higher energy as follows: 7.66 kcal/mol with **8c** [O(1)-C(2)-N(3)-N(4) –167.2°; C(2)-N(3)-N(4)-C(5) –162.0°], 10.12 kcal/mol with **9c** [O(1)-C(2)-N(3)-N(4) –170.6°; C(2)-N(3)-N(4)-C(5) –153.4°], and 6.54 kcal/mol with **10c** [O(1)-C(2)-N(3)-N(4) –157.4°; C(2)-

N(3)-N(4)-N(5) 23.6°]. c) An analogous conformer was located in the case of **8c** [O(1)-C(2)-N(3)-N(4) −0.4°; C(2)-N(3)-N(4)-C(5) 175.2°] as was found, *vice versa*, a non-planar one in the case of **10c** [O(1)-N(2)-N(3)-N(4) −10.5°; C(2)-N(3)-N(4)-N(5) 149.3°]; both conformers are slightly higher in energy (by 0.70 and 1.48 kcal/mol) than those depicted in Figure 1.

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