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Synthesis of *N*-[1-(2-Hydroxyethyl)-1*H*-tetrazol-5-yl]-*N*-methylhydrazine as Polymeric Precursor

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A nitrogen-rich polymer was formed from the reaction of hexamethylene diisocyanate and *N*-[1-(2-hydroxyethyl)-1*H*-tetrazol-5-yl]-*N*-methylhydrazine (**3**) monomers. Compound **3** was synthesized by a nucleophilic substitution of the methylated sulfur atom of 4-[2-(acetoxy)ethyl]-2-methylthiosemicarbazide (**10**) with sodium azide and final deprotection of the formed *N*-[1-2-(acetoxyethyl)-1*H*-tetrazol-5-yl]-*N*-methylhydrazine (**13**). Moreover, the isomer 4-(2-azidoethyl)-2-methylsemicarbazide (**18**) to **3** was synthesized. Compounds **3**, **10**, **13** and 4-[2-(trimethylsilyloxy)ethyl]-2-methylthiosemicarbazide (**15**) were characterized by using vibrational spectroscopy (IR, Raman), mass spectrometry and multinuclear NMR spectroscopy. The crystal structures of **3**, **10** and **13** were determined by using single-crystal X-ray diffraction. The molecular weights of the polymers were determined by GPC.

Introduction

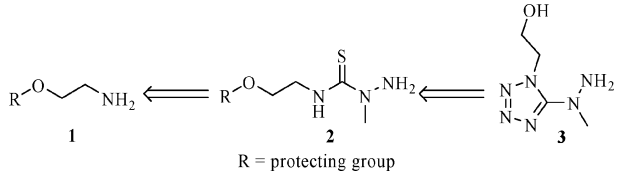
To date, nitrogen-rich polymers are used as binder in energetic compositions[1] and as gas-generating agents.[2] Furthermore, nitrogen-rich polymers are used for biomedical applications[3] and antifoggants in photographic materials.[4] Within the wide range of applied nitrogen-rich polymers, compounds containing tetrazole moieties are rare. Tetrazoles are predestined monomers for this kind of polymers, especially due to their high nitrogen content and the sufficiently high thermal stability, along with their energetic character. One example for tetrazole-containing polymers is poly(vinyltetrazole), either obtained by radical polymerization of 1-vinyl-1*H*-tetrazole[5] or by [2+3] cycloaddition reaction of hydrazoic acid with poly(vinylnitrile).[6] One disadvantage of poly(vinyltetrazole) is the lack of solubility or melting point, which prevents practical applications. Nevertheless, copolymers (e.g. with styrene) of vinyltetrazole are in use.[7] Other tetrazole-containing polymers are poly(1-vinyl-1*H*-hydroxytetrazole)[5] or a polycondensate with N^1-[1-(4-aminophenyl)-1*H*-tetrazol-5-yl]benzene-1,4-diamine.[4]

Most nitrogen-rich polymers are synthesized by radical polymerization. Therefore, the investigation of derivatives of tetrazoles, containing at least two functional groups, suitable as monomer for polycondensation reactions, could lead to new, useful compounds. The advantage of polycondensation or polyaddition reactions, compared to the radical polymerization is the simpleness of derivatization. By variation of one monomer, the nitrogen-rich polymer can be adjusted to the application needed.

In order to gain a high nitrogen content, *N*-[1-(2-hydroxyethyl)-1*H*-tetrazol-5-yl]-*N*-methylhydrazine was synthesized. N^1-Substituted tetrazolylhydrazines were reported by Atherton and Lambert.[8] In contrast to the well-known derivatives of aminotetrazole,[9] alkylated tetrazolylhydrazines are rarely known.[10] Experiments showed, that an alkylation of the tetrazole moiety by alkyl halides, analogously to known alkylations of aminotetrazole,[8] are not possible, due to the reactivity of the hydrazine moiety. In this work we present a five-step synthesis starting with ethanolamine to lead to *N*-[1-(2-hydroxyethyl)-1*H*-tetrazol-5-yl]-*N*-methylhydrazine.

Results and Discussion

In order to obtain *N*-[1-(2-hydroxyethyl)-1*H*-tetrazol-5-yl]-*N*-methylhydrazine (**3**), an improved way developed by Weigand,[11] similar to the synthesis by Atherton and Lambert,[8] was applied (Scheme 1).



Scheme 1. Retrosynthetic pathway to *N*-[1-(2-hydroxyethyl)-tetrazol-5-yl]-*N*-methylhydrazine.

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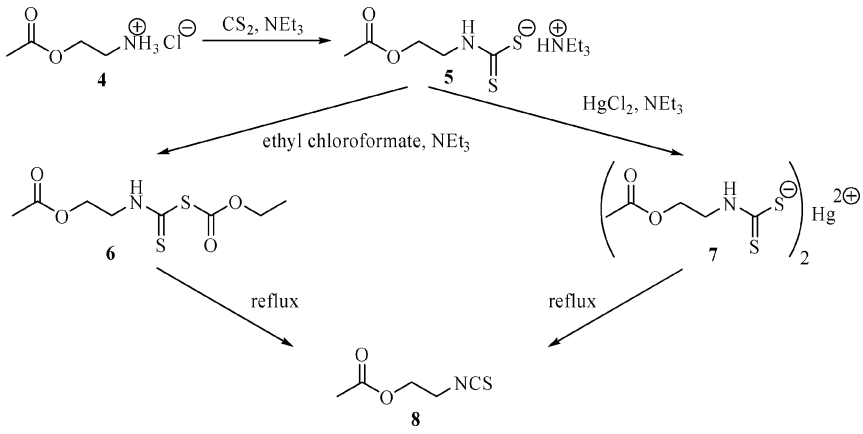
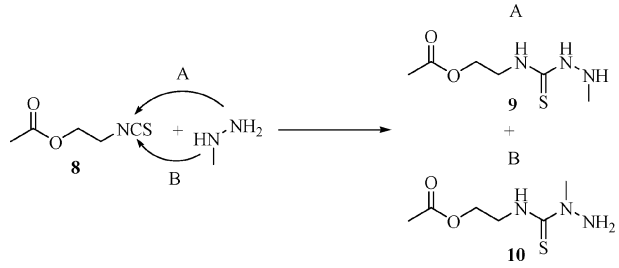


Scheme 2. Synthesis of 2-isothiocyanatoethyl acetate **8**.

In the first step towards the synthesis of **3**, it is necessary to protect ethanolamine to avoid a cyclization reaction due to a possible intramolecular attack of the hydroxy group at the electrophilic isothiocyanate formed later. On applying different protecting groups, only the acetyl group proved to be suitable. Based on 2-aminoethyl acetate, which is required to form the thiosemicarbazide **2**, several different ways to afford **8** have been published.[12] Compound **8** was obtained by desulfuration of the dithiocarbamate **5** by either mercury(II) chloride[13] or ethyl chloroformate[14] (Scheme 2).

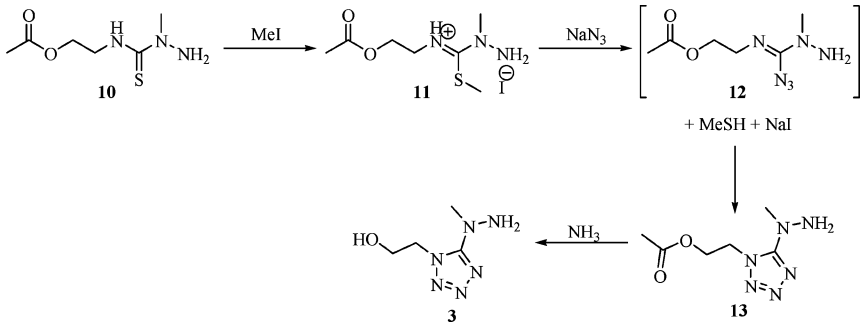
Compound **8** was purified by distillation. A common way to synthesize thiosemicarbazides is the reaction between derivatives of hydrazine and isothiocyanates.[15] 4-[2-(Acetoxy)-ethyl]-2-methylthiosemicarbazide (**10**) was obtained from the reaction of monomethylhydrazine with the isothiocyanate moiety of **8**. Under kinetic control, it was possible to selectively obtain **10** at 0 °C, whereas carrying out the reaction at elevated temperatures yielded a mixture of both isomers **9** and **10** (Scheme 3), as shown by ^{1}H NMR studies.

In order to obtain tetrazole **13**, it was necessary to methylate the sulfur atom of **10** and thus to convert it into a leaving group. The resulting methylthio group is replaced by azide (from a suspension of sodium azide in ethanol). The resulting azido amine **12** undergoes an electrocyclic ring closure to form the tetrazole **13**. Compound **13** had to be purified by column chromatography, before it was deprotected by treatment with concentrated ammonia at ambient temperature for 1 h (Scheme 4).



Scheme 3. Synthesis of 4-[2-(acetoxy)ethyl]-2-methylthiosemicarbazide (**10**).

Compounds **10**, **13** and **3** were characterized by single-crystal X-ray diffraction (Table 3). Compound **10** (Figure 1) crystallizes in the monoclinic space group $P2_1/n$ with four molecules per unit cell. The bond lengths and angles are in accordance with values observed for thiosemicarbazides as reported in the literature.[16] The crystal structure reveals intermolecular interactions between each of the thiosemicarbazide moieties and the acetyl groups. The structure is stabilized by four hydrogen bonds. Three intermolecular hydrogen bonds exist between three different N3 donor atoms to the sulfur acceptor atom to form a two-dimensional layer. The fourth hydrogen bond between the donor atom N1 to the acceptor O2 connects the layers along the *c* axis.



Scheme 4. Synthesis of *N*-[1-(2-hydroxyethyl)-1*H*-tetrazol-5-yl]-*N*-methylhydrazine (**3**).

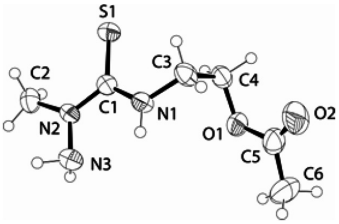


Figure 1. Molecular structure of **10**. Thermal ellipsoids are drawn at the 50% probability level.

Compound **13** (Figure 2) crystallizes in the monoclinic space group $P2_1/n$ with four molecules per unit cell. As mentioned before, the bond lengths and angles are consistent with comparable values of tetrazoles in the literature.[17] Again, the acetyl groups and tetrazole moieties are facing each other. Thereby the acetyl moieties are situated between two layers of tetrazoles. The structure is stabilized by two different hydrogen bonds: one between the donor atom N6 and the acceptor atom N4, connecting the tetrazole moieties, the other between the donor atom N6 and the acceptor atom O2 of the opposing molecule.

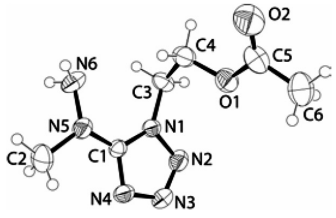


Figure 2. Molecular structure of **13**. Thermal ellipsoids are drawn at the 50% probability level.

Compound **3** (Figure 3) crystallizes in the monoclinic space group $P2_1/c$ with four molecules per unit cell. Compared to compound **13**, the N4–N3–N2 angle is about 5.5° smaller than the corresponding angle of **13**. The other angles and bond lengths show no difference compared to values from the literature.[17] In the solid state, the molecules form dimers by an intermolecular hydrogen bond between N4 as acceptor and O1 as donor atom. The dimers are connected by a hydrogen bond between the donor atom N6 and the acceptor atom N2 along the *b* axis. These tubular-like structures are connected by a hydrogen bond between the donor atom N6 and the acceptor atom O1.

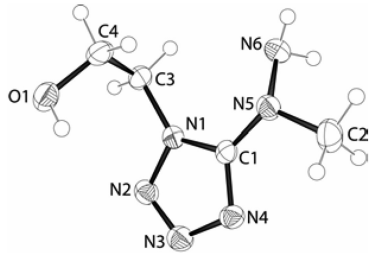
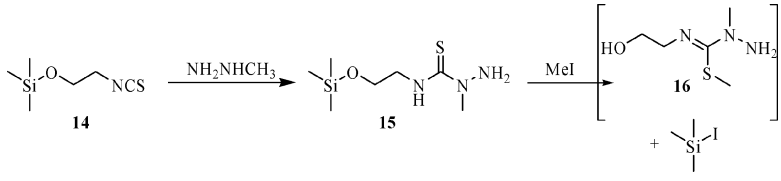


Figure 3. Molecular structure of **3**. Thermal ellipsoids are drawn at the 50% probability level.

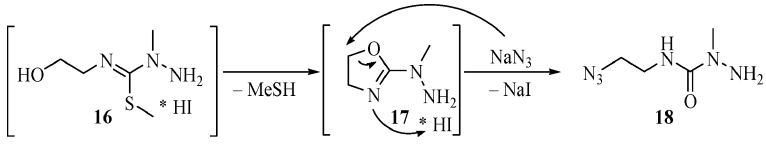
In order to point out the importance of the protecting group, a more labile protecting group was chosen to obtain the free hydroxy group during the methylation step. We applied the trimethylsilyl group, due to its increased lability towards acidic conditions and temperature.[18] The corresponding [2-(isothiocyanato)ethoxy]trimethylsilane (**14**) was prepared according to Kricheldorf et al.[19] Addition of monomethylhydrazine in ethereal solution yielded 2-methyl-4-[2-(trimethylsilyloxy)ethyl]thiosemicarbazide (**15**). The formation of hydrogen iodide while maintaining a temperature of 80 °C (4 h) during the methylation step of the thiosemicarbazide **15** ensured the cleavage of the trimethylsilyloxy group to give **16** (Scheme 5).

In the following step, a nucleophilic displacement of the methylthio group took place to afford the intermediate five-membered ring **17**. Sodium azide was added to the reaction mixture, and the azide anion caused a ring opening by nucleophilic attack at the oxygen-bearing CH_2 group to lead to 4-(2-azidoethyl)-2-methylsemicarbazide (**18**) (Scheme 6).

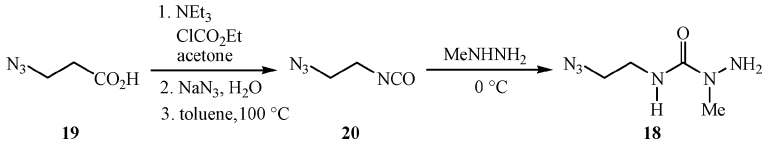
The product was purified by column chromatography, and a pale yellow liquid was obtained. The analysis (IR, NMR) showed no evidence for a tetrazole; however, an azide group could unambiguously be detected, together with small signals of decomposition products. In contrast to the analytical data of the previously mentioned tetrazole **3**, the IR spectrum showed a very strong band at 2104 cm^{-1} (Figure 4).[20] To verify the structure of **18**, we synthesized this compound from 3-azidopropionic acid (**19**) according to



Scheme 5. Synthesis of (*Z*)-1-amino-3-(2-hydroxyethyl)-1,2-dimethylisothiourea (**16**).



Scheme 6. Formation of 4-(2-azidoethyl)-2-methylsemicarbazide (**18**).



Scheme 7. Synthesis of **18** from **19**.

Weinstock's[21] procedure of the Curtius reaction, followed by treatment of the corresponding isocyanate **20** with methylhydrazine (Scheme 7). A comparison of the ^{1}H and ^{13}C NMR data is given in Table 1.

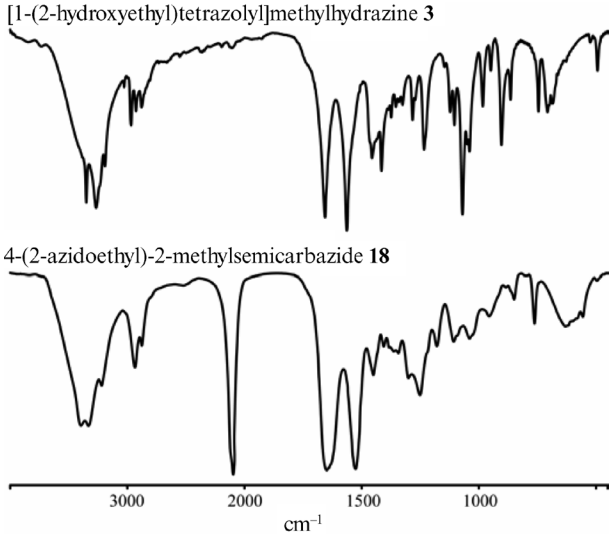


Figure 4. IR spectra of **3** and **18**; the signal appearing at 2104 cm^{-1} indicates the azide group.

Table 1. ^{1}H and ^{13}C NMR data of compounds **18** and **3** in [D$_6$]-DMSO.

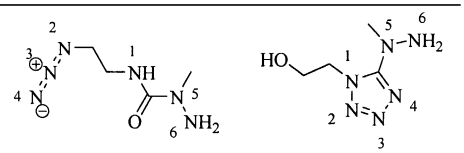
		18			**3**	
	^{1}H		^{13}C	^{1}H		^{13}C
CH_3	s	2.91	37.7	s	3.09	44.4
CH_2	q	3.18	39.1	t	3.72	50.8
$NNCH_2$	t	3.28	50.8	t	4.49	59.5
NH_2	s	4.41	–	s	4.82	–
OH/NH	br. t	6.89	–	br. s	4.96	–
C_q	–	–	159.2	–	–	159.2

In Table 2, the ^{15}N NMR spectroscopic data are shown. The shifts are consistent with common values for tetrazoles (in case of **3**[22]) and azides (in case of **18**).[23]

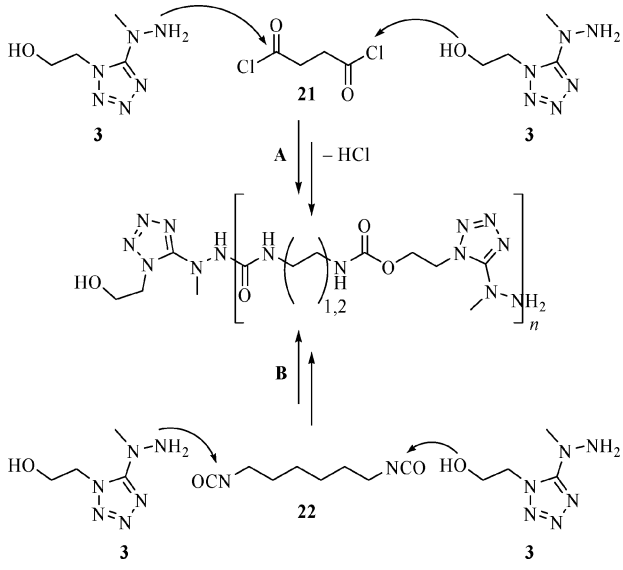
With **3** being a bifunctional tetrazole, containing a hydroxy group and a hydrazine moiety, there are different possibilities for a polycondensation to occur. Succinyl chloride (**21**) and hexamethylene diisocyanate (**22**) were chosen to study the reaction with **3** (Scheme 8).

Two different methods of polymerization were investigated: polycondensation in solution and bulk. The experiments revealed, that the polycondensation in solution was not suitable, because either low molecular weight fragments or starting material were detected. In turn, the polymers were synthesized by melting the monomers and annealing them for several hours.

Table 2. ^{15}N NMR data of **18** and **3** data in [D$_6$]DMSO.



	18	**3**
N1	–304.2	–174.5
N2	–310.7	–21.9
N3	–131.8	–11.0
N4	–172.5	–100.1
N5	–286.0	–313.3
N6	–304.7	–301.6



Scheme 8. Polycondensation and polyaddition of **3**. The attack of two hydrazine moieties or two hydroxy groups at **21** or **22** are also possible.

With succinyl chloride as a monomer (Method A, Scheme 8), only low molecular weights could be obtained. The average molecular weight M_n was found to be 996 g/mol. The measurement was carried out by using a DMSO solution containing 5 g of LiBr per L as eluent. The elemental analysis of the polymer showed significant differences to the calculated data (calcd. C 35.42, H 5.57, N 41.37; found C 27, H 5, N 28). These differences are expected to be a result of the high chlorine content of the polymer, since the hydrogen chloride formed during the polycondensation can undergo an acid/base reaction with the hydrazine moiety of the tetrazole. Hence, the deactivated amino group does not participate in any esterification reactions necessary for the formation of long polymers any longer.

To avoid the formation of hydrogen chloride and the resulting deactivation of the hydrazine moiety, hexamethylene diisocyanate was chosen as monomer for a polyaddition reaction (Method B, Scheme 6). The polymerization was carried out in bulk, by melting **3** at 100 °C and subsequent addition of **22**. The melt was kept at 120 °C for 1 h, and the polymer was obtained as prudish foam. The molecular weights of the polymers were determined by a GPC measurement. As eluent, dimethylformamide containing 0.01 M lithium nitrate was used. With a molecular weight distribution M_w of 5850 g/mol the obtained polymer was much longer than the corresponding polymer with **21** as monomer. The polydispersity was determined to be 3.21. The softening point of the polymer was found at 55 °C, the melting area between 190 and 245 °C, yielding a clear and colorless liquid. Above 260 °C the polymer underwent decomposition. The elemental analysis was in agreement with the calculated values (calcd. C 44.16, H 6.79, N 34.33; found C 43.26, H 6.82, N 32.81). Taking into account these results, the formed hydrogen chloride during the synthesis according to Method A can be determined to be responsible for the partial decomposition of the polymer during the polycondensation process.

Conclusions

The polymer of *N*-[1-(2-hydroxyethyl)-1*H*-tetrazol-5-yl]-*N*-methylhydrazine (**3**) and hexamethylene diisocyanate (**22**) was readily prepared in high yields. The nitrogen-rich polymer possesses a nitrogen content of 33%, accompanied by a high thermal stability (260 °C). Moreover, no sensitivity towards friction or impact can be observed. The investigated polymer can easily be converted into several derivatives by using different diisocyanates as monomers. Thereby the formed polymers can be adjusted to the desired application. A probable mechanism for the formation of **3** has been suggested, and furthermore the isomer 4-(2-azidoethyl)-2-methylsemicarbazide (**18**) was synthesized.

Experimental Section

General: All chemical reagents and solvents of analytical grade were obtained from Sigma–Aldrich or Acros Organics and used as supplied. 2-Aminoethyl acetate (**1**) was synthesized according to a literature procedure,[24] as were 2-isothiocyanatoethyl acetate (**8**)[25] and 3-azidopropionic acid (**19**).[26] ^{1}H, ^{13}C and ^{15}N NMR spectra were recorded with a JEOL Eclipse 400 instrument. The spectra were measured in [D$_6$]DMSO, $CDCl_3$ or D_2O. The chemical shifts are given relative to tetramethylsilane (^{1}H, ^{13}C) or nitromethane (^{15}N) as external standards. Coupling constants (*J*) are given in Hertz (Hz). Infrared (IR) spectra were recorded with a Perkin–Elmer Spectrum One FT-IR instrument and KBr pellets or NaCl plates at room temperature. Raman spectra were recorded with a Perkin–Elmer Spectrum 2000R NIR FT-Raman instrument equipped with an Nd:YAG laser (1064 nm). The intensities are reported in percentages relative to the most intense peak and are given in parentheses. Elemental analyses were performed with a Netsch Simultaneous Thermal Analyzer STA 429. Melting points were determined by differential scanning calorimetry (Linseis DSC PT-10 instrument). Measurements were performed at a heating rate of 5 °C min^{-1} in closed aluminium containers with a hole (1 μm) on the top for gas release with a nitrogen flow of 5 mL min^{-1}. The reference sample was a closed aluminium container. The molecular weights were measured by Fa. PSS, Mainz by using a TSP P1000 HPLC pump with 1.0 mL min^{-1} flow, a TSP AS3000 injection system with 50 μL volume of injection and a Showdex Differential Refractometer RI 71 as detector. The analysis was done with PSS-WinGPC Unity, version 7.2. PSS-GRAM, 10 μm 30 Å, ID 8.0 mm × 50 mm, PSS-GRAM, 10 μm 30 Å, ID 8.0 mm × 300 mm, PSS-GRAM, 10 μm 100 Å, ID 8.0 mm × 300 mm and PSS-GRAM, 10 μm 3000 Å, ID 8.0 mm × 300 mm were used as columns. DMF containing 0.01 M $LiNO_3$ or DMSO containing 5 g L^{-1} of the compound were used as eluents. The calibration was done by using a polystyrene standard.

4-[2-(Acetoxy)ethyl]-2-methylthiosemicarbazide (10): 2-Isothiocyanatoethyl acetate (**8**) (7.3 g, 50 mmol) was dissolved in diethyl ether (10 mL), and a solution of monomethylhydrazine (2.3 g, 50 mmol) and diethyl ether (5 mL) was added dropwise at 0 °C. After stirring for 1 h, the product separated as colorless solid; **10** was purified by recrystallization from ethanol (8.6 g, 90%). M.p. 81 °C. IR (KBr): $\tilde{\nu}$ = 3323 (s), 3271 (m), 3183 (w), 2924 (w), 1736 (vs), 1634 (m), 1620 (m), 1526 (s), 1442 (m), 1384 (m), 1370 (m), 1276 (m), 1243 (s), 1144 (m), 1048 (s), 926 (w), 908 (w), 877 (w), 812 (w), 693 (w), 607 (w) cm^{-1}. Raman (200 mW, 25 °C): $\tilde{\nu}$ = 3323 (100), 3267 (96), 3186 (89), 3000 (57), 2960 (75), 2937 (77), 1728 (26), 1626 (31), 1456 (29), 1435 (30), 1378 (23), 1294 (18), 1221 (15), 1148 (13), 1088 (10), 1069 (10), 1054 (11), 993 (11), 910 (11), 871 (13), 815 (38), 665 (54), 645 (18), 566 (12), 478 (34) cm^{-1}. ^{1}H NMR ([D$_6$]-DMSO): δ = 2.01 (s, 3 H, CC*H*$_3$), 3.44 (s, 3 H, NC*H*$_3$), 3.67 (q, 2 H, C*H*$_2$), 4.10 (t, 2 H, C*H*$_2$), 4.88 (N*H*$_2$), 8.28 (t, 1 H, N*H*) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 21.3 (C*C*H$_3$), 43.1 (N*C*H$_3$), 43.7 (N*C*H$_2$), 63.2 (O*C*H$_2$), 170.9 (*C*O), 181.8 (*C*S) ppm. MS (DEI$^+$): *m*/*z* (%) = 191.1 (18), 131.0 (67), 130.0 (10), 116.0 (18), 115.0 (27), 114.0 (33), 104.0 (10), 89.0 (16), 87.0 (9), 86.0 (27), 85.0 (36), 74.0 (9), 69.0 (20), 60.0 (11), 59.0 (9), 57.1 (10), 45.9 (100), 44.8 (26), 43.7 (11), 42.6 (86), 41.5 (9); calcd. for $C_6H_{13}N_3O_2S$ [M] 191.0728, found 191.0735. $C_6H_{13}N_3O_2S$ (191.25): calcd. C 37.68, H 6.85, N 21.97, S 16.77; found C 37.70, H 6.71, N 21.90, S 16.75.

***N*-[1-(2-Acetoxyethyl)-1*H*-tetrazol-5-yl]-*N*-methylhydrazine (13):** 4-[2-(Acetoxy)ethyl]-2-methylthiosemicarbazide (**10**) (2.3 g, 12 mmol) was suspended in ethanol (40 mL), and iodomethane (1.9 g, 13 mmol) was added. The mixture was stirred under reflux for 4 h. After cooling to 20 °C, sodium azide (2.6 g, 40 mmol) was added, and the mixture was stirred under reflux for further 12 h. The solvent was removed, and the resulting oil was extracted with dichloromethane. The organic phases were collected, and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (SiO_2, ethanol/diethyl ether, 1:9, R_f = 0.17). The product was obtained as colorless crystals (860 mg, 36%). M.p. 77.9–79.5 °C. IR (KBr): $\tilde{\nu}$ = 3434 (w), 3357 (m), 3263 (w), 2996 (w), 2965 (w), 2903 (w), 1732 (vs), 1645 (s), 1560 (m), 1467 (m), 1443 (m), 1409 (m), 1391 (m), 1260 (s), 1157 (w), 1126 (w), 1107 (m), 1040 (m), 994 (m), 939 (m), 909 (m), 739 (w), 697 (w), 686 (w), 635 (vs), 608 (vs), 489 (w) cm^{-1}. Raman (200 mW, 25 °C): $\tilde{\nu}$ = 3357 (25), 3263 (46), 3032 (36), 2994 (69), 2983 (62), 2961 (65), 2935 (82), 2791 (27), 1722 (76), 1643 (42), 1566 (30), 1467 (51), 1407 (54), 1338 (30), 1286 (76), 1270 (70), 1231 (43), 1155 (21), 1130 (32), 1108 (80), 1053 (28), 998 (27), 938 (33), 817 (70), 699 (100), 634 (96), 526 (45) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 1.83 (s, 3 H, CC*H*$_3$), 3.12 (s, 3 H, NC*H*$_3$), 4.09 (N*H*$_2$), 4.28 (t, 2 H, C*H*$_2$), 4.62 (t, 2 H, C*H*$_2$) ppm. ^{13}C NMR ($CDCl_3$): δ = 20.6 (C*C*H$_3$), 44.7 (N*C*H$_3$), 47.2 (N*C*H$_2$), 61.7 (O*C*H$_2$), 158.6 (*C*$_q$), 170.7 (*C*O) ppm. ^{15}N NMR ($CDCl_3$): δ = –0.3 (N3), –16.8 (N2),

–90.1 (N4), –175.1 (N1), –298.5 (NH_2), –312.5 (NCH_3) ppm. MS (DEI^+): *m/z* (%) = 200.2 (22) [M], 158.2 (9), 115.1 (5), 87.1 (83), 69.1 (12), 43.1 (100), 15.1 (13); calcd. for $C_6H_{12}N_6O_2$ [M] 200.1, found 200.2. $C_6H_{12}N_6O_2$ (200.20): calcd. C 36.00, H 6.04, N 41.98; found C 36.00, H 5.87, N 41.36.

***N*-[1-(2-Hydroxyethyl)-1*H*-tetrazol-5-yl]-*N*-methylhydrazine (3):** *N*-[1-(2-Acetoxyethyl)-1*H*-tetrazol-5-yl]-*N*-methylhydrazine (**13**) (320 mg, 1.6 mmol) was dissolved in 0.1 M aqueous potassium hydroxide solution (30 mL) and stirred at ambient temperature for 1 h. The solvent was removed and the obtained oil extracted with acetonitrile. After recrystallization from acetonitrile, colorless crystals formed (150 mg, 59%). M.p. 111.0–117.8 °C. IR (KBr): $\tilde{\nu}$ = 3350 (s), 3266 (s), 2967 (w), 2926 (w), 2878 (w), 1656 (vs), 1563 (vs), 1455 (m), 1415 (m), 1373 (m), 1340 (w), 1325 (w), 1282 (m), 1233 (m), 1122 (m), 1104 (m), 1069 (vs), 1039 (m), 983 (m), 948 (w), 903 (m), 864 (m), 745 (m), 707 (m), 684 (m), 493 (m) cm^{-1}. Raman (200 mW, 25 °C): $\tilde{\nu}$ = 3351 (40), 3232 (38), 3193 (34), 3028 (32), 2976 (100), 2928 (37), 2882 (38), 2809 (24), 1654 (41), 1566 (35), 1466 (56), 1418 (47), 1378 (32), 1352 (34), 1284 (66), 1268 (59), 1231 (30), 1105 (55), 1071 (29), 987 (19), 950 (23), 864 (52), 692 (91), 633 (54), 523 (28), 498 (27) cm^{-1}. ^1H NMR ([D$_6$]DMSO): δ = 3.09 (s, 3 H, NCH_3), 3.72 (t, 2 H, OCH_2), 4.49 (t, 2 H, NCH_2), 4.82 (s, 2 H, NH_2), 4.96 (br. t, 1 H, O*H*) ppm. ^{13}C NMR ([D$_6$]-DMSO): δ = 44.4 (*C*H$_3$), 50.8 (O*C*H$_2$), 59.5 (N*C*H$_2$), 159.2 (C_q) ppm. ^{15}N NMR (D_2O): δ = –11.0 (N3), –21.9 (N2), –100.1 (N4), –174.5 (N1), –301.6 (NH_2), –313.3 (NCH_3) ppm. MS (DEI^+): *m/z* = 158.1 [M],143.1, 127.1, 113.1, 87.1, 69.1, 55.1, 43.1, 31.1, 28.1; calcd. for $C_4H_{10}N_6O$ [M] 158.1, found 158.1. $C_4H_{10}N_6O$ (158.16): calcd. C 30.38, H 6.37, N 53.14; found C 30.43, H 6.46, N 52.23.

4-{2-[(Trimethylsilyl)oxy]ethyl}-2-methylthiosemicarbazide (15): Ethanolamine (1.2 g, 20 mmol) was dissolved in ethyl acetate (15 mL), and triethylamine (4.1 g, 40 mmol) was added at 0 °C. Chlorotrimethylsilane (4.3 g, 40 mmol) was added dropwise with vigorous stirring. After stirring at ambient temperature for 30 min, the solid was filtered off and washed with ethyl acetate (20 mL). After the addition of carbon disulfide (1.9 g, 25 mmol), the solution was stirred at 0 °C for 1 h and at room temperature for an additional hour. Then chlorotrimethylsilane (2.3 g, 21 mmol) and triethylamine (2.0 g, 20 mmol) were added dropwise. The reaction mixture was refluxed for 1 h. The solid was filtered off and washed twice with ethyl acetate. The solvent was removed under reduced pressure. A solution of monomethylhydrazine (0.9 g, 20 mmol) in diethyl ether (3 mL) was added dropwise at 0 °C to the resulting yellow-brownish oil, dissolved in diethyl ether (5 mL). After stirring at 0 °C for 30 min and at room temperature for further 1.5 h, the solvent was removed under reduced pressure and the product slowly crystallized off the dark oil. Recrystallization from diethyl ether yielded **15** as colorless solid (0.8 g, 17%). M.p. 84–90 °C. IR (KBr): $\tilde{\nu}$ = 3317 (s), 3249 (m), 3178 (w), 3149 (m), 2961 (w), 2873 (w), 1643 (m), 1528 (vs), 1367 (m), 1303 (s), 1262 (m), 1251 (s), 1213 (w), 1164 (s), 1081 (vs), 1049 (vs), 895 (s), 866 (s), 839 (vs), 748 (m), 707 (vw) cm^{-1}. ^1H NMR ([D$_6$]DMSO): δ = 0.08 (s, 6 H, SiCH_3), 3.62–3.90 (m, 7 H, CH_3, 2 CH_2) ppm. ^{13}C NMR ([D$_6$]-DMSO): δ = –0.53 (Si*C*H$_3$), 43.80 (*C*H$_3$), 47.39 (*C*H$_2$), 62.51 (*C*H$_2$), 182.11 (*C*S) ppm. MS (DEI^+): *m/z* (%) = 221.1 (8) [M], 160.0 (21), 131.0 (29), 117.1 (8), 116.0 (36), 115.0 (12), 114.0 (83), 105.0 (12), 101.0 (12), 89.0 (20), 86.0 (15), 75.0 (12), 73.0 (74), 46.0 (100), 45.0 (9); calcd. for $C_7H_{19}N_3OSSi$ [M] 221.1018, found 221.1006. $C_7H_{19}N_3OSSi$ (221.39): calcd. C 37.97, H 8.65, N 18.98, S 14.48; found C 37.54, H 8.79, N 18.98, S 14.48.

4-(2-Azidoethyl)-2-methylsemicarbazide (18) from 15: 4-{2-[(Trimethylsilyl)oxy]ethyl}-2-methylthiosemicarbazide (**15**) (1.0 g, 4.5 mmol) was dissolved in ethanol (15 mL), and methyl iodide (0.6 g, 4.5 mmol) was added. After refluxing for 4 h, the reaction mixture was cooled to 40 °C, and sodium azide (0.4 g, 6.8 mmol) was added. The suspension was refluxed for 18 h. The solvent was removed under reduced pressure, and the residue was extracted with dichloromethane. The solvent was removed under reduced pressure and the resulting oil purified by column chromatography (dichloromethane/ethyl acetate, 1:1, R_f = 0.2) (0.4 g, 56%). IR (KBr): $\tilde{\nu}$ = 3400 (m), 3314 (m), 3208 (m), 2933 (m), 2874 (m), 2104 (vs), 1652 (vs), 1520 (vs), 1451 (m), 1403 (m), 1359 (m), 1300 (m), 1247 (m), 1174 (m), 1106 (m), 1053 (s), 1028 (vs), 1009 (s), 957 (m), 849 (w), 821 (w), 761 (m), 627 (m), 555 (m) cm^{-1}. ^1H NMR ([D$_6$]-DMSO): δ = 2.91 (s, 3 H, NCH_3), 3.18 (q, *J* = 5.7 Hz, 2 H, CH_2NH), 3.28 (t, *J* = 5.7 Hz, 2 H, CH_2N$_3$), 4.41 (s, 2 H, NH_2), 6.89 (br. t, 1 H, N*H*) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 37.7 (*C*H$_3$), 39.1 (*C*H$_2$NH), 50.8 (*C*H$_2$N$_3$), 159.2 (*C*=O) ppm; assignments of carbon signals were proved by 2D ^{13}C,^1H shift correlation. ^{15}N NMR ([D$_6$]DMSO): δ = –310.7 (N2), –304.7 (v. br., N6), –304.2 (d, *J* = 92 Hz, N1), –286.0 (N5), –172.5 (N4), –131.8 (t, *J* = 4 Hz, N3) ppm; assignments of nitrogen signals were proved by ^1H-decoupled ^{15}N NMR spectra and 2D ^{15}N,^1H shift correlations optimized for *J* = 90 and 3 Hz. MS (DEI^+): *m/z* (%) = 158.2 (8) [M], 149.1 (6), 129.1 (40), 114.1 (41), 102.1 (12), 73.1 (14), 60.1 (39), 46.1 (100), 45.1 (48), 30.1 (75), 26.1 (30); calcd. for $C_6H_{12}N_6O_2$ [M] 158.1, found 158.2.

4-(2-Azidoethyl)-2-methylsemicarbazide (18) from 19: 3-Azidopropionic acid (**19**) (3.47 g, 30.1 mmol) was treated with ethyl chloroformate and triethylamine in acetone and then with sodium azide in water as described by Weinstock.[21] After heating the corresponding acyl azide in dry toluene at 100 °C, half of the solvent was removed under reduced pressure to obtain a solution of **20**[27] in toluene, which is free of acetone. Otherwise, the 2-azidoethylcarbamoyl(methyl)hydrazone of acetone will be formed from the final product **19** and acetone. The solution of **20** was treated with methylhydrazine (1.38 g, 30 mmol) in dry toluene (10 mL) at 0 °C and

Table 3. Selected crystal data for **10**, **13** and **3**.

	10	**13**	**3**
Empirical formula	$C_6H_{13}N_3O_2S$	$C_6H_{12}N_6O_2$	$C_4H_{10}N_6O$
M_r [g mol^{-1}]	191.25	200.22	158.18
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/n$
a [Å]	6.8896(8)	11.808(2)	7.7148(12)
b [Å]	7.0185(7)	7.9679(16)	7.5255(10)
c [Å]	20.2201(19)	11.460(2)	12.7433(18)
β [°]	89.808(8)	112.64(3)	100.655(13)
V [Å^3]	977.73(18)	995.2(3)	727.09(18)
Z	4	4	4
F(000)	408	424	336
$\rho_{calcd.}$ [g cm^{-3}]	1.299	1.336	1.445
μ [mm^{-1}]	0.300	0.104	0.111
2θ [°]	53.98	49.99	51.99
Index range	$-8 \le h \le 8$	$-14 \le h \le 13$	$-9 \le h \le 9$
	$-8 \le k \le 8$	$-9 \le k \le 9$	$-5 \le k \le 9$
	$-25 \le l \le 25$	$-13 \le l \le 13$	$-13 \le l \le 15$
λ	0.71073	0.71073	0.71073
T [K]	200(2)	200(2)	200(2)
Reflections collected	10765	8920	3647
Unique reflections	2124	1742	1424
Parameters	138	153	141
S	1.119	1.126	1.074
R_{int}	0.0819	0.0460	0.0281
R_1/wR_2 [$I > 2\sigma(I)$]	0.0655/0.1454	0.0428/0.1030	0.0344/0.0858
R_1/wR_2	0.0826/0.1568	0.0495/0.1082	0.0464/0.0938

stirred at room temperature for 16 h. After removal of the solvent under vacuum, **19** (2.17 g, 46%) was isolated as an oil.

Polymerization of 3 and 22: *N*-[1-(2-Hydroxyethyl)-1*H*-tetrazol-5-yl]-*N*-methylhydrazine (**3**) (500 mg, 3.2 mmol) was mixed with hexamethylene diisocyanate (**22**) (531 mg, 3.2 mmol) and heated to 120 °C for 1 h. The polymer was obtained as hard, sproudish foam (960 mg, 93%). M.p. 190–245 °C, decomposition point 260 °C. IR (KBr): $\tilde{\nu}$ = 2926 (w), 2851 (w), 1636 (vs), 1539 (m), 1454 (w), 1261 (w), 1099 (w), 1034 (w), 803 (vw), 591 (w) cm^{-1}. $C_8H_{15}N_8O_3$ (271.26): calcd. C 44.16, H 6.79, N 34.33; found C 43.05, H 6.76, N 33.45. M_w = 5850 g/mol.

Crystal Structure Analysis: The crystallographic data were collected with an Oxford Xcalibur3 diffractometer equipped with a Spellman generator (voltage 50 kV, current 40 mA) and a Kappa CCD area detector with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The structure was solved by direct methods (SHELXS-97)[28] and refined (SHELXL-97).[29] All non-hydrogen atoms were refined anisotropically. Further details are listed in Table 3. CCDC-695558 (**10**), -695556 (**13**) and -695557 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

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