Hydrogen Bonding of 2-Tetrazenes, 1

First Synthesis and Investigation of Two Hydroxyalkyl-Substituted 2-Tetrazenes

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Received February 11, 1998

Keywords: Ab initio calculations / Hydrogen bonds / NMR spectroscopy / Thermolysis / Transition states

Two members of previously unknown hydroxyalkyl-2-tetrazenes (**1a**, **2a**) have been synthesized and hydrogen bonding of these novel difunctional compounds has been investigated by spectroscopic (IR, ^{1}H NMR, ^{15}N NMR) and theoretical methods. The structures of **1a** and its bis(trimethylsilyl) derivative **1b** were determined by X-ray analysis. In the crystalline state, molecules **1a** are associated by O–H···O hydrogen bonds that form a three-dimensional network. Ab initio HF and DFT as well as semiempirical SCF calculations show that O–H···N hydrogen bonds of 2-tetrazenes are medium strong. The δ-^{15}N data and the quantum chemical calculations indicate that the amino nitrogen atoms of a 2-tetrazene are involved in intermolecular hydrogen bonding to a larger extent than the azo nitrogen atoms; the corresponding energy difference of the two types of hydrogen bonds is about 3 kJ mol^{-1}. The hydrogen bonds can either stabilize or destabilize 2-tetrazenes thermodynamically depending on which nitrogen atoms are involved. Complexation of 1,1,4,4-tetramethyl-2-tetrazene with methanol is accompanied by only minor changes in geometric parameters whereas systematic effects on the electronic structure are more distinct. Transition states for N–N bond cleavage are stabilized to a larger extent making such compounds rather sensitive for thermal decomposition.

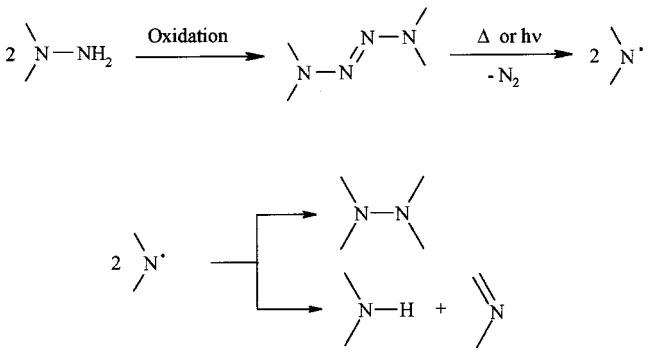
Introduction

2-Tetrazenes[1][2][3][4] are composed of a chain of four nitrogen atoms with a central double bond. This functional group is isoelectronic with the butadiene dianion, i.e. in the planar structure there are three occupied π MOs, of which the highest (HOMO) is antibonding. Therefore, their thermodynamic stability is closely related to the shape and the energy of the π MOs.[5][6][7][8][9]

2-Tetrazenes were described for the first time in 1878 by E. Fischer[10] and have received since then considerable attention as sources of aminyl radicals and their products.[11][12] The most important method to prepare 2-tetrazenes is the oxidative coupling of 1,1-disubstituted hydrazines (Scheme 1).[2][3][4] The parent compound, N_4H_4, was generated in 1975 from 1,1,4,4-tetrakis(trimethylsilyl)-2-tetrazene.[13] It is a colourless solid that decomposes above about 0°C into dinitrogen and hydrazine as well as ammonium azide.

By thermal and photolytic fragmentation 2-tetrazenes loose dinitrogen.[1][2][6][7][8][9][14][15] The primarily generated aminyl radicals[11][12][16] show mainly two reactions: Either

Scheme 1. Reaction scheme for synthesis and decomposition of 2-tetrazenes



they dimerize affording hydrazines or they disproportionate to amines and imines. While tetraalkyl- and alkyl-aryl-2-tetrazenes are stable to above 100°C, decomposition of tetraaryl-2-tetrazenes commences already at about 40°C.[1] In some instances, substituent effects have been studied.[17][18] Electron acceptor groups seem to increase the thermal stability. Photoelectron spectroscopic studies of 2-tetrazenes revealed a relation between electronic structure and thermodynamic stability,[6][7] and according to this car-

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  1434–193X/98/0707–1431 $ 17.50+.50/0

bonyl substituents should stabilize the 2-tetrazene system.[15] Since such compounds decompose, however, more easily than simple tetraalkyl-2-tetrazenes, their transition states for thermolysis must be even more stabilized than their ground states. Hydroxy groups should be of even larger influence on the electronic structure and accordingly on the thermodynamic and thermal stability because of their ability to form inter- and intramolecular hydrogen bonds. Although several other functional groups can be combined with the 2-tetrazene unit,[1][2] to our knowledge no hydroxy-substituted alkyl- or aryl-2-tetrazene was prepared before our present study.

Results and Discussion

Synthesis of Hydroxyalkyl-2-tetrazenes

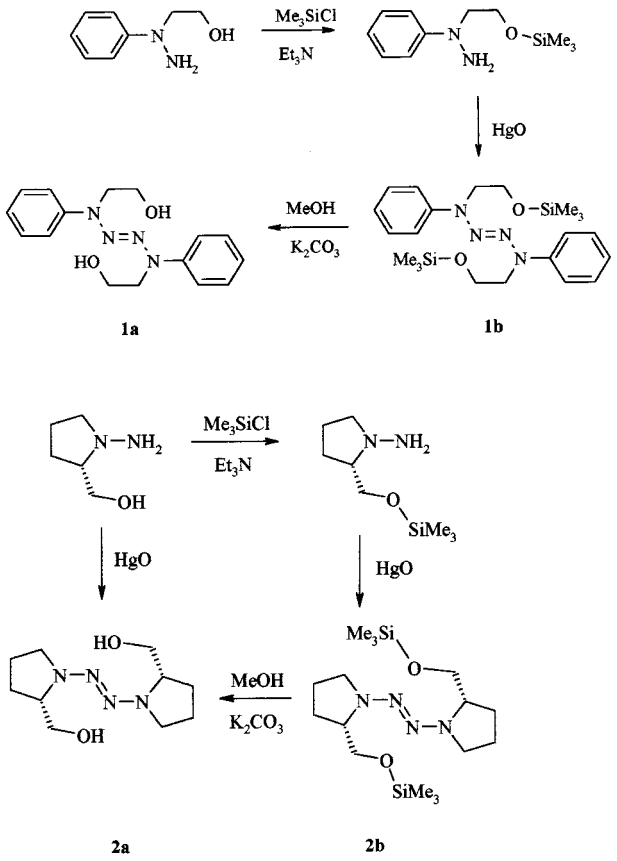
We have synthesized two hydroxyalkyl-2-tetrazenes (Scheme 2) which seem to have some unusual properties and might be used for interesting theoretical and practical investigations. Preliminary tests readily indicated that it is difficult to prepare hydroxy-substituted 2-tetrazenes from the corresponding hydrazines directly by oxidative coupling.[2] Starting from a variety of hydroxyalkyl- or hydroxyaryl-substituted hydrazines, the corresponding 2-tetrazenes could not be isolated. However, strong evolution of dinitrogen indicated that they were formed as unstable intermediates. This was supported by identification of their decomposition products in the reaction mixture. Also several attempts starting from trimethylsilyl-protected hydroxyalkylhydrazines failed, while synthesis of a methoxyalkyl-2-tetrazene (**2c**) by this method was successful without problems.[8] Only in one case (**2a**) we were finally able to generate the corresponding 2-tetrazene directly from the hydroxyalkylhydrazine. In two cases the trimethylsilyl-protected 2-tetrazenes could be obtained and removal of the protecting groups afforded the first two hydroxyalkyl-2-tetrazenes **1a** and **2a** (Scheme 2).

(*S*)-(−)-1-Amino-2-(hydroxymethyl)pyrrolidine[19] was used as starting material for **2a** which could be obtained by direct oxidation. It was, however, impossible to purify the product because it decomposed on distillation in high vacuum or during column chromatography. Better results were obtained when the alcoholic group of the starting compound was protected. Then **2a** was generated in pure form from the protected hydroxyalkyl-2-tetrazene **2b** which could be purified by vacuum distillation. For the synthesis of **1a** only the latter path was followed. Starting material was 1-(hydroxyethyl)-1-phenylhydrazine which firstly was silylated and then oxidized to the 2-tetrazene **1b** from which **1a** was liberated.

1a is a solid (m.p. 133−134°C, decomp.) and an X-ray crystal analysis could be performed (see below). The individual molecules are associated by hydrogen bonds between the hydroxy groups. ^{1}H-NMR spectroscopy indicates that in [D$_6$]DMSO solution intermolecular association dominates while in $CDCl_3$ solution intramolecular H bonds are favoured.

2a was obtained as a viscous oil. The IR spectrum of a capillary liquid film shows broad absorption of the OH

Scheme 2. Synthesis of hydroxyalkyl-2-tetrazenes **1a** and **2a**

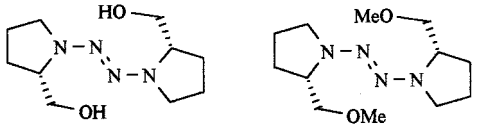


groups at 3365 cm^{-1}. In $CDCl_3$ solution three ν_{OH} bands are found with variable intensities depending on concentration: 3620 cm^{-1} (free OH groups), 3420 cm^{-1} (intermolecular association) and 3150 cm^{-1} (intramolecular association), indicating stronger intermolecular and somewhat weaker intramolecular H bonds.

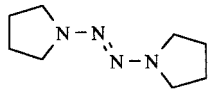
An important information about hydrogen bonding in **2a** is obtained by ^{15}N-NMR spectroscopy[20] (Figure 1). Comparison of the δ-^{15}N values of **2a**, its dimethoxy derivative **2c**[8] and 1,2-dipyrrolidinodiazene (**3**) indicates that the substituents cause inverse effects on the chemical shifts of the azo and the amino nitrogen atoms. While the δ-^{15}N values of the former atoms increase in the series **3** → **2c** → **2a**, for the latter they decrease. However, the effect of the hydroxymethyl groups is always larger than that of the methoxymethyl groups, which is in particular apparent for the azo nitrogen atoms. These findings indicate that hydrogen bonding in **2a** which under these experimental conditions is probably predominantly intermolecular involves all nitrogen atoms. Protonation shifts[20] of tertiary amines are positive ($\Delta\delta \approx 10-20$) whereas those of imines are negative and numerically much larger ($\Delta\delta \approx -100$). Accordingly, the high-field shift of the azo nitrogen atoms of **2a** of 4.8 ppm (relative to **2b**) and the corresponding low-field shift of the amino nitrogen atoms of 3.6 ppm can be explained with a preferential involvement of the latter atoms in H bonds. If we assume that the observed hydrogen bond shift relative

to the protonation shift is a measure of the abundance of such a hydrogen bond, the relation between amino−H bonds and azo−H bonds should be 3.6/10:4.8/100 ≈ 10:1. This would correspond to a difference in energy of the two types of N···H bonds of roughly 3 kJ mol^{-1}. The signals observed for **2c** and **3** are close to those reported recently for a tetraazido-substituted tetraalkyl-2-tetrazene.[21] ^{15}N-NMR spectra of **1a** have not been measured because of too low solubility in $CDCl_3$.

Figure 1. δ-^{15}N data [ppm] of 2-tetrazenes **2a**, **2c** and **3**



	2a	**2c**
Amino-N	-230.7	-234.3
Azo-N	11.5	16.3



3

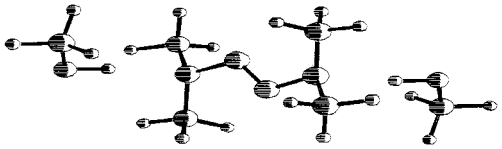
Amino-N	-238.4
Azo-N	17.2

Inter- and Intramolecular Hydrogen Bonding in 2-Tetrazenes

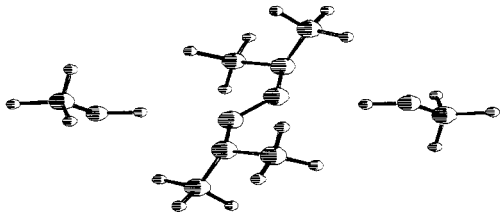
Our present investigation on hydroxy-substituted 2-tetrazenes allows the conclusion that hydroxy groups may exert delicate effects that either stabilize or destabilize the tetrazene system by hydrogen bonding. Until now hydrogen bonding of such compounds has not been investigated. In principle, 2-tetrazenes can form H bonds with all of their four nitrogen atoms, however, one would expect that primarily the azo nitrogen atoms are involved because of the delocalization of the electron lone-pairs of the amino nitrogen atoms. H bonds of the former nitrogen atoms will stabilize the 2-tetrazene unit by increasing the Coulomb attraction for the π electrons. On the other hand, hydrogen bonds to the amino nitrogen atoms will weaken the resonance energy of the π-electron system. sp^2-Hybridized nitrogen atoms as in imines[22] and azo compounds[23] are good H bond acceptors. 2-Tetrazenes are split by acids.[24][25]

In order to investigate the structure and strength of different hydrogen bonds of 2-tetrazenes, we have performed quantum chemical calculations on complexes of tetramethyl-2-tetrazene (TMT) with two molecules of methanol either involving the amino (complex **I**) or the azo nitrogen atoms (complex **II**). All systems were assumed to be centrosymmetric (point group C_i). We have used the semiempirical PM3 method as well as the ab initio Hartree-Fock (HF) method and the Becke3LYP (B3LYP) method of the density functional theory (DFT) with the basis set 6−31+G**. The last method includes electron correlation which is necessary to obtain reliable results. According to all methods, complex **I** is more stable than complex **II** (PM3: $\Delta\Delta H_f = -3.8$ kJ mol^{-1}, B3LYP: $\Delta E = -5.7$ kJ mol^{-1}). The two complexes, as calculated by the B3LYP method, are depicted in Figure 2, selected structure parameters of free TMT and the complexes are summarized in Table 1. In the ab initio HF calculations for complex **II** either a shallow minimum or a saddle point was found, depending on the basis set. Therefore, the corresponding results are not reported in the following sections.

Figure 2. Complexes of tetramethyl-2-tetrazene with two molecules of methanol showing hydrogen bonds to the amino (**I**) or the azo nitrogen atoms (**II**) (B3LYB results)



Complex **I**



Complex **II**

In complex **I**, the two methanol molecules are located above and below the 2-tetrazene molecule, and the OH groups are directed to N^1 and N^4, respectively, which are clearly pyramidalized (sum of bond angles: 343°). In complex **II**, the OH groups of the two methanol molecules are located near the plane of the four nitrogen atoms while the alcoholic methyl groups are again above and below the tetramethyl-2-tetrazene molecule. According to their geometric parameters (O−H and N···H distances, O−H···H angles, Table 1) the hydrogen bonds in both complexes can be characterized as "normal".[22][23] Only minor changes of bond distances and bond angles of the tetrazene molecule are observed between free TMT and its complexes **I** and **II** (Table 1), and in most cases inverse shifts are found. In **I** the N-N bond is lengthened by 0.009 A and the N=N bond is shortened a little relative to that of TMT, while in **II** the

Table 1. Total energy E (au), selected structure parameters – bond lengths (A) and angles (°) – and orbital energies (eV) of tetramethyl-2-tetrazene (TMT), complexes **I** and **II** (B3LYP/6−31+G**/ results)

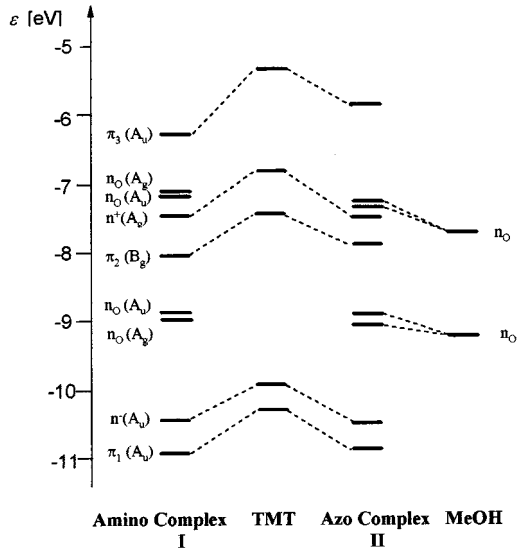
	TMT	Complex **I**	Complex **II**
E	−378.5982599	−610.0840039	−610.0818385
N−N	1.378	1.387	1.374
N=N	1.257	1.253	1.262
N−C	1.458	1.466	1.459
O−H		0.974	0.973
N···H		2.011	2.091
N=N−N	114.1	114.0	115.1
N−N−C	110.9	110.1	111.6
	118.4	118.0	119.1
C−N−C	116.1	115.1	116.0
=N−N···H		107.8	
N=N···H			134.3
O−H···N		167.2	169.7
N=N−N−C	151.7	149.5	147.9
	13.8	14.7	8.3
N=N−N···H		−99.5	
N−N=N···H			−38.2
=N−N···H−O		174.2	
N=N···H−O			164.3
π_3 (A_u)	−5.32	−6.22	−5.81
n^+ (A_g)	−6.81	−7.44	−7.53
π_2 (A_g)	−7.44	−8.03	−7.93

N=N bond length increases by 0.005 Å and the N−N bond remains nearly unchanged.

More clearly than in the geometric structure the effects of hydrogen bonding are reflected in the electronic structure. The energies of the three highest occupied MOs are included in Table 1; an orbital correlation diagram for TMT, methanol and their complexes **I** and **II** is shown in Figure 3. Compared with the ionization potentials of TMT[7] and methanol[26] measured by photoelectron spectroscopy, the absolute values calculated by the B3LYP method are too small by 2−3 eV, however, the sequence and the spacing of the MOs relate excellently to the experimental data. As is obvious from the data given in Table 1, the orbitals of TMT are stabilized by hydrogen bonding while the n_O orbitals of methanol are destabilized. However, a decrease of the energy separation of the antibonding π_3 MO and the bonding π_2 MO is found for **I** while for **II** the energy difference remains unchanged. PM3 calculations lead to similar results. In accord with our earlier findings[6] of the relationship between electronic structure and thermodynamic stability and with our expectations regarding stabilizing and destabilizing H bonds (see above), we can conclude that in **I** the 2-tetrazene unit is destabilized while in **II** its stability is not affected.

The energy of the complexes **I** and **II** compared to the sum of the energies of their components permits an estimation of the strength of the different H bonds. According to PM3 **I** is stabilized relative to the starting compounds by $\Delta\Delta H_f = -30.9$ kJ mol^{-1}, while the ab initio result is $\Delta E^{HF} = -36.2$ kJ mol^{-1} and according to B3LYP it is $\Delta E = -42.0$ kJ mol^{-1}. The corresponding values for **II** are −27.1 kJ mol^{-1} (PM3) and $\Delta E = -36.3$ kJ mol^{-1} (B3LYP). These data lead to the conclusion that a H bond of an alcoholic OH group to an amino nitrogen atom of a 2-tetrazene has an energy of 15−21 kJ mol^{-1}, while to a H bond of an azo nitrogen atom an energy value of 13−18 kJ mol^{-1} can be ascribed. The most reliable values, obtained by the B3LYP method, correspond to the upper limits. According to these data, the O−H···N bonds of 2-tetrazenes are characterized as medium strong, and the amino-nitrogen atoms are more basic than the azo nitrogen atoms. This unexpected result for the difference in the strength of the two H bonds of about 3 kJ mol^{-1} corresponds very well to the value estimated for **2a** from δ-^{15}N values (see above). Since the strength of both types of O−H···N hydrogen bonds is lower than that of alcoholic O−H···O hydrogen bonds,[22][23] intermolecular association of hydroxyalkyl-2-tetrazenes will primarily employ the latter type.

Figure 3. Orbital correlation diagram for 1,1,4,4-tetramethyl-2-tetrazene (TMT), methanol and their complexes **I** and **II**

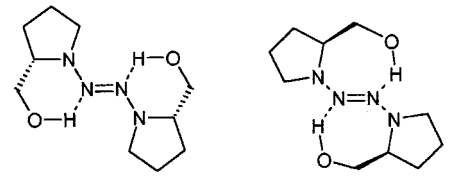


For **2a** different types of intramolecular H bonds are possible, some examples are depicted in Figure 4 as results of PM3 calculations. Structures involving the amino nitrogen atoms of the pyrrolidine rings are less favourable. From these results it can be concluded that isolated molecules of **2a** form intramolecular H bonds of type **III**, and this should be the structure of **2a** in the gas phase or in diluted solution that would have a somewhat stabilized 2-tetrazene unit because of these favourable H bonds. On the other hand, in the pure form and in concentrated solution (as in the ^{15}N-NMR measurements, see above) the molecules of **2a** should be associated by H bonds between the hydroxy groups and to a lesser extent between hydroxy groups and amino atoms of the pyrrolidine rings which would be unfavourable with regard to stability.

X-ray Structure Analysis of 1a and 1b

The crystalline compounds **1a** and **1b** were analysed by X-ray crystallography. Structure diagrams of **1a** and **1b** are depicted in Figures 5 and 7, respectively; the packing of the molecules in the crystals is shown in Figures 6 and 8. Selected structure parameters are given in Table 2.

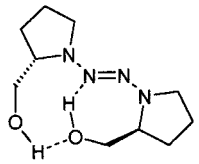
Figure 4. Intramolecular hydrogen bonds in hydroxyalkyl-2-tetrazene **2a** (AM1 and PM3 results)



III **IV**

ΔH_f(PM3): -153.8 -132.5 kJ mol^{-1}

ΔH_f(AM1): -109.2 -90.5 kJ mol^{-1}



V

ΔH_f(PM3): -148.0 kJ mol^{-1}

ΔH_f(AM1): -88.6 kJ mol^{-1}

Both compounds crystallize in triclinic, centrosymetric space groups with four and two formula units for **1a** and **1b** in the unit cell, respectively. In **1a** molecule I is disordered at the C(1), C(2) atoms, the O(1) atom has the same position for both groups, the disordered atoms C(1′) and C(2′) have lower occupancies (0.4). In contrast to I, molecules II and III are not disordered. They occupy a centre of symmetry and are crystallographically centrosymmetric. The different conformations of the three molecules are expressed by their respective different O−C−C−N torsional angles (Table 2), as also depicted in Figure 5 (a−c). The hydrogen bond pattern of the molecules in **1a** is responsible for the differences of the conformations as shown in Figure 6: the centrosymmetric molecules II and III [C2*x*, N2*x*, C3*x*, N3*x*, *x* = numbers according to the schemes given in Figure 5 (b and c)] are interconnected via OH···O hydrogen bonds in chains, and each of these are surrounded by four non-centrosymmetric molecules I (C*x*, N*x*), situated above the planes of molecules II and III. Thus, additional hydrogen bonds exist in the (001) direction along the 2_1-axes and produce a three-dimensional hydrogen bond network.

In **1b** two cystallographically centrosymmetric molecules were found (Figure 7), the non-equivalence of the molecules is demonstrated by the difference in the O−C−C−N torsion angles (O1−C2−C1−N1 −74.9° and O2−C13−C12−N3 −62.8°), which are similar to molecule II in **1a**, the interplanar angles of the nitrogen frameworks to the phenyl rings are 16.4° (C6−C11) and 15.0° (C17−C22) which is also similar to the geometry of molecule II in **1a** (see below). A trimethylsilyl group of one molecule points towards a phenyl group of a neighbour

Figure 5. Molecular structures of different molecules of crystalline 2-tetrazene **1a** (50% ellipsoid presentation): (a) molecule I, (b) molecule II, (c) molecule III

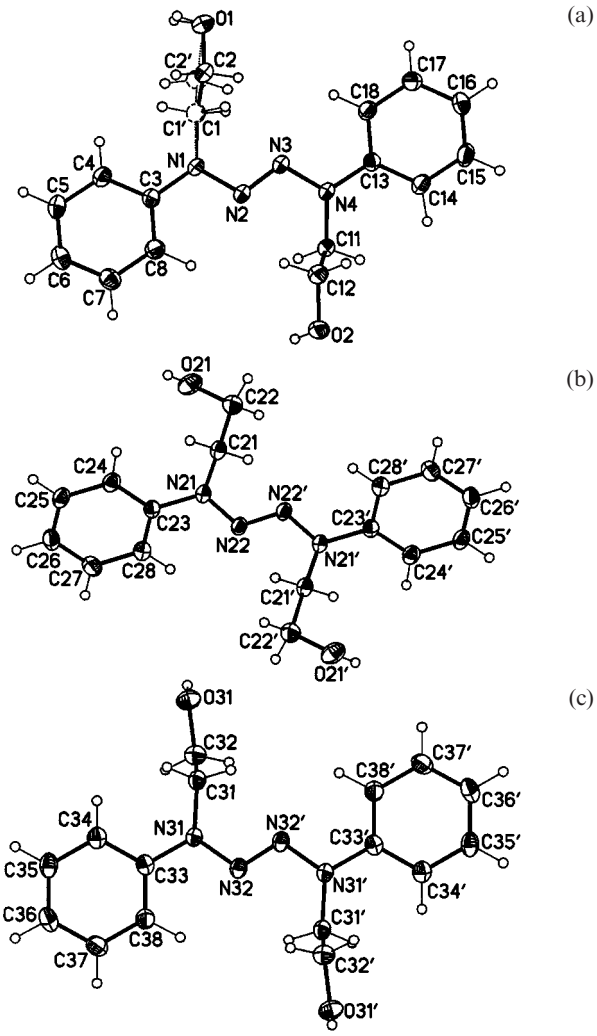
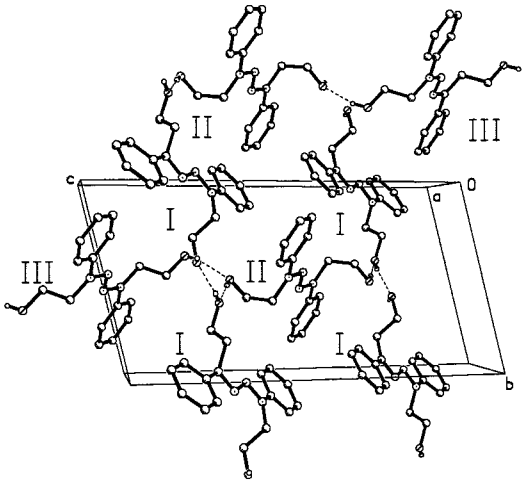


Figure 6. Packing diagram of **1a**, hydrogen atoms which are not involved in hydrogen bonding are omitted



molecule and vice versa, the arrangement is shown in Figure 8.

Table 2. Selected structure parameters of compounds **1a** and **1b** from X-ray analyses

1a[a]		**1b**	
Bond lengths			
N(1)−N(2)	1.364(1)	N(1)−N(2)	1.376(5)
		N(3)−N(4)	1.376(5)
N(2)−N(3)	1.254(3)	N(2)−N(2′)	1.266(6)
		N(4)−N(4′)	1.260(6)
N(1)−C(1)	1.459(9)	N(1)−C(1)	1.465(5)
		N(3)−C(9)	1.445(4)
N(1)−C(3)	1.411(2)	N(1)−C(3)	1.401(4)
		N(3)−C(11)	1.407(4)
Bond angles			
N(1)−N(2)−N(3)	112.6(1)	N(1)−N(2)−N(2′)	113.5(3)
		N(3)−N(4)−N(4′)	112.7(3)
N(2)−N(1)−C(1)	119.8(9)	N(2)−N(1)−C(1)	119.0(3)
		N(4)−N(3)−C(9)	121.1(3)
N(2)−N(1)−C(3)	115.1(1)	N(2)−N(1)−C(3)	116.5(3)
		N(4)−N(3)−C(11)	115.2(3)
C(1)−N(1)−C(3)	123.7(4)	C(1)−N(1)−C(3)	124.3(3)
		C(9)−N(3)−C(11)	123.7(3)
Torsional angles			
N(1)−N(2)−N(3)−N(4)	179.1(2)	N(1)−N(2)−N(2′) −N(1′)	180.0(0)
C(1)−N(1)−N(2)−N(3)	−25.0(3)	C(1)−N(1)−N(2)−N(2′)	7.3(6)
C(11)−N(4)−N(3)−N(2)	4.3(2)	N(3)−N(4)−N(4′)−N(3′)	180.0(0)
C(21)−N(21)−N(22)−N(22′)	−4.6(3)	C(12)−N(3)−N(4)−N(4′)	5.2(6)
C(31)−N(31)−N(32)−N(32′)	−4.5(3)	C(17)−N(3)−N(4)−N(4′)	176.2(4)
C(3)−N(1)−N(2)−N(32′)	172.5(2)	C(6)−N(1)−N(2)−N(2′)	174.7(4)
C(13)−N(4)−N(3)−N(2)	−166.9(2)		
C(23)−N(21)−N(22)−N(22′)	−179.6(1)		
C(33)−N(31)−N(32)−N(32′)	175.2(2)		
O(1)−C(2)−C(1)−N(1)	−178.5(2)		
O(2)−C(12)−C(11)−N(4)	−178.8(1)		
O(21)−C(22)−C(21)−N(21)	67.6(2)		
O(31)−C(32)−C(31)−N(31)	169.4(1)		

[a] Data except torsion angles were averaged for equivalent bonds, the numbering is referred to one half of molecule I. Data for C(1′) and C(2′) were not included because of higher uncertainties.

Figure 7. Molecular structure of 2-tetrazene **1b** showing two independent molecules in a parallel arrangement

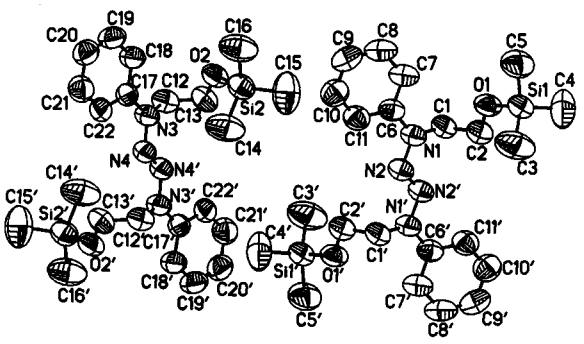
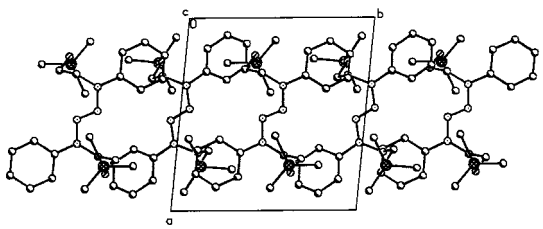


Figure 8. Packing diagram of **1b**, presentation without hydrogen atoms



Compared to the unsubstituted parent compound, N_4H_4,[27] there are clear structural changes: The bond distance of the azo nitrogen atoms increases from 1.205 Å in N_4H_4 to 1.254 Å in **1a** and 1.263 Å in **1b**. On the other hand, the bond length of the formal N−N single bond decreases from 1.429 Å (N_4H_4) to 1.364 Å (**1a**) and 1.376 Å (**1b**). The structures of two 1,4-diaryl-1,4-di-*tert*-butyl-2-tetrazenes which have been analysed by Nelsen et al.[28] show similar geometric parameters as **1a** and **1b**. In tetraisopropyltetrazenium hexachloroantimonate, which was analysed by Bock et al.,[9] the different NN bonds are nearly equally long (1.281 and 1.306 Å). The close resemblance with the data calculated for TMT (Table 1) is obvious. The amino nitrogen atoms of **1a** and **1b** have planar configurations as is indicated by the sum of the bond angles at these atoms for which values between 359 and 360° are found. The four nitrogen atoms of the 2-tetrazene units and its directly bonded C atoms show an essentially coplanar arrangement; torsional angle deviate by less than 25° from 0 or 180°. The phenyl rings are slightly rotated against the N_4 plane (**1a**: 17.2 and 19.4° molecule I, 6.8° molecule II and 11.3° molecule III; **1b**: 16.4 and 15.0°).

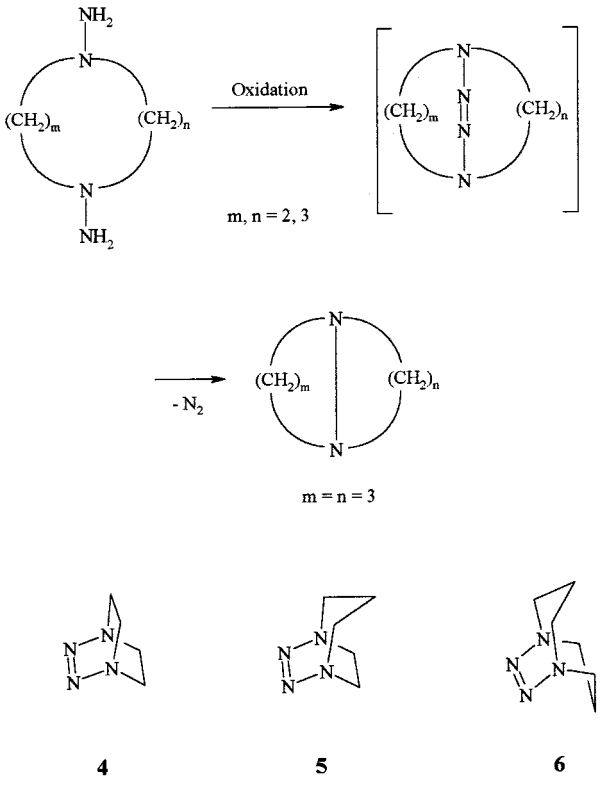
Structure and Stability of Hydroxylalkyl-2-Tetrazenes

The 2-tetrazene unit contains a preformed dinitrogen molecule, and the ease to liberate it depends on the molecular structure of the tetrazene. In a linear arrangement of the four nitrogen atoms, the bonding properties of π_2 and the

antibonding properties of π_3 nearly counterbalance each other forcing the molecule to decompose readily. Bending of the N_4-chain will increase the energy separation and the bonding or antibonding character of π_2 and π_3, respectively, and the 2-tetrazene becomes more stable. This relationship between N−N=N bond angle, properties of π_2 and π_3, and thermal stability was found for TMT and cyclic 1,4-dimethyl-2-tetrazenes of which only three ring systems (five- to seven-membered rings) are known.[6][7] These results certainly allow the general conclusion that for the thermal stability of 2-tetrazenes the energy separation of π_2 and π_3 is essential.

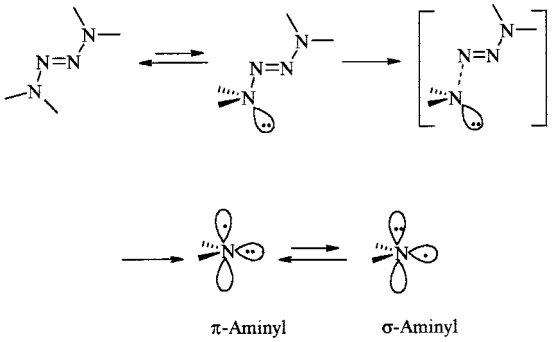
Although, in principle, the 2-tetrazene unit can be incorporated in a bicyclic molecule, attempts to synthesize such compounds as **4**−**6** (Scheme 3) by oxidation of the corresponding monocyclic dihydrazines in highly diluted solution failed.[29] However, at least one of these compounds (**6**) was probably generated as an unstable intermediate, because its decomposition product, 1,4-diazabicyclo[3.3.0]octane, was identified in the reaction mixture. These bicyclic 2-tetrazenes are model systems for the transition state of thermolysis of 2-tetrazenes (see below). They are unstable because conjugation of the electron lone-pairs on the bridge-head nitrogen atoms with the azo group is switched off. The decomposition of 2-tetrazenes is obviously related to that of azo compounds,[30][31][32][33][34] and a concerted fragmentation as well as a two-step-mechanism has to be considered.[35][36][37]

Scheme 3. Unstable bicyclic 2-tetrazenes



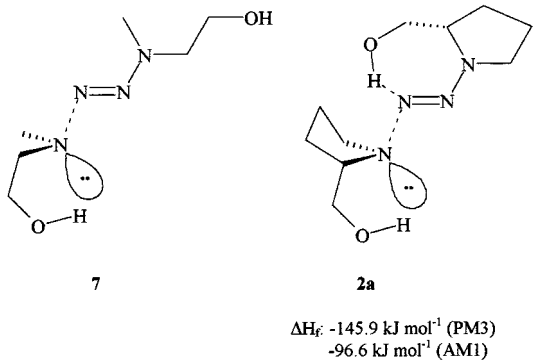
In the decomposition of acyclic 2-tetrazenes conformational effects are important.[17] In order to generate the aminyl radical in the more stable π electron configuration, rotation about the N−N single bond is necessary, and the structure of the transition state will probably have a similar conformation (Scheme 4).

Scheme 4. Decomposition path of a 2-tetrazene



This model is consistent with the observation that decomposition is more rapid in polar than in unpolar solvents.[37][38] In hydroxy-substituted 2-tetrazenes it is quite obvious that generally the twisted conformation with a non-conjugated electron lone-pair on N^1 or N^4 can be better stabilized than the untwisted conformation by intra- and/or intermolecular hydrogen bonds. Because of this, most hydroxy-substituted 2-tetrazenes should be less stable towards thermal decomposition although they might be thermodynamically more stable than similar 2-tetrazenes without such substituents. This is visualized in Scheme 5 for 1,4-bis(2-hydroxyethyl)-1,4-dimethyl-2-tetrazene (**7**) and **2a**. In this twisted conformation **2a** is less stable than in its ground state **III** (Figure 4) by about 7.9 (PM3) or 12.6 (AM1) kJ mol^{-1}. Intramolecular hydrogen bonding in the transition state of **2a** is probably less effective than in **7** which until now could not be synthesized, even not with trimethylsilyl-protected hydroxy groups. In compound **1a**, the phenyl groups lower the basicity of the amino nitrogen atoms and hydrogen bonding will accordingly be less effective also in the twisted conformation making the molecule more resistant against decomposition. The highly ordered transition states should be confirmed by negative activation entropies for thermolysis which remain to be measured.

Scheme 5. Transition states for N−N cleavage of hydroxyalkyl-2-tetrazenes **2a** and **8**



ΔH_f: -145.9 kJ mol^{-1} (PM3)
-96.6 kJ mol^{-1} (AM1)

Conclusion

Our present results lead to the conclusion that certain hydroxyalkyl-substituted 2-tetrazenes can be prepared by standard procedures.[2][3][4] The tetrazene unit in these compounds is affected by hydrogen bonding induced by the hydroxy groups. This can lead to stabilization or destabilization of the ground state of the molecules as well as of their transition states for thermolysis by inter- and/or intramolecular H bonds. However, in general stabilization of the transition state by these effects will be more effective because it is more polar than the ground state. This is consistent with the observation that most hydroxyalkyl-substituted 2-tetrazenes seem to be rather unstable towards thermolysis. Hydrogen bonding induces only minor structural changes of the 2-tetrazene unit, but has a pronounced effect on the energy of the characteristic molecular orbitals.

Hydroxy-substituted 2-tetrazenes are obviously well suited to study in detail some important aspects of hydrogen bonding. In particular, stabilization and destabilization of molecules by H bonds, which is reflected in energy changes of bonding and antibonding molecular orbitals, is vital in supramolecular chemistry, for example in enzymatic and pharmacologic processes like substrate and drug activation, and needs more detailed explanation.[22][23]

We thank Mrs. *Kerstin Spieker*, Mrs. *Sonja Engelmann* and Mr. *Uwe Albersmeyer* for synthetic work. This work was supported by the *Fonds der Chemischen Industrie*, Frankfurt am Main

Experimental Section

General: Melting points (uncorrected) were determined with a Büchi 510 apparatus. − The ^{1}H-, ^{13}C- and ^{15}N-NMR spectra were recorded on a Varian XL-200 or a Bruker AMX 300 spectrometer. The following frequencies were used: 200 or 300 MHz (^{1}H), 50.3 or 75.5 MHz (^{13}C), and 30.4 MHz (^{15}N). The spectra were measured as solutions in a 5 mm (^{15}N: 10 mm) tube at room temp. with the solvents $CDCl_3$ or [D_6]DMSO. The chemical shifts are reported in units of parts per million (δ) relative to tetramethylsilane (^{1}H, ^{13}C) or nitromethane (^{15}N) as internal standard. Coupling constants *J* are given in Hz. − Infrared (IR) spectra were recorded on a Perkin Elmer 1600 instrument. Only the most significant absorptions are given. − Electron impact mass spectra (MS) were obtained with a Hewlett Packard HP 5971A MSD instrument (70 eV). The intensities are reported as a percentage relative to the base peak after the corresponding *m/z* value. − Elemental analyses were performed with a Carlo Erba 1106 instrument. − Optical activity (specific rotation $[\alpha]_D^{20}$) was determined with a Polartronik Universal instrument of Schmid & Haensch. − Semiempirical PM3[39] and AM1[40] calculations were performed with the MOPAC[41] program package (version 6.1, IBM version of MOPAC 6.00), ab initio HF[42] and Becke3LYP[43] calculations with the program GAUSSIAN 94.[44] Geometries were fully optimized at the respective levels of theory.

X-ray Structure Analysis of **1a** *and* **1b**: The accurate structure determinations of **1a** and **1b** were carried out with a Nicolet R3m/V- and a Siemens P4 diffractometer, respectively. Both computer controlled instruments used graphite monochromated Mo-K_α radiation. The structures were solved by direct methods and all atoms except hydrogen atoms were refined anisotropically. Scattering factors were corrected for anomalous dispersion by Cromer and Lieberman.[45] The refinements based on F^2 were performed by the full-matrix least-squares method on a SGI IRIS Indigo workstation with the crystallographic software SHELXTL-Plus.[46] Selected data of the structure analyses of **1a** and **1b** are summarized in Table 3. Further details of the crystal structure investigations have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101082. These include lists of atomic coordinates, selected bond lengths and angles and equivalent isotropic displacement parameters. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: int. code + 44(1223)336−033; e-mail: deposit@ccdc.cam.ac.uk).

Table 3. Summary of the crystallographic data for compounds **1a** and **1b**

	1a	**1b**
Formula	$C_{16}H_{20}N_4O_2$	$C_{22}H_{36}N_4O_2Si_2$
M_r	300.36	444.73
Color	yellow	yellow
Crystal shape	prisms	prisms
Crystal size (mm)	0.38 × 0.31 × 0.24	0.31 × 0.27 × 0.23
Crystal system	triclinic	triclinic
Space group	*P*1(No 2)	*P*1(No 2)
a (A)	7.212(1)	11.191(2)
b (A)	10.609(2)	11.739(2)
c (A)	20.481(4)	11.860(2)
α (°)	103.45(2)	63.306(11)
β (°)	97.28(2)	78.301(13)
γ (°)	90.29(2)	89.96(2)
V (A^3)	1510.7(5)	1355.8(4)
Z	4	2
ρ_{calcd} (g cm^{-3})	1.321	1.089
T (K)	123(1)	298(2)
λ (A)	0.71073	0.71073
μ (mm^{-1})	0.090	0.153
F(000)	640	480
2θ range (°)	4< 2θ < 50	3.92 < 2θ < 60.00
Colld. reflections	5479	3634
Indep. reflections	5315	3419
Obsvd. reflections	4290	2304
Parameters refined	366[a]	272
Goodness-of-fit on F^2	1.308	0.925
*R*1/*wR*2 [*I*>2σ(*I*)]	0.0470/0.1237	0.0563/0.1518
*R*1/*wR*2 (all data) ◦	0.0611/0.1748	0.0931/0.2089
Resid. el. density (e A^{-3})	0.397/−0.307	0.214/−0.238

[a] The phenyl groups were calculated as ridid, the hydrogen atoms as riding groups, carbon atoms C(1) and C(2) were given a SOF = 0.6 and the complementary vlues for C(1′) and C(2′), together with the fixed hydrogen atoms.

The starting materials for the synthesis of compounds **1a**, **1b** and **2a**, **2b**, 1-(hydroxyethyl)-1-phenyl-hydrazine[47] and (*S*)-(−)-1-amino-2-(hydroxymethyl)pyrrolidine,[19] were prepared according to literature procedures.

1-(Trimethylsiloxyethyl)-1-phenylhydrazine: 1-(Hydroxyethyl)-1-phenylhydrazine (17.22 g, 0.11 mol) and triethylamine (55.5 ml, 0.40 mol) were dissolved in absolute THF (100 ml). Trimethylsilyl chloride (14.21 g, 0.13 mol) was added dropwise keeping the temp. below 30°C. Stirring continued at room temp. for 6 h. The precipitate (triethylammonium chloride) was filtered off and washed with THF. The solvent was removed in vacuo below 30°C. The residue was distilled in high vacuum through a Vigreux column. Yield 20.48 g (83%), b.p. 97−99°C/0.03 hPa. − ^{1}H NMR ($CDCl_3$): δ = 0.12 [s, 9 H, $Si(CH_3)_3$], 3.59 (t, *J* = 6 Hz, 2 H, N−CH_2), 3.80 (b, 2 H, NH_2), 3.90 (t, *J* = 6 Hz, 2 H, O−CH_2), 6.78 (t, *J* = 8 Hz, 1 H, C^4H), 6.99 (d, *J* = 8 Hz, 2 H, C^2H), 7.26 (t, *J* = 7 Hz, 2 H, C^3H). − ^{13}C NMR ($CDCl_3$): δ = −0.6 ($Si(CH_3)_3$), 57.6 (N−CH_2), 60.1 (O−CH_2), 112.1 (C^3), 117.9 (C^4), 129.0 (C^2), 151.8 (C^1). − IR

(liquid film): $\tilde{\nu}$ = 3342 (NH_2), 3090, 3062, 2955, 2901, 1597 cm^{-1}. − $C_{11}H_{20}N_2OSi$ (224.38): calcd. C 58.88, H 8.98, N 12.48; found C 59.13, H 8.67, N 12.51.

1,4-Bis(trimethylsiloxyethyl)-1,4-diphenyl-2-tetrazene (**1b**): To a solution of 1-(trimethylsiloxyethyl)-1-phenylhydrazine (4.70 g, 21 mmol) in diethyl ether (40 ml) yellow mercury(II) oxide (6.50 g, 30 mmol) was added with stirring in portions within 45 min. Stirring continued for 30 min. The solids were filtered off and washed with diethyl ether. The filtrate was dried with sodium sulfate and then the solvent was distilled off in vacuo. The residue solidified on cooling. Recrystallizatzion from absolute ethanol afforded yellowish needles. Yield 2.20 g (47%), m.p. 53°C. − ^{1}H NMR ($CDCl_3$): δ = 0.13 [s, 18 H, $Si(CH_3)_3$], 3.92 (t, *J* = 8 Hz, 4 H, N−CH_2), 4.26 (t, *J* = 8 Hz, 4 H, O−CH_2), 6.98 (m, 2 H, C^4H), 7.34 (m, 8 H, C^2H, C^3H). − ^{13}C NMR ($CDCl_3$): δ = −0.6 [$Si(CH_3)_3$], 48.6 (N−CH_2), 58.0 (O−CH_2), 114.6 (C^3), 120.6 (C^4), 129.0 (C^2), 145.9 (C^1). − IR (liquid film): ν = 3036, 2956, 2872, 1595, 1364 cm^{-1}. − $C_{22}H_{36}N_4O_2Si_2$ (444.72): calcd. C 59.42, H 8.16, N 12.60; found C 59.52, H 8.33, N 12.53.

1,4-Bis(hydroxyethyl)-1,4-diphenyl-2-tetrazene (**1a**): A mixture of **1b** (2.11 g, 4.8 mmol) and methanol (25 ml, 0.62 mol) was dissolved in diethyl ether (5 ml) and cooled in an ice bath to 0°C. Potassium carbonate (a spatula-tipfull) was added and the mixture was stirred for 1 h at 0°C. The solid was filtered off and half of the solvent of the filtrate was distilled off in vacuo. Cooling affords yellow needles which were washed with cold methanol and dried in vacuo. Yield 1.28 g (90%), m.p. 133−134°C (decomp.). − ^{1}H NMR ($CDCl_3$): δ = 3.66 (t, *J* = 7 Hz, 4 H, N−CH_2), 4.13 (t, *J* = 7 Hz, 4 H, O−CH_2), 4.55 (b, 2 H, OH), 6. 89 (m, 2 H, C^4H), 7.31 (m, 8 H, C^2H, C^3H). − ^{13}C NMR ($CDCl_3$): δ = 48.2 (N−CH_2), 56.4 (O−CH_2), 114.2 (C^3), 120.2 (C^4), 129.0 (C^2), 145.6 (C^1). − IR (liquid film): ν = 3275 (OH), 3050, 2955, 1594, 1357 cm^{-1}. − MS (70 eV, EI); *m/z* (%): 300 (9) [M^+], 272 (6) [$M^+ - N_2$], 241 (5) [$M^+ - N_2 - CH_3O$], 137 (11) [$C_6H_5NHC_2H_4OH^+$], 106 (100) [$C_6H_5NHCH_2^+$], 77 (24) [$C_6H_5^+$], 51 (6) [$C_4H_3^+$], 28 (8) [N_2^+]. − $C_{16}H_{20}N_4O_2$ (300.36): calcd. C 63.98, H 6.71, N 18.65; found C 63.87, H 7.00, N 18.56.

(S)-1-Amino-2-(trimethylsiloxymethyl)pyrrolidine: THF (50 ml), triethylamine (51 ml, 0.37 mol) and (*S*)-(−)-1-amino-2-(hydroxymethyl)pyrrolidine[19] (10.17 g, 87.6 mmol) were placed in a 250 ml three-necked flask. To this solution trimethylsilyl chloride (13.3 ml) was added dropwise in 30 min keeping the temp. below 30°C. After stirring for 7.5 h the colourless precipitate was filtered off and washed with THF. The filtrate was distilled. Yield 11.58 g (70%), b.p. 76−79°C/1.3 Pa. − ^{1}H NMR ($CDCl_3$): δ = 0.12 [s, 9 H, $Si(CH_3)_3$], 1.4−2.1 (m, 4 H, C^3H_2, C^4H_2), 2.25−2.45 (m, 2 H, C^5H_2), 3.0−3.2 (s, 2 H, NH_2), 3.2−3.35 (m, 1 H, C^2H), 3.4−3.8 (m, 2 H, O−CH_2). − ^{13}C NMR ($CDCl_3$): δ = 0.51 ($Si(CH_3)_3$), 21.40 (C^4), 26.85 (C^3), 60.82 (C^5), 66.41 (C^2), 70.76 (O−CH_2).

(S,S)-1,2-Bis[2-(trimethylsiloxymethyl)pyrrolidino]diazene (**2b**): To a solution of (*S*)-1-amino-2-(trimethylsiloxymethyl)pyrrolidine (3.06 g, 16.3 mmol) in absolute diethyl ether (40 ml) yellow mercury(II) oxide (5.28 g, 24.4 mmol) was added with stirring in 3 h. Then ether (30 ml) was added and stirring at 20°C continues for 9 h. The solids were filtered off and washed with ether. The filtrate was dried with sodium sulfate and then distilled. Yield 1.64 g (54%), b.p. 135°C/0.5 Pa. − ^{1}H NMR ($CDCl_3$): δ = 0.11 [m, 9 H, $Si(CH_3)_3$], 1.7−2.1 (m, 4 H, C^3H_2, C^4H_2), 3.0−3.2 (m, 1 H, C^2H), 3.4−3.9 (m, 4 H, C^5H_2, O−CH_2). − ^{13}C NMR ($CDCl_3$): δ = −0.41 [$Si(CH_3)_3$], 22.12 (C^4), 27.10 (C^3), 50.23 (C^5), 63.03 (C^2), 64.91 (O−CH_2). − MS (70 eV; EI): *m/z* (%): 372 (70) [M^+], 269 (41) [$M^+ - CH_2OSi(CH_3)_3$], 172 (18), 156 (86), 103 (100), [$(CH_3)_3SiOCH_2^+$], 73 (93) [$(CH_3)_3Si^+$].

(S,S)-1,2-Bis[2-(hydroxymethyl)pyrrolidino]diazene (**2a**): (a) From **2b**: **2b** (0.50 g, 1.34 mmol) was treated with methanol (10 ml) and potassium carbonate (3 mg) at 0°C for 45 min. The volatile components were removed in vacuo and *tert*-butyl methyl ether (3 ml) was added to the residue. The mixture was filtered and the solvent removed in vacuo, yield 0.14 g (46%). The colourless oil decomposes at 140°C in vacuo.

(b) From (*S*)-1-amino-2-(hydroxymethyl)pyrrolidine: To (*S*)-1-amino-2-(hydroxymethyl)pyrrolidine (10.2 g, 88 mmol) red mercury(II) oxide (28.0 g, 0.13 mol) was added with stirring in portions. The elemental mercury was filtered off, the filtrate dried with potassium carbonate, and the solvent distilled off in vacuo, yield 6.7 g (67%). By ^{1}H-NMR spectroscopy a purity of the sample of 94% was determined. − $[\alpha]_D^{20}$ = 340 (*c* = 0.4704 and 0.7978 g per 100 ml in $CHCl_3$). − ^{1}H NMR ($CDCl_3$): δ = 1.5−2.1 (m, 8 H, C^3H_2, C^4H_2), 3.0−3.3 (m, 2 H, C^2H), 3.4−3.9 (m, 10 H, C^5H_2, NH_2, OH). − ^{13}C NMR ($CDCl_3$): δ = 22.16 (C^4), 26.32 (C^3), 50.13 (C^5), 63.59 (C^2), 65.77 (O−CH_2). − IR (liquid film): ν = 3350 (ν_{CH}), 2950, 2870, 1440, 1330, 1040 cm^{-1}. − MS (70 eV, EI): *m/z* (%): 228 (70) [M^+], 197 (26) [$M^+ - CH_2OH$], 169 (23) [$M^+ - CH_2OH - H_2O$], 100 (11) [$C_5H_{10}NO^+$], 82 (30) [$C_5H_8N^+$], 70 (100) [$C_4H_8N^+$], 57 (22), 41 (43), 31 (44), 28 (27) [N_2^+]. − $C_{10}H_{20}N_4O_2$ (228.3): calcd. C 52.61, H 8.83, N 24.54; found C 52.74, H 8.70, N 23.03.

Syntheses of *(S,S)-1,2-bis[2-(methoxymethyl)pyrrolidino]diazene* (**2c**) and *1,2-pyrrolidinodiazene* (**3**) were described previously.[8]

Cyclic dihydrazines, used as starting materials in the attempted syntheses of bicyclic 2-tetrazenes **3**−**6**, were prepared from the corresponding diazacycloalkanes following standard procedures.[48][49]

1,4-Diaminopiperazine: M.p. 115°C (ref.[50] 117−119°C). − ^{1}H NMR ($CDCl_3$): δ = 2.61 (s, 8 H, N−CH_2−C), 2.99 (s, 4 H, NH_2, disappears on treatment with D_2O). − ^{13}C NMR ($CDCl_3$): δ = 58.86 (N−CH_2). − MS (70 eV, EI); *m/z* (%): 116 [M^+], 100 [$M^+ - NH_2$], 83.

1,4-Diaminohexahydro-1,4-diazepine: B.p. 70−75°C/0.13 Pa. − ^{1}H NMR ($CDCl_3$): δ = 1.61 (q, 2 H, C−CH_2−C), 2.68 (t, 4 H, N−CH_2−C), 2.72 (s, 4 H, N−CH_2), 3.07 (bs, 4 H, N−CH_2). − ^{13}C NMR ($CDCl_3$): δ = 23.96 (C−CH_2−C), 59.13 (N−CH_2−C), 60.28 (N−CH_2).

1,5-Diaminooctahydro-1,5-diazocine: B.p. 86°C/2.7 Pa. − ^{1}H NMR ($CDCl_3$): δ = 1.72 (q, 4 H, C−CH_2−C), 2.78 (t, 8 H, N−CH_2−C), 3.20 (s, 4 H, N−CH_2). − ^{13}C NMR ($CDCl_3$): δ = 25.3 (C−CH_2−C), 59.2 (N−CH_2). − IR (liquid film): ν = 3300, 3140 (ν_{NH}), 2930, 2830 (ν_{CH}), 1600, 1555, 1455, 1430, 1360, 1110, 940, 840, 815 cm^{-1}. − $C_6H_{18}N_4Cl_2$ (dihydrochloride) (217.1): calcd. C 33.19, H 8.36, N 25.80; found C 33.98, H 8.64, N 25.47.

Oxidation of the dihydrazines was carried out with different reagents.[29] $K_3Fe(CN)_6$ in aqueous 2 N KOH (0.17 mol l^{-1}) at −2°C, HgO (red) in CH_2Cl_2 (34 mmol l^{-1}) at −10, −5, 20, and 40°C, $Pb(OAc)_4$ in CH_2Cl_2 at −30°C. Nitrogen-rich polymeric products were obtained which might indicate intermolecular 2-tetrazene formation.

1,5-Diazabicyclo[3.3.0]octane was identified as a product in low yield (< 1%) in the oxidation of 1,5-diaminooctahydro-1,5-diazocine; the product was identical with a sample synthesized independently.[51] B.p. 37−40°C/1066 Pa (ref.[51] 74−75°C/3466 Pa). − MS (70 eV, EI); *m/z*: 114 [M^+], 97, 85, 70, 57, 43.

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