

# Hydrogen Bonding of 2-Tetrazenes, 2 [1]. Synthesis and Structural Studies of Hydroxyalkyl-Substituted 2-Tetrazenes\*

Bernd Porath<sup>a</sup>, Paul Rademacher<sup>a</sup>, Roland Boese<sup>b</sup>, and Dieter Bläser<sup>b</sup>

<sup>a</sup> Institut für Organische Chemie, Universität Essen,  
Universitätsstrasse 5-7, D-45117 Essen, Germany

<sup>b</sup> Institut für Anorganische Chemie, Universität Essen,  
Universitätsstrasse 5, D-45117 Essen, Germany

Reprint requests to Prof. Dr. Paul Rademacher. Fax: +49-(0)201-183-4252.

E-mail: paul.rademacher@uni-essen.de

Z. Naturforsch. **57 b**, 365–376 (2002); received January 30, 2002

Hydroxyalkyl-2-tetrazenes, Hydrogen Bonding, Conformational Analysis

Five hydroxyethyl-2-tetrazenes (**1** - **5**) and their methyl ethers (**6** - **10**) have been synthesized and hydrogen bonding in these compounds has been investigated by theoretical and spectroscopic (IR, <sup>1</sup>H NMR, <sup>15</sup>N NMR) methods. The structure of 1,1,4,4-tetrakis(2-hydroxyethyl)-2-tetrazene (**4**) was determined by X-ray diffraction analysis. Several conformations with intramolecular hydrogen bonds were investigated by ab initio B3LYP as well as semiempirical SCF calculations. In all cases, conformers with OH...N hydrogen bonds with azo nitrogen atoms as acceptors (conformers **A**, **B**, **C**) are found as most stable. In compounds with small or flexible N<sup>1</sup>- and N<sup>4</sup>-substituents R besides the hydroxyethyl group (**3**, **4**), hydrogen bonds forming six-membered rings, with the R groups taking syn positions at the N<sup>1</sup>-N<sup>2</sup> and N<sup>3</sup>-N<sup>4</sup> bonds (conformer **A**), are preferred over those with seven-membered rings and R taking anti positions (conformer **B**). Steric interaction in the other compounds (**1**, **2**, **5**) leads to destabilization of conformers **A** and conformers **B** become more stable. A special case is presented by compound **4** which has only hydroxyethyl substituents on the 2-tetrazene unit. In the most stable conformer (**4C**) there are two OH...O and one OH...N hydrogen bonds. By IR solution measurements intra- and intermolecular hydrogen bonds could be distinguished. Association shifts  $\Delta\delta$  measured by <sup>1</sup>H NMR spectroscopy, indicate that the investigated compounds exhibit comparable association properties with intermolecular association clearly prevailing. <sup>15</sup>N NMR spectra of compounds **1** - **10** in two solvents have been measured if solubility was sufficient. The data indicate that all nitrogen atoms of **1** - **5** participate in H bonding. In the crystalline state, molecules **4** adopt a conformation without intramolecular H bonds (**4D**) and are associated by intermolecular OH...O hydrogen bonds that form a three-dimensional network. An untypical decomposition pattern was discovered for benzyl derivatives **5** and **10**.

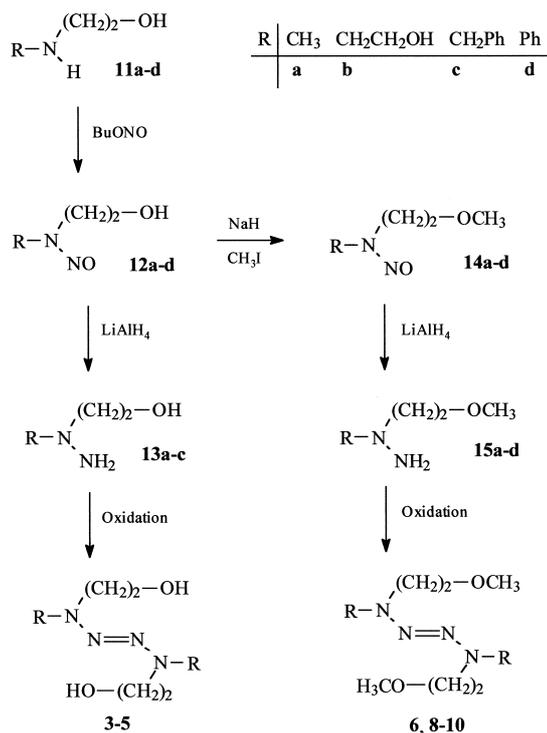
## Introduction

2-Tetrazenes [2 - 5] are composed of a four nitrogen chain with a central double bond. They are iso-electronic with the butadiene-dianion, which means that in the planar structure there are three occupied  $\pi$  MOs, of which the highest (HOMO) is antibonding. Therefore, their thermodynamic stability is closely related to the shape and the energy of the  $\pi$  MOs [1, 6 - 11]. 2-Tetrazenes were described for the first

time in 1878 by E. Fischer [12] and have since then received considerable attention as sources of aminyl radicals and products derived thereof [13, 14]. The most important method to prepare 2-tetrazenes is oxidative coupling of 1,1-disubstituted hydrazines [3 - 5]. The parent compound, N<sub>4</sub>H<sub>4</sub>, was generated in 1975 from 1,1,4,4-tetrakis(trimethylsilyl)-2-tetrazene [15].

Recently, we have synthesized two members of previously unknown hydroxyalkyl-2-tetrazenes (**1**, **2**) and investigated hydrogen bonding [16] of these novel difunctional compounds by spectroscopic (IR, <sup>1</sup>H NMR, <sup>15</sup>N NMR) and theoretical methods [1]. The structures of **2** and its bis(tri-

\* Presented in part at the 5th Conference on Iminium Salts (ImSaT-5), Stimpfach-Rechenberg (Germany), September 11 - 13, 2001.

Scheme 1. Synthesis of 2-tetrazenes **3 - 6, 8 - 10**.

methylsilyl) ether were determined by X-ray analysis. It was shown that OH---N hydrogen bonds of 2-tetrazenes are medium strong. From  $\delta(^{15}\text{N})$  data and quantum chemical calculations it was concluded 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 H bonds is about  $3 \text{ kJ mol}^{-1}$ . This is in accordance with a higher gas-phase basicity of the former nitrogen atoms [17].

We have now synthesized three additional hydroxyalkyl-2-tetrazenes (**3 - 5**) and investigated hydrogen bonding in these compounds. Some additional studies have been performed on compounds **1** and **2**. As reference systems without H bonding the corresponding methyl ethers (**6 - 10**) were included in the study. Structures **1 - 10** are summarized in Table 1.

## Results and Discussion

### Syntheses

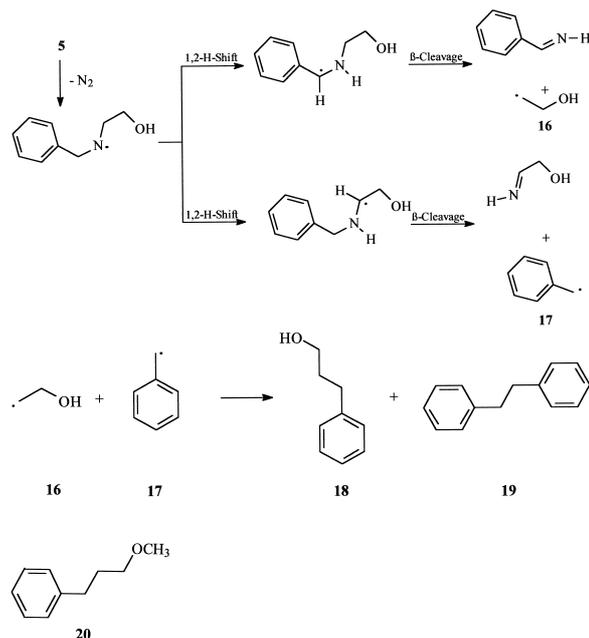
Compounds **1** [1], **2** [1], and **7** [9] were prepared as described previously. Compounds **3 - 6**,

Table 1. Constitution of compounds **1 - 10**.

	X =	OH	OCH <sub>3</sub>
		<b>1</b>	<b>6</b>
		<b>2</b>	<b>7</b>
		<b>3</b>	<b>8</b>
		<b>4</b>	<b>9</b>
		<b>5</b>	<b>10</b>

**8 - 10** were synthesized by oxidation of the corresponding 1,1-disubstituted hydrazines. The latter compounds were obtained by N-nitrosation of the corresponding secondary amines **11** followed by reduction according to literature methods [3-5]. The procedure is outlined for compounds **3 - 6, 8 - 10** in Scheme 1.

The two benzyl derivatives **5** and **10** were found to be so unstable that only small amounts could be isolated. The decomposition products indicate a way of fragmentation uncharacteristic for 2-tetrazenes, with benzyl (**17**) and hydroxyethyl (**16**) or methoxyethyl radicals as reactive intermediates (Scheme 2). Thus, bibenzyl (**19**) and 3-phenylpropanol (**18**) or 3-methoxypropylbenzene (**20**), respectively, were detected as by-products together with several other compounds. To our knowledge, such a decomposition pattern of a 2-tetrazene has not been observed previously.

Scheme 2. Decomposition of 2-tetrazene **5**.

### Quantum chemical computations

In the previous communication [1] we have shown that all N atoms of a 2-tetrazene can act as an acceptor of hydrogen bonds with the amino nitrogen atoms being preferred over the azo nitrogen atoms. For compounds **1 - 5**, various structures with intramolecular hydrogen bonds are possible. We have studied these conformations with the aid of B3LYP calculations with special consideration of intramolecular OH---N and OH---O hydrogen bonds. This hybrid density functional method is well suited for studying hydrogen bonds although

Table 2. Absolute energies  $E$  [au] and relative energies  $\Delta E$  [kJ mol<sup>-1</sup>] of conformers **A - D** of 2-tetrazenes **1 - 5** (B3LYP/6-31+G\*\* results).

2-Tetra- zene	— Conformer —			
	<b>A</b>	<b>B</b>	<b>C</b>	<b>D</b>
<b>1</b>	-991.156902	-991.167500	-991.164956	-991.162300
$\Delta E$	27.82	0.00	6.68	13.65
<b>2</b>	-762.523346	-762.527020	-762.524264	-762.519650
$\Delta E$	9.64	0.00	7.23	19.34
<b>3</b>	-607.672539	-607.668549	-607.667958	-607.663746
$\Delta E$	0.00	10.47	12.03	23.08
<b>4</b>	-836.737928	-836.733899	-836.741772	-836.736499
$\Delta E$	10.09	20.67	0.00	13.84
<b>5</b>	-1069.794301	-1069.794640	-1069.792329	-1069.790015
$\Delta E$	0.89	0.00	6.07	12.14

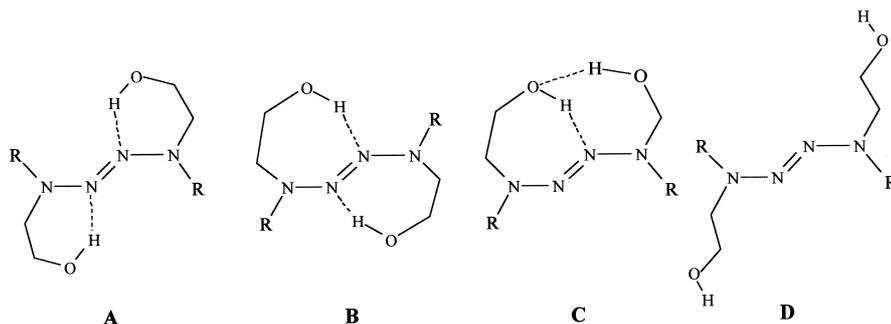
Table 3. Structure parameters of O-H---N hydrogen bonds in conformers **A - C** of 2-tetrazenes **1 - 5**.

Con- former	O-H [pm]	OH---N [pm]	N---O [pm]	O-H---N [°]
<b>1A</b>	97.1	216.8	277.7	135.2
<b>1B</b>	96.9	220.9	287.4	141.7
<b>1C</b>	96.8	287.5	309.2	93.7
<b>2A</b>	97.2	210.3	291.0	139.4
<b>2B</b>	97.5	196.0	287.2	154.5
<b>2C</b>	97.6	196.0	280.4	143.3
<b>3A</b>	97.0	210.9	270.5	134.1
<b>3B</b>	97.4	196.5	286.7	153.0
<b>3C</b>	97.6	192.8	277.5	143.7
<b>4A</b>	97.4	194.3	277.2	141.4
<b>4B</b>	97.2	208.7	291.9	142.6
<b>4C</b>	97.8	188.4	275.8	147.2
<b>5A</b>	96.9	217.4	293.0	133.9
<b>5B</b>	97.2	201.2	288.9	149.1
<b>5C</b>	98.0	180.8	272.4	154.1

weak van der Waals interactions are not adequately taken into account [18].

For all compounds four conformations (**A - D**, Scheme 3) were considered. In **A** the intramolecular OH---N hydrogen bonds form six-membered rings, while in **B** they exhibit seven-membered rings. In conformation **C** there is an intramolecular OH---O hydrogen bond and in **D** there are no hydrogen bonds. The geometry of the respective conformers was optimized; the absolute and relative energies are summarized in Table 2. We refrain from presenting excessive data, but will discuss the results mainly with respect to intramolecular hydrogen bonding. Structure parameters of the O-H---N hydrogen bonds in conformers **A - C** are presented in Table 3. As an example, these conformers are depicted for compound **4** as ball and stick diagrams in Fig. 1. Some additional structure parameters are reported for **4** together with experimental results (see below).

For all compounds, conformers with intramolecular OH---N hydrogen bonds were found as most stable, and these conformers are about 10 - 20 kJ mol<sup>-1</sup> more stable than those without H bonds (**D**). In compounds with small or flexible substituents **R** (**3**, **4**), the hydrogen bonds forming six-membered rings (**A**) are preferred over those with seven-membered rings (**B**), whereas in the other compounds (**1**, **2**, **5**) the former conformation is sterically destabilized so that **B** becomes most stable. Steric destabilization in **A** may become so large that



Scheme 3. Conformations **A** - **D** of compounds **1** - **10**.

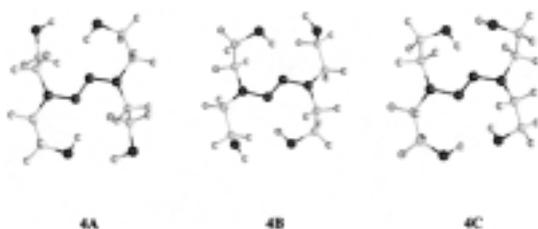


Fig. 1. Conformers **A** - **C** of compound **4**.

conformation **C** or even **D** may be more stable. The main reason for this destabilization is that in **A** both substituents **R** are in syn positions of the N-N bonds of the 2-tetrazene unit, whereas in **B** they are in anti positions. In conformer **C** this holds only for one substituent **R**. Compound **4** with four hydroxyethyl substituents on the 2-tetrazene unit clearly presents a special case with conformer **C** being most stable (see below).

Conformer **1A** differs in the orientation of the phenyl groups relative to the 2-tetrazene unit from the other conformers. While in **1B** - **1D** the phenyl groups take nearly coplanar positions, in **1A** they are approximately perpendicular to this group so that  $\pi$ -conjugation is removed. In conformer **1C** the OH...N interaction is rather weak as indicated by the unfavourable O-H...N angle and the large N...O distance (Table 3). This is compensated by the OH...O interaction with a relatively short OH...O distance (201.9 pm) and a wide O-H...O angle (156.2°). Since there are four hydroxyethyl groups in compound **4**, additional conformations are possible with intramolecular OH...O hydrogen bonds. **4A** has a symmetric tetracyclic structure with two OH...N and two OH...O hydrogen bonds. The most stable conformer (**4C**) is unsymmetrical with a tricyclic structure. While two hydroxyethyl groups form an O-H...N and an O-H...O hydrogen bond

as indicated in Scheme 3, the other two are only linked by an O-H...O hydrogen bond (Fig. 1). In the latter grouping, the OH...O distance has a value of 210.7 pm and the O-H...O angle is 160.9°. In compound **5**, the two types of conformations with intramolecular OH...N hydrogen bonds forming six- or seven-membered rings, respectively, are of similar strength. In **5B** the OH...N distance (201.2 pm) is shorter than in **5A** (217.4 pm), and the O-H...N angle is larger in **5B** (149.1°) than in **5A** (133.9°). In all structures, the phenyl groups are approximately perpendicular to the plane of the N<sub>4</sub> chain. In this orientation repulsive interactions between the hydroxyethyl groups and the phenyl rings are avoided. Finally, a short comment is given for the OH...O bond in conformation **C** of **1** - **5**. The OH...O distance varies between 202 and 215 pm and the O...O distance between 294 and 307 pm which corresponds to an O-H...O angle of 147 to 162°.

For the methyl ethers **6** - **10**, structures similar to those of the corresponding 2-tetrazene alcohols without intramolecular hydrogen bonds (**1D** - **5D**) were calculated as the most stable conformers.

#### Spectroscopic investigations

It has been shown by spectroscopic measurements (IR, <sup>1</sup>H, <sup>15</sup>N NMR) that hydroxyalkyl-2-tetrazenes form intra- and intermolecular hydrogen bonds [1]. In their IR spectra (liquid film or in KBr), compounds **1** - **5** exhibit strong and broad absorption bands at 3300 - 3500 cm<sup>-1</sup> that are characteristic for hydroxy groups intermolecularly associated by hydrogen bonds. Compounds **2**, **3** and **5** are sufficiently soluble in chloroform so that IR spectra at different concentrations up to high dilution (50.0 - 0.1%) could be measured. With increasing dilution, the intensity of the afore-mentioned band de-

Table 4.  $^1\text{H}$  chemical shifts  $\delta$  [ppm] of hydroxy groups and association shifts  $\Delta\delta$  [ppm] of 2-tetrazenes **1**, **3** - **5** in  $[\text{D}_6]\text{DMSO}$  and  $\text{CDCl}_3$ .

Compound	$[\text{D}_6]\text{DMSO}$ (1 M)	$\text{CDCl}_3$ (0.02 M)	$\Delta\delta$
<b>1</b>	4.9	1.8	3.1
<b>3</b>	4.6	2.0	2.6
<b>4</b>	4.5	1.6	2.9
<b>5</b>	4.7	2.1	2.6

Table 5.  $^{15}\text{N}$  chemical shifts  $\delta$  [ppm] of amino and azo nitrogen atoms of 2-tetrazenes **1** - **5** and their methyl ethers **6** - **10** and  $\Delta\delta(^{15}\text{N})$  values in  $[\text{D}_6]\text{DMSO}$  and  $\text{CDCl}_3$ .

2-Tetrazene	$\text{CDCl}_3$ (1 M)		$[\text{D}_6]\text{DMSO}$ (1 M)	
	$\delta(\text{amino-N})$	$\delta(\text{azo-N})$	$\delta(\text{amino-N})$	$\delta(\text{azo-N})$
<b>1</b>	*	*	-230.5	-8.3
<b>6</b>	-231.9	-8.4	*	*
<b>2</b>	-230.7	11.5	-235.2	13.1
<b>7</b>	-234.3	16.3	-236.0	13.6
$\Delta\delta(2 - 7)$	3.6	-4.8	0.8	-0.5
<b>3</b>	-256.1	13.4	-256.8	14.1
<b>8</b>	-257.1	15.1	-257.2	13.9
$\Delta\delta(3 - 8)$	1.1	-1.7	0.4	0.2
<b>4</b>	*	*	-252.7	6.9
<b>9</b>	-252.4	7.5	-252.8	6.7
$\Delta\delta(4 - 9)$			0.1	0.2
<b>5</b>	-246.3	7.0	-247.1	7.8
<b>10</b>	-247.4	8.4	-247.7	7.6
$\Delta\delta(5 - 10)$	1.1	-1.4	0.6	0.2

\* Not determined because of too low solubility.

creases and its position is shifted by about  $75\text{ cm}^{-1}$  to higher frequencies. Simultaneously, sharp bands at  $3630$  and  $3155\text{ cm}^{-1}$  appear corresponding to O-H vibrations of free and intramolecularly associated hydroxy groups, respectively.

By  $^1\text{H}$  NMR spectroscopy inter- and intramolecular hydrogen bonds can be distinguished [19 - 21]. While chemical shifts of hydrogen atoms in intermolecular hydrogen bonds are characterized by strong variations with concentration, the corresponding shifts for intramolecular hydrogen bonds are only small. We have measured  $^1\text{H}$  NMR spectra of compounds **1**, **3** - **5** in  $[\text{D}_6]\text{DMSO}$  (1 M) and in  $\text{CDCl}_3$  (0.02 M) and have determined association shifts  $\Delta\delta$  (Table 4). The data indicate that the investigated compounds exhibit comparable association properties with intermolecular association clearly prevailing.

Important indications about the nitrogen atoms to act as acceptors in hydrogen bonds can be ob-

tained from  $^{15}\text{N}$  chemical shifts  $\delta(^{15}\text{N})$  of the hydroxyalkyl-2-tetrazenes compared with their methyl ethers [1]. We have measured the  $\Delta\delta(^{15}\text{N})$  values of compounds **1** - **10** in  $[\text{D}_6]\text{DMSO}$  and  $\text{CDCl}_3$  solutions (Table 5). For compounds **1** and **4** solubility in  $\text{CDCl}_3$  is insufficient for  $^{15}\text{N}$  NMR spectroscopic measurements, and the same holds for compound **6** and  $[\text{D}_6]\text{DMSO}$ . In  $[\text{D}_6]\text{DMSO}$ , the  $\Delta\delta(^{15}\text{N})$  values are always smaller than in  $\text{CDCl}_3$  indicating that in the former solvent associations of the hydroxy groups with solvent molecules are prevailing. The larger  $\Delta\delta(^{15}\text{N})$  values measured for  $\text{CDCl}_3$  solutions can thus be attributed to OH---N hydrogen bonds. In order to estimate the significance of these values, the data are compared with protonation shifts [1, 22 - 25]. While tertiary amines show positive protonation shifts of about 10 - 20 ppm, those of imines are negative and numerically much larger ( $\Delta\delta \approx -100$  ppm). As an example, Schiff bases with strong intramolecular phenolic OH---N hydrogen bonds are mentioned for which  $\Delta\delta(^{15}\text{N})$  values of about -20 to -30 ppm have been measured [26].

Since the  $\Delta\delta(^{15}\text{N})$  values observed for  $\text{CDCl}_3$  solutions (Table 5) are rather small, in particular for compounds **3/8** and **5/10**, no detailed interpretation regarding the strength of the different OH---N hydrogen bonds seems to be possible. However, the fact that numerically smaller values are found for  $[\text{D}_6]\text{DMSO}$  than  $\text{CDCl}_3$  solutions, is in accordance with mainly OH---O association in the former solvent. Only for compounds **2/7** the  $\Delta\delta(^{15}\text{N})$  values measured in  $\text{CDCl}_3$  are significantly larger than in  $[\text{D}_6]\text{DMSO}$  which is an indication of stronger participation of both amino and azo nitrogen atoms in hydrogen bonding in compound **2** [1]. The different behaviour of this chiral compound can certainly be explained with a more rigid structure favouring OH---H interactions.

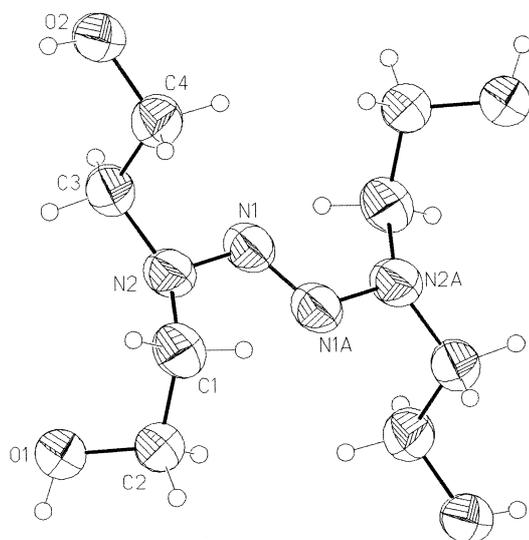
#### X-ray structure analysis of **4**

Compound **4** was analysed by X-ray crystallography. The crystallographic data and the results are given in Table 6. A structure diagram with the atom numbering scheme is depicted in Fig. 2. The packing of the molecules is shown in Fig. 3. The compound crystallizes in the monoclinic space group  $P2_1/n$  with two formula units in the unit cell.

Selected structure parameters from the X-ray structure analysis are summarized in Table 7 to-

Table 6. Crystallographic data of 2-tetrazene **4**.

Formula	C <sub>8</sub> H <sub>20</sub> N <sub>4</sub> O <sub>4</sub>
<i>M<sub>r</sub></i>	236.28
Colour	pale yellow
Crystal description	block
Crystal size [mm]	0.52, 0.47, 0.43
Crystal system	monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> [Å]	5.1915(13)
<i>b</i> [Å]	6.834(2)
<i>c</i> [Å]	16.745(3)
β	92.264(11)
<i>V</i> [Å <sup>3</sup> ]	593.6(2)
<i>Z</i>	2
ρ <sub>calcd.</sub> [g cm <sup>-3</sup> ]	1.3222
λ [Å]	0.71073
<i>T</i> [K]	293(2)
μ [mm <sup>-1</sup> ]	0.105
<i>F</i> (000)	256
2θ Range [°]	4.86 < 2θ < 60.00
Collected reflections	3065
Independent reflections	1732
Obsvd. reflections	1343
Parameters refined	74
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.040
<i>R</i> 1/ <i>wR</i> 2 [ <i>I</i> > 2σ( <i>I</i> )]	0.0585 / 0.1650
<i>R</i> 1/ <i>wR</i> 2 (all data)	0.0707 / 0.1767
Resid. el. density [e Å <sup>-3</sup> ]	0.206/−0.195

Fig. 2. Molecular structure of 2-tetrazene **4** with atom numbering.

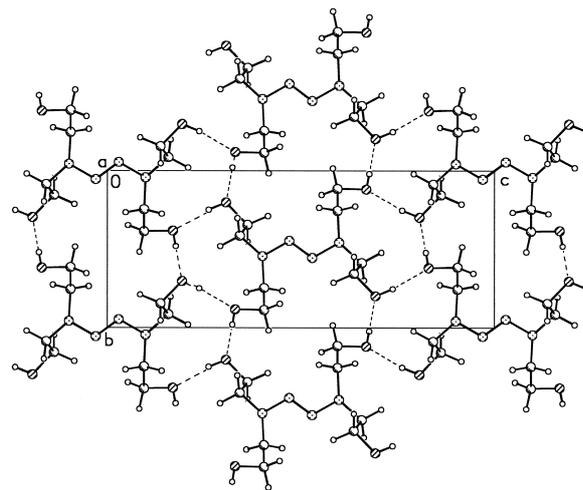
gether with the results of B3LYP and PM3 calculations obtained for conformation **4D**.

The structure parameters determined for the 2-tetrazene unit are in good agreement with those

Table 7. Selected structure parameters of 2-tetrazene **4** from X-ray crystal structure analysis (XRA) and quantum chemical calculations (B3LYP, PM3).

	XRA	B3LYP <sup>a</sup>	PM3 <sup>a</sup>
Bonds lengths (pm)			
N(1)-N(1A)	124.7(2)	125.5	123.4
N(1)-N(2)	136.6(2)	137.9	140.6
N(2)-C(1)	145.1(2)	147.1	150.4
N(2)-C(3)	143.9(2)	146.8	150.3
C(1)-C(2)	149.8(2)	152.8	153.6
C(3)-C(4)	150.0(2)	152.9	153.4
O(1)-C(2)	140.2(2)	142.3	140.9
O(2)-C(4)	141.1(2)	142.9	140.2
Bond angles (°)			
N(1A)-N(1)-N(2)	113.90(2)	114.5	116.9
N(1)-N(2)-C(1)	119.01(12)	119.0	118.8
N(1)-N(2)-C(3)	111.07(11)	110.8	110.6
C(1)-N(2)-C(3)	120.14(12)	118.3	112.5
Torsional angles (°)			
N(2A)-N(1A)-N(1)-N(2)	180.00(2)	180.0	180.0
N(1A)-N(1)-N(2)-C(1)	14.14(0.20)	18.8	39.6
N(1A)-N(1)-N(2)-C(3)	160.12(0.14)	161.2	171.9

<sup>a</sup> Conformer **4D**.

Fig. 3. Packing of molecules **4** in the crystal.

found previously for compound **1** [1]. The data in Table 6 indicate that the molecular structure of compound **4**, as calculated for the conformation without intramolecular hydrogen bonds (**4D**), is reproduced fairly well by both quantum chemical methods. However, deviations from the observed parameters are considerably smaller for the *ab initio* (B3LYP) than the semi-empirical method (PM3). While for the former method bond lengths are uniformly too

large by 0.8 - 3.0 pm, for the latter method deviations between -1.3 and +6.4 pm are found. Both theoretical methods confirm the slightly pyramidal configuration of the amino nitrogen atoms. The sum of the bond angles at these atoms was calculated as 348.1° (B3LYP) and 341.9° (PM3) and observed as 350.2° (XRA). For the torsional angles, the PM3 results too deviate more than the B3LYP values which are in excellent agreement with the experimental ones.

In the crystalline state, molecules **4** are associated by OH...O hydrogen bonds. It is obvious from energetic reasons that no intramolecular OH...N bonds are present. The molecules form a three-dimensional network. The 2-tetrazene units are ordered centrosymmetrically parallel above each other, and all hydroxy groups act as hydrogen donors as well as acceptors in the hydrogen bonds. In this way, a ladder-like motive is built with the N<sub>4</sub> chains as steps. These strands are connected at both sides with two other strands which are inverted and displaced by a half step width. Thus, each 2-tetrazene molecule is associated with six other molecules by hydrogen bonds.

## Conclusions

2-Tetrazenes with hydroxyalkyl groups are well suited to study in detail some important aspects of hydrogen bonding. In the liquid and solid state, the pure compounds are associated by intermolecular OH...O hydrogen bonds, while isolated molecules form intramolecular OH...N hydrogen bonds. In the latter, mainly for steric reasons the azo nitrogen atoms are preferred as acceptors over the amino nitrogen atoms.

## Experimental Section

### General methods

Melting points (uncorrected) were determined with an Electrothermal 9100 apparatus. The <sup>1</sup>H, <sup>13</sup>C and <sup>15</sup>N NMR spectra were recorded on a Bruker Avance DRX 500 spectrometer. The following frequencies were used: 500.13 MHz (<sup>1</sup>H), 125.76 MHz (<sup>13</sup>C), and 50.6 MHz (<sup>15</sup>N). The spectra were measured as solutions in a 5 mm tube at 20 °C with the solvents CDCl<sub>3</sub> or [D<sub>6</sub>]DMSO. The chemical shifts are reported in units of parts per million (δ) relative to tetramethylsilane (<sup>1</sup>H, <sup>13</sup>C) or nitromethane (<sup>15</sup>N) as internal standard. Coupling constants *J* are given in Hz. Infrared (IR) spectra were recorded on

a BIORAD FTIR spectrometer FTS 135. Only the most significant absorptions are given. Electron impact mass spectra (MS) were obtained with a Fisons VG Prospec instrument (70 eV). The intensities are reported as a percentage relative to the base peak after the corresponding *m/z* value. GC/MS analyses were carried out making use of a gas chromatograph HP 5890 Series II of Hewlett-Packard that was connected with a quadrupole mass spectrometer HP 5971A MSD. Elemental analyses were performed with a Carlo Erba EA 1110 CHNS-O instrument.

Semi-empirical PM3 [27] calculations were performed with the MOPAC 93 [28] program package, Becke3LYP [29] HF/DFT calculations with the program GAUSSIAN 98 [30]. In the latter method the basis set 6-31+G(d,p) was used. Geometries were fully optimized at the respective levels of theory.

The X-ray structure determination of compound **4** was carried out with a Siemens P4 diffractometer. The computer controlled instrument used graphite monochromated Mo-K<sub>α</sub> radiation. The structure was solved by direct methods and all atoms except hydrogen atoms were refined anisotropically. Scattering factors were corrected for anomalous dispersion by Cromer and Lieberman [31]. The refinements based on *F*<sup>2</sup> were performed by the full-matrix least-squares method with the crystallographic software SHELXL-97 [32]. Hydrogen atoms were treated with a riding model on idealized geometries with the 1.2 fold isotropic displacement parameters of the equivalent *U*<sub>ij</sub> of the corresponding carbon atom. Hydroxy hydrogen atom positions were taken from a Fourier-map and also refined as riding groups. Further details of the crystal structure investigations have been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publication no. CCDC-177474. 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 The Director, CCDC, 12 Union Road, Cambridge CB25Z, UK (Fax: Int. code + 44(1223) 336-033; e-mail: deposit@ccdc.cam.ac.uk).

### (2-Hydroxyethyl)methylnitrosamine (**12a**)

Butyl nitrite (43.3 g, 0.450 mol) was added dropwise to a solution of 2-methylamino-ethanol (**11a**) (30.0 g, 0.400 mol) in absolute THF (250 ml) at a temperature of 0 °C. Stirring continued at 20 °C for 2 d. The solvent and butanol were removed *in vacuo* in an evaporator at a bath temperature below 40 °C. The yellow crude material was distilled in high vacuum. Yield 37.7 g (91%); b. p. 105 °C / 0.04 hPa. The compound forms a syn / anti mixture (≈ 3:1). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 3.07 (s, 3 H, CH<sub>3</sub>), 3.3 - 3.6 (br, 1 H, OH), 3.7 - 3.8 (m, 4 H, NCH<sub>2</sub>,

OCH<sub>2</sub>), 3.83 (s, 3 H, CH<sub>3</sub>), 3.91 (t, <sup>3</sup>J = 6 Hz, 2 H, NCH<sub>2</sub>), 4.17 (t, <sup>3</sup>J = 6 Hz, 2 H, OCH<sub>2</sub>). – <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>): δ = 32.6 (CH<sub>3</sub>), 40.5 (CH<sub>3</sub>), 47.9 (NCH<sub>2</sub>), 56.0 (NCH<sub>2</sub>), 58.3 (OCH<sub>2</sub>), 60.0 (OCH<sub>2</sub>). – IR (liquid film): ν = 3385 (s, O-H), 2941 (s, C-H), 2878 (s, C-H), 1437 (m, N=O), 1387 (m), 1332 cm<sup>-1</sup> (s, δ (O-H)).

#### 1-(2-Hydroxyethyl)-1-methylhydrazine (13a)

Under argon, LiAlH<sub>4</sub> (11.4 g, 0.300 mol) is suspended in absolute THF (200 ml) at reflux temperature. At 50–55 °C, a solution of nitrosamine **12a** (26.0 g, 0.250 mol) in absolute THF (80 ml) is added slowly. The mixture is refluxed for 2.5 h. Excess LiAlH<sub>4</sub> is hydrolysed with a solution of sodium hydroxide (4.8 g) in water (20 ml). The hydroxide precipitate is filtered off and extracted with THF (100 ml). The combined filtrates are dried over sodium sulfate. The solvent is removed in an evaporator below 30 °C (bath temperature). The crude material is distilled through a 20 cm Vigreux column in high vacuum. Yield 12.1 g (54%); b. p. 45–46 °C/0.03 hPa. – <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 2.51 (s, 3 H, CH<sub>3</sub>), 2.56 (t, <sup>3</sup>J = 5 Hz, 2 H, NCH<sub>2</sub>), 3.77 (t, <sup>3</sup>J = 5 Hz, 2 H, OCH<sub>2</sub>), 3.0–3.5 (br, 3 H, OH, NH<sub>2</sub>). – <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>): δ = 51.4 (CH<sub>3</sub>), 61.5 (NCH<sub>2</sub>), 62.2 (OCH<sub>2</sub>). – IR (liquid film): δ = 3312 (s, O-H, NH<sub>2</sub>), 2945 (s, C-H), 2838 (s, C-H), 2788 (m, C-H), 1610 (m, δ (NH<sub>2</sub>)), 1458 cm<sup>-1</sup> (m).

#### 1,4-Bis(2-hydroxyethyl)-1,4-dimethyl-2-tetrazene (3)

Under argon, hydrazine **13a** (3.15 g, 35.0 mmol) is dissolved in absolute diethyl ether (40 ml). With stirring, yellow mercury(II) oxide (8.67 g, 40.0 mmol) is added in several portions at 20 °C. Stirring is continued for 1 h. Mercury and mercury oxide are filtered off and the filtrate is dried over sodium sulfate. The solvent is removed in an evaporator *in vacuo*. The crude material is purified by chromatography on neutral aluminium oxide with a mixture of CH<sub>2</sub>Cl<sub>2</sub>-CH<sub>3</sub>OH (50:1) as eluent. Yield 1.38 g (45%); colourless oil. – <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 2.57 (s, 6 H, CH<sub>3</sub>), 3.24 (t, <sup>3</sup>J = 5 Hz, 4 H, NCH<sub>2</sub>), 3.73 (t, <sup>3</sup>J = 5 Hz, 4 H, OCH<sub>2</sub>), 3.0–3.2 (br, 2 H, OH). – <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>): δ = 38.4 (CH<sub>3</sub>), 61.5 (NCH<sub>2</sub>), 62.2 (OCH<sub>2</sub>). – IR (liquid film): ν = 3368 (s, O-H), 2962 (s, C-H), 2879 (s, C-H), 1608 (w, N=N), 1466 (m), 1271 (s, δ (O-H)), 1040 cm<sup>-1</sup> (s, C-O). – MS (70 eV, EI): *m/z* = 176 (35) [M<sup>+</sup>], 149 (8) [M<sup>+</sup> - HCN], 145 (12) [M<sup>+</sup> - CH<sub>2</sub>OH], 102 (20) [M<sup>+</sup> - CH<sub>2</sub>OH - C<sub>2</sub>H<sub>5</sub>N], 116 (38) [M<sup>+</sup> - 2 (C<sub>2</sub>H<sub>4</sub>O)], 56 (26) [C<sub>3</sub>H<sub>6</sub>N<sup>+</sup>], 45 (25) [C<sub>2</sub>H<sub>5</sub>O<sup>+</sup>], 44 (100) [C<sub>2</sub>H<sub>6</sub>N<sup>+</sup>], 28 (22) [N<sub>2</sub><sup>+</sup>], 15 (21) [CH<sub>3</sub><sup>+</sup>]. – MS (high resolution): *m/z* = 176.1254 (calcd. 176.1273). – C<sub>6</sub>H<sub>16</sub>N<sub>4</sub>O<sub>2</sub> (176.22): calcd. C 40.90, H 9.15, N 31.79; found C 41.24, H 9.24, N 29.42.

#### Bis(2-hydroxyethyl)nitrosamine (12b)

By the procedure described for **12a**, diethanolamine (**11b**) (42.1 g, 0.400 mol) was reacted with butyl nitrite (51.6 g, 0.500 mol) in absolute THF (200 ml) at a temperature of 0 °C. Stirring continued at 20 °C for 5 h and then at 50 °C for 36 h. The solvent and butanol were removed *in vacuo* in an evaporator. Last traces of butanol were removed by stirring the crude material at 80 °C/0.1 hPa for 6 h. Yield 52.0 g (97%). – <sup>1</sup>H NMR (500 MHz, [D<sub>6</sub>]DMSO): δ = 3.45 (t, <sup>3</sup>J = 5 Hz, 2 H, NCH<sub>2</sub>), 3.6–3.8 (m, 4 H, NCH<sub>2</sub>, OCH<sub>2</sub>), 4.18 (t, <sup>3</sup>J = 5 Hz, 2 H, OCH<sub>2</sub>), 4.6–5.2 (br, 2H, OH). – <sup>13</sup>C NMR (126 MHz, [D<sub>6</sub>]DMSO): δ = 46.4 (NCH<sub>2</sub>), 54.9 (NCH<sub>2</sub>), 56.7 (OCH<sub>2</sub>), 58.7 (OCH<sub>2</sub>). – IR (liquid film): ν = 3381 (s, O-H), 2945 (s, C-H), 2878 (s, C-H), 1440 (w, N=O), 1386 (m), 1335 (s), 1120 cm<sup>-1</sup> (s, C-O).

#### 1,1-Bis(2-hydroxyethyl)hydrazine (13b)

By the procedure described for **13a**, nitrosamine **12b** (26.8 g, 0.200 mol) is reduced with LiAlH<sub>4</sub> (11.5 g, 0.300 mol) in absolute THF (250 ml). Yield 3.7 g (15%); b. p. 90 °C/7\*10<sup>-4</sup> hPa. – <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 2.62 (t, <sup>3</sup>J = 5 Hz, 4 H, NCH<sub>2</sub>), 3.64 (t, <sup>3</sup>J = 5 Hz, 4 H, OCH<sub>2</sub>), 3.8–5.0 (br, 4 H, OH, NH<sub>2</sub>). – <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>): δ = 59.9 (NCH<sub>2</sub>), 62.6 (OCH<sub>2</sub>). – IR (liquid film): ν = 3400 (m, O-H), 3343 (m, N-H), 2927 (s, C-H), 2879 (s, C-H), 2816 (s, C-H), 1608 (m, δ (NH<sub>2</sub>)), 1458 (m), 1118 cm<sup>-1</sup> (s, C-O).

#### 1,1,4,4-Tetrakis(2-hydroxyethyl)-2-tetrazene (4)

By the procedure described for **3**, hydrazine **13b** (4.33 g, 36.0 mmol) is oxidized with yellow mercury(II) oxide (10.83 g, 50.0 mmol) in THF (50 ml). The crude material is purified by chromatography on neutral aluminium oxide with a mixture of CH<sub>2</sub>Cl<sub>2</sub>-CH<sub>3</sub>OH (50:1) as eluent. Recrystallization from CH<sub>2</sub>Cl<sub>2</sub>-CH<sub>3</sub>OH (20:3) afforded colourless crystals. Yield 0.78 g (18%); m. p. 68–70 °C. – <sup>1</sup>H NMR (500 MHz, [D<sub>6</sub>]DMSO): δ = 3.23 (t, <sup>3</sup>J = 5 Hz, 8 H, NCH<sub>2</sub>), 3.47 (q, <sup>3</sup>J = 5 Hz, 8 H, OCH<sub>2</sub>), 4.53 (t, <sup>3</sup>J = 6 Hz, 4 H, OH). – <sup>13</sup>C NMR (126 MHz, [D<sub>6</sub>]DMSO): δ = 54.8 (NCH<sub>2</sub>), 58.9 (OCH<sub>2</sub>). – IR (KBr): ν = 3301 (s, O-H), 2925 (s, C-H), 2881 (s, C-H), 1455 (s), 1332 (s, δ (OH)), 1139 cm<sup>-1</sup> (s, C-O). – MS (70 eV, EI): *m/z* = 236 (48) [M<sup>+</sup>], 104 (7) [C<sub>4</sub>H<sub>10</sub>NO<sub>2</sub><sup>+</sup>], 74 (97) [C<sub>4</sub>H<sub>11</sub>NO<sub>2</sub><sup>+</sup> - CH<sub>3</sub>O], 56 (100) [C<sub>3</sub>H<sub>6</sub>N<sup>+</sup>], 45 (51) [C<sub>2</sub>H<sub>5</sub>O<sup>+</sup>], 30 (55) [CH<sub>2</sub>NH<sub>2</sub><sup>+</sup>], 28 (32) [N<sub>2</sub><sup>+</sup>]. – C<sub>8</sub>H<sub>20</sub>N<sub>4</sub>O<sub>4</sub> (236.27): calcd. C 40.67, H 8.53, N 23.71; found C 40.62, H 8.77, N 23.99.

#### Benzyl-(2-hydroxyethyl)nitrosamine (12c)

By the procedure described for **12a**, 2-(benzylamino)-ethanol (**11c**) (60.5 g, 0.400 mol) was reacted with butyl

nitrite (43.3 g, 0.450 mol) in chloroform (250 ml). Stirring continued at 20 °C for 5 h and then at 50 °C for 72 h. Yield 72.7 g (100%, crude material, used without further purification). The compound forms a syn/anti mixture ( $\approx 3:1$ ). –  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 2.72 (t,  $^3J$  = 5 Hz, 2 H,  $\text{NCH}_2$ ), 3.18 (br, 3 H,  $\text{NCH}_2$ , OH), 3.55 (t,  $^3J$  = 5 Hz, 2 H,  $\text{NCH}_2$ ), 3.62 (t,  $^3J$  = 5 Hz, 2 H,  $\text{OCH}_2$ ), 3.75 (s, 2 H,  $\text{NCH}_2$ ), 4.13 (t,  $^3J$  = 5 Hz, 2 H,  $\text{OCH}_2$ ), 7.0 - 7.5 (m, 5 H, ArH). –  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 46.0 ( $\text{NCH}_2$ ), 47.3 ( $\text{NCH}_2$ ), 53.7 ( $\text{NCH}_2$ ), 57.3 ( $\text{NCH}_2$ ), 59.0 ( $\text{OCH}_2$ ), 59.0 ( $\text{OCH}_2$ ), 127.8 ( $\text{C}_{\text{arH}}$ ), 128.1 ( $\text{C}_{\text{arH}}$ ), 128.2 ( $\text{C}_{\text{arH}}$ ), 128.5 ( $\text{C}_{\text{arH}}$ ), 128.8 ( $\text{C}_{\text{arH}}$ ), 128.9 ( $\text{C}_{\text{arH}}$ ), 134.8 ( $\text{C}_{\text{ar}}$ ), 135.0 ( $\text{C}_{\text{ar}}$ ). – IR (liquid film):  $\nu$  = 3401 (s, O-H), 3065 (m, Ar-H), 3032 (m, Ar-H), 2943 (m, C-H), 2884 (m, C-H), 1451 (s, N=O), 1341  $\text{cm}^{-1}$  (s,  $\delta$  (O-H)).

#### *1-Benzyl-1-(2-hydroxyethyl)hydrazine (13c)*

By the procedure described for **13a**, nitrosamine **12c** (36.0 g, 0.200 mol) is reduced with  $\text{LiAlH}_4$  (9.5 g, 0.250 mol) in THF (300 ml). Yield 26.8 g (81%, crude material, used without further purification). –  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 2.69 (t,  $^3J$  = 5 Hz, 2 H,  $\text{NCH}_2$ ), 2.8 - 3.1 (br, 3 H, NH, OH), 3.68 (s, 2 H,  $\text{NCH}_2$ ), 3.82 (t,  $^3J$  = 5 Hz, 2 H,  $\text{OCH}_2$ ), 7.2 - 7.4 (m, 5 H, ArH). –  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 59.6 ( $\text{NCH}_2$ ), 62.4 ( $\text{OCH}_2$ ), 68.1 ( $\text{NCH}_2$ ), 127.6 ( $\text{C}_{\text{arH}}$ ), 128.6 ( $\text{C}_{\text{arH}}$ ), 129.2 ( $\text{C}_{\text{arH}}$ ), 136.6 ( $\text{C}_{\text{ar}}$ ). – IR (liquid film):  $\nu$  = 3327 (s, O-H,  $\text{NH}_2$ ), 3062 (s, Ar-H), 3028 (s, Ar-H), 2940 (s, C-H), 2822 (s, C-H), 1602 (m,  $\delta$  ( $\text{NH}_2$ )), 1453 (s), 1048 (m, C-O).

#### *1,4-Dibenzyl-1,4-bis(2-hydroxyethyl)-2-tetrazene (5)*

Under argon, hydrazine **13c** (8.32 g, 50.0 mmol) is dissolved in absolute ethanol (200 ml) and cooled to  $-15^\circ\text{C}$ . A solution of 1,4-benzoquinone (6.50 g, 60.0 mmol) in absolute ethanol (200 ml) is added dropwise so that the temperature does not rise above  $-10^\circ\text{C}$ . Stirring is continued for 1 h at this temperature. The solvent is removed in an evaporator *in vacuo* below  $40^\circ\text{C}$  (bath temperature). The black residue is treated with chloroform (300 ml) and washed five times with sodium hydroxide solution (5%, 100 ml). The organic solution is dried with potassium carbonate. The solvent is removed *in vacuo* in an evaporator. The brown residue is purified by chromatography on neutral aluminium oxide with a mixture of  $\text{CH}_2\text{Cl}_2$ - $\text{CH}_3\text{OH}$  (50:1) as eluent. Recrystallization (four times) from petrol ether/ethyl acetate (3:2) afforded fine brownish needles. Yield 1.22 g (15%); m. p. 52 - 53 °C. –  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 2.3 - 2.5 (br, 2 H, OH), 3.33 (t,  $^3J$  = 5 Hz, 4 H,  $\text{NCH}_2$ ), 3.69 (t,  $^3J$  = 5 Hz, 4 H,  $\text{OCH}_2$ ), 4.45 (s, 4 H,  $\text{NCH}_2$ ), 7.1 - 7.4 (m, 10 H, ArH). –  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 54.5 ( $\text{NCH}_2$ ), 56.8 ( $\text{NCH}_2$ ), 61.0 ( $\text{OCH}_2$ ), 127.1 ( $\text{C}_{\text{arH}}$ ), 128.1 ( $\text{C}_{\text{arH}}$ ), 128.4 ( $\text{C}_{\text{arH}}$ ), 137.7

( $\text{C}_{\text{ar}}$ ). – IR (KBr):  $\nu$  = 3369 (s, O-H), 3086 (m, Ar-H), 3062 (m, Ar-H), 3029 (m, Ar-H), 2930 (s, C-H), 2885 (s, C-H), 1603 (s, C=C), 1495 (s), 1355 (s,  $\delta$  (O-H)), 1046 (s, C-O), 699 (s,  $\delta$  (Ar-H)<sub>o.o.p.</sub>), 734  $\text{cm}^{-1}$  (s,  $\delta$  (Ar-H)<sub>o.o.p.</sub>). – MS (70 eV, EI):  $m/z$  = 328 (68) [ $\text{M}^+$ ], 150 (60) [ $\text{C}_6\text{H}_5\text{CH}_2\text{NC}_2\text{H}_4\text{OH}^+$ ], 120 (42) [ $\text{C}_6\text{H}_5\text{CH}_2\text{NC}_2\text{H}_4\text{OH}^+$  -  $\text{CH}_3\text{O}$ ], 106 (28) [ $\text{C}_6\text{H}_5\text{CH}_2\text{NC}_2\text{H}_4\text{OH}^+$  -  $\text{C}_2\text{H}_5\text{O}$ ], 91 (100) [ $\text{C}_6\text{H}_5\text{CH}_2^+$ ], 77 (5) [ $\text{C}_6\text{H}_5^+$ ], 65 (20) [ $\text{C}_5\text{H}_5^+$ ], 45 (20) [ $\text{C}_2\text{H}_5\text{O}^+$ ], 28 (10) [ $\text{N}_2^+$ ]. –  $\text{C}_{18}\text{H}_{24}\text{N}_4\text{O}_2$  (328.41): calcd. C 65.83, H 7.37, N 17.06; found C 65.52, H 7.17, N 17.50.

#### *N-Nitroso-N-(2-hydroxyethyl)aniline (12d)*

By the procedure described for **12a**, *N*-(2-hydroxyethyl)aniline (**11d**) (54.8 g, 0.400 mol) is reacted with butyl nitrite (43.3 g, 0.450 mol) in diethyl ether (250 ml). Yield 65.1 g (98%, crude material, used without further purification). –  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 2.72 (br, 1 H, OH), 3.77 (t,  $^3J$  = 5 Hz, 2 H,  $\text{NCH}_2$ ), 4.17 (t,  $^3J$  = 5 Hz, 2 H,  $\text{OCH}_2$ ), 7.35 - 7.50 (m, 3 H, ArH), 7.55 - 7.70 (m, 2 H, ArH). –  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 47.9 ( $\text{OCH}_2$ ), 58.8 ( $\text{NCH}_2$ ), 120.4 ( $\text{C}_{\text{arH}}$ ), 127.7 ( $\text{C}_{\text{arH}}$ ), 129.5 ( $\text{C}_{\text{arH}}$ ), 142.0 ( $\text{C}_{\text{ar}}$ ). – IR (liquid film):  $\nu$  = 3422 (s, O-H), 3067 (m, Ar-H), 2945 (s, C-H), 2885 (s, C-H), 1596 (s, C=C), 1450 (s, N=O), 1076  $\text{cm}^{-1}$  (s, C-O).

#### *N-Nitroso-N-(2-methoxyethyl)aniline (14d)*

By the procedure described for **14a**, *N*-nitroso-*N*-(2-hydroxyethyl)aniline (**12d**) (41.5 g, 0.250 mol) is reacted with iodomethane (42.6 g, 0.300 mol) and sodium hydride (7.2 g, 0.300 mol) in absolute THF (400 ml). Yield 42.6 g (95%, crude material, used without further purification). –  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 3.28 (s, 3 H,  $\text{CH}_3$ ), 3.53 (t,  $^3J$  = 5 Hz, 2 H,  $\text{NCH}_2$ ), 4.17 (t,  $^3J$  = 5 Hz, 2 H,  $\text{OCH}_2$ ), 7.3 - 7.5 (m, 3 H, ArH), 7.6 - 7.7 (m, 2H, ArH). –  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 45.4 ( $\text{OCH}_2$ ), 58.8 ( $\text{CH}_3$ ), 68.3 ( $\text{NCH}_2$ ), 120.3 ( $\text{C}_{\text{arH}}$ ), 127.3 ( $\text{C}_{\text{arH}}$ ), 129.3 ( $\text{C}_{\text{arH}}$ ), 142.2 ( $\text{C}_{\text{ar}}$ ). – IR (liquid film):  $\nu$  = 3060 (m, Ar-H), 3019 (m, Ar-H), 2986 (s, C-H), 2894 (s, C-H), 2831 (s, C-H), 1592 (s, C=C), 1457 (s, N=O), 1380 (s), 1127  $\text{cm}^{-1}$  (s, C-O).

#### *1-(2-Methoxyethyl)-1-phenylhydrazine (15d)*

By the procedure described for **13a**, *N*-nitroso-*N*-(2-methoxyethyl)aniline (**14d**) (44.2 g, 0.245 mol) is reduced with  $\text{LiAlH}_4$  (9.5 g, 0.250 mol) in THF (300 ml). Yield 13.82 g (34%); b. p. 98 - 102 °C/ $6 \times 10^{-5}$  hPa. –  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 3.36 (s, 3 H,  $\text{CH}_3$ ), 3.61 (t,  $^3J$  = 5 Hz, 2 H,  $\text{NCH}_2$ ), 3.68 (t,  $^3J$  = 5 Hz, 2 H,  $\text{OCH}_2$ ), 3.7 - 3.9 (br, 2 H,  $\text{NH}_2$ ), 6.78 (t,  $^3J$  = 7 Hz, 1 H, ArH), 6.99 (d,  $^3J$  = 8 Hz, 2 H, ArH), 7.25 (t,  $^3J$  = 8 Hz, 2 H, ArH).

–  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 55.1 (OCH<sub>2</sub>), 58.9 (CH<sub>3</sub>), 70.5 (NCH<sub>2</sub>), 112.9 (C<sub>ar</sub>H), 117.9 (C<sub>ar</sub>H), 128.9 (C<sub>ar</sub>H), 151.3 (C<sub>ar</sub>). – IR (liquid film):  $\nu$  = 3340 (s, N-H), 3059 (m, Ar-H), 3021 (m, Ar-H), 2928 (s, C-H), 2880 (s, C-H), 2830 (s, C-H), 1597 (m,  $\delta$  (NH<sub>2</sub>)), 1497 (s, C=C), 1452 (m), 1117  $\text{cm}^{-1}$  (s, C-O).

#### 1,4-Bis(2-methoxyethyl)-1,4-diphenyl-2-tetrazene (6)

By the procedure described for **3**, 1-(2-methoxyethyl)-1-phenylhydrazine (**15d**) (4.99 g, 30.0 mmol) is oxidized with yellow mercury(II) oxide (8.66 g, 40.0 mmol) in diethyl ether (40 ml). The product is obtained as fine yellowish needles by recrystallization from diethyl ether. Yield 2.41 g (49%); m. p. 107 °C. –  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 3.39 (s, 6 H, CH<sub>3</sub>), 3.71 (t,  $^3J$  = 6 Hz, 4 H, OCH<sub>2</sub>), 4.26 (t,  $^3J$  = 6 Hz, 4 H, NCH<sub>2</sub>), 6.9 - 7.0 (m, 2 H, ArH), 7.2 - 7.4 (m, 8 H, ArH). –  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 46.6 (OCH<sub>2</sub>), 59.1 (CH<sub>3</sub>), 68.4 (NCH<sub>2</sub>), 114.7 (C<sub>ar</sub>H), 120.7 (C<sub>ar</sub>H), 129.1 (C<sub>ar</sub>H), 145.9 (C<sub>ar</sub>). – IR (KBr):  $\nu$  = 3057 (s, Ar-H), 3040 (m, Ar-H), 2978 (s, C-H), 2933 (s, C-H), 2898 (s, C-H), 1594 (s, C=C), 1491 (s), 1037  $\text{cm}^{-1}$  (s, C-O). – MS (70 eV, EI):  $m/z$  = 328 (23) [ $\text{M}^+$ ], 300 (3) [ $\text{M}^+ - \text{N}_2$ ], 255 (3) [ $\text{M}^+ - \text{N}_2 - \text{C}_2\text{H}_5\text{O}$ ], 151 (7) [ $\text{C}_6\text{H}_5\text{NHC}_2\text{H}_4\text{OCH}_3^+$ ], 150 (9) [ $\text{C}_6\text{H}_5\text{NC}_2\text{H}_4\text{OCH}_3^+$ ], 106 (36) [ $\text{C}_6\text{H}_5\text{NC}_2\text{H}_4\text{OCH}_3^{++} - \text{C}_2\text{H}_5\text{O}$ ], 77 (22) [ $\text{C}_6\text{H}_5^+$ ], 45 (100) [ $\text{C}_2\text{H}_5\text{O}^+$ ], 28 (6) [ $\text{N}_2^+$ ]. –  $\text{C}_{18}\text{H}_{24}\text{N}_4\text{O}_2$  (328.41): calcd. C 65.83, H 7.37, N 17.06; found C 66.07, H 7.27, N 17.10.

#### (2-Methoxyethyl)methylnitrosamine (14a)

Under argon, iodomethane (35.5 g, 0.250 mol) is added to a solution of (2-hydroxyethyl)methylnitrosamine (**12a**) (18.2 g, 0.175 mol) in absolute THF (300 ml). The solution is cooled to –60 °C and sodium hydride (7.2 g, 0.300 mol) is added. The mixture is vigorously stirred and allowed to warm to 20 °C. When the exothermic reaction has ended, stirring is continued for 30 min. Then excess sodium hydride is destroyed with water (10 ml). The solvent is removed *in vacuo* in an evaporator and the residue is treated with dichloromethane (100 ml) and water (100 ml). The layers are separated and the aqueous solution is extracted two times with dichloromethane (75 ml). The combined organic phases are dried with sodium sulfate, and the solvent is removed in an evaporator. The residue is distilled *in vacuo*. Yield 18.5 g (86%); b. p. 90 - 92 °C/18 hPa. The compound forms a syn / anti mixture ( $\approx 1.5:1$ ). –  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 3.06 (s, 3 H, NCH<sub>3</sub>), 3.24 (s, 3 H, NCH<sub>3</sub>), 3.31 (s, 3 H, OCH<sub>3</sub>), 3.43 (t,  $^3J$  = 5 Hz, 2 H, NCH<sub>2</sub>), 3.70 - 3.75 (m, 4 H, NCH<sub>2</sub>, OCH<sub>2</sub>), 3.78 (s, 3 H, OCH<sub>3</sub>), 4.26 (t,  $^3J$  = 5 Hz, 2H, OCH<sub>2</sub>). –  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 32.3 (CH<sub>3</sub>), 40.4 (CH<sub>3</sub>), 44.9 (NCH<sub>2</sub>), 53.2 (NCH<sub>2</sub>), 58.6

(OCH<sub>2</sub>), 58.7 (OCH<sub>2</sub>), 68.7 (OCH<sub>3</sub>), 70.6 (OCH<sub>3</sub>). – IR (liquid film):  $\nu$  = 2986 (s, C-H), 2930 (s, C-H), 2894 (s, C-H), 2831 (s, C-H), 1457 (s, N=O), 1380 (s), 1127  $\text{cm}^{-1}$  (s, C-O).

#### 1-(2-Methoxyethyl)-1-methylhydrazine (15a)

By the procedure described for **13a**, nitrosamine **14a** (17.7 g, 0.150 mol) is reduced with  $\text{LiAlH}_4$  (7.6 g, 0.200 mol) in THF (250 ml). Yield 7.70 g (49%); b. p. 55 °C/30 hPa. –  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 2.43 (s, 3 H, NCH<sub>3</sub>), 2.55 (t,  $^3J$  = 5 Hz, 2 H, NCH<sub>2</sub>), 2.90 (b, 2 H, NH<sub>2</sub>), 3.28 (s, 3 H, OCH<sub>3</sub>), 3.48 (t,  $^3J$  = 5 Hz, 2H, OCH<sub>2</sub>). –  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 50.3 (NCH<sub>3</sub>), 58.7 (OCH<sub>3</sub>), 61.8 (NCH<sub>2</sub>), 70.6 (OCH<sub>2</sub>). – IR (liquid film):  $\nu$  = 3327 (s, N-H), 2944 (s, C-H), 2882 (s, C-H), 2835 (s, C-H), 1604 (m,  $\delta$  (NH<sub>2</sub>)), 1459 (m), 1127  $\text{cm}^{-1}$  (s, C-O).

#### 1,4-Bis(2-methoxyethyl)-1,4-dimethyl-2-tetrazene (8)

By the procedure described for **3**, hydrazine **15a** (2.60 g, 25.0 mmol) is oxidized with yellow mercury(II) oxide (6.50 g, 30.0 mmol) in diethyl ether (40 ml). The crude material is purified by high-vacuum distillation. Yield 1.77 g (69%); b. p. 75 °C / 0.02 hPa. –  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 2.75 (s, 6 H, NCH<sub>3</sub>), 3.27 (s, 6 H, OCH<sub>3</sub>), 3.30 (t,  $^3J$  = 5 Hz, 4 H, NCH<sub>2</sub>), 3.50 (t,  $^3J$  = 5 Hz, 4 H, OCH<sub>2</sub>). –  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 38.2 (NCH<sub>3</sub>), 54.6 (NCH<sub>2</sub>), 58.6 (OCH<sub>3</sub>), 70.4 (OCH<sub>2</sub>). – IR (liquid, film):  $\nu$  = 2963 (s, C-H), 2917 (s, C-H), 2877 (s, C-H), 1601 (w, N=N), 1464 (m), 1121  $\text{cm}^{-1}$  (s, C-O). – MS (70 eV, EI):  $m/z$  = 204 (48) [ $\text{M}^+$ ], 176 (4) [ $\text{M}^+ - \text{N}_2$ ], 159 (22) [ $\text{M}^+ - \text{C}_2\text{H}_5\text{O}$ ], 131 (8) [ $\text{M}^+ - \text{C}_3\text{H}_7\text{NO}$ ], 116 (38) [ $\text{M}^+ - 2(\text{C}_2\text{H}_4\text{O})$ ], 73 (12) [ $\text{C}_3\text{H}_7\text{NO}^+$ ], 56 (26) [ $\text{C}_3\text{H}_6\text{N}^+$ ], 45 (100) [ $\text{C}_2\text{H}_5\text{O}^+$ ], 44 (55) [ $\text{C}_2\text{H}_6\text{N}^+$ ], 28 (22) [ $\text{N}_2^+$ ]. – MS (high resolution):  $m/z$  = 204.1578 (calcd. 204.1586). –  $\text{C}_8\text{H}_{20}\text{N}_4\text{O}_2$  (204.27): calcd. C 47.04, H 9.87, N 27.43; found C 46.56, H 9.90, N 26.91.

#### Bis(2-methoxyethyl)nitrosamine (14b)

By the procedure described for **14a**, nitrosamine **12b** (26.8 g, 0.200 mol) is methylated with iodomethane (71.0 g, 0.500 mol) and sodium hydride (14.4 g, 0.600 mol) in absolute THF (400 ml). Yield 30.3 g (95%, crude material, used without further purification). –  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 3.25 (s, 3 H, CH<sub>3</sub>), 3.32 (s, 3 H, CH<sub>3</sub>), 3.40 (t,  $^3J$  = 5 Hz, 2 H, NCH<sub>2</sub>), 3.68 (t,  $^3J$  = 5 Hz, 2 H, OCH<sub>2</sub>), 3.81 (t,  $^3J$  = 5 Hz, 2 H, OCH<sub>2</sub>), 4.32 (t,  $^3J$  = 5 Hz, 2H, NCH<sub>2</sub>). –  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 44.5 (NCH<sub>2</sub>), 52.9 (NCH<sub>2</sub>), 58.7 (CH<sub>3</sub>), 58.8 (CH<sub>3</sub>), 68.8 (OCH<sub>2</sub>), 70.7 (OCH<sub>2</sub>). – IR (liquid film):  $\delta$  = 2986 (s, C-H), 2933 (s, CH), 2895 (s, C-H), 2830 (s, C-H), 1454 (s, N=O), 1357 (s), 1119  $\text{cm}^{-1}$  (s, C-O).

*1,1-Bis(2-dimethoxyethyl)hydrazine (15b)*

By the procedure described for **13b**, nitrosamine **14b** (29.6 g, 0.200 mol) is reduced with LiAlH<sub>4</sub> (11.5 g, 0.300 mol) in THF (250 ml). Yield 13.1 g (44%); b. p. 50–53 °C/1\*10<sup>-3</sup> hPa. – <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 2.69 (t, <sup>3</sup>J = 5 Hz, 4 H, NCH<sub>2</sub>), 2.8 – 3.1 (br, 2 H, NH<sub>2</sub>), 3.28 (s, 6 H, CH<sub>3</sub>), 3.53 (t, <sup>3</sup>J = 5 Hz, 4 H, OCH<sub>2</sub>). – <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>): δ = 58.8 (CH<sub>3</sub>), 60.7 (NCH<sub>2</sub>), 70.8 (OCH<sub>2</sub>). – IR (liquid film): ν = 3344 (m, NH<sub>2</sub>), 2977 (s, C-H), 2926 (s, C-H), 2877 (s, C-H), 2815 (s, C-H), 1607 (m, δ (NH<sub>2</sub>)), 1458 (m), 1119 cm<sup>-1</sup> (s, C-O).

*1,1,4,4-Tetrakis(2-methoxyethyl)-2-tetrazene (9)*

By the procedure described for **3**, hydrazine **15b** (5.20 g, 35.0 mmol) is oxidized with yellow mercury(II) oxide (10.83 g, 50.0 mmol) in THF (50 ml). The crude material is purified by chromatography on neutral aluminium oxide with a mixture of hexane and ethyl acetate (5:2) as eluent. Yield 3.52 g (69%). – <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 3.30 (s, 12 H, CH<sub>3</sub>), 3.43 (t, <sup>3</sup>J = 5 Hz, 8 H, NCH<sub>2</sub>), 3.50 (t, <sup>3</sup>J = 5 Hz, 8 H, OCH<sub>2</sub>). – <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>): δ = 52.2 (NCH<sub>2</sub>), 58.7 (CH<sub>3</sub>), 70.5 (OCH<sub>2</sub>). – IR (liquid, film): ν = 2977 (s, C-H), 2923 (s, C-H), 2888 (s, C-H), 2815 (s, C-H), 1577 (w, N=N), 1460 (s), 1119 cm<sup>-1</sup> (s, C-O). – MS (70 eV, EI): *m/z* = 292 (12) [M<sup>+</sup>], 88 (14) [C<sub>4</sub>H<sub>10</sub>NO<sup>+</sup>], 45 (100) [C<sub>2</sub>H<sub>5</sub>O<sup>+</sup>], 31 (9) [CH<sub>3</sub>O<sup>+</sup>], 29 (16) [C<sub>2</sub>H<sub>5</sub><sup>+</sup>], 28 (7) [N<sub>2</sub><sup>+</sup>], 15 (7) [CH<sub>3</sub><sup>+</sup>]. – C<sub>12</sub>H<sub>28</sub>N<sub>4</sub>O<sub>4</sub> (292.38): calcd. C 49.30, H 9.65, N 19.16; found C 48.04, H 9.26, N 17.54.

*Benzyl-(2-methoxyethyl)nitrosamine (14c)*

By the procedure described for **14b**, nitrosamine **13c** (36.0 g, 0.200 mol) is methylated with iodomethane (35.5 g, 0.250 mol) and sodium hydride (6.0 g, 0.250 mol) in THF (350 ml). Yield 36.4 g (94%, crude material, used without further purification). The compound forms a syn / anti mixture (≈1.5:1). – <sup>1</sup>H NMR (500 MHz, [D<sub>6</sub>]DMSO): δ = 3.16 (s, 3 H, CH<sub>3</sub>), 3.20 (s, 3 H, CH<sub>3</sub>), 3.31 (t, <sup>3</sup>J = 5 Hz, 2 H, NCH<sub>2</sub>), 3.6 – 3.7 (m, 4 H, NCH<sub>2</sub>, OCH<sub>2</sub>), 4.29 (t, <sup>3</sup>J = 5 Hz, 2 H, OCH<sub>2</sub>), 4.83 (s, 2 H, OCH<sub>2</sub>), 5.36 (s, 2 H, NCH<sub>2</sub>), 7.0 – 7.5 (m, 5 H, ArH). – <sup>13</sup>C NMR (126 MHz, [D<sub>6</sub>]DMSO): δ = 42.1 (NCH<sub>2</sub>), 46.4 (NCH<sub>2</sub>), 51.1 (NCH<sub>2</sub>), 55.6 (NCH<sub>2</sub>), 57.7 (CH<sub>3</sub>), 57.8 (CH<sub>3</sub>), 67.3 (OCH<sub>2</sub>), 68.8 (OCH<sub>2</sub>), 127.1 (C<sub>ar</sub>H), 127.4 (C<sub>ar</sub>H), 128.0 (C<sub>ar</sub>H), 128.3 (C<sub>ar</sub>H), 128.5 (C<sub>ar</sub>H), 128.6 (C<sub>ar</sub>H), 134.7 (C<sub>ar</sub>), 135.3 (C<sub>ar</sub>). – IR (liquid film): ν = 3065 (m, Ar-H), 3032 (m, Ar-H), 2931 (s, C-H), 2895 (s, C-H), 2831 (m, C-H), 1455 (s, N=O), 1118 cm<sup>-1</sup> (s, C-O).

*1-Benzyl-1-(2-methoxyethyl)hydrazine (15c)*

By the procedure described for **13b**, nitrosamine **14c** (35.3 g, 0.181 mol) is reduced with LiAlH<sub>4</sub> (9.5 g, 0.250 mol) in THF (300 ml). Yield 30.1 g (92%, crude material, used without further purification). – <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 2.73 (t, <sup>3</sup>J = 5 Hz, 2 H, NCH<sub>2</sub>), 2.8 – 3.0 (br, 2 H, NH<sub>2</sub>), 3.34 (s, 3 H, CH<sub>3</sub>), 3.60 (t, <sup>3</sup>J = 5 Hz, 2 H, OCH<sub>2</sub>), 3.71 (s, 2 H, NCH<sub>2</sub>), 7.2 – 7.4 (m, 5 H, ArH). – <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>): δ = 58.7 (CH<sub>3</sub>), 59.0 (NCH<sub>2</sub>), 66.5 (NCH<sub>2</sub>), 70.8 (OCH<sub>2</sub>), 127.2 (C<sub>ar</sub>H), 128.2 (C<sub>ar</sub>H), 129.2 (C<sub>ar</sub>H), 137.2 (C<sub>ar</sub>). – IR (liquid film): ν = 3339 (m, NH<sub>2</sub>), 3062 (m, Ar-H), 3028 (m, Ar-H), 2925 (s, C-H), 2816 (s, C-H), 1602 (m, δ (NH<sub>2</sub>)), 1453 (s), 1118 cm<sup>-1</sup> (m, C-O).

*1,4-Dibenzyl-1,4-bis(2-methoxyethyl)-2-tetrazene (10)*

By the procedure described for **5**, hydrazine **15c** (9.02 g, 50.0 mmol) is oxidized with benzoquinone (6.50 g, 60.0 mmol) in ethanol (400 ml). After removal of the solvent the brown crude material was crystallized at -20 °C. Recrystallization from little petrol ether (five times) afforded brownish needles. Yield 1.17 g (13%); m. p. 29 – 30 °C. – <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 3.28 (s, 6 H, CH<sub>3</sub>), 3.37 (t, <sup>3</sup>J = 6 Hz, 4 H, NCH<sub>2</sub>), 3.48 (t, <sup>3</sup>J = 6 Hz, 4 H, OCH<sub>2</sub>), 4.46 (s, 4 H, NCH<sub>2</sub>), 7.1 – 7.4 (m, 10 H, ArH). – <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>): δ = 60.0 (NCH<sub>2</sub>), 56.4 (NCH<sub>2</sub>), 58.7 (CH<sub>3</sub>), 70.5 (OCH<sub>2</sub>), 126.8 (C<sub>ar</sub>H), 128.1 (C<sub>ar</sub>H), 128.3 (C<sub>ar</sub>H), 138.4 (C<sub>ar</sub>). – IR (KBr): δ = 3061 (m, Ar-H), 3026 (m, Ar-H), 2975 (s, C-H), 2882 (s, C-H), 2845 (s, C-H), 1603 (s, C=C), 1503 (s), 1118 (s, C-O), 733 (s, δ(Ar-H)<sub>o.o.p.</sub>), 699 cm<sup>-1</sup> (s, δ(Ar-H)<sub>o.o.p.</sub>). – MS (70 eV, EI): *m/z* = 356 (66) [M<sup>+</sup>], 164 (76) [C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>NC<sub>2</sub>H<sub>4</sub>OCH<sub>3</sub><sup>+</sup>], 120 (10) [C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>NHCH<sub>2</sub>], 91 (100) [C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub><sup>+</sup>], 77 (3) [C<sub>6</sub>H<sub>5</sub><sup>+</sup>], 65 (11) [C<sub>5</sub>H<sub>5</sub><sup>+</sup>], 59 (39) [C<sub>3</sub>H<sub>7</sub>O<sup>+</sup>], 45 (25) [C<sub>2</sub>H<sub>5</sub>O<sup>+</sup>], 29 (12) [C<sub>2</sub>H<sub>5</sub><sup>+</sup>]. – C<sub>20</sub>H<sub>28</sub>N<sub>4</sub>O<sub>2</sub> (356.47): calcd. C 67.39, H 7.92, N 15.72; found C 66.91, H 7.81, N 16.14.

*Oxidation of hydrazine 13c with mercury(II) oxide*

By the procedure described for **3**, hydrazine **13c** (4.99 g, 30.0 mmol) is oxidized with yellow mercury(II) oxide (8.66 g, 40.0 mmol) in absolute diethyl ether (40 ml). After removal of the solvent, a crude material (4.26 g) was obtained. GC/MS analysis indicated a complex mixture of decomposition products with only a small amount of 2-tetrazene **5** (*m/z* = 328). The main components were 3-phenylpropanol (**18**) and dibenzyl (**19**).

*3-Phenylpropanol (18)*. MS (70 eV, EI): *m/z* = 136 (37) [M<sup>+</sup>], 118 (58) [M<sup>+</sup> - OH], 117 (100) [M<sup>+</sup> - H<sub>2</sub>O], 105 (16) [M<sup>+</sup> - CH<sub>3</sub>O], 92 (48) [C<sub>7</sub>H<sub>8</sub><sup>+</sup>], 91 (80) [C<sub>7</sub>H<sub>7</sub><sup>+</sup>], 77 (15) [C<sub>6</sub>H<sub>5</sub><sup>+</sup>].

*Bibenzyl (19)*. MS (70 eV, EI):  $m/z = 182$  (35) [ $M^+$ ], 91 (100) [ $C_7H_7^+$ ], 65 (9) [ $C_5H_5^+$ ].

*Oxidation of hydrazine 15c with mercury(II) oxide*

By the procedure described for **3**, hydrazine **15c** (5.41 g, 30.0 mmol) is oxidized with yellow mercury(II) oxide (8.66 g, 40.0 mmol) in absolute diethyl ether (40 ml). After removal of the solvent, a crude material

(4.59 g) was obtained. GC/MS analysis indicated a complex mixture of decomposition products of 2-tetrazene **10** ( $m/z = 328$ ). The main components were 3-methoxypropylbenzene (**20**) and bibenzyl (**19**).

*3-Methoxypropylbenzene (20)*. MS (70 eV, EI):  $m/z = 150$  (3) [ $M^+$ ], 119 (7) [ $M^+ - OCH_3$ ], 118 (100) [ $M^+ - OCH_3 - H$ ], 92 (27) [ $C_7H_8^+$ ], 91 (50) [ $C_7H_7^+$ ], 45 (32) [ $C_2H_5O^+$ ].

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