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Synthesis and characterization of novel triazenes from the reaction of the cyclic aminal 1,3,6,8-tetraazatricyclo[4.3.1.1^{3,8}]undecane (TATU) with diazonium ions

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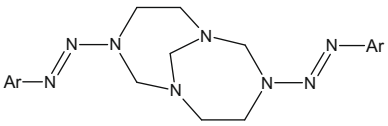
ABSTRACT

The reaction of the cyclic aminal 1,3,6,8-tetraazatricyclo[4.3.1.1^{3,8}]undecane (TATU, **4**) with diazonium salts resulted in the formation of a new series of bis-triazenes, namely 3,8-bis[(4-methoxyphenyl)diazenyl]-1,3,6,8-tetraazabicyclo[4.3.1]decane **6a**, 3,8-bis[(2-methoxyphenyl)diazenyl]-1,3,6,8-tetraazabicyclo[4.3.1]decane **6b**, 3,8-bis(*p*-tolyldiazenyl)-1,3,6,8-tetraazabicyclo[4.3.1]decane **6c**. When aniline derived diazonium salt **5d** was coupled with TATU, 3,8-bis(phenyldiazenyl)-1,3,6,8-tetraazabicyclo[4.3.1]decane **6d** and bis[1,5-bis-((*E*)-phenyldiazenyl)-1,3,5-triazepan-3-yl]methane **7** were obtained. These compounds were characterized by HR-MS, ^{1}H and ^{13}C NMR and 2D-NMR. Additionally, the structure of compound **7** was confirmed by X-ray crystallography.

Triazenes are a unique class of polyazo compounds containing three consecutive nitrogen atoms with a double bond between N1 and N2 (R–N1 = N2–N3–R′R″). The two most widely utilized methods for the synthesis of triazenes are the coupling of aryl diazonium salts to primary or secondary amines and the addition of organometallic reagents to alkyl azides.[1] Triazenes have been used for many purposes, such as anticancer agents,[2] as coupling partners in combinatorial chemistry,[3] as protecting groups for amines in organic synthesis[4] and in the formation of novel heterocycles.[5]

Vaughan reported on the reaction of diazonium salts with formaldehyde/ethylenediamine mixtures to afford the cage-like bis-triazenes of type 3,8-di-[2-aryl-1-azenyl]-1,3,6,8-tetraazabicyclo[4.4.1]undecane **1**.[6] The formation of the bis-triazene **1** was attributed to the coupling of the diazonium ion to the aminal cage 1,3,6,8-tetraazatricyclo[4.4.1.1^{3,8}]dodecane (TATD, **2**), which is formed in situ from the condensation of ethylenediamine and formaldehyde.[6] Alternatively, a similar reaction of diazonium salts with either hexamethylenetetramine (urotropine) or an aqueous mixtures of ammonia-formaldehyde affords 3,7-bis(arylazo)-1,3,5,7-tetraazabicyclo[3.3.1]nonanes **3**.[7] We recently communicated an efficient one-pot synthesis of the aminal cage 1,3,6,8-tetraazatricyclo[4.3.1.1^{3,8}]undecane (TATU, **4**).[8] While TATD has been the subject of much theoretical and experimental investigation,[9] TATU has been less extensively studied.[10] As a part of our continuing studies on the reactions of macrocyclic aminals, we planned to investigate the reaction of TATU and diazonium ions, applying Vaughan's methodology.[6]



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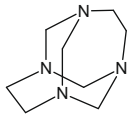

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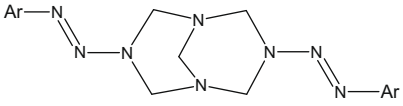

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Following the literature procedure,[6] the reaction of TATU and diazonium salts **5a**–**b** afforded complex mixtures, from which were unable to isolate the expected bis-triazenes **6a**–**d**. On one hand, when diazonium salts with electron-withdrawing groups such as *p*-nitro or *p*-bromine were used the triazenes **1** and **3** were the major recognizable products. These results prompted us to examine the mode of reaction of this the aminal cage **4** with the diazonium ions.

Since cyclic aminals such as TATU **4** undergo facile Brönsted acid-catalyzed ring cleavage, we reasoned that the reaction with diazonium salts failed due to the low pH of the medium.[11] Thus, on the basis of the work developed by Vaughan's group[12] we explored different reaction conditions by varying the pH. The optimized conditions include the careful addition of an aqueous solution of the appropriate diazonium salt[13] to a saturated sodium carbonate solution of TATU over 20 min. After the reaction stirred for approximately 30 min, the resulting precipitate was isolated by vacuum filtration, washed with water, dried, and purified by

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recrystallization to afford a new type of bis-triazenes, namely 3,8-di(2-aryl-1-azenyl)-1,3,6,8-tetrazabyciclo[4.3.1]decanes **6a–d**.[14] This method works well with electron-rich diazonium salts but failed with electron-poor salts. In addition, when the diazonium salt derivate of aniline **5d** was used, the desired triazene **6d** was obtained, along with the unexpected compound bis-[1,5-bis-((*E*)-phenyldiazenyl)-1,3,5-triazepan-3-yl]methane **7**.

All compounds have been completely characterized by ^{1}H and ^{13}C NMR, melting point, and HR-MS. When necessary, COSY, HMQC or HSQC, HMBC and NOESY experiments were conducted and all results are consistent with the proposed formulations. Furthermore, the structure of *tetrakis*-triazene **7** was unequivocally confirmed by X-ray crystallography.

The bis-triazenes **6a–d** contain bicyclic structures with a seven-membered ring bridged to a six-membered ring and the structures are unsymmetrical. Additionally, the compounds present an unusual type of chirality, where the geometrical rigidity (similar to Tröger's bases[15]) and nonplanar structure have created a chiral environment for geminal protons or N-substituted groups (i.e., for CH_2 of the NCH_2CH_2N group). This results in diastereomers (the non-equivalence of geminal protons), which causes the assignments of these protons to become complicated. In this context, a NOESY was conducted to unambiguously assign the non-equivalent CH_2 geminal protons and to establish the nature of the conformational structure of this bicyclic system. The foregoing correlations led to the conclusion that the preferred conformation of a 1,3,6,8-tetraazabicyclo[4.3.1]decane system is a chair–chair conformation (Fig. 1).

At ambient temperature, the ^{13}C NMR spectra of compounds **6a–d** in $CDCl_3$ showed resonances for each aryl group in the aromatic region. The aliphatic region exhibited singlets due to methyl groups (for **6a–c**) but lacked some methylene signals or displayed peaks that were low or broad. The ^{13}C chemical shifts for these carbons were obtained from cross sections of 2D heteronuclear $\{^{1}H–^{13}C\}$ HSQC or HMQC spectra. We believe that the lacking of these signals is due to an equilibrium of the rotamers arising from restricted rotation around the N2–N3 bond of the triazene.[16] This hypothesis was confirmed by the analysis of ^{1}H and ^{13}C NMR spectra at low temperatures in $CDCl_3$. When the temperature of the solution of **6a** in $CDCl_3$ was lowered, the signals in the aliphatic region of the spectrum broadened and partially resolved at 213 K.

The reaction mechanism for the formation of 3,8-bis-(2-aryl-1-diazenyl)-1,3,6,8-tetraazabicyclo[4.3.1]decane **6a–d** is believed to occur by the route shown in Scheme 1, which is analogous to the previously reported mechanism for the formation of **1** and **3**.[7,17] However, under these reaction conditions, the predominant

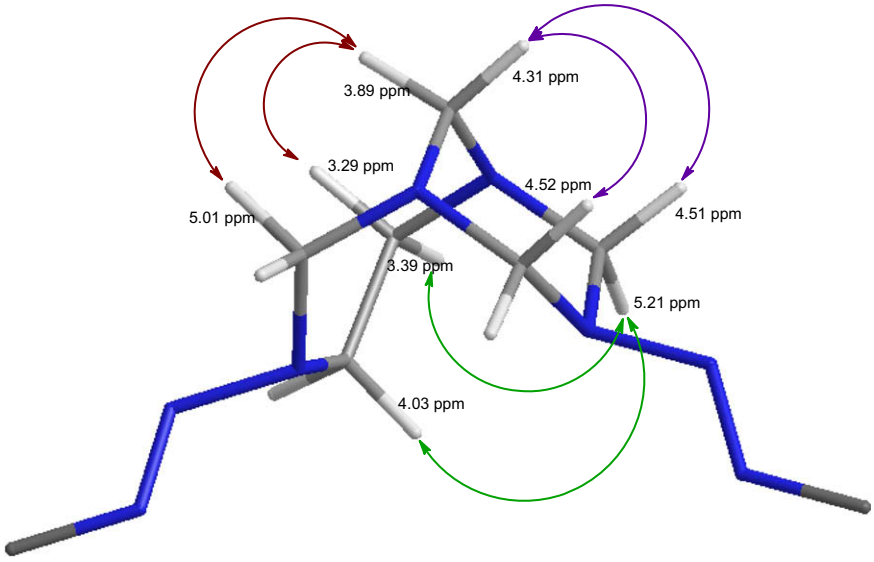
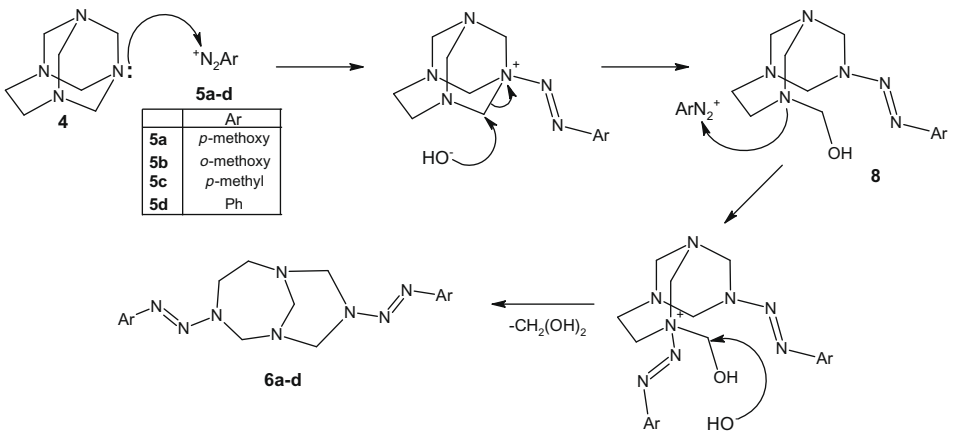


Figure 1. Selected key **6a** NOESY correlations.



Scheme 1. Synthetic pathway for 3,8-bis-(2-aryl-1-diazenyl)-1,3,6,8-tetraazabicyclo[4.3.1]decanes **6**.

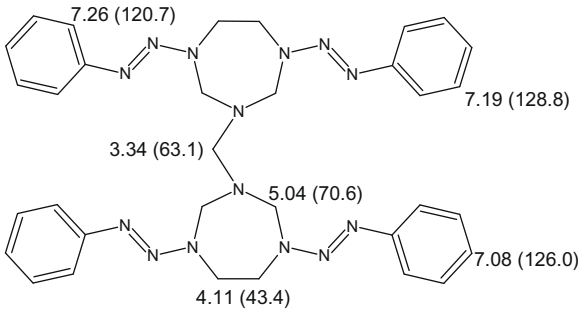


Figure 2. ^{1}H NMR (^{13}C) ppm spectroscopic data for **7** in $CDCl_3$.

species in the basic solution is TATU **4**. The reaction sequence is initiated by attack on the electrophilic diazonium ion by one of the two equivalent nitrogen atoms in TATU **4** that have the most sp^3 character.[10b] Next, nucleophilic attack at the adjacent methylene by the hydroxyl group results in the formation of hemiaminal **8**. After attack on the diazonium ion by the hemiaminalic nitrogen, one molecule of formaldehyde hydrate is eliminated, affording the observed bis-triazenes **6a–d**.

Only one report exists on the direct synthesis of *tetrakis*-triazenes.[18] We now report that compound **7**, a novel *tetrakis*-triazene, has been isolated from the reaction of the cyclic aminal TATU **4** with a diazonium salt **5d**. We also present the X-ray crystal structure of **7** here. This new *tetrakis*-triazene **7** was isolated by crystallization in $CHCl_3$/EtOH as an amorphous solid. The simplicity of ^{1}H NMR spectra indicated that the molecule is highly symmetric. The cross-peak in the HMQC two dimensional spectrum was taken into account when assigning ^{13}C NMR signals (Fig. 2). The ^{1}H NMR spectrum exhibits three signals in the aliphatic region with relative intensities of 8:8:2. The more shielded aminal hydrogen at 3.34 ppm exists as a singlet and corresponds to the two hydrogen atoms of the methylene bridge between the two rings of the triazepane. Another singlet at 4.11 ppm corresponds to the protons of the ethylene moiety of the triazepane. An eight-proton singlet at 5.04 ppm was assigned to the equivalent methylene groups (NCH_2N) in the triazepane rings. These signals show a cross-peak in the HMQC contour plot with the signal at 63.1, 43.3 and 70.6 ppm, respectively, in the carbon domain. HR-MS (*m/z* 630. 2940) suggested a molecular formula of $C_{33}H_{38}N_{14}$.

Table 1
Selected bond lengths (Å) and bond angles (°) for **7**

Bond lengths (Å)		Bond angles (°)	
N1–N2	1.3352(17)	N2–N1–C28	113.87(12)
N2–N3	1.2716(17)	N2–N1–C25	120.57(13)
N4–N5	1.3361(18)	C28–N1–C25	124.82(12)
N5–N6	1.2673(18)	N5–N4–C27	115.74(12)
N9–N10	1.3490(19)	N5–N4–C26	121.92(13)
N10–N11	1.273(2)	C27–N4–C26	118.76(13)
N12–N13	1.359(4)	N10–N9–C31	117.62(16)
N13–N14	1.264(3)	N10–N9–C30	113.74(13)
		C30–N9–C31	126.47(15)
		N13–N12–C32	124.6(4)
		N13–N12–C33	110.5(3)
		C32–N12–C33	119.5(4)
		C27–N7–C28	114.34(12)
		C27–N7–C29	112.55(12)
		C28–N7–C29	112.85(12)
		C30–N8–C33	113.35(12)
		C30–N8–C29	112.88(12)
		C33–N8–C29	112.69(12)

Crystals suitable for X-ray analysis were readily grown in ethyl acetate. The structure of **7** was unambiguously determined by X-ray crystallography (Fig. 3)[19] and selected bonds lengths and angles are given in Table 1. In concordance with reported data,[20] Figure 3 shows that the configuration around the N=N bonds (e.g., N2–N3 or N5–N6) are '*anti*' and these bonds are significantly shorter (ca. 1.27 Å) than the N–N bonds (e.g., N1–N2 or N4–N5) (ca. 1.34 Å). Other notable features of the structure in Figure 3 include bond angles around N1, N4, N9 and N12, which are close to sp^2-hybridization [$\sum\alpha \cong 360°$]. In contrast, the bond angles around the nitrogen atom bridge (N7 and N8) are close to an sp^3 geometry [$\sum\alpha = 339.7°$ around N7, and 338.9° around N8].

As shown in Scheme 2 the formation of **7** could be explained by the coupling of the diazonium salt **5d** to 3,3′-methylenebis-1,3,5-

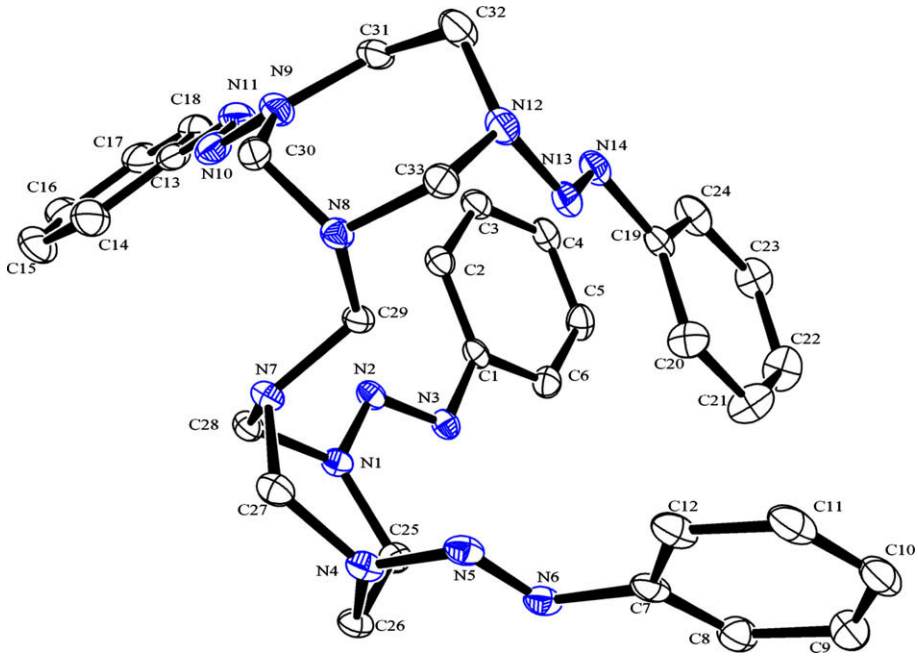
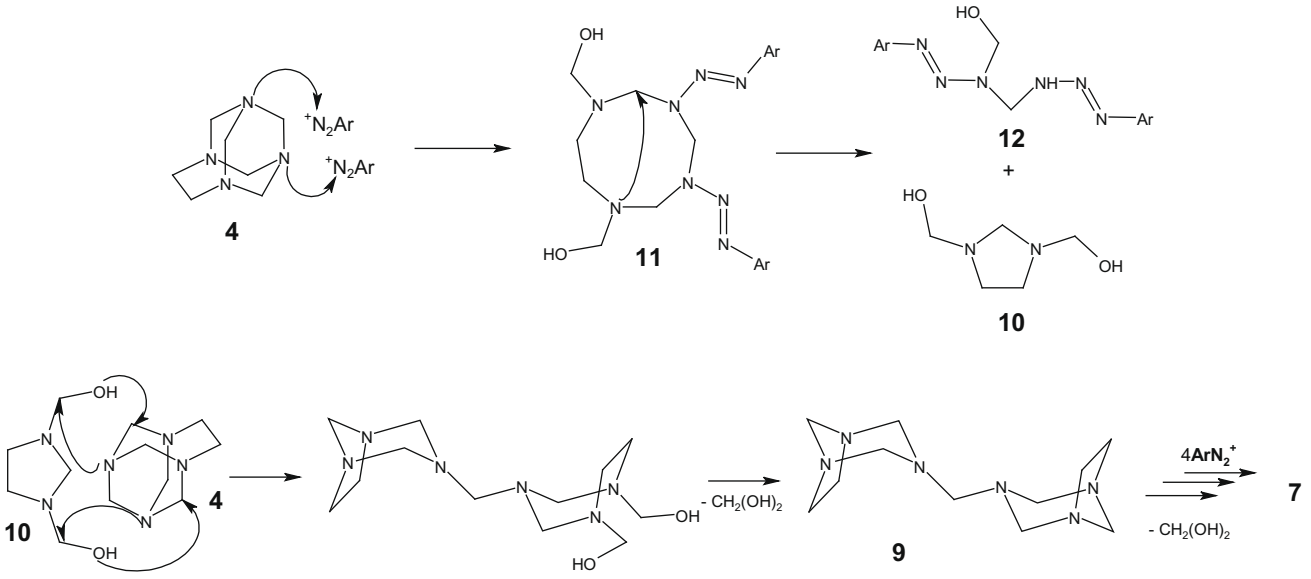


Figure 3. Molecular structure of **7**. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres.



Scheme 2. Proposed pathway for bis[1,5-bis-((*E*)-phenyldiazenyl)-1,3,5-triazepan-3-yl]methane **7** formation.

triazabicyclo[3.2.1]octane **9**. Alternatively, we speculated that the more nucleophilic nitrogen (most sp^3 character)[10b] atoms in TATU **4** simultaneously attack two molecules of the diazonium salt **5d** to form **11**. This macrocycle then undergoes intramolecular nucleophilic attack to yield **10** and open chain by-products, such as **12**, which we have not been able to isolate. Finally, the formation of compound **9** can be explained by the reaction of imidazolidine-1,3-diyldimethanol **10** with TATU **4**.

In conclusion, we have demonstrated that the use of a basic medium provides a mild and effective method for the coupling of diazonium ions with TATU **4**. The successful synthesis of bis-triazenes **6a–d** and *tetrakis*-triazene **7** provides an alternative method for the preparation of bis-triazenes and paves the way for the preparation of these types of compounds from cyclic aminals.

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14. *3,8-Bis-[(4-methoxyphenyl)diazenyl]-1,3,6,8-tetraazabicyclo [4.3.1]decane* (**6a**): yield 55%, mp 122–123 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21 (d, J = 8.76 Hz, 2H), 7.15 (d, J = 8.64 Hz, 2H), 6.75 (d, J = 8.88 Hz, 2H), 6.71 (d, J = 8.76 Hz, 2H), 5.34 (d, J = 13.08 Hz, 1H), 5.21 (d, J = 13.07 Hz, 1H), 5.15 (d, J = 13.63 Hz, 1H), 5.01 (d, J = 13.89 Hz, 1H), 4.52 (d, J = 13.24 Hz, 1H), 4.51 (d, J = 13.24 Hz, 1H), 4.31 (d, J = 14.04 Hz, 1H), 4.03 (m, 1H), 3.89 (d, J = 14.08 Hz, 1H), 3.85 (m, 1H), 3.77 (s, 6H), 3.39 (m, 1H), 3.29 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.2, 157.8, 144.3, 143.9, 121.8, 121.7, 113.8, 73.7, 70.6, 66.9, 66.0, 55.4, 55.4, 50.4, 47.3. HR-EIMS *m/z*: calcd for $C_{20}H_{26}N_8O_2$: 410.4732, found: 410.2162. *3,8-Bis-[(2-methoxyphenyl)diazenyl]-1,3,6,8-tetraazabicyclo[4.3.1]decane* (**6b**): yield 48%, mp 107–110 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18 (d, J = 7.0 Hz, 1H), 7.08 (d, J = 8.2 Hz, 1H), 7.04 (d, J = 8.2 Hz, 1H), 6.95 (d, J = 7.1 Hz, 1H), 6.85 (d, J = 7.9 Hz, 2H), 6.79 (t, J = 6.7 Hz, 1H), 6.63 (t, J = 6.9 Hz, 1H), 5.40 (d, J = 10.8 Hz, 1H), 5.26 (d, J = 13.5 Hz, 2H), 5.02 (d, J = 14.0 Hz, 1H), 4.62 (d, J = 12.0 Hz, 1H), 4.59 (d, J = 12.0 Hz, 1H), 4.32 (d, J = 14.0 Hz, 1H), 4.07 (t, J = 11.7 Hz, 1H), 3.90 (d, J = 12.0 Hz, 1H), 3.90 (m, 1H), 3.84 (s, 3H), 3.76 (s, 3H), 3.46 (d, J = 14.9 Hz, 1H), 3.33 (t, J = 12.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.2, 153.1, 140.2, 139.7, 127.1, 126.6, 120.8, 120.7, 119.2, 118.8, 112.0, 111.8, 73.9, 71.3, 66.0 (broad), 56.1, 50.2, 47.7. HR-EIMS *m/z*: calcd for $C_{20}H_{26}N_8O_2$: 410.4732, found: 410.2168. *3,8-Bis(p-tolyldiazenyl)-1,3,6,8-tetraazabicyclo[4.3.1]decane* (6c): yield 60%, mp 104–105 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.16 (d, J = 8.04 Hz, 2H), 7.10 (d, J = 7.84 Hz, 2H), 7.02 (d, J = 8.12 Hz, 2H), 6.99 (d, J = 8.00 Hz, 2H), 5.34 (d, J = 12.96 Hz, 1H), 5.24 (d, J = 12.76 Hz, 1H), 5.15 (d, J = 13.44 Hz, 1H), 5.03 (d, J = 13.80 Hz, 1H), 4.54 (d, J = 10.08 Hz, 1H), 4.51 (d, J = 12.06 Hz, 1H), 4.31 (d, J = 14.04 Hz, 1H), 3.99 (m, 1H), 3.92 (m, 1H), 3.88 (d, J = 14.00 Hz, 1H), 3.37 (m. 1H), 3.31 (m, 1H), 2.29 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.2, 147.8, 135.9, 135.3, 129.2, 129.2, 120.6, 120.6, 74.0(not obs), 70.4(not obs), 66.5(not obs), 50.2(not obs), 47.3(not obs), 21.0, 21.0. HR-EIMS *m/z*: calcd for $C_{20}H_{26}N_8$: 378.4744, found: 378.2124. *3,8-Bis(phenyldiazenyl)-1,3,6,8-tetraazabicyclo[4.3.1]decane* (**6d**): yield 36%, mp 134–136 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.17 (m, 10H), 5.37 (m, 1H), 5.29 (m, 1H), 5.22 (d, J = 14.04 Hz, 1H), 5.03 (d, J = 13.84 Hz, 1H), 4.58 (d, J = 11.72 Hz, 1H), 4.55 (d, J = 12.8 Hz, 1H), 4.34 (d, J = 14.08 Hz, 1H), 4.02 (m, 1H), 3.90 (d, J = 14.04 Hz, 1H), 3.82 (m, 1H), 3.45 (m, 1H), 3.31 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.5, 150.0, 128.6, 126.2, 125.7, 120.8, 120.8, 74.0, 71.0, 65.9(not obs), 50.3, 47.4. HR-EIMS *m/z*: calcd for $C_{18}H_{22}N_8$: 350.4212, found: 350.1985. *Bis-[1,5-bis-((E)-phenyldiazenyl)-1,3,5-triazepan-3-yl]methane* (**7**): yield 32%, mp 195–197 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26 (d, J = 6.92 Hz, 8H), 7.19 (t, J = 7.72 Hz, 8H), 7.08 (t, J = 7.20 Hz, 4H), 5.04 (s, 8H), 4.11 (s, 8H), 3.34 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.0, 128.8, 126.0, 120.7, 70.6 (no obs.), 63.1 (not obs), 43.3 (not obs). HR-EIMS *m/z*: calcd for $C_{33}H_{38}N_{14}$: 630.7492, found: 630.2940.
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19. Crystal data for compound **7**, $C_{33}H_{38}N_{14}$, were collected using a Bruker Appex-II diffractometer at 100 K, $M_r = 630.77$, triclinic, *P1*, $a = 10.8032(7)$ Å, $b = 13.3808(7)$ Å, $c = 13.4206(7)$ Å, $V = 1643.27(18)$ Å^3, $Z = 2$, Dx = 1.275 g/cm^3, X-ray source Mo Kα (radiation), $\lambda = 0.7107$ Å, $F(0\,0\,0) = 668$, colourless prism $0.44 \times 0.32 \times 0.18$ mm. The structure solution was obtained by direct methods and was refined with anisotropic thermal parameters using full-matrix least squares procedures on F^2 to give $R = 0.043$, $wR = 0.116$ for 5991 independent observed reflections and 458 parameters. Crystallographic data (excluding structure factors) for the given structure in this Letter have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 751350. Copies of these data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44(0) 1223 336033 or email: deposit@ccdc.cam.ac.uk).

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