# Synthesis of lariat aminotriazolophanes using carbonoxysulfide

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The synthesis is described of some new aminotriazolophanes based on resorcinol and glutaric acid scaffolds by cyclisation reactions between various 1,ω-dihaloalkanes and the crown precursors 1,3-bis [(4-amino-5-oxy-1, 2,4-triazole-3-yl) methyleneoxy] benzene and 1,3-bis(4-amino-5-oxo-1,2,4-triazol-3-yl) propane. The latter were synthesised using carbonoxysulfide as a reactant. The syntheses of heterophanes were carried out regioselectively and the compounds were obtained in good yields.

**Keywords:** lariat aminotriazolophane, resorcinol, glutaric acid dihydrazide, carbonoxysulfide, cyclisation

Macrocyclic organic molecules, containing heteroatoms, are widely recognised as components of host–guest complexes. The simplest crown ethers and their derivatives are used as ion selective reagents in a number of separation and catalytic processes and as model reagents for molecular recognition.[1]

For more than three decades, macrocyclic polyether compounds (crown ethers) have been synthesised and utilised in alkali and alkaline earth metal cation determinations due to their superior binding ability for these metal ions.[2] Attachment of a side arm with potential metal ion coordination sites leads to better complexing agents called lariat ethers.[3] Such lariat ethers are designed to enhance the cation binding ability or selectivity of crown ethers by providing the potential for three-dimensional complexation, thereby mimicking the dynamic complexation processes exhibited by natural macrocyclic ionophores. When the side arm contains an acidic group, a proton-ionisable lariat ether is produced in which the ligand provides not only a polyether binding site for metal ion complexation, but also the requisite anion for formation of an electro-neutral complex.[4] Such proton-ionisable lariat ethers exhibit markedly enhanced solvent extraction of alkali and alkaline earth metal cations and their transport across liquid membranes compared to non-ionisable analogues when the aqueous solutions contain metal chlorides, nitrates and sulfates.[5]

Incorporation of heterocyclic subunits provides rigidity to the macrocycle and assists in increasing the stability of complexes formed with both metals and organic cations.[2] The observation that certain triazoles were capable of inhibiting fog formation[6] in photographic emulsions and that others were useful as anticonvulsants[6] and herbicides,[6] has led to renewed attention particularly by the chemical industry, to simple and fused triazole systems. 1,2,4-Triazoles also have potent antimicrobial activity.[6]

Carbonoxysulfide (COS)[7] is a gaseous reagent which facilitates the synthesis of novel heterocycles, that are difficult to prepare by other routes.

A wide variety of biologically active heterocyclic compounds have been synthesised in our laboratory in recent years, by the use of carbonoxysulfide.[8-11] Recently, we have been successful in demonstrating the use of carbonoxysulfide in the synthesis of simple unsymmetrical aminotriazoles, containing oxygen as well as sulfur heteroatoms.[12,13] These have then been used to synthesise fused ring systems and also spiro compounds.

In continuation of our earlier work, we now report a facile regioselective synthesis of aminotriazolophanes using carbonoxysulfide and involving N-alkylation.

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## Results and discussion

Resorcinol was reacted with ethyl bromoacetate in acetone in the presence of potassium carbonate to give 1,3-bis[ethoxy-carbonylmethoxy-phenoxy)-acetic acid ester[14] (**1**) as a pale yellow solid in 96% yield (Scheme 1). Treatment of compound **1** with hydrazine hydrate (99%) gave the corresponding hydrazide **2** in 85% yield (Scheme 1).

Compound **2** was then reacted with COS in ethanolic potassium hydroxide solution for 4h to afford the corresponding dipotassium salt of thiocarbazinic acid. The dried salt was then fused with hydrazine hydrate (0.02 moles) at 110–120 °C in an oil bath for 3 h to give 1, 3-bis [(4'-amino-5'-oxo-1, 2, 4-triazol-3-yl) methyleneoxy] benzene **3** in 66% yield.

Glutaric acid dihydrazide[15] **6** was also employed for the synthesis of novel lariat aminotriazolophanes. In this case, glutaric acid dihydrazide **6** was first reacted with COS in presence of triethylamine to afford triethylammonium salt of respective thiocarbazinic acid. It was then treated with benzyl chloride to afford its benzyl ester **7**. The benzyl ester was then reacted with hydrazine hydrate in an oil bath at 120–125 °C for 4 h to afford the crown precursor **8**.

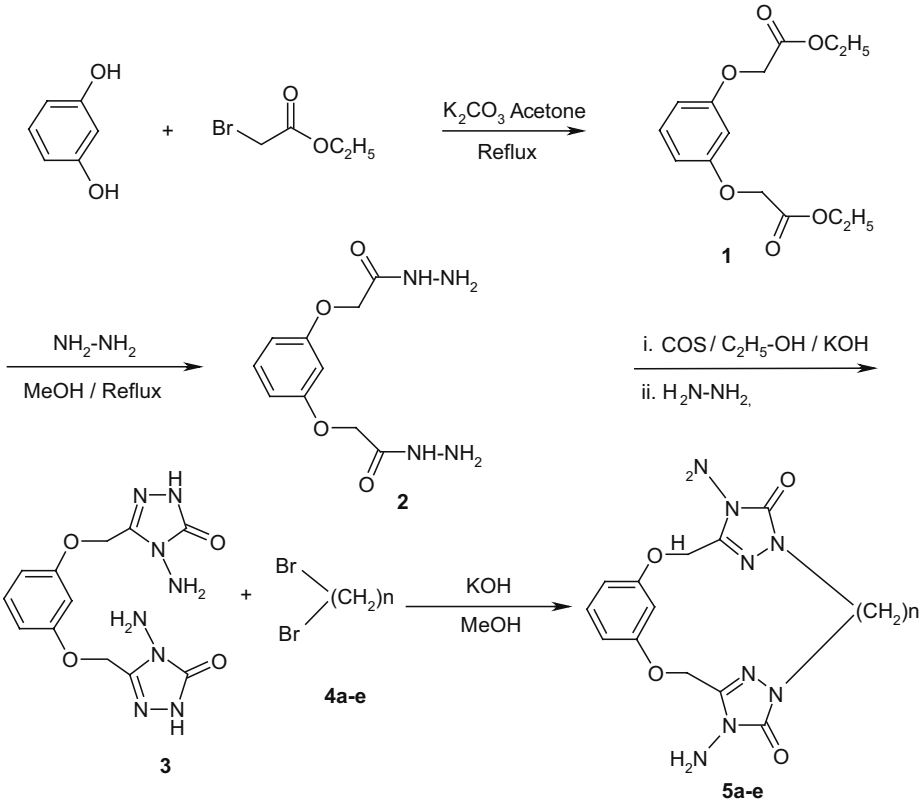
Heterophanes were then synthesised from crown precursors **3** and **8** by there reaction with different 1,ω-dihaloalkanes using high dilution techniques. 1,ω-Dihaloalkanes were added dropwise with stirring to the methanolic solution of dipotassium salt of **3** and **8,** to afford the desired macrocycles **5a–e** and **9a,b** respectively**.**

## Experimental

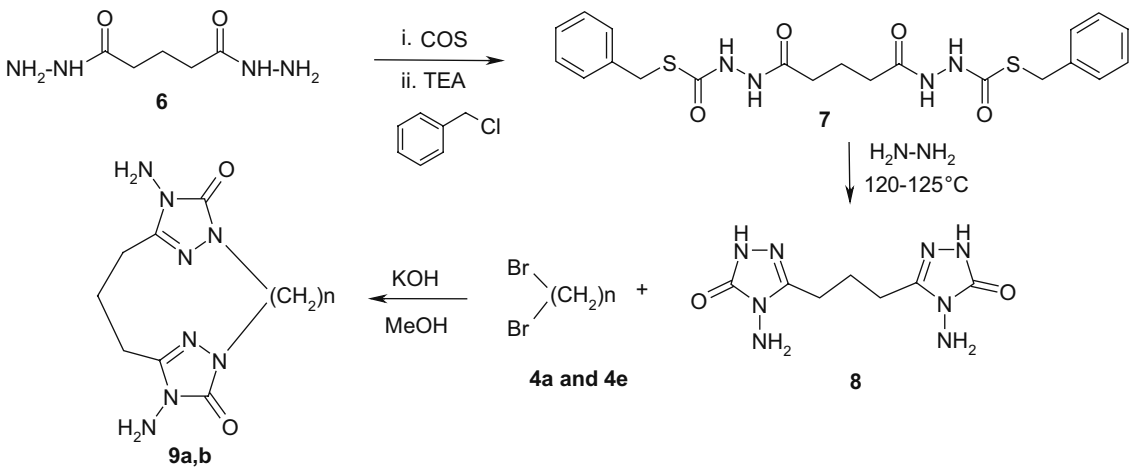
*General experimental procedure*

All chemicals were obtained from E-Merck and Qualigens. Solvents were purified according to reported methods. The progress of the reactions was followed with TLC using silica gel SILG/UV 254 plates. Chromatography was carried on a column over silica gel 60, 0.063–0.200 mm (70–230 mesh ASTM). IR spectra were run on a Perkin Elmer 257-FTIR 1600 spectrophotometer using potassium bromide (KBr) discs. The $^{1}H$ and $^{13}C$ NMR (300 MHz) were run on a JEOL AL-300 spectrometer (δ in ppm, *J* in Hz). Mass spectra were recorded on a Shimadzu GCMS-QP 2010. The C, H, N, S analysis of the compounds were carried out at UICT, analytical chemistry department, Mumbai and are in agreement with the theoretical values. Melting points were taken in open capillaries and are uncorrected.

*Synthesis of 1,3-bis[ethoxycarbonylmethoxy-phenoxy]-acetic acid* **(1):** Resorcinol (11.01 g, 0.1 mmol) and ethyl bromoacetate (16.7 g, 0.2 mmol) were refluxed under stirring at 78 °C in acetone (100 ml) in the presence of potassium carbonate (41.4 g, 0.3 mmole) for 12 h. The reaction mixture was then filtered and solvent was removed under reduced pressure. An oily compound was obtained which was then dissolved in dichloromethane and washed with 2% NaOH solution, aqueous $NH_4Cl$ and finally with distilled water. It was then dried over sodium sulfate and concentrated. Recrystallisation of the residue from ethyl acetate–petroleum ether afforded **1** as off-white crystalline compound; yield: 21.33 g (96%); m.p. 42–44 °C.



**Scheme 1**



**Scheme 2**

*Synthesis of hydrazide* **(2):** Compound **1** (5.64 g, 0.02 moles) was dissolved in methanol (25 ml) and refluxed with hydrazine hydrate (99%, 2.0 g, 0.04 moles) for 4 h. Compound **2** was separated out as a colourless solid, which was filtered, washed with cold methanol, and recrystallised from hot water to give colourless crystals of **2**; yield: 85%; m.p. 220 °C. IR (KBr, in $cm^{-1}$) 3442, 1610, 1420, 1338 and 1283. $^1$H NMR (DMSO-$d_6$) δ 4.33 (s, 4H, 2 x ring-C$\underline{H}_2$-O), 4.45 (s, 4H, 2 x –N–N$\underline{H}_2$, $D_2O$ exchangeable), 6.55 to 7.21 (m, 4H, ArH) and 9.33 (s, 2H, –NH, $D_2O$ exchangeable). $^{13}$C NMR (DMSO-$d_6$) 66.24 and 66.27 (2 x ring-$CH_2$-O), 101.85, 112.34, 130.06 and 158.89 (Ar-C) and 166.56 ppm (2 x >C=O). Anal. Found C, 46.9; H,5.2; N,21.6.Calcd for $C_{10}H_{14}N_4O_4$: C, 47.2; H,5.55; N,22.0%.

*Synthesis of phane precursor 1,3-bis [ (4-amino-5-oxy-1,2,4-triazol-3-yl) methyleneoxy] benzene* **(3)**: Compound **2** (2.86 g, 0.01 mole) was dissolved in ethanolic (20 ml) potassium hydroxide (1.12 g, 0.02 moles) and a dry stream of carbonoxysulfide was then passed through it for 3 h. The dipotassium salt of the respective thiocarbamic acid separated out. This was then filtered and washed with acetone–pet ether solution (1 : 1). The dried salt was then immediately fused with hydrazine hydrate (1.0 g, 0.02 moles) at 110–120 °C in an oil bath for 3 hr. The reaction mixture was then cooled to room temperature and poured onto crushed ice and acidified with dil. hydrochloric acid (to pH = 7). An off-white solid was obtained which was filtered, washed with water and crystallised from DMF–water (1 : 1) mixture.

*Analytical data for compound* **3:** Yield 53%. m.p. 270 °C. IR (KBr, $cm^{-1}$) 3270 ($NH_2$ stret.), 1708 (C=O) and 1596 (C=N stret) $cm^{-1}$. $^1$H NMR (DMSO-$d_6$): δ 5.67 (s, 4H, 2x–N–$NH_2$, $D_2O$ exchangeable), 5.29 (s, 4H, 2 x ring–C$\underline{H}_2$–O), 7.03 to 7.60 (4H, aromatic protons) and 12.14 (s, 2H, –NH, $D_2O$ exchangeable). $^{13}$C NMR (DMSO-$d_6$): 60.10 (2x ring–$\underline{C}H_2$–O), 102.38, 108.34 and 130.49 (aromatic carbons), 144.82 (2x O–$CH_2$–$\underline{C}$=N), 154.74 & 159.24(2x–ArC–O–$CH_2$) and 167.07 ppm (2 x >C=O). $\underline{MS}$: $M^+$ at *m/z* 334. The other prominent peaks were at *m/z* 290, 274, 226, 135, 91 and 77. Anal. Found C,42.8; H,4.05; N,33.3.Calcd for $C_{12}H_{14}N_8O_4$: C,43.1; H,4.2; N,33.5%.

*N'-[5-(N'-benzylsulfanylcarbonyl-hydrazino)-5-oxo-pentanoyl]-hydrazinecarbothioic acid S-benzyl ester* **(7):** Glutaric acid dihydrazide **6** (1.6 g, 0.01 mole) and triethylamine (2.02 g, 0.02 mole) were dissolved in dimethylformamide (20 ml). A dry stream of COS

was then bubbled through for 30 min at 0–5 °C. Benzyl chloride (2.52 g, 0.02 mole) was added to the reaction mixture and COS gas was passed for further 3 h. A triethylammonium salt separated out. It was then filtered and the filtrate was poured onto crushed ice. A colourless solid was obtained which was filtered, washed with water and dried. Purification by column chromatography using ethylacetate: heptane (1:3) as the eluent afforded a colourless solid. Yield 53%. m.p.151 °C**.** $^1$H NMR (DMSO-$d_6$) δ 1.50 (s, 2H, CO–$CH_2$–$CH_2$), 2.18 (s, 4H, 2 x CO–$CH_2$), 4.10 and 4.18 (2 s, S-$CH_2$), 7.20 to 7.50 (10H, ArH) and 9.711, 9.812 & 9.966 (3 s, 4H, –NH, $D_2O$ exchangeable). $^{13}$C NMR in (DMSO-$d_6$) 22.36, 32.30 & 33.12(2x $CH_2$), 122.38, 126.58, 128.52 and 139.49 (ArC), 166.23, 172.22, 172.68 and 173.01 ppm (4 x >C=O). Anal. Found C,54.4; H, 4.95; N,12.0; S,13.6; Calcd for $C_{21}H_{24}N_4O_4S_2$: C,54.8; H, 5.25; N,12.2; S,13.9%.

*Synthesis of 1,3-bis(4-amino-5-oxo-1,2,4-triazol-3-yl) propane* **(8):** Compound **7** (4.60 g, 0.01 mole) was heated with hydrazine hydrate (99%, 0.96 ml, 0.03 mole) at 120–130 °C for 4 h. The reaction mixture was then cooled and washed with ethyl acetate to remove unreacted compound **7**. It was then washed with water and finally crystallised from hot water to afford an off white coloured solid.

*Analytical data for compound* **(8):** Colourless solid**;** Yield: 50%; m.p. 270–272 °C. $^1$H NMR (DMSO-$d_6$) δ 2.40 (2H, ring–$CH_2$–$CH_2$), 3.51 (4H, 2x ring–$CH_2$), 5.09 (s, 4H, 2x–N–$NH_2$) and 11.35 (s, 2H, –NH, $D_2O$ exchangeable). $^{13}$C NMR in (DMSO-$d_6$) 17.55 and 20.74 (3 methylenic carbons), 148.06 (2x–C=N) and 154.50 and 154.80 ppm (2 x >C=O). Anal. Found C,34.8; H, 4.85; N,46.4. Calcd for $C_7H_{12}N_8O_2$: C,35.0; H, 5.0; N, 46.65%.

*Regioselective synthesis of the macrocycles: General procedure*
1,3-Bis[(4-amino-1,2,4-triazole-5-one) methyleneoxy] benzene, (0.01 mole) was dissolved in potassium hydroxide (0.02 mole) in aqueous methanol (200 ml, 20 : 80). 1, ω-dibromo alkane (0.01 mole) dissolved in methanol (10 ml) was then added dropwise under stirring. The reaction mixture was then refluxed at 70 °C for 6 h. On cooling a white solid was obtained in the reaction mixture. This was filtered, washed with water and dried. Compounds **9a,b** were also synthesised using the high dilution technique as described above.

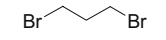
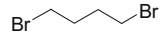
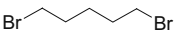
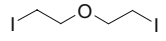
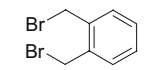
*Analytical data for $1^4$,$5^4$-diamino-8(1,3)-benzena-7,9-dioxa-1,5(1,3)-di(5-oxo-1,2,4-triazola)-decaphane* **(5a):** An off-white coloured solid; Yield: 45%; m.p. 145. $^1$H NMR (DMSO-$d_6$): δ 1.98. (*p*, 2H, *J* = 6.5 Hz–N–$CH_2$–$CH_2$), 3.72 (*t*, 4H, *J* = 6.5 Hz,–N–$CH_2$), 4.91 (*s*, 4H, –O–$CH_2$), 5.38(s, 4H,–N–$NH_2$) and 6.64 to 7.20 (m, 4H, aromatic protons). $^{13}$C NMR (DMSO-$d_6$) 25.24(–N–$CH_2$–$CH_2$), 44.28(–N–$CH_2$), 60.10 and 68.45 (2x ring–$CH_2$–O), 102.02, 108.29 and 130.02 (ArC), 143.13 and 143.20 (2x O–$CH_2$–C=N), 152.70 (ArC–O–$CH_2$) and 158.47 and 158.91 ppm (2 x >C=O). Anal. Found C, 47.8; H, 4.5; N, 29.6. Calcd for $C_{15}H_{18}N_8O_4$: C, 48.1; H, 4.85; N, 29.9%.

*Analytical data for $1^4$,$6^4$-diamino-8(1,3)-benzena-8,10-dioxo-1,6(1,3)-di(5-oxo-1,2,4-triazola)-cycloundecaphane* **(5b):** Colourless solid; Yield: 60%; m.p. 133–135 °C. $^1$H NMR (DMSO-$d_6$) δ 1.57 (quintet, 4H, *J* = 7 Hz, 2x–N–$CH_2$–$CH_2$), 3.68 (t, 4H, *J* = 7 Hz, 2x–N–$CH_2$), 4.91 (s, 4H,–O–$CH_2$), 5.39 (s, 4H. –N–$NH_2$) and 6.64 to 7.20 (aromatic protons). $^{13}$C NMR (DMSO-$d_6$) 25.24 (2x–N–$CH_2$–$CH_2$), 44.25(2x–N–$CH_2$), 57.73 and 59.64 (2x ring–$CH_2$–O), 105.02, 108.45 and 130.02 (ArC), 143.13 (O–$CH_2$-C=N), 152.70 (2x ArC–O–$CH_2$) and 158.91 ppm (>C=O). Mass spectrum showed molecular ion peak $M^+$ at *m/z* 388. The other prominent peaks were at *m/z* 290, 274, 226, 135, 91 and 77. Anal. Found C, 49.2; H,4.8; N,28.6. Calcd for $C_{16}H_{20}N_8O_4$: C, 49.5; H,5.2; N,28.85%.

*Analytical data for $1^4$,$7^4$-diamino-9(1,3)-benzena-9,11-dioxa-1,7(1,3)-di(5-oxo-1,2,4-triazola-cyclododecaphane* **(5c):** Pale brown solid; Yield: 47%,; m.p. 120–122 °C. $^1$H NMR (DMSO-$d_6$) δ 1.80 (quintet, 2H, *J* = 6.5 Hz,N–$CH_2$–$CH_2$–$CH_2$), 3.10 (quintet, 4H, *J* = 6.5 Hz,–N–$CH_2$–$CH_2$), 3.68 (t, 4H,*J* = 6.5 Hz,–N–$CH_2$), 4.90(s, 4H,–O–$CH_2$), 5.45 (s, 4H,–N–$NH_2$) and 6.66 to 7.50 (aromatic protons). $^{13}$C NMR (DMSO-$d_6$) 22.76 (–N–$CH_2$–$CH_2$–$CH_2$), 27.69 and 28.57 (2x–N–$CH_2$–$CH_2$), 44.82 and 44.84(2x–N–$CH_2$), 59.48 and 59.82 (2x–O–$CH_2$), 107.96, 111.31 and 130.18 (aromatic carbons), 143.19(–C=N), 152.82 (ArC–O–$CH_2$) and 159.06 ppm (>C=O). Anal. Found C, 50.4; H,5.2; N,27.5. Calcd for $C_{17}H_{22}N_8O_4$: C, 50.7; H,5.5; N,27.85%.

*Analytical data for $1^4$,$7^4$-diamino-4(1,3)-benzena-3,5-dioxa-1,7(1,3)-di(5-oxo-1,2,4-triazola-cycloheptadecaphane* **(5d):** A colourless solid; yield: 54%; m.p. 197–199°C. $^1$H NMR ($CDCl_3$) δ 1.20 to 1.62 (m, 16H, 8$CH_2$), 3.26 (quintet, 4H, *J* = 6.5 Hz –N–$CH_2$), 3.56 (s, 4H,–O–$CH_2$), 4.97 (s, 4H,–N–$NH_2$) and 6.15 to 7.24 (aromatic protons). $^{13}$C NMR ($CDCl_3$) 25.48, 25.63, 26.51, 26.79, 27.43, 27.94, 28.52 and 29.64 (8C, –N–$CH_2$–chain carbons), 45.65 (2x–N–$CH_2$), 72.64 (2x–O–$CH_2$), 110.83, 121.30, 126.87 and 129.91 (aromatic carbons), 142.49 and 142.61(2x–C=N), 153.01 (ArC–O–$CH_2$) and 158.85 ppm (>C=O). Anal. Found C, 55.6; H,6.5; N,23.4. Calcd for $C_{22}H_{32}N_8O_4$: C, 55.9; H,6.8; N,23.7%.

**Table 1**

| Entry | Compound No. | Structure |
|---|---|---|
| 1 | **4a** |  |
| 2 | **4b** |  |
| 3 | **4c** |  |
| 4 | **4d** |  |
| 5 | **4e** |  |

*Analytical data for $1^4$,$7^4$-diamino-4(1,3),9(1,2)-dibenzena-3,5-dioxa-$1^5$,$7^5$-dioxo-(1,7)(1,3)-1,2,4-triazola-cyclodecaphane* **(5e):** Pale brown solid**;** yield: 47%; m.p. 110–112 °C. $^1$H NMR (DMSO-$d_6$): δ 3.43 (s, 4H, 2x–N–$CH_2$), 4.59 and 4.68 (s, 4H, 2x–O–$CH_2$), 4.93 and 5.05 (s, 4H,–N–$NH_2$) and 6.47 to 7.66 (aromatic protons). $^{13}$C NMR (DMSO-$d_6$) 45.42 (–N–$CH_2$), 57.57 and 59.68 (2x–O–$CH_2$), 102.56, 128.38, 128.89, 129.23, 129.63, 129.87 to 130.03 (aromatic carbons), 142.34(–C=N), 152.785 (ArC–O–$CH_2$) and 158.905 ppm (>C=O). Mass spectrum gave molecular ion peak M + at *m/z* 436. The other major fragments were at *m/z* 420, 379, 324, 216, 117, 104, 91 and 77. Anal. Found C, 54.9; H,4.3; N,25.4. Calcd for $C_{20}H_{20}N_8O_4$: C, 55.0; H,4.6; N,25.7%.

*Analytical data for $1^4$,$5^4$-diamino-1,5(1,3)-di(5-oxo-1,2,4-triazola) cyclononaphane* **(9a):** An off-white solid**;** yield: 35%; m.p. 160–161 °C. IR (KBr, in $cm^{-1}$) 3300, 3209, 2938, 1706 (C=O, stretching) and 1642(C=N, stretching). $^1$H NMR (DMSO-$d_6$) δ 0.995 (*quintet*, 2H, *J* = 7.0 Hz, ring–$CH_2$–$CH_2$), 1.495(*quintet*, 4H, *J* = 6.5 Hz, 2x–N–$CH_2$–$CH_2$), 2.835(*triplet*, 4H, *J* = 7.0, ring–$CH_2$), 3.56(*triplet*, 4H, *J* = 6.5 Hz, 2x–N–$CH_2$) and 5.33(s, 4H, 2x–N–$NH_2$, $D_2O$-exchangeable). Mass spectrum (DI method) exhibited M + ion at *m/z* 294. The other main fragments were at *m/z* 278, 263, 140, 122 and 94. Anal. Found C, 44.5; H,5.9; N,37.7. Calcd for $C_{11}H_{18}N_8O_2$: C, 44.9; H,6.2; N,38.1%.

*Analytical data for $1^4$,$5^4$-diamino-3(1,3)benzena-1,5(1,3)-di(5-oxo-1,2,4-triazola)cyclo octaphane* **(9b):** An off-white solid**;** yield: 33%; m.p. 120–122 °C. IR (KBr, in $cm^{-1}$) 3316, 3211, 1701 (>C=O str), 1701 and 1584. $^1$H NMR (DMSO-$d_6$) δ 2.18 (*quintet*, 2H, *J* = 7.0 Hz, 2x–$CH_2$–$CH_2$), 3.69 (*triplet*, 4H, *J* = 7.0 Hz, 2x–$CH_2$), 4.39(s, 4H, 2x–N–$CH_2$), 5.30 (4H, 2x–N–$NH_2$, $D_2O$ exchangeable) and 7.28–7.38 (m, 4H, ArH). $^{13}$C NMR (DMSO-$d_6$) 14.17 (ring–$CH_2$–$CH_2$), 20.86 (2x ring–$CH_2$), 45.38(2x–N–$CH_2$), 126.61, 127.33 and 128.93 (ArC), 147.77 (2x >C=N) and 153.16 ppm (2x >C=O). Anal. Found C, 52.3; H,5.0; N,32.4. Calcd for $C_{15}H_{18}N_8O_2$: C,52.6; H,5.3; N,32.7%.

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