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ORIGINAL ARTICLE

Synthesis and structural characterization of 18-, 19-, 20- and 22-membered Schiff base macrocycles

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Abstract Six new dioxadiaza macrocyclic Schiff bases with 18-, 19-, 20- and 22-membered rings have been synthesized from diamine and dialdehyde building blocks. An X-ray diffraction study and molecular modelling (at the HF/6-31G(d,p) level of theory) have been performed to determine their molecular geometries and structural configurations. According to the theoretical studies the most stable conformers of the macrocycles are those, in which the lone pair electrons localized on the nitrogen atoms are *exo*-oriented, and those on the oxygen atoms are *endo*-oriented with respect to the cavity. In order to obtain more proper metal ion receptors with all lone pair electrons directed into the cavity, two Schiff base macrocycles have been reduced to the corresponding diamines, of which one could be isolated only as a very stable oxaazacyclophane borane adduct.

Keywords Schiff bases · Macrocycles · Oxaazacyclophanes · Molecular modelling

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Introduction

The interest in exploring new metal ion complexes with macrocycles containing nitrogen and oxygen donor atoms has been increasing, because they result very attractive for supramolecular and coordination chemistry. Particularly important are systems that are related to bioactive molecules such as metalloporphyrins, corrins and antibiotics [1, 2].

A convenient route for the construction of polyoxaaza macrocycles is Schiff base condensation, a method that has been developed already for the synthesis of one of the first macrocycles employed for metal complexation. Varying the number, position and orientation of the donor atom lone pair electrons within the polyoxaaza macrocycles as well as the cavity size, highly selective receptors for a variety of metal ions can be designed [2]. On the other hand, through the proper choice of building blocks for the formation of the Schiff base macrocycles it is possible to obtain compounds with attractive and sophisticated structures, which could be employed for creating new materials such as chemical sensors, catalysts, liquid crystals, and pharmaceutical substances [3–5].

Many synthetic protocols for the preparation of tetra- [6–11], penta- [12–32], hexa-, and polydentate Schiff base macrocyclic compounds involve metal ions as templating agents that orient all or part of the ligand donor atoms into an optimal conformation for the ring closure [1, 2, 33–41]. However, the template synthetic method can have the disadvantage that stable metal-complexed macrocycles are generated, thus making the preparation of the metal-free ligand difficult. Therefore, during the last two decades, considerable effort has been made to develop metal-free methods for the synthesis of macrocycles [2, 42], in particular to overcome the common problem that the desired product is obtained in very low yield.

We are interested in new synthetic [43–45] and semi-synthetic [46–50] macrocycles containing oxygen and nitrogen atoms in order to study their coordinating capacity towards metal cations as well as their ability to act as hosts for neutral and charged guest atoms and molecules. We report herein on the synthesis and structural characterization of six new Schiff base dioxadiaza macrocycles and some of their hydrogen-reduced amine analogues.

Experimental section

All reagents for synthesis were purchased from commercial suppliers and used without further purification. NMR spectra were recorded on 400 MHz Bruker AVANCE 400 and Varian UNITY INOVA spectrometers. Chemical shifts (δ) are reported in ppm relative to tetramethylsilane and J values are given in Hertz. Mass spectra were recorded on a high resolution Jeol MStation 700 mass spectrometer using the FAB^+ technique. Infrared spectra were recorded on a Perkin-Elmer Spectrum GX FTIR spectrophotometer. Melting points are uncorrected.

X-ray crystallography

Compound **3** was crystallized from ethanol and the oxaazacyclophane-borane adduct **10** from chloroform. X-ray diffraction studies were performed at 293(2) K on a BRUKER-AXS APEX diffractometer with a CCD area detector (MoK_α, $\lambda = 0.71073$ Å, monochromator: graphite). Frames were collected via ω/ϕ-rotation at 10 s per frame (SMART) [51]. The measured intensities were reduced to F^2 and corrected for absorption with SADABS (SAINT-NT) [52]. Structure solution, refinement, and data output were carried out with the SHELXTL-NT software package [53]. Non-hydrogen atoms were refined anisotropically, while hydrogen atoms were placed in geometrically calculated positions using a riding model. The N–H and B–H hydrogen atoms in compound **10** have been localized by difference Fourier maps. The crystals of compound **10** were weak and contained solvent molecules ($CHCl_3$), thus giving somewhat elevated R values.

Details of the crystal structure determination and solution refinement of **3** ($C_{28}H_{22}N_2O_2$): colourless rectangular prism with dimensions $0.52 \times 0.20 \times 0.16$ mm^3, $M = 418.48$ g mol^{-1}, orthorhombic, $P2_12_12_1$, $a = 9.4764(13)$, $b = 10.7696(14)$, $c = 21.506(3)$ Å, $V = 2{,}194.8(5)$ Å^3, $Z = 4$, $\rho_{calc} = 1.266$ mg/m^3, $\mu = 0.080$ mm^{-1}, 2430 independent reflections measured, 1719 reflections observed with $I \geq 2\sigma(I)$, parameters refined 289, $R = 0.078$, $R_w = 0.1338$, goodness of fit = 1.158. Details of the crystal structure determination and solution refinement of **10** ($C_{28}H_{40}B_2N_2O_2 \cdot CHCl_3$): [50] colourless rectangular prism with dimensions $0.35 \times 0.23 \times 0.18$ mm^3, $M = 577.61$ g mol^{-1}, triclinic, P-1, $a = 10.3152(10)$, $b = 10.9207(11)$, $c = 15.6942(16)$ Å, $\alpha = 110.262(2)$, $\beta = 98.274(2)$, $\gamma = 101.512(2)$, $V = 1{,}580.9(3)$ Å^3, $Z = 2$, $\rho_{calc} = 1.213$ mg/m^3, $\mu = 0.318$ mm^{-1}, 5548 independent reflections measured, 3824 reflections observed with $I \geq 2\sigma(I)$, parameters refined 367, $R = 0.1228$, $R_w = 0.2416$, goodness of fit = 1.253.

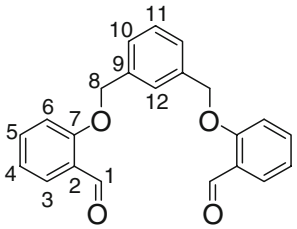
Crystallographic data for **3** and **10** have been deposited at the Cambridge Crystallographic Data Center as CCDC No. 663938 and No. 650762 respectively. Copies of the data can be obtained free of charge upon application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (e-mail: deposit@ccdc.cam.ac.uk).

Computational methods

The geometry of each stationary point was fully optimized using the Gaussian 03 software package [54] with the double zeta 6-31G(d,p) basis set. All stationary points were characterized as minima as proved by an analysis of the harmonic vibrational frequencies, using analytical second derivatives. All of the structures were visualized with the Chemcraft 1.5 program [55].

Dialdehyde **1**

This compound was prepared by a modified procedure to that reported previously [56, 57] A solution of salicylaldehyde (1.00 g, 8 mmol) in anhydrous DMF (5 mL) was added to a suspension of K_2CO_3 (in excess) in the same solvent (25 mL). The suspension was kept under nitrogen and stirred at 80 °C during 30 min. Then, a solution of α,α′-dibromo-*m*-xylene (1.08 g, 4 mmol) in anhydrous DMF (5 mL) was added slowly to the mixture and the resulting suspension was then stirred at 80 °C. The reaction was monitored by TLC (heptane:acetone 60:40) until a single product was observed and the starting material disappeared. The suspension was filtered in order to remove the potassium salt. The filtrate was evaporated in vacuum to dryness and acetone was added until a precipitate appeared. A light-brown solid was obtained after filtration, acetone washing, and drying in vacuum.

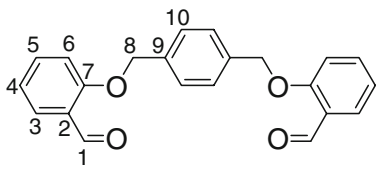


1

Yield: 95%; m.p. 112–114° (from acetone); ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C, TMS): δ = 10.56 (s, 2 H, H-1), 7.86 ppm (dd, ^3J(H–H) = 7.6 Hz, ^4J(H–H) = 2 Hz, 2 H; H-3), 7.57 ppm (d, ^3J(H–H) = 7.6 Hz, 2 H; H-10), 7.54 ppm (dt, ^4J(H–H) = 1.6 Hz, ^3J(H–H) = 8 Hz, 2 H; H-5), 7.45 ppm (t, ^3J(H–H) = 7.6 Hz, 1 H; H-11), 7.46 ppm (s, 1 H; H-12), 7.08 ppm (t, ^3J(H–H) = 7.6 Hz, 2 H; H-4), 7.05 ppm (d, ^3J(H–H) = 8 Hz, 2 H; H-6), 5.23 ppm (s, 4 H; H-8); ^{13}C NMR (400 MHz, DMSO-d_6, 25 °C; δ, ppm): δ = 189.8 (C-1), 161.0 (C-7), 136.9 (C-9), 136.1 (C-10), 129.4 (C-12), 128.9 (C-3), 127.3 (C-11), 126.2 (C-5), 125.3 (C-2), 121.3 (C-6), 113.1 (C-4), 70.4 (C-8); IR (KBr, cm^{-1}): ν = 3014 (w), 2935 (w), 2878 (m), 2765 (w), 1668 (s), 1600 (s), 1482 (s), 1459 (s), 1403 (m), 1369 (m), 1303 (s), 1288 (s), 1233 (s), 1185 (m), 1164 (m), 1104 (m), 1008 (s), 898 (m), 846 (m), 821 (m), 790 (m), 773 (m), 711 (s); FAB-MS: m/z (%) 347 ([M$^+$], 25), 307 (21), 289 (13), 225 (45), 224 (13), 197 (16), 195 (11), 154 (100), 136 (64), 121 (9), 106 (6); Elem anal. Calcd for $C_{22}H_{18}O_4$ (346.38): C, 76.29; H, 5.24; O, 18.48; found: C, 75.96; H, 5.24.

Dialdehyde **2**

Compound **2** was prepared in a similar manner to that described for dialdehyde **1** using α,α'-dibromo-*m*-xylene (1.08 g, 4 mmol) and salicylaldehyde (1.00 g, 8 mmol). The product was obtained as white crystals in higher yield (see below) to that reported previously in the literature (84%) [57].

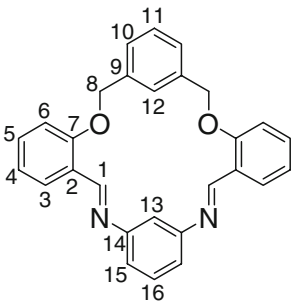


2

Yield: 98%; m.p. 188–190 °C (from acetone); ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C, TMS): δ = 10.57 (s, 2 H; H-1), 7.87 ppm (dd, ^3J(H–H) = 8.0 Hz, ^4J(H–H) = 1.8 Hz, 2 H; H-3), 7.56 ppm (dt, ^3J(H–H) = 8.0 Hz, ^4J(H–H) = 1.8 Hz, 2 H; H-5), 7.50 ppm (s, 4 H, H-10), 7.07 ppm (t, ^3J(H–H) = 8.0 Hz, 2 H; H-4), 7.05 ppm (d, ^3J(H–H) = 8.0 Hz, 2 H; H-6), 5.24 ppm (s, 4 H; H-8); ^{13}C NMR (400 MHz, DMSO-d_6, 25 °C; δ, ppm): δ = 189.9 (C-1), 161.1 (C-7), 136.4 (C-9), 136.1 (C-5), 128.8 (C-3), 127.9 (C-10), 125.4 (C-2), 121.3 (C-4), 113.2 (C-6), 70.3 (C-8); IR (KBr, cm^{-1}): ν = 2936 (w), 2850 (m), 2763 (m), 1687 (s), 1599 (s), 1488 (s), 1458 (s), 1401 (m), 1376 (s), 1307 (s), 1286 (s), 1242 (s), 1191 (s), 1164 (s), 1102 (s), 1009 (s), 994 (s), 866 (m), 851 (m), 803 (m), 779 (s); FAB-MS: m/z (%) 345 ([M$^+$], 28), 329 (1), 307 (22), 289 (14), 273 (2), 260 (2), 242 (2), 225 (9), 219 (5), 192 (100), 165 (4). Elem anal. Calcd for $C_{22}H_{18}O_4$ (346.38): C, 76.29; H, 5.24; O, 18.48; found: C, 76.10; H, 5.24.

Macrocycle **3**

Compound **3** was synthesized from **1** (0.16 g, 0.46 mmol) and 1,3-benzenediamine (0.05 g, 0.46 mmol). The reaction mixture was stirred in ethanol under high pressure during 24 h at 70 °C. A considerable amount of yellow crystals appeared during the reaction, which were removed by filtration and then washed with ethanol and dried in vacuum.

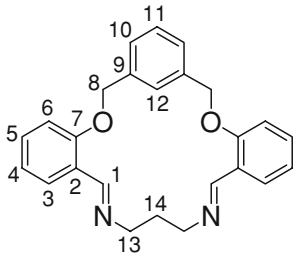


3

Yield: 31%; m.p. 311–314 °C (from ethanol); ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C, TMS): δ = 9.07 (s, 2 H; H-1), 8.22 ppm (dd, ^3J(H–H) = 8 Hz, ^4J(H–H) = 2 Hz, 2 H; H-3), 7.94 ppm (s, 1 H, H-12), 7.49 ppm (dt, ^3J(H–H) = 8 Hz, ^4J(H–H) = 2 Hz, 2 H; H-5), 7.35 ppm (m, 3 H, H-10, H-11), 7.21 ppm (dt, ^3J(H–H) = 8 Hz, ^4J(H–H) = 2 Hz, 2 H; H-15), 7.17 ppm (t, ^3J(H–H) = 8 Hz, 1 H; H-16), 7.12 ppm (d, ^3J(H–H) = 8 Hz, 2 H; H-6), 7.10 ppm (t, ^3J(H–H) = 8 Hz, 2 H; H-4), 6.90 ppm (t, ^4J(H–H) = 2 Hz, 1 H; H-13), 5.09 ppm (s, 4 H, H-8); ^{13}C NMR (400 MHz, DMSO-d_6, 25 °C; δ, ppm): δ = 158.5 (C-1), 157.2 (C-7), 153.6 (C-14), 136.6 (C-9), 132.7 (C-5), 128.9 (C-16), 128.8 (C-3), 128.4 (C-11), 127.0 (C-10), 124.3 (C-12), 121.5 (C-4), 121.2 (C-15), 112.1 (C-2), 112.0 (C-13), 108.2 (C-6), 71.2 (C-8); IR (KBr, cm^{-1}): ν = 3063 (w), 3006 (w), 2928 (w), 2876 (w), 1615 (s), 1599 (s), 1574 (s), 1478 (s), 1456 (s), 1368 (s), 1299 (s), 1265 (s), 1226 (s), 1162 (s), 1145 (m), 11034 (s), 1006 (s), 964 (m), 864 (m), 763 (s); FAB-MS: m/z (%) 419 ([M$^+$], 15), 391 (7), 346 (5), 341 (5), 329 (3), 307 (100), 289 (38), 273 (7), 260 (5), 235 (5), 219 (9). Elem anal. Calcd for $C_{28}H_{22}N_2O_2$ (418.49): C, 80.35; H, 5.30; N, 6.69; O, 7.66; found: C, 80.45; H, 5.29; N, 6.92.

Macrocycle **4**

Compound **4** was prepared in an analogous manner to that described for macrocycle **3**, using **1** (0.16 g, 0.46 mmol) and 1,3-propanediamine (0.342 g, 0.46 mmol). The product was obtained as a white solid.

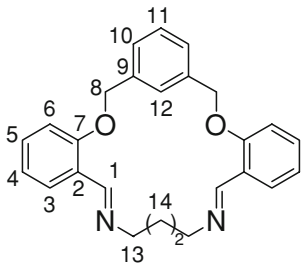


4

Yield: 39%; m.p. 95–197 °C (from ethanol); ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C, TMS): δ = 8.83 (s, 2 H; H-1), 8.02 ppm (dd, ^3J(H–H) = 8 Hz, ^4J(H–H) = 2 Hz, 2 H; H-3), 7.92 ppm (s, 1 H; H-12), 7.38 ppm (dt, ^3J(H–H) = 8 Hz, ^4J(H–H) = 2 Hz, 2 H; H-5), 7.28 ppm (m, 3 H; H-10 and H-11), 7.03 ppm (d, ^3J(H–H) = 8 Hz, 2 H; H-6), 7.01 ppm (t, ^3J(H–H) = 8 Hz, 2 H; H-4), 5.20 ppm (s, 4 H; H-8), 3.59 ppm (t, 4 H; H-13), 2.25 ppm (m, 2 H; H-14); ^{13}C NMR (400 MHz, DMSO-d_6, 25 °C; δ, ppm): δ = 161.8 (C-1), 157.0 (C-7), 137.5 (C-9), 131.8 (C-5), 128.2 (C-3), 127.6 (C-11), 126.0 (C-12), 125.0 (C-10), 124.0 (C-2), 121.2 (C-4), 112.0 (C-6), 69.3 (C-8), 57.2 (C-13), 29.7 (C-14); IR (KBr, cm^{-1}): v = 3680 (w), 3654 (w), 3446 (m), 2911 (w), 2886 (w), 1640 (s), 1598 (s), 1489 (m), 1449 (s), 1371 (m), 1290 (m), 1241 (s), 1044 (m), 752 (m); FAB-MS: m/z (%) 385 ([M$^+$], 100), 369 (2), 341 (2), 309 (9), 307 (57), 289 (26), 273 (5), 260 (3), 242 (3), 235 (4), 219 (5), 207 (2), 202 (1). Elem anal. Calcd for $C_{25}H_{24}N_2O_2$ (384.47): C, 78.08; H, 6.29; N, 7.29; O, 8.34; found: C, 78.48; H, 6.29; N, 7.27.

Macrocycle **5**

Compound **5** was prepared in an analogous manner to that described for macrocycle **3**, using **1** (0.16 g, 0.46 mmol) and 1,4-butanediamine (0.037 g, 0.46 mmol). The product was obtained as a pale yellow solid.

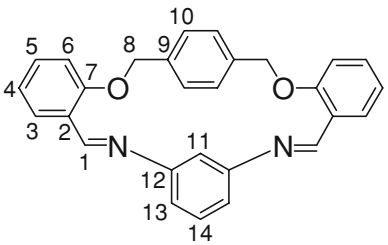


5

Yield: 44%; m.p. 97–102 °C (from ethanol); ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C, TMS): δ = 8.80 (s, 2 H; H-1), 7.97 ppm (dd, ^3J(H–H) = 8 Hz, ^4J(H–H) = 2 Hz, 2 H; H-3), 7.75 ppm (s, 1 H; H-12), 7.41 ppm (dt, ^3J(H–H) = 8 Hz, ^4J(H–H) = 2 Hz, 2 H; H-5), 7.31 ppm (m, 3 H; H-10 and H-11), 6.97 ppm (t, ^3J(H–H) = 8 Hz, 2 H; H-4), 6.93 ppm (d, ^3J(H–H) = 8 Hz, 2 H; H-6), 5.16 ppm (s, 4 H; H-8), 3.67 ppm (t, 4 H; H-13), 1.26 ppm (q, 4 H; H-14); ^{13}C NMR (400 MHz, DMSO-d_6, 25 °C; δ, ppm): δ = 157.6 (C-1), 156.7 (C-7), 137.6 (C-9), 131.6 (C-5), 128.4 (C-11), 127.3 (C-3), 126.5 (C-12), 125.3 (C-10), 124.7 (C-2), 121.1 (C-4), 111.9 (C-6), 69.5 (C-8), 60.5 (C-13), 27.0 (C-14); IR (KBr, cm^{-1}): v = 3331 (w), 3029 (w), 2938 (s), 2839 (s), 1638 (s), 1599 (s), 1581 (m), 1488 (s), 1456 (s), 1372 (s), 1342 (m), 1298 (s), 1286 (s), 1242 (s), 1156 (s), 1111 (m), 1017 (s), 999 (s), 789 (m), 749 (s); FAB-MS: m/z (%) 399 ([M$^+$], 7), 329 (29), 277 (22), 222 (8), 208 (6), 174 (37), 172 (24), 132 (45), 104 (100), 78 (54), 77 (28), 65 (6).

Macrocycle **6**

Compound **6** was prepared in an analogous manner to that described for compound **3**, using **2** (0.16 g, 0.46 mmol) and 1,3-benzenediamine (0.05 g, 0.46 mmol). The product was obtained as a yellow solid.



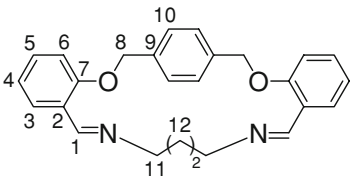
6

Yield: 53%; m.p. 161–164 °C (from ethanol); ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C, TMS): δ = 8.64 (s, 2 H; H-1), 8.10 (dd, ^3J(H–H) = 8 Hz, ^4J(H–H) = 2 Hz, 2 H; H-3), 7.48 ppm (dt, ^3J(H–H) = 8 Hz, ^4J(H–H) = 2 Hz, 2 H; H-5), 7.34 ppm (t, ^3J(H–H) = 8 Hz, 1 H; H-14), 7.33 (t, ^3J(H–H) = 8 Hz, 2 H; H-4), 7.24 ppm (s, 4 H; H-10), 7.15 ppm (dd, ^3J(H–H) = 8 Hz, ^4J(H–H) = 2 Hz, 2 H; H-13), 7.10 ppm (d, ^3J(H–H) = 8 Hz, 2 H; H-6), 6.51 ppm (t, ^4J(H–H) = 2 Hz, 1 H; H-11), 5.14 ppm (s, 4 H; H-8); ^{13}C NMR (400 MHz, DMSO-d_6, 25 °C; δ, ppm): δ = 159.9 (C-1), 156.6 (C-7), 153.0 (C-12), 137.4 (C-9), 132.9 (C-5), 129.6 (C-10), 129.3 (C-14), 127.5 (C-3), 126.0 (C-4), 122.9 (C-13), 121.9 (C-11), 114.7 (C-2), 105.9 (C-6), 73.6 (C-8); IR (KBr, cm^{-1}): v = 3057 (w), 3034 (w), 2942 (w), 2878 (w), 1614 (s), 1598 (s), 1573 (s), 1483 (s), 1452 (s), 1420 (m), 1360 (s), 1261 (s), 1160 (s), 1138 (m), 1100 (s), 1038 (m), 985 (s), 955 (s), 893 (m), 855 (m), 748 (s); FAB-MS: m/z (%) 419 ([M$^+$], 100), 418 (16), 314 (3), 307 (83), 289 (42), 230 (9), 219 (12), 207 (40), 190 (14);

Elem anal. Calcd for $C_{28}H_{22}N_2O_2$ (418.49): C, 80.36; H, 5.30; N, 6.69; O, 7.65; found: C, 79.96; H, 5.26; N, 6.78.

Macrocycle **7**

Compound **7** was prepared in an analogous manner to that described for compound **3** using **2** (0.16 g, 0.46 mmol) and 1,4-butanediamine (0.037 g, 0.46 mmol). The product was obtained as a white solid.

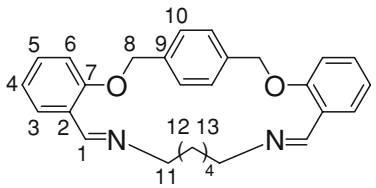


7

Yield: 30%; m.p. 175–178 °C (from ethanol); NMR characterization studies could not be performed because of insolubility of the compound in most common solvents; IR (KBr, cm^{-1}): ν = 3066 (w), 3027 (w), 2930 (s), 2854 (m), 2830 (m), 1644 (s), 1598 (s), 1577 (m), 1518 (m), 1438 (s), 1456 (s), 1374 (s), 1340 (m), 1298 (s), 1281 (s), 1250 (s), 1234 (s), 1160 (m), 1036 (s), 1008 (s), 750 (s); FAB-MS: m/z (%) 399 ([M^+], 31), 391 (4), 371 (3), 345 (6), 307 (100), 289 (52), 273 (9), 235 (10), 196 (4), 192 (12), 165 (10). Elem anal. Calcd. for $C_{26}H_{26}N_2O_2$ (398.5): C, 78.36; H, 6.58; N, 7.03; O, 8.03; found: C, 78.32; H, 6.68; N, 7.09.

Macrocycle **8**

Compound **8** was prepared in an analogous manner to that described for compound **3** using **2** (0.16 g, 0.46 mmol) and 1,6-hexanediamine (0.053 g, 0.46 mmol). The product was obtained as a white powder.

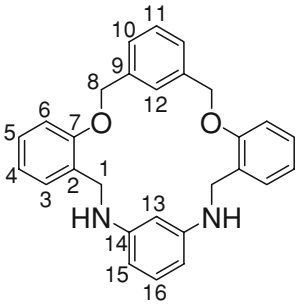


8

Yield: 86%; m.p. 164–166 °C (from ethanol); ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C, TMS): δ = 8.72 (s, 2 H; H-1), 7.82 ppm (dd, ^3J(H–H) = 8 Hz, ^4J(H–H) = 2 Hz, 2 H; H-3), 7.43 ppm (s, 4 H; H-10), 7.38 ppm (dt, ^3J(H–H) = 8 Hz, ^4J(H–H) = 2 Hz, 2 H; H-5), 7.04 ppm (d, ^3J(H–H) = 8 Hz, 2 H; H-6), 7.01 ppm (t, ^3J(H–H) = 8 Hz, 2 H; H-4), 5.16 ppm (s, 4 H; H-8), 3.61 ppm (t, 4 H; H-11), 1.71 ppm (m, 4 H; H-12) 1.38 ppm (m, 4 H; H-13); ^{13}C NMR (400 MHz, DMSO-d_6, 25 °C; δ, ppm): δ = 157.9 (C-1), 156.7 (C-7), 131.6 (C-9), 127.8 (C-5), 127.7 (C-3), 127.5 (C-10), 126.1 (C-2), 121.5 (C-4), 113.1 (C-6), 70.3 (C-8), 61.1 (C-11), 29.6 (C-12), 26.2 (C-13); IR (KBr, cm^{-1}): ν = 3398 (w), 3071 (w), 3034 (w), 2926 (m), 2880 (m), 2824 (m), 1911 (w), 1802 (w), 1688 (w), 1633 (s), 1598 (s), 1579 (s), 1519 (w), 1486 (s), 1452 (s), 1371 (s), 1296 (s), 1284 (s), 1239 (s), 1158 (s), 1105 (s), 1042 (s), 1003 (s), 799 (s), 749 (s); FAB-MS: m/z (%) 427 ([M^+], 100), 426 (9), 322 (3), 307 (18), 289 (12), 273 (2), 257 (2), 242 (2), 222 (5), 208 (7), 204 (12), 202 (7), 165 (4). Elem anal. Calcd for $C_{28}H_{30}N_2O_2$ (426.55): C, 78.84; H, 7.09; N, 6.57; O, 7.50; found: C, 78.49; H, 6.99; N, 6.72.

Macrocycle **9**

The diamine **9** was synthesized from the reaction of Schiff base **3** (0.050 g, 0.11 mmol) and $LiBH_4$ (0.005 g, 0.11 mmol) in dry THF (10 mL) as solvent. The mixture was first stirred at 60 °C during 7.5 h and then overnight at room temperature. Then, a little amount of water was added, the solvents were evaporated in vacuum and a chloroform-water extraction was performed. A white solid was recovered after the organic phase had been evaporated.



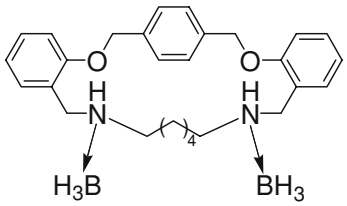
9

Yield: 84%; m.p. 210–212 °C (from chloroform); ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C, TMS): δ = 7.64 (s, 1 H; H-12), 7.43 ppm (dd, ^3J(H–H) = 8 Hz, ^4J(H–H) = 2 Hz, 2 H; H-3), 7.29 ppm (m, 3 H; H-10 and H-11), 7.09 ppm (dt, ^3J(H–H) = 8 Hz, ^4J(H–H) = 2 Hz, 2 H; H-5), 6.93 ppm (t, ^3J(H–H) = 8 Hz, 1 H; H-16), 6.87 ppm (t, ^3J(H–H) = 8 Hz, 2 H; H-4), 6.78 ppm (d, ^3J(H–H) = 8 Hz, 2 H; H-6), 6.07 ppm (dd, ^3J(H–H) = 8 Hz, ^4J(H–H) = 2 Hz, 2 H; H-15), 5.85 ppm (t, ^4J(H–H) = 2, 1 H; H-13), 5.18 ppm (s, 4 H; H-8), 4.33 ppm (s, 4 H; H-1), 1.55 ppm (s, 2 H; N–H); ^{13}C NMR (400 MHz, DMSO-d_6, 25 °C; δ, ppm): δ = 155.9 (C-7), 149.2 (C-14), 138.1 (C-9), 129.5 (C-16), 128.7 (C-11), 128.6 (C-3), 127.9 (C-5), 127.8 (C-2), 126.5 (C-12), 125.2 (C-10), 120.9 (C-4), 111.9 (C-6), 103.5 (C-15), 97.2 (C-13), 69.6 (C-8), 43.0 (C-1); IR (KBr, cm^{-1}): ν = 3433 (s), 3034 (w), 2917 (m), 1612 (s), 1590 (s), 1519 (s), 1486 (s), 1458 (s), 1361 (m), 1306 (s), 1219 (s), 1155 (m), 1062 (m), 1035 (s), 810 (s), 924 (m),

810 (s), 778 (s), 755 (s); FAB-MS: m/*z* (%) 422 ([M^+], 20), 420 (17), 401 (48), 341 (33), 327 (59), 281 (100), 267 (41), 207 (74), 191 (45).

Oxaazacyclophane borane adduct **10**

Details of the synthesis and characterization of this compound were recently reported by our group [50].



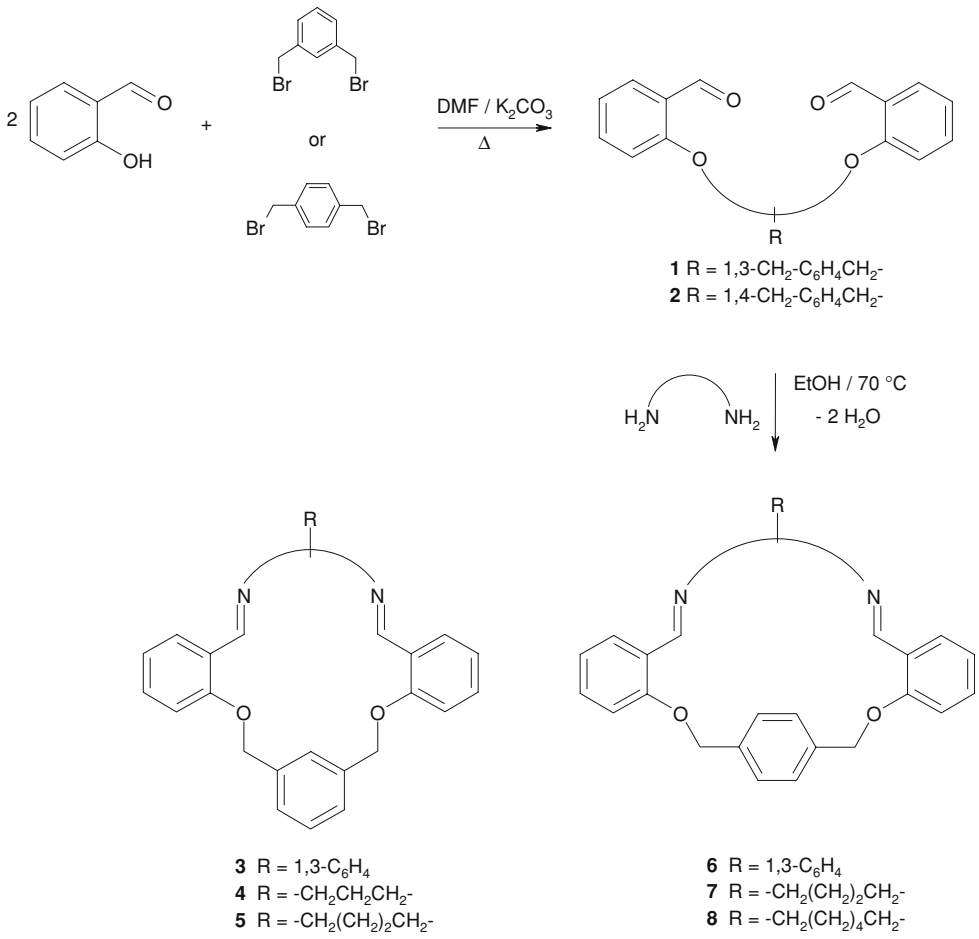
10

Results and discussion

Following the two-step protocol shown in Scheme 1, the Schiff base macrocycles **3–8** were synthesized. Reaction of salicylaldehyde with α,α′-dibromo-*m*-xylene and α,α′-dibromo-*p*-xylene gave the corresponding dialdehydes **1** and **2**, which were then condensed with diamines having a nitrogen separation proper for the ring closure. In the case of the *m*-xylylene dialdehyde derivative, 1,3-benzenediamine, 1,3-propanediamine and 1,4-butanediamine were chosen, while for the *p*-xylylene dialdehyde derivative 1,3-benzenediamine, 1,4-butanediamine and 1,6-hexanediamine have been employed, in order to obtain a series of compounds that might be suitable for the complexation of at least one metal ion within the cavity. In such a way dioxadiaza macrocycles having ring sizes varying from 18 to 22 members have been obtained (18 for **3** and **4**, 19 for **5** and **6**, 20 for **7** and 22 for **8**).

The formation of the Schiff base compounds could be evidenced by the IR spectra that showed intense bands at $\nu = 1615$, 1640, 1638, 1614, 1644 and 1633 cm^{-1} for compounds **3–8**, respectively, which correspond to the stretching vibration of the C=N bonds. The ^1H NMR spectra showed single signals for the protons corresponding to the –HC=N– group at 9.07, 8.83, 8.80, 8.64 and 8.72 ppm for compounds **3–6** and **8**, respectively. Compound **7** is insoluble in most of the common organic solvents and could therefore not be characterized via this

Scheme 1 Synthetic protocol used for the synthesis of compounds **1–8**



spectroscopic method. In the ^{13}C NMR spectra, the signal corresponding to the imine group was observed at $\delta = 158.5$, 161.8, 157.6, 159.9 and 157.9 ppm for **3–6** and **8**, respectively. FAB$^+$ mass spectrometry gave peaks at m/z = 419, 385, 399, 419, 399 and 427 that correspond to the $[M + H]^+$ ions of compounds **3–8**, respectively.

Since the new Schiff bases contain two nitrogen and two oxygen donor atoms, a theoretical study was carried out to evaluate the orientation of the lone pair electrons on the donor atoms in order to know if the synthesized compounds are suitable to coordinate metal atoms. We explored all possibilities taking into account that the imine C=N bond can have *E* and *Z* configuration, and found that the *E* isomers have lower energy when compared to the *Z* isomers. There are two different configurations for the *E* isomers, which differ in the orientation of the lone pair electrons located at the nitrogen atoms. The lowest energy was found for those structures where the lone pair electrons

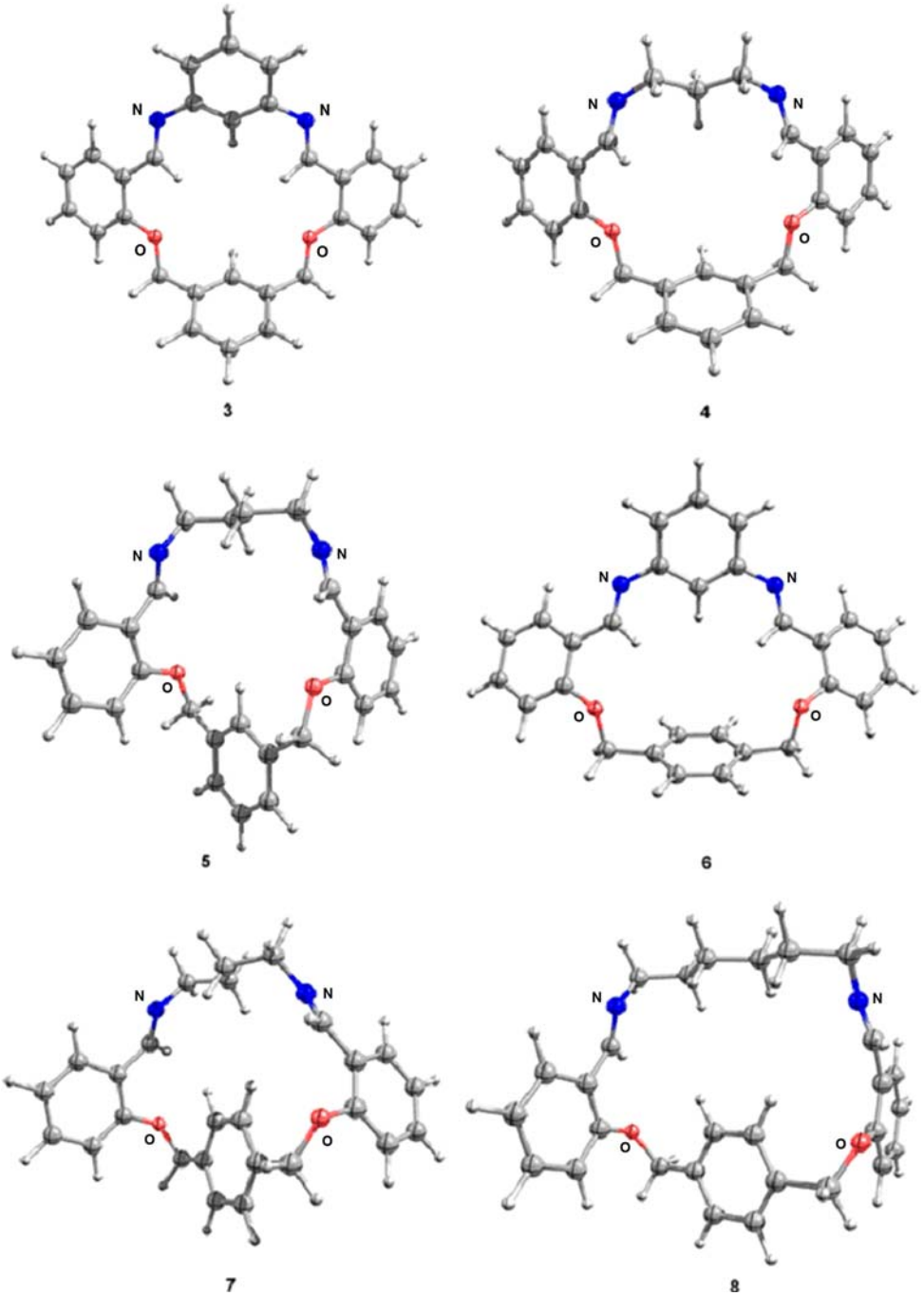


Fig. 1 Geometry-optimized molecular structures for compounds **3–8** using ab initio calculations at the HF/6-31G(d,p) level of theory

on the nitrogen atoms are oriented towards the periphery of the macrocycle (*exo*), while the lone pair electrons of the oxygen atoms are oriented into the cavity (*endo*) (Fig. 1). Structures **3**, **4** and **6** belong to the point group C_s, while **5**, **7** and **8** belong to the point group C_2.

This is supported by the X-ray structure of compound **3**. From Fig. 2 it can be seen that the orientation of the donor atoms is in agreement with the calculated structure shown in Fig. 1.

Apparently, in this arrangement the annular tension in the central heterocycle is minimized and there is an attractive interaction between the imine hydrogen atoms and the oxygen atoms within the macrocycle. The NBO (Natural Bond Orbitals) analysis suggests, for the case of structure **3**, that the lone pair electrons of the oxygen atoms are delocalized mainly into the aromatic ring of the salicylidene fragment: $n_O \rightarrow \pi^*_{C=Carom}$ (Fig. 3a). The stabilization energy E(2) for this interaction is 39.04 kcal/mol. The C–H···O intraannular interaction is much smaller, E(2) = 0.94 kcal/mol, and results from a delocalization of the $n_O \rightarrow \sigma^*_{H-C}$ type (Fig. 3b).

The theoretical study discussed before suggests that the lone pair electrons on the nitrogen atoms are *exo*-oriented, which reduces the possibility for coordination to a metal atom located within the cavity. However, an option to achieve the reorientation of the nitrogen lone pair electrons is reduction of the C=N bond. In order to explore this possibility, Schiff bases **3** and **8** were reduced with $LiBH_4$ to the corresponding diamines. While reduction of compound **3** gave the expected free diamine **9** in good yield (84%), the reduction of **8** provided the oxaazacyclophane-borane adduct **10** that shows considerable stability in air and towards hydrolysis [50]. Both compounds have been characterized by spectroscopic methods (IR, ^1H and ^{13}C NMR) and FAB^+ mass spectrometry. In the case of compound **10** it was also possible to establish the molecular structure by X-ray crystallography (Fig. 4). As we can see from Fig. 4, in this case at least one nitrogen lone pair electron can be directed into the cavity.

Conclusions

The above discussion has shown that Schiff base macrocyclic structures can be formed easily in two steps of synthesis, which then can be reduced in order to increase the affinity toward metal atoms. Diimine **8** showed a different behavior in the reaction with $LiBH_4$, when compared to its analogue **3**, and resulted in the formation of a very stable oxaazacyclophane-borane adduct.

Preliminary experiments with metal salts, such as copper, nickel and zinc perchlorate, have shown that some of the macrocyclic hosts described herein are capable of metal complexation. On the other hand, it is important to emphasize that diamines prepared from the corresponding Schiff bases could also serve as receptors for anions, in particular if the nitrogen atoms are protonated. We are currently working on complexation studies of the

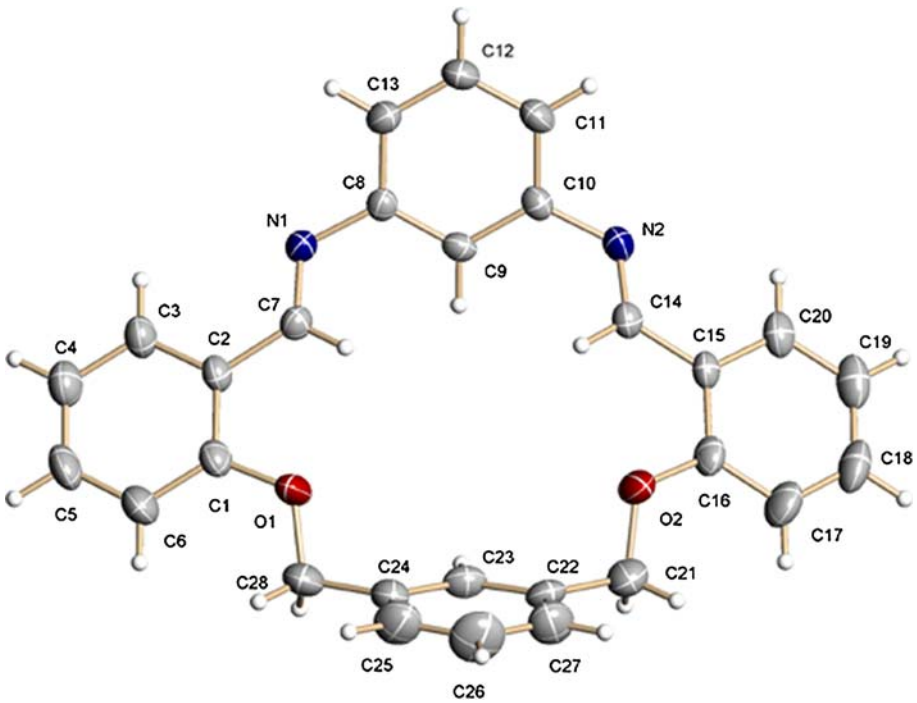


Fig. 2 Perspective view of the molecular structure of macrocycle **3**

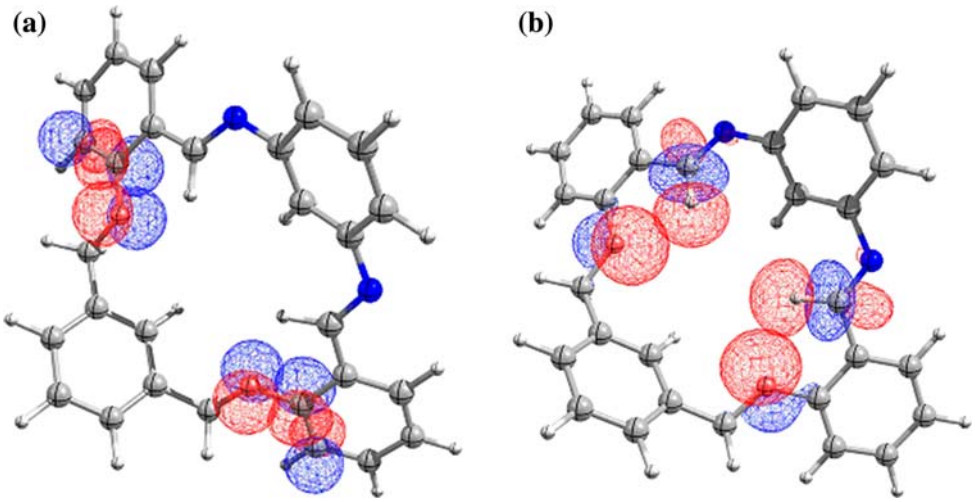


Fig. 3 Orthogonal NBOs for the oxygen lone pair at the HF/6-31G(d,p) level of theory: **a** $n_{\pi O}$ interacting with the $\pi^*_{C=Carom}$ antibond, and **b** $n_O \rightarrow \sigma^*_{H-C}$

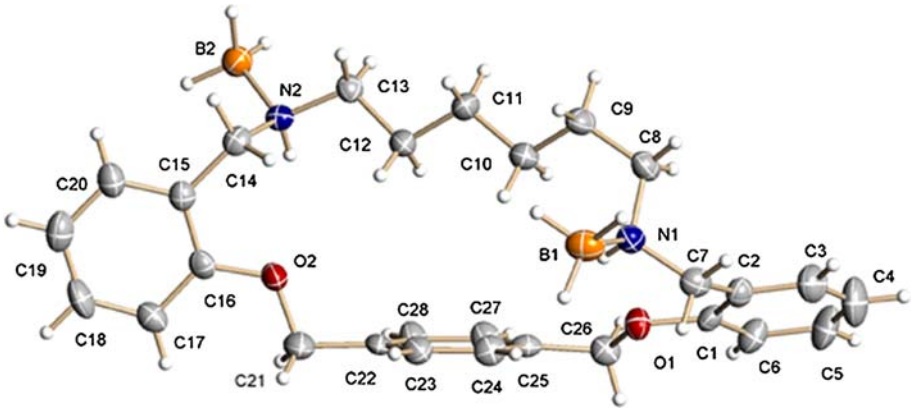


Fig. 4 Perspective view of the molecular structure of compound **10** [50]

macrocyclic hosts and on the preparation of further macrocyclic Schiff bases and their hydrogen-reduced amine analogues with improved structures and additional binding sites, in order to generate hosts with a more specific capability for guest complexation in organic and aqueous media.

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