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Jeong Kim $^{\rm a}$, Leonard F. Lindoy $^{\rm b}$, Tae-Ho Ahn $^{\rm a}$ & Gyu-Sung Choi $^{\rm c}$

^a Department of Chemistry, Seonam University, Namwon, 590-711, Korea

^b School of Chemistry, University of Sydney, N.S.W., 2006, Australia

^c Department of Chemistry, Gyungnam University, Masan, 631-701, Korea Published online: 19 Apr 2010.

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New N₂O₂- and N₂O₃-Macrocycle Ligands Incorporating *p*-Xylyl Groups

Jeong Kim,¹ Leonard F. Lindoy,^{2,*} Tae-Ho Ahn,¹ and Gyu-Sung Choi³

¹Department of Chemistry, Seonam University, Namwon 590-711, Korea ²School of Chemistry, University of Sydney, N.S.W., 2006, Australia ³Department of Chemistry, Gyungnam University, Masan 631-701, Korea

ABSTRACT

The synthesis and characterization of four dibenzo-substituted macrocycles incorporating mixed nitrogen and oxygen heteroatoms as well as one or two xylyl groups are reported. The X-ray structure of one product containing two xylyl functions is presented.

Key Words: Macrocycle; Synthesis; X-ray structure.

In past studies, we investigated the interaction of mixed donor macrocyclic ligands incorporating oxygen/nitrogen donor sites with a range of

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^{*}Correspondence: Leonard F. Lindoy, School of Chemistry, University of Sydney, N.S.W. 2006, Australia; Fax: +61 2 9351 7067; E-mail: lindoy@chem.usyd.edu.au.

first-row transition and post transition metal ions.^[1–3] We now report the synthesis and characterization of a new series of related macrocyclic ligands **1** through **4**, in which one or two xylyl groups have been incorporated in their ring structures. These semiflexible ring systems, incorporating both π -aryl and hydrogen-bond acceptor sites (or donor sites in the respective protonated forms) constitute a class of "hybrid" macrocycles of potential application as receptors for small molecules and ions.

Condensation of the respective dialdehydes 5 through 8 and α, α' diamino-p-xylene in methanol yielded the corresponding cyclic Schiff base products; these were not isolated but were reduced in situ by step-wise addition of sodium borohydride to the reaction solution. All reactions proceeded smoothly. The respective ring-closing reactions were not carried out under high dilution conditions. Thin layer chromatography on silica gel [employing triethylamine/ethyl acetate (1:3) as eluent] of the crude products coupled with their low-resolution mass spectra indicated that small yields of the corresponding 2:2 condensation products were also formed under the conditions employed. These 2:2 by-products exhibit little solubility in warm acetonitrile, while the monomeric products are more soluble (and are readily crystallized from this solvent), thus providing a means for the purification of the latter. The high-resolution mass spectra (HRMS) and ¹H- and ¹³C-NMR spectra of the respective products in each case are consistent with the assigned structures, with there being no evidence for the presence of imine groups.

The X-ray structure of 1, crystallized from acetonitrile, is shown in Fig. 1. The bond lengths and angles are unremarkable. The dihedral angles between each xylyl aromatic plane and the least squares plane defined by O(1), O(8),



Figure 1. X-ray structure of 1. Thermal ellipsoids are scaled to 30% probability.

N(12), and N(19) are c. 85° for the aryl ring in the -NHCH₂C₂H₄CH₂NHstring (namely, close to perpendicular to the O₂N₂ least squares plane), and c. 29° for the aryl group in the -OCH₂C₂H₄CH₂O- string. Overall, while there appears to be little preorganization of the xylyl groups for π -interaction with an included guest, this is likely to be little impediment to such binding given that inspection of CPK (Corey-Pauling-Koltun) models indicates that free rotation is possible around each of the xylyl methylene groups in this structure.

EXPERIMENTAL

¹H- and ¹³C-NMR spectra were recorded in (D)chloroform on a Bruker AC-300 spectrometer at 300 and 75 MHz, respectively. High-resolution mass spectra were obtained on a Jeol JMS HX-100 mass spectrometer. Melting points are uncorrected. All solid products were dried over phosphorus pentoxide in a vacuum.

Macrocycle Synthesis

Dialdehyde 5 (Fig. 2)

This was prepared (in higher yield) by a modified procedure to that reported previously.^[4] Salicylaldehyde (2.44 g, 0.02 mol) and α, α' -dibromo*p*-xylene (2.64 g, 0.01 mol) were dissolved in acetonitrile, and potassium carbonate (5.5 g, 0.04 mol) was added. The mixture was heated at the reflux for 2 h then filtered. The solution was cooled to room temperature, and the precipitate that formed was filtered off and washed with 10% aqueous sodium hydroxide solution (3 × 100 mL) and recrystallized from acetonitrile to yield colorless crystals (2.41 g, 84%). M.p. 192–194°C (lit. 191°C).^[6] The ¹H-NMR was identical to that reported previously;^{[6] 13}C-NMR δ 190.30, 156.47, 137.92, 136.10, 130.21, 129.15, 128.54, 127.21, 120.55, 110.50, 69.85.

Dialdehydes 6 through 8 (Fig. 2)

These were prepared and characterized as described previously.^[5,7]

Macrocycle 1 (Fig. 2)

Dialdehyde **5** (3.46 g, 0.01 mol) was dissolved in dry methanol (100 mL), and $\alpha \alpha'$ -diamino-*p*-xylene (1.36 g, 0.01 mol) dissolved in methanol (50 mL) was added dropwise. The mixture was refluxed for 2 h then filtered. Sodium





borohydride (1.9 g, 0.05 mol) was added to this solution in small portions at room temperature. The solvent was removed on a rotary evaporator, and the residue was dissolved in dichroromethane (100 mL), which was shaken with water (3 × 100 mL). The organic phase was separated and dried over anhydrous sodium sulfate. The solvent was again removed using a rotary evaporator, and the product that remained was recrystallized from acetonitrile to yield colorless crystals (1.58 g, 35%). M.p. 135–136°C [Found: m/z450.2308 (EI), C₃₀H₃₀N₂O₂ requires *M*, 450.2307]; $\delta_{\rm H}$ 6.94–7.40 (m, 16H, aromatic H), 5.05 (s, 4H, ArOCH₂), 3.82 (s, 4H, NCH₂ArCH₂N), 3.76

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(s, 4H, Ar**CH**₂NCH₂Ar), 1.91 (s, 2H, NH); &C 156.86, 138.31, 136.32, 130.69, 128.41, 128.22, 127.35, 120.75, 110.82, 69.40, 52.86, 49.20.

Macrocycle 2 (Fig. 2)

In a similar manner to that described above, dialdehyde **6** (2.70 g, 0.01 mol) and α, α' -diamino-*p*-xylene (1.36 g, 0.01 mol) yielded the product as colorless crystals after recrystallization from ethanol (1.42 g, 38%). M.p. 142–143°C; [Found: m/z 374.1996 (EI), C₂₄H₂₆N₂O₂ requires *M*, 374.1994]; $\delta_{\rm H}$ 6.71–7.39 (m, 12H, aromatic H), 4.17 (s, 4H, ArOCH₂), 3.87 (s, 4H, NCH₂ArCH₂N), 3.44 (s, 4H, ArCH₂NCH₂Ar), 1.81 (s, 2H, NH); $\delta_{\rm C}$ 156.64, 136.23, 131.73, 131.04, 127.71, 126.89, 121.74, 113.10, 68.19, 65.23, 61.06.

Macrocycle 3 (Fig. 2)

In a similar manner to that described above, dialdehyde **8** (2.84 g, 0.01 mol) and α, α' -diamino-*p*-xylene (1.36 g, 0.01 mol) yielded the product as colorless crystals after recrystallization from ethanol (0.97 g, 25%). M.p. 113–114°C; [Found: m/z, 388.2150 (EI), C₂₅H₂₈N₂O₂ requires *M*, 388.2151]; $\alpha_{\rm H}$ 6.75–7.24 (m, 12H, aromatic H), 4.02 (s, 4H, ArOCH₂), 3.72 (s, 4H, NCH₂ArCH₂N), 3.63 (s, 4H, ArCH₂NCH₂Ar), 2.15 (quintet, 2H, OCH₂CH₂CH₂O), 1.76 (s, 2H, NH); $\delta_{\rm C}$ 156.72, 138.92, 130.12, 128.47, 128.21, 128.02, 120.59, 111.18, 64.57, 52.79, 48.65, 29.34.

Macrocycle 4 (Fig. 2)

In a similar manner to that described above, dialdehyde **7** (3.12 g, 0.01 mol) and α , α' -diamino-*p*-xylene (1.36 g, 0.01 mol) yielded the product as colorless crystals after recrystallization from ethanol (1.67 g, 40%). M.p. 130–132°C; [Found: m/z, 418.2257 (EI), C₂₆H₃₀N₂O₃ requires *M*, 418.2256]; $\delta_{\rm H}$ 6.77–7.31 (m, 12H, aromatic H), 3.98 (t, 4H, ArOCH₂), 3.78 (s, 4H, NCH₂ArCH₂N), 3.70 (s, 4H, ArCH₂NCH₂Ar), 3.66 (t, 4H, ArOCH₂CH₂), 1.99 (s, 2H, NH); $\delta_{\rm C}$ 156.92, 138.96, 130.48, 128.84, 128.42, 128.28, 121.02, 111.85, 70.10, 67.91, 52.90, 47.97.

X-ray Structure of Macrocycle 1

Data were collected at 295(2) K using a Bruker P4 diffractometer employing graphite-monochromated Mo-K α radiation generated from a sealed tube (0.71073 Å). The intensities of three standard reflections did not change significantly during the data collection. A multiscan empirical absorption correction was applied to the data using the program SADABS.^[8] The structure was solved by direct methods using SHELXS-97^[9] then refined and extended with SHELXL-97.^[9] The structure is illustrated in Fig. 1, the latter showing 30% probability amplitude displacement envelopes for the nonhydrogen atoms. All nonhydrogen atoms were refined with anisotropic displacement parameters, whereas the hydrogen atoms were constrained at estimated positions.

Crystal data: $C_{30}H_{30}N_2O_2$, M = 450.56, triclinic, space group P1 (#2), a = 9.6540(16) Å, b = 10.0092(19) Å, c = 13.960(3) Å, $\alpha = 84.23(2)^{\circ}$, $\beta = 72.754(15)^{\circ}$, $\gamma = 68.424(17)^{\circ}$, V = 1198.0(4) Å³, $D_c = 1.249$ g cm⁻³, Z = 2, crystal size $0.4 \times 0.3 \times 0.2$ mm, μ (Mo-K α) 0.078 mm⁻¹, T (Empirical)_{min,max} = 0.4551, 0.4762, $2\theta_{max} = 54.0$, hkl range -11 to 11, -11 to 12, -16 to 17, $N_{ind} = 4709$ ($R_{merge} = 0.0263$), $N_{obs} = 2903$ ($I > 2\sigma(I)$), $N_{var} = 343$, residuals R1(F) = 0.0512, $wR2(F^2) = 0.1309$, GoF(all) = 1.018, $\Delta \rho_{min,max} = -0.155$, 0.165 e^{-} Å⁻³. The refinement residuals are defined as $R1 = \Sigma ||F_0| - |F_c|| / \Sigma |F_0|$ for $F_0 > 2\sigma(F_0)$ and $wR2 = {\Sigma[w(F_0^2 - F_c^2)^2] / \Sigma[w(F_c^2)^2]^{1/2}$, where $w = 1/[\sigma^2(F_0^2) + (0.0518P)^2 + 0.1348P]$, $P = (F_0^2 + 2F_c^2) / 3$. CCDC deposition No. 219088.

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