Electronic Supplementary Information

1D Water chain stabilized by meso-expanded calix[4]pyrrole

B. Sathish Kumar and Pradeepta K. Panda*

School of Chemistry, University of Hyderabad, Hyderabad, India, 500046 Email: <u>pkpsc@uohyd.ernet.in; pradeepta.panda@gmail.com</u>

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1) Instrumentation and reagents:

NMR spectra were recorded on a Bruker Avance-400 MHz FT NMR spectrometer using tetramethylsilane (TMS, $\delta = 0$) as an internal standard at room temperature. Mass spectral determinations were carried out by Shimadzu-LCMS-2010 mass spectrometer and elemental analysis was obtained through Thermo Finnigan Flash EA 1112 analyzer. HRMS data were recorded with Bruker Maxis spectrometer. Melting points were determined on MR-Vis+ visual melting point range apparatus from LABINDIA instruments private limited. IR spectra were recorded on a JASCO-FT-IR model 5300 and NICOLET 5700 FT-IR spectrometer. DTA-TG analysis was done on NETZSCH STA 409 PC/PG.

Crystallographic data for **1** and **4** were collected on BRUKER SMART-APEX CCD diffractometer. Mo–K α ($\lambda = 0.71073$ Å) radiation was used to collect X-ray reflections on the single crystal. Data reduction was performed using Bruker SAINT^{S1} software. Intensities for absorption were corrected using SADABS^{S2} and refined using SHELXL-97 ^{S3} with anisotropic displacement parameters for non-H atoms. Hydrogen atoms on O and N were experimentally located in difference electron density maps. All C–H atoms were fixed geometrically using HFIX command in SHELX-TL. A check of the final CIF file using PLATON^{S4} did not show any missed symmetry.

Crystallographic data (excluding the structure factor) for structures 1 and 4 in this paper have been deposited in the Cambridge Crystallographic Data Centre as supplementary publication number **CCDC 1007110, 1007111** respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

X-ray powder diffraction of crystals of 1 was recorded on Bruker D8 Advance diffractometer (Sl. No. 204795), detector: PSD: LynxEye, source: Cu-K α 1(λ = 1.5406 Å) at 40 kV and 30 mA. Diffraction patterns were collected over a 2 θ range of 5-42 ° at a scan rate of 5° min⁻¹. DIFFRAC^{*plus*} EVA was software used for data analysis provided by Bruker-AXS.

The solvents used in the NMR was purchased from Sigma-Aldrich^{\mathbb{R}} and used as such.

^{S1} SAINT, version 6.45 /8/6/03, Bruker AXS, 2003.

^{S2} Sheldrick, G. M.; *SADABS*, Program for Empirical Absorption Correction of Area Detector Data, University of Göttingen, Germany, **1997**.

^{S3} Sheldrick, G. M.; *SHELXS-97* and *SHELXL-97*, Programs for the Solution and Refinement of Crystal Structures, University of Göttingen, Germany, **1997**.

^{S4} (a) A. L. Spek, *PLATON, A Multipurpose Crystallographic Tool*, Utrecht University, Utrecht, The Netherlands, **2002**; (b) A, L, Spek, *J. Appl. Cryst.* **2003**, *36*, 7-13.

2) Synthesis:

1) Synthesis of compound 4

Method A:



To the solution of compound $2^{[1]}$ (100 mg, 0.633 mmol) in (20 mL) of dry tetrahydrofuran containing triethylamine (23 µL, 0.019 mmol) was added 5% Pd/C (67 mg, 0.032 mmol). Then reaction mixture was purged with H₂ gas with balloon. This was stirred under H₂ gas atmosphere with balloon for 18 h. Then the reaction mixture was filtered through celite and solvent was removed in rotary evaporator. The crude product was purified by Kugel Rohr distillation under high vacuum at 100-120 °C, desired product obtained as white solid (65 mg, 64%).

Method B:



Compound $3^{[2]}$ (500 mg, 2.65 mmol), potassium hydroxide (1 g, 26.5 mmol) and dry ethylene glycol (20 mL) were taken in two neck round bottom flask equipped with reflux condenser having nitrogen inlet. To this hydrazine hydrate 98% (1.3 mL, 26.5 mmol) was added. Then the reaction mixture was heated to reflux and it was stirred for 4 h. Then reaction mixture was cooled to room temperature and poured in ice cold water. Compound was extracted with dichloromethane (2 x 20 mL). Then combined organic layers were concentrated in rotary evaporated. Pure product was obtained in same way as method A (0.236 g, 55% yield).

Melting point: 108-110 °C; FTIR Data (KBr): 3356, 2924, 1024, 792 cm⁻¹. ¹H-NMR (400 MHz, CDCl₃): δ in ppm 7.82 (s, 2H, NH), 6.64-6.63 (brs, 2H, pyrrole α -CH), 6.16-6.14 (brs, 2H, pyrrole β -CH), 5.99 (brs, 2H, pyrrole β -CH), 2.94 (brs, 4H, -CH₂). ¹³C-NMR (100 MHz, CDCl₃): δ in ppm 131.84, 116.59, 108.31, 105.36, 28.078. HRMS exact mass calcd. for C₁₀H₁₂N₂ (M+H) 161.1079, found: 161.1078. Elemental analysis: calcd. C: 74.97; H: 7.55; N: 17.48, found C: 74.85; H: 7.61; N: 17.32.

2) Synthesis of compound 1



Compound 4 (300 mg, 1.875 mmol) was dissolved in dry dichloromethane (45 mL), to this dry acetone (6.9 mL, 93.75 mmol) was added under nitrogen atmosphere. Then borontrifluoride diethyletherate (58 μ L, 0.468 mmol) was added and stirred at room temperature. Reaction was monitored by TLC, after 1 h starting material was finished. The reaction was stopped by quenching with sodium bicarbonate solution (10 mL). The organic layer was separated and concentrated in rotary evaporator. The crude product was purified by silica gel column chromatography by eluting with 10-20 % ethylacetate in hexane. After evaporation of the solvent, the pure product was obtained as a white solid (117 mg, 32% yield).

¹H-NMR (400 MHz, CDCl₃): δ in ppm 7.29 (s, 4H, NH), 5.92-5.91 (brs, 4H, pyrrole β-CH), 5.80-5.78 (brs, 4H, pyrrole β-CH), 2.72 (brs, 8H, -CH₂), 1.51 (s, 12H, CH₃). ¹H-NMR (400 MHz, CD₃CN): δ in ppm 7.91 (s, 4H, NH), 5.82 (brs, 4H, pyrrole β-CH), 5.68 (brs, 4H, pyrrole β-CH), 2.65 (brs, 8H, -CH₂), 1.48 (s, 12H, CH₃). ¹³C-NMR (100 MHz, CDCl₃): δ in ppm 138.72, 131.28, 105.50, 103.03, 35.42, 29.03, 27.09. HRMS exact mass calcd. for $C_{26}H_{32}N_4$ (M+H) 401.2705, found: 401.2705.

Melting point: Bulk sample: 170-172 °C (dec).

Crystal sample: 178-180 °C (dec);

FTIR Data (KBr): Bulk sample: 3438.05, 3108.45, 2967.96, 2930.14, 2865.30, 1987.37, 1573.9, 1228.08, 768.8 cm⁻¹. Crystal sample: 3486.68, 3384.02, 3227.32, 2962.56, 2892.31, 1638.74,

1573.90, 1206.47, 1038.96, 768.80 cm⁻¹.

Elemental analysis:

| Sample | Elements | Calculated % | Observed % |
|---------------------------------|----------|--------------|-------------------|
| Bulk | C | 77.96 | 77.85 |
| $(C_{26}H_{32}N_4)$ | Н | 8.05 | 8.12 |
| | N | 13.99 | 14.10 |
| Crystal | C | 71.53 | 71.46 |
| $(C_{26}H_{32}N_4 \cdot 2H_2O)$ | Н | 8.31 | 8.38 |
| | N | 12.83 | 12.75 |













Figure S5: ¹³C NMR spectrum of compound 1 in $CDCl_3$.

4) Crystal structures :



Figure S6: ORTEP-POVray diagram of **4** top view (left) and side view (right). Thermal ellipsoids are scaled upto 35% probability level. Color code: blue: N, grey: C and white: H.

| D-H A | d(D-H) | d(H···A) | d(D···A) | <(DHA) |
|--------------------|---------|----------|----------|--------|
| N(2)-H(2)-O(2) | 0.90(2) | 2.17(2) | 3.063(2) | 171(2) |
| N(4)-H(4)-O(1) | 0.91(2) | 2.19(2) | 3.066(2) | 161(2) |
| O(1)-H(34A)···O(1) | 0.99(2) | 1.88(2) | 2.859(2) | 169(3) |
| O(1)-H(34B)···O(2) | 0.99(1) | 1.90(3) | 2.824(2) | 154(3) |
| O(2)-H(36B)-O(1) | 0.99(2) | 1.84(2) | 2.824(2) | 169(2) |
| O(2)-H(36A)···O(2) | 0.99(2) | 1.83(3) | 2.806(2) | 165(3) |
| O(2)-H(36B)-O(1) | 0.99(2) | 1.84(2) | 2.824(2) | 169(2) |
| O(1)-H(34B)-O(2) | 0.99(1) | 1.90(3) | 2.824(2) | 154(3) |

Table S2: Hydrogen bong distances and angles of $1 \cdot (2H_20)$

5) DTA-TG Analysis:

5.1) For Crystal sample: 1·2H₂O:

DTA-TG was measured at the scanning rate of 10 °C min⁻¹ under nitrogen. 8.25% water is present in $1.2H_2O$ theoretically, 7.24% of mass change was observed at 80-140 °C.



Figure S7: TGA profile and its differential curve of 1.2H₂O

5.2) For Bulk sample 1:

DTA-TG was measured at the scanning rate of 10 $^{\circ}$ C min⁻¹ under nitrogen. 3.09 % of mass change was observed at 80-140 $^{\circ}$ C.



Figure S8: TGA profile and its differential curve of bulk sample 1

6) Comparison of IR spectra:



Figure S9: Comparison of IR spectra of bulk sample and crystal



Figure S10: Elemental analysis spectra of bulk sample 1



Figure S11: Elemental analysis spectra of crystal sample 1.2H₂O



Figure S12: Powder X-ray diffraction plots of crystal sample $1 \cdot 2H_2O$ at variable temperature. (a-c) heating; (c-e) cooling.