

Synthesis and X-ray structure of new molecular clips based on diphenylglycoluril

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A pair of new molecular clips based on diphenylglycoluril and 1, 2-dihydroindazol-3-one have been synthesised. Their structures and conformations were confirmed by single crystal X-ray diffraction.

Keywords: diphenyl glycoluril, molecular clip, 1, 2-dihydro-indazol-3-one

The design and synthesis of novel receptors with different molecular cavities is one of the major challenges in host–guest chemistry.¹ Glycoluril is an important building block for supramolecular chemistry, and its derivatives have been used as the basis for various molecular clips.^{2–4} Most molecular clips based on diphenylglycoluril have been derived from benzene, hydroquinone and their relatives. They possess good symmetry with the aromatic walls and show good binding properties for aromatic guests, especially, for dihydroxybenzene, by hydrogen bonding, π – π stacking interactions and a so-called ‘cavity-effect’.^{5,6}

We now report the synthesis and X-ray structure of a pair of new molecular clip from diphenylglycoluril and 1, 2-dihydroindazol-3-one. The deep U-shaped cavity in their structures provides great potential for binding aromatic guest molecules.

The synthesis of the title clip molecules **4a** and **4b** is shown in Scheme 1. The structures and conformations of compound **4a** and **4b** were further elucidated by their single crystal X-ray diffraction, as shown in Figs 1 and 2.

The crystals of **4a** and **4b** were obtained by slow evaporation of their solution in chloroform/methanol (20:1, v/v) mixtures. The crystal structures of **4a** and **4b** clearly revealed that they have well-defined geometry due to the rigidity that the fused rings confer on the molecule. The distance between the two carbonyl oxygens (O2–O3) of the glycoluril ring in **4a** and **4b** amounts to 5.341 Å and 5.461 Å, respectively, which indicates that two carbonyl groups of glycoluril ring are good hydrogen-acceptors for 1, 3-dihydroxy-substituted aromatic guests.² The dihedral angle between two phenyl rings of the sidewalls in **4a** and **4b** are 58.01° and 29.11°, and the distance between the centroids of two phenyl rings of the sidewalls in

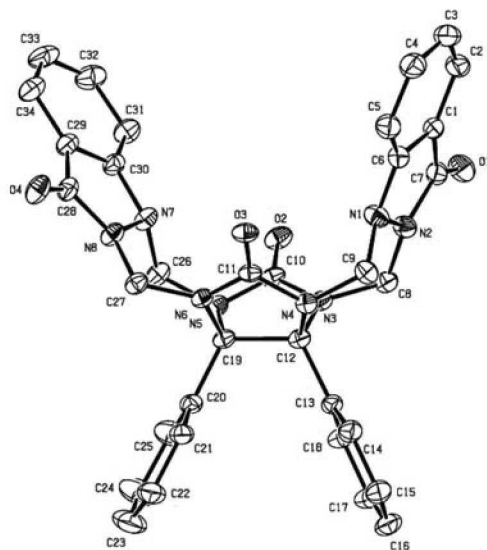
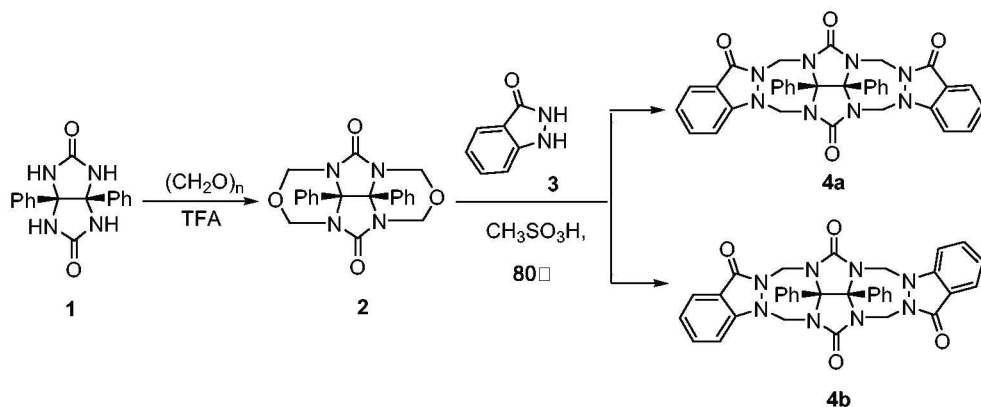


Fig. 1 The crystal structure of **4a**.

4a and **4b** are 7.838 Å and 6.845 Å, respectively. These values are suitable for the complexation of an aromatic ring by π – π stacking interactions.⁷

In conclusion, a pair of new molecular clips derived from diphenylglycoluril have been synthesised. Their structures and conformations were confirmed by single crystal X-ray diffraction. Both have great potential to bind aromatic guest



Scheme 1

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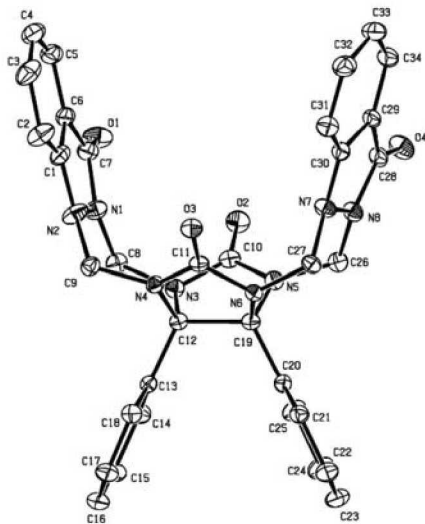


Fig. 2 The crystal structure of **4b**.

molecules. Further studies on their binding properties are in progress.

Experimental

General

All reagents obtained from commercial sources were of AR grade. Melting points were determined with XT4A micromelting point apparatus and were uncorrected. The ^1H NMR was recorded on a Mercury Plus-400 spectrometer with TMS as internal reference and CDCl_3 as solvent. IR were recorded on a Perkin-Elmer PE-983 IR spectrometer as KBr pellets with absorption in cm^{-1} . MS were obtained with Finnigan Trace MS instrument using EI method. Elemental analyses were carried out on a Vario EL III instrument.

Synthesis

Diphenylglycoluril **1**,⁸ and glycoluril cyclic ether **2**⁹ were prepared as the literature method.

General procedure for preparation of **4a** and **4b**

Anhydrous MeSO_3H (10 mL) was added to a flask containing compound **3** (0.367 g, 2.74 mmol), and the mixture was stirred at 80°C until homogeneous. Compound **2** (0.518 g, 1.37 mmol) was added in one portion and the flask was sealed and heated at 80°C for 3 h. The reaction mixture was allowed to cool and then poured into water (100 mL). The pale precipitate was collected by filtration using a medium fritted funnel, and washed with water (50 mL) and dried under vacuum. Flash chromatography gave compound **4a** (0.273 g, 32.8%) and **4b** (0.187 g, 22.4%) as white solids. The physical and spectra data of the compounds **4a** and **4b** are as follows.

4a. M.p. $>300^\circ\text{C}$ (dec.). TLC ($\text{CHCl}_3/\text{CH}_3\text{OH}$, 20:1), R_f 0.49. IR (KBr, cm^{-1}): 2924, 1748, 1752, 1674, 1649, 1463, 1384, 1263, 1151, 877, 756. δ_{H} (400 MHz, $\text{DMSO}-d_6$) 7.60–7.52 (m, 4 H, ArH), 7.45–7.40 (m, 2 H), 7.25–7.15 (m, 10 H, ArH), 7.10–7.02 (m, 2 H), 6.22 (d, $J = 14.4$, 2 H, NCH_2N), 6.04 (d, $J = 15.2$, 2 H, NCH_2N), 4.86 (d, $J = 15.2$, 2 H, NCH_2N), 4.76 (d, $J = 14.4$, 2 H, NCH_2N). MS (EI): $m/z = 611$ [$\text{M} + \text{H}$] $^+$. Anal. Calcd for $\text{C}_{34}\text{H}_{26}\text{N}_8\text{O}_4$ (610.21): C, 66.88; H, 4.29; N, 18.35. Found: C, 66.63; H, 4.18; N, 18.07%.

4b. M.p. $>300^\circ\text{C}$ (dec.). TLC ($\text{CHCl}_3/\text{CH}_3\text{OH}$, 20:1), R_f 0.24. IR (KBr, cm^{-1}): 3064, 1730, 1667, 1620, 1460, 1384, 1260, 1154, 874, 750. δ_{H} (400 MHz, $\text{DMSO}-d_6$) 7.60–7.50 (m, 4 H, ArH), 7.42–7.39 (m, 2 H), 7.25–7.15 (m, 10 H, ArH), 7.07–7.02 (m, 2 H), 6.20 (d, $J = 14.8$, 2 H, NCH_2N), 6.03 (d, $J = 15.2$, 2 H, NCH_2N), 4.85 (d, $J = 15.2$, 2 H, NCH_2N), 4.73 (d, $J = 14.8$, 2 H, NCH_2N). MS (EI): $m/z = 611.3$ [$\text{M} + \text{H}$] $^+$. Anal. Calcd for $\text{C}_{34}\text{H}_{26}\text{N}_8\text{O}_4$ (610.21): C, 66.88; H, 4.29; N, 18.35. Found: C, 66.55; H, 4.24; N, 17.88%.

X-ray diffraction study of **4a** and **4b**

A white crystal of the title compound **4a** and **4b** were each mounted on a glass fibre in a random orientation at 295(2) K, respectively. The determination of the unit cell and the data collection were performed with MoK α radiation ($\lambda = 0.71073$ Å) on a Bruker Smart Apex-CCD diffractometer with a ψ - ω scan mode. The structure was solved by direct methods with SHELXS-97 program and expanded by Fourier technique. The non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were placed at the calculated positions.

Crystal data for 4a: $\text{C}_{36}\text{H}_{28}\text{Cl}_6\text{N}_8\text{O}_4$, $M = 849.36$, Triclinic, space group P-1, $a = 9.6598(9)$, $b = 13.2119(12)$, $c = 15.3667(14)$ Å, $\alpha = 97.875(2)^\circ$, $\beta = 97.643(2)^\circ$, $\gamma = 104.726(2)^\circ$, $V = 1849.8(3)$ Å 3 , $Z = 2$, $D_c = 1.525$ g cm^{-3} , Reflections collected: 17111, independent reflections: 7205 [$R_{\text{int}} = 0.0656$] Final R indices [$I > 2\sigma(I)$]: $R^1 = 0.0622$, $wR^2 = 0.1584$. R indices (all data): $R^1 = 0.0995$, $wR^2 = 0.1812$. CCDC 294988.

Crystal data for 4b: $\text{C}_{34}\text{H}_{26}\text{N}_8\text{O}_5$, $M = 634.63$, Monoclinic, space group C_2/c , $a = 11.2685(10)$, $b = 24.869(2)$, $c = 21.381(2)$ Å, $\alpha = 90^\circ$, $\beta = 100.407(2)^\circ$, $\gamma = 90^\circ$, $V = 5893.3(9)$ Å 3 , $Z = 8$, $D_c = 1.431$ g cm^{-3} , Reflections collected: 21072, independent reflections: 5188 [$R_{\text{int}} = 0.0360$], Final R indices [$I > 2\sigma(I)$]: $R^1 = 0.0578$, $wR^2 = 0.1590$. R indices (all data): $R^1 = 0.0798$, $wR^2 = 0.1770$. CCDC 279808.

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