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Synthesis and crystal structure of a novel molecular clip from diphenylglycoluril and phthalhydrazide

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A novel molecular clip from diphenylglycoluril and phthalhydrazide has been synthesised. Its structure and conformation was confirmed by single crystal X-ray diffraction.

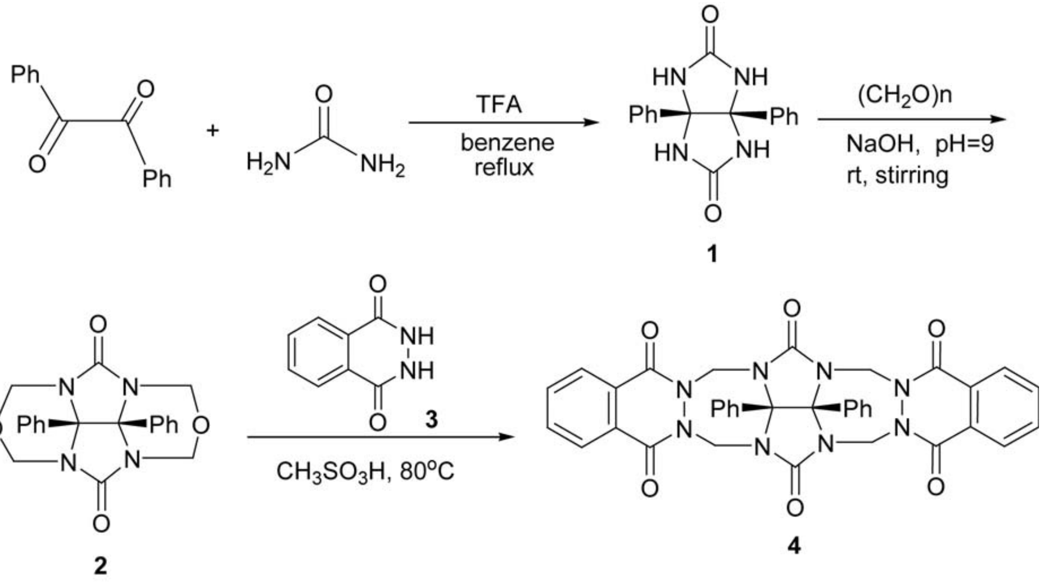
Keywords: diphenylglycoluril, phthalhydrazide, molecular clip

Natural receptors play a fundamental role in molecular recognition, catalysis, and transport processes. Artificial receptors have been developed to mimic these functions.[1,2] The rigid concave shape of glycoluril makes it a versatile building block to construct various supramolecular structures, such as molecule capsules,[3] molecule clips,[4] and the cucurbit[n]uril family of macrocycles.[5] Glycoluril-based clips with a preorganised cleft and rigid aromatic arms have been proved to be effective receptors for hydroxybenzene derivatives,[6,7]metal ions,[8–10] and anions.[11] In order to expand the range of possible guest structure, we report here the synthesis and X-ray structure of a new molecular clip from diphenylglycoluril and phthalhydrazide.

The title molecule clip **4** was prepared by reacting the glycoluril cyclic ether **2** with phthalhydrazide **3** using $MeSO_3H$ as an acid and solvent at 80 °C (Scheme 1). It was characterised by its NMR spectra. The ^1H NMR spectrum of **4** in DMSO-*d*6 shows two pairs of well-defined doublets with equal intensity for the protons of methylene at $\delta = 6.62$ ppm ($J = 15.2$ Hz) and $\delta = 4.72$ ppm ($J = 15.2$ Hz), indicating that molecule possess good symmetry and the four bridging methylene have the same chemical environment. The IR and MS for the product are in good agreement with the title compound. In addition, its structure and conformation was confirmed by single crystal X-ray diffraction, as shown in Fig. 1.

Crystals of **4** were obtained by slow evaporation of solution in chloroform–methanol mixtures. The structure analysis showed that in the crystal, the asymmetric unit contained two independent molecules A and B (Fig. 1). There were some small differences in their structures and conformations. In molecule A, the distance between the carbonyl oxygens (O_2–O_3) of the glycoluril ring amounts to 5.363 Å, the dihedral angle between two phenyl rings of the sidewalls is 35.74°, and the distance between the centroids of two phenyl rings of the sidewalls is 6.766 Å; In molecule B, the distance between the carbonyl oxygens (O_5–O_6) of the glycoluril ring amounts to 5.415 Å, the dihedral angle between two phenyl rings of the sidewalls is 34.14°, and the distance between the centroids of two phenyl rings of the sidewalls is 6.593 Å. As can be seen compound **4** is similar to Nolte's molecular clips,[12,13] but has a deeper cavity. Hence molecule **4** is a potential synthetic receptor for some neutral molecules through π-π stacking and hydrogen bond interactions. Moreover, because compound **4** has more N and O atoms in its U-shaped cavity than the previous molecular clips,[14] it is also a potential synthetic receptor for metal ions.

In conclusion, a new clip molecule from diphenylglycoluril and phthalhydrazide was synthesised. Its structure and conformation was also confirmed by single crystal X-ray diffraction. Further studies on its molecular recognition are in progress.



Scheme 1 Synthesis of clip molecule **4**.

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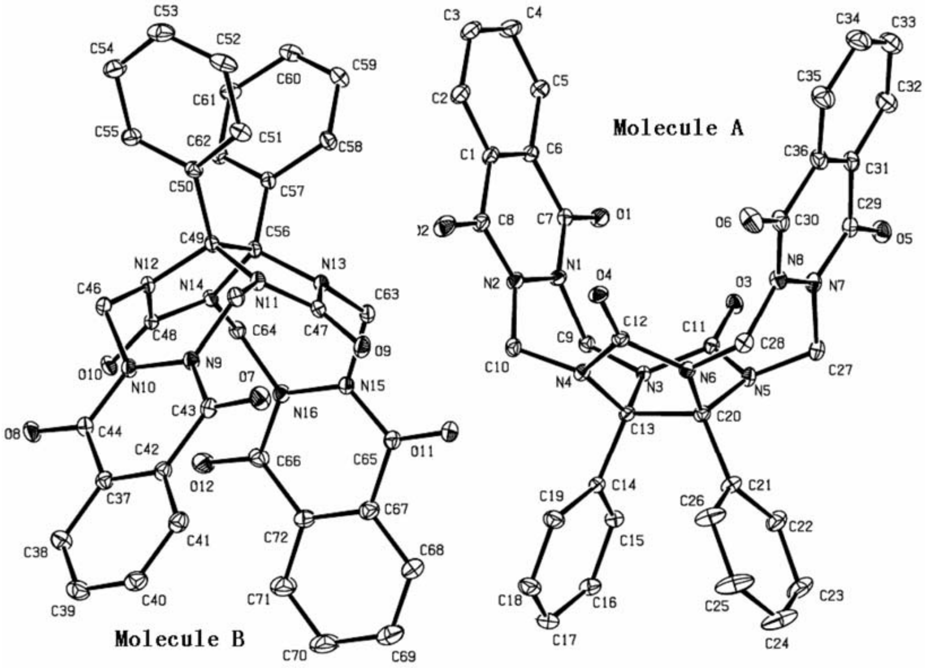

Fig. 1 The crystal structure of **4**. solvent molecules omitted for clarity.

Experimental

General

All reagents obtained from commercial sources were of AR grade. The melting point was determined with an XT4A micromelting point apparatus and was uncorrected. The ^{1}H NMR spectra were recorded on a Mercury Plus-400 spectrometer with TMS as internal reference and DMSO-*d6* as solvent. IR spectra 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

Diphenyl glycoluril **1**[15] and cyclic ether **2**[16] were prepared as the literature method.

Preparation of molecular clip **4**: Anh. $MeSO_3H$ (10 mL) was added to a flask containing phthalhydrazide **3** (0.36g, 2.74 mmol), and the mixture was stirred at 80 °C until homogeneous. Compound **2** (0.52g, 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 through a medium fritted funnel and washed with water (50 mL) and dried under vacuum. Flash chromatography (MeOH/$CHCl_3$, 1: 20) gave compound **4** (0.59g, yield: 65%) as a white solid. M.p. >300 °C. IR (KBr): 3025, 2924, 1741, 1650, 1608, 1452, 1429, 1298, 1130cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.11–8.08 (m, 4H, ArH), 7.95–7.92 (m, 4H, ArH), 7.23–7.17 (m, 10H, ArH), 6.62 (d, *J* = 15.2, 4H, NCH_2N), 4.72 (d, *J* = 15.2, 4H, NCH_2N). EI-MS: *m/z* = 668 $[M + 2H]^{2+}$. Anal. Calcd for $C_{36}H_{26}N_8O_6$ (666.2): C, 64.86; H, 3.93; N, 16.81; Found: C, 64.70; H, 3.85; N, 16.71%.

X-ray diffraction study of **4**

Crystals were obtained by slow evaporation from chloroform–methanol solution (20:1 v/v). A colourless crystal of the title compound **4** having approximate dimensions of 0.30mm × 0.20 mm × 0.10mm was mounted on a glass fibre in a random orientation at 292(2) K. The determination of unit cell and the data collection were performed with MoKα radiation (λ = 0.71073 Å) on a Bruker Smart APEX-CCD diffactometer with a ψ–ω scan mode. A total of 36637 reflections were collected in the range of $1.18 < \theta < 26.00°$ at room temperature, and 13537 were independent (R_{int} = 0.0691), of which 6751 observed reflections with $I > 2\sigma(I)$ were used in the structure determination and refinements. The structure was solved by direct methods using the SHELXS-97 program and expanded by Fourier technique. The non-hydrogen atoms were refined anisotropically, and the location of the hydrogen atoms were determined by a theoretical calculation. A full-matrix least-squares refinement gave the final $R^1 = 0.0613$, $wR^2 = 0.1433$ $[W = 1 / [\sigma^2(F_o^2) + (0.0880P)^2 + 0.0000P]$ where $P = (Fo^2 + 2Fc^2)/3$, $(\Delta/\sigma)_{max} = 0.000$, $S = 0.899$, $(\Delta\rho)_{max} = 0.598$, $(\Delta\rho)_{min} = 0.462$ e/ Å^3. All calculations were performed on a PC with SHELXS-97 program. *Crystal data*: $C_{74}H_{54}Cl_6N_{16}O_{12}$, *M* = 1572.03, Triclinic, space group *P*-1, *a* = 14.1307(12), *b* = 14.6268(12), *c* = 17.9728(15) Å, α = 87.514(2)°, β = 73.552(2)°, γ = 76.403(2)°, *V* = 3461.8(5)Å^3, *Z* = 2, D_c = 1.508g cm^{-3}, μ = 0.327mm^{-1}. The data have been deposited as CCDC 279807 which contains the supplementary crystallographic information for this paper. These data can be obtained free of charge at www.ccdc. cam.ac.uk/conts/ retrieving.html or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB21EZ, UK; fax: +44(0)1223-336033; e-mail: deposit@ccdc.cam.ac.uk.

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