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ORIGINAL PAPER

Synthesis and Crystal Structure of a New Diphenylglycoluril Derivative

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Abstract The title compound has been synthesized by alkylation of diphenylglycoluril with *o*-xylylenedihalides followed by Sonogashira cross-coupling reaction. The yielded product 2 was investigated with X-ray crystallographic, NMR, EI-MS, and IR techniques. The crystal belongs to a triclinic system, space group *P*-1 with unit cell parameters $a = 10.5057(8)$ Å, $b = 12.6915(9)$ Å, $c = 13.3426(10)$ Å, $\alpha = 83.8540(10)^{\circ}$, $\beta = 87.9360(10)^{\circ}$, $\gamma = 75.5700(10)^{\circ}$, $V = 1712.9(2)$ Å^3, $Z = 2$, $D_c = 1.322$, $M_r = 681.59$, $\mu = 0.232$ mm^{-1}, $F(000) = 708$, $R_1 = 0.0586$ and $wR_2 = 0.1470$.

Keywords Diphenylglycoluril · Crystal structure · Dimeric aggregates · Hydrogen bond · π–π stacking

Introduction

Glycoluril recently has become an important building block for supramolecular chemistry [1–11]. Many of supramolcular systems are based on glycoluril, making use of its molecular curvature and self-complementary H-bonded ureid moiety. Rebek have previously used the H-bonded potential of glycoluril itself to design the self-assembly molecule encapsules [12–14] and engineer the formation of H-bonded tapes in the crystal [15]. Our groups have also reported glycoluril derivatives to form linear H-bonded tapes by exclusive heterochiral recognition processes [16]. These results have suggested that glycoluril derivatives have significant potential as a building block in studies of crystal engineering.

Experimental

General Methods

Melting point was determined with XT4A micromelting point apparatus and was uncorrected. NMR Spectra were measured on Plus-400 instruments operating at 400 MHz for ^{1}H and 100 MHz for ^{13}C. MS was measured on a Finnigan Trace MS spectrometer. IR was recorded on a PE-983 infrared spectrometer as KBr pellet with absorption in cm^{-1}. The Diphenylglycoluril and 2,3-bis(bromomethyl)-1-4-dibromo-benzene were prepared according to the methods reported [17, 18]. DMSO was dried and distilled under N_2 over calcium hydride (CaH_2) before use. Potassium tert-butoxide and phenylacetylene were commercially available from Acros Organics, and other chemicals were used as received without further purification.

Synthesis of the Title Compound

Scheme 1 shows the synthetic route for the title compound 2. Diphenylglycoluril was alkylated with 2,3-bis(bromomethyl)-1-4-dibromo-benzene using t-BuOK as base in anhydrous DMSO to give intermediate 1 in 30% yield. The coupling reaction between 1 and phenylacetylene was readily accomplished using $Pd(PPh_3Cl_2)_2$ and CuI as catalysts in the presence of Et_3N in DMF at 100 °C, and the expected compound 2 was obtained. The structure of 2 was confirmed by ^{1}H NMR, ^{13}C NMR, MS and IR.

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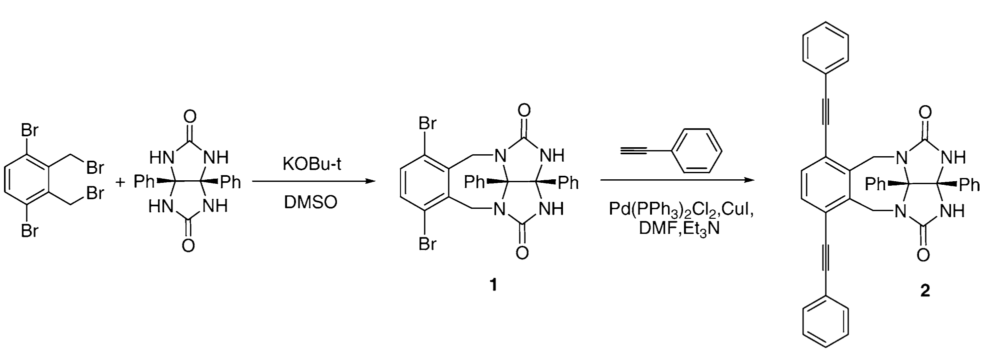
Scheme 1 Synthetic route for the preparation of the title compound



Compound 1

Diphenylglycoluril (2.94 g, 10 mmol) was dissolved in anhydrous DMSO (40 mL) under argon, and t-BuOK (4.48 g, 40 mmol) was added. After the reaction was stirred for 1 min, 2,3-bis(bromomethyl)-1-4-dibromo-benzene (0.84 g, 2 mmol) was added in one portion and stirring was continued for 3 h. The reaction mixture was poured into 0.1 N HCl (1 L) and extracted with EtOAc (3 × 400 mL). The extracts were washed with brine and dried over anhydrous $MgSO_4$. After filtration and rotary evaporation, the residue was purified by flash chromatography (SiO_2, $CHCl_3$/MeOH = 50:1) to give 1 (0.33 g, 30%) as a white solid. M.p. > 300 °C. TLC ($CHCl_3$/MeOH = 50:1) *Rf* 0.48. IR (KBr, cm^{-1}): 3569w, 34089w, 3264w, 3066w, 1722 s, 1691 s, 1466 s, 1324w, 1161w, 974w, 779w. ^1H NMR (400 MHz, $CDCl_3$): δ 7.35–7.07 (m, 12H), 5.84 (s, 2H), 5.64 (*d*, $J = 16.0$, 2H), 4.05 (*d*, $J = 16.0$, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.6, 138.1, 136.4, 133.8, 133.1, 129.2, 129.0, 128.9, 128.1, 127.8, 127.1, 124.0, 87.8, 78.8, 44.4. EI-MS: m/z 558 (2, $[M + H]^+$), 104 (100).

Compound 2

To a solution of $Pd(PPh_3)_2Cl_2$ (36 mg, 0.05 mmol), CuI (19 mg, 0.10 mmol) and compound 1 (279 mg, 0.50 mmol) in freshly distilled Et_3N (15 mL) and DMF (25 mL) under Ar atmosphere at room temperature, were added phenylethynylene (204 mg, 2 mmol). The mixture was warmed to 110 °C for 12 h (monitored by TLC), and then the solvent was removed under reduced pressure. The solid residue was purified by flash chromatography (SiO_2, $CHCl_3$–MeOH, 50:1) to give 2 (218 mg, 0.365 mmol, 73%) as a white solid. M.p. > 300 °C. TLC ($CHCl_3$/MeOH = 30:1) *Rf* 0.48. IR (KBr, cm^{-1}): 3375w, 3062w, 1705 s, 1457 s, 1428 m, 1363w, 757 m, 691 m. ^1H NMR (400 MHz, CDCl3): δ 7.64–7.03 (m, 22H), 5.92 (s, 2H), 5.83 (*d*, $J = 16.0$, 2H), 4.05(*d*, $J = 16.0$, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.8, 138.8, 136.5, 133.3, 131.7, 131.4, 129.0, 128.8, 128.7, 128.5, 128.3, 128.1, 127.9, 127.1, 123.6, 123.0, 95.1, 88.3, 87.3, 77.3, 42.1. MS(ESI): m/z 597 ($[M + H]^+$), 619 ($[M + Na]^+$).

X-ray Crystal Structure Determination

Crystals suitable for X-ray structure determination were obtained via slow evaporation of its solution in dichloride methane. Crystal data were collected with Mo Kα radiation ($\lambda = 0.71073$ Å) on a BRUKER SMART APEX-CCD

Table 1 Crystal data and structure refinement of 2

CCDC No.	666025
Empirical formula	$C_{41}H_{30}Cl_2N_4O_2$
Formula weight	681.59
Temperature (K)	292(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	*P*-1
Unit cell dimensions	$a = 10.5057(8)$ Å
	$b = 12.6915(9)$ Å
	$c = 13.3426(10)$ Å
	$\alpha = 83.8540(10)^\circ$
	$\beta = 87.9360(10)^\circ$
	$\gamma = 75.5700(10)^\circ$
Volume (Å^3)	1712.9(2)
Z	2
Density (calculated) (mg/m^3)	1.3222
Absorption coefficient (mm^{-1})	0.232
F_{000}	708
θ range for data collection, Deg	1.67–27.00
Index ranges	$-13 \le h \le 13$
	$-16 \le k \le 16$
	$-17 \le l \le 16$
Reflections collected	17830
Independent reflections	7391[*R*(int) = 0.0610]
Absorption correction	Multiscan
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	7391/8/476
Goodness-of-fit on F^2	0.963
Final *R* indices [I > 2σ(I)]	$R_1 = 0.0586$, $wR_2 = 0.1470$
R indices (all data)	$R_1 = 0.0933$, $wR_2 = 0.1657$
Largest diff. Peak and hole, *e* (A^{-3})	0.225 and −0.371

diffractometer with a ψ–ω scan mode. A total of 17830 reflections were collected in the range of $1.67 < \theta < 27.00°$ at room temperature, and 7391 were independent (Rint = 0.0610), of which 4592 observed reflections with $I > 2\sigma(I)$ were used in the structure determination and refinements. Lattice determination and data collection were carried out using SMART version 5.625 software. Date reduction and absorption corrections were performed with SAINT version 6.45 and SADABS version 2.03, respectively [19]. Structure solution and refinement were made by SHELXTL version 6.14 software package [20]. The non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were generated geometrically with C–H bond distances of 0.93–0.97 according to criteria described in the SHELXTL manual. They were included in the refinement with $U_{iso}(H) = 1.2U_{eq}(C)$. The final full-matrix

Table 2 Selected bond lengths (Å) and angles (°) for **2**

C(1)–C(2)	1.365(3)	C(2)–C(1)–C(6)	120.1(2)
C(2)–C(3)	1.372(4)	N(2)–C(27)–C(34)	99.97(14)
C(6)–C(7)	1.434(3)	C(3)–C(4)–C(5)	119.8(2)
C(7)–C(8)	1.192(3)	C(8)–C(7)–C(6)	177.4(2)
C(10)–C(23)	1.508(3)	C(7)–C(8)–C(9)	173.1(2)
C(11)–C(13)	1.364(3)	C(11)–C(9)–C(8)	118.01(18)
C(17)–C(18)	1.378(3)	C(10)–C(9)–C(8)	121.73(18)
C(23)–N(1)	1.469(2)	C(12)–C(10)–C(9)	119.34(17)
C(24)–N(2)	1.452(2)	C(10)–C(12)–C(24)	121.24(17)
C(25)–O(1)	1.213(2)	C(12)–C(14)–C(15)	122.00(18)
C(25)–N(3)	1.354(3)	C(16)–C(15)–C(14)	175.6(2)
C(25)–N(1)	1.385(3)	C(15)–C(16)–C(17)	179.7(3)
C(26)–O(2)	1.225(2)	N(1)–C(23)–C(10)	115.06(15)
C(34)–N(4)	1.441(2)	N(2)–C(24)–C(12)	113.84(15)
C(34)–N(3)	1.449(3)	N(3)–C(25)–N(1)	107.43(17)
C(37)–C(38)	1.373(3)	O(2)–C(26)–N(2)	125.87(19)
C(41)–Cl(1)	1.703(7)	N(2)–C(26)–N(4)	107.99(16)

Table 3 Selected torsion angles (°) for non-hydrogen atoms

C6–C1–C2–C3	−0.5(5)	N4–C34–C35–C40	−159.29(19)
C1–C2–C3–C4	1.2(5)	N3–C34–C35–C40	−28.1(3)
C4–C5–C6–C7	−178.2(2)	O1–C25–N1–C27	−168.74(18)
C2–C1–C6–C5	57.6(5)	N3–C25–N1–C27	12.2(2)
C10–C9–C11–C13	−2.9(3)	O2–C26–N2–C24	−1.7(3)
C24–C12–C14–C15	0.2(3)	N4–C26–N2–C24	177.17(3)
C14–C15–C16–C17	−82(51)	N4–C26–N2–C27	8.2(2)
C15–C16–C17–C22	91(51)	C12–C24–N2–C26	114.1(2)
N1–C27–C28–C33	−158.38(18)	C12–C24–N2–C27	−77.9(2)
N2–C27–C28–C33	−30.5(2)	C28–C27–N2–C26	103.24(18)
C28–C27–C34–N4	−98.14(18)	C34–C27–N2–C26	−19.5(2)
N1–C27–C34–N3	20.89(17)	C28–C27–N2–C24	−66.1(2)
N2–C27–C34–N3	−94.20(16)	C34–C27–N2–C24	171.14(15)
N4–C34–C35–C36	25.1(3)	O2–C26–N4–C34	−172.2(2)
N3–C34–C35–C36	156.3(2)	N2–C26–N4–C34	8.9(2)

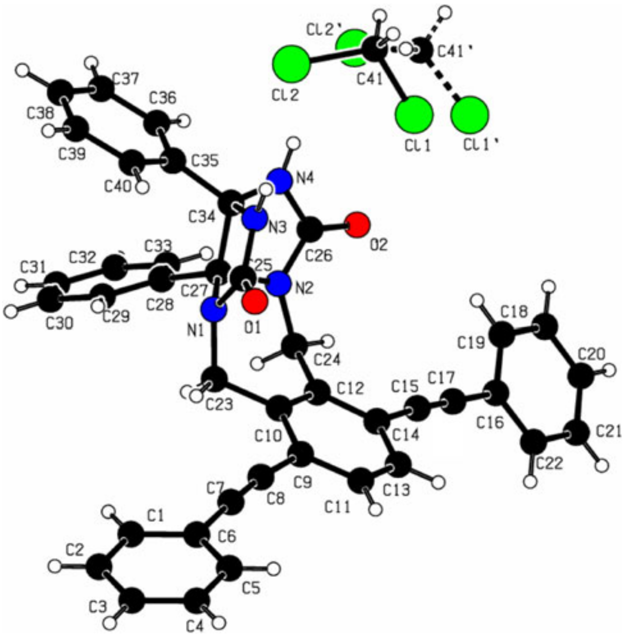


Fig. 1 Crystalline structure of compound 2 and solvent molecules

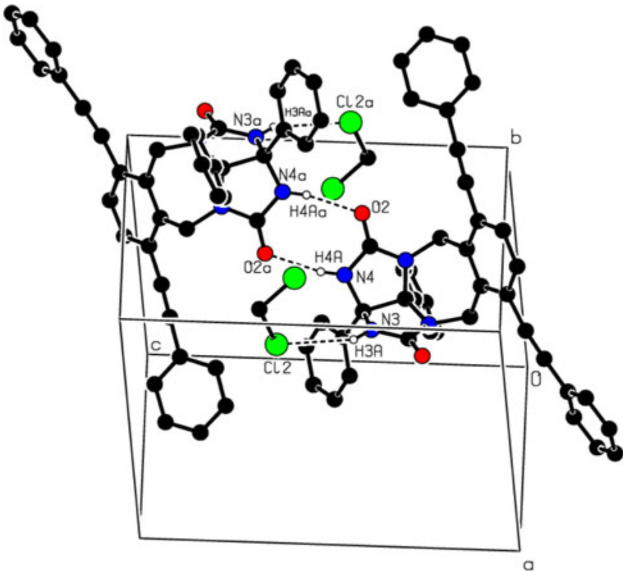


Fig. 2 Part of the crystal structure of 2, showed the formation of the dimeric aggregates via hydrogen bond interactions

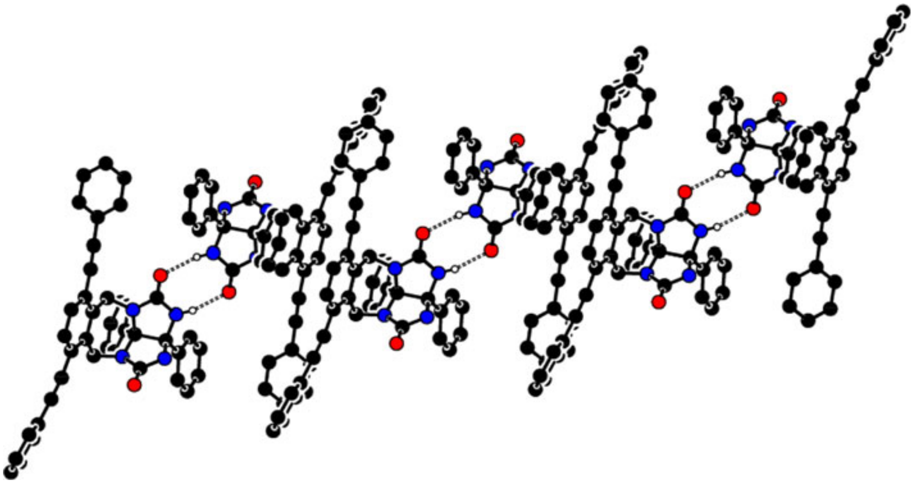


Fig. 3 The packing arrangement viewed down the *a*-axis. Hydrogen bonds are shown by dashed lines

least-square refinement on F^2 converged with $R_1 = 0.0586$ and $wR_2 = 0.1470$ for 4592 observed reflections [$I \geq 2\sigma(I)$]. The crystallographic data obtained and experimental details employed were summarized in Table 1.

Results and Discussion

Selected bond distances and bond angles are listed in Table 2. Selected torsion angle are given in Table 3. An ORTEP view of the molecule with the atomic numbering (thermal ellipsoids drawn at 30% probability) is shown in Fig. 1.

The compound has a well-defined geometry due to the rigidity that the fused rings confer on the molecule. The bond distances and bond angles of the title compound are in good agreement with the corresponding values obtained in case of related glycoluril derivatives [21–23]. The angle between the mean planes defined by the five-membered rings is 111.3°. The distance between two carbonyl oxygen atoms (O_1–O_2) of the glycoluril moiety is 5.72 Å. Interestingly, both ethynyls are tortuose with torsion angles of 173.1° and 175.6°. The phenyl ring C (C9–C14) of the sidewall and phenyl ring D (C1–C6) of the side chain is not coplanar with a dihedral angle of 23.5°. The phenyl ring C (C9–C14) is twisted with respect to ring E (C17–C22) making a dihedral angle of 33.4°.

Viewed from Fig. 2, the two molecule 2 are dimerizated via self-association by the formation of two N–H···O=C interactions ($d = 2.04$ Å and $\theta = 167.5°$) to yield the $R_2^2(8)$ hydrogen bonding motif commonly observed in the crystal structures of amides. Interestingly, the other two N–H do not form the further H-bonded interaction to the tape formation, whereas the N–H form the N–H···Cl intermolecular H-bonded interactions with the solvent dichloride methane. Besides, the benzene ring in the sidewall of two molecules is almost parallel, which is favorable for the edge face phenyl embraces π–π interactions between the dimeric structures (Fig. 3). The distance between the planes of the two sidewall benzene rings is 3.63 Å.

Supplementary Material

CCDC-666025 contains the supplementary crystallographic data for this article. 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 CB2 1EZ, UK; fax: +44(0)1223-336033; e-mail: deposit@ccdc.cam.ac.uk.

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References

1. Rowan AE, Elemans JAAW, Nolte RJM (1999) Acc Chem Res 32:955
2. Hof F, Craig SL, Nuckolls C, Rebek J Jr (2002) Angew Chem Int Ed 41:1488
3. Kölbel N. Menger F.M. *Chem Commun* 2001, 275
4. Fremann WA, Mock WL, Shih NYJ (1981) Am Chem Soc 103:7367
5. Wu A, Chakraborty A, Witt D, Lagona J, Damkaci F, Ofori MA, Chiles JK, Fittinger JC, Isaacs LJ (2002) Org Chem 67:5817
6. Lagona J, Fettinger JC, Isaacs L (2003) Org Lett 5:3745
7. Kim J, Jung I-S, Kim S-Y, Lee E, Kang J-K, Sakamoto S, Yamaguchi K, Kim KJ (2000) Am Chem Soc 122:540
8. Day A, Arnold AP, Blanch RJ, Snushall BJ (2001) Org Chem 66:8094
9. Kang J, Jo J-H, In S (2004) Tetrahedron Lett 45:5225

10. Wu A, Mukhopadhyay P, Chakraborty A, Fittinger JC, Isaacs LJ (2004) Am Chem Soc 126:10035
11. Yin G. Wang Z. Chen Y. Wu A. Pan Y.(2006) *Synlett* 49
12. Wyler R, de Mendoza J, Rebek J Jr (1993) Angew Chem Int Ed 32:1699
13. Branda N, Wyler R, Rebek J Jr (1994) Science 263:1267
14. Branda N, Grotzfeld RM, Valdes C, Rebek J Jr (1995) J Am Chem Soc 117:85
15. Johnson D.W. Palmer L.C. Hof F. Lovine P.M. Rebek J Jr. *Chem Commun* 2002, 2228
16. Wu A, Fettinger JC, Isaacs L (2002) Tetrahedron 58:9769
17. Smeets JWH, Sijbesma RP, Niele FGM, Spek AL, Smeets WJJ, Nolte RJMJ (1987) Am Chem Soc 109:928
18. Lai YH, Yap AHT (1993) J Chem Soc Perkin Trans 2:1373
19. Sheldrick GM (2001) SADABS. Version 2.10. Bruker AXS Inc, Madison
20. Sheldrick GM (1997) SHELXL-97, Program for Crystal Refinement. Universität Göttingen, Germany
21. Wang Z-G, Zhou B-H, Chen Y-F, Yin G-D, Li Y-T, Wu A-X, Isaacs LJ (2006) Org Chem 71:4502
22. She N-F, Guo H-Z, Wang Z-G, Wu A-X (2005) Acta Crystallogr: sect E E61:o2549
23. Johnson DW, Hof F, Palmer LC, Martin T, Obst U, Rebek J Jr (2003) Chem Commun 14:1638