

Synthesis and Structure of a Novel Thiacalix[4]arene based Triazine Derivative

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Using thiacalix[4]arene and 1,3-bis-(dichloro-s-triazinyloxy)benzene as a starting materials, a novel thiacalix[4]arene based triazine derivative has been designed and synthesized. This nucleophilic displacement reaction occurred in mild condition. The conformation of 1,3-alternate was confirmed by NMR spectra and X-ray crystal structure analyses. Moreover, it formed a unique π -electron-deficient cavity has the potential to recognize cations and anions.

Key Words: Thiacalix[4]arene, Triazine, Synthesis, Structure.

INTRODUCTION

Thiacalix[4]arene, as a kind of thiacalixarenes, has attracted considerable attention in the fast-growing field of supramolecular chemistry. Four sulfur atoms instead of the methylene bridges make it has many novel features comparing with classical calixarenes, such as larger cavity, more flexibility, considerably different conformational behaviour, chemical modification of bridges and excellent coordination abilities¹. We have reported some fluorescent sensors based on thiacalix[4]arene modified with different functional groups². Much effort have been done to develop of new functional thiacalix[4]arenes and worthwhile to continue devote to do.

Triazine-based derivatives are valuable in molecular recognition and self-assembly research, because of it providing both hydrogen bond donor and acceptor sites for the selective binding of guest molecules³. Recent research indicated that a potential application of triazine act as an electron-deficient π -aromatic component to interact with anion species. In view of the high reactivity of a cyanuric halide toward nucleophilic reagents in a controlled fashion, we utilized the synthetic advantage of it to linking desired moiety with thiacalix[4]arene. Yielding a cleft formed by π -electron deficient triazine rings, we envisioned that this π -electron-deficient cavity would act as a receptor to interact with anions through π -anion interactions. Herein, we report the synthesis of the novel thiacalix[4]arene linked with triazine.

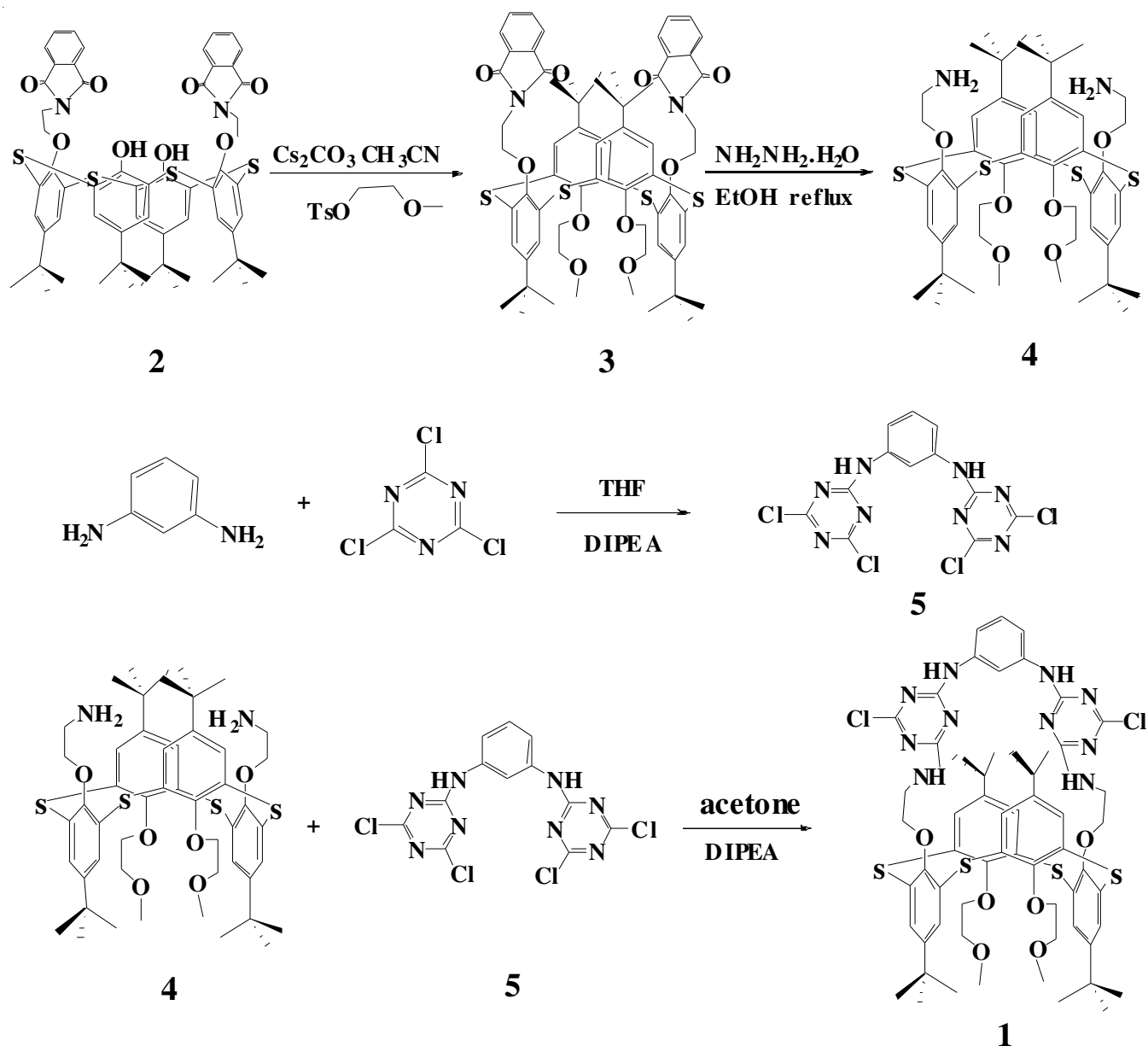
EXPERIMENTAL

All the reagents used in the study were dried or purified according to standard procedures prior to use. Melting points

were determined on a XT-4 binocular microscope (Beijing Tech Instrument Co. China) and were uncorrected. ¹H and ¹³C NMR spectra were measured on a Varian Nova-400 NMR spectrometer at room temperature. ESI-MS spectra were recorded on an Agilent HPLC-MSD-Trap-VL spectrometer. Crystal X-ray diffraction was conducted on a Bruker Smart ApexII CCD diffractometer. The X-ray datas were collected with graphite-Monochromated MoK α radiation ($\lambda = 0.071073$ Å) in ϕ and ω scan modes. The structure solution was solved by direct methods using SHELX-97 software packages. Hydrogen atoms were not refined and were placed either theoretically or found in the Fourier difference maps. 7 Water molecules in the unit cell have been taken into account to SQUEEZE option of the PLATON program. The crystallographic data in this paper have been deposited with the Cambridge crystallographic data centre as supplementary publication number CCDC(857542).

Synthesis: Compound (2), (3), (4) and (5) were synthesized following the literature procedures^{3,4}.

Synthesis of compound 1: At room temperature, solutions of 2 (461.5 mg, 0.5 mmol) in acetone (50 mL) and 3 (202 mg, 0.5 mmol) in acetone (50 mL) were added dropwise at the same time and the same rate to a solution of DIPEA (387 mg, 3 mmol) in 150 mL acetone during 6 h. After addition of two reactants, took about 24 h until the starting materials were consumed (**Scheme-I**). The solvents were removed and the residue was chromatographed with mixture of petroleum ether/ethyl acetate (6:1, v/v) as the mobile phase to give pure product 1 220 mg, yielding 37 %. m.p. > 300 °C; ¹H NMR (CDCl₃, 400 MHz), δ (ppm): 1.14 (s, 18H, C(CH₃)),



Scheme-I: Synthesis of compound 1

1.32 (s, 18H, C(CH₃)), 3.16 (t, $J = 6.8$ Hz, 4H, OCH₂), 3.31 (s, 6H, CH₃), 3.63-3.71 (m, 4H, OCH₂), 4.05-4.12 (m, 8H, OCH₂), 7.16 (br, 1H, NH), 7.23 (br, 1H, NH), 7.31 (t, $J = 8.0$ Hz, 1H, Ar-H), 7.37 (s, 4H, Ar-H), 7.42-7.46 (m, 2H, Ar-H), 7.51 (s, 4H, Ar-H), 7.61 (s, 1H, Ar-H); ¹³C NMR (CDCl₃, 400 MHz), δ (ppm): 30.98 (CH₃), 31.15 (CH₃), 31.20 (CH₃), 34.17 (C), 34.28 (C), 58.82 (NCH₂), 67.27 (OCH₂), 69.98 (OCH₂), 70.63 (OCH₂), 127.91 (Ar-C), 128.05 (Ar-C), 128.59 (Ar-C), 128.98 (Ar-C), 129.16 (Ar-C), 129.61 (Ar-C), 130.90 (Ar-C), 138.33 (Ar-C), 139.33 (Ar-C), 145.99 (Ar-C), 146.08 (Ar-C), 146.76 (Ar-C), 165.40 (Ar-C), 165.74 (Ar-C), 169.00 (Ar-C); IR (KBr, $\nu_{\max}$, cm⁻¹): 3413, 3283, 2962, 2873, 1573, 1541, 1437, 1240, 1087, 1033, 805; ESI-MS: m/z 1277 [M+Na]⁺.

RESULTS AND DISCUSSION

The single crystal of compound 1 was obtained by slow crystallization from its ethyl acetate/n-hexane (80:1 v/v) solution. The molecular structure for **1** is presented in Fig. 1,

a selection of bond distances/angles and crystallographic data can be found in Tables 1 and 2. X-ray diffraction studies reveal that the thiacalix[4]arene adopted a 1,3-alternate conformation, which was also confirmed by NMR spectra. For every two opposite benzene rings of thiacalix[4]arene framework, the dihedral angle and centroid distance are 32.14(16)°, 6.08 Å and 41.37(16)°, 6.83 Å, respectively. The four bridging sulfur atoms on thiacalix[4]arene skeleton lie in the same plane. The average distance between two neighbouring sulfur atoms in **1** is 5.57 Å. Triazine rings are twisted out of plane with the inclined angles exist between the two triazine ring planes and the benzene ring is 13.69(19)°, 27.02(18)° respectively. In the center of the cavity, there is a water molecule, the Intra-molecular hydrogen-bond N(9)...H(9)...O(1W) were formed between water oxygen and the hydrogen amino group with the very short distance of 2.20 Å. The average bond lengths and bond angles of the bridging nitrogen atoms indicated that four linking nitrogen atoms adopted an sp² configuration.

TABLE-1
 X-RAY CRYSTALLOGRAPHIC DATA OF COMPOUND 1

Formula	C ₆₂ H ₉₀ N ₁₀ O ₁₄ Cl ₂ S ₄ ·8H ₂ O	D (calcd.) g cm ⁻³	1.124
Formula weight	1398.56	μ, mm ⁻¹	0.261
Temperature (K)	293(2)	F(000)	2960
Wavelength, Å	0.71073	θ range, °	1.55 to 25.00
Crystal system	Monoclinic	h, k, l range	-18 < h < 18
Space group	P 21/n		-29 < k < 29
a (Å)	15.6034(7)		-23 < l < 20
b (Å)	24.9078(11)	Z	4
c (Å)	19.4826(9)	Reflection collected	13178
α, °	90.00	Independent reflection	8354
β, °	97.318(2)	R _{int}	0.0509
γ, °	90.00	R1, wR2 [I > 2σ(I)]	0.0652, 0.1928
V, Å ³	7510.2(6)	R1, wR2 (all data)	0.0980, 0.2107

 TABLE-2
 SELECTED BOND DISTANCES (Å) AND ANGLES (°)

N6-C50	1.462(4)	N6-H6	0.86	C51-N7-H7	116
N6-C54	1.326(4)	N7-H7	0.86	C48-N7-C51	127.9(3)
N7-C48	1.456(5)	N9-H9	0.86	C56-N9-H9	115
N7-C51	1.330(4)	N9-H9	0.86	C62-N9-H9	115
N9-C56	1.346(4)	C50-N6-H6	119	C56-N9-C62	129.6(3)
N9-C62	1.429(4)	C54-N6-H6	119	C53-N10-H10	113
N10-C53	1.347(5)	C50-N6-C54	121.9(3)	C58-N10-H10	113
N10-C58	1.395(4)	C48-N7-H7	116	C53-N10-C58	133.5(3)

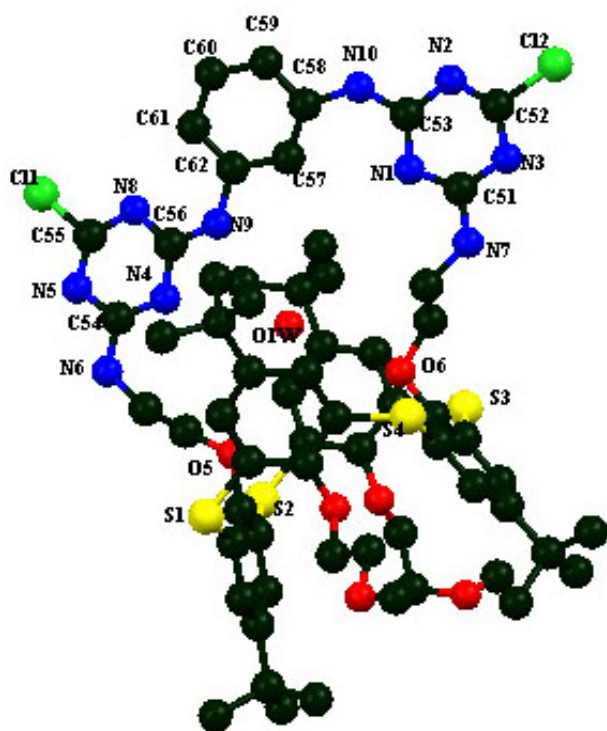


Fig. 1. Molecular structure of compound 1

Conclusion

In summary, a novel 1,3-alternate-25,27-[(*N,N'*-bis-(chloro-*s*-triazinyl)-*m*-phenyl-enediamine)minoethoxy]-26,28-bis-(2-methoxyethyl)-thiacalix[4]arene had been first synthesized under very mild conditions. It's structure was

characterized by IR, NMR, MS spectrometry and X-ray diffraction. The spectroscopy and X-ray single crystallography data showed that the new thiacalix[4]arene derivative adopted a 1,3-alternate conformation. The thiacalix[4]arene platform with the segment of *N,N'*-bis-(dichloro-*s*-triazinyl)-*m*-phenylenediamine formed a unique π -electron-deficient cavity. It was envisioned that the introduction of ether groups on to the benzene rings would give rise to a functionalized cavity. In addition, the macrocyclic framework contains multiple triazine and secondary amine moieties, which are potential hydrogen bond acceptors and donors, respectively. Most noticeably, the cavity such as **1** is composed of all two electron-deficient triazine walls. It might be useful in complexation with highly electron-rich species. The study of the molecular recognition property of the functionalized thiacalix[4]arene is in progress and will be reported in due course.

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