

Synthesis and Structure of a Host-Guest Inclusion System between C-propyl-o-toluidine-methyl-resorcin[4]arene and Ethanol Solvate

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Abstract

Tetra-bromo-methyl-resorcin[4]arene cavitands were synthesized and C-2 position amine functionalized to obtain C-propyl-o-toluidine-methyl-resorcin[4]arene cavitand **4**, and the crystal containing one solvate molecule of ethanol was obtained in a dichloromethane-ethanol solvent system, its structure crystallized in the monoclinic space group $P2_1/n$, with $a = 12.521(3) \text{ \AA}$, $b = 21.738(6) \text{ \AA}$, $c = 25.353(6) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 102.372(4)^\circ$, $\gamma = 90^\circ$, and $Z = 4$. The compound was determined by single-crystal X-ray diffraction and characterized by ^1H NMR, FT-IR and elemental analyses.

Keywords

Resorcin[4]arene, Cavitand, Amine Functionalized, Dichloromethane-Ethanol

1. Introduction

As a new generation of supramolecules, calixarenes are particularly active in the field of preparation of cavitands by chemists. The application of resorcin[4]arene in host-guest chemistry is becoming more and more extensive, and the exploration of the synthesis and modification of supramolecular compounds of resorcin[4]arene supramolecular compounds has attracted the keen interest of chemical synthesis workers. With the exploration of resorcin[4]arenes and their derivatives, resorcin[4]arene derivatives have been used to synthesize nanoparticles [1], catalysis [2], affinity materials [3], sensing [4], and molecular capsules [5] [6], which were due to the dominant conformation of resorcin[4]arene that is easy to modify various groups. For example, functionalized groups such as oxy-

gen-containing groups [7] [8], nitrogenous groups [9] [10], sulfur-containing groups [11] [12], and phosphorus-containing groups [13] [14] can be introduced into Tetra-bromo-methyl-resorcin[4]arene by simple electrophilic reaction.

At present, there have been many reports on the introduction of nitrogen-containing groups at the C-2 position of resorcin[4]arene [15] [16], among which, halogen-modified resorcin[4]arenes are often obtained by nucleophilic substitution reaction to obtain organic amine-modified resorcin[4]arenes, and Mannich condensation reaction with formaldehyde can also be used to synthesize resorcin[4]arenes with oxazine structure, which indicates that the research on nitrogen-containing group modification is still relatively popular, and can functionalize calix[4]arenes to improve their utilization. Kashapov *et al.* [17] [18] have explored three different methods to enhance the solubility of resorcin[4]arenes in water. The first method is to ionize the hydroxyl group of resorcin[4]arenes hydrocarbons under the action of alkali. The second is a supramolecular approach, which takes advantage of the high water solubility of N-methylglucosamine. The third method is solubilization in surfactant solution, which modifies the C-2 position of the cavity with amino acid groups to enhance the water solubility of resorcin[4]arenes hydrocarbons.

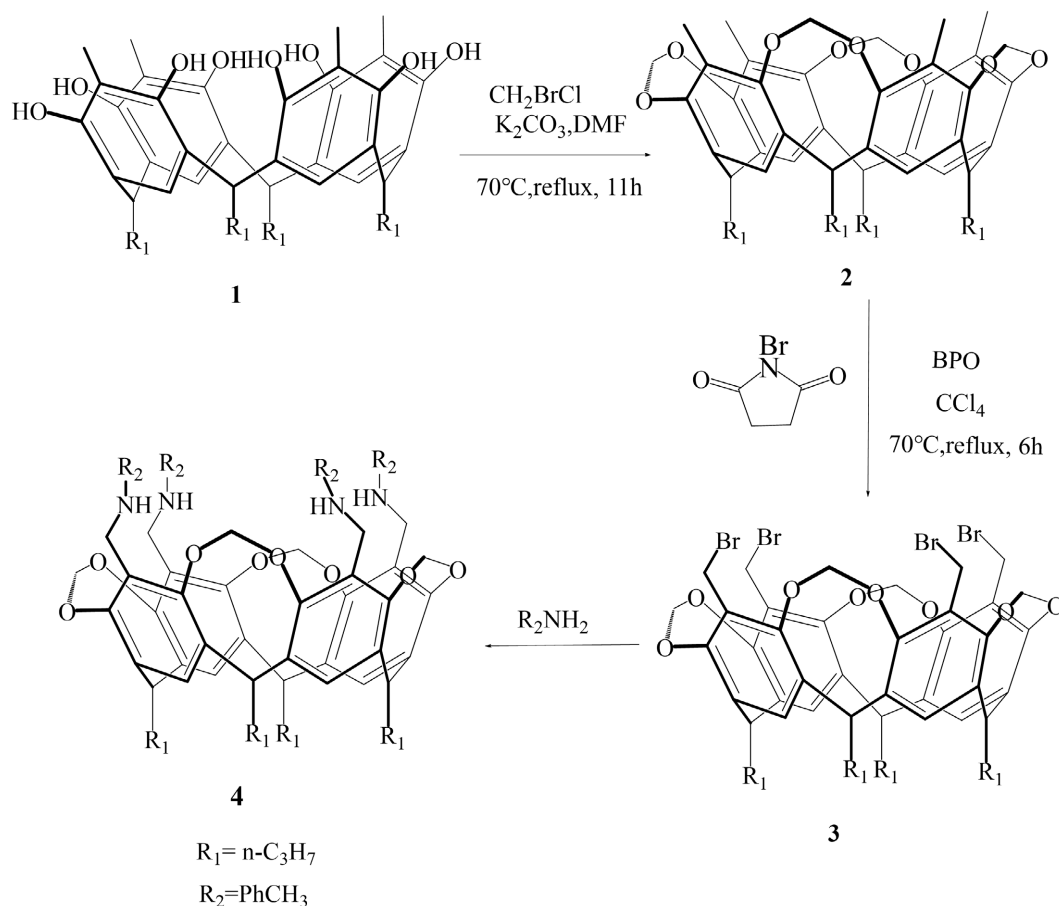
Liu *et al.* [19] synthesized diisobutylamine methyl-modified resorcin[4]arene compounds. The aromatic hydrocarbon molecule of the hydroquinone resorcin[4]arenes in the middle of the compound is bowl-shaped, the longer N-diisobutyl substituent can enlarge the macrocyclic cavity, so that the cup aromatic can wrap the solvent molecule, and the longer alkyl chain increases the stereo obstruction of the upper edge of resorcinol and forms a closed space through free folding, which can not only stabilize the guest molecule in the cavity, but also improve the kinetic stability of the whole resorcinol molecule.

Fox [20] [21] research group used amine to replace bromo-methyl-cavitands, and reacted with CS₂ in a solvent with THF/H₂O = 2:1 to synthesize dithiocarbamate functionalized cavitands. This compound can be stabilized by adding potassium hydroxide to obtain potassium salt. Herein, amine-modified resorcin[4]arene has a good research prospect, and our research group is also full of strong interest in it and has done corresponding research. In this paper, o-methylaniline resorcin[4]arene cavitand **4** was synthesized, and the crystal structure of the amine-modified compound was obtained in the mixed solvent of dichloromethane and ethanol. It can be seen that the o-methylaniline resorcin[4]arene cavitand selectively encapsulates a molecule of ethanol in the structure (Scheme 1).

2. Experimental Section

2.1. Materials

All reagents, unless otherwise stated, were purchased as analysis grade and used without further purification. All synthesis reactions were carried out under nitrogen protection. Compounds **1** - **3** were synthesized by referring to the methods in



Scheme 1. Synthetic route of compounds **1**, **2**, **3** and tetramethylene amine cavitand **4**.

the literature [22]. ^1H nuclear magnetic resonance (NMR) spectra were recorded on a Bruker ALX 400 MHz using tetramethylsilane as internal standard. Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet 6700 spectrophotometer in the $400 - 4000 \text{ cm}^{-1}$ region using KBr pellets. Elemental analyses were carried out using a Perkin-Elmer 2400 CHN analyzer.

2.2. Preparation of Complex 4

The synthesis of compounds **1**, **2** and **3** was synthesized according to the literature [22] method, and tetramethylene toluidine cavitand **4** was prepared by treating compound **3** with excess amines (Scheme 1).

Take 20 mL of *o*-toluidine (50%) in a 50 mL flask at room temperature, weigh **3** (0.235 g, 0.28 mmol) and add it to ethylamine in a small amount and multiple times within 15 minutes, stir until **3** is completely dissolved, stir for 1 h, remove excess *o*-toluidine under reduced pressure, dissolve it with dichloromethane, wash it with deionized water, add an appropriate amount of anhydrous magnesium sulfate to dry, and remove the solvent product under reduced pressure as a white powdery solid. Chemical formula: $\text{C}_{76}\text{H}_{84}\text{O}_8\text{N}_4$, Yield: 0.30 g, 85%. ^1H NMR (400 MHz, CDCl_3 , ppm, ppm) δ 7.08 - 7.18 (m, 8H, Ar-*H*), 7.03 (d, $J = 7.1$ Hz, 4H, Ar-*H*), 6.81 (d, $J = 8.0$ Hz, 4H, Ar-*H*), 6.67 (t, $J = 7.2$ Hz, 4H, Ar-*H*), 5.99 (d,

$J = 6.9$ Hz, 4H, OCH_2), 4.80 (t, $J = 8.1$ Hz, 4H, Ar_2CHCH_2), 4.40 (d, $J = 6.9$ Hz, 4H, OCH_2), 4.10 (s, 8H, ArCH_2), 2.20 (dd, $J = 15.1, 7.9$ Hz, 8H, CHCH_2CH_2), 2.10 (s, 12H, ArCH_3), 1.38 (dd, $J = 14.7, 7.3$ Hz, 8H, $\text{CH}_2\text{CH}_2\text{CH}_3$), 1.01 (t, $J = 7.3$ Hz, 12H, CH_2CH_3). Anal. Calc. for $(\text{C}_{76}\text{H}_{84}\text{O}_8\text{N}_4)$: C 77.26; H 7.17; N 4.74%. found: C 77.23; H 7.19; N 4.76%.

2.3. X-Ray Crystallography

Single crystal data for compound **4-EtOH** obtained from the tetramethylene amine cavitand **4** encapsulated with ethanol were determined on the Bruker SMART APEX 2000 CCD surface detection X-single crystal diffractometer. Moderately sized, regular-shaped, transparent and crack-free crystals were selected and fixed at the tip of the glass capillary, and single crystal data were collected at a monochromatic Mo- $K\alpha$ ray with a diffractive light source of $\lambda = 0.71073$ Å at 296(2) K. The collected data was restored [23] by the SSAINT software and then integrated by the SADABS [24] program, and the structure was solved by direct methods using SHELXS-97 and refined by least squares on F^2 (SHELXL-97) [25] [26]. Non-hydrogen atoms were corrected by various anisotropic modifications, and the position of hydrogen atoms were determined by theoretical hydrogenation ($\text{C}_{\text{sp}^2}\text{-H} = 0.93$ Å, $\text{C}_{\text{sp}^3}\text{-H} = 0.96$ Å). The crystallographic data and structure refinement are given in **Table 1**.

3. Results and Discussion

3.1. Syntheses and Characterizations

Methods in the synthesis of tetramethylene toluidine cavitands [19] [27], Bromo-treated tetramethylene toluidine cavitands were prone to occur nucleophilic substitution reaction, and the synthesis method was relatively simple and the reaction speed was relatively fast. In this reaction, tetramethylene bromide cavitand can be dissolved in primary amine, no additional solvent was required, dissolved with dichloromethane, washed with deionized water, dried and removed solvent to obtain tetramethylenetoluidine cavitand. The cavitand **4** has a polyhydrophobic group, and the single crystal of compound **4-EtOH** was volatilized by using dichloromethane and ethanol mixed solvent as the crystallization system. FT-IR spectrum of complex **4** showed the existence of both contractive vibration peak of N-H in the range of $3318 - 3438$ cm^{-1} and a strong absorption peak of C-N at around 1164 cm^{-1} as shown in **Figure 1**. In the ^1H NMR spectrum of complex **4** as shown in **Figure 2**, the chemical shift of ArH protons exhibited as a singlet at 7.13 ppm, indicating of the C_{4v} isomer. The bridging Ar_2CHCH_2 protons exhibited as a triplet at around 4.80 ppm. The chemical shift of ArH on methylaniline exhibited as multiple peaks between 6.67 - 7.18 ppm. The bridging $\text{Ar}_2\text{CH}_2\text{NH}$ protons exhibited as a singlet at approximately 4.10 ppm.

3.2. Crystal Structures

Complex **4-EtOH** crystallizes in the monoclinic space group $P2_1/n$, **Table 1**

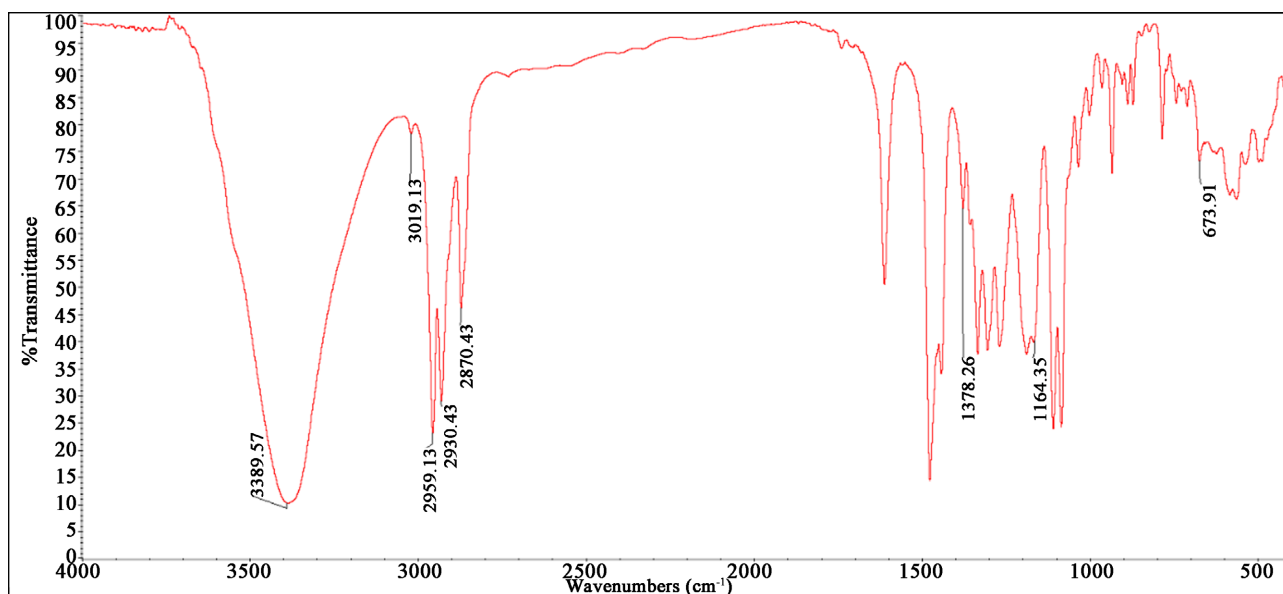


Figure 1. Infrared spectra of 2,8,14,20-tetramethylo-toluidine-5,11,17,23-tetrapropyl-cavitand.

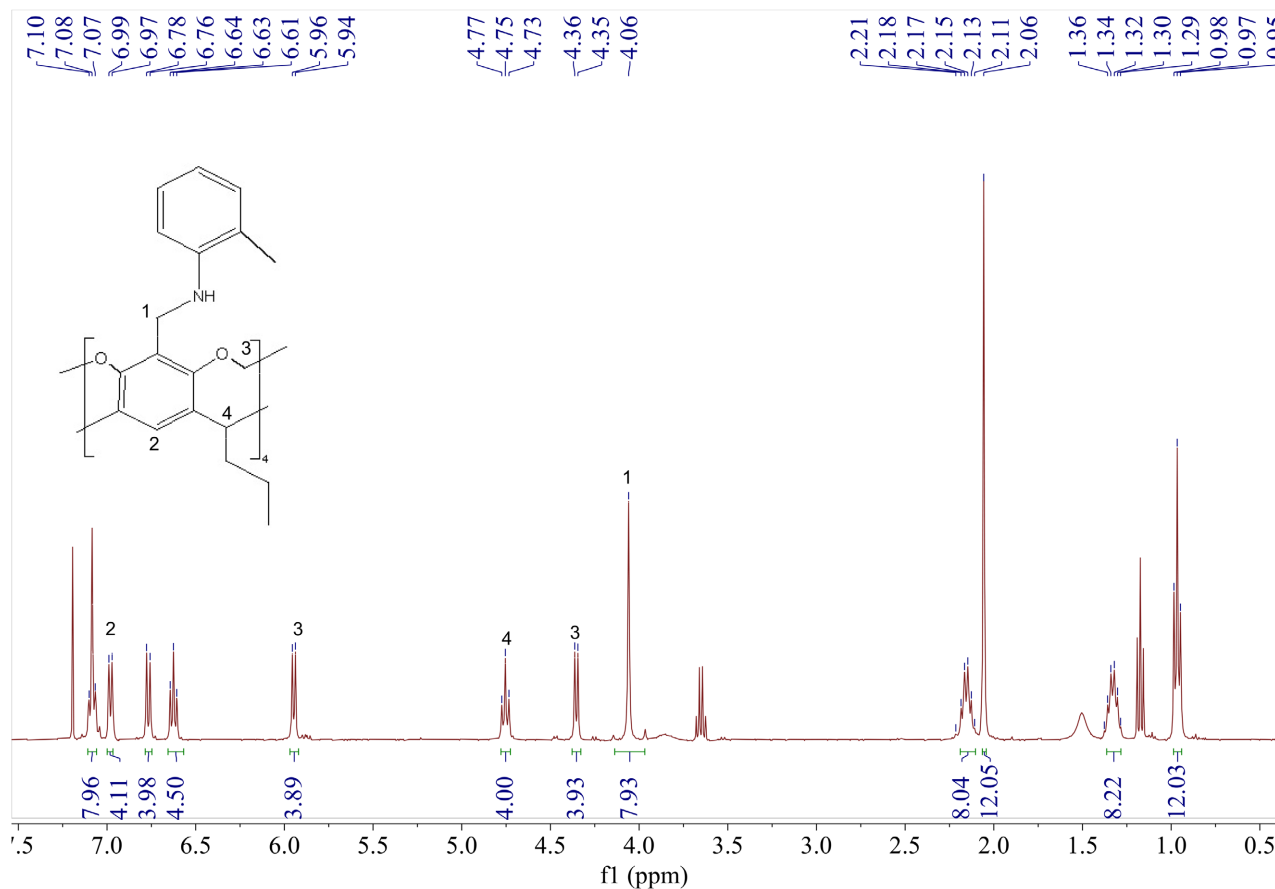


Figure 2. Nuclear magnetic hydrogen spectrum of 2,8,14,20-tetramethylo-toluidine-5,11,17,23-tetrapropyl-cavitand.

shows the specific data. The multi-component complex **4-EtOH** consists of a 2,8,14,20-tetra-*n*-propyl-5,11,17,23-tetramethylene *o*-toluidine cavitand molecule and an ethanol molecule, as shown in **Figure 3**. The arrangement structure

Table 1. Crystallographic data for compound **4-EtOH**.

Compound	4-EtOH
Empirical formula	C ₇₈ H ₉₀ O ₉ N ₄
Formula weight	1204.50
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	12.521(3) Å
<i>b</i> (Å)	21.738(6) Å
<i>c</i> (Å)	25.353(6) Å
α (°)	90
β (°)	102.372(4)
γ (°)	90
Volume (Å ³)	6741(3)
<i>Z</i>	4
<i>T</i> (K)	296(2)
Absorption coefficient (mm ⁻¹)	0.077
Density (calcd) (g/cm ³)	1.187
F(000)	2580.0
Reflections collected	41,890
Independent reflections	15,362
<i>R</i> (int)	0.1015
Data/restraints/parameters	15362/3/830
Final <i>R</i> ^a , <i>wR</i> ^{2b} [<i>I</i> ≥ 2σ(<i>I</i>)]	0.1064, 0.2836
<i>R</i> ^a , <i>wR</i> ^{2b} (all data)	0.2704, 0.3961
GoF ^c	0.956
Final diff. features (e/Å ³)	0.770, -0.399

Note: ^a $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; ^b $wR2 = \left[\sum w(|F_o|^2 - |F_c|^2)^2 / \sum w|F_o|^2 \right]^{1/2}$;

^c $GoF = \left[\sum w(|F_o| - |F_c|)^2 / (N_{obs} - N_{param}) \right]^{1/2}$.

of *o*-toluidine at the upper edge of the cavitand can have a variety of isomers, which were caused by the different orientation of C-N-C and the torsionable benzene ring, **Table 2** shows the partial bond length and bond angle of compound **4-EtOH**. It can be seen that the plane of the benzene ring containing N(1) and N(3) is perpendicular to the plane of the upper edge of the cavity, with the N atom facing towards the interior of the cavity, where the bond length of N(1)-C(46) is 1.390(8) Å, the bond length of N(1)-C(45) is 1.469(7) Å, slightly longer than the bond length of N(1)-C(46), and the bond angle C(46)-N(1)-C(45)

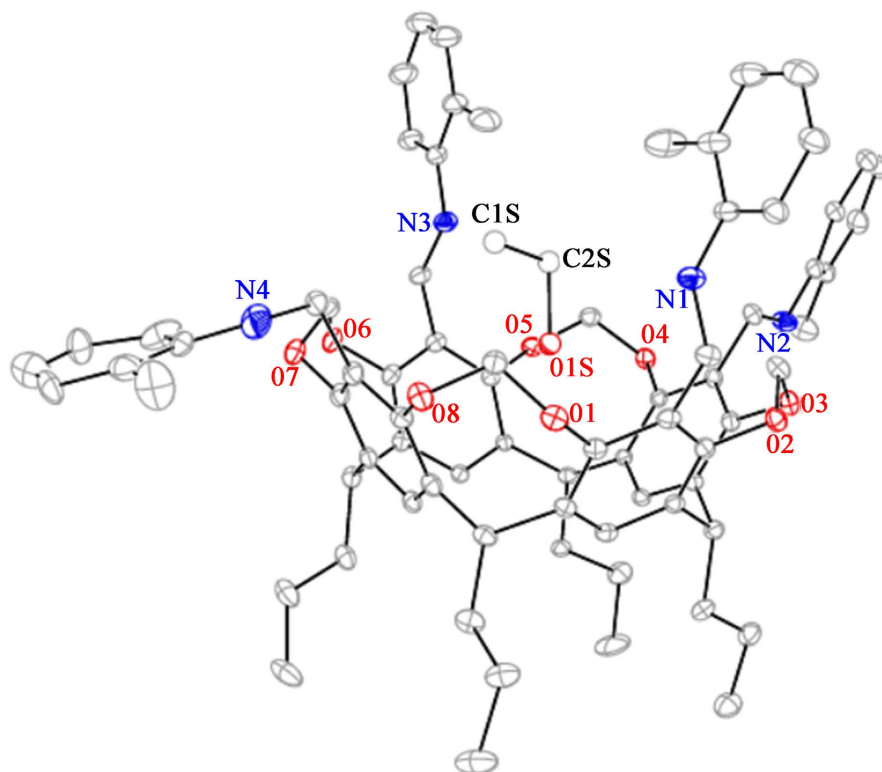


Figure 3. The asymmetric unit of multi-component complex **4-EtOH**.

is $120.3(5)^\circ$, and the bond length of N(3)-C(62) is $1.401(8)$ Å and the bond length of N(3)-C(61) is $1.446(7)$ Å. Neither the bond angle nor N(1)-N is quite the same, while the bond angle C(62)-N(3)-C(61) is $121.7(5)^\circ$, which is slightly larger than that of C(46)-N(1)-C(45); The plane of the benzene ring containing N(2) is perpendicular to the plane of the upper edge of the cavity, with the N atom facing towards the outside of the cavity, and the bond lengths of N(2)-C(54) are $1.379(7)$ Å and N(2)-C(53) are $1.456(7)$, the bond lengths being the same as those of N(1)-C. The bond angle C(54)-N(2)-C(53) is $120.8(5)^\circ$, which is also the same as that of C-N(1)-C. The plane of the benzene ring containing N(4) is roughly parallel to the plane of the upper edge of the cavity, with the N atom facing the outside of the cavity, and the bond length of N(4)-C(70) is $1.381(9)$ Å. The bond length of N(4)-C(69) is $1.455(9)$ Å, and the bond angle of C(70)-N(4)-C(69) is $126.6(7)^\circ$, which is greater than that of the previous three. The bond angle of the ethanol molecule O(1S)-C(2S)-C(1S) is $110.1(10)^\circ$.

Four *o*-tolubenzene were connected to resorcalix[4]arene by nitrogen atoms, and two phenolic hydroxyl groups were connected with methylene groups, which makes the amine-modified methyl cavitand have different properties than resorcalix[4]arene. From the crystal structure of compound **4-EtOH**, it can be seen that the upper edge C-2 position was connected to the hydrophobic aromatic group, the hydrophilic phenolic hydroxyl group at the upper edge were bridged by methylene, the lower edge was a hydrophobic hydrocarbon group, thereby changing the properties of resorcalix[4]arene. The methylene bridged *o*-toluidine

Table 2. Partial bond length (Å) and bond angle (°) of compound **4-EtOH**.

Bond lengths			
N(1)-C(46)	1.390(8)	N(3)-C(61)	1.446(7)
N(1)-C(45)	1.469(7)	N(3)-H(3)	0.8600
N(1)-H(1)	0.8600	N(4)-C(70)	1.381(9)
N(2)-C(54)	1.379(7)	N(4)-C(69)	1.455(9)
N(2)-C(53)	1.456(7)	N(4)-H(4)	0.8600
N(2)-H(2)	0.8600	O(1S)-C(2S)	1.542(10)
N(3)-C(62)	1.401(8)	O(1S)-H(1S)	0.8200
Bond angles			
C(46)-N(1)-C(45)	120.3(5)	N(2)-C(53)-H(53A)	109.6
C(46)-N(1)-H(1)	119.8	N(2)-C(53)-H(53B)	109.6
C(45)-N(1)-H(1)	119.8	N(2)-C(54)-C(55)	121.5(6)
C(54)-N(2)-C(53)	120.8(5)	N(2)-C(54)-C(59)	118.7(6)
C(54)-N(2)-H(2)	119.6	N(3)-C(61)-C(14)	111.4(5)
C(53)-N(2)-H(2)	119.6	N(3)-C(61)-H(61A)	109.3
C(62)-N(3)-C(61)	121.7(5)	N(3)-C(61)-H(61B)	109.4
C(62)-N(3)-H(3)	119.1	C(67)-C(62)-N(3)	118.5(7)
C(61)-N(3)-H(3)	119.1	C(63)-C(62)-N(3)	121.4(7)
C(70)-N(4)-C(69)	126.6(7)	N(4)-C(69)-C(20)	112.0(6)
C(70)-N(4)-H(4)	116.7	N(4)-C(69)-H(69A)	109.2
C(69)-N(4)-H(4)	116.7	N(4)-C(69)-H(69B)	109.2
N(1)-C(45)-C(2)	111.7(4)	C(71)-C(70)-N(4)	117.1(9)
N(1)-C(45)-H(45A)	109.3	C(75)-C(70)-N(4)	123.2(8)
N(1)-C(45)-H(45B)	109.3	C(2S)-O(1S)-H(1S)	109.3
C(47)-C(46)-N(1)	122.2(6)	O(1S)-C(2S)-C(1S)	110.1(10)
N(1)-C(46)-C(51)	117.8(6)	O(1S)-C(2S)-H(2S1)	109.8
N(2)-C(53)-C(8)	110.4(5)	O(1S)-C(2S)-H(2S2)	109.7

deepens the internal cavity of the resorcalix[4]arene, and the larger space opens up the possibility of housing guest molecules, as shown in **Figure 4(a)**, compound **4-EtOH** contains an ethanol molecule can be clearly seen.

As shown in **Figure 4(b)**, the upper edge of the resorcalix[4]arene was connected to four o-toluaniline, and the steric resistance of the upper edge is very large, so that the adjacent resorcalix[4]arene units can only be arranged in the opposite direction of the cup mouth to reduce the steric hindrance. The two layers of resorcalix[4]arenes were also arranged by the cup mouth to the bottom of the cup due to the influence of steric hindrance. The upper and lower layers of

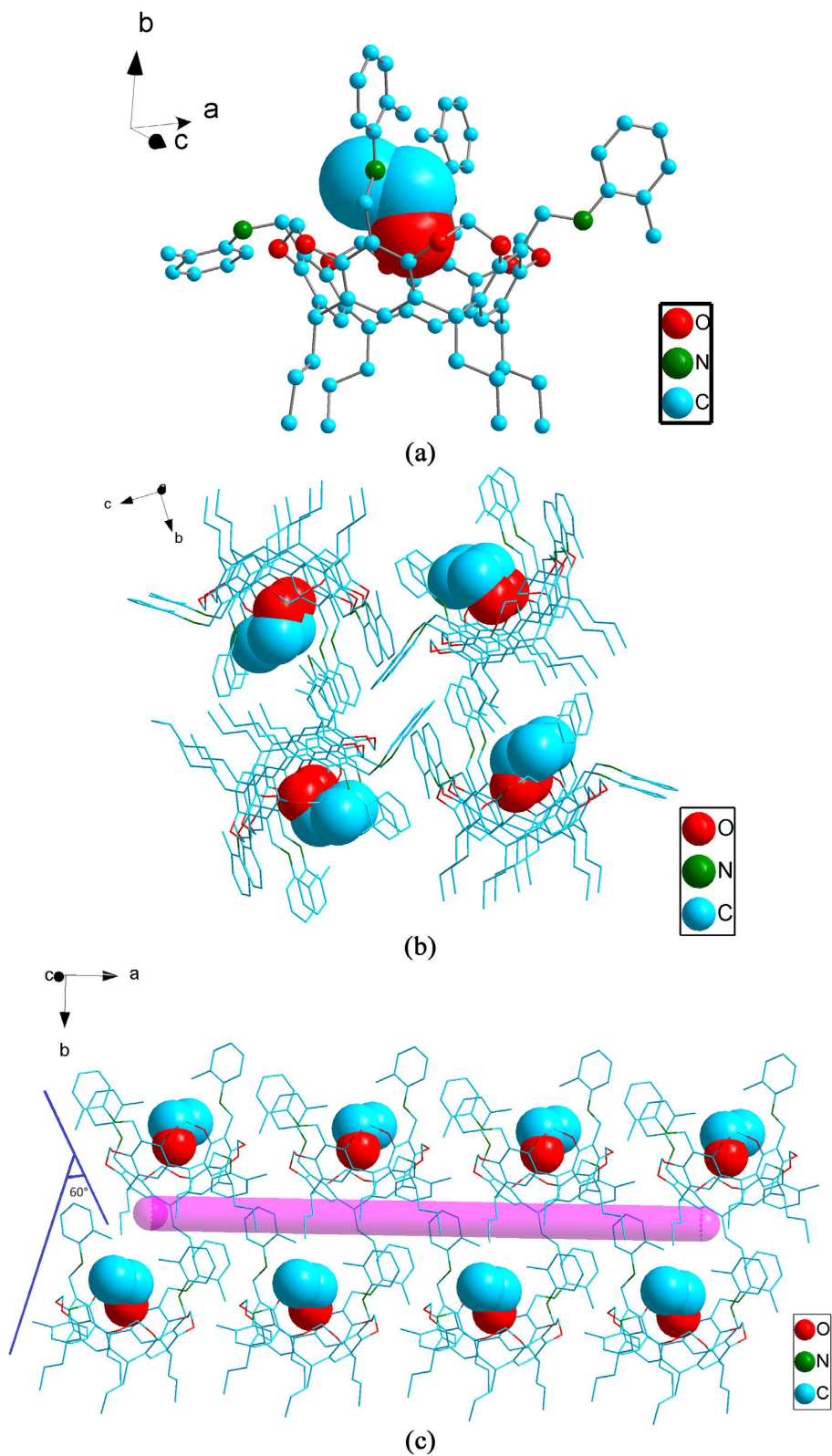


Figure 4. (a) Molecular structure of multi-component complex **4-EtOH** in stick presentations from side view. (b) Crystal structure stacking diagram of compound **4-EtOH** along the a-axis. (c) Alternate permutation structures of multi-component complex **4-EtOH** in stick and filling presentations from side view.

resorcalix[4]arene units between the one-dimensional chain were not parallel in **Figure 4(c)**, there was an angle of about 60°, the crystal arrangement adopts this dislocation arrangement because the upper edge of the resorcalix[4]arene has an aromatic group, the lower edge has a chain hydrocarbon group, and the dislocation arrangement ensures the crystallographic stability of the structure.

4. Conclusion

In summary, o-methylaniline resorcalix[4]arene cavitand **4** was synthesized with high yield by reacting tetrabromomethyl cavitand with o-toluidine in this paper, and characterized by IR spectra, ¹H NMR and elemental analysis. Compound **4** crystallized in a mixed solvent of dichloromethane and ethanol, the cavity of the cavitand was encapsulated with an ethanol molecule, and the crystal structure of **4-EtOH** was determined by X-ray single crystal diffractometry. The adjacent cavitand objects were arranged in the opposite direction of the cup mouth, the cup-in-line arrangement between the two layers of cavitand objects was arranged by the cup mouth to the bottom of the cup, the resorcalix[4]arene units between the one-dimensional chain of the upper and lower layers of acupuncture objects were not parallel, and the dislocation arrangement of about 60° angle was adopted.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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