

## Crystal structures of two thiacalix[4]arene derivatives anchoring four thiadiazole groups

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**Abstract.** The crystal structures of two thiacalixarene derivatives anchoring thiadiazole functional groups at lower rim,  $C_{60}H_{72}O_4S_{12}N_8$  (**1**),  $C_{64}H_{80}O_4S_{12}N_8$  (**2**), have been determined by single crystal X-ray diffraction. The thiacalix[4]arene framework in both **1** and **2** adopts the 1,3-alternate conformation. Compound **1** forms a 1-D chain by weak hydrogen bonding (C–H···N) interactions between two thiadiazole groups in two different molecules. The chains are further connected to form a 2-D network through sulfur–sulfur (S···S) interactions. The lattice water molecules which exist as dimers by forming hydrogen bonds (O–H···O) promote a 3-D supramolecular structure through weak hydrogen bonding (O–H···S) interactions between the lattice water dimers and the 2-D networks. On the other hand, compound **2**, based on dimer which is formed by weak hydrogen bonding (C–H···S) interactions, is extended to a 1-D chain through sulfur–sulfur (S···S) interactions. The dimers of lattice methanol molecules linked by hydrogen bonds (O–H···O) act as bridges to link the 1-D chains into a 2-D network through weak hydrogen bonding (C–H···N) interactions.

**Keywords.** Thiacalixarene; thiadiazole; crystal structure; weak interaction.

### 1. Introduction

As novel members of the well-known calixarene family<sup>1–4</sup> thiacalixarenes since their discovery in 1997; have attracted considerable interest as an alternative to ‘classic’ calixarenes by providing sites for functionalization not only on the aromatic rings but also on the bridging sulfur atoms.<sup>5</sup> By virtue of electron-rich sulfur bridges, thiacalixarenes possess additional coordination sites and flexible cavity dimensions as well as high affinity to transition metal ions compared with analogous calixarenes, and thus are considered to be superior to the classical calixarenes.<sup>6,7</sup> The conformational preferences of thiacalix[4]arene derivatives in the solid state are controlled by the groups attached to the thiacalixarene framework, presence of guest molecule(s), solvent of crystallization and other factors.<sup>8,9</sup> In a previous paper, we have synthesized novel thiacalixarene derivatives bearing thiadiazole functional groups at lower rims.<sup>10</sup> In the present study, we report the crystal structures of two

thiacalix[4]arene derivatives which form supramolecular structures through intermolecular interactions.

### 2. Experimental

#### 2.1 Synthesis of $C_{60}H_{72}O_4S_{12}N_8$ (**1**), $C_{64}H_{80}O_4S_{12}N_8$ (**2**)

Compounds **1** and **2** (figure 1) were synthesized as white powder as per the reported procedure.<sup>10</sup> A sample of **1** or **2** ~30 mg was dissolved in 30 mL chloroform. Several drops of methanol were added and the solution was allowed to evaporate for slowly a week at room temperature to obtain single crystals suitable for X-ray diffraction analysis.

#### 2.2 X-ray structure determination

X-ray single-crystal data collections for **1** and **2** were performed with a Bruker SMART APEX II CCD diffractometer equipped with a graphite monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å) by using  $\phi$ - $\omega$  scan technique at room temperature. The structures were solved by direct methods and refined

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by the full-matrix least-squares refinement on  $F^2$  using with SHELXL-97 package.<sup>11–13</sup> Intensity data were corrected for empirical absorption. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms of water molecules were located by Fourier map, and then refined by riding mode. The other hydrogen atoms were assigned with common isotropic displacement factors and included in the final refinement by use of geometrical restrains. A summary of the crystallographic data are given in table 1. The  $R$  factors for both the structures are quite high presumably due to poor quality of the crystals. Selected bond distances and angles are given in tables 2 and 3, respectively. The geometrical parameters of hydrogen bonding and other intermolecular interactions are listed in table 4.

### 3. Results and discussion

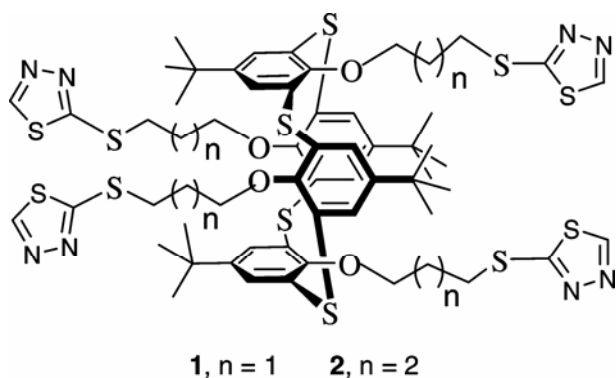
#### 3.1 Structure of $C_{60}H_{72}O_4S_{12}N_8$ (**1**)· $CHCl_3$ · $H_2O$

The thiacalix[4]arene framework adopts the 1,3-alternate conformation. As seen from figure 2, the asymmetric unit consists of one thiacalix[4]arene molecule and one chloroform and one water molecules. The dihedral angle between the two thiadiazole rings on the same plane defined by the four sulfur atoms of thiacalix[4]arene framework is  $77.3^\circ$ ,  $10.9^\circ$ , respectively. For every two opposite benzene rings of thiacalix[4]arene framework, the dihedral angle and centroid distance are  $48.48(1)^\circ$ ,  $6.43(3)$  Å,  $54.89(2)^\circ$ ,  $6.53(3)$  Å, respectively. The four sulfur atoms on thiacalix[4]arene skeleton lie in the same plane with a mean deviation of 0.08 Å. The distance between two opposite sulfur atoms as well as oxygen atoms are  $7.93(3)$  Å,  $7.87(3)$  Å,

$4.25(7)$  Å,  $3.98(2)$  Å, respectively. In the crystal structure, the molecules are linked to form 1-D chain structure by weak hydrogen bonding ( $C_{50}-H_{50}\cdots N_4 = 3.25$  Å and  $C_{60}-H_{60}\cdots N_5 = 3.40$  Å) interactions<sup>14</sup> between thiadiazole nitrogen atoms and hydrogen atoms of methyl groups attached to another thiadiazole ring (figure 3). The adjacent 1-D chains are further connected to form a 2-D network through weak sulfur–sulfur ( $S_6\cdots S_{11} = 3.59$  Å)<sup>15</sup> interactions between sulfur atoms in the thiadiazole rings and 2-positional mercapto sulfur atoms (as seen from supplementary material figure S1). The lattice water molecules, which exist as dimers through hydrogen bondings ( $O_5-H_2\cdots O_5 = 2.28$  Å), promote the formation of a 3-D network by weak hydrogen bonding ( $O_5-H_1\cdots S_{12} = 3.78$  Å)<sup>16,17</sup> interactions between the lattice water dimers and 2-D networks (see figure S2 and figure S3 of supplementary material). The lattice chloroform molecules do not play any roles in the supramolecular structures.

#### 3.2 Structure of $C_{64}H_{80}N_8O_6S_{12}$ (**2**)· $2CH_3OH$

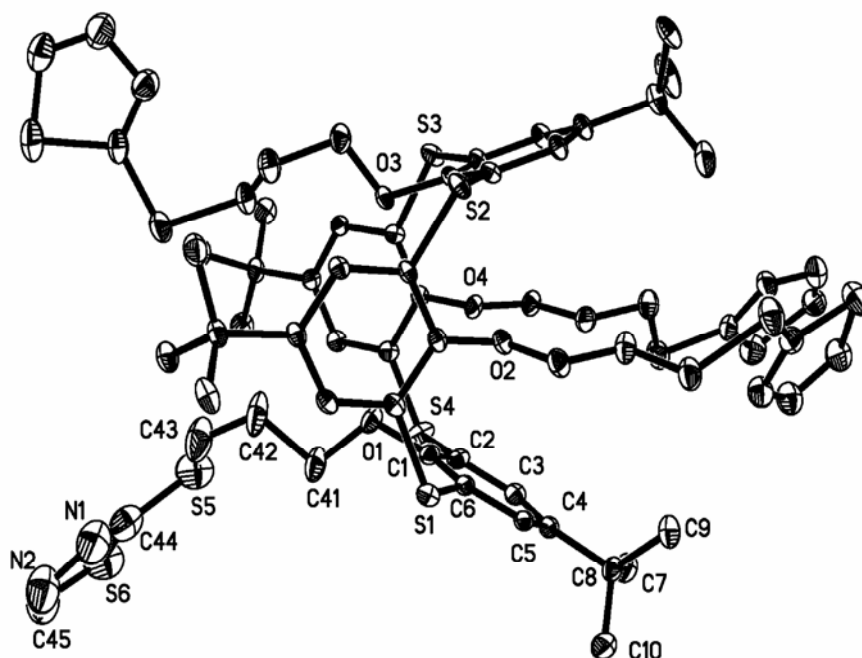
As shown in figure 4, the asymmetric unit of the compound  $C_{64}H_{80}N_8O_6S_{12}$  (**2**)· $2CH_3OH$  contains one thiacalix[4]arene molecule and two methanol molecules. The dihedral angle between the two thiadiazole rings on the same side is  $82.0^\circ$ ,  $25.0^\circ$ , respectively. For every two opposite benzene rings of thiacalix[4]arene framework, the dihedral angle and centroid distance are  $43.74(2)^\circ$ ,  $6.28(7)$  Å,  $50.26(2)^\circ$ ,  $6.44(6)$  Å, respectively. The four sulfur atoms on calix[4]arene skeleton lie in the same plane with the mean deviation of 0.19 Å. The distance between the two opposite sulfur atoms as well as oxygen atoms are  $7.90(3)$  Å,  $7.80(2)$  Å,  $4.18(7)$  Å,  $4.14(6)$  Å, respectively. Two molecules of **2** are connected to form a dimer through two weak hydrogen bonding ( $C_{49}-H_{49}\cdots S_2 = 3.70$  Å)<sup>18</sup> interactions involving the hydrogen atoms from alkyl chains and the sulfur atoms of thiacalix[4]arene framework. These dimers are assembled into 1-D chain structure by sulfur–sulfur ( $S\cdots S = 3.65$  Å)<sup>14</sup> interactions between the sulfur atoms from adjacent mercaptothiadiazole groups (see figure S4 of supplementary material). The lattice methanol molecules exist in dimers by hydrogen bondings ( $O_5-H_5\cdots O_6 = 3.05$  Å and  $O_6-H_6\cdots O_5 = 3.05$  Å). Subsequently, a 2-D network is generated through weak hydrogen bonding ( $C_{65}-H_{65}\cdots N_2 = 3.35$  Å and  $C_{46}-H_{46}\cdots O_6 = 3.42$  Å)



**Figure 1.** The structures of compounds **1** and **2**.

**Table 1.** Crystal data and structure refinement parameters for **1** and **2**.

| Compound                                   | <b>1</b>  | <b>2</b>   |
|--|---|--|
| Formula                                    | C <sub>61</sub> H <sub>75</sub> N <sub>8</sub> O <sub>4</sub> S <sub>12</sub> ( <b>1</b> )·H <sub>2</sub> O·CHCl <sub>3</sub> | C <sub>64</sub> H <sub>80</sub> N <sub>8</sub> O <sub>6</sub> S <sub>12</sub> ( <b>2</b> )·2CH <sub>3</sub> OH |
| Formula weight                             | 1491.36   | 1474.16  |
| <i>T</i> (K)                               | 273(2)  | 291(2)   |
| Space group                                | <i>P</i> $\bar{1}$  | <i>P</i> $\bar{1}$   |
| Crystal system                             | Triclinic   | Triclinic  |
| Cell constants                             |   |  |
| <i>a</i> (Å)                               | 15.448(8)   | 15.858(2)  |
| <i>b</i> (Å)                               | 15.640(8)   | 16.247(2)  |
| <i>c</i> (Å)                               | 15.878(8)   | 16.472(2)  |
| $\alpha$ (°)                               | 106.702(7)  | 71.279(2)  |
| $\beta$ (°)                                | 91.659(8)   | 86.046(2)  |
| $\gamma$ (°)                               | 93.213(7)   | 72.668(2)  |
| Volume (Å <sup>3</sup> )                   | 3664(3)   | 3835.4(8)  |
| <i>Z</i>                                   | 2   | 2  |
| Density (g/cm <sup>3</sup> )               | 1.352   | 1.276  |
| Absorption coefficient (mm <sup>-1</sup> ) | 0.518   | 0.394  |
| <i>F</i> (000)                             | 1560  | 1560   |
| Sizes (mm)                                 | 0.35 × 0.27 × 0.08  | 0.45 × 0.35 × 0.11   |
| $\theta$ (°)                               | 2.46 to 25.50   | 2.30 to 25.50  |
| Limiting indices                           | -18 ≤ <i>h</i> ≤ 18, -18 ≤ <i>k</i> ≤ 18, -19 ≤ <i>l</i> ≤ 19   | 19 ≤ <i>h</i> ≤ 18, -19 ≤ <i>k</i> ≤ 19, -19 ≤ <i>l</i> ≤ 19   |
| Reflections collected/unique               | 27209/13486 [ <i>R</i> (int) = 0.1029]  | 29467/14138 [ <i>R</i> (int) = 0.0563]   |
| Data/restraints/parameters                 | 13486/881/876   | 14138/537/84   |
| GOF  | 0.964   | 1.021  |
| <i>R</i> <sub>1</sub>                      | 0.1024  | 0.0939   |
| <i>WR</i> <sub>2</sub>                     | 0.2421  | 0.2453   |

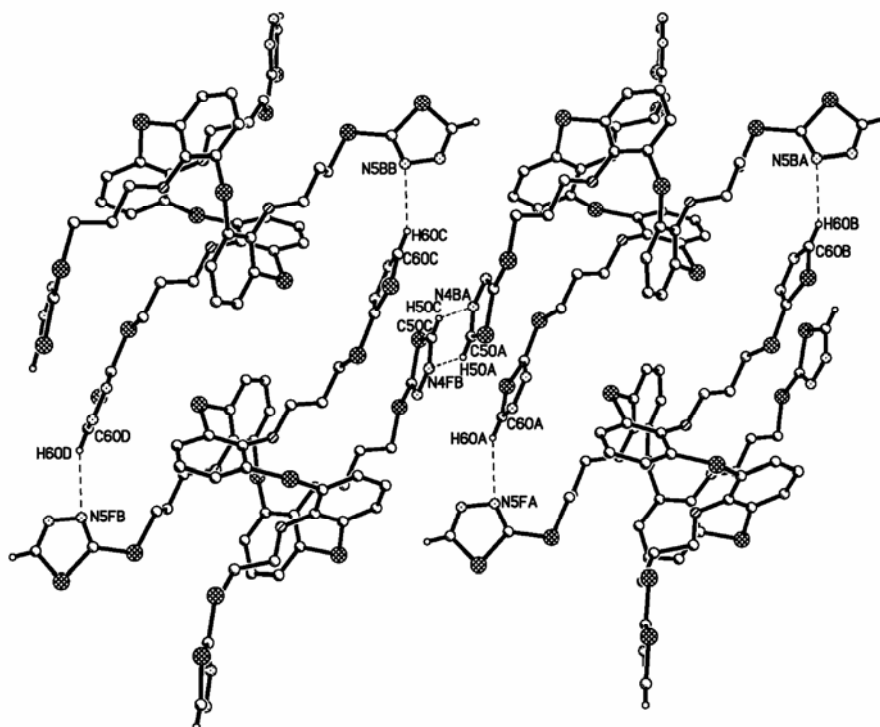
**Figure 2.** ORTEP of compound **1** with 15% probability (one chloroform and one water molecules as well as all hydrogen atoms and *t*-butyl groups are deleted for clarity).

**Table 2.** Selected bond lengths (Å) of **1** and **2**.

| <b>1</b>    |          |             |          | <b>2</b>    |          |             |          |
|-------------|----------|-------------|----------|-------------|----------|-------------|----------|
| C(21)–C(22) | 1.390(8) | C(51)–C(52) | 1.50(1)  | C(21)–C(22) | 1.379(8) | S(3)–C(31)  | 1.769(6) |
| C(25)–C(26) | 1.402(8) | C(52)–C(53) | 1.52(1)  | C(21)–C(26) | 1.402(8) | S(3)–C(25)  | 1.769(6) |
| C(27)–C(28) | 1.50(1)  | S(2)–C(22)  | 1.780(6) | C(22)–C(23) | 1.400(8) | S(9)–C(57)  | 1.794(9) |
| C(22)–C(23) | 1.395(8) | S(2)–C(16)  | 1.799(6) | C(53)–C(54) | 1.488(9) | S(9)–C(56)  | 1.801(9) |
| O(3)–C(21)  | 1.384(7) | S(9)–C(54)  | 1.73(1)  | C(54)–C(55) | 1.58(1)  | S(10)–C(58) | 1.669(8) |
| C(23)–C(24) | 1.387(8) | S(9)–C(53)  | 1.809(8) | C(55)–C(56) | 1.49(1)  | S(10)–C(57) | 1.688(8) |
| O(3)–C(51)  | 1.414(8) | S(10)–C(55) | 1.66(1)  | C(23)–C(24) | 1.350(8) | N(5)–C(57)  | 1.289(8) |
| C(24)–C(25) | 1.405(9) | S(10)–C(54) | 1.716(8) | C(23)–C(27) | 1.551(8) | N(5)–N(6)   | 1.397(8) |
| C(24)–C(27) | 1.561(9) | N(5)–C(54)  | 1.30(1)  | C(24)–C(25) | 1.401(8) | N(6)–C(58)  | 1.260(9) |
| N(5)–N(6)   | 1.34(1)  | N(6)–C(55)  | 1.26(1)  | C(25)–C(26) | 1.393(8) | C(27)–C(28) | 1.47(1)  |

**Table 3.** Selected bond angles (deg) of **1** and **2**.

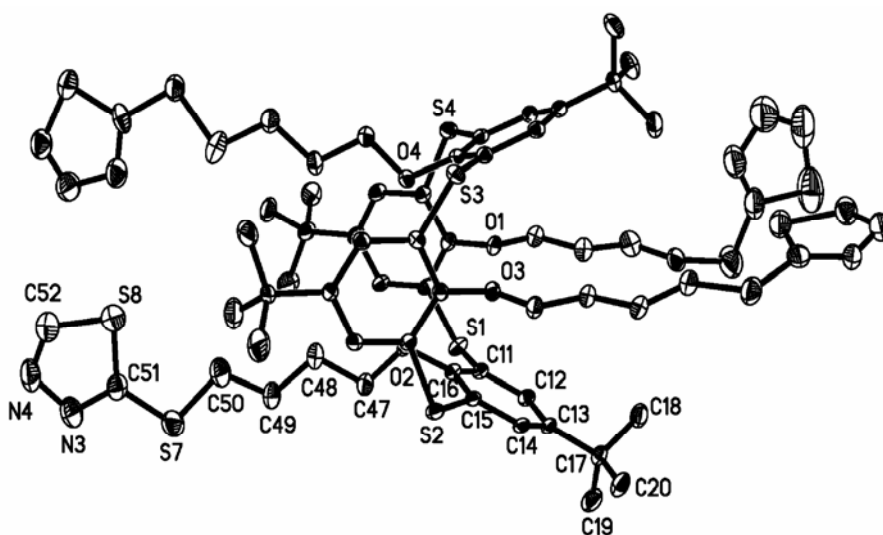
| <b>1</b>          |          | <b>2</b>          |          |
|-------------------|----------|-------------------|----------|
| C(23)–C(22)–S(2)  | 115.5(4) | C(26)–C(21)–S(2)  | 122.9(4) |
| C(26)–C(21)–O(3)  | 120.2(6) | O(3)–C(26)–C(25)  | 121.0(5) |
| C(21)–C(26)–S(3)  | 122.7(5) | O(3)–C(53)–C(54)  | 107.8(6) |
| O(3)–C(51)–C(52)  | 110.2(7) | C(53)–C(54)–C(55) | 111.6(6) |
| C(51)–C(52)–C(53) | 112.2(6) | C(56)–C(55)–C(54) | 109.4(7) |
| C(52)–C(53)–S(9)  | 112.6(6) | C(55)–C(56)–S(9)  | 110.7(7) |
| N(5)–C(54)–S(9)   | 125.1(7) | S(10)–C(57)–S(9)  | 126.5(5) |
| S(10)–C(54)–S(9)  | 122.5(6) | N(5)–C(57)–S(9)   | 120.0(7) |
| C(22)–S(2)–C(16)  | 106.8(3) | C(26)–O(3)–C(53)  | 115.0(4) |
| C(26)–S(3)–C(32)  | 109.6(3) | C(57)–S(9)–C(56)  | 98.0(4)  |
| C(54)–S(9)–C(53)  | 101.9(4) | C(15)–S(2)–C(21)  | 108.5(3) |
| C(21)–O(3)–C(51)  | 113.0(5) | C(31)–S(3)–C(25)  | 107.7(3) |

**Figure 3.** 1-D chain of compound **1** formed by C–H...N interactions (chloroform and water molecules as well as all *t*-butyl groups are deleted and only the hydrogen atoms involved in hydrogen bonding are shown for clarity).

**Table 4.** Geometrical parameters of hydrogen bonds for **1** and **2** (Å, deg).

| Compounds | D–H...A           | <i>d</i> (D–H) | <i>d</i> (H...A) | <i>d</i> (D...A) | ∠(D–H...A) |
|-----------|-------------------|----------------|------------------|------------------|------------|
| <b>1</b>  | O5–H2W...O5(a)    | 0.96           | 1.78             | 2.28(3)          | 108.0      |
|           | C50–H50...N4(b)   | 0.93           | 2.54             | 3.25(1)          | 147.0      |
|           | C60–H60...N5(c)   | 0.93           | 2.55             | 3.40(2)          | 153.0      |
|           | O5B–H1B...S12A(d) | 0.962          | 2.903            | 3.78(7)          | 179.7      |
| <b>2</b>  | O5–H5...O6        | 0.82           | 2.33             | 3.05(5)          | 146.0      |
|           | O6–H6...O5        | 0.82           | 2.45             | 3.05(5)          | 130.0      |
|           | C46–H46...O6(e)   | 0.93           | 2.55             | 3.42(3)          | 156.0      |
|           | C65–H65A...O6     | 0.96           | 2.45             | 3.14(7)          | 129.0      |
|           | C65–H65B...N2(f)  | 0.95           | 2.43             | 3.35(5)          | 162.0      |
|           | C49B–H49D...S2A   | 0.97           | 2.93             | 3.70             | 147.2      |
|           | C49A–H49B...S2B   | 0.97           | 2.93             | 3.70             | 147.2      |

Symmetry codes: a:  $1-x, -y, -z$ ; b:  $2-x, 1-y, 2-z$ ; c:  $2-x, 1-y, 1-z$ ; d:  $-x+2, -y+1, -z+1$ ; e:  $x, 1+y, -1+z$ ; f:  $1-x, 1-y, -z$ .

**Figure 4.** ORTEP of compound **2** with 15% probability (two methanol molecules and all hydrogen atoms are omitted for clarity).

interactions,<sup>16,17</sup> which act as bridges to link the 1-D chains and methanol dimers (see supplementary material figure S5).

#### 4. Conclusion

In summary, crystal structures of two thiacalix[4]arene derivatives anchoring thiadiazole functional groups at lower rims,  $C_{60}H_{72}O_4S_{12}N_8$  (**1**),  $C_{64}H_{80}O_4S_{12}N_8$  (**2**), have been determined by single-crystal X-ray diffraction. The thiacalix[4]arene platforms in both compounds **1** and **2** adopt simple 1,3-alternate conformation. This may be ascribed to the introduction of a long chain, which prevents the rotation of the aryl rings in thiacalixarene skeleton. Both structures of  $C_{60}H_{72}O_4S_{12}N_8$  (**1**)·CHCl<sub>3</sub>·H<sub>2</sub>O and

$C_{64}H_{80}N_8O_6S_{12}$  (**2**)·2CH<sub>3</sub>OH display 3-D and 2-D supramolecular network respectively through intermolecular interactions.

#### Acknowledgements

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#### Supplementary materials

Crystallographic data for **1** (CCDC-642372) and **2** (CCDC-642374) reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary materials. Copies of this

material can be obtained free of charge from Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

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