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A New Tubular Arrangement of a Dimethylsilyl Bridged Calix[4]resorcinarene

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The functionalization of calix[4]resorcinarene 1 ($R_1 = H$, $R_2 = Me$) with dichlorodimethylsilane leads to the formation of the dimethylsilyl-bridged cavitand 2 which, during the work up of the reaction product, encapsulates a molecule of water. $2 \cdot H_2O$ crystallizes in the C2/c system ($a = 23.892$ Å, $b = 8.493$ Å, $c = 43.035$ Å, $\beta = 100.05°$, reflections: 5385, 2376 ($F > 4.0\ \sigma(F)$), $R = 9.17\%$, calculated density $= 1.213$ Mg/m^3) with eight molecules per unit cell. The main feature of the crystal packing is the alternating pairs of up-down disposed cavitands along the *c* direction and well developed columns in the *b* direction. The molecules of water are completely encapsulated, but there are some close contacts with the methylene bridge from the upper molecule. Molecular orbital calculations show that the lowest energy conformer of cavitand 2 is that with all four silicon atoms oriented inward and the energies of the other conformers are so high that they cannot be accessed at normal temperature. *Ab initio* calculated electrostatic potentials correlate well with the relative positions of the cavitands in the crystal structure.

Keywords: Crystal structure, functionalized calix[4]resorcinarene, molecular structure, AM1, *ab initio* molecular orbital, supramolecular packing

INTRODUCTION

The chemistry of resorcinarenes has seen impressive developments during the last few years due to their conformational and complexation properties reflected in high structural recognition abilities [1–4, and references therein]. In this respect, the title of the review of Böhmer: "**Calixarenes, Macrocycles with (almost) Unlimited Possibilities**" [3] characterizes most expressively this extremely dynamic field of supramolecular chemistry.

Calix[4]resorcinarenes 1 (the official IUPAC name is: 2,8,14,20-tetraalkylpenta-cyclo[19.3.1.$1^{3,7}.1^{9,13}.1^{15,19}$] octacosa-1(25)3,5,7(28),9,11,13(27), 15,17,19(26),21,23-dodecaene-4,6,10,12,16,18,22, 24-octol) may present many isomeric (stereoisomeric) forms arising from the combination of five conformations: crown (cone), chair (a flattened partial cone), boat (flattened cone), diamond (1,2 alternate), and saddle (1,3 alternate) [2] with the

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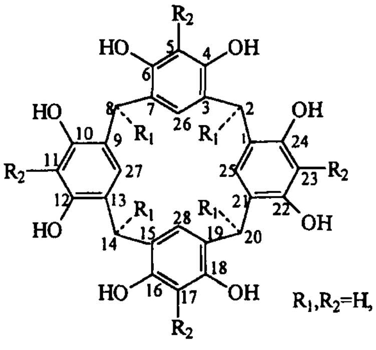
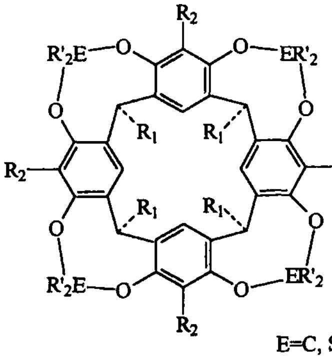


R_1,R_2=H, alkyl

1



E=C, Si

2

relative configuration (*cis-cis-cis, cis-cis-trans, cis-trans-trans*, and *trans-cis-trans*), and the individual configurations (axial or equatorial) of the substituents R_1. The magnitude of the barrier for interconversion between the possible conformers increases on the esterification of the phenolic OH groups [5–10]. The resorcinarenes derived from formaldehyde ($R_1 = \mathrm{H}$) are more flexible and their conformational mobility in apolar solvents has been assigned to a rapid interconversion of crown conformers [11]. In polar solvents (like pyridine) the saddle conformation seems to be stabilized due to the disruption of the hydrogen bonds between neighbouring phenol rings by the solvent [12].

Extensive studies on the rotational barriers and the pathways for conformational interconversions on related calix[4]arenes by using the CHARM [13] and MM3 [14] empirical force fields confirm the high mobility of such systems, the calculations yielding energy barriers close to those determined experimentally. These molecules act as host in the crown conformation, so improving the host properties implies the stabilization of this conformation. One way to do this is the of the rigidification of the system by functionalization of the phenolic OH groups of 1 with bis(electrophiles) such as $ClCH_2Br$, or R_2SiCl_2 (see Refs. [15,16] for $R_1 = \mathrm{Me}$, $R_2 = \mathrm{H}$) to afford the formation of cavitands 2.

Recently Murayama and Aoki [17a] reported a resorcin[4]arene ($R_1 = \mathrm{Et}$, $R_2 = \mathrm{H}$) dimer (encapsulating a tetraethylammonium cation) hold together by hydrogen bonding through eight water molecules. A similar assembly was found for eight propanol molecules by Atwood *et al.* [17b]. A very elegant assembling of six of C-methylcalix[4]-resorcinarene ($R_1 = \mathrm{Me}$, $R_2 = \mathrm{H}$, in cone conformation) and eight water molecules in a shell-like octahedral cubic spheroid observed by MacGillivray and Atwood [18] suggests a potentially greater variety of supramolecular associations available by just modifying the ratio of water and resorcinarene.

In view of our current interest in new types of systems with controlled host properties [19–22] we have synthesized **2** by functionalizing **1** in the "upper rim" with dichlorodimethylsilane. In this paper we report the results on structure of **2** ($E = \mathrm{Si}$, $R' = \mathrm{Me}$), which is the first cavitand from this class with no substituents at the methylene bridges ($R_1 = \mathrm{H}$, $R_2 = \mathrm{Me}$). The absence of substituents at positions 2,8,14,20 restricts the number of possible configurational isomers and affords also a different type of packing than in similar systems. In order to better understand the molecular properties and to get an idea about the main factors affecting the packing in the crystal structure, we performed semiempirical AM1 [23] and *ab initio* molecular orbital calculations on **2**.

EXPERIMENTAL

Synthesis

Resorcinarene **1** was obtained according to a procedure previously reported by Sverker [24].

For the synthesis of **2** we adopted the method applied for similar systems by Cram and coworkers [25]. Thus, a solution of 2.23 ml (1.84 mmol) of dichlorodimethylsilane in 50 ml of tetrahydrofuran was added dropwise over 18 h to a vigorously stirred suspension of 2.00 g (3.67 mmol) of **1** and 9.17 ml of triethylamine in 200 ml of tetrahydrofuran. The mixture was stirred additionally for 24 h and then the solvent was removed in vacuo. Orange crystals were obtained after washing the solid residue with 1000 mL of distillate water and than with a mixture (3 portions of 25 ml) of dichloromethane:hexane (3:1). Suitable crystals for X-ray analysis were grown from dichloromethane. M.p. > 300°, ^{1}H NMR ($CDCl_3$ δ 7.15 (2, 4H), 4.27 (d, 2H J = 13.06), 3.35(d, 2H J = 13.06), 1.93 (s, 12H), 0.52(s, 12H), −0.60(s, 12H). FAB$^+$ mass spectra: 768 m/z.

X-ray Structure

A crystal with dimensions of 0.32 × 0.20 × 0.10 mm was selected, mounted on fiber glass and collocated on a Siemens P4/PC four-circle diffractometer with CuKα radiation ($\lambda = 1.54178$). The cell parameters were determined with 42 reflections ($11.117 < 2\theta < 37.221$), and the space group found is monoclinic, $C2/c$, with the following parameters: $a = 23.892(5)$, $b = 8.493(9)$, $c = 43.035(9)$, $\beta = 100.05(2)$, $V = 8599(2)$, Density (calculated) = 1.213 g cm^{-1}, $Z = 8$. Other data set characteristics: $F(000) = 3328$, $\mu = 1.697\ \text{mm}^{-1}$, final R $\Sigma[Fo - Fc]/\Sigma Fo$=9.2% (469 parameters), wR $[\Sigma[Fo - Fc]^2/\Sigma Fo^2]^{1/2} = 10.3\%$ for 2376 observed reflections with $F \geq 4\ \sigma F$ in the range $3 \leq \theta \leq 110°$, $T = 298°K$. The intensity were corrected for background, Lorentz and polarization effects. The structure was solved [26] by direct methods and refined by full-matrix least-square with anisotropic temperature factors for the all non-hydrogen atoms. The hydrogen atoms were included at idealized positions with fixed temperature factor $U = 0.08\ \text{Å}^2$. The residual electron density from a final difference Fourier synthesis as $0.73\ eA^{-3}$ and $-0.40\ eA^{-3}$. The water molecule is disordered.

Supplemental material includes details of the structure determinations and tables with fractional coordinates, bond lengths and bond angles for $2 \cdot H_2O$.

Theoretical Investigations

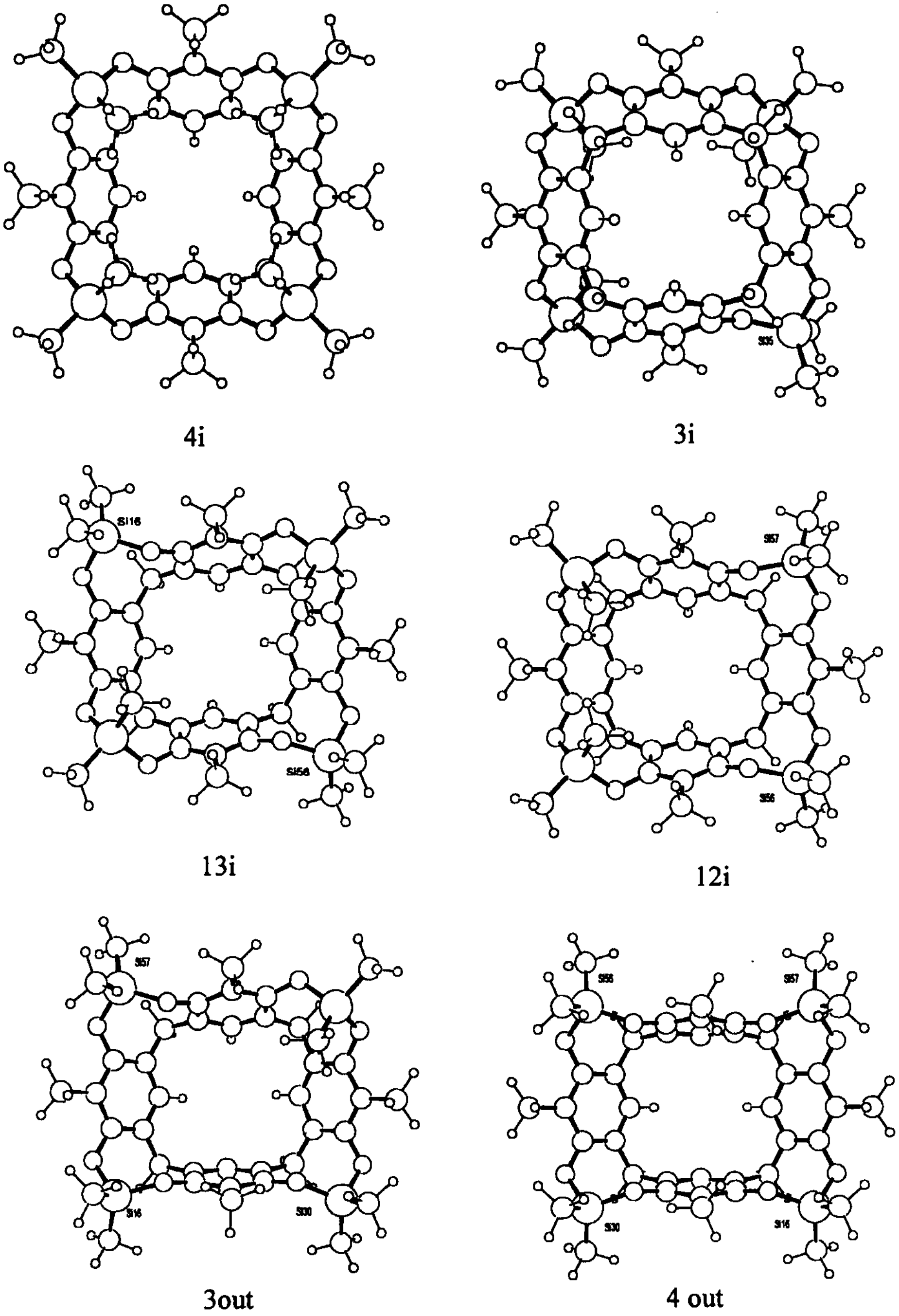
All calculations have been performed by using the Gaussian 94 package [27]. Six conformations of **2** and **3** ($E = C$, $R' = Me$) (with the EMe_2 groups arranged as: all in (4i), three in (3i), 2 in {12i (vicinal) and 13i (opposite)}, 3 out (3o) and four out (4o) have been fully optimized within the framework of AM1 method. A single point RHF/STO-3G//AM1 *ab initio* calculation was then used to evaluate the electrostatic potential around the most stable conformer of **2** (2ai).

RESULTS AND DISCUSSION

Figure 1 shows the "gas phase" structures of the five conformers of **2** (4i, 3i, 12i, 13i, 3o, 4o) as found from the AM1 optimizations, and Table I lists their enthalpies of formation, along with those of **3**.

The distance between two opposite (inward oriented) methyl groups in the most stable conformer (4i) is 6.83 Å, and this changes slightly (to 7.15 Å) in 3i. With two $SiMe_2$ outward, in 12i this distance is increased to 9.5A, and no more opening of the ring is noticed when three or all four $SiMe_2$ groups flip outward (in 4out for example, the shortest Me... Me distance over the upper rim of the bowl is of 6.8 Å). This should have important practical consequences because only a limited range of molecules with shapes confining to these geometry restrictions can be accommodated by **2**, and hence a very good specificity might be expected.

The enthalpy data show that the effect of rigidification is similar for the $SiMe_2$ and CMe_2 groups: both prefer the *all in* conformation (4i), and the opening of the structure (by moving



4i 3i

13i 12i

3out 4 out

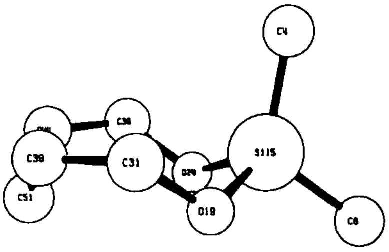
FIGURE 1 The AM1 optimized structures of six conformations of **2**. The outward-oriented $SiMe_2$ groups are marked. Note that there is no important opening of the capsule when more $SiMe_2$ groups orient outward.

these groups out) results in penalties in the enthalpies of formation of the same order for both **2** and **3**. The *all in* conformation found here is related to the preference of the four C_5O_2Si eight-membered rings to adopt the boat-crown (BC) conformation (see Ref. [28] for a recent

TABLE I Enthalpies of formation (kcal/mol) of **2** and **3**. $\Delta\Delta H$ are relative to the most stable conformer found by the AM1 optimization

Conformer	4i	3i	13i	12i	3out	4out
$SiMe_2$	− 483.533	− 476.911	− 471.518	− 470.612	− 465.818	− 460.695
$\Delta\Delta H$	0.000	6.622	12.015	12.921	17.715	22.838
CMe_2	− 206.889	− 200.844	− 195.013	− 191.812	− 188.520	− 183.315
$\Delta\Delta H$	0.000	6.035	11.876	15.077	18.369	23.574

analysis of the related cyclooctane conformations studied at various HF *ab initio* levels). Thus, while the outward orientation of silicon implies that the C_5O_2Si ring adopts the unfavorable boat-boat (BB) conformation **4**, its inward orientation allows the BC (most favored) **5** conformation.



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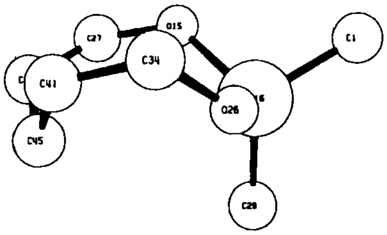


5

It is interesting to note that there is an almost perfect linear correlation between the $\Delta\Delta H$ and HOMO values for these conformers (see Fig. 2).

Both lines have the same slope, and, since the volume of $SiMe_2$ is larger than that of CMe_2 it is reasonable to suppose than this dependence has an electronic rather than steric origin.

Solid State Structure

Figure 3 illustrates the molecular structure and a view of packing along the *b* axis.

The main feature of this crystal packing is the arrangement of the resorcinarenes in columns. The packing is different from that found in other columnar unbridged [29–32] or bridged [16, 33–39] resorcinarenes *by alternating pairs of bowls "up" and "down"* **6**.

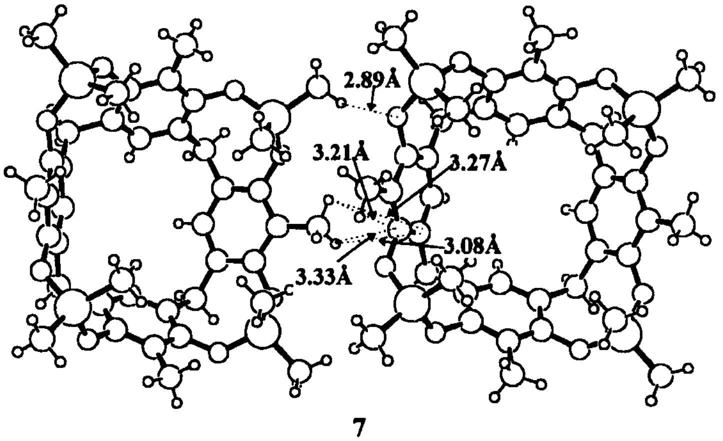
6

Thus, long cavities-somehow similar to that encountered in the carbon tubes are formed along the *b* direction (clearly visible in Fig. 3b), and the molecules of water are completely encapsulated within the resorcinarene bowls.

For a more clear view, and to emphasize some short intermolecular $H_2CH...O$ and $H_2C...C$(phenyl) contacts, three different arrangement of two neighbor bowls are shown in Schemes **7**–**9**. Thus **7** and **8** display an up-up (or a down-down) and an up-down pair (*a*, *c* direction), respectively, and **9** an up-up pair in the *b* direction.

These arrangements are closely related to the electrostatic potential exhibited by **2**. Figure 4 shows the ±12.55 kcal/mol electrostatic potential isovalue surfaces (blue- for the negative value) as calculated by the RHF/STO-3G//AM1 method.

One distinct region is associated with the carbon atoms from the four phenyl groups and the eight oxygen atoms (blue color) and the other one (red) is related to the hydrogen atoms from the methyl, methylene or phenyl groups). Thus **7** and **8** reflect such electrostatic attractions between groups of opposite charges.



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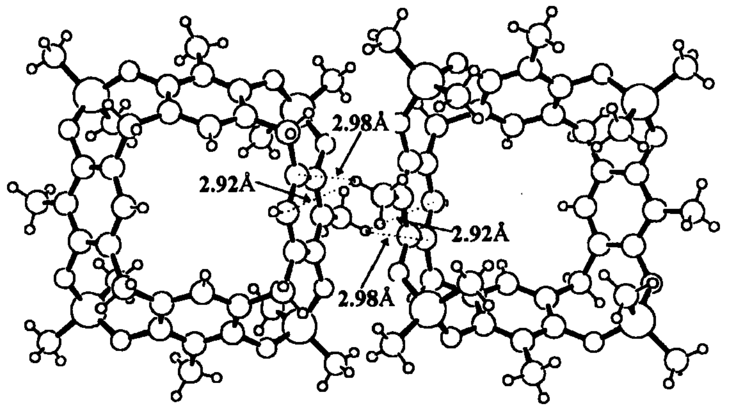

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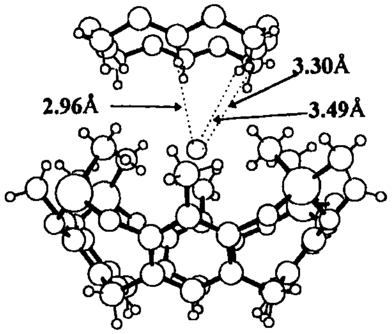


9

The shortest intermolecular contacts are well in the range of non-bonded aliphatic C—H... C(π) distances (2.5–3.5 Å) recently analyzed by Leszczynsky's group [40] and the $H_2CH...O$ distances are also within the sum of the van der Waals radii of an oxygen atom and a methyl group (3.40 Å, *cf.* Ref. [41]) On the basis of the electrostatic potentials only weak repulsive

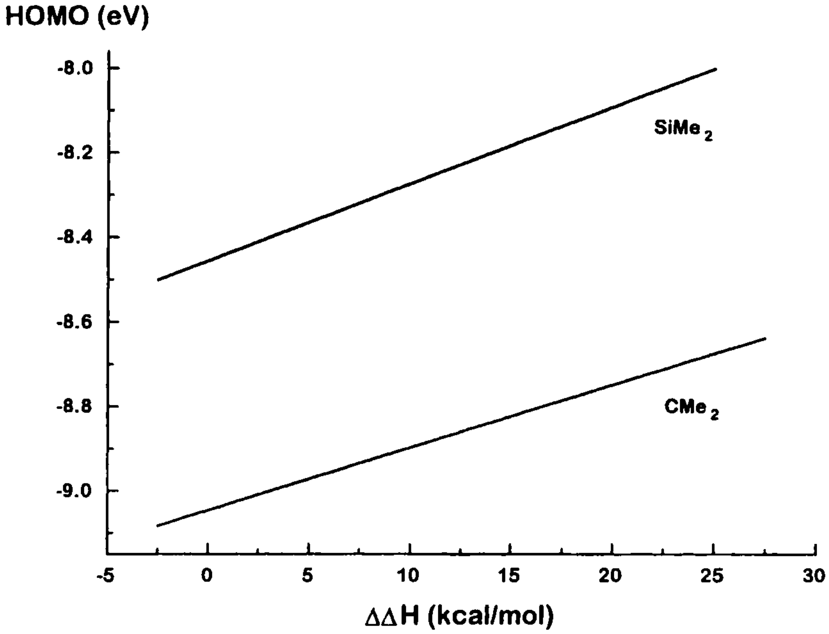


FIGURE 2 The variation of HOMO energies with the relative heat of formations of conformations of 2 ($SiMe_2$) and 3 (CMe_2).

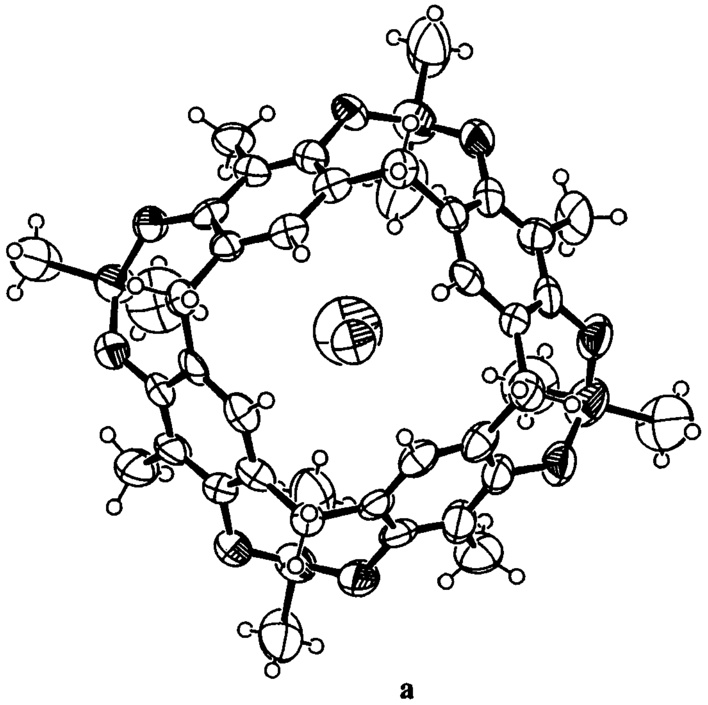
interactions between the two resorcinarenes are expected in 9, but it is also possible that the oxygen atom of the guest molecule interacts attractively with the hydrogen atoms situated at the lower rim of the vicinal molecule. The intermolecular O... H distances of 2.30-3.50 Å support this assumption.

A gross estimate of the interaction energy in these three positions has been obtained by partial optimization of the structures of **7**-**9** by using the Sybyl package from Spartan 5.0 [42], and calculating the interaction energy as the difference between the steric energy of the "dimer" and twice the energy of the isolated resorcinarene. The relative interaction energies are −14.63, −15.12 and −7.62 kcal/mol for **7**, **8** and **9**, respectively, in agreement with the qualitative expectations based on the electrostatic potentials.

A notable characteristic of this structure is the encapsulation of one molecule of water. This is by our best knowledge the first example of a complete encapsulation of a nonlinear guest in **2**, since previous reports [16, 43], indicated only a partial inclusion of linear fragments of CS_2 or PhC≡CH in the cavity of the host.

Since the position of the hydrogen atoms is not determined experimentally, we proceeded in optimizing the water-resorcinarene 1 : 1 complex with the aid of AM1 method and the resulted optimized structure is shown in Figure 5.

Usually, semiempirical optimizations of weakly bonded systems lead to the separation of the components (or to very loose optima [44]). In this case, however, the inward oriented methyl groups prevent the elimination of the water and thus we were able to locate the shown optimum. The overall interaction energy between the water and the host (estimated as the difference of enthalpies of formation: $\Delta H_{complex} - \Delta H_{resorcinarene} - \Delta H_{water}$) gives a small value (0.85 kcal/mol). However, due to the four inward oriented Me groups the barrier for expelling the molecule of water in the solid state, is high enough to keep it trapped under the normal conditions.



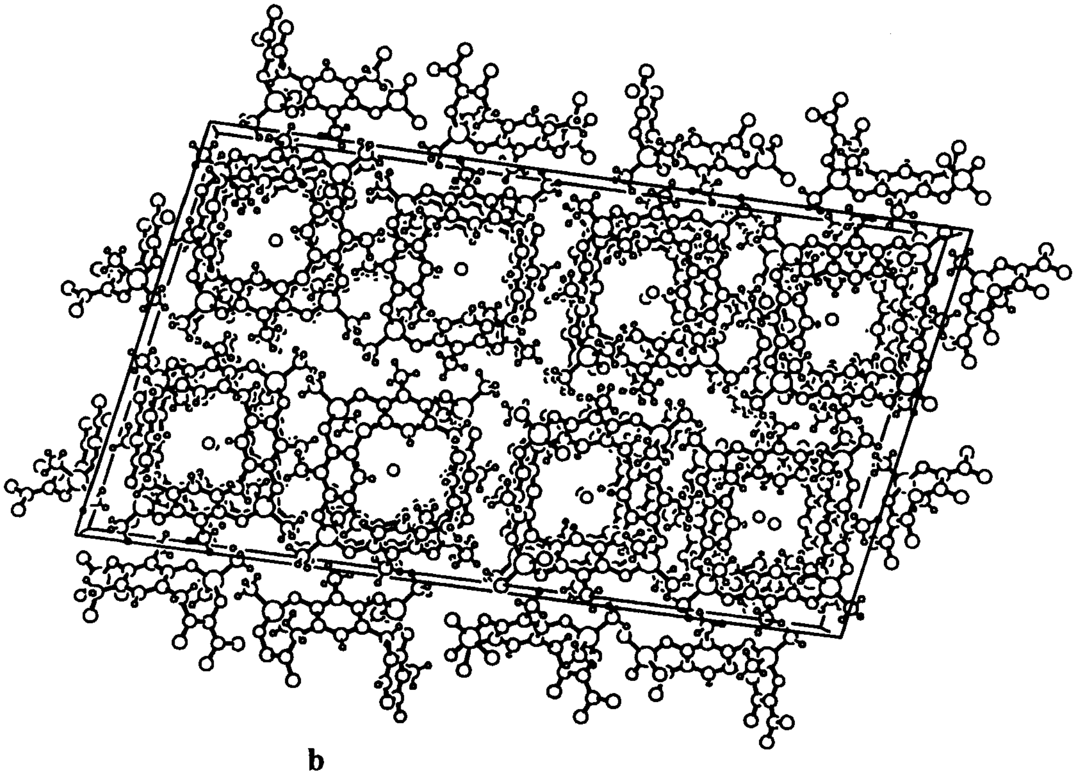


FIGURE 3 The molecular structure of $2 \cdot H_2O$ (a) and a view of the crystal packing down to *b* axis (b).

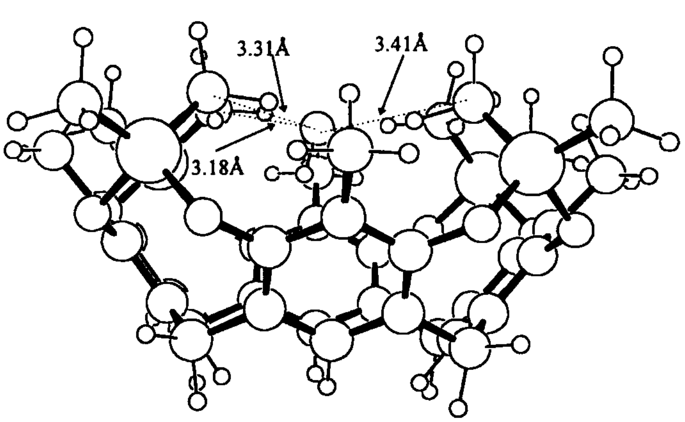


FIGURE 5 The AM1 optimized structure of $2{\cdot}H_2O$ complex. Note the Me. . .O short contacts, which are below the sum of the van der Waals radii.

Acknowledgments

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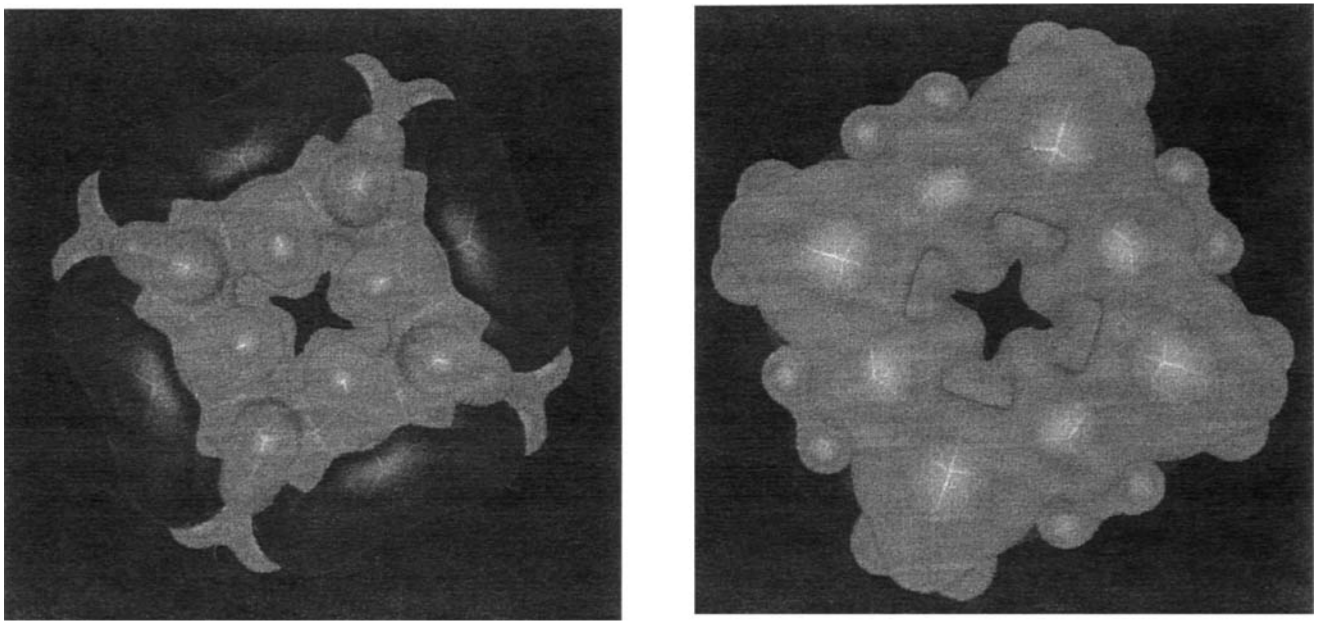

FIGURE 4 The electrostatic potential map of $-12.55\,\text{kcal/mol}$ (blue) and $+12.55\,\text{kcal/mol}$ (red) as seen from the lower rim (left) and upper rim (right) of **2**.

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