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Thiabowls: Synthesis, Molecular Structure, and Novel Supramolecular Architecture of Trithia-[3]-Peristylane

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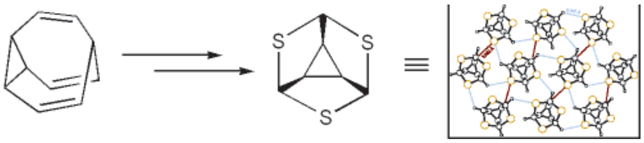
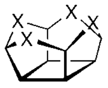
ABSTRACT



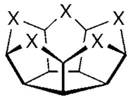
A synthesis of trithia-[3]-peristylane, $C_6H_6S_3$, a novel C_{3v} symmetric thiabowl, from the exotic hydrocarbon bullvalene has been accomplished. The X-ray crystal structure of this trithiabowl displays an unprecedented supramolecular architecture in the solid state with 12 CH⋯S interactions involving all of its six hydrogen atoms and the two lone pairs on each of the three sulfur atoms.

[*n*]-Peristylanes **1a**−**4a** are a class of aesthetically pleasing and topologically novel molecular entities in which the carbon atoms of an inner [*n*]-membered ring clasp the alternate corners of an outer [2*n*]-membered ring. Such a fascinating union generates a range of "bowl"-shaped molecular constructs of potential C_{nv} symmetry, having $[n + 1]$-number of rings, a fluted rim, and walls composed exclusively of five-membered rings.[1] We have recently conceived a new family of heterocyclic analogues of **1a**−**4a** in which all the methylene groups on the rim of the bowl are replaced by a heteroatom.[2] The resulting heterobowls **1b**,**c**,**d**−**4b**,**c**,**d** are endowed with two chemically distinct surfaces made up of a hydrophobic base and a hydrophilic rim.

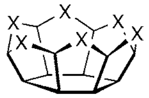
1a. $X=CH_2$
b. X= O
c. X= NR
d. X= S



2a-d



3a-d



4a-d

These heterobowls **1b**,**c**,**d**−**4b**,**c**,**d** are not only expected to be more stable than their carba-analogues **1a**−**4a**, due to the elimination of HC−CH_2 torsional strain but also harbor the potential to exhibit strong attraction for metal ions and small molecules and can be regarded as a new class of ionophores.

In pursuit of the target structures **1b**,**c**,**d**−**4b**,**c**,**d**, we have recently accomplished the synthesis of triaza-[3]-peristylane **1c**,[2a] tetraoxa-[4]-peristylane **2b**,[2b] tetrathia-[4]-peristylane **2d**,[2c] and pentaoxa-[5]-peristylane **3b**.[2d−f,3] Oxaperistylanes **2b** and **3b** have been found to show a very interesting supramolecular architecture in the solid-state dictated by a

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† Indian Institute of Science.
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[1] (a) Olah, G. A. *Cage Hydrocarbons*; John Wiley and Sons: New York, 1990. (b) Osawa, E.; Yonemitsu, O. *Carbocyclic Cage Compounds*; VCH: New York, 1992. (c) Hopf, H. *Classics in Hydrocarbon Chemistry*; Wiley-VCH: Weinheim, 2000.

[2] (a) Mehta, G.; Vidya, R.; Sharma, P. K.; Jemmis, E. D. *Tetrahedron Lett.* **2000**, *41*, 2999. (b) Mehta, G.; Vidya, R.; Venkatesan, K. *Tetrahedron Lett.* **1999**, *40*, 2417. (c) Mehta, G.; Gagliardini, V.; Schaefer, C.; Gleiter, R. *Tetrahedron Lett.* **2003**, *44*, 9313. (d) Mehta, G.; Vidya, R. *Tetrahedron Lett.* **1997**, *38*, 4173. (e) Mehta, G.; Vidya, R. *Tetrahedron Lett.* **1997**, *38*, 4177. (f) Mehta, G.; Vidya, R. *J. Org. Chem.* **2001**, *66*, 6905.

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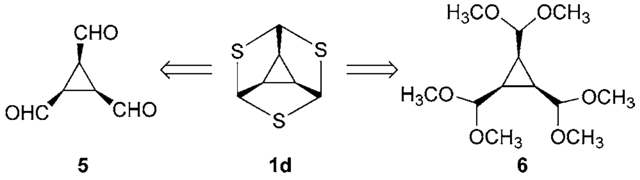
network of CH···O interactions.[2b,d–f,3] On the other hand, tetrathia-[4]-peristylane **2d** has a multicolumnar arrangement in the solid-state sustained by S···S and CH···S interactions.[2c] These interesting observations have motivated us to undertake the synthesis of other heterobowls, particularly trithia-[3]-peristylane **1d**, to further probe the involvement of chalcogen−chalcogen and CH···S interactions in these fascinating systems. We report here the first synthesis of trithiabowl (trithia-[3]-peristylane) **1d**, $C_6H_6S_3$, and find that in the solid state it reveals a unique and novel supramolecular architecture in which all of its six hydrogen atoms and three sulfur atoms participate in CH···S interactions.

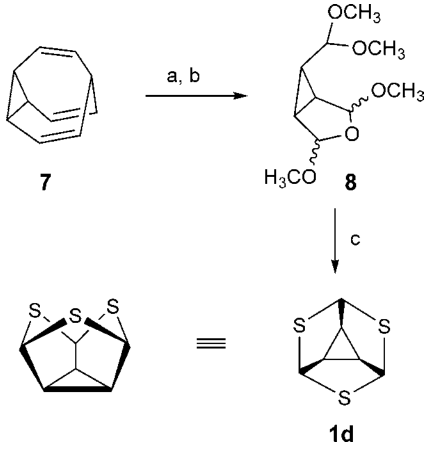
Our synthetic approach to trithia-[3]-peristylane **1d** was centered on harnessing the remarkable propensity of Lawesson's reagent [2,4-bis(4-methoxyphenyl)-1,3-dithiaphosphetane-2,4-disulfide, LR][4] to effect oxygen−sulfur exchange in carbonyl group or their synthetically equivalent acetal-containing substrates.[2c,5] Thus, it was surmised that either all *cis*-1,2,3-cyclopropane tricarboxaldehyde **5** or its ketal **6** could lead to trithiabowl **1d** through reaction with LR, Scheme 1. However, all *cis*-cyclopropane derivatives **5** or **6** are unknown and access to them in itself is a challenging proposition. In this context, our attention was drawn to the beautiful hydrocarbon[6] bullvalene **7** in which the cyclopropane ring is locked through three cis-disposed vinyl arms and could be disengaged through an oxidative maneuver to give **5** or its equivalent derivative. Consequently, bullvalene **7**[6] was subjected to ozonolysis, and further stirring the reaction mixture with Amberlyst 15 resin furnished the cyclic acetal **8** in 65% yield possibly through the intermediacy of **5**, Scheme 2.[7] When **8** was treated with LR[2c,5] under sonication conditions, trithia-[3]-peristylane **1d** was isolated in 25% yield, Scheme 2.[7] Although **1d** was realized in low yield, it is quite remarkable that all the oxygens in **8** were replaced by three sulfur atoms with concomitant cyclization in a single-pot reaction.

Scheme 1. Retrosynthetic Approaches toward Trithia-[3]-peristylane **2d**



The ^1H and ^{13}C NMR spectra of **1d** exhibited two signals each, as expected for the C_{3v} symmetric structure. In the ^1H NMR spectrum, the cyclopropane and the rim hydrogens resonated at δ 3.81(s) and 5.46(s), respectively. Similarly, the ^{13}C NMR signals for the cyclopropane and the rim carbons were at δ 61.2 and 66.0, respectively. It is interesting to note that the observed chemical shifts in both ^1H and ^{13}C NMR spectra of **1d** deviated from the expected range.

Scheme 2[a]



[a] Reagents and conditions: (a) O_3, MeOH, −78 °C; Me_2S, −78 °C to rt. (b) Amberlyst 15, rt, 12 h, 65%; (c) Lawessons's reagent, PhMe, sonication, rt, 12 h, 25%.

To probe the electronic structure of **1d**, its He(I) photoelectron (PE) spectrum was recorded, which showed two peaks at lower energy to which we assign three transitions (8.1, 8.2, and 9.5 eV) followed by a broad band between 10.1 and 10.4 eV. The first three transitions are assigned to ionization events from the lone pairs at the sulfur centers on the basis of comparison with the PE data for thioethers[8a] and 1,3-dithianes.[8b] For the detailed assignment we compared the recorded ionization energies ($I_{v,j}$) with the orbital energies derived from SCF calculations [HF/6-311G(d)] (Koopmans' approximation[9]) based on the optimized [C_{3v} , B3LYP/6-311G(d)] structure[10,11] of **1d** as summarized in Table 1. These calculations predict for the highest occupied MOs, five levels belonging to the MOs 15e, 13a1, and 14e. The MOs 15e and $13a_1$ are linear combinations of the three 3p orbitals on the sulfur centers as shown in Figure 1. The 14e linear

Table 1. Comparison between Recorded Vertical Ionization Energies ($I_{v,j}$) and Calculated Orbital Energies ϵ_j[a]

$I_{v,j}$	assignment	$-\epsilon_j$ (HF−SCF)
8.3, 8.4	15e	8.99
9.5	$13a_1$	10.31
10.1, 10.4	14e	11.05

[a] All values in eV.

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(3) (a) Wu, H.-J.; Wu, C.-Y. *Tetrahedron Lett.* **1997**, *38*, 2493. (b) Wu, H.-J.; Wu, C.-Y. *J. Org. Chem.* **1999**, *64*, 1576.

(4) Perregaard, J.; Scheibye, S.; Meyer, H. J.; Thomsen, I.; Lawesson, S. O. *Bull. Soc. Chim. Belg.* **1977**, *86*, 679.

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(7) All compounds reported here were characterized on the basis of their spectral (IR and ^1H and ^{13}C NMR and mass) data.

(8) (a) Gleiter, R.; Spanget-Larsen, J. *Top. Curr. Chem.* **1979**, 86, 139. (b) Kobayashi, M.; Gleiter, R.; Coffen, D. L.; Bock, H.; Schulz, U.; Stein, U. *Tetrahedron* **1977**, *33*, 433.

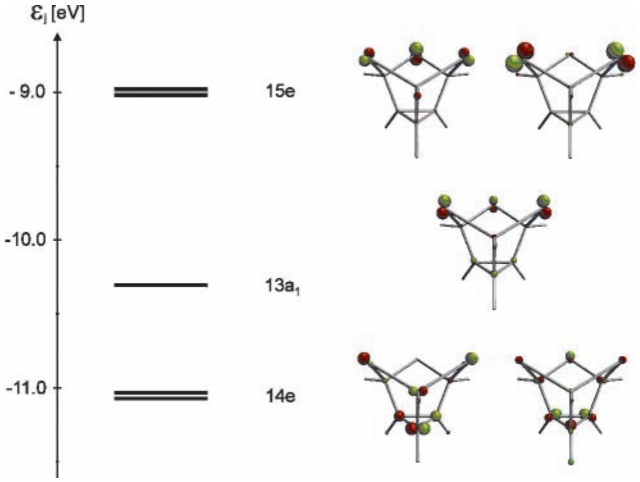

Figure 1. Calculated highest occupied molecular orbitals and their energies ϵ_j.

combinations can be described as Walsh-type orbitals centered at the three-membered ring. The assignment of the first two peaks to 15e and $13a_1$ is also in line with the half-width of the first two peaks (2:1). The energy of HOMO is of interest with regard to the potential complexation properties of **1d**.

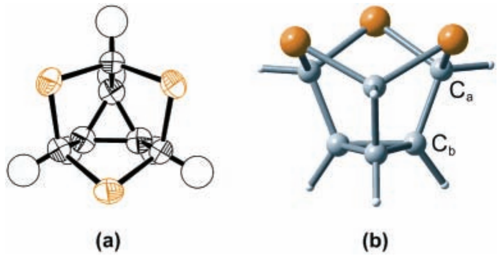

Figure 2. (a) ORTEP drawing of **1d**. Transannular sulfur−sulfur distances: 3.034 Å. (b) Optimized [B3LYP/6-311G(d)] C_{3v} symmetric structure of **1d**. Calculated bond lengths (bond lengths from the crystal structure are given in the bracket): C_b-C_b 1.506 Å (1.505 Å), C_a-C_b 1.535 Å (1.528 Å), C_a-S 1.851 Å (1.822 Å).

The X-ray data[12] on microcrystals of **1d**, which belonged to the $R3/c$ space group, revealed its nearly C_{3v} symmetry and closely resembled its calculated structure, Figure 2. The packing pattern in trithiabowl **1d** reveals a large number of close intermolecular contacts that are within the range of van der Waals interactions and CH⋯S hydrogen bonds.[13−15] Interestingly, there are no short S⋯S contacts in this structure. Each of the three sulfur atoms present in **1d** is involved in two different C−H⋯S contacts in a bifurcated manner through its two lone pairs; one of the interactions is with the C−H of the bottom cyclopropane ring (C−H⋯S distance 3.092 Å, angle 154°) and the other is with the rim C−H of the bowl (C−H⋯S distance 3.047 Å, angle 161°). Although, the C−H⋯S distances are marginally longer (~0.1 Å) than the sum of the van der Waals radii of sulfur and hydrogen atoms, the linearity of the bond qualifies it to be a hydrogen bond, albeit a weak (soft) one.[13,14] When viewed along the diagonal between the *a* and *b* axes, two chainlike connectivities between the molecules of **1d**, mediated by the two types of C−H⋯S interactions mentioned above, can be seen (Figure 3). In the same *ab* plane, a top-to-bottom columnar arrangement of the bowls can also be visualized; however, the molecules of **1d** in the column are

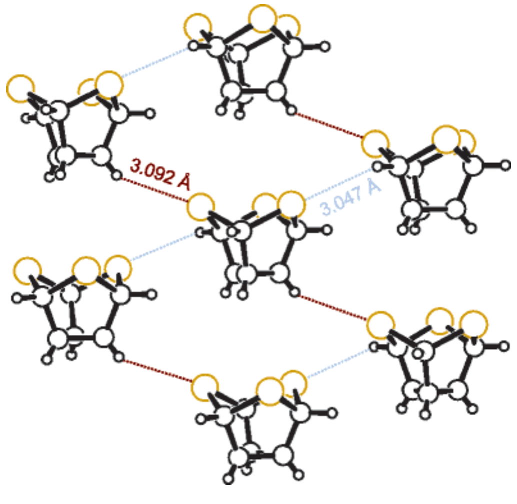

Figure 3. C−H⋯S interactions viewed along the diagonal between *a* and *b* axes.

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(9) Koopmans, T. *Physica* **1934**, *1*, 104.

(10) Geometry of **1d** was fully optimized resulting in a C_{3v} symmetry using the DFT (B3LYP) method applying a 6-311G(d) basis set with the Gaussian 98 program.[11] Frequency calculations were carried out to confirm the nature of the stationary point, yielding no imaginary frequency for the minimum.

(11) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.

(12) Crystal data. Structure was solved by direct methods (SIR92) on an APEX SMART instrument. Refinement was by full-matrix least-squares using SHELXL-97. Crystal system, trigonal; space group, $R3/c$; cell parameters, $a = b = 10.0157(10)$ Å, $c = 11.9343$ (23) Å; $V = 1036$ Å^3; cell formula units (Z) = 3; $T = 273$ K; $\lambda = 0.71073$ Å; $\mu = 9.598$ cm^{-1}; $R_1 = 0.0277$ for 482 $F_o > 4\mathrm{sig}(F_o)$ and 0.0289 for all 495 data $wR_2 = 0.0686$, GOF = S = 1.151, Restrained GOF = 1.150 for all data. Crystallographic data have been deposited in the Cambridge Crystallographic Data Center (CCDC-215516).

(13) In the present case, we have used the cutoff limit of ~3.0 Å for CH⋯S interactions. However, it has been suggested[14] that the cutoff limit for these distances can be stretched up to ~3.2 Å to qualify for a potential hydrogen bond. No S⋯S contacts were observed within the limit of ~3.6 Å.

(14) (a) Steiner, T. *Angew. Chem., Int. Ed.* **2002**, *41*, 48. (b) Jeffrey, G. *An Introduction to Hydrogen Bonding*; Oxford University Press: Oxford, 1997.

not directly connected but held in place through the network of soft C−H···S bonds, Figure 3. In its two-dimensional arrangement, molecules of trithiabowl **1d** form a planar sheet along the *c* axis, sustained by 3.047 Å-type as well as 3.092 Å-type C−H···S interactions, Figure 4.

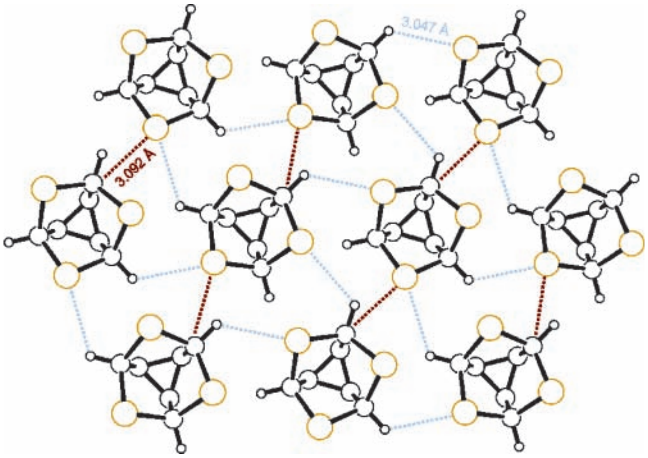

Figure 4. Planar two-dimensional sheet structure through C−H···S (3.047 Å, angle 161°, blue; 3.092 Å, angle 154°, red) contacts seen along the *c* axis.

These sheets stack in three dimensions as shown in Figure 5 and are held together by both types of soft C−H···S hydrogen bonds. The involvement of all three sulfur atoms in bifurcated C−H···S interactions with the cyclopropane ring and rim hydrogens of the neighboring molecules, when considered in the light of the threefold symmetry axis present in **1d**, makes 12 C−H···S interactions per molecule, and this spectacular arrangement is displayed in Figure 6. We like to believe that the packing pattern in **1d** represents a unique supramolecular architecture in which all possible modes of C−H···S interactions per molecule are observed.

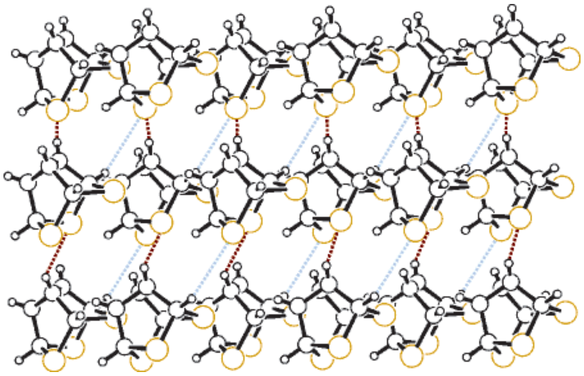

Figure 5. Stacking of sheets in three dimensions through soft C−H···S (3.047 Å, angle 161°, blue; 3.092 Å, angle 154°, red) interactions seen along the *b* axis.

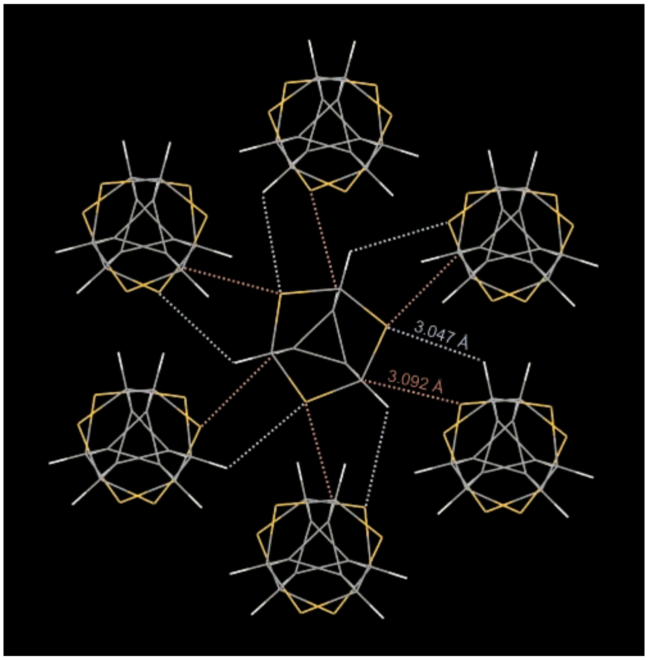

Figure 6. All possible C−H···S interactions (12 per molecule) in trithia-[3]-peristylane **1d**.

In short, we have achieved the first synthesis of trithia-[3]-peristylane **1d**. Its optimized and X-ray crystal structure data reveal its expected C_{3v} symmetry. In the solid state, **1d** exhibits a unique and beautiful architecture in which all of its six hydrogens and three sulfur atoms participate through 12 C−H···S interactions.

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