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Supertetrahedral cubane $C_{32}H_8$ and supertetrahedral dodecahedrane $C_{80}H_{20}$ with tetrahedral C_4H fragments in the vertices

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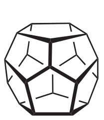
The DFT B3LYP/6-311+G(d,p) calculations predict novel stable hydrocarbon cage structures of ‘supertetrahedral’ cubane $C_{32}H_8$ and dodecahedrane $C_{80}H_{20}$ in which the CH vertices are replaced by the tetrahedral C_4H fragments.

Due to their aesthetically attractive symmetrical convex regular polyhedron structures (Platonic bodies) and non-standard bonding, the highly strained cage molecules of tetrahedrane **1**, cubane **2** and dodecahedrane **3** are of considerable interest to organic synthetic and theoretically oriented chemists.[1]

1, T_d

2, O_h



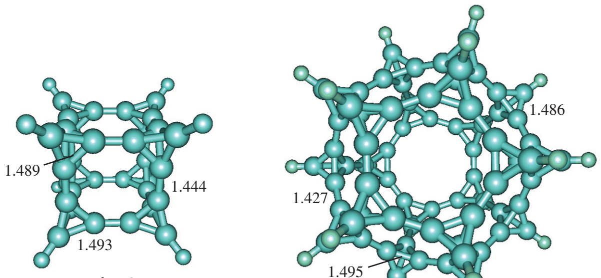
3, I_h

The synthesis of tetrahedrane,[2] cubane[3] and dodecahedrane[4] remains the top of the art of preparative organic chemistry. Currently, cage structures also attract attention as potential systems for capturing various atoms and ions in their cavities to form endohedral complexes.[5] Special interest[6–8] has been drawn to endohedral hydrocarbons, in particular, those with the smallest hydrocarbon cages $M@C_{20}H_{20}$ (where M = H, He, Ne, Ar, Li, Li^+, Be, Be^+, Na, Na^+, Mg, Mg^+ and Mg^{2+}).

The T_d structure of tetrahedrane **1** is not a global minimum on the potential energy surface (PES).[9] However, due to sufficient kinetic stability of its structure, tetrahedrane can be used as a building block[10] for the construction of composite molecules, such as bis(tetrahedrane),[11] tetra(tetrahedranyltetrahedrane), (cyclohexane, adamantane) and other systems[10] constructed by replacing tetrahedral carbons in saturated hydrocarbon molecules by the tetrahedranyl fragments C_4H_3.

Here we report a computational design of novel stable cage structures **4** and **5** constructed on the basis of cubane **2** and dodecahedrane **3**, in which all vertex CH groups are replaced by the tetrahedral fragments C_4H.

The calculations have been carried out with the aid of the density functional theory (B3LYP/6-311+G**).[12] The vibration analysis confirmed that the cage structures of **4** and **5** correspond to energy minima on the PESs. The geometries of **4** and **5** found by calculations are shown in Figure 1, and the energy characteristics are listed in Table 1.



4, O_h

5, I_h

Figure 1 Geometrical parameters of cage structures **4** and **5** calculated by the DFT (B3LYP/6-311+G**) method. The bond lengths are given in angström units.

Table 1 Energy characteristics of cage compounds **2**–**5** calculated by the DFT (B3LYP/6-311+G**) method.[a]

Structure, symmetry	E_{tot} (a.u.)	E_{ZPE} (a.u.)	ω_1/cm^{-1}	$E_{HOMO-LUMO}/eV$
2, O_h	–309.53270	0.13272	617 (E_u)	7.3
3, I_h	–774.35952	0.35701	480 (H_g)	6.9
4, O_h	–1222.94455	0.25221	105 (E)	4.2
5, I_h	–3057.65717	0.63285	85 (H_g)	6.2

[a] E_{tot} is the total energy (1 a.u. = 627.5095 kcal mol^{-1}); ZPE is the harmonic zero-point correction; ω_1 is the smallest harmonic vibrational frequency; $E_{HOMO-LUMO}$ is the energy gap between the frontier orbitals.

The calculated C–C bond lengths in the eight-membered rings of the molecule of **4** (1.444 and 1.489 Å) are significantly shorter than those in cubane **2**, as found at the same level of theory (1.570 Å) or experimentally determined with the use of electron diffraction[13] and microwave spectroscopy[14] (1.571 Å). The calculated C–C bond lengths in the C_4H fragment (1.493 Å) are close to those of tetrahedrane **1** (1.479 Å, B3LYP/6-311+G**) and 1.495–1.508 Å [X-ray diffraction data for tetrakis(trimethylsilyl)tetrahedrane].[2] The C–C bond lengths in dodecahedrane **3** obtained theoretically (1.554 Å, B3LYP/6-311+G**) and experimentally (1.535–1.541 Å, X-ray diffraction)[4] are also notably longer than those in **5**. The calculated distances between the opposite carbon atoms in the molecules of **4** and **5** are 5.2 and 7.3 Å, respectively, which indicates the presence of a rather spacious cavity in the molecules. The minimum harmonic frequencies calculated for compounds **4** and **5** are significantly lower than the corresponding frequencies of cubane **2** and dodecahedrane **3**, pointing thus to the greater flexibility of the former structures. This finding is consistent with the narrower gap between the frontier HOMO and LUMO orbitals of **4** and **5**, as compared with cubane **2** and dodecahedrane **3** (see Table 1).

Thus, the calculations performed showed that supertetrahedral analogues **4** and **5** of cubane **2** and dodecahedrane **3** represent a new type of stable hydrocarbon systems having sufficiently large internal cavities for the formation of various endohedral complexes.

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References

1 (*a*) M. Hargittai and I. Hargittai, *Symmetry through the Eyes of a Chemist*, 3rd edn., Springer, Berlin, 2009, ch. 3, pp. 97–167; (*b*) H. Hopf, *Classics in Hydrocarbon Chemistry*, Wiley-VCH, Weinheim, 2000.

2 G. Maier, J. Neudert, O. Wolf, D. Pappusch, A. Sekiguchi, M. Tanaka and T. Matsuo, *J. Am. Chem. Soc.*, 2002, **124**, 13819 and references therein.

3 P. E. Eaton and T. W. Cole, *J. Am. Chem. Soc.*, 1964, **86**, 962.

4 J. C. Gallucci, C. W. Doecke and L. A. Paquette, *J. Am. Chem. Soc.*, 1986, **108**, 1343 and references therein.

5 (*a*) *Endofullerenes*, eds. T. Akasaka and S. Nagase, Kluwer, Dordrecht, 2002; (*b*) I. S. Neretin and Yu. L. Slovokhotov, *Russ. Chem. Rev.*, 2004, **73**, 455 (*Usp. Khim.*, 2004, **73**, 492).

6 R. J. Cross, M. Saunders and H. Prinzbach, *Org. Lett.*, 1999, **1**, 1479.

7 M. Mascal, *J. Org. Chem.*, 2002, **67**, 8644.

8 D. Moran, F. Stahl, E. D. Jemmis, H. F. Schaefer III and P. v. R. Schleyer, *J. Phys. Chem. A*, 2002, **106**, 5144.

9 R. Haunschild and G. Frenking, *Mol. Phys.*, 2009, **8**–**12**, 911 and references therein.

10 R. M. Minyaev, *Izv. Akad. Nauk, Ser. Khim.*, 2012, 1657 (in Russian).

11 A. Sekiguchi, in *Strained Hydrocarbons*, ed. H. Dodziuk, Wiley-VCH Verlag, Weinheim, 2009, ch. 2.6.

12 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, *Gaussian 03, Revision E.01*, Gaussian, Inc., Wallingford CT, 2004.

13 A. Almenningen, T. Jonvik, H. D. Martin and T. Urbanek, *J. Mol. Struct.*, 1985, **128**, 239.

14 E. Hirota, Y. Endo, M. Fujitake, E. W. Della, R. E. Pigou and J. S. Chickos, *J. Mol. Struct.*, 1988, **190**, 235.

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