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# Cubanoids: Computer–Aided Molecular Design of Compact Hydrocarbons Constructed by Assembling Cubane Units

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# Cubanoids: Computer–Aided Molecular Design of Compact Hydrocarbons Constructed by Assembling Cubane Units[#]

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**Abstract**

**Motivation.** Except for percubyl–cubane, whose structure has been predicted some time ago, there exists a structural gap in the number of compact hydrocarbon molecules that may be thought to exist between the discrete cubane molecule and bulk supercubane. In this paper we have designed a novel series of molecules which are constructed by assembling discrete numbers of $C_8$ units. Their corresponding molecular and electronic structures along with their harmonic normal modes of vibration have been analyzed with the aid of quantum chemical calculations.

**Method.** Semiempirical (PM5) quantum chemical calculations were employed for the geometry optimizations. Single–point calculations with the HF/3–21G method were subsequently performed to check the orbital energies.

**Results.** Six novel hydrocarbon structures have been designed and their stabilities assessed with the aid of quantum chemical calculations. No imaginary vibrational frequency has been found for any of these molecules.

**Conclusions.** The structural gap between the discrete cubane molecule and bulk supercubane has been filled by designing a series of novel, compact and stable hydrocarbons. We shall call them cubanoids.

**Keywords.** Cubanoids; hydrocarbons; CAMD; semiempirical quantum chemisty; PM5; MOPAC2002.

**Abbreviations and notations**

| | |
|---|---|
| MO, molecular orbital | HF, Hartree–Fock |
| PM5, Parametric Method number 5 | NDDO, neglect of diatomic differential overlap |
| HOMO, Highest–occupied molecular orbital | LUMO, Lowest–unoccupied molecular orbital |
| DFT, density functional theory | H–L, HOMO–LUMO energy gap |

## 1 INTRODUCTION

The design of hydrocarbon molecules can be traced back to 1865, when the organic chemist Kekulé successfully solved the enigma behind the structure of benzene by proposing the notorious hexagon formula [1]. His proposal, which has been said being originated from a dream, is even more amazing if we think that it happened long before the advent of both X–ray crystal structure analysis (the structures of NaCl and KCl crystals were firstly solved by William Lawrence Bragg in

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[#] Dedicated to Professor Nenad Trinajstić on the occasion of the 65th birthday.

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1913) and digital computers. In 1970 the Japanese chemist Eiji Osawa was the first to theoretically predict the beautiful icosahedral structure of buckminsterfulllererene, $C_{60}$ [2]. Shortly after, in 1975, Bochvar and Gal'pern arrived at similar conclusions [3]. The discovery of $C_{60}$ had to wait until 1985, when the team of Kroto, Smalley, and Curl – awarded the Nobel Prize for Chemistry in 1996 – produced convincing evidence of its presence in their mass spectra [4]. As often happens, Osawa's paper went unnoticed and it surfaced only after that the experimental discovery took place [5]. More recently, the molecular structures of star–shaped Helvetane and Israelane molecules [6] as well as those of Archimedene [7] and toroidal fullerenes [8] have been conceived with the aid of both computer–aided molecular design (CAMD) [9,10] and molecular orbital (MO) calculations [11]. The beauty and fascination of these molecules lies in their 3D structures, which represent atomic–scale miniatures of macroscopic objects, namely a soccer ball in the case of $C_{60}$, Swiss' cross for Helvetane, David's star for Israelane, and so forth.

A different approach to designing new molecules is that of assembling small building blocks, rather than thinking at the macroscopic 3D object that they should resemble. In this paper we shall employ the cubane molecule as the building block for the construction of a novel series of spherical–like, compact hydrocarbon structures. Cubane ($C_8H_8$), which has been synthesized in 1964 by Eaton and Cole [12], is a highly strained molecule made of eight C−H moieties arranged at the corners of a cube (Figure 1). Its molecular structure was originally solved by Fleischer [13] with the aid of X–ray crystal structure analysis. Since then, several cubane derivatives have been prepared by replacing one or more hydrogen atoms with different chemical groups to yield functionalized cubanes [14] as well as with cubyl groups so as to yield cubyl–cubanes [15].

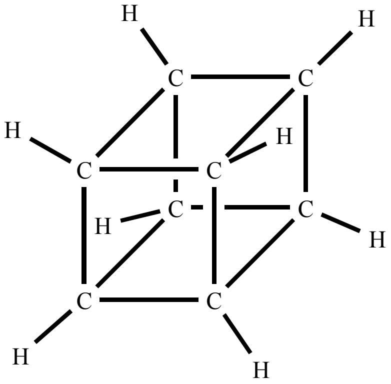

**Figure 1.** Chemical structure of the cubane molecule.

A crystalline polymorph of diamond and graphite called supercubane has also been proposed [16] for which periodic DFT calculations predict a density of 2.9 g/cm$^3$, a value that is intermediate between those of graphite (2.1 g/cm$^3$) and diamond (3.6 g/cm$^3$) [17]. The simplest non–periodic model of supercubane is represented by percubyl–cubane (vide infra). This molecule comprises a central $C_8$ unit surrounded by eight cubyl moieties that are bonded to its corners through C−C bonds. Theoretical calculations performed by Vlahacos and Jensen [18] at the HF/STO–3G level of theory yielded for percubyl–cubane an equilibrium geometry of *O* symmetry in which the dihedral angles for the intercube C−C bonds are rotated 15° from those of the body–centered supercubane structure originally proposed by Burdett and Lee [16].

To the best of our knowledge, no other compact 3D hydrocarbon structure containing a discrete number of cubane units has been so far designed. In what follows, we show that highly symmetrical molecules made of $C_8$ units can be conceived. Their structural, electronic, and vibrational properties have been investigated with the aid of semiempirical MO calculations. Several of these newly designed species appear to be highly strained molecules albeit the absence of negative frequencies indicates them to be local minima. These novel hydrocarbon molecules, which we shall call *cubanoids*, are expected to fill the structural gap that there exists between the discrete cubane molecule and the periodic structure of bulk supercubane.

## 2 MATERIALS AND METHODS

All the semiempirical MO calculations were performed with the MOPAC2002 software package [19]. Among the available semiempirical methods based on the neglect of diatomic differential overlap (NDDO) approximation [20] we employed the newly developed Parametric Method Number 5 (PM5) of Stewart [21], which represents an improvement of the widely used PM3 method [22]. The default criteria for terminating all optimizations were increased by a factor of 100 (keyword PRECISE). Vibrational frequencies were computed for all of the cubanoid structures (keyword FORCE) so as to check whether the newly designed geometries are local minima. The optimized structure of cubane compares well with those of previous theoretical studies where higher level *ab initio* methods have been employed (vide infra). Orbital energies and thermochemical properties derived from semiempirical methods are, however, less accurate than those computed with either ab initio HF or DFT methods. Hence, we have performed a series of single–point calculations on the PM5 optimized structures by employing the HF/3–21G method as implemented in the Gaussian 98 software package [23]. Note that, as a difference from ab initio and DFT methods, semiempirical methods give the heat of formation (HOF) of the molecule thus implicitly assuming that the electronic energy has the status of enthalpy. When accurate HOF values are wanted for comparison with experiments, they should be computed by employing isodesmic equations [24]. Pre– and post–processing operations were performed with the aid of the WinMOPAC (version 3.5) and XMO graphical user interfaces [25].

## 3 RESULTS AND DISCUSSION

Table 1 summarizes the results of our semiempirical MO computations on the molecules herein investigated. Let us start with cubane, whose geometry has been optimized to assess the performance of the PM5 method with respect to more expensive electronic structure methods such as DFT. PM5 yields for cubane the C−C and C−H bond lengths of 1.571 and 1.087 Å, respectively. The C−C bond length is well within those of 1.556 and 1.592 Å as calculated with the SVWN/6–31G* and B3LYP/6–31G* methods, respectively [26]. The C−H bond length is almost the same as that of 1.086 Å calculated by Ball with the B3LYP/6–31G* method. This satisfactory structural comparison indicates that the PM5 method is enough accurate for the molecular design of compact hydrocarbons derived from cubane. The HOMO, LUMO, and HOMO–LUMO gap PM5 energies of cubane are also given in Table 1 along with those computed from single–point HF/3–21G calculations (in parenthesis). The HOMO energies computed with the PM5 and HF/3–21G methods compare quite well with each other whereas this is not the case for the LUMO energies which are separated by ~4 eV. As a result, the HOMO–LUMO gap obtained with the PM5 method (12.831 eV) is considerably smaller than that calculated with the HF/3–21G method (17.119 eV).

**Table 1.** Results of semiempirical PM5 MO calculations on cubane, percubyl–cubane (PCC), and the newly designed cubanoids **1**–**6**. The heat of formation (HOF) is in kcal/mol, the HOMO, LUMO, and HOMO–LUMO (H–L) gap energies in eV, and the frequency of the lowest–lying harmonic vibrational mode in cm$^{-1}$. The energy values obtained from single–point *ab initio* calculations with the HF/3–21G method are given in parenthesis.

| Molecule | Formula | HOF | HOMO | LUMO | H–L gap | Symmetry | $\nu_1$ |
|---|---|---|---|---|---|---|---|
| **Cubane** | $C_8H_8$ | 105.32 | –10.174 (–10.526) | 2.657 (6.593) | 12.831 (17.119) | $O_h$ | 552 |
| **PCC** | $C_{72}H_{56}$ | 961.18 | –9.324 (–8.441) | 2.046 (5.354) | 11.370 (13.795) | O | 37 |
| **1** | $C_{72}H_{32}$ | 1485.37 | –8.631 (–7.605) | 1.240 (4.446) | 9.871 (12.050) | $O_h$ | 129 |
| **2** | $C_{84}H_{56}$ | 864.10 | –8.867 (–8.036) | 2.156 (5.001) | 11.023 (13.037) | $C_i$ | 72 |
| **3** | $C_{72}H_{32}S_{12}$ | 1154.50 | –8.066 (–7.608) | –0.093 (4.052) | 7.973 (11.660) | $C_i$ | 56 |
| **4** | $C_{64}H_{40}$ | 1067.21 | –9.180 (–8.472) | 1.843 (4.366) | 11.023 (12.838) | $O_h$ | 117 |
| **5** | $C_{76}H_{64}$ | 767.99 | –9.537 (–9.314) | 2.443 (4.777) | 11.980 (14.091) | $C_{2h}$ | 63 |
| **6** | $C_{64}H_{40}S_{12}$ | 1033.66 | –8.551 (–8.368) | –0.233 (3.645) | 8.318 (12.012) | $C_{2h}$ | 49 |

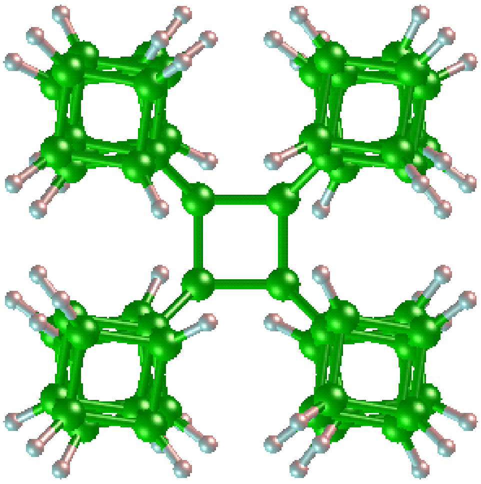

**Figure 2.** Optimized structure of percubyl–cubane (PCC).

Next, we optimized the structure of percubyl–cubane (PCC) that is shown in Figure 2. In agreement with a previous theoretical study [18], the relaxed geometry of PCC possesses *O* symmetry. The cubyl groups are rotated by 44° through the C−C bonds connecting each of them to the central $C_8$ unit. The HOMO–LUMO energy gap calculated for PCC with the PM5 method corresponds to 11.370 eV, a value which is ~2.4 eV smaller than that calculated with the HF/3–21G method (see Table 1). The HOF of PCC is about nine times larger than that calculated for cubane (note that the number of hydrogen atoms in PCC is not a multiple of that in cubane). Hence, the PCC molecule is expected to possess almost the same strain as that of cubane.

Additional cubyl units may be added to PCC so as to obtain a radial–like structure. This, however, is not a compact structure since the resulting molecule would be characterized by a certain degree of conformational flexibility. One (and the only possible) way of making a compact structure out of PCC is that of connecting its neighboring cubyl units. In practice, this could be achieved by means of condensation reactions on substituted PCC molecules. The removal in PCC of neighboring pairs of hydrogen atoms and subsequent formation of C−C bonds yields the optimized cubanoid structure **1** shown in Figure 3. This highly symmetric, compact structure belongs to the $O_h$ point group of symmetry. The C−C bond distances connecting the internal to the external cubane moieties correspond to 1.34 Å while the C−C bond lengths among neighboring cubane moieties on the outer–sphere correspond to 1.57 Å. The latter C−C bonds are responsible for the deformation of the external $C_8$ cages whose C•••C distances along two of the triagonals (3D diagonals) are at 2.85 and 2.46 Å, respectively. This, along with the large HOF calculated for this molecule (1485.37 kcal/mol), indicates that its geometry is subject to a very large strain. Despite this, however, our vibrational analysis did not result in any negative harmonic frequency. The lowest vibrational mode ($\nu_1$) has a frequency of 129 $cm^{-1}$ and is doubly degenerate with $1E_u$ symmetry. The HOMO–LUMO energy gap corresponds to 9.871 eV, which is ~2 eV smaller than that calculated with the HF/3–21G method (see Table 1).

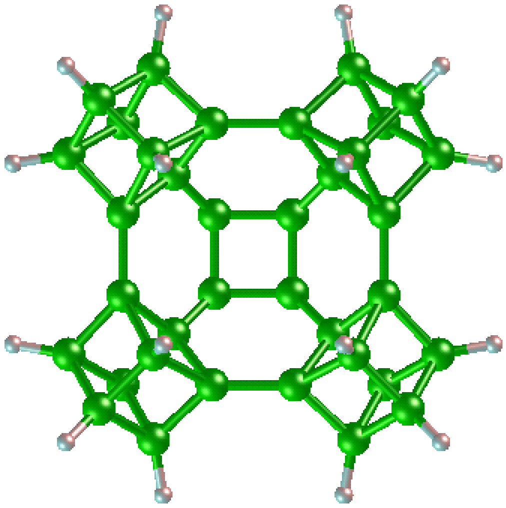

**Figure 3.** Optimized structure of cubanoid **1**.

We found that the strain in **1** can be relieved considerably when either methylene or sulfur bridging moieties are being inserted between neighboring $C_8$ units. The optimized structures of the resulting cubanoids **2** ($\nu_1$ = 72 cm$^{-1}$) and **3** ($\nu_1$ = 56 cm$^{-1}$) are shown in Figure 4. Both compact structures possess $C_i$ symmetry. Owing to the presence of twelve bridging methylene or sulfur moieties, the outer $C_8$ units of **2** and **3** are not anymore distorted as it was observed in the case of **1**. Here, the C•••C distance along one of the triagonals is ~0.1 Å longer than those of the others, thus indicating that the distortion of the $C_8$ cage is minimal.

Furthermore, the HOF of **2** (864.10 kcal/mol) is ~100 kcal/mol lower than that calculated for PCC (961.18 kcal/mol) despite the larger number of carbon atoms. This result indicates that the introduction of bridging methylene moieties into **1** removes the strain to which this hydrocarbon is subject. The C−C bond length connecting the inner cube of **2** with the outer cubes corresponds to 1.444 Å while the C−C bonds connecting each methylene bridge to the neighboring $C_8$ cage are at 1.477 Å. The HOMO–LUMO energy gaps computed for **2** and **3** with the PM5 method are rather different, being 11.023 and 7.973 eV, respectively.

The difference between these energy gaps corresponds to ~3 eV and is reduced to ~1.4 eV when single–point HF/3–21G calculations are performed. This energy difference is likely being a consequence of electronic effects arising from the replacement of the bridging methylene moieties with isolobal sulfur atoms. In this regard, we notice that the HOMO of **3** is localized on four bridging sulfur atoms (two opposing pairs) whereas the HOMO of **2** is localized on the carbon atoms of the inner $C_8$ cage. The minimum separation between sulfur atoms in **3** corresponds to 3.228 Å.

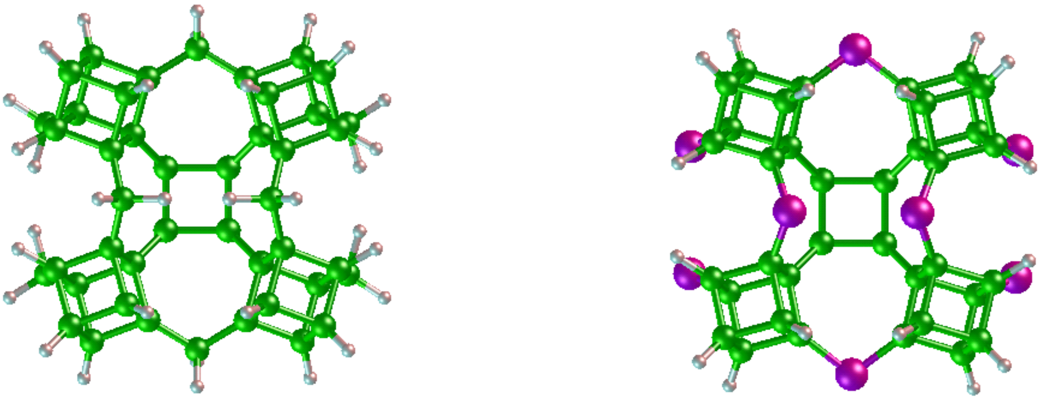

**Figure 4.** Optimized structures of cubanoids **2** (left) and **3** (right).

The structures of cubanoids **1**–**3** are all characterized by possessing a $C_8$ unit at their respective cores. It is interesting to check whether removal of the central cubane units destabilizes their molecular structures. To test this hypothesis, we removed the carbon atoms of the inner $C_8$ unit of **1**–**3** and saturated the open valences of the eight carbon atoms with hydrogen atoms. The optimized structure of the cubanoid molecule, **4** ($\nu_1$ = 117 cm$^{-1}$), derived from **1** upon removal of its central $C_8$ unit, is shown in Figure 5.

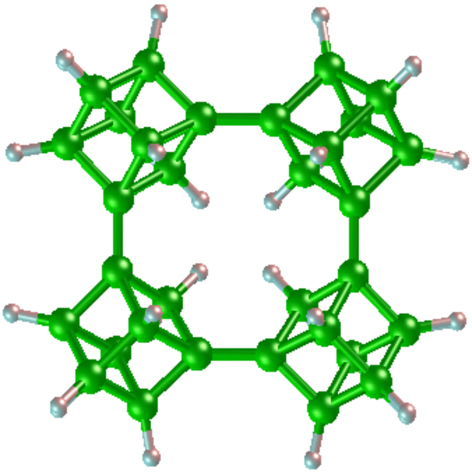

**Figure 5.** Optimized structure of cubanoid **4** derived from **1** upon removal of the inner $C_8$ cage.

The C−C bond lengths connecting neighboring $C_8$ units are at 1.481 Å. Each $C_8$ unit is still subject to a considerable amount of strain, as indicated by the different values of the C•••C distances along the triagonals, which differ by ~0.2 Å. This is confirmed by the large value computed for the HOF (1067.21 kcal/mol) of **4** which is about ten times larger than that of cubane (Table 1). The closest separation among the hydrogen atoms occupying the central cavity of cubanoid **4** corresponds to 1.448 Å.

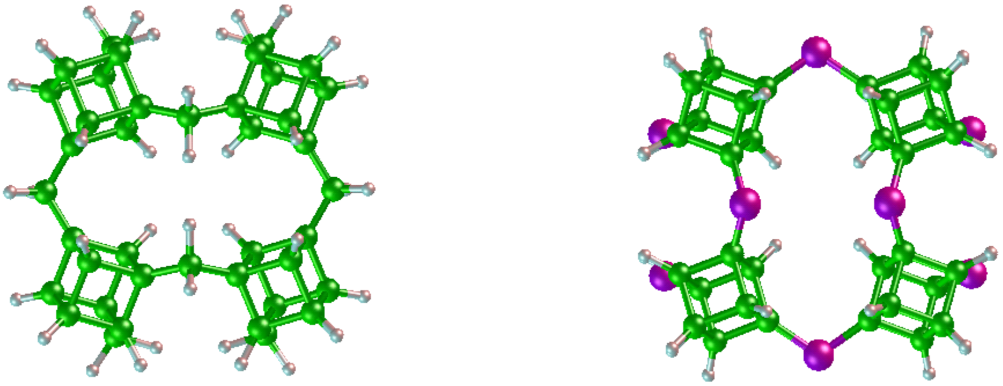

**Figure 6.** Optimized structures of cubanoids **5** (left) and **6** (right) derived from **2** and **3**, respectively, upon removal of their corresponding inner $C_8$ cages.

Two other core–free cubanoids can be obtained upon removal of the central $C_8$ units of **2** and **3**, respectively. Their optimized structures are shown in Figure 6. As reported in Table 1, the HOF of cubanoid **5** ($\nu_1 = 63$ cm$^{-1}$) is only 767.99 kcal/mol thereby indicating again that inserting methylene units into **4** has the effect to decrease its corresponding strain. If sulfur atoms rather than methylene units are being inserted into **4**, cubanoid **6** ($\nu_1 = 49$ cm$^{-1}$) is obtained. We notice that the HOMO–LUMO energy gap of **6** is ~3.7 eV smaller than that of **5** and it reduces to ~2 eV when single–point HF/3–21G calculations are performed. This difference in the energy gap is again attributable to the valence electrons of the bridging sulfur atoms. As observed for the HOMO level of **3**, we notice that also the HOMO of **6** is localized on four bridging sulfur atoms (two opposing pairs) whereas the HOMO of **5** is localized on the eight inner C−H moieties (each pertaining to a $C_8$ unit) pointing toward the empty core. The minimum separation between sulfur atoms in **6** corresponds to 3.904 Å, which is ~0.7 Å longer than that in **3**.

## 4 CONCLUSIONS

With the aid of semiempirical quantum chemical calculations we have successfully designed a series of compact hydrocarbons containing discrete numbers of cubane units. These novel molecules, which we shall call *cubanoids*, are expected to fill the structural gap that there exists between the cubane molecule and the periodic structure of bulk supercubane. If synthesized, they might be useful as building blocks for the production of novel nano–materials.

### Acknowledgment

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### Supplementary Material

The Cartesian coordinates of the optimized molecular structures of cubanoids **1–6** along with those of both cubane and percubyl–cubane (PCC) are collected in the file ‘cubanoids–xyz.txt’.

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## Biographies

**Fabio Pichierri** is associate professor (untenured position) of Computational Chemistry at Tohoku University. After obtaining a Ph.D. degree in Chemical Sciences from the University of Trieste (Italy), Dr. Pichierri moved to Japan in 1996 where he undertook postdoctoral research at RIKEN (The Institute of Physical and Chemical Research) and at the research center of Mitsubishi Chemical Corporation. In January 2003 he joined Tohoku University under the 21–st century Center of Excellence (COE) program "Giant Molecules and Complex Systems" of the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of Japan. His scientific interests lay in the applications of computational quantum chemistry methods to molecular recognition phenomena, molecular design and, more recently, molecular–scale devices and machines (Computational Nanoscience & Nanotechnology). Dr. Pichierri is a member of the Chemical Society of Japan (CSJ), the Japanese Society of Applied Physics (JSAP), the Materials Research Society (MRS) of US and a life member of the World Association of Theoretically Oriented Chemists (WATOC). F.P. is married and the father of two children.