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Cubic Fuels?

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Abstract
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Keywords
high energy density materials, rocket fuels

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Cubic Fuels?

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ABSTRACT: The cubic molecules C\textsubscript{4}O\textsubscript{4}, N\textsubscript{8}, and Si\textsubscript{8}R\textsubscript{8} are considered as possible high-energy propellants. The potential energy surface minimum for C\textsubscript{4}O\textsubscript{4} is found to be incapable of supporting any bound vibrational levels. N\textsubscript{8}’s decomposition to 4 N\textsubscript{2} is mapped in detail, but the initial barrier of its rather complicated dissociation is too modest to allow hope for its handling in bulk quantity. Si\textsubscript{8}H\textsubscript{4} is found to be the most promising additive among the four R’s considered, but simulation of its combustion in an LH\textsubscript{2}/LOX rocket gives only a 6-s specific impulse enhancement. © 2000 John Wiley & Sons, Inc

Key words: high energy density materials; rocket fuels

Introduction

Chemists have long been interested in high-symmetry molecules for their beauty and frequently interesting properties. Any number of cubic molecules are therefore known, including many transition-metal or heavy main-group-based systems. Examples taken from the journal Organometallics during 1996 include (C\textsubscript{p}V\textsubscript{1})N\textsubscript{4} [1], (C\textsubscript{pRu})\textsubscript{2}S\textsubscript{4} [2], Mes\textsubscript{8}In\textsubscript{7}P\textsubscript{2} [3], and (C\textsubscript{pGa})\textsubscript{2}Se\textsubscript{4} [4], illustrating the point that cubes are a well-established structural motif and may contain a wide variety of atoms.

The present study investigates several cubic species in regards to their potential utility as rocket fuels. Such high-energy density materials (HEDM) must meet three important criteria: large energy release for some chemical process including but not limited to unimolecular decay or combustion, appreciable stability to permit handling before use, and light weight to maximize payload. Meeting the first two goals simultaneously is a challenge, and the weight criterion limits potential HEDM candidates to lighter elements. Although the ultimate goal might be regarded as finding a chemical reaction to replace the liquid hydrogen/liquid oxygen engine employed on the space shuttle, a shorter term aim is the identification of additives that might reduce the volume of cryogenic propellants required.
Put in the language of physical chemistry, we seek a system possessing a large exothermicity but with a sufficiently large activation energy to make the reactants metastable, composed of light elements. Since the potential fuels are high-energy species, we must also be concerned with other potential surfaces of the same or different spin multiplicity crossing the reaction barrier, as internal conversion or spin-orbit coupling may provide alternate reactive pathways that destroy metastability. An example close to the subject of this study is tetrahedral $N_4$, which CCSD(T) [5] and multi-configuration self-consistent field (MCSCF) [6] computations predict has a barrier to decomposition to $2 N_2$ of 61–63 kcal/mol. Yarkony [7] has shown that a triplet surface cuts through this barrier about 28 kcal/mol above $N_4$, with a sufficiently large spin-orbit coupling element to permit crossing onto the triplet surface, effectively halving the barrier.

The present work is composed of four parts, following a brief summary of the computational protocol. The first is a survey of cubane isoelectronic species formed from one or two second-row elements. The results of this discussion highlight three molecules that have been proposed previously as HEDM or explosive materials, and so we investigate the decomposition pathways of the two most energetic. Finally, a proposal that the experimentally known third-row system $Si_8$ ($t$-butyl)$_8$ might have a sufficiently large combustion exothermicity to overcome its heavier weight is considered.

### Computational Methods

Since we are in the main considering very large reaction energies, sometimes on large molecules, the level of theory used is fairly modest. The majority of the computations are closed-shell SCF [8] [restricted Hartree–Fock (RHF)] followed by second-order Møller–Plesset perturbation corrections (MP2) [9]. One open-shell case is treated with restricted open-shell Hartree Fock (ROHF)-based perturbation theory according to the restricted MP2 (RMP2) formalism [10]. The 6-31G (d) basis set [11] is used throughout. Minima and transition states are demonstrated as such by computation of the force constant matrix (zero or one imaginary frequency, respectively). Reaction mechanisms are proved by tracing the intrinsic reaction coordinate (IRC), which connects reactants to saddle point to products [12]. All computations have been performed with the GAMESS program package [13].

### Survey of Cubane Analogs

The prototype cubic structure is no doubt cubane, $C_8H_8$, first synthesized in 1964 [14]. A recent computational study [15] contains references to available experimental structural, infrared (IR), and Raman data, and Eaton [16] has reviewed the synthesis and reactivity of cubanes. Cubane is a strained dense hydrocarbon and therefore of interest in the HEDM program in its own right, leading to efforts to synthesize it in large quantities [17]. A recent popular article in the New York Times (July 15, 1997) summarizes some of the potential uses of cubanes as a drug or fuel and its interesting “plastic” phase transition near the melting point [18]. Before going on, it is worth mentioning that a promising line of research toward more energetic systems is NO$_2$ substitution for H in cubane [19–22], with up to 6 NO$_2$ groups added at present [22]. The functionalization of cubane has recently been reviewed [23].

Here we consider several isoelectronic systems, inspired by literature proposals of molecules such as $N_8$, $H_2C_4N_4$, and $C_6O_4$. Figure 1 shows all possible corner pieces that may be constructed from the elements B, C, N, and O, each of which is isoelectronic to the CH corner of the parent cubane. The second row of the figure is constructed by deprotonation of the first. If we then ignore the two corner pieces with formal charges of two, and form all possible neutral cubic molecules either of type $X_8$ possessing $O_h$ symmetry or type $X_3Y_4$ possessing $T_d$ symmetry (alternating corners), the possible second-row cubane analogs shown in Table I are generated. The first three entries are formed with neutral corner pieces, the final four from formally charged corners.

Table I includes the energetics for the unimolecular decomposition reaction of each cubane analog to four triply bonded molecules, e.g., $C_8H_8 \rightarrow 4HCCH$. This decomposition is certainly not the only potential energy release mechanism; for example, combustion of cubane will be considered below. Note also that the decomposition reaction does not measure just the strain energy of the cubes, as it also involves the energy difference between $\sigma$ bonds in the cubane and $\pi$ bonds in
the always colinear triple bonded products. This accounts for the initially surprising observation that the cubane decomposition with respect to 4HCCH is endothermic. Both the reaction used and the modest computational level employed mean the data in Table I should be regarded mainly as a survey intended to identify the most energetic candidates.

Three species stand out in Table I: HC\textsubscript{N} as well as its slightly less stable ionic counterpart C\textsubscript{NH} which has a sizable exothermicity, and C\textsubscript{O} whose decompositions are predicted to be extremely exothermic. The decomposition reactions of the latter two species will therefore be considered in more detail in the next two sections.

The heavier congeners already exist, namely (t-butyl)\textsubscript{C\textsubscript{4}P\textsubscript{4}} [30, 31] and (t-butyl)\textsubscript{Si\textsubscript{4}P\textsubscript{4}} [31].

### Table I

<table>
<thead>
<tr>
<th>Reaction</th>
<th>RHF\textsuperscript{b}</th>
<th>MP2\textsuperscript{b}</th>
<th>R\textsuperscript{c}</th>
<th>HOMO\textsuperscript{d}</th>
<th>LUMO\textsuperscript{d}</th>
<th>ν (min)\textsuperscript{e}</th>
</tr>
</thead>
<tbody>
<tr>
<td>H\textsubscript{8}C\textsubscript{6} \rightarrow 4 HCCH</td>
<td>76.9</td>
<td>97.4</td>
<td>1.559</td>
<td>−0.382</td>
<td>+0.234</td>
<td>688</td>
</tr>
<tr>
<td>(HC\textsubscript{2})\textsubscript{2}N\textsubscript{4} \rightarrow 4 HCN</td>
<td>−99.8</td>
<td>−83.6</td>
<td>1.486</td>
<td>−0.392</td>
<td>+0.194</td>
<td>708</td>
</tr>
<tr>
<td>N\textsubscript{8} \rightarrow 4 N\textsubscript{2}</td>
<td>−518.7</td>
<td>−466.9</td>
<td>1.466</td>
<td>−0.446</td>
<td>+0.088</td>
<td>727</td>
</tr>
<tr>
<td>B\textsubscript{2}N\textsubscript{2}H\textsubscript{6} \rightarrow 4 HBNH</td>
<td>141.4</td>
<td>157.4</td>
<td>1.586</td>
<td>−0.414</td>
<td>+0.223</td>
<td>541</td>
</tr>
<tr>
<td>(HB)\textsubscript{4}O\textsubscript{4} \rightarrow 4 HBO</td>
<td>83.1</td>
<td>84.3</td>
<td>1.522</td>
<td>−0.495</td>
<td>+0.192</td>
<td>537</td>
</tr>
<tr>
<td>C\textsubscript{4}N\textsubscript{4} \rightarrow 4 CNH</td>
<td>−198.3</td>
<td>−155.3</td>
<td>1.535</td>
<td>−0.332</td>
<td>+0.181</td>
<td>657</td>
</tr>
<tr>
<td>C\textsubscript{4}O\textsubscript{4} \rightarrow 4 CO</td>
<td>−409.4</td>
<td>−358.0</td>
<td>1.519</td>
<td>−0.439</td>
<td>+0.098</td>
<td>167</td>
</tr>
</tbody>
</table>

\textsuperscript{a}The 6-31G(d) basis set has been used.
\textsuperscript{b}Reaction exothermicities, in kcal/mol. Zero-point corrections are not included. MP2 results are from RHF geometries.
\textsuperscript{c}RHF bond distance in the cube, in angstroms.
\textsuperscript{d}RHF orbital energy, in hartree, for highest occupied and lowest unoccupied molecular orbitals, for the cube.
\textsuperscript{e}Smallest RHF vibrational frequency, in wavenumbers, for the cube. For all cubes, this was a doubly degenerate mode.

\textbf{C\textsubscript{4}O\textsubscript{4}}

The hypothetical molecule C\textsubscript{4}O\textsubscript{4} has previously been proposed as an HEDM candidate by Evangelisti [32, 33]. It has the second largest unimolecular decomposition energy in Table I, but there are other signs that it is not particularly stable. The energy of the lowest unoccupied molecule orbital (LUMO) is fairly low, and C\textsubscript{4}O\textsubscript{4} has by far the lowest vibrational frequency of all the cubes. The results presented in Table I are essentially identical to those given by Evangelisti [33], who used somewhat larger basis sets and reported also that the MP2 frequencies for C\textsubscript{4}O\textsubscript{4} were all positive. Larger basis sets and use of MP2 raise the lowest vibrational frequency to about 280 wave numbers [33]. Localized orbitals for the present RHF/6-31G(d) wave functions show 12 identical CO σ bonds and one lone pair pointing outward at each of the C or O corners.

Kinetic stability requires more than a positive definite force field; in addition, the lowest barrier out of all possible decomposition reactions must be substantial. C\textsubscript{4}O\textsubscript{4} has a transition state possessing \textit{D\textsubscript{2h}} symmetry for dissociation into two cyclic C\textsubscript{2}O\textsubscript{2} rings. This transition state, not illustrated...
here because it is virtually indistinguishable from the $T_d$ cubic minimum, can be thought of as the rhombi of two opposite faces separated by stretching the four other faces of the cube. At the RHF/6-31G(d) saddle point, the eight bond distances in the top and bottom faces are 1.5138 Å, while the other four bond distances are 1.5305. These values are very little changed from the twelve 1.5192-Å bonds in the cube minimum. The RHF analytic frequency along the dissociative mode is 168 $\text{cm}^{-1}$, and the RHF energy is 0.000015 hartree above the cubic structure. [MP2/6-31G(d) at the RHF geometries gives an energy separation of 0.000015 hartree.] Since the RHF energy barrier is just 0.002 kcal/mol, and the cubic minimum’s smallest frequency is 167.3 $\text{cm}^{-1}$ = 0.48 kcal/mol, it is clear this cube’s shallow minimum does not support any bound vibrational levels. We were also able to locate a second-order saddle point in $S_4$ symmetry whose RHF energy is 0.000079 hartree above the cube (imaginary frequencies 323$i$ and 270$i$), indicating a second readily accessible decomposition route. Therefore, $\text{C}_4\text{O}_4$ is not an observable molecule.

By taking extra numerical care, it is possible to trace the IRC connecting the $D_{2d}$ saddle point to the $T_d$ minimum. In the other direction, the $D_{2d}$ reaction path necessarily leads to two four-membered $\text{C}_2\text{O}_2$ rings [each is locally planar $D_{2h}$ at the RHF/6-31G(d) level]. The $\text{C}_2\text{O}_2$ ring is a minimum energy structure, and two such rings lie 151 kcal/mol below $\text{C}_4\text{O}_4$, and therefore still 258 kcal/mol above 4 CO. Thus one might postulate cyclic $\text{C}_2\text{O}_2$ as a HEDM candidate. Bartlett’s group [34] has considered this ring, along with other isomers, and Evangelisti [33] has considered a tetrahedral $\text{C}_4\text{O}_2$. We have located the transition state connecting this ring to 2 CO, which occurs in the $C_2$ point group (alternating CO bond distances of 1.2467 and 1.5738 Å, a slightly nonplanar, imaginary frequency is 863$i$), with an RHF barrier of 7.6 kcal/mol. The dissociative mode clearly leads to 2 CO. The barrier is modest from a practical view (handling of this potential fuel), but we now have a high-energy species with a nonzero barrier to dissociation.

Reinvestigation at the MP2/6-31G(d) level of theory shows that the $\text{C}_2\text{O}_2$ ring puckers into a $C_{2v}$ geometry, and its four bond lengths are 1.394 Å. The transition state has a nearly unchanged structure, namely a puckered $C_2$ dissociation (CO distances 1.317 and 1.512, imaginary frequency is 386$i$) leading to 2 CO. The MP2/6-31G(d) barrier is reduced to 0.47 kcal/mol, and harmonic zero-

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Because $N_2$ is a very stable molecule, strained species such as $N_4$ [5–7] and $N_8$ have been proposed as HEDM candidates, releasing their energy by unimolecular decomposition to $N_2$. The cube $N_8$ was first suggested in 1981 [35] as a small portion of a work proposing cubic $P_8$, a molecule we later investigated ourselves [36]. In the early 1990s, Engleke [37] and Bartlett et al. [38] proposed $N_8$ as an HEDM material, based on a high energy relative to 4 $N_2$, a positive definite force field, and stability for one dissociative pathway. Engleke’s group [37] investigated a $D_{4h}$ pathway, the symmetry-forbidden concerted separation to four diatoms, and found that this pathway has a high barrier of 100–160 kcal/mol. Bartlett’s group [38] did a formal symmetry analysis (but no computations) for both a $D_{2h}$ and a $D_{2d}$ pathway and found them to be Woodward–Hoffman forbidden. Clearly the $O_h$ symmetry group of $N_8$ has many other subgroups, and thus these limited studies are not definite proof of kinetic stability.

In the years since, many groups [39–46] have considered cubic $N_8$. These studies mainly focus on equilibrium properties such as structure, frequencies, or energy, with the notable exception of a 1997 study by Evangelisti and Roos [44] that investigated the decomposition mechanism. A number of the works cited here also consider tetrahedral $N_4$ [35, 40, 42, 45], in addition to the three key references we have already given [5–7].

A number of these studies have considered isomeric structures for $N_8$ other than a cube [39–43, 46]. A total of 10 different minima on the $N_8$ surface have been located to date, and it is now established that azidopentazole (a five-membered ring with an azide side chain) is the lowest energy isomer [41, 42]. Two nearly equal energy isomers lie about 15 kcal/mol above this, octaazapentalene [39–42, 46] (two fused aromatic five-membered rings) and diazidodiimide [41, 42] ($N_8$—$N=$...
Nguyen and Ha’s CCSD(T) result indicates the latter is perhaps the more stable of these two.

Experimental work on purely nitrogen species is sparse. The very recent report by Christe of the novel cation \( N^+_2 \) (with counterion \( AsF_5^- \)) was described as only the third all-nitrogen species ever obtained in isolable yield, and the first since azide ion \( N_3^- \) in 1890. Not surprisingly, this new salt is explosive. \( N^+_2 \) has a structure consisting of \( N_2 \) and \( N_3 \) pieces, and thus if it were combined with an azide counterion, the most likely structure would be the diazidodiimide isomer just mentioned. Thus, after nearly two decades of computational studies on \( N_8 \), we may finally be on the verge of experimental entree into the \( N_8 \) system.

Evangelisti and co-workers have considered the decomposition of cubic \( N_8 \) using CASSCF wave functions, followed by CASPT2, together with some density function theory (DFT) results. Their study proposed a mechanism involving a series of five minima including the initial cube and terminating at octaazapentalene, locating transition states between these minima. Vibrational frequencies were computed for all stationary points, and inspection of the imaginary frequency normal modes of the transition states was used to assign the mechanism. Their main result is that only the first of these transition states lies at a higher energy than cubic \( N_8 \), and this initial barrier to dissociation is modest. The CASSCF transition state was found to have \( C_{2v} \) symmetry, and lies 9.3 kcal/mol above the cube. CASPT2 single-point corrections raise this to 22.4 kcal/mol.

The present study’s contributions to the problem of cubic \( N_8 \)'s stability are the computation of IRC paths to prove conclusively the reaction mechanism, and the demonstration that the dissociation mechanism does lead eventually to \( 4 N_2 \). We will also briefly consider the role of the lowest triplet state. The level of theory is more modest than that used by Evangelisti and co-workers [44], as we will present both RHF/6-31G(d) and MP2/6-31G(d) reaction paths. Explicitly tracing the reaction paths leads to a different mechanism, although the initial steps are in agreement with those already proposed [44].

Figure 2 shows the RHF/6-31G(d) dissociation of cubic \( N_8 \) into \( 4 N_2 \). Structures at the various stationary points in Figure 2 are shown in Figure 3. The initial stages of the reaction consist of the concerted opening of two opposite bonds on one of the faces of the cube to form 2. In contrast, the opposite face then opens one bond at a time forming first 4 and then 6, which is the all-nitrogen analog to cyclooctatetraene [39, 40, 42, 46]. This part of the reaction is nearly identical to that presented by Evangelisti and co-workers [44], except that their initial transition state 1 has \( C_{2v} \) symmetry. These workers report a transition state connecting 6 to the octaazapentalene isomer (whose CASPT2 barrier, relative to 6 is 37.3 kcal/mol), but they do not carry the dissociation through the final stages to \( 4 N_2 \). Nguyen and Ha [41] have located the transition state, also with a modest barrier, that connects octaazapentalene to the azidopentazole isomer. These two literature reports are indicated with dotted lines in Figure 2.

The final stages of the RHF mechanism begin by dissociation of one \( N_2 \) from the eight-membered ring, to give the diazide \( N_2-N_3 \). Our RHF barrier for loss of \( N_2 \) from 6 is 30.7 kcal/mol, somewhat lower than that of Evangelisti and co-workers [44]. The approximate location of a valley-ridge inflection (VRI) point causing a bifurcation to a lower symmetry lower energy path is indicated. The energies of three low-energy isomers of \( N_8 \) which are not on the direct pathway for dissociation are added for reference. The two dotted surfaces have been explored in the literature, but not in the present work.
FIGURE 3. RHF/6-31G(d) structures along the reaction \( \text{N}_8 \rightarrow 4\text{N}_2 \). Bond distances are in angstroms, and imaginary frequencies for transition states are in wavenumbers. For reference, the RHF distance in cubic \( \text{N}_8 \) is 1.466 and in diatomic \( \text{N}_2 \) is 1.078. Structure numbers correspond to those in Figure 2. Arrows in transition states indicate directions of imaginary normal modes.

FIGURE 4. MP2/6-31G(d) potential surface for the dissociation of cubic \( \text{N}_8 \) to \( 4\text{N}_2 \). All energies are in kcal/mol and do not include zero-point corrections. Numerals refer to structures in Figure 5. Structures similar to Figure 2 but with a changed symmetry are indicated by primes, new structures have numbers higher than 9. Two sample points, A and B, along the quadruple dissociation are also illustrated in Figure 5.

smaller than Evangelisti and co-workers’ [44] barrier for rearrangement of 6 to octaazaazapentalene. Since the imaginary frequency modes for all transition states in Figure 2 happen to be totally symmetric, every IRC segment shown possesses the symmetry of the adjacent saddle point. The IRC connecting 7 to 8 thus begins in \( \text{C}_s \) symmetry, which leads to a cis geometry for \( \text{N}_3-\text{N}_3 \). Since this conformation is a rotational transition state, the \( \text{C}_s \) reaction path bifurcates to \( \text{C}_1 \) symmetry, eventually leading to trans \( \text{N}_3-\text{N}_3 \). We approximately located the valley–ridge inflection point [48] where the bifurcation occurs and then followed a \( \text{C}_1 \) path to the minimum energy structure of \( \text{N}_3-\text{N}_3 \). This six-atom molecule explodes into 3 \( \text{N}_2 \), an interesting but not unprecedented triple fragmentation [49].

The MP2/6-31G(d) potential energy surface is presented in Figure 4, with corresponding structures in Figure 5. Structure numbers are the same as those used for the RHF results just described, and cases where the point group is changed are indicated by addition of a prime. New structures have numbers higher than nine. Two key differences are a lower barrier and different symmetry for the initial barrier \( \text{I}' \), and explosion to four diatoms after barrier \( \text{I}'' \).

The initial barrier \( \text{I}' \) occurs in a higher point group, \( D_{2d} \), but comparison with the \( \text{C}_2 \) RHF structure 1 shows only a small difference, in that the back face is twisting instead of remaining square. The key result of this section is that this initial MP2 barrier is small, as after zero-point energy correction, the activation energy is just +15.4 kcal/mol. The energy of the lowest triplet state is shown slicing 0.2 kcal/mol below the top of the singlet state’s barrier. This curve was ob-
Returning to the later stages of the singlet state decomposition, the next few ripples on the surface are dictated by 1's higher symmetry, as the $S_4$ axis in $D_{2d}$ becomes the main $C_4$ axis in $D_{4h}$ as we reach two planar $N_4$ rings, 10. In fact, the initial stages of the MP2 $N_8$ decomposition are nearly identical to the breakup of $C_4O_4$ already discussed. There are two sets of perpendicular $C_2$ axes in $D_{4h}$: one $C_2$ axis through an edge bond is preserved as that bond reforms in 12. The $C_2$ axis in 2 with two bonds reformed is through a face center, so 13 necessarily has neither $C_2$ axis. The transition state $3'$ leading away from 2 possesses a mirror plane not present on the RHF surface, and rather than leading to the shallow fused $4 + 6$ ring minimum, it explodes into four $N_2$. We are unaware of any other such transition structure leading to a quadruple decomposition. Since the imaginary mode of $3'$ looks as if it should lead to the fused rings, we have illustrated two representative points on the IRC. The reason for the explosion from $3'$ is that RHF structure 4 is not a minimum on the MP2 surface, in fact ordinary MP2 geometry optimization from RHF structure 4 also leads to explosion.

The right-hand side of Figure 4 illustrates what happens to the octaazacyclooctatetraene isomer 6, which is no longer on the direct $N_8$ decomposition pathway. Isomer 6 has only a very small activation energy to decomposition, +1.5 kcal/mol after zero-point correction. Structure $7'$ was located by starting from the RHF $C_7$ geometry of 7, in which symmetry the MP2 transition state has two imaginary frequencies. So, $7'$ was located imposing no symmetry constraint, and the IRC leading to $8'$ was also run in $C_1$ symmetry. However, the $7'$ saddle point possesses $C_2$ symmetry, breaking only one bond initially (the opening bond is 1.774 Å). $8'$ has a torsion angle of 141° compared to 180° in 8, but apart from $7'$ all structures are similar to Figure 3 and are not pictured here. Structure $9'$ remains a transition state for triple dissociation.

Our efforts have been focused on the decomposition of the $N_8$ cube, and we find it and one of its low-energy isomers (6, octaazacyclooctatetraene) to have small barriers for decomposition, +15.4 and +1.5 kcal/mol, respectively. Our result for cubic $N_8$ is in general agreement with that of Evangelisti and co-workers [44], whose CASPT2 barrier for $N_8$ was +22.4 kcal/mol. Thus neither the cube nor the eight-membered ring is a good HEDM candidate, as handling concerns for bulk quantities dictate a unimolecular decomposition barrier of 30–35 kcal/mol.

The three lowest energy isomers of $N_8$ did not play a role in the cube’s decomposition, so we have not obtained any results for their decomposition barriers. However, our results for the energies of these three isomers have been included in Figures 2 and 4, showing each lies well above 4 $N_2$. Recent experimental results [47] raise hope for the synthesis of at least the diazidodimide isomer, and any further computational attention should be directed toward the decomposition mechanisms of these lowest energy isomers.
Due to the strength of SiO bonds, the combustion of elemental silicon to solid amorphous SiO$_2$ ($\Delta H_f^{\circ}$ (298) = $-215.9$ kcal/mol) is more energetic than combustion of elemental carbon to gaseous CO$_2$ ($\Delta H_f^{\circ}$ = $-94.1$ kcal/mol). Based on this large room temperature difference, along with a suggestion that the operating temperature ($\approx 2500$ K) of the LH2/LOX shuttle main engine is low enough to lead to condensed phase products rather than gaseous SiO$_2$ ($\Delta H_f^{\circ}$ = $-77.0$), we consider here several silicon-based cubes, in spite of their large molecular weights.

The cubic structure octasilacubane Si$_8$H$_8$ (OSC) was first proposed based on theoretical computations of Nagase in 1987 [50] and confirmed by synthesis of a substituted silicon cube in 1988 [51]. Additional theoretical studies [52–54] confirmed that the cube was a relatively unstrained structure and include the important result that the cubic isomer of Si$_8$H$_8$ is the most stable of the 22 considered [54]. This is in marked contrast to the C$_8$H$_8$ system, where 15 isomers are found to be more stable than cubane [54]. Additional experimental studies [55–63] explored the photophysical properties and extended the range of ligands, to include the well-characterized compound t-butyloctasilacubane TBOSC [50].

Here we consider four silicon cubes, namely OSC H$_8$Si$_8$, methyloctasilacubane (MOSC) (CH$_3$)$_6$Si$_8$, TBOSC ((CH$_3$)$_5$C$_2$Si)$_8$, and silyloctasilacubane (SOSC) (SiH$_3$)$_6$Si$_8$ in comparison to cubane itself, and RJ-4. RJ-4 is a ramjet fuel mixture, whose primary component is C$_{12}$H$_{30}$, a methylcyclopentadiene dimer. Some traditional difficulties with proposed fuels are not present for OSC compounds. Synthesis of TBOSC proceeds with 20% yield in a straightforward manner [57], and one might well suppose the side products are malformed cubes usable as fuel material. Handling is not a problem, as TBOSC is stable to heating in vacuum to 250°C and stable more than a month at room temperature in vacuum [60b]. The purple TBOSC crystals “change to a yellow solid if they are left out in the air for a few days” [60b]. Because of this mild air sensitivity, and since the proposed energy release is combustion, we consider here the possibility of using TBOSC or other R$_4$Si$_8$ compounds as an additive to the liquid H$_2$ (LH2) component of a LH2/LOX rocket. We thus address two questions: Is OSC stable in contact with H$_2$? How energetic are the OSC combustion reactions?

Figure 6 shows the potential energy surface for the hydrogenation reaction Si$_8$H$_8$ + H$_2$ → Si$_8$H$_{10}$. The larger, second barrier corresponds to the direct insertion of H$_2$ into an Si—Si bond, and the transition state’s structure is quite similar to that for the prototype reaction H$_2$ + Si$_2$H$_6$ → 2SiH$_4$, apart from constraints imposed by the cube. The previous computations [64] show that the cube has modified the energetics somewhat, as the prototype reaction’s barrier is +84 kcal/mol, and overall exothermicity is $-5$ kcal/mol. Tracing the IRC shows that at its initial stages, the reaction proceeds first by opening of the Si—Si bond to give an intermediate, with H$_2$ bound only weakly, followed by reaction of the H$_2$ to yield new SiH bonds. The zwitterionic intermediate Si$_8$H$_8$ that is shown in Figure 6 complexed to H$_2$ can be optimized by itself, and its energy plus H$_2$ is just 0.35 kcal/mol higher than the Si$_8$H$_{10}$ intermediate shown in Figure 6. The initial saddle point shown on the Si$_8$H$_{10}$ surface can also be located as an Si$_8$H$_8$ transition state. These two structures may be artifacts of our using closed-shell wave func-

![FIGURE 6. Potential energy surface for hydrogenation of Si$_8$H$_8$. MP2/6-31G(d) barrier heights are in kcal/mol, after correction with RHF zero-point energies. (Less accurate RHF results in parenthesis). Direct addition of H$_2$ leads to hydrogens attached at adjacent Si atoms. A similar species with H atoms on opposite corners of a face is 10 kcal/mol more stable.](image-url)
tions. Finally, an additional structure with a Z-shaped upper face is shown in Figure 6. This species is more stable than the direct H insertion product, lying 37.6 kcal/mol below H$_2$ + OSC. Similar Z-shaped structures have been reported [59]. The question of OSC's stability in liquid H$_2$ is answered in the affirmative by the large barriers found in Figure 6.

We turn then to the question of how large the exothermicity of the combustion reaction of these species is. For this, we must obtain estimates for their heats of formation. This is done by use of isodesmic reactions [65] involving species with experimentally known heats of formation (apart from the cubes). The energies of the isodesmic reactions are obtained at the MP2/6-31G(d) level using RHF/6-31G(d) geometries, and corrected for zero-point energy with RHF/6-31G(d) frequencies. The resulting energy data and key structural results for each cube are summarized in Table II. The size of TBOSC precludes computation of either a force field or MP2 energetics, as 6-31G(d) contains 776 basis functions, although we did optimize its structure. Instead we estimate TBOSC’s heat of formation from group additivity relations, using the final isodesmic reaction shown, for $n = 1$ and $n = 2$ (opposite corners). The heats of formation for OSC itself, and one and two t-butyl groups are thus computed to be 138.2, 104.1, and 70.2 kcal/mol. Since the increment per t-butyl group is $-34.1$ and $-33.9$, we assume a constant group increment of $-34$, and thus estimate TBOSC’s heat of formation as $-134$ kcal/mol. This is likely to be an underestimate since the first two t-butyl additions do not induce any steric crowding.

Note that our procedure generates a heat of formation for cubane of 149 kcal/mol which is in good agreement with 298° gas-phase experimental results, +148.71 ± 1.0 [66] or an indirect estimate +159 ± 1.2 [67]. Bond distances for cubane and TBOSC are in good agreement with the experimental values 1.575 [68] and 2.388 [57]. We find no evidence to support the reported polymorphic form of TBOSC [60a], as geometry optimizations started at the average Si—Si distance 2.493 Å, which has been reported for this “β form” [60a] revert to a structure with the shorter Si—Si distance reported in Table II.

Given the heats of formation, we can find the heats of combustion for the following:

Cubane: C$_8$H$_8$ + 16 O$_2$ → 8 CO$_2$ + 4 H$_2$O
OSC: Si$_8$H$_8$ + 10 O$_2$ → 8 SiO$_2$ + 4 H$_2$O
MOSC: Si$_8$(CH$_3$)$_8$ + 22 O$_2$ → 8 SiO$_2$ + 8 CO$_2$ + 12 H$_2$O
SOSC: Si$_8$(SiH$_3$)$_8$ + 22 O$_2$ → 16 SiO$_2$ + 12 H$_2$O
TBOSC: Si$_8$(C(CH$_3$)$_3$)$_8$ + 58 O$_2$ → 8 SiO$_2$ + 32 CO$_2$ + 36 H$_2$O

### TABLE II

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$R^b$</th>
<th>$E$ (RHF)$^c$</th>
<th>$E$ (MP2)$^c$</th>
<th>ZPE$^d$</th>
<th>$\Delta H_f$(298)$^e$</th>
<th>$\Delta H_f$(0)$^e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_8$H$_8$</td>
<td>O$_h$</td>
<td>1.5590</td>
<td>-307.39391</td>
<td>-308.41377</td>
<td>90.86</td>
<td>149.1</td>
</tr>
<tr>
<td>Si$_8$H$_8$</td>
<td>O$_h$</td>
<td>2.4018</td>
<td>-2315.94762</td>
<td>-2316.61099</td>
<td>51.04</td>
<td>138.2</td>
</tr>
<tr>
<td>Si$_8$(CH$_3$)$_8$</td>
<td>O$_h$</td>
<td>2.4097</td>
<td>-2628.29080</td>
<td>-2630.02689</td>
<td>206.64</td>
<td>20.6</td>
</tr>
<tr>
<td>Si$_8$(SiH$_3$)$_8$</td>
<td>O$_h$</td>
<td>2.4076</td>
<td>-4636.64197</td>
<td>-4637.99567</td>
<td>145.02</td>
<td>160.4</td>
</tr>
<tr>
<td>Si$_8$H$_7$(t-butyl)</td>
<td>C$_{3v}$</td>
<td>2.4012</td>
<td>-2472.08730</td>
<td>-2473.29089</td>
<td>127.57</td>
<td>104.1</td>
</tr>
<tr>
<td>Si$_8$H$_7$(t-butyl)$_2$</td>
<td>D$_{3d}$</td>
<td>2.4054</td>
<td>-2628.22685</td>
<td>-2629.97060</td>
<td>204.09</td>
<td>70.2</td>
</tr>
<tr>
<td>Si$_8$(t-butyl)</td>
<td>O$_h$</td>
<td>2.4402</td>
<td>-3565.01197</td>
<td>-3566.01197</td>
<td>-134</td>
<td>-87</td>
</tr>
</tbody>
</table>

$^a$ RHF/6-31G(d) geometry is used throughout.
$^b$ RHF bond distances in the cubes. An average value is given for the two low symmetry cubes.
$^c$ In hartree units.
$^d$ Zero-point energy, in kcal/mol, at 0°, from unscaled RHF frequencies.
$^e$ In kcal/mol, using frequencies scaled by 0.89.
$^f$ See text for group additivity approximation used.
Using experimental heats of formation for CO₂, H₂O, and SiO₂ in both gaseous and solid states gives the results in Table III. The data are compared to a ramjet fuel RJ-4 [17b] and liquid and solid hydrogen. The traditional chemistry units kcal/mol must be converted into more pragmatic units such as cal/g or cal/cc of fuel in order to assess a fuel’s energy content. For rocket applications, one must carry liquid O₂ (LOX), and the final two columns of Table III include the weight and volume of oxidant. Depending on the extent to which OSC forms condensed-phase product in the engine nozzle (some mixture of gaseous and liquid SiO₂ is to be expected), the performance of OSC (−1782 to −3794 cal/g) approximates that for LH₂, −3208. LH₂, however, is very bulky due to its small density, and while only TBOSC has an experimental density available, it is clear that all four Si cubes greatly exceed LH₂’s performance of −1360 cal/cc. Addition of carbon content to the cubes (MOSC, TBOSC) tends to degrade performance if, as hypothesized, condensed-phase SiO₂ is formed. From a practical viewpoint (SiH bonds readily oxidize, thus limiting handling characteristics), the experimentally unknown MOSC is the best candidate, as it has the smallest organic group, maximizing Si content.

A simulation program [69] has been used to determine the optimal percentage of four possible additives: OSC, SOSC, MOSC, and TBOSC, based on the calculated specific impulse, Iₛₚ. The Iₛₚ is an overall figure of merit for a propellant’s performance (usually reported in units of seconds). Iₛₚ is proportional to the square root of the energy released, inversely proportional to the square root of the average molecular weight of exhaust, and depends somewhat on the engine and nozzle geometry. The inputs to this program are the molecular weights and chemical formulas of the species, and their heats of formation at 0 K (close to the initial temperature of the liquid propellants). The program determines that the optimal percentage of either MOSC or TBOSC (both carbon containing species) is zero. MOSC is marginal at best, a 0.1% mole fraction of SOSC additive gives a 2-s improvement over the specific impulse (Iₛₚ) of the pure LH₂/LOX engine. The accepted value for the optimum sea-level Iₛₚ for a system using LOX/LH₂ as the propellant, with a chamber pressure of 1000 PSI, and nozzle area expansion ratio of 40 is 389 s [70]. The parent Si₉H₆ (OSC) gives the best simulation result, an improvement in this Iₛₚ of 6 s. Generally speaking, additives should produce an improvement of 20 s over LH₂/LOX to be considered worthy of experimental trials.

Although its overall Iₛₚ result is disappointing, we present here further details from the OSC sim-
ulation. This gives the optimal fuel mole fraction percentage of LH2/OSC/LOX as 87.8/1.2/11.0 (weight percentage is 21.76/35.00/43.24). For comparison, the pure LH2/LOX engine operates at a mole percentage 80/20, to produce the optimal amount of hot H2 molecules in the exhaust, as light species in the exhaust maximize Tp. In other words, the fuel mixture is intended to produce maximum thrust, rather than stoichiometric combustion. The OSC simulation predicts an engine chamber temperature of 2650 K and yields the following products (gases unless otherwise indicated):

<table>
<thead>
<tr>
<th></th>
<th>H2</th>
<th>SiO2()</th>
<th>H2O</th>
<th>SiO</th>
<th>H</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt %</td>
<td>86.31</td>
<td>8.05</td>
<td>3.83</td>
<td>1.49</td>
<td>0.32</td>
</tr>
<tr>
<td>wt %</td>
<td>21.96</td>
<td>61.00</td>
<td>8.72</td>
<td>8.27</td>
<td>0.04</td>
</tr>
</tbody>
</table>

Traces of OH, Si, SiH, and gaseous SiO2 (wt % 0.004) are the only other exhaust species predicted. The overall process thus amounts to combustion of OSC heating an exhaust consisting of a nearly unchanged number of molecules of H2. LH2’s presence is crucial, as simulation of pure OSC/LOX predicts a higher operating temperature and therefore a greatly increased fraction of gaseous SiO2. In addition to serving as a working fluid, the LH2 reduces the average molecular weight of the exhaust.

Conclusions

Results for the several types of cubic species presented here may be summarized as follows:

1. C4O4’s existence is doubtful since its dissociation barrier was found to be much smaller than its lowest vibrational frequency.
2. N8’s MP2/6-31G(d) barrier to dissociation was found to be about +15 kcal/mol, in reasonable agreement with Evangelisti and co-workers’ [44] earlier CASPT2 value of +22. While this molecule might be observable spectroscopically, this small barrier makes the prospect of synthesizing bulk quantities for use as a propellant seem dim.
3. Cubes containing only Si and H lead to modest improvements in LH2/LOX specific impulse. The handling stability imparted by carbon-containing substituents unfortunately leads to poorer performance in the rocket simulations.

4. Two other high-energy molecules encountered during this research are the four-membered ring C4O2 and the eight-membered ring octaazacyclotetraene. Both have small dissociation activation energies, +0.01 and +1.5 kcal/mol, respectively, and are therefore unlikely HEDM species.

Speculation for further research that might arise from the results presented above includes the following:

1. Since its decomposition exothermicity energy is not nearly as high as C4O4 and N8, the Hammond postulate implies the decomposition barrier for H4C4N4 may be more substantial than that found for the first two, and a computational study of its decomposition mechanism would be worthwhile.
2. The three lowest energy isomers of N8 do not appear in the cube’s decomposition mechanism, and since at least one of these now seems experimentally accessible, their decomposition pathways should be revisited.
3. The notion of combustion of Si compounds seems validated, but any Si-based fuel must have a higher heat of formation than the Si cubes, which are actually rather stable, in complete contrast to the N8 or C4O4 cubes.

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References

This is a one-dimensional adiabatic isentropic equilibrium program with full two-variable grid search capabilities.