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Cubic C₈: An observable allotrope of carbon?

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Abstract: Ab initio and density-functional theory calculations have been used to investigate the structure, electronic properties, spectra and reactivity of cubic C₈, which is predicted to be aromatic by Hirsch's rule. Although highly strained and with a small amount of diradical character, the carbon cube represents a surprisingly deep minimum and should therefore be observable as an isolated molecule. It is, however, very reactive, both with itself and triplet oxygen. Calculated infrared, Raman and UV/vis spectra are provided to aid identification of cubic C₈ should it be synthesised.

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Introduction

Hirsch's rule ^[1,2,3,4,5,6] states that molecules with $2(N+1)^2$ valence electrons can display spherical aromaticity. One candidate that fulfills this criterion is cubic C₈, which has 32 valence electrons ($N = 3$). Cubic C₈-moieties have been suggested to form the fundamental carbon unit in a high-pressure *bcc*-carbon nanocrystalline phase^[7,8,9,10] sometimes known as "superdense carbon", first isolated by Strel'nitskii et al.^[11] and investigated in series of theoretical studies.^[12,13,14] Cubic C₈ and its isomers have been the subject of several theoretical studies.^[15,16,17,18,19,20,21,22,23,24,25,26,27,28,29] The very early MINDO/3 results of Minyaev^[15] do not agree with later DFT, MP2 or coupled-cluster calculations, neither in the geometries of the minima, nor in the relative stabilities of singlet and triplet states. Initial MP2 calculations by Jensen^[17] agreed quite well with reference coupled-cluster calculations but gave a distorted C₈-cage for the cubic isomer. Nyrönen and Suantomo^[19] found that the *O_h* C₈-isomer is a minimum at the B3LYP and MP2 levels of theory, both with the 6-31G(d) basis set, but a transition state at HF/6-31G(d). Jones^[20] found its lowest vibrational frequency to be 720 cm⁻¹ using the BP86 functional with a TZVP basis set. Several of these studies have been concerned with analogies between C₈ and B₄N₄^[17,21] and others with the aromaticity of 3D clusters.^[22,27] Most estimates of the relative energy of cubic C₈ use the puckered ring structure found by Ragavachari and Binkley^[30] as the reference.

We now report a high-level calculational characterization of cubic C₈ designed to test its viability as an isolated molecule, its relative stability and its electronic and spectroscopic properties. Our aim is to provide as complete a characterization as possible of the yet hypothetical molecule to aid identification in future experimental studies.

Results and Discussion

Structure and Normal Vibrations

The cubic (*O_h*) structure of C₈ proves to be a surprisingly deep minimum (*vide infra*). The C–C bond length is quite independent of the calculational formalism used (but not of the basis set) and varies between 1.45 and 1.53 Å (see the Supporting Information). The "best" (RCCSD(t)/aug-cc-pVTZ) value of 1.487 Å indicates some multiple C–C bond character despite the extremely strained coordination of each individual carbon atom. This shortening is more pronounced than that found for "banana" bonds, such

as in cyclopropane,^[31] although the cage strain also contributes to the bond-shortening effect. The optimized bond length is unusually sensitive to the basis set and generally tends to be longer at a given calculational level with double- ξ than with triple- ξ basis sets.

The most facile normal vibration calculated for the O_h structure is not degenerate (A_{2u} , shown schematically in Figure 1) at most levels of theory. However, not all methods agree on the nature of the lowest mode, as described below.

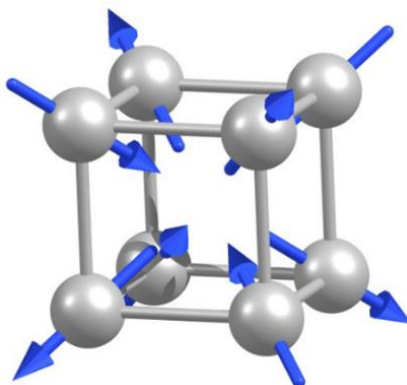


Figure 1. The lowest-frequency vibration (A_{2u}) calculated at most levels of theory for cubic C_8 (O_h).

Electronic Structure

The CASSCF(14x14)/ANO-RCC-VDZP//CCSD(T)/aug-cc-pVDZ-calculated energy orbital energies of cubic C_8 are shown in Figure 2.

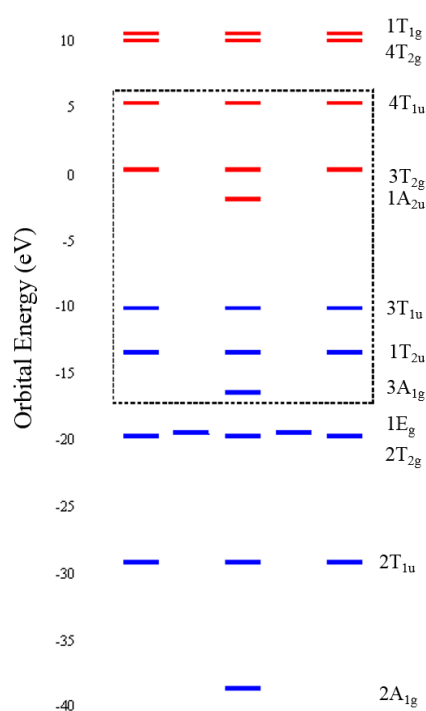


Figure 2. CASSCF(14×14)/ANO-RCC-VDZP valence energy-level diagram at the CCSD(T)/aug-cc-pVDZ-optimized geometry. The blue energy levels indicate occupied orbitals and the red ones virtual. The core-orbital configuration is $1A_{1g}^2 1T_{1u}^6 1T_{2g}^6 1A_{2u}^2$. The dashed box indicates the active space for the CAS-SCF calculations. Full details are given in the Supporting Information.

The energy-level pattern is consistent with the expectation that the 32-electron system should be aromatic.^[1-6]

The HOMO-2 ($3A_{1g}$) is the familiar A_{1g} orbital described by Hirsch for small inorganic clusters. It is delocalized over the entire cage, as shown in Figure 3.

The results of CASSCF calculations depend strongly on the type of orbitals used (canonical and quasi-canonical) and on the basis set but there is general agreement that the HOMOs in the $^1A_{1g}$ ground state are triply degenerate ($3T_{1u}$) and the LUMO is not degenerate ($1A_{2u}$). The formally unoccupied orbitals contain 0.8 electrons in the CASSCF calculations, suggesting that cubic C_8 is essentially a singlet biradical. Restricted Hartree-Fock, but not restricted DFT calculations exhibit RHF → UHF instability.

However, the CASSCF wavefunction gives a far larger multi-reference character than all other methods investigated. The coefficient of the Hartree-Fock configuration in the CISD/cc-pVTZ wavefunction is 0.898 but decreases to 0.808 if the smaller cc-pVDZ basis set is used. These contributions are essentially independent of whether the basis sets are augmented with diffuse functions. Using UHF broken symmetry reference wavefunctions decreases the coefficient of the Hartree-Fock wavefunction in the ground state to approximately 0.6 for both basis sets, so that post-Hartree-Fock calculations with restricted reference wavefunctions must be considered most reliable. In support of this assumption, the T1 diagnostic^[32] in CCSD calculations of cubic C_8 lies in the range 0.0112 to 0.0126 with basis sets that range from 6-31G(d) to aug-cc-pVTZ. The accepted value at which a single-reference coupled-cluster calculation is no longer reliable is 0.02. Thus, this diagnostic suggests clearly that coupled-cluster calculations with an RHF reference wavefunction should be reliable.

We can conclude from our extensive calculations (described in the Supporting Information) that CASSCF and/or small basis sets overemphasize the multi-reference character of cubic C_8 and that high-level post-SCF calculations with adequate basis sets should give reliable results.

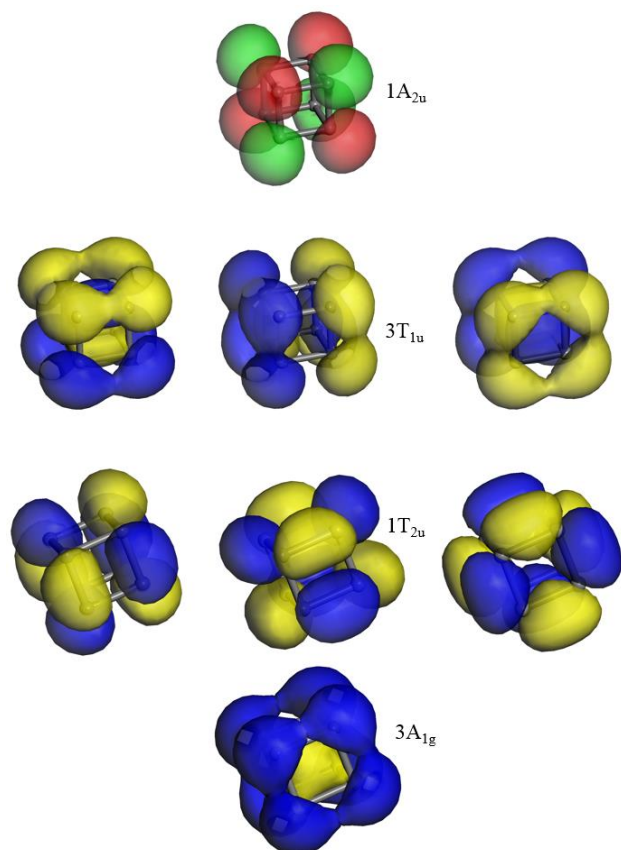


Figure 3. The highest seven occupied orbitals and the LUMO of cubic C_8 .

Calculated total energies using restricted and unrestricted reference wavefunctions are shown in the Supporting Information. As RCCSD(T) and UCCSD(T) calculations agree within approximately 10 kcal mol^{-1} in energy and give very similar vibrational frequencies, the restricted results will be discussed below for post-SCF formalisms.^[33] The Møller-Plesset calculations with unrestricted reference wavefunctions diverge strongly from all others. Restricted Hartree-Fock wavefunctions for the lower symmetry structures depicted in Scheme 2 are generally stable.

The CASPT2(14×14)/ANO-RCC-VDZP calculated vertical Born-Oppenheimer singlet-triplet energy difference for cubic C_8 is only 1.3 eV, in good agreement with 1.4 eV found at CCSD(T)/aug-cc-pVTZ and in strong contrast to the RHF/aug-cc-pVTZ HOMO-LUMO gap of 8.67 eV. Note that the triplet state is Jahn-Teller distorted. Adiabatic excitation to the D_{2h} -symmetrical triplet minimum requires 0.82 eV (0.77 eV at CCSD(T)/aug-cc-pVDZ).

The best calculated adiabatic electron affinity of cubic C_8 is 2.99 eV (CCSD(T)/aug-cc-pVDZ, 2.77 eV at CAS(14×14)PT2/ANO-RCC-VDZP). This is higher than the experimental value for C_{60} (2.689 eV^[34]) and is quite remarkable for a molecule as



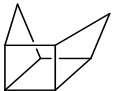

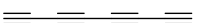
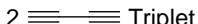
small as C_8 . The radical anion has O_h symmetry, as expected from the orbital diagram shown in Figure 1, with longer bonds (1.533 Å) than the neutral species.



The corresponding radical cation is a Jahn-Teller species with at least one minimum with D_{4h} symmetry. The optimized geometry shows four short (1.436 Å) and eight long (1.498 Å) bonds. The calculated vertical and adiabatic ionization potentials are close to 9.9 eV (both CCSD(T)/aug-cc-pVDZ and CASPT2(14×14)/ANO-RCC-VDZP).

Stability

A summary of the calculated thermodynamics of cubic C_8 is shown in Table 1. Cubic C_8 is found to be approximately 50 kcal mol⁻¹ per carbon atom more strained than C_{60} -fullerene and to lie approximately 100 kcal mol⁻¹ higher in energy than both the monocyclic and linear C_8 -isomers. Heats of formation per atom for graphite, diamond, C_{60} , cubic C_8 and gaseous carbon are 0.0, 1.9, 14.7, 61.6, and 87.6 kcal mol⁻¹, respectively. However, cubic C_8 is found to be more stable than all the polycyclic isomers investigated and stable towards dissociation into two singlet cyclic C_4 molecules.

Table 1. Summary of the RCCSD(T)/aug-cc-pvdz calculated energetics of cubic C_8 .

Quantity/Reaction	Energy (kcal mol ⁻¹)
Heat of Formation ($\Delta H_f^\circ(298)$)	492.4
Heat of Formation per carbon atom	61.6
Energies relative to cubic C_8	
	-98.3
	+17.6
	+40.0
	+9.4
	-92.6
2  Triplet	+41.3

2  Singlet	+60.4
2  Singlet	+39.9
4 C2	+308.1
<hr/>	
7.5 C ₈ → C ₆₀ (energy per carbon atom)	-51.4

Vibrational Spectroscopy

The calculated (RCCSD(T)/aug-cc-pVDZ) infrared spectrum exhibits just one peak at 1064 cm⁻¹ (intensity 17.33 km mol⁻¹, corresponding to a triply degenerate T_{1u} vibration). Four vibrations are calculated to be Raman-active. The spectra are summarized in Table 2.

Table 2. Summary of the vibrational spectra of cubic C₈ calculated within the harmonic approximation.

Frequency [cm ⁻¹]			Vibration	IR intensity ^[a]	Raman intensity ^[b]
<i>B3LYP</i>					
<i>RCCSD(T)</i>					
<i>cc-pVDZ</i>	<i>cc-pVDZ</i>	<i>aug-cc-pVDZ</i>			
247	364	245	A_{2u}	0	0
668	650	621	E_u	0	0
756	668	646	T_{2g}	0	50.6 (30.5)
849	870	842	T_{2u}	0	0
1054	1024	996	T_{2g}	0	4.8 (2.9)
1131	1086	1064	T_{1u}	17.3 (32.5) ^[c]	0
1230	1172	1148	E_g	0	31.0 (18.7)
1228	1176	1159	A_{1g}	0	67.0 (40.4)

^[a] Calculated within the harmonic approximation at CCSD(T)/cc-pVDZ [km mol⁻¹]

^[b] Calculated within the harmonic approximation at B3LYP/cc-pVDZ [$\text{\AA}^4 \text{amu}^{-1}$] ($[10^{-13} \text{m}^4 \cdot \text{kg}^{-1}]$ in parentheses)

^[c] B3LYP value.

The RCCSD(T)-calculated frequency of the lowest vibration mode depends strongly on the basis set. For instance, the calculated frequency for this vibration changes from 364 cm⁻¹ using the cc-pVDZ basis set to 246 cm⁻¹ on the addition of diffuse functions to give aug-cc-pVDZ. The calculated harmonic frequencies for cubic C₈ are very sensitive to both basis set and calculational level. Two general trends are discernible. Firstly that the lowest three vibrations are almost always A_{2u} , E_u and T_{2g} , although the order varies. The A_{2u} is most sensitive to open-shell and basis-set effects, so that it sometimes becomes imaginary, especially with RHF-based methods and small basis

sets. The consensus order of the three lowest vibrations is $A_{2u} < E_u < T_{2g}$. Secondly, the results of post-SCF calculations using restricted and unrestricted (broken symmetry) reference HF wavefunctions have essentially converged (both energies and frequencies) at the CCSD(T) level with augmented basis sets. The lowest three frequencies calculated at different levels are given in Table 3.

Car-Parrinello Molecular-Dynamics (CPMD) simulations of gas phase C_8 at 1000 K for 22 ps showed that the C_8 cube remains perfectly stable; no structural rearrangements were observed. The infrared spectrum calculated from the dipole-dipole correlation function of a simulation at 300 K, which includes anharmonic contributions, is shown in Figure 4. It is dominated by a single intense peak at 1062 cm^{-1} (the T_{1u} mode) with some weak contributions at 620 , $1350/1380$ and 1640 cm^{-1} .

Table 3. The calculated frequencies and symmetries of the three lowest normal vibrations for cubic C_8 at different levels of calculation. Imaginary frequencies and the corresponding irreducible representations are underlined.

Method/basis set	Three Lowest Frequencies (cm^{-1})			Symmetry
RHF/6-31G(d)	<u>-897.3</u>	696.0	825.0	<u>A_{2u}</u> , E_u , T_{2g}
UHF/6-31G(d)	754.9	800.1	1022.1	T_{2g} , E_u , A_{2u}
RMP2/6-31G(d)	135.4	666.4	755.9	A_{2u} , E_u , T_{2g}
UMP2/6-31G(d)	278.3	650.0	655.7	A_{2u} , E_u , T_{2g}
RMP2/cc-pVDZ	601.4	677.8	1025.3	T_{2g} , E_u , T_{2g}
UMP2/cc-pVDZ	392.0	640.6	643.8	A_{2u} , T_{2g} , E_u
RMP2/aug-cc-pVDZ	577.8	652.5	997.8	T_{2g} , E_u , T_{2g}
UMP2/aug-cc-pVDZ	206.3	612.1	619.8	A_{2u} , E_u , T_{2g}
RMP3/aug-cc-pVDZ	663.4	775.5	779.8	E_u , A_{2u} , T_{2g}
UMP3/aug-cc-pVDZ	634.9	657.9	887.5	A_{2u} , E_u , T_{2g}
B3LYP/6-31G(d)	135.5	666.4	755.9	A_{2u} , E_u , T_{2g}
B3LYP/6-31G(2df,p)	172.3	664.1	749.6	A_{2u} , E_u , T_{2g}
B3LYP/cc-pVDZ	246.9	668.0	756.8	A_{2u} , E_u , T_{2g}
B3LYP/aug-cc-pVDZ	247.9	666.2	754.7	A_{2u} , E_u , T_{2g}
B3LYP/aug-cc-pVTZ	258.9	677.6	766.4	A_{2u} , E_u , T_{2g}
B3LYP/aug-cc-pVQZ	269.9	679.0	763.4	A_{2u} , E_u , T_{2g}
B3LYP/CBSB7	214.5	673.4	761.4	A_{2u} , E_u , T_{2g}
RCCSD/aug-cc-pVDZ	<u>-204.1</u>	641.5	719.5	<u>A_{2u}</u> , E_u , T_{2g}
UCCSD/aug-cc-pVDZ	276.0	638.3	673.2	A_{2u} , E_u , T_{2g}
RCCSD/cc-pVTZ	<u>-69.5</u>	683.0	765.5	<u>A_{2u}</u> , E_u , T_{2g}
RCCSD(T)/cc-pVDZ	362.6	647.6	662.7	A_{2u} , E_u , T_{2g}
UCCSD(T)/cc-pVDZ	364.2	650.3	667.4	A_{2u} , E_u , T_{2g}
RCCSD(T)/aug-cc-pVDZ	245.6	620.7	646.0	A_{2u} , E_u , T_{2g}
UCCSD(T)/aug-cc-pVDZ	247.2	621.4	650.1	A_{2u} , E_u , T_{2g}

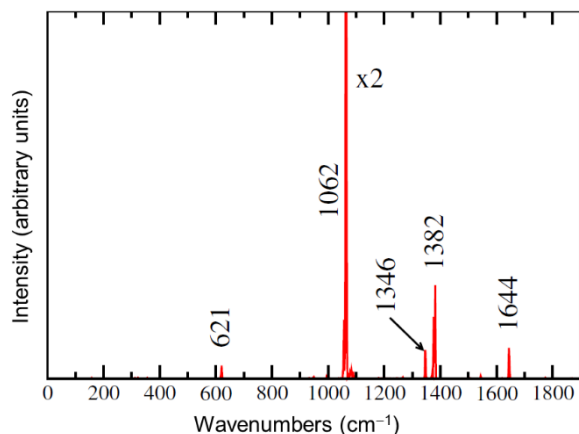


Figure 4. Calculated infrared spectrum for cubic C_8 from a CPMD simulation. For details, please see the Supporting Information.

UV/vis Spectroscopy

UV-spectra were calculated with EOM-CCSD and SAC-CI using the aug-cc-pVTZ basis set. The results are shown in Figure 5. Details of the calculations are given in the Supporting Information.

The lowest-energy allowed transition into the $1A_{2u}$ -LUMO of cubic C_8 would be from the $3A_{1g}$ HOMO-2, and therefore of relatively high energy. Different types of excited-state calculations give quite consistent results. The single intensive band in the calculated spectrum corresponds to a mixture of $1T_{2u} \rightarrow 3T_{2g}$ (HOMO-1 \rightarrow LUMO+1) and $3T_{1u} \rightarrow 3T_{2g}$ (HOMO \rightarrow LUMO+1) transitions. Figure 5 shows that both techniques predict a single absorption at 234 and 256 nm for EOM-CCSD and SAC-CI, respectively, at our “best” bond length of 1.487 Å.

However, even a small change in the bond length can shift the absorption maxima significantly. The dashed lines in Figure 5 show the calculated spectra at a bond length of 1.447 Å. The 0.04 Å shortening of the C-C bond shifts the absorption maximum by approximately 20 nm to shorter wavelengths in both cases. This extreme sensitivity to the C-C bond length should result in vibrationally broadened absorption peaks.

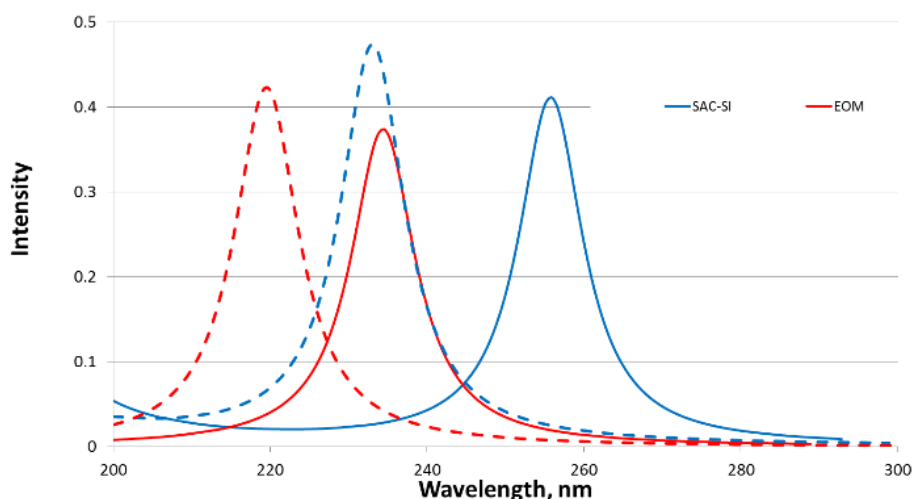


Figure 5. SAC-CI (blue) and EOM-CCSD (red) calculated UV/vis spectra for cubic C_8 . The aug-cc-pVTZ basis set was used. The full lines give the results calculated at a C-C bond length of 1.487 Å, the dashed lines at 1.447 Å. Further details of the calculations and of the representation of the spectra are given in the Supporting Information.

Nuclear Magnetic Resonance

Gauge-Independent Atomic Orbital (GIAO) calculations of the ^{13}C chemical shift for cubic C_8 at the B3LYP/aug-cc-pVDZ and PW91PW91/IGLO-III levels of density-functional theory predict chemical shifts of approximately 280 ppm relative to tetramethyl silane (See Supporting Information). This value is extreme, but not unexpected. It is, however, very unlikely to be measurable. Nucleus-Independent Chemical Shift (NICS)^[35] values are also reported in the Supporting Information but are not very informative for such a three-dimensional structure.

Crystalline phase

Condensed phases of C_8 molecules were studied by periodic plane-wave DFT calculations (for details, please see the Supporting Information). Three different crystalline arrangements of C_8 molecules were considered: face-to-face, edge-to-edge and corner-to-corner stacking. This results in ideal simple-cubic (sc), face-centered-cubic (fcc) and body-centered-cubic (bcc) lattices, respectively, with one C_8 molecule in the primitive unit cell. The effects of varying the lattice constant for these three cases are shown in Figure 6.

In the face-to-face and edge-to-edge stacking, the C_8 molecules only interact by weak dispersion forces. A double minimum is observed for both structures in the PBE+D potential-energy profiles. This is probably not an artefact of the empirical Grimme D2

dispersion correction to the PBE functional. A double minimum is also present in the local-density approximation (LDA). In this case, dispersion forces are not included explicitly; nevertheless LDA is used in studies of graphite since it yields reasonable results for the graphite interlayer spacing due to fortuitous error cancellation.^[36,37]

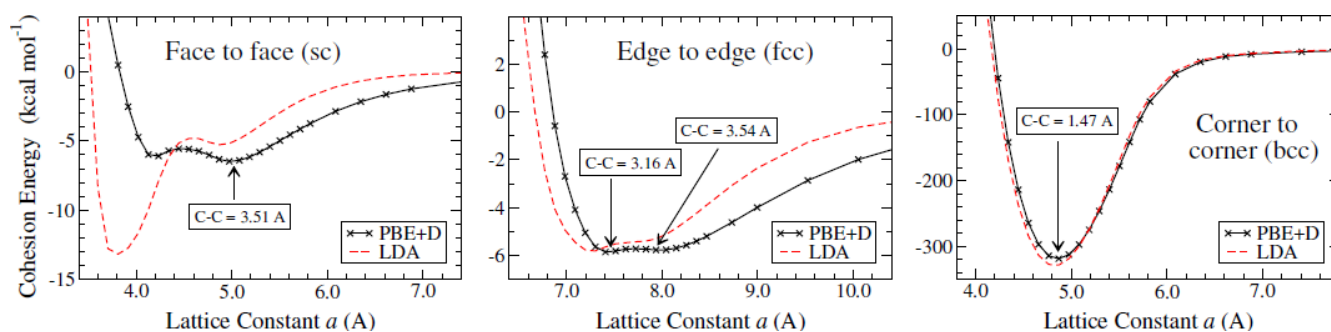


Figure 6. Potential-energy profiles obtained for the cubic crystalline phases of C_8 . For details, see the text and Supporting Information.

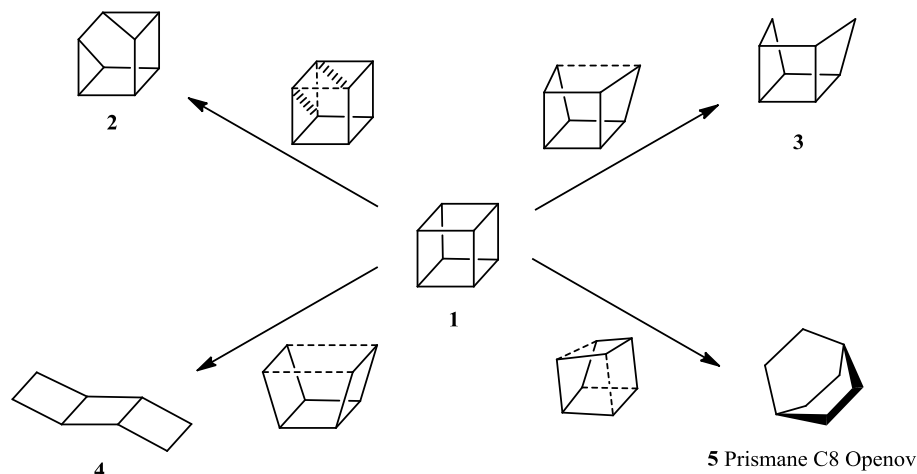
At the outer minimum, the C-C distance between the C_8 cubes of 3.54 and 3.55 Å is only slightly larger than the interlayer distance of 3.37 Å in graphite.

For the cohesion energy of the C_8 molecules in the sc and fcc lattices, we obtain 5.9 and 6.5 kcal mol⁻¹, respectively. This amounts to 31 and 35 meV per carbon atom, which is about the exfoliation energy in graphite (experimental values vary between 35 and 52 meV/atom^[36]). At the inner minimum, the C-C distance between the C_8 cubes is about 0.4 Å shorter than at the outer one, but the cohesion energy is approximately the same within the accuracy of the calculations. Some small rehybridization of the carbon *sp*-orbitals can be seen, which leads to an elongation of the C-C bond within the C_8 molecules by about 0.03 Å.

In the corner-to-corner stacking, on the other hand, strong covalent bonds between the cubes are formed. The C-C bond length between the cubes (1.47 Å) becomes shorter than that within the cubes, which is considerably lengthened (1.58 Å), and the cohesion energy increases to 318.7 kcal mol⁻¹. Although the C_8 condensation energy is quite high, the C_8 -bcc structure is still less stable than diamond by 15.6 kcal mol⁻¹ per carbon atom.

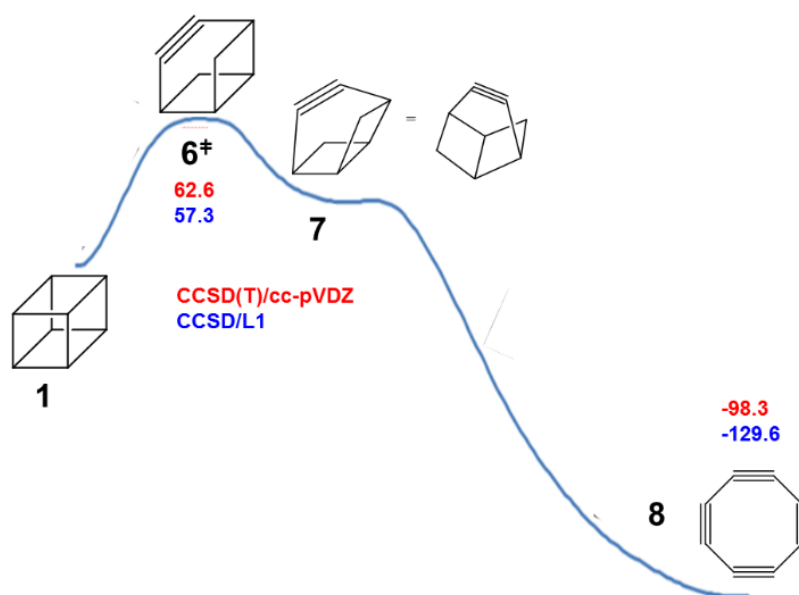
The C_8 -bcc structure is also higher in energy by 5.8 kcal mol⁻¹ than the sodalite structure with six atoms per unit cell proposed as an alternative structure for carbon with cubic symmetry.^[14]

Rearrangement reactions



Scheme 1. Possible rearrangement pathways for cubic C_8 .

The lowest-frequency vibrational mode described above is highly symmetrical and is unlikely to lead to a cage rearrangement because this would require three or more bonds to be broken concertedly. We therefore investigated possible rearrangement pathways that involve elongating one bond (**3**), two parallel bonds on one face of a cube (**4**), three bonds to form “prismane C_8 ” (**5**) and several more (e.g. **2**) by relaxed geometry scans followed by transition-state searches from the highest point at the CCSD/L1 level of theory.

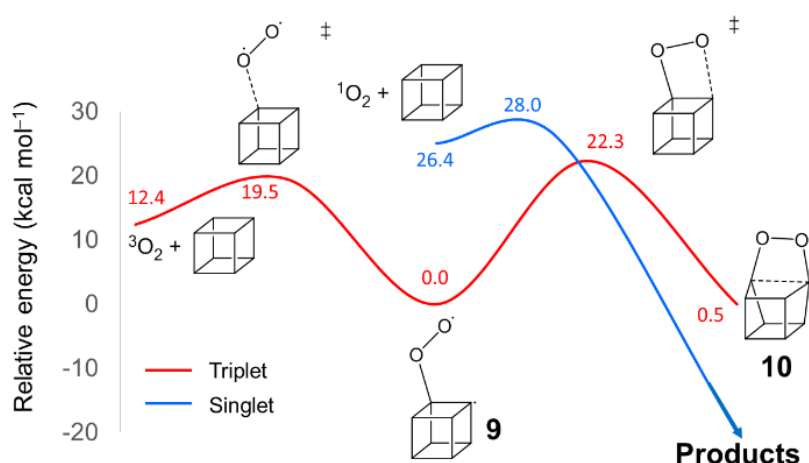


Scheme 2. Rearrangement pathway and energy of stationary points in kcal mol⁻¹ (CCSD(T)/cc-pVDZ).

The lowest rearrangement barrier found is 57.5 kcal mol⁻¹. The transition state **6**[‡] leads to the C₂-symmetrical structure **7**. Following the reaction path away from cubic C₈ by intrinsic reaction coordinate (IRC) calculations leads first through a very flat region in which an intermediate and a second transition state were found at CCSD/L1. The barrier for this second rearrangement was calculated to be just 0.35 kcal mol⁻¹. This intermediate does not exist at all levels of theory. The final product of rearrangement is the monocyclic C_{4h} symmetrical C₈-ring **8** mentioned above.

Oxidation by triplet O₂

The reaction of C₈ with ³O₂ is 13 kcal mol⁻¹ exothermic and has a barrier of only 7 kcal mol⁻¹ at B3LYP/6-311+G*. The product is triplet peroxide **9**, which can rearrange to the dioxetane **10** by breaking the propellane bond and then fragment further. The calculated barrier for this process is around 22 kcal mol⁻¹. Spin-crossing from the triplet to the singlet state can occur close to the transition state for this last reaction. ¹O₂ addition to the C₈ cube is indicated to be very facile with a barrier of only 1.6 kcal mol⁻¹. These results indicate that, although the C₈ cube sits in a surprisingly deep energy well on the rearrangement potential- energy hypersurface, it is extremely reactive and will polymerize or react with oxygen extremely easily.



Scheme 3. Oxidation process and energy of stationary points in kcal mol⁻¹ (B3LYP/6-311+G*).

Conclusions

The above studies suggest that cubic C₈ should be observable as an isolated molecule in the absence of oxygen. It is calculated to be highly strained but nonetheless a quite

deep local minimum with a rearrangement barrier of 57 kcal mol⁻¹. Its orbital energy-level diagram suggests aromaticity, as expected from Hirsch's rule, but CAS-SCF calculations suggest a small amount of singlet diradical character with a low (0.8 eV) adiabatic singlet-triplet gap. It has a high (~3 eV) electron affinity and an unexceptional (10 eV) ionization potential. We have presented calculated UV/vis and infrared spectra. Periodic DFT calculations suggest that cubic C₈ cannot exist in a molecular crystalline phase, but rather will polymerize to the bcc or sodalite carbon phases. CPMD calculations at 1,000 K confirm that isolated cubic C₈ molecules should not rearrange easily.

Efforts are underway in our laboratories to synthesize and characterize cubic C₈. We note in this context that a promising precursor, 1,2,4,7-tetraiodocubane, is known.^[38]

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