Assignment

Chemical and Physical properties of endohedrally doped nanodiamonds

Objective: The semiempirical electronic structure Parametric Method 3 (PM3) at the www.nanoHUB.org website is introduced to the student in this assignment. In particular, this semiempirical method is applied to study dopant semiconductor materials intercalated in two types of nanodiamond (**ND**) complexes: hydrogenated (**HNDs**) and dehydrogenated (**DHDs**). Selected dopants **M** [**M**=Be, Mg, Ca, Si, O, S] [will be compared. The chemical stabilities are elucidated in terms of (a) stabilization and complexion energies, (b) first ionization energies based on Koopmans' theorem and (c) examination of the electron charge density. The optical properties of the final geometries will also be quantitatively estimated using the semiempirical electronic method **C**NDO/**I**NDO (**C**omplete/**I**ntermediate Neglect of Differential Overlap) also at the www.nanoHUB.org website.

Introduction: Nanodiamonds are interesting due to their excellent mechanical, electronic and optical properties.[1-3] Often the content of impurities (*dopants*) is used to classify nanodiamonds, including hydrogenated and dehydrogenated nanodiamonds. These carbon nanostructures emerge as promising candidates for building blocks in nanoscience and nanotechnology. Envisioned applications include optoelectronics components, miniaturized mechanical devices (cantilevers), biological materials (imaging purposes) and as light-emitting semiconductors.[4] Typical nanodiamonds have 5000 atoms and are 3 nm in diameter. These are too large to be studied in this class, so instead we consider much smaller, but equivalent, structures that have less than 30 carbon atoms.

In this exercise, we will use electronic structure calculations to study hydrogenated and dehydrogenated nanodiamonds doped and compare our results with **HNDs** and **DHDs**. The structural and optical properties and the changes in these properties that arise as a result of chemical functionalization will be investigated. In order to assess the quality of our calculations it is common to contrast the results with other theoretical studies based on similar methods. Thus, we will consider structures of C_{29} and $C_{29}H_{24}$ doped with silicon, oxygen and sulfur ions whose geometries and energies have been previously studied.[5]

Stabilization characteristics of the systems will be calculated by considering the change in energy from the initial (E_0) and final (E_f) configurations or the "relaxation energy" (E_{relax}). A large relaxation energy indicates that the initial structure was very unstable, compared to the final, relaxed structure. The complexion energy (E_b) will be calculated by the difference in energy between the nanodiamond complexes, **HND** ($C_{20}H_{20}$@M) and **ND** (C_{20}@M) minus the undoped species ($C_{20}H_{20}$ or C_{20}) and **M** (M=O, for example) as depicted in **Scheme 1**.

Scheme 1

$$E_b = E_{C_{20}H_{20}M} - E_{C_{20}H_{20}} - E_M \quad \text{(a)}$$

$$E_b = E_{C_{20}M} - E_{C_{20}} - E_M \quad \text{(b)}$$

With these schematics in mind, we will elucidate the reactivities of the complexes and study which group is thermodynamically favored. The optical properties of the doped hydrated and dehydrogenated systems will also be investigated.

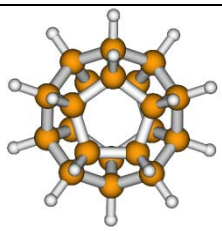
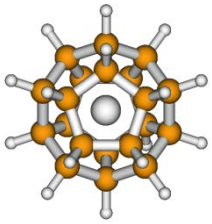
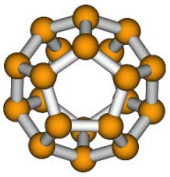
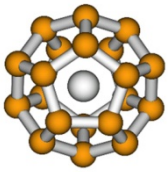
a.) Hydrogenated (**HNDs**) Complex					
	$C_{20}H_{20}$	**+**	**O**	**=**	**$C_{20}H_{20}$ @O**
b.) Dehydrogenated (**DHDs**) Complex					
	C_{20}	**+**	**O**	**=**	**C_{20} @O**

Chart 1. Structures of hydrogenated (a) and dehydrogenated (b) nanodiamond complexes. Carbon and hydrogen atoms are depicted as orange and white.

Procedure

For this particular exercise we will use the program QC-Lab accessible at the NanoHub (www.nanohub.org). The atomic coordinates of the complexes that we will study are available on the class blackboard site (https://courses.northwestern.edu) in the folder named *CA* (Computer Assignments), subfolder *Nanodiamonds*. Remember to save the final equilibrium coordinates as shown in (**Figure 8**). They will be used to determine the complexes optical properties using CNDO/INDO.

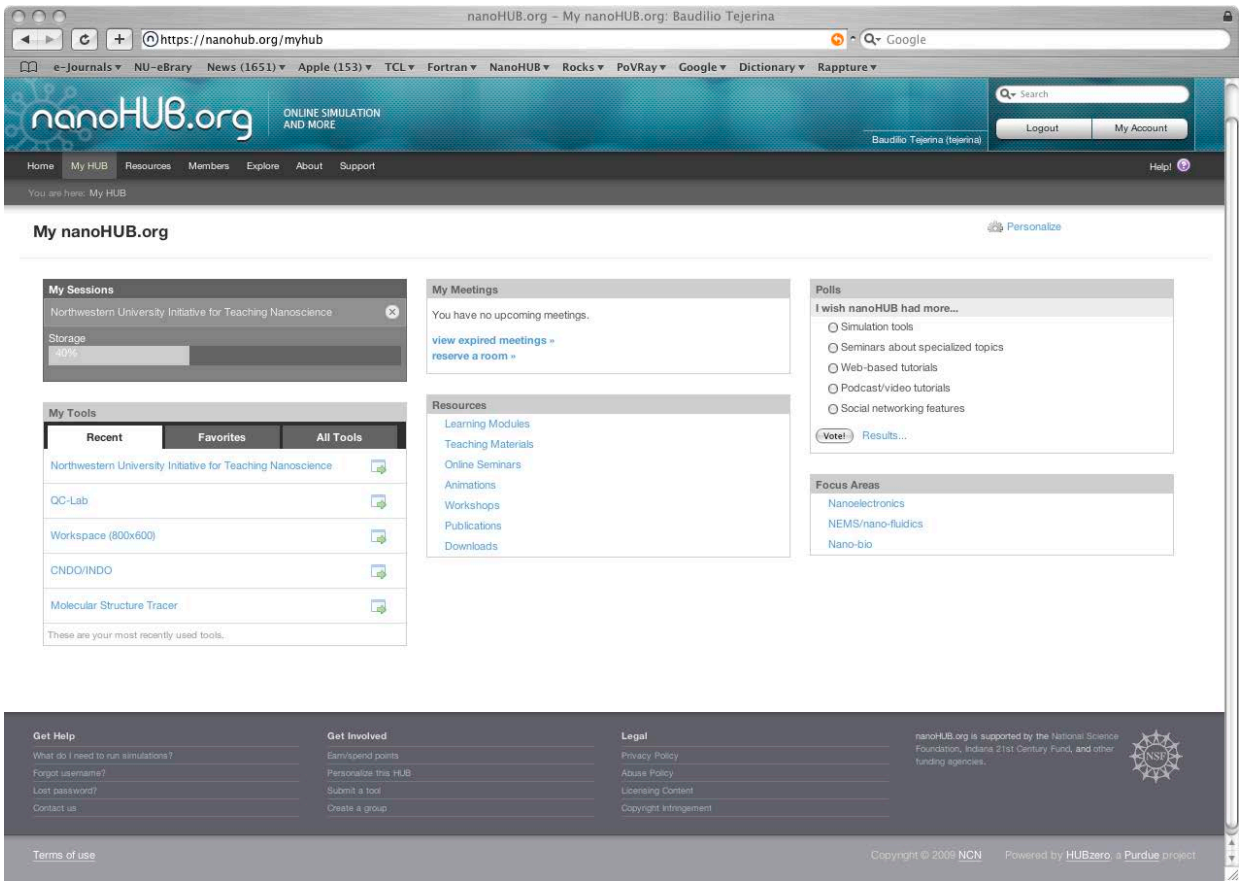


Figure 1: NanoHUB window showing *My HUB*. The programs are listed on the tab *All Tools* of the menu *My Tools*. Selecting the star next to the name of the desired tool, marks it as *Favorite* and a link to it is placed in the *Favorites* folder. The button launches the application.

1. The CNDO/INDO program interface.

After logging into the nanoHUB, select the option My HUB (see **Figure 1**). On the menu My Tools select the tab All Tools and locate the application QC-Lab. If you click on the star next to the name, the application will be marked as Favorite and placed in the Favorites folder.[6]

At this point you may start the application by clicking on the Launch Tool button. The window with the program's GUI will appear as illustrated in **Figure 2**. The Popout feature of the tool (located on the upper right hand side of the window) may be activated by clicking on the button; it will create a dedicated window to the tool on your local computer that facilitates the work.[7] If you wish to continue working on the current project from a different location or computer, you may close the browser and even shut down the computer; when you log back into the NanoHUB all be as you left it. Even if a job was running, it will continue running on the background or, most likely, it will have finished the calculation in the meantime. Do not however click on the Close button, unless you wish to terminate the current QC-Lab session for good.

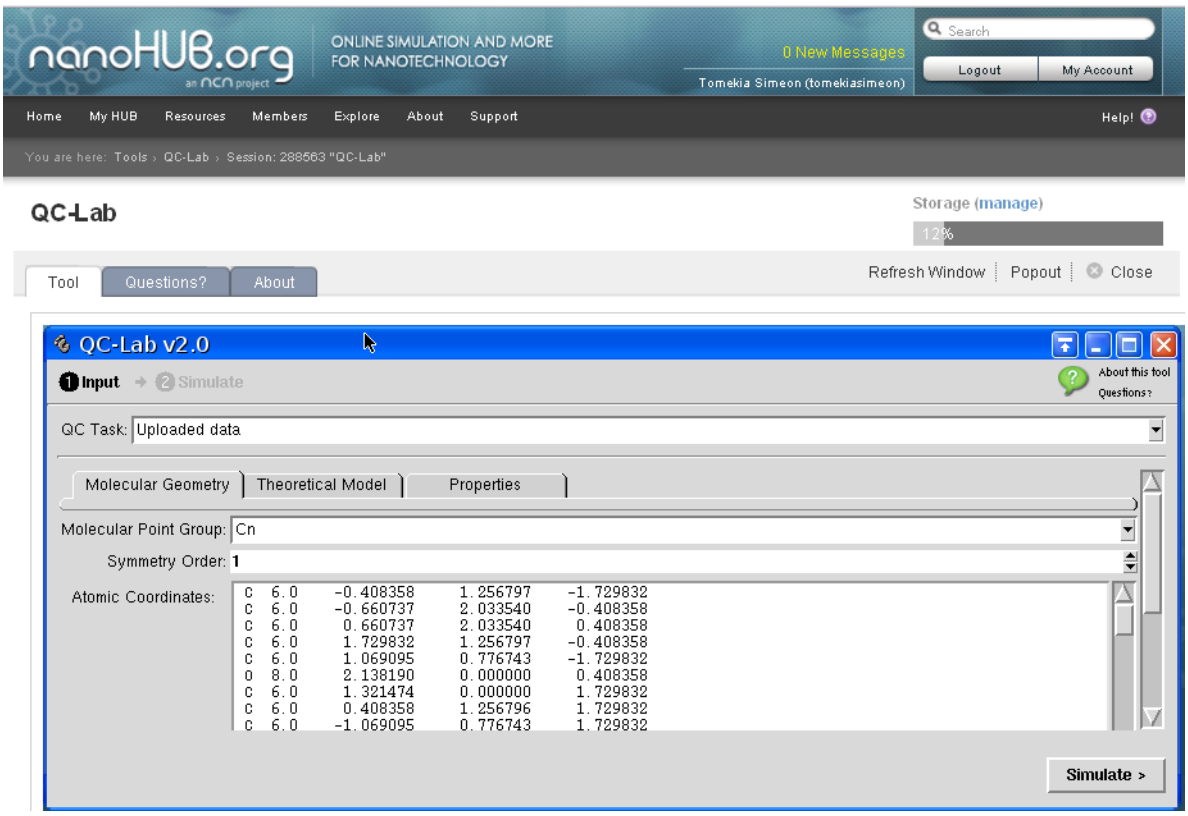


Figure 2: Initial window of the QC-Lab program interface on the web browser.

2. - Definition of the model.

2a. - Molecular geometry, electric charge, and spin multiplicity.

To illustrate the use of the QC-Lab program, let us consider the $C_{20}H_{20}$@O complex, a nanodiamond, with a spherical shape. The structure, extracted from the experimental, X-ray structure of the material,[8] is given in Cartesian coordinates in the file $C_{20}H_{20}$@O.xyz located on the directory "Assignments/Doped/NanoDiamonds" on Blackboard. Download the file to your computer and then upload the coordinates to the QC-Lab program: on the *QC-Lab Job* menu, located on main window of the tool (see **Figure 3**a), select *Upload…* and follow the instructions to pass the $C_{20}H_{20}$@O.xyz file to the QC-Lab program. During the computations, we will ignore the symmetry of all complexes.

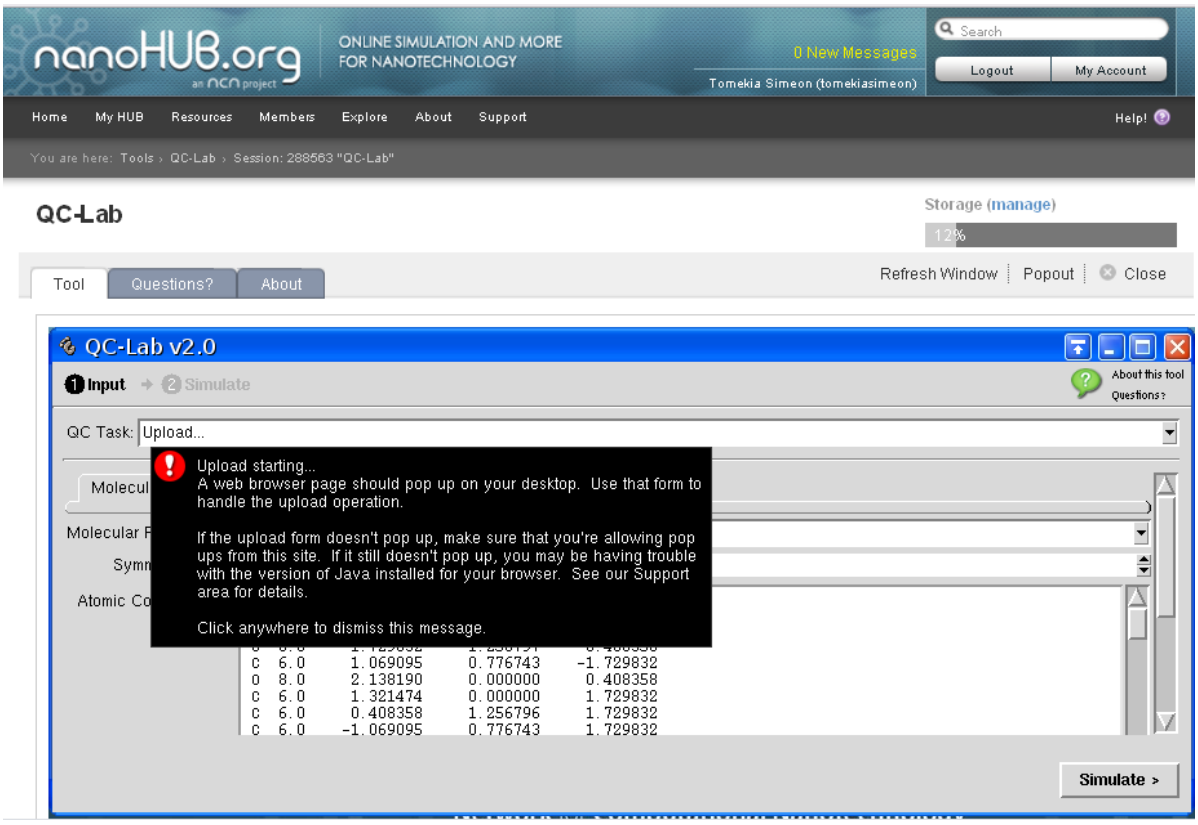


Figure 3a. Displaying the GUI for uploading atomic coordinates.

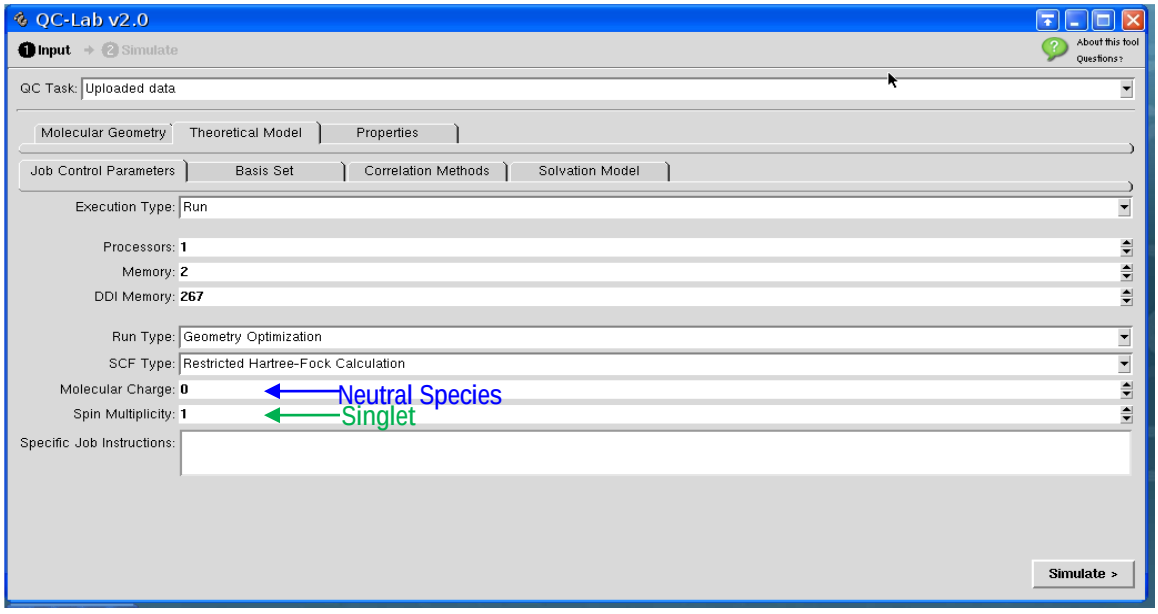


Figure 3b: Defining the chemical model: charge and spin multiplicity. Once the structure has been entered, the electric charge and the spin multiplicity of the system must be specified. Enter the appropriate values for the *Charge* and *Multiplicity*. In the case of the $C_{20}H_{20}$@O complex we will assume that the system is neutral (*Charge=0*) and all the electrons are paired with opposite spins.[9]

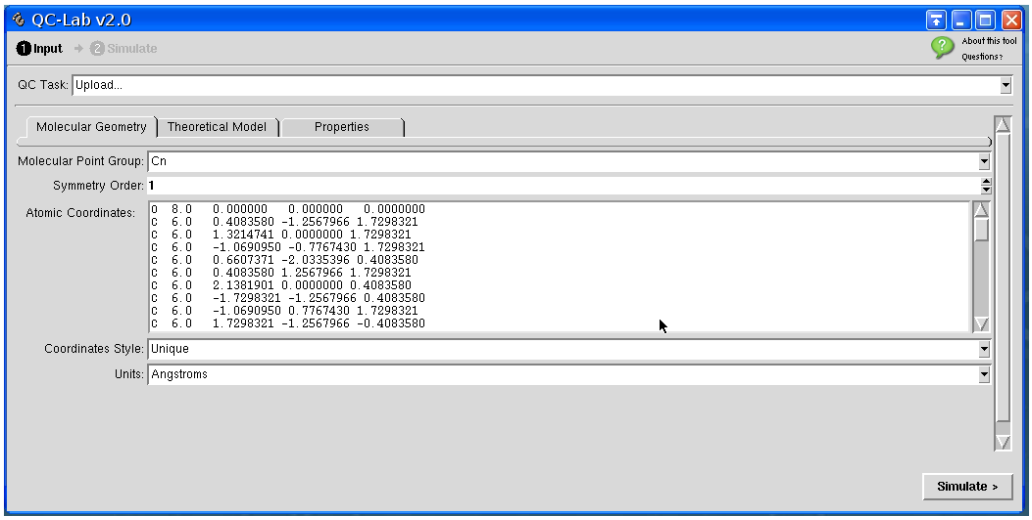


Figure 4a: Structural model for the neutral $C_{20}H_{20}$@Ca complex.

2. Simulation parameters.

Computational chemistry utilizes mathematical equations and/or algorithms to quantatively describe the physical and chemical phenomena in molecular systems. In computational chemistry, chemists use computer software packages to investigate the structures, reactions, and many physicochemical properties of molecules that are of experimental interest based on the Schrödinger equation (SE).[10]

In *ab initio* methods, fundamental properties of molecular systems are calculated from first principles by solving various approximations of the Schrödinger equation to describe their basic structure. Semi-empirical methods are based on the Hartree-Fock[11,12] formalism but utilize many approximations and some parameters from empirical (experimental) data to provide an initial structure for the mathematical models. The Schrödinger equation is solved iteratively using the SCF or Self-Consistent Field method. **Figure 4 (a-b)** shows the parameters that control the calculation. In the SCF method, the wave function is recomputed cyclically until the associated energy converges that is, the difference in energy between two consecutive iterations drops below a predefined threshold.

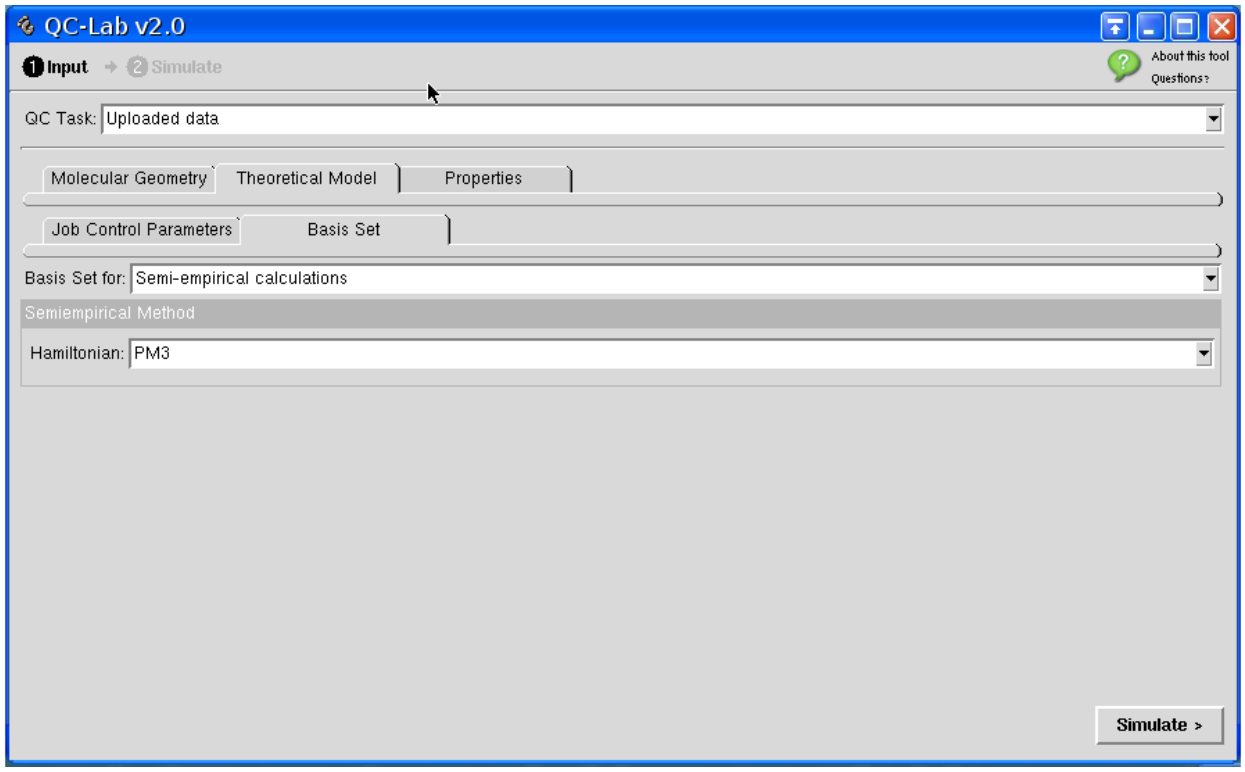


Figure 4b: To complete the description of the system, we have to provide the theoretical approach that we will utilize in the computation. In our study we will calculate the wave function by solving the Schrödinger equation using the approximate, semi empirical method PM3 (Parametric Method 3).

Analysis of the results

After the computation has finished, a new window will automatically appear showing the picture of the structure (atomic configuration) of the system under study (See **Figure 5**).

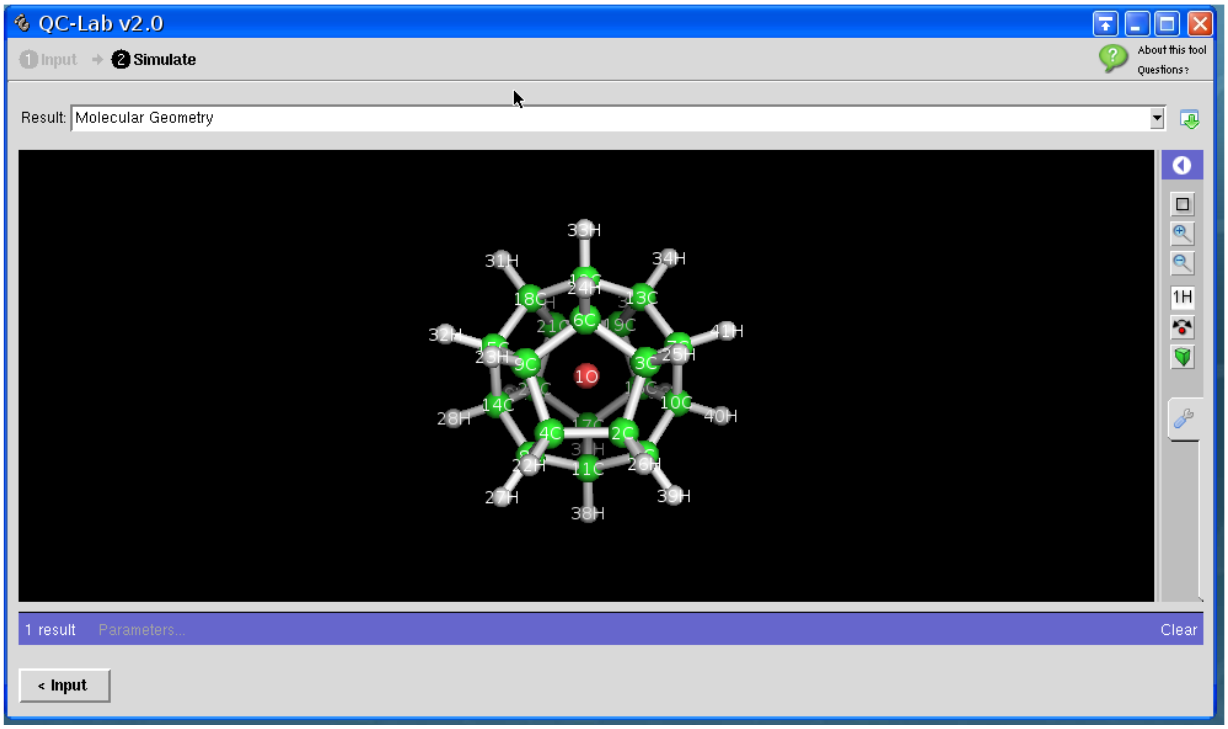


Figure 5: Structure of the particle $C_{20}H_{20}$@O complex showing the atomic labels. Please note that counting starts at '0' so the atom 6C in the picture corresponds to the 7C in the Output Log file**.**

Total Energy

In order to verify that the calculation has been successfully completed we must make sure that the SCF procedure has converged. On the *Result* menu, select the option Output Log. The window contains the description of the system and the results of the calculation. You may either download its content to your local computer for further reference (advisable), or search for specific information on-line using the built-in 'Find:' button located at the lower part of the window. For instance, search for the text "total energy"; if the string is found, its first appearance will be highlighted (see **Figure 6**). In the example, the SCF took 10 iterations to find a solution for the semiempirical PM3 Hartree-Fock equation. The total energy, sum of the electronic and nuclear energies, is –108.8113936998 hartrees.

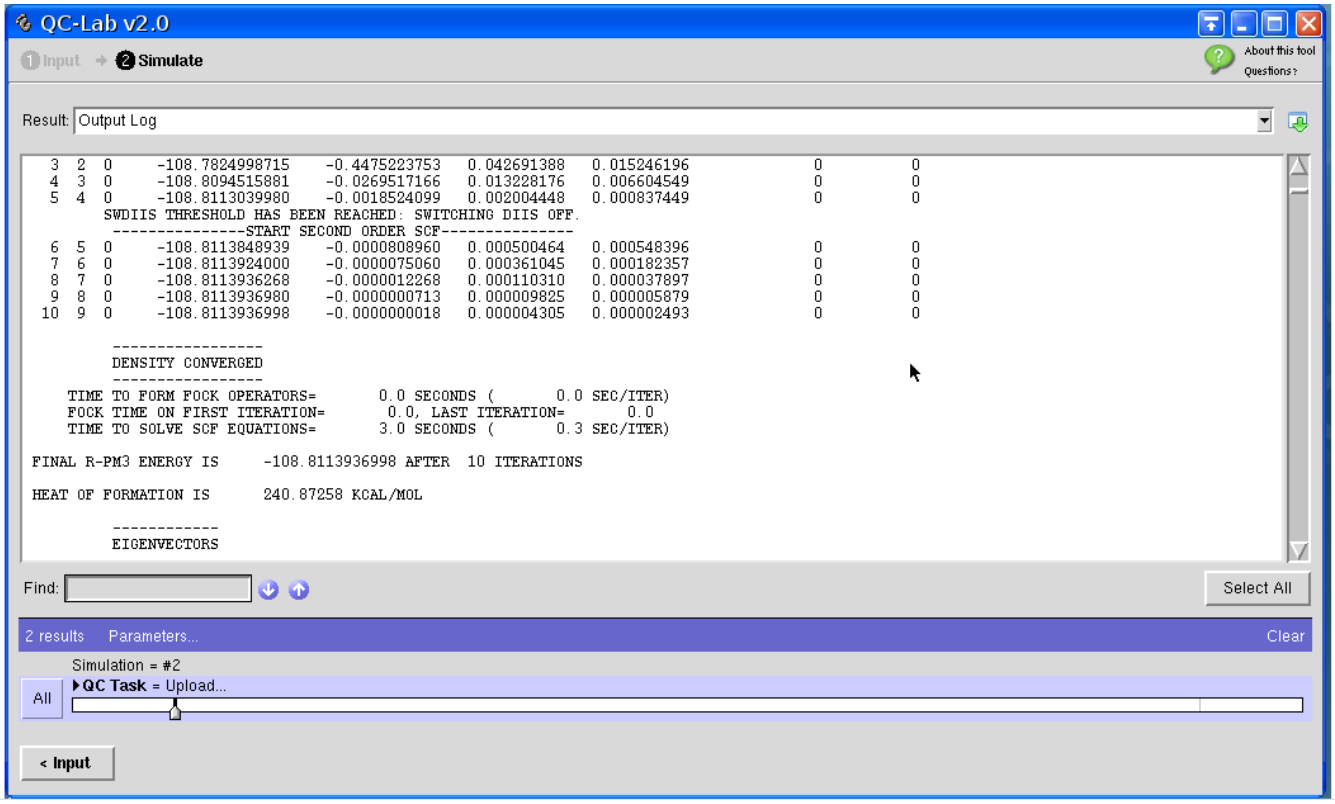


Figure 6. Output log showing the converged “FINAL R-PM3 ENERGY”.

Charge distribution.
The reactivity of a molecule may be inferred from its electron density distribution. One way to quantify such a distribution is by means of a *charge population analysis*. The charge at each atomic center is assigned by the sum of its nuclear charge (atomic number) and the number of electrons occupying the orbital's belonging to that atom. **Figure 7** shows the resulting *Orbital Occupancy* of the converged wave function. The numerical values obtained for the $C_{20}H_{20}$@O system are shown in the column labeled *Charge*, highlighted on **Figure 7**. In the log file window, the population analysis section may be located by searching for the string "MOPAC CHARGES". Use the last set of "MOPAC CHARGES" when collecting data.

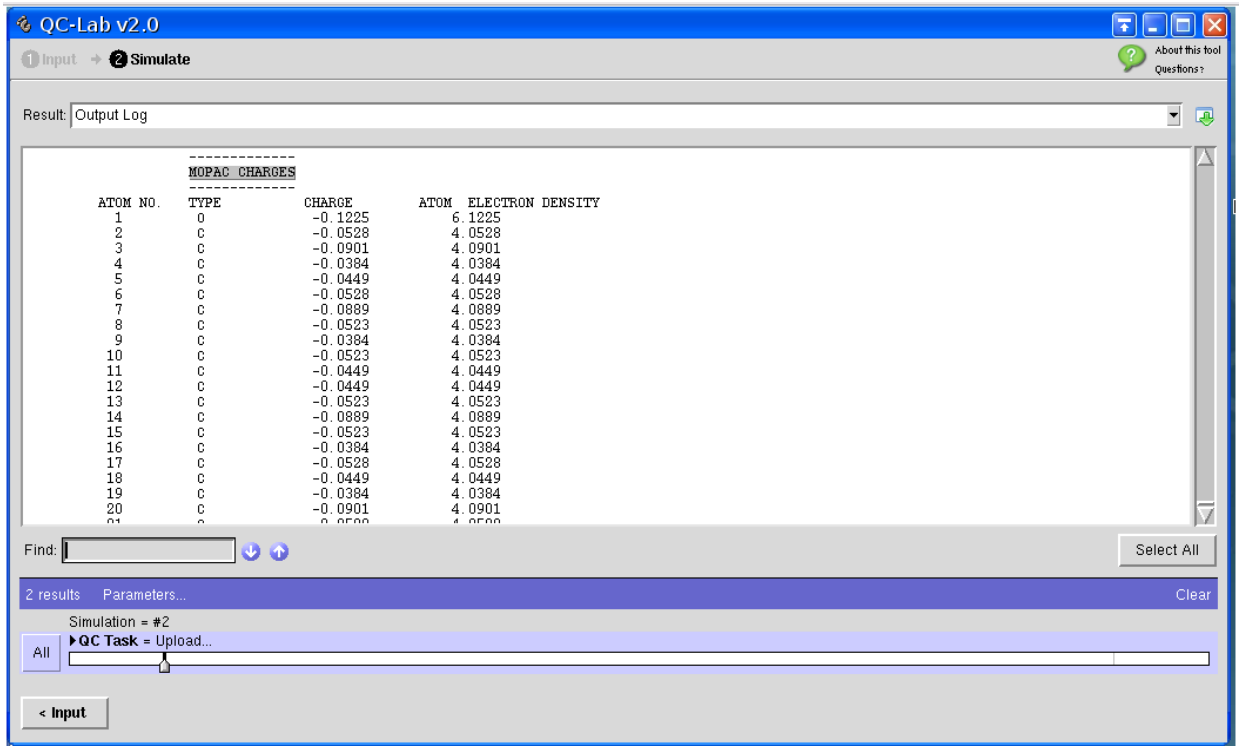
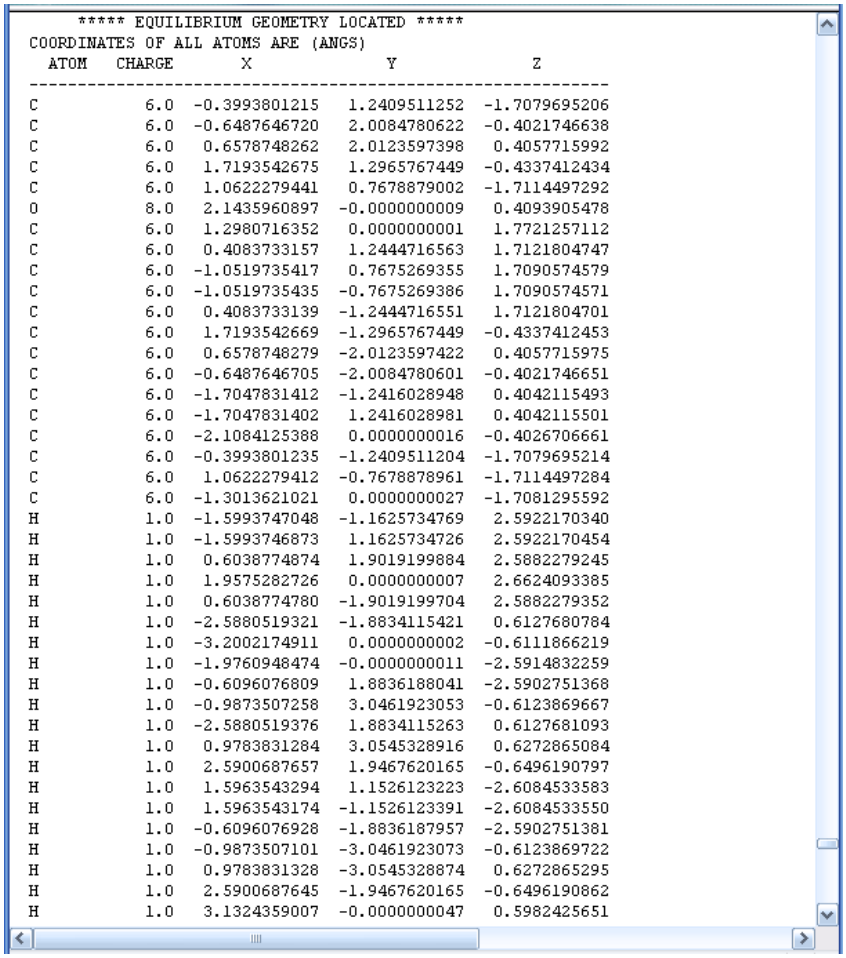


Figure 7: Atomic charge population analysis of the $C_{20}H_{20}$@O particle. Please note that the atomic labels in this table differ from those shown on the structure in **Figure 5** by one unit, thus C(7) in the table corresponds to C(6) on the figure.

Based on the electron population analysis, we may define an *electrostatic* criterion to predict which centers in the $C_{20}H_{20}$@O will likely react with nucleophilic (e.g., positive C atoms will attract nucleophilic ligands) species and which will react with electrophilic species. Although these electrostatic interactions may seem to be a reasonable argument to predict the initiating step of a reaction, it may not be sufficient, as *electronic* factors (i.e., which orbital's can combine to form bonds) are also in effect. Indeed electronic factors may dominate in the overall mechanism and change the direction of the reaction predicted by electrostatic factors alone. In a chemical process, the total energy is the factor that determines which product is more stable.



***** EQUILIBRIUM GEOMETRY LOCATED *****
COORDINATES OF ALL ATOMS ARE (ANGS)

ATOM	CHARGE	X	Y	Z
C	6.0	-0.3993801215	1.2409511252	-1.7079695206
C	6.0	-0.6487646720	2.0084780622	-0.4021746638
C	6.0	0.6578748262	2.0123597398	0.4057715992
C	6.0	1.7193542675	1.2965767449	-0.4337412434
C	6.0	1.0622279441	0.7678879002	-1.7114497292
O	8.0	2.1435960897	-0.0000000009	0.4093905478
C	6.0	1.2980716352	0.0000000001	1.7721257112
C	6.0	0.4083733157	1.2444716563	1.7121804747
C	6.0	-1.0519735417	0.7675269355	1.7090574579
C	6.0	-1.0519735435	-0.7675269386	1.7090574571
C	6.0	0.4083733139	-1.2444716551	1.7121804701
C	6.0	1.7193542669	-1.2965767449	-0.4337412453
C	6.0	0.6578748279	-2.0123597422	0.4057715975
C	6.0	-0.6487646705	-2.0084780601	-0.4021746651
C	6.0	-1.7047831412	-1.2416028948	0.4042115493
C	6.0	-1.7047831402	1.2416028981	0.4042115501
C	6.0	-2.1084125388	0.0000000016	-0.4026706661
C	6.0	-0.3993801235	-1.2409511204	-1.7079695214
C	6.0	1.0622279412	-0.7678878961	-1.7114497284
C	6.0	-1.3013621021	0.0000000027	-1.7081295592
H	1.0	-1.5993747048	-1.1625734769	2.5922170340
H	1.0	-1.5993746873	1.1625734726	2.5922170454
H	1.0	0.6038774874	1.9019199884	2.5882279245
H	1.0	1.9575282726	0.0000000007	2.6624093385
H	1.0	0.6038774780	-1.9019199704	2.5882279352
H	1.0	-2.5880519321	-1.8834115421	0.6127680784
H	1.0	-3.2002174911	0.0000000002	-0.6111866219
H	1.0	-1.9760948474	-0.0000000011	-2.5914832259
H	1.0	-0.6096076809	1.8836188041	-2.5902751368
H	1.0	-0.9873507258	3.0461923053	-0.6123869667
H	1.0	-2.5880519376	1.8834115263	0.6127681093
H	1.0	0.9783831284	3.0545328916	0.6272865084
H	1.0	2.5900687657	1.9467620165	-0.6496190797
H	1.0	1.5963543294	1.1526123223	-2.6084533583
H	1.0	1.5963543174	-1.1526123391	-2.6084533550
H	1.0	-0.6096076928	-1.8836187957	-2.5902751381
H	1.0	-0.9873507101	-3.0461923073	-0.6123869722
H	1.0	0.9783831328	-3.0545328874	0.6272865295
H	1.0	2.5900687645	-1.9467620165	-0.6496190862
H	1.0	3.1324359007	-0.0000000047	0.5982425651

Figure 8: Final geometry and restarting incomplete SCF calculations.

Restarting Computations (copy and paste new geometries and rerun):
It is possible that the energy will not converge in the specified number of SCF iterations. In these cases, it is possible to restart and continue the calculation from the end of the previous one. To do so, first locate the SCF steps in the *Output Log* similar to the EQUILIBRIUM GEOMETRY shown in **Figure 8**, most importantly, make sure that the energy shows a convergent trend. Copy and paste this last string of coordinates and rerun the calculation.

Cartesian coordinates: The Cartesian coordinates of the structures are available at the end of this document.

A. Total and Complexion Energies

1. The files HNDsM.xyz and DHDsM.xyz contain the coordinates for the separate components of the hydrogenated and dehydrogenated complexes, respectively. Using the semi empirical method CNDO, calculate the electronic structures and tabulate the total and binding energies of the clusters as a function of the complex (**HNDs** and **DHDs**) with the various dopants. The complexion energy (E_b) will be calculated by the difference in energy between the doped nanodiamond complexes, $C_{20}H_{20}$@M and
C_{20}@M minus **M** [**M**=Be, Mg, Ca, Si, O, S] depicted in **Scheme 1** and **2** (ref. **Chart 1**). Calculate the results for **M** [**M**=**D1** and **D2**].

Based on the results, propose a complexion energy trend for the **HNDs** and **DHDs** complexes. In other works, how does complexation energy vary as one move from left to right in the periodic table? Also, how does the complexation energy vary depending on whether the ND is hydrogenated or not?

B. Electronic properties

1. From the electronic structure calculation outputs for $C_{20}H_{20}$@M and C_{20}@M complexes [M=Be, Mg, Ca, Si, O, S] (using the files in the classroom folder) determine:
(a) The atomic charge for **M** [**M**=**D1** and **D2**].
(b) The HOMO, LUMO and HOMO-LUMO gap (eV) energies.
(c) The dipole moment.

2. From the results, explain why the excitation of an electron from the HOMO to LUMO is easier in doped complexes than in the case of $C_{20}H_{20}$ and C_{20}.

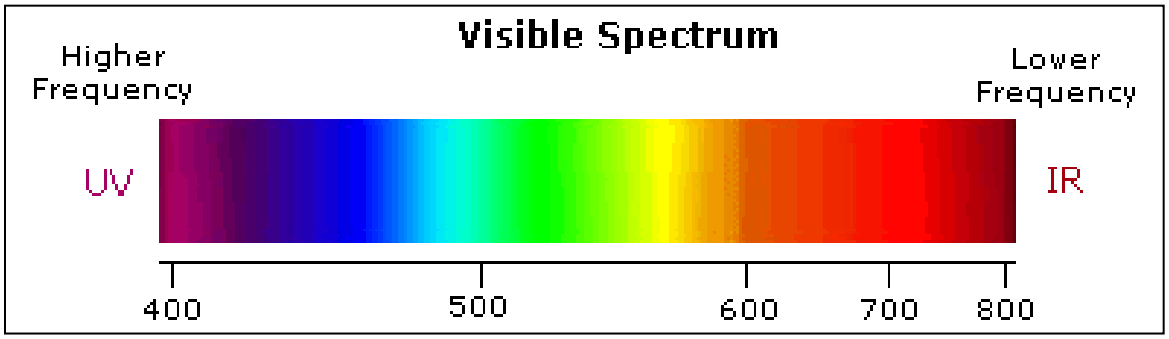
3. Compare the **HNDs** and **DHDs** atomic charge analysis for **M** [**M**=**D1** and **D2**]. Comment on the charge-transfer mechanisms between the dopant and carbon framework. What conclusions can you make concerning the hydrogenated and dehydrogenated complexes donor/acceptor and reactivity interactions?

C. Optical characterization of doped nanodiamonds.

Nanodiamonds (**NDs**) powders produced by denotation are considered the most versatile platform for biomedical applications because they exhibit low or no cytotoxicity.[13] **NDs** are characterized according to the content of impurities (*dopants*), such as nitrogen and boron atoms in the material. Recently, blue ($\lambda_{em} \approx 450nm$), red ($\lambda_{em} \approx 700nm$), and green ($\lambda_{em} \approx 530nm$) fluorescent **NDs** have been produced and characterized for use as cellular markers and/or labels.[13, 14, 15]

To understand and determine the spectra of **NDs** and the relationship of conjugation to color, we will analyze the spectra in and near the visible part of the spectrum. Ultraviolet-visible spectroscopy (UV=200-400 nm and visible=400-800 nm) corresponds to electronic excitations between the energy levels that corresponds to the molecular orbitals of the systems. In particular, transitions involving p orbitals and lone pairs (n=non-bonding).

The two lowest energy transitions are achieved by the energies available in the 200 to 800nm spectrum. The lowest energy transition is that between the **h**ighest **o**ccupied **m**olecular **o**rbital (**HOMO**) and the **l**owest **u**noccupied **m**olecular **o**rbital (**LUMO**) in the ground state. The absorption of the EM radiation excites an electron the **LUMO** and creates an excited state. The more highly conjugated the system, the smaller the **HOMO-LUMO** gap, $\Delta E_{H\text{-}L}$, and therefore the lower the frequency and longer the wavelength.



Violet: 400-420 nm **Indigo: 420-440 nm** **Blue: 440-490 nm**
Green: 490-570 nm **Yellow: 570-584 nm** **Orange: 585-620 nm**
Red: 620-780 nm

Figure 9. Depiction of electromagnetic radiation in range of wavelength for visible light. Colors that can be produced by visible light of wavelengths also shown. Wavelengths in nm.

a. Plot the UV/Vis spectra of the **M** [**M**=**D1** and **D2**] complexes **HND** and **DND** and discuss how this spectroscopic technique may be used to identify and distinguish the composition and stereochemistry of two isomeric species.
b. Place the predicted absorption color and transition of **M** [**M**=**D1** and **D2**] **HNDs** and **DNDs**.
c. Which **NDs** exhibited the least and greatest energy transitions? Why

i References

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4. J.-Y. Raty, G. Galli, C. Bostedt, T. W. van Buuren, L. J. Terminello, *Phys. Rev. Lett.* **2007**, *90*, *037401*.
5. A. S. Barnard, S. P. Russo, I. K. Snook, *J. Chem. Phys*. **2003**,*118*, 10725.
6. Alternatively, you may call the program directly, www.nanohub.org/tools/cndo, or through the utility NUITNS (Northwestern University Initiative for Teaching NanoScience). The package NUITNS is located on www.nanohub.org/tools/nuitns and provides access to a group of complementary programs aimed to the study of molecular systems by electronic structure methods.
7. To reattach the window to the browser click again on the *Popout* button.
8. Karttunen, A. J.; Linnolahti, M.; Pakkanen, *J. Phys. Chem. C* **2008**, *112*, 16324.
9. Remember that the spin multiplicity of a system is defined by the number 2S+1 where S is the sum of the individual electron spins.
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13. Yu, S. J.; Kang, M. W.; Chang, H. C.; Chen, K. Yu, Y. C. *J. Am. Chem. Soc*. **2005**, *127*, 17604.
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Endohedral Doped Nanodiamonds

***Best to view with Molden and/or MacMolPt on the www.nanohub.org**

Hydrogenated Nanodiamonds (HNDs)

$C_{20}H_{20}$

C 6.0 0.4083580 -1.2567966 1.7298321
C 6.0 1.3214741 0.0000000 1.7298321
C 6.0 -1.0690950 -0.7767430 1.7298321
C 6.0 0.6607371 -2.0335396 0.4083580
C 6.0 0.4083580 1.2567966 1.7298321
C 6.0 2.1381901 0.0000000 0.4083580
C 6.0 -1.7298321 -1.2567966 0.4083580
C 6.0 -1.0690950 0.7767430 1.7298321
C 6.0 1.7298321 -1.2567966 -0.4083580
C 6.0 -0.6607371 -2.0335396 -0.4083580
C 6.0 0.6607371 2.0335396 0.4083580
C 6.0 1.7298321 1.2567966 -0.4083580
C 6.0 -2.1381901 0.0000000 -0.4083580
C 6.0 -1.7298321 1.2567966 0.4083580
C 6.0 1.0690950 -0.7767430 -1.7298321
C 6.0 -0.4083580 -1.2567966 -1.7298321
C 6.0 -0.6607371 2.0335396 -0.4083580
C 6.0 1.0690950 0.7767430 -1.7298321
C 6.0 -1.3214741 0.0000000 -1.7298321
C 6.0 -0.4083580 1.2567966 -1.7298321
H 1.0 -1.6097170 -1.1695279 2.6045769
H 1.0 -1.6097170 1.1695279 2.6045769
H 1.0 0.6148572 1.8923359 2.6045769
H 1.0 1.9897197 0.0000000 2.6045769
H 1.0 0.6148572 -1.8923359 2.6045769
H 1.0 -2.6045769 -1.8923359 0.6148572
H 1.0 -3.2194341 0.0000000 -0.6148572
H 1.0 -1.9897197 0.0000000 -2.6045769
H 1.0 -0.6148572 1.8923359 -2.6045769
H 1.0 -0.9948598 3.0618638 -0.6148572
H 1.0 -2.6045769 1.8923359 0.6148572
H 1.0 0.9948598 3.0618638 0.6148572
H 1.0 2.6045769 1.8923359 -0.6148572
H 1.0 1.6097170 1.1695279 -2.6045769
H 1.0 1.6097170 -1.1695279 -2.6045769
H 1.0 -0.6148572 -1.8923359 -2.6045769
H 1.0 -0.9948598 -3.0618638 -0.6148572
H 1.0 0.9948598 -3.0618638 0.6148572
H 1.0 2.6045769 -1.8923359 -0.6148572
H 1.0 3.2194341 0.0000000 0.6148572

$C_{20}H_{20}Be$

C 6.0 0.4083580 -1.2567966 1.7298321
C 6.0 1.3214741 0.0000000 1.7298321
C 6.0 -1.0690950 -0.7767430 1.7298321
C 6.0 0.6607371 -2.0335396 0.4083580
C 6.0 0.4083580 1.2567966 1.7298321
C 6.0 2.1381901 0.0000000 0.4083580
C 6.0 -1.7298321 -1.2567966 0.4083580
C 6.0 -1.0690950 0.7767430 1.7298321
C 6.0 1.7298321 -1.2567966 -0.4083580
C 6.0 -0.6607371 -2.0335396 -0.4083580
C 6.0 0.6607371 2.0335396 0.4083580
C 6.0 1.7298321 1.2567966 -0.4083580
C 6.0 -2.1381901 0.0000000 -0.4083580
C 6.0 -1.7298321 1.2567966 0.4083580
C 6.0 1.0690950 -0.7767430 -1.7298321
C 6.0 -0.4083580 -1.2567966 -1.7298321
C 6.0 -0.6607371 2.0335396 -0.4083580
C 6.0 1.0690950 0.7767430 -1.7298321
C 6.0 -1.3214741 0.0000000 -1.7298321
C 6.0 -0.4083580 1.2567966 -1.7298321
H 1.0 -1.6097170 -1.1695279 2.6045769
H 1.0 -1.6097170 1.1695279 2.6045769
H 1.0 0.6148572 1.8923359 2.6045769
H 1.0 1.9897197 0.0000000 2.6045769
H 1.0 0.6148572 -1.8923359 2.6045769
H 1.0 -2.6045769 -1.8923359 0.6148572
H 1.0 -3.2194341 0.0000000 -0.6148572
H 1.0 -1.9897197 0.0000000 -2.6045769
H 1.0 -0.6148572 1.8923359 -2.6045769
H 1.0 -0.9948598 3.0618638 -0.6148572
H 1.0 -2.6045769 1.8923359 0.6148572
H 1.0 0.9948598 3.0618638 0.6148572
H 1.0 2.6045769 1.8923359 -0.6148572
H 1.0 1.6097170 1.1695279 -2.6045769
H 1.0 1.6097170 -1.1695279 -2.6045769
H 1.0 -0.6148572 -1.8923359 -2.6045769
H 1.0 -0.9948598 -3.0618638 -0.6148572
H 1.0 0.9948598 -3.0618638 0.6148572
H 1.0 2.6045769 -1.8923359 -0.6148572
H 1.0 3.2194341 0.0000000 0.6148572
Be 4.0 0.00000 0.00000 0.000000

$C_{20}H_{20}Mg$	$C_{20}H_{20}Ca$
C 6.0 0.4083580 -1.2567966 1.7298321 C 6.0 1.3214741 0.0000000 1.7298321 C 6.0 -1.0690950 -0.7767430 1.7298321 C 6.0 0.6607371 -2.0335396 0.4083580 C 6.0 0.4083580 1.2567966 1.7298321 C 6.0 2.1381901 0.0000000 0.4083580 C 6.0 -1.7298321 -1.2567966 0.4083580 C 6.0 -1.0690950 0.7767430 1.7298321 C 6.0 1.7298321 -1.2567966 -0.4083580 C 6.0 -0.6607371 -2.0335396 -0.4083580 C 6.0 0.6607371 2.0335396 0.4083580 C 6.0 1.7298321 1.2567966 -0.4083580 C 6.0 -2.1381901 0.0000000 -0.4083580 C 6.0 -1.7298321 1.2567966 0.4083580 C 6.0 1.0690950 -0.7767430 -1.7298321 C 6.0 -0.4083580 -1.2567966 -1.7298321 C 6.0 -0.6607371 2.0335396 -0.4083580 C 6.0 1.0690950 0.7767430 -1.7298321 C 6.0 -1.3214741 0.0000000 -1.7298321 C 6.0 -0.4083580 1.2567966 -1.7298321 H 1.0 -1.6097170 -1.1695279 2.6045769 H 1.0 -1.6097170 1.1695279 2.6045769 H 1.0 0.6148572 1.8923359 2.6045769 H 1.0 1.9897197 0.0000000 2.6045769 H 1.0 0.6148572 -1.8923359 2.6045769 H 1.0 -2.6045769 -1.8923359 0.6148572 H 1.0 -3.2194341 0.0000000 -0.6148572 H 1.0 -1.9897197 0.0000000 -2.6045769 H 1.0 -0.6148572 1.8923359 -2.6045769 H 1.0 -0.9948598 3.0618638 -0.6148572 H 1.0 -2.6045769 1.8923359 0.6148572 H 1.0 0.9948598 3.0618638 0.6148572 H 1.0 2.6045769 1.8923359 -0.6148572 H 1.0 1.6097170 1.1695279 -2.6045769 H 1.0 1.6097170 -1.1695279 -2.6045769 H 1.0 -0.6148572 -1.8923359 -2.6045769 H 1.0 -0.9948598 -3.0618638 -0.6148572 H 1.0 0.9948598 -3.0618638 0.6148572 H 1.0 2.6045769 -1.8923359 -0.6148572 H 1.0 3.2194341 0.0000000 0.6148572 Mg 12.0 0.00000 0.000000 0.00000	C 6.0 0.4083580 -1.2567966 1.7298321 C 6.0 1.3214741 0.0000000 1.7298321 C 6.0 -1.0690950 -0.7767430 1.7298321 C 6.0 0.6607371 -2.0335396 0.4083580 C 6.0 0.4083580 1.2567966 1.7298321 C 6.0 2.1381901 0.0000000 0.4083580 C 6.0 -1.7298321 -1.2567966 0.4083580 C 6.0 -1.0690950 0.7767430 1.7298321 C 6.0 1.7298321 -1.2567966 -0.4083580 C 6.0 -0.6607371 -2.0335396 -0.4083580 C 6.0 0.6607371 2.0335396 0.4083580 C 6.0 1.7298321 1.2567966 -0.4083580 C 6.0 -2.1381901 0.0000000 -0.4083580 C 6.0 -1.7298321 1.2567966 0.4083580 C 6.0 1.0690950 -0.7767430 -1.7298321 C 6.0 -0.4083580 -1.2567966 -1.7298321 C 6.0 -0.6607371 2.0335396 -0.4083580 C 6.0 1.0690950 0.7767430 -1.7298321 C 6.0 -1.3214741 0.0000000 -1.7298321 C 6.0 -0.4083580 1.2567966 -1.7298321 H 1.0 -1.6097170 -1.1695279 2.6045769 H 1.0 -1.6097170 1.1695279 2.6045769 H 1.0 0.6148572 1.8923359 2.6045769 H 1.0 1.9897197 0.0000000 2.6045769 H 1.0 0.6148572 -1.8923359 2.6045769 H 1.0 -2.6045769 -1.8923359 0.6148572 H 1.0 -3.2194341 0.0000000 -0.6148572 H 1.0 -1.9897197 0.0000000 -2.6045769 H 1.0 -0.6148572 1.8923359 -2.6045769 H 1.0 -0.9948598 3.0618638 -0.6148572 H 1.0 -2.6045769 1.8923359 0.6148572 H 1.0 0.9948598 3.0618638 0.6148572 H 1.0 2.6045769 1.8923359 -0.6148572 H 1.0 1.6097170 1.1695279 -2.6045769 H 1.0 1.6097170 -1.1695279 -2.6045769 H 1.0 -0.6148572 -1.8923359 -2.6045769 H 1.0 -0.9948598 -3.0618638 -0.6148572 H 1.0 0.9948598 -3.0618638 0.6148572 H 1.0 2.6045769 -1.8923359 -0.6148572 H 1.0 3.2194341 0.0000000 0.6148572 Ca 20.00 0.0000000 0.000000 0.00000

$C_{20}H_{20}Si$	$C_{20}H_{20}O$
C 6.0 0.4083580 -1.2567966 1.7298321	C 6.0 0.4083580 -1.2567966 1.7298321
C 6.0 1.3214741 0.0000000 1.7298321	C 6.0 1.3214741 0.0000000 1.7298321
C 6.0 -1.0690950 -0.7767430 1.7298321	C 6.0 -1.0690950 -0.7767430 1.7298321
C 6.0 0.6607371 -2.0335396 0.4083580	C 6.0 0.6607371 -2.0335396 0.4083580
C 6.0 0.4083580 1.2567966 1.7298321	C 6.0 0.4083580 1.2567966 1.7298321
C 6.0 2.1381901 0.0000000 0.4083580	C 6.0 2.1381901 0.0000000 0.4083580
C 6.0 -1.7298321 -1.2567966 0.4083580	C 6.0 -1.7298321 -1.2567966 0.4083580
C 6.0 -1.0690950 0.7767430 1.7298321	C 6.0 -1.0690950 0.7767430 1.7298321
C 6.0 1.7298321 -1.2567966 -0.4083580	C 6.0 1.7298321 -1.2567966 -0.4083580
C 6.0 -0.6607371 -2.0335396 -0.4083580	C 6.0 -0.6607371 -2.0335396 -0.4083580
C 6.0 0.6607371 2.0335396 0.4083580	C 6.0 0.6607371 2.0335396 0.4083580
C 6.0 1.7298321 1.2567966 -0.4083580	C 6.0 1.7298321 1.2567966 -0.4083580
C 6.0 -2.1381901 0.0000000 -0.4083580	C 6.0 -2.1381901 0.0000000 -0.4083580
C 6.0 -1.7298321 1.2567966 0.4083580	C 6.0 -1.7298321 1.2567966 0.4083580
C 6.0 1.0690950 -0.7767430 -1.7298321	C 6.0 1.0690950 -0.7767430 -1.7298321
C 6.0 -0.4083580 -1.2567966 -1.7298321	C 6.0 -0.4083580 -1.2567966 -1.7298321
C 6.0 -0.6607371 2.0335396 -0.4083580	C 6.0 -0.6607371 2.0335396 -0.4083580
C 6.0 1.0690950 0.7767430 -1.7298321	C 6.0 1.0690950 0.7767430 -1.7298321
C 6.0 -1.3214741 0.0000000 -1.7298321	C 6.0 -1.3214741 0.0000000 -1.7298321
C 6.0 -0.4083580 1.2567966 -1.7298321	C 6.0 -0.4083580 1.2567966 -1.7298321
H 1.0 -1.6097170 -1.1695279 2.6045769	H 1.0 -1.6097170 -1.1695279 2.6045769
H 1.0 -1.6097170 1.1695279 2.6045769	H 1.0 -1.6097170 1.1695279 2.6045769
H 1.0 0.6148572 1.8923359 2.6045769	H 1.0 0.6148572 1.8923359 2.6045769
H 1.0 1.9897197 0.0000000 2.6045769	H 1.0 1.9897197 0.0000000 2.6045769
H 1.0 0.6148572 -1.8923359 2.6045769	H 1.0 0.6148572 -1.8923359 2.6045769
H 1.0 -2.6045769 -1.8923359 0.6148572	H 1.0 -2.6045769 -1.8923359 0.6148572
H 1.0 -3.2194341 0.0000000 -0.6148572	H 1.0 -3.2194341 0.0000000 -0.6148572
H 1.0 -1.9897197 0.0000000 -2.6045769	H 1.0 -1.9897197 0.0000000 -2.6045769
H 1.0 -0.6148572 1.8923359 -2.6045769	H 1.0 -0.6148572 1.8923359 -2.6045769
H 1.0 -0.9948598 3.0618638 -0.6148572	H 1.0 -0.9948598 3.0618638 -0.6148572
H 1.0 -2.6045769 1.8923359 0.6148572	H 1.0 -2.6045769 1.8923359 0.6148572
H 1.0 0.9948598 3.0618638 0.6148572	H 1.0 0.9948598 3.0618638 0.6148572
H 1.0 2.6045769 1.8923359 -0.6148572	H 1.0 2.6045769 1.8923359 -0.6148572
H 1.0 1.6097170 1.1695279 -2.6045769	H 1.0 1.6097170 1.1695279 -2.6045769
H 1.0 1.6097170 -1.1695279 -2.6045769	H 1.0 1.6097170 -1.1695279 -2.6045769
H 1.0 -0.6148572 -1.8923359 -2.6045769	H 1.0 -0.6148572 -1.8923359 -2.6045769
H 1.0 -0.9948598 -3.0618638 -0.6148572	H 1.0 -0.9948598 -3.0618638 -0.6148572
H 1.0 0.9948598 -3.0618638 0.6148572	H 1.0 0.9948598 -3.0618638 0.6148572
H 1.0 2.6045769 -1.8923359 -0.6148572	H 1.0 2.6045769 -1.8923359 -0.6148572
H 1.0 3.2194341 0.0000000 0.6148572	H 1.0 3.2194341 0.0000000 0.6148572
Si 14.0 0.000000 0.0000000 0.000000	O 8.0 0.000000 0.000000 0.0000000

$C_{20}H_{20}S$ C 6.0 0.4083580 -1.2567966 1.7298321 C 6.0 1.3214741 0.0000000 1.7298321 C 6.0 -1.0690950 -0.7767430 1.7298321 C 6.0 0.6607371 -2.0335396 0.4083580 C 6.0 0.4083580 1.2567966 1.7298321 C 6.0 2.1381901 0.0000000 0.4083580 C 6.0 -1.7298321 -1.2567966 0.4083580 C 6.0 -1.0690950 0.7767430 1.7298321 C 6.0 1.7298321 -1.2567966 -0.4083580 C 6.0 -0.6607371 -2.0335396 -0.4083580 C 6.0 0.6607371 2.0335396 0.4083580 C 6.0 1.7298321 1.2567966 -0.4083580 C 6.0 -2.1381901 0.0000000 -0.4083580 C 6.0 -1.7298321 1.2567966 0.4083580 C 6.0 1.0690950 -0.7767430 -1.7298321 C 6.0 -0.4083580 -1.2567966 -1.7298321 C 6.0 -0.6607371 2.0335396 -0.4083580 C 6.0 1.0690950 0.7767430 -1.7298321 C 6.0 -1.3214741 0.0000000 -1.7298321 C 6.0 -0.4083580 1.2567966 -1.7298321 H 1.0 -1.6097170 -1.1695279 2.6045769 H 1.0 -1.6097170 1.1695279 2.6045769 H 1.0 0.6148572 1.8923359 2.6045769 H 1.0 1.9897197 0.0000000 2.6045769 H 1.0 0.6148572 -1.8923359 2.6045769 H 1.0 -2.6045769 -1.8923359 0.6148572 H 1.0 -3.2194341 0.0000000 -0.6148572 H 1.0 -1.9897197 0.0000000 -2.6045769 H 1.0 -0.6148572 1.8923359 -2.6045769 H 1.0 -0.9948598 3.0618638 -0.6148572 H 1.0 -2.6045769 1.8923359 0.6148572 H 1.0 0.9948598 3.0618638 0.6148572 H 1.0 2.6045769 1.8923359 -0.6148572 H 1.0 1.6097170 1.1695279 -2.6045769 H 1.0 1.6097170 -1.1695279 -2.6045769 H 1.0 -0.6148572 -1.8923359 -2.6045769 H 1.0 -0.9948598 -3.0618638 -0.6148572 H 1.0 0.9948598 -3.0618638 0.6148572	

Dehydrogenated Nanodiamonds (DNDs)	
C_{20}	**C_{20}@Be**
C 6.0 0.4083580 -1.2567966 1.7298321 C 6.0 1.3214741 0.0000000 1.7298321 C 6.0 -1.0690950 -0.7767430 1.7298321 C 6.0 0.6607371 -2.0335396 0.4083580 C 6.0 0.4083580 1.2567966 1.7298321 C 6.0 2.1381901 0.0000000 0.4083580 C 6.0 -1.7298321 -1.2567966 0.4083580 C 6.0 -1.0690950 0.7767430 1.7298321 C 6.0 1.7298321 -1.2567966 -0.4083580 C 6.0 -0.6607371 -2.0335396 -0.4083580 C 6.0 0.6607371 2.0335396 0.4083580 C 6.0 1.7298321 1.2567966 -0.4083580 C 6.0 -2.1381901 0.0000000 -0.4083580 C 6.0 -1.7298321 1.2567966 0.4083580 C 6.0 1.0690950 -0.7767430 -1.7298321 C 6.0 -0.4083580 -1.2567966 -1.7298321 C 6.0 -0.6607371 2.0335396 -0.4083580 C 6.0 1.0690950 0.7767430 -1.7298321 C 6.0 -1.3214741 0.0000000 -1.7298321 C 6.0 -0.4083580 1.2567966 -1.7298321	C 6.0 0.4083580 -1.2567966 1.7298321 C 6.0 1.3214741 0.0000000 1.7298321 C 6.0 -1.0690950 -0.7767430 1.7298321 C 6.0 0.6607371 -2.0335396 0.4083580 C 6.0 0.4083580 1.2567966 1.7298321 C 6.0 2.1381901 0.0000000 0.4083580 C 6.0 -1.7298321 -1.2567966 0.4083580 C 6.0 -1.0690950 0.7767430 1.7298321 C 6.0 1.7298321 -1.2567966 -0.4083580 C 6.0 -0.6607371 -2.0335396 -0.4083580 C 6.0 0.6607371 2.0335396 0.4083580 C 6.0 1.7298321 1.2567966 -0.4083580 C 6.0 -2.1381901 0.0000000 -0.4083580 C 6.0 -1.7298321 1.2567966 0.4083580 C 6.0 1.0690950 -0.7767430 -1.7298321 C 6.0 -0.4083580 -1.2567966 -1.7298321 C 6.0 -0.6607371 2.0335396 -0.4083580 C 6.0 1.0690950 0.7767430 -1.7298321 C 6.0 -1.3214741 0.0000000 -1.7298321 C 6.0 -0.4083580 1.2567966 -1.7298321 Be 4.0 0.00000 0.00000 0.000000
C_{20}@Mg	**C_{20}@Ca**
C 6.0 0.4083580 -1.2567966 1.7298321 C 6.0 1.3214741 0.0000000 1.7298321 C 6.0 -1.0690950 -0.7767430 1.7298321 C 6.0 0.6607371 -2.0335396 0.4083580 C 6.0 0.4083580 1.2567966 1.7298321 C 6.0 2.1381901 0.0000000 0.4083580 C 6.0 -1.7298321 -1.2567966 0.4083580 C 6.0 -1.0690950 0.7767430 1.7298321 C 6.0 1.7298321 -1.2567966 -0.4083580 C 6.0 -0.6607371 -2.0335396 -0.4083580 C 6.0 0.6607371 2.0335396 0.4083580 C 6.0 1.7298321 1.2567966 -0.4083580 C 6.0 -2.1381901 0.0000000 -0.4083580 C 6.0 -1.7298321 1.2567966 0.4083580 C 6.0 1.0690950 -0.7767430 -1.7298321 C 6.0 -0.4083580 -1.2567966 -1.7298321 C 6.0 -0.6607371 2.0335396 -0.4083580 C 6.0 1.0690950 0.7767430 -1.7298321 C 6.0 -1.3214741 0.0000000 -1.7298321 C 6.0 -0.4083580 1.2567966 -1.7298321 Mg 12.0 0.00000 0.000000 0.000000	C 6.0 0.4083580 -1.2567966 1.7298321 C 6.0 1.3214741 0.0000000 1.7298321 C 6.0 -1.0690950 -0.7767430 1.7298321 C 6.0 0.6607371 -2.0335396 0.4083580 C 6.0 0.4083580 1.2567966 1.7298321 C 6.0 2.1381901 0.0000000 0.4083580 C 6.0 -1.7298321 -1.2567966 0.4083580 C 6.0 -1.0690950 0.7767430 1.7298321 C 6.0 1.7298321 -1.2567966 -0.4083580 C 6.0 -0.6607371 -2.0335396 -0.4083580 C 6.0 0.6607371 2.0335396 0.4083580 C 6.0 1.7298321 1.2567966 -0.4083580 C 6.0 -2.1381901 0.0000000 -0.4083580 C 6.0 -1.7298321 1.2567966 0.4083580 C 6.0 1.0690950 -0.7767430 -1.7298321 C 6.0 -0.4083580 -1.2567966 -1.7298321 C 6.0 -0.6607371 2.0335396 -0.4083580 C 6.0 1.0690950 0.7767430 -1.7298321 C 6.0 -1.3214741 0.0000000 -1.7298321 C 6.0 -0.4083580 1.2567966 -1.7298321 Ca 20.00 0.0000000 0.000000 0.00000

C_{20}@Si

C 6.0 0.4083580 -1.2567966 1.7298321
C 6.0 1.3214741 0.0000000 1.7298321
C 6.0 -1.0690950 -0.7767430 1.7298321
C 6.0 0.6607371 -2.0335396 0.4083580
C 6.0 0.4083580 1.2567966 1.7298321
C 6.0 2.1381901 0.0000000 0.4083580
C 6.0 -1.7298321 -1.2567966 0.4083580
C 6.0 -1.0690950 0.7767430 1.7298321
C 6.0 1.7298321 -1.2567966 -0.4083580
C 6.0 -0.6607371 -2.0335396 -0.4083580
C 6.0 0.6607371 2.0335396 0.4083580
C 6.0 1.7298321 1.2567966 -0.4083580
C 6.0 -2.1381901 0.0000000 -0.4083580
C 6.0 -1.7298321 1.2567966 0.4083580
C 6.0 1.0690950 -0.7767430 -1.7298321
C 6.0 -0.4083580 -1.2567966 -1.7298321
C 6.0 -0.6607371 2.0335396 -0.4083580
C 6.0 1.0690950 0.7767430 -1.7298321
C 6.0 -1.3214741 0.0000000 -1.7298321
C 6.0 -0.4083580 1.2567966 -1.7298321
Si 14.0 0.000000 0.0000000 0.000000

C_{20}@O

C 6.0 0.4083580 -1.2567966 1.7298321
C 6.0 1.3214741 0.0000000 1.7298321
C 6.0 -1.0690950 -0.7767430 1.7298321
C 6.0 0.6607371 -2.0335396 0.4083580
C 6.0 0.4083580 1.2567966 1.7298321
C 6.0 2.1381901 0.0000000 0.4083580
C 6.0 -1.7298321 -1.2567966 0.4083580
C 6.0 -1.0690950 0.7767430 1.7298321
C 6.0 1.7298321 -1.2567966 -0.4083580
C 6.0 -0.6607371 -2.0335396 -0.4083580
C 6.0 0.6607371 2.0335396 0.4083580
C 6.0 1.7298321 1.2567966 -0.4083580
C 6.0 -2.1381901 0.0000000 -0.4083580
C 6.0 -1.7298321 1.2567966 0.4083580
C 6.0 1.0690950 -0.7767430 -1.7298321
C 6.0 -0.4083580 -1.2567966 -1.7298321
C 6.0 -0.6607371 2.0335396 -0.4083580
C 6.0 1.0690950 0.7767430 -1.7298321
C 6.0 -1.3214741 0.0000000 -1.7298321
C 6.0 -0.4083580 1.2567966 -1.7298321
O 8.0 0.000000 0.000000 0.0000000

C_{20}@S

C 6.0 0.4083580 -1.2567966 1.7298321
C 6.0 1.3214741 0.0000000 1.7298321
C 6.0 -1.0690950 -0.7767430 1.7298321
C 6.0 0.6607371 -2.0335396 0.4083580
C 6.0 0.4083580 1.2567966 1.7298321
C 6.0 2.1381901 0.0000000 0.4083580
C 6.0 -1.7298321 -1.2567966 0.4083580
C 6.0 -1.0690950 0.7767430 1.7298321
C 6.0 1.7298321 -1.2567966 -0.4083580
C 6.0 -0.6607371 -2.0335396 -0.4083580
C 6.0 0.6607371 2.0335396 0.4083580
C 6.0 1.7298321 1.2567966 -0.4083580
C 6.0 -2.1381901 0.0000000 -0.4083580
C 6.0 -1.7298321 1.2567966 0.4083580
C 6.0 1.0690950 -0.7767430 -1.7298321
C 6.0 -0.4083580 -1.2567966 -1.7298321
C 6.0 -0.6607371 2.0335396 -0.4083580
C 6.0 1.0690950 0.7767430 -1.7298321
C 6.0 -1.3214741 0.0000000 -1.7298321
C 6.0 -0.4083580 1.2567966 -1.7298321
S 16.0 0.000000 0..00000 0.000000