



COMPUTATIONAL STUDIES ON CAGE/NON-CAGE STRUCTURES OF OCTACARBORANE DIANION SERIES

Vibha Kumar*, Seema Baniwal, Deepa Saini

Pt. L. M. S. Campus, Sri Dev Suman Uttarakhand University, Rishikesh - 249 201, India.

*Corresponding Author email: vibhasingh25@gmail.com

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ABSTRACT

Only cage structures of octacarborene have been reported in the literature, some stable non-cage structures for the same have been found for the first time in this work. A complete isoelectronic dianion series of carboranes of $B_8H_8^{2-}$ have been investigated, each time a B-H unit being replaced by a bare carbon hence forming a dianion series of general formula $C_nB_{8-n}H_{8-n}^{2-}$ ($n=1-8$). The work has been carried out using Gaussian98 software at Hartree-Fock and DFT levels using 6-31G basis sets both with and without polarization functions.

Keywords: Carboranes, dianions, boranes, deltahedra.

INTRODUCTION

Different workers in the past have studied three different deltahedra of *closo*-carboranes i.e., $C_2B_6H_8$ [1, 2, 3, 4, 5], $CB_7H_8^-$ [2, 3, 4] and $C_3B_5H_7$ [3] of the *closo*-borane $B_8H_8^{2-}$. Only 1,7- $C_2B_6H_8$, isomer amongst the several isomers possible for $C_2B_6H_8$ is known experimentally and it has been prepared and characterized [4, 6] by pyrolysis of 1,3-dicarbonylborane in diphenyl ether [7].

Carborane are clusters compounds which are made up of boron and carbon atoms [8]. They are obtained by replacing one B-H unit of a borane by a carbon atom. The geometrical structures of carboranes are similar to those of boron hydrides, the difference lies in the presence of one or more boron atoms by carbon atoms [9]. *Closo*-carboranes have polyhedral structures with triangular faces like those of *closo*-boranes [10-13]. Like many of the related boranes, these clusters are polyhedra and are similarly classified according to Wade-Mingos rules [14-20] as *closo*-, *nido*-, *arachno*-, *hypho*-, etc. The *closo*-carboranes, having the general formula, $C_nB_{8-n}H_n$, have structures in which all the polyhedral faces are triangles, therefore these are also called deltahedra.

In this work a series of dianion carboranes with eight central atoms (carbon and boron) $C_xB_nH_n^{2-}$ ($x+n=8$, $x=1-7$) was studied. In all the recent studies on carboranes only cage compounds have been studied and no mention of non-cage compounds is seen anywhere, however in this work some stable non-cage compounds

have been identified and studied along with cage compounds.

MATERIALS AND METHODS

Geometry optimization of all the carboranes were carried out at the Hartree-Fock and DFT/B3LYP level using the Gaussian98 software package [21]. The nature of each stationary point was probed by analytical frequency calculations. All the minima were found to have zero imaginary frequency.

RESULT AND DISCUSSION

A dianion *closo*-carboranes series related to $B_8H_8^{2-}$ with the formula $CB_7H_7^{2-}$, $C_2B_6H_6^{2-}$, $C_3B_5H_5^{2-}$, $C_4B_4H_4^{2-}$, $C_5B_3H_3^{2-}$, $C_6B_2H_2^{2-}$, and C_7BH^{2-} was studied. This series involves successive substitution of a B-H unit with a carbon atom. We investigated the isoelectronic dianion series of carboranes of general formula $C_nB_{8-n}H_{8-n}^{2-}$, where all the possible values of n from 2 to 8 were tried out. Thus in all cases the sum of carbon and boron atoms was equal to eight. As one carbon was replaced by a boron, one hydrogen was also removed as one carbon equals to a B-H unit in terms of number of electrons. All possible starting structures corresponding to each formula were generated starting from each stable form of $B_8H_8^{2-}$ by this method and geometry optimization was performed in each case. All the calculations were performed at RHF/6-31G and

B3LYP/6-31G* method. Frequency analysis was also run to check the stability of the molecules.

CB₇H₇²⁻

In case of the carborane of molecular formula CB₇H₇²⁻ only a single stable form was found to exist, while various other possible structures studied

possessed one or more imaginary frequencies and therefore are not being discussed here. The structure is shown in the figure 1 has a C_s symmetry and has a cage structure. The energy obtained shows that it is higher in energy than the corresponding CB₇H₈⁻ structure. The energies at two levels are given in table 1.

Table 1: Energies of CB₇H₇²⁻ at RHF and B3LYP level

S. No.	Symmetry	Energy(Hartrees) RHF/6-31G	Dipole moment	Energy(Hartrees) B3LYP/6-31G*	Dipole moment
1.	C _s	-214.4268736	1.3823	-216.2062946	0.8604

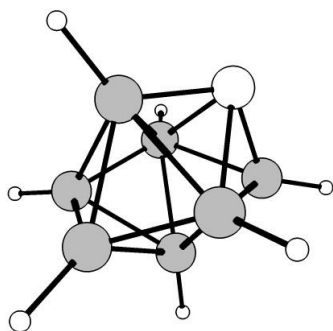


Fig. 1: Structure of CB₇H₇²⁻

C₂B₆H₆²⁻

To obtain structures with the formula C₂B₆H₆²⁻ starting structures two B–H units were replaced by carbons in each stable form of B₈H₈²⁻. All possible pair of boron positions of the stable forms of the molecule B₈H₈²⁻ were substituted in turn, and the structures so obtained were optimized. Frequency analysis performed shows that among the various possible structures

obtained only five are stable forms of the dianion, and these are shown in figure 2.

Out of five structures found three are cage structures and two are non-cage structures and of the two non-cage structures one is a planar ring structure and the other has a puckered ring shape. The energies obtained shows that among the three cage structures obtained two are more stable than the non-cage structures while the third cage structure is less stable than the non-cage structures.

Table 12 gives the energies of the various isomers of C₂B₆H₆²⁻. The structures in the figure are arranged in the order of increasing energy. It is also interesting to note that literature mentions only the cage compounds, and non-cage carboranes have not been investigated at all, we have obtained some non-cage compounds and some of them are more stable than some of the cage compounds.

Structure 3 and 4 in figure 2 have got different shapes on optimization on the two different basis sets.

Table 2: Energies of C₂B₆H₆²⁻ at RHF and B3LYP level

S. No.	Symmetry	Energy(Hartrees) RHF/6-31G	Relative Energies (kcal/mol)	Dipole moment	Energy(Hartrees) B3LYP/6-31G*	Relative Energies (kcal/mol)	Dipole moment
1.	C ₁	-226.9506831	0.00	102616	-228.7851628	0.00	0.8918
2.	C _{2v}	-226.9192767	19.71	2.5285	-228.7578322	0.027	1.6492
3.	C _s	-226.9154846	22.08	2.3589	-228.7483105	23.21	0.6619
4.	C _{2v}	-226.9130257	23.63	5.6809	-228.7340799(1)	32.05	502466
5.	C _s	-226.8986852	32.62	2.0644	-228.7065074	49.35	1.8004

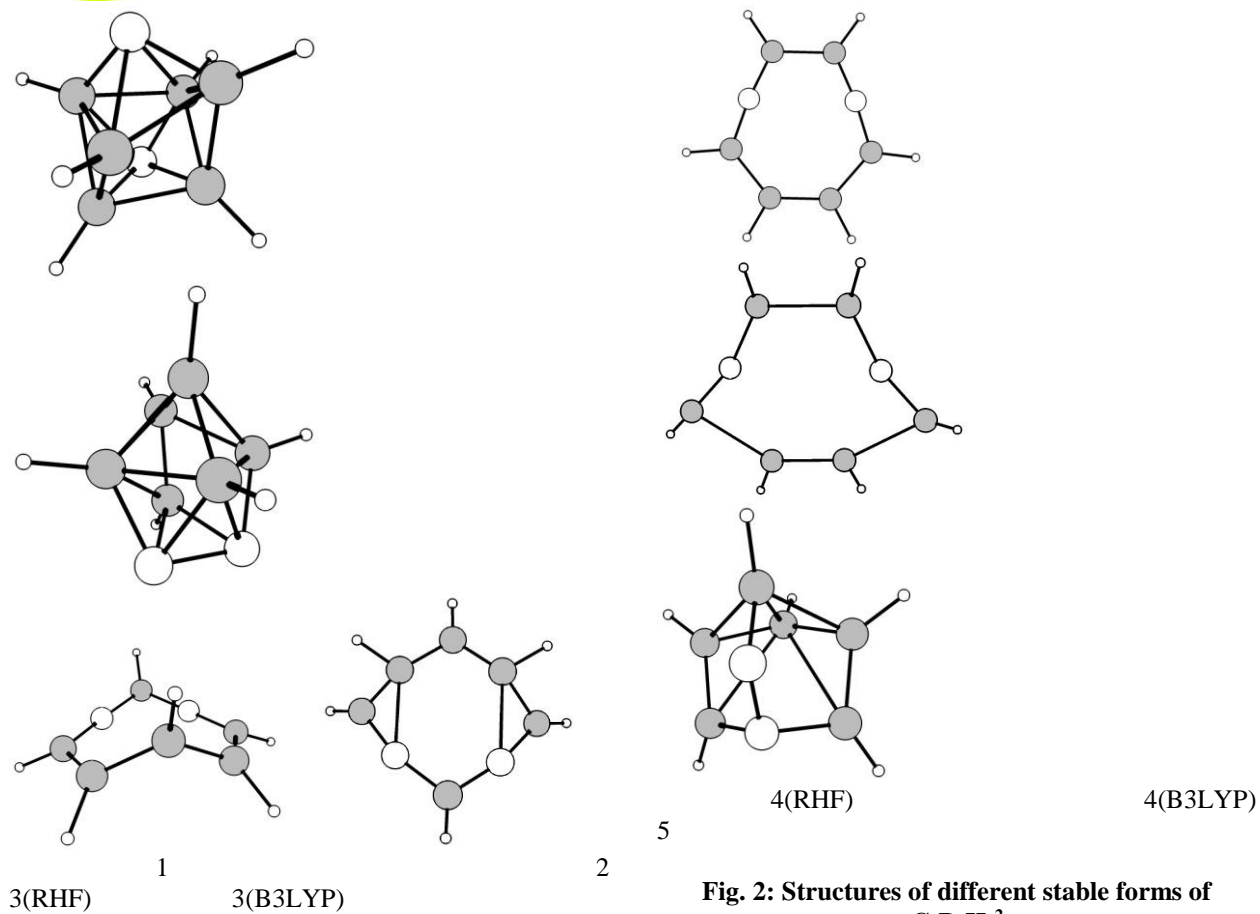


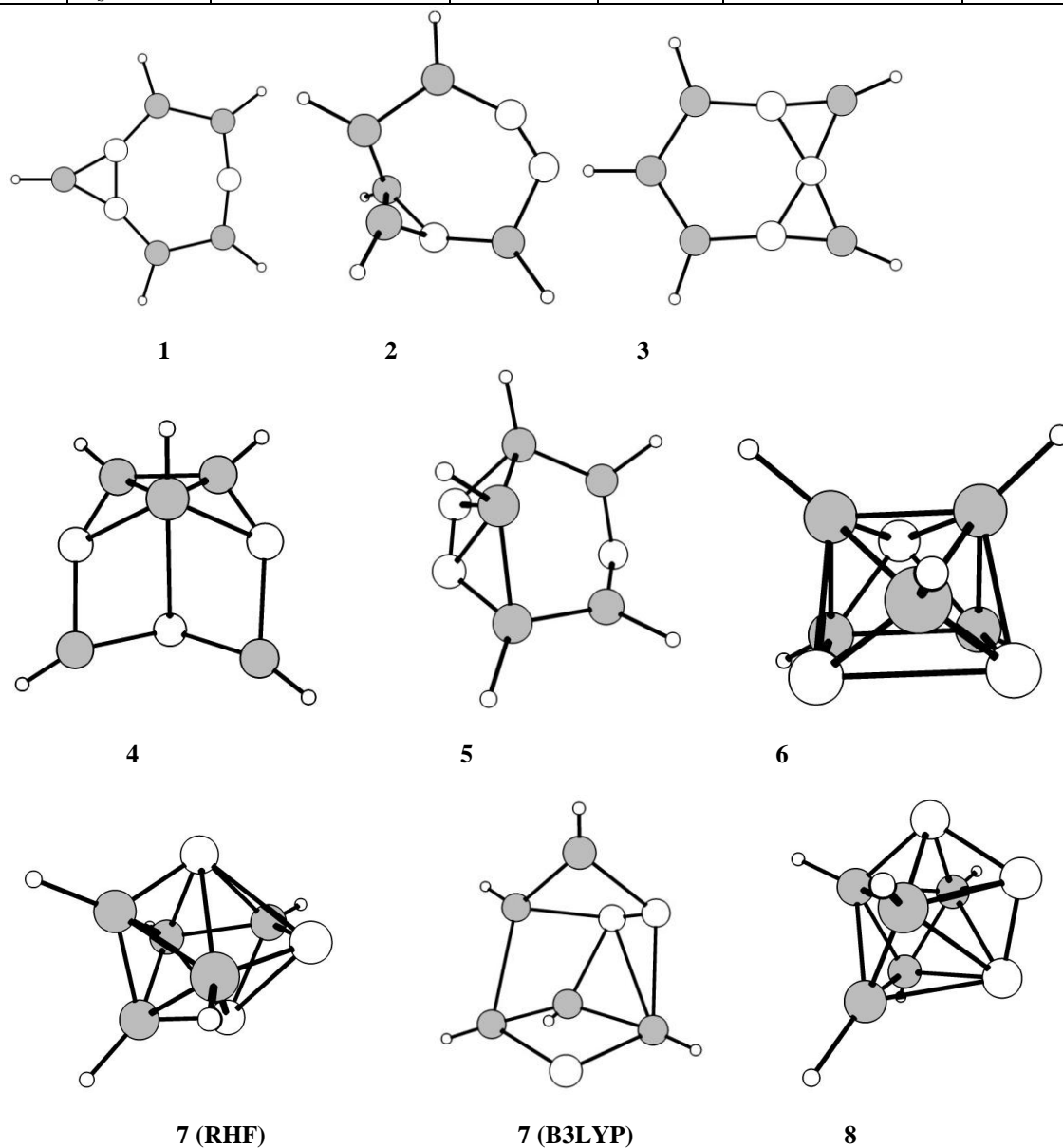
Fig. 2: Structures of different stable forms of $C_2B_6H_6^{2-}$

$C_3B_5H_5^{2-}$

In the compounds of formula $C_3B_5H_5^{2-}$ three B–H units of $B_8H_8^{2-}$ are replaced by three carbons. Optimizing all the structures so generated eight stable isomers of $C_3B_5H_5^{2-}$ were found which are shown in figure 3. Others isomers found were not stable as they possess one or more imaginary frequencies. Out of eight stable isomers obtained only three are cage structures and five are non-cage structures. It is seen that the non-cage structures are more stable than the cage structure. The energies of the stable forms are given in table 3. Structure 7 has got different shapes on two different levels, and structure 6 is found to have one imaginary frequency at RHF and structure 7 at B3LYP level respectively, while both are stable on the other levels.

Table 3: Energies of $C_3B_5H_5^{2-}$ at RHF and B3LYP level

S. No.	Symmetry	Energy(Hartrees) RHF/6-31G	Relative Energies (kcal/mol)	Dipole moment	Energy(Hartrees) B3LYP/6-31G*	Relative Energies (kcal/mol)	Dipole moment
1.	C_s	-239.5508768	0.00	0.1044	-241.388671	0.00	0.1557
2.	C_I	-239.5288489	13.82	2.9117	-241.3727441	9.99	1.414
3.	C_s	-239.5176997	20.82	7.8377	-241.375193	8.46	6.3702
4.	C_s	-239.5130932	23.71	1.416	-241.3725375	10.12	0.526
5.	C_s	-239.4792036	44.97	0.2861	-241.3355418	33.33	1.8756
6.	C_s	-239.4385997(1)	70.45	0.9349	-241.3339035	34.36	0.496
7.	C_I	-239.4010988	93.98	2.3638	-241.3264881(1)	39.02	1.7231
8.	C_s	-239.3884017	101.95	2.5249	-241.2850325	65.03	1.8048

**Fig. 3: Structures of different stable forms of $C_3B_5H_5^{2-}$**

$C_4B_4H_4^{2-}$

All possible sets of four B–H units were replaced by carbon in $B_8H_8^{2-}$ to generate starting structures which were then optimized and frequency calculations performed to verify that they correspond to

minima on the PES. Frequency calculation shows that three out of eight forms obtained are stable i.e., possess zero imaginary frequency and are minima on the potential energy surface, the remaining ones possess one or more imaginary frequencies. The energies and the relative energies are given in table 4. The stable forms of the molecule observed have C_{2v} , C_s and D_{2d} symmetries respectively and are shown in figure 4.

Table 4: Energies of $C_4B_4H_4^{2-}$ at RHF and B3LYP level

S. No.	Symmetry	Energy(Hartrees) RHF/6-31G	Relative Energies (kcal/mol)	Dipole moment	Energy(Hartrees) B3LYP/6-31G*	Relative Energies (kcal/mol)	Dipole moment
1.	C_{2v}	-251.1659961	0.00	0.00	-254.0572901	0.00	0.00
2.	C_s	-250.9986802	104.99	3.1784	-253.9189326	86.82	1.276
3.	D_{2d}	-250.9400132	141.81	0.00	-253.892417	103.46	0.00

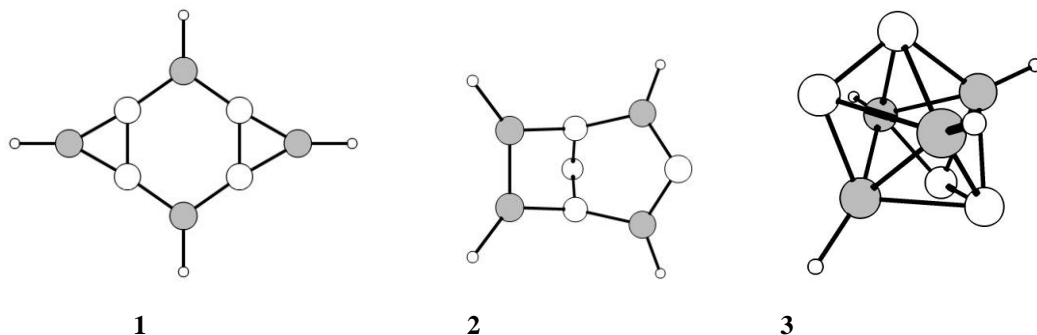


Fig. 4: Structures of different stable forms of $C_4B_4H_4^{2-}$

The structure with the symmetry C_{2v} is the most stable out of all the three stable forms obtained, however this is not a cage structure, another non-cage structure of the symmetry C_s is also obtained and is more stable than the cage structure of D_{2d} symmetry.

$C_5B_3H_3^{2-}$

In this case four stable structures were obtained by the usual method. The energies and relative energies

of the various forms of $C_5B_3H_3^{2-}$ are given in table 5. Here all of the stable forms of the molecule have either C_1 or C_s symmetry as shown in figure 5. Other forms were also observed but were not found to be stable as they possessed one or more imaginary frequencies. All the four stable isomers of the dianion $C_5B_3H_3^{2-}$ obtained are non-cage structures.

Table 5: Energies of $C_5B_3H_3^{2-}$ at RHF and B3LYP level

S. No.	Symmetry	Energy(Hartrees) RHF/6-31G	Relative Energies (kcal/mol)	Dipole moment	Energy(Hartrees) B3LYP/6-31G*	Relative Energies (kcal/mol)	Dipole moment
1.	C_s	-264.7055942	0.00	3.8658	-266.6409603	0.00	2.3372
2.	C_1	-264.7047702	0.52	2.5445	-266.6409603	7.75	1.1059
3.	C_s	-264.6808379	15.53	2.1659	-266.623195	11.14	1.7939
4.	C_1	-264.6440543	38.61	3.0248	-266.599429	26.06	1.7288

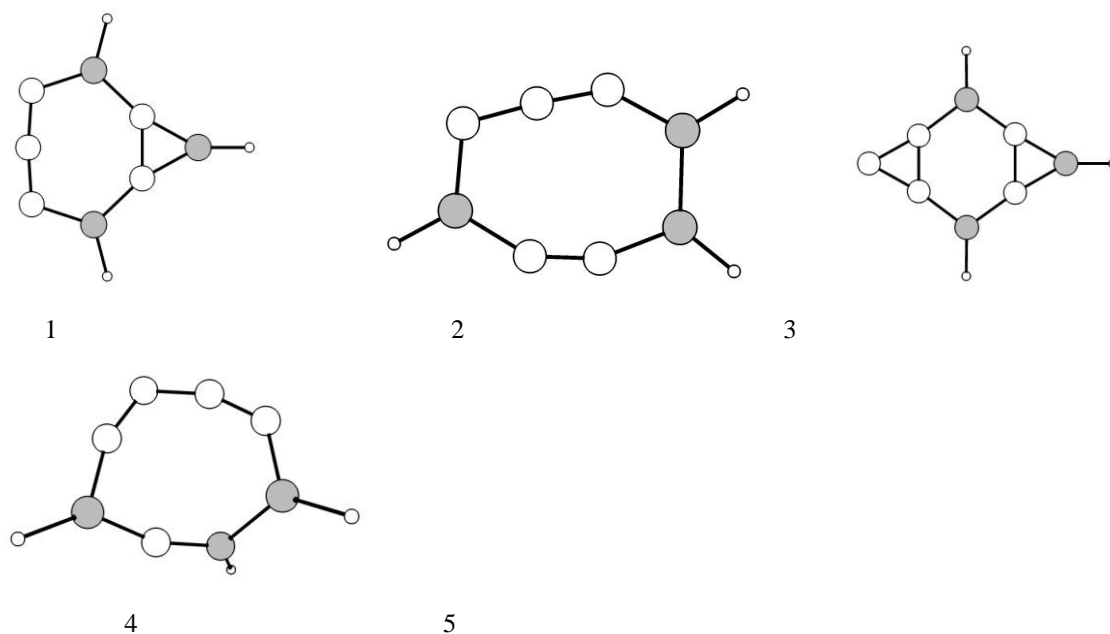


Fig. 5: Structures of different stable forms of $C_5B_3H_3^{2-}$

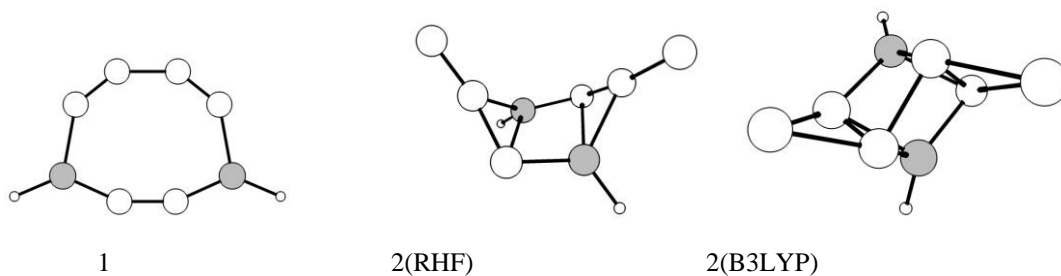
$C_6B_2H_2^{2-}$

In case of the molecules of the formula $C_6B_2H_2^{2-}$ five stable forms with C_2 and C_1 symmetry were found. The energies and the relative energies are given in table 6. The structures of the stable forms are shown in figure 6. All the structures obtained are non-cage structures. Structure 2 and 3 have different shapes on the two different levels. Structure 4 is found to be

stable on B3LYP level but it did not converge on RHF level. Structure 3 is the lowest energy form on RHF level while the lowest energy form on B3LYP level is structure 1.

Table 6: Energies of $C_6B_2H_2^{2-}$ at RHF and B3LYP level

S. No.	Symmetry	Energy(Hartrees) RHF/6-31G	Relative Energies (kcal/mol)	Dipole moment	Energy(Hartrees) B3LYP/6-31G*	Relative Energies (kcal/mol)	Dipole moment
1.	C_2	-277.2134875	65.78	3.2637	-279.1911219(1)	0.00	1.0686
2.	C_2	-277.1090695	131.31	1.4306	-279.0449568(1)	91.72	1.9752
3.	C_1	-277.3183232	0.00	4.2358	-279.1733941	11.12	0.8867
4.	C_2	Fluctuating	-	-	-279.1541673	23.18	1.7514
5.	C_1	-277.0655948(1)	158.58	0.9697	-279.1049212	54.09	0.1688



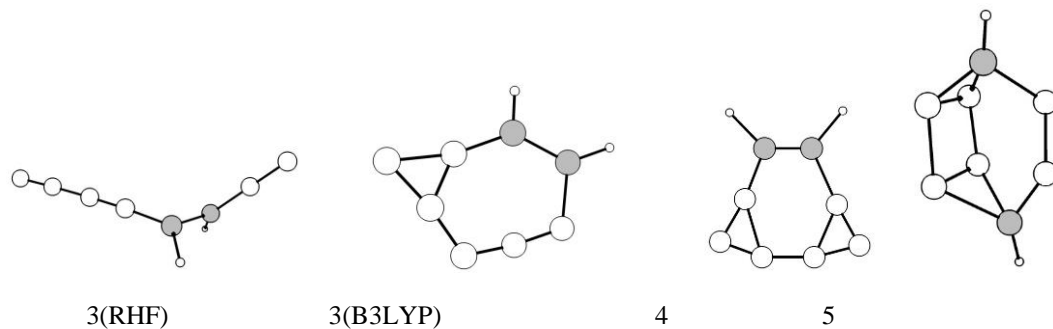


Fig. 6: Structures of different stable forms of $C_6B_2H_2^{2-}$

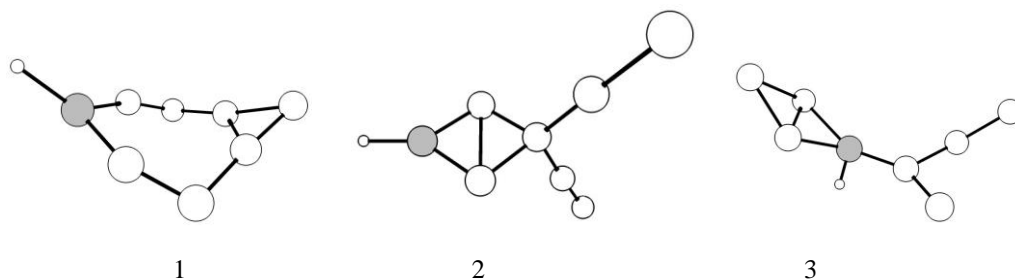
C_7BH^{2-}

There is only one boron and hydrogen remaining and rest all the B-H units have been replaced by carbons. Five isomers of this dianion have been obtained on optimizing the various structures obtained after substituting five carbons in place of five B-H units and both of them are minima on the PES. The structures of

the isomers obtained are shown in figure 7 and their energies are given in table 7. The energies obtained shows that structure 1 is the lowest energy structure on B3LYP level while structure 4 is the lowest energy structure on RHF level and important point to note is that again all the isomers obtained are non-cage structures. Structure 4 and 5 have different shapes on the two different levels.

Table 7: Energies of C_7BH^{2-} at RHF and B3LYP level

S. No.	Symmetry	Energy(Hartrees) RHF/6-31G	Relative Energies (kcal/mol)	Dipole moment	Energy(Hartrees) B3LYP/6-31G*	Relative Energies (kcal/mol)	Dipole moment
1.	C_s	-289.6811909	75.82	3.1935	-291.756098	0.00	0.8653
2.	C_{2v}	-289.7147968	54.73	8.3968	-291.7515083	2.88	7.6248
3.	C_1	-289.7110485	57.08	5.7143	-291.7413489	9.25	4.8021
4.	C_1	-289.8020223	0.00	3.5531	-291.625046	82.23	1.2587
5.	C_s	-289.6894356	70.64	2.2146	-291.5958186	100.57	1.888



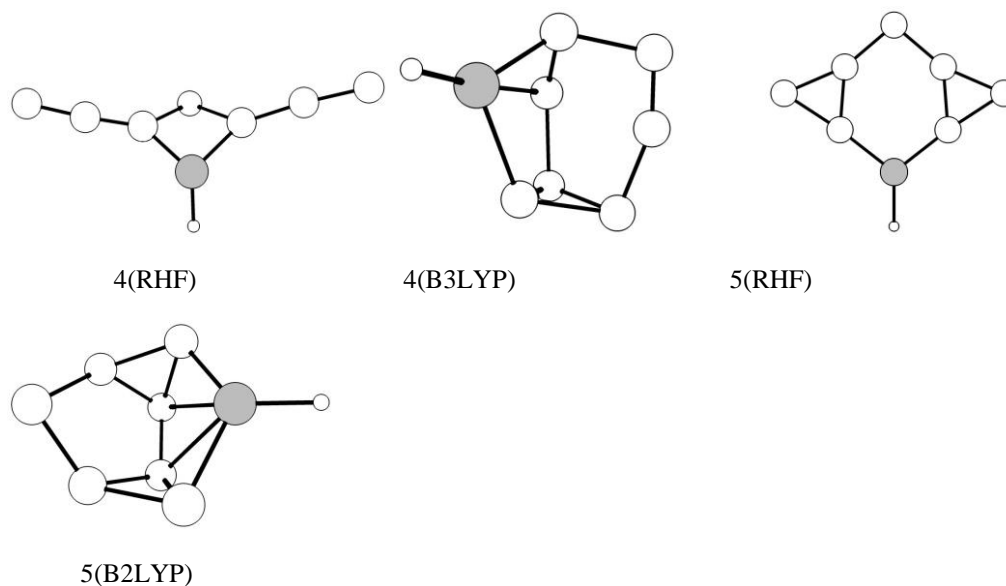


Fig. 7: Structures of different stable forms of $C_7BH_2^-$

Conclusion

From this piece of work, it has been found out that along with cage structures, non-cage structures also exist in octacarboranes dianions, and energy optimization of both of these types of structure shows that the non-cage

compounds are stable as well and as the number of carbon increases by replacing a B-H unit with carbon the stability of non-cage structures increases and that of cage compounds decreases.

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