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Investigation of closo-carboranes isoelectronic with $B_{11}H_{11}^{2-}$

Vibha Kumar[1]*, Pompozhi Protasis Thankachan[2]
[1]**Department of Chemistry, Government P.G. College, New Tehri, Uttarakhand, 249148, (INDIA)**
[2]**Department of Chemistry, Indian Institute of Technology Roorkee, Roorkee 247667, (INDIA)**
E-mail : vibhasingh25@gmail.com

ABSTRACT

The relative stabilities of the *closo*-carboranes isoelectronic with the borane $B_{11}H_{11}^{2-}$ were evaluated at the RHF/6-31G* and D95V** level and B3LYP/6-31G* and D95V** level by comparing their relative energies. Starting with the mono-*closo*borane, $CB_{10}H_{11}^{-}$ the sequential replacement of BH groups by a C unit led to the di- the tri- and the tetra-closocarborane. All the possible positional isomers were investigated and further the frequency calculation was run to filter the unstable isomers.

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KEYWORDS

Borane;
Carborane;
Closocarborane;
Mono-closoborane.

INTRODUCTION

The eleven-vertex polyhedral borane $B_{11}H_{11}^{2-}$ has been of interest due to its remarkable fluxional behavior in solution[1-4]. Studies have also been carried out on the *closo*-carboranes related to the borane $B_{11}H_{11}^{2-}$ these carboranes have polyhedral structures with triangular faces[5,6]. Among 11-vertex *closo*-carboranes, the carboranes with one and two carbons i.e, $CB_{10}H_{11}^{-}$ and $C_2B_9H_{11}$ have been studied theoretically[7,8]. Five positional isomers are possible for $CB_{10}H_{11}^{-}$, but only one isomer i.e., 2- $CB_{10}H_{11}^{-}$ has been synthesized[9] and characterized by ^{11}B NMR[10]. According to empirical valence rules of Williams[11] carbon prefers site with lower connectivity, so the order of stability should be 2-$CB_{10}H_{11}^{-}$ > 10-$CB_{10}H_{11}^{-}$ > 8-$CB_{10}H_{11}^{-}$ > 5-$CB_{10}H_{11}^{-}$ > 1-$CB_{10}H_{11}^{-}$ as the second and third positions have the lowest coordination number among all the positions. This position is coordinated to five other atoms, position one has the highest coordination number of seven and all other sites have a coordination number of six.

Schleyer et al.[7] performed optimization on all the five isomers mentioned above but could obtain only four of them as the optimization of one of the isomer 5-$CB_{10}H_{11}^{-}$ led to the most stable form i.e., 2-$CB_{10}H_{11}^{-}$. Frequency calculation performed by them showed that only three out of the four were local minima, and one of the isomer 1-$CB_{10}H_{11}^{-}$ possessed an imaginary frequency.

Dicarborane 2,3-$C_2B_9H_{11}$ has also been synthesized[8] but has not been characterized by X-ray crystallography as the compound forms an isotropic plastic mesophase at room temperature[8]. However two X-ray structures are available for the substituted $C_2B_9H_{11}$: one for 2,3-Me_2-2,3-$C_2B_9H_9$[12] and the other for 10-Br-4,7-$(OH)_2$-2,3-Me_2-2,3-$C_2B_9H_9$[13] the molecules possess the same symmetry as 2,3-$C_2B_9H_{11}$. The structure of molecule 2,3-$C_2B_9H_{11}$ has been optimized by Schleyer and Najafian[7] at RMP2/6-31G* level, by Mackie et al.[14] using MP2/6-311+G* method and by Kononova et al[8] at DFT B3LYP/6-311++G** level.

According to Kononova and co-workers[8] monocarborane species 2-$CB_{10}H_{11}^{-}$ though possess-

ing 2n+2 electrons for skeletal bonding lacks four two-center B−B bonds and according to them cannot be regarded as a genuine deltahedral *closo*-carborane. This species is however fluxional in nature[15] as shown by its ^{11}B NMR spectra in solution which is averaged. The reason for fluxionality being the absence of two-center B−B bonds. But the molecule 2,3-$C_2B_9H_{11}$ is found not to be fluxional[8]. In literature work on only two carboranes i.e., the monocarboranes and the dicarboranes of $B_{11}H_{11}{}^{2-}$ have been reported. In the present work we tried to investigate the carboranes iso-electronic with $B_{11}H_{11}{}^{2-}$ and having three and four car-bons i.e, $C_3B_8H_{10}$ and $C_4B_7H_9$.

COMPUTATIONAL METHODS

Geometry optimization of all the polyhedral struc-tures with molecular formula $B_{11}H_{11}{}^{2-}$ and their corre-sponding carboranes were carried out using 6-31G* and D95V** basis sets at RHF and B3LYP levels us-ing Gaussian 98W software package[16]. The nature of each stationary point was probed by analytical fre-quency calculations. (Single point calculations of the geometries optimized at B3LYP/6-31G** level were also done at MP4D, MP4SDQ and MP2 levels to see any significant change in the energetic.)Single point (SP) calculations were also done at the geometries optimized at the B3LYP/6-31G** level at the MP4D, MP4SDQ and MP2 levels to see if any significant change in the energetics is observed.

RESULTS AND DISCUSSION

In literature two carboranes have been reported one in which one B−H unit is replaced by carbon and the second in which two B−H units are replaced by
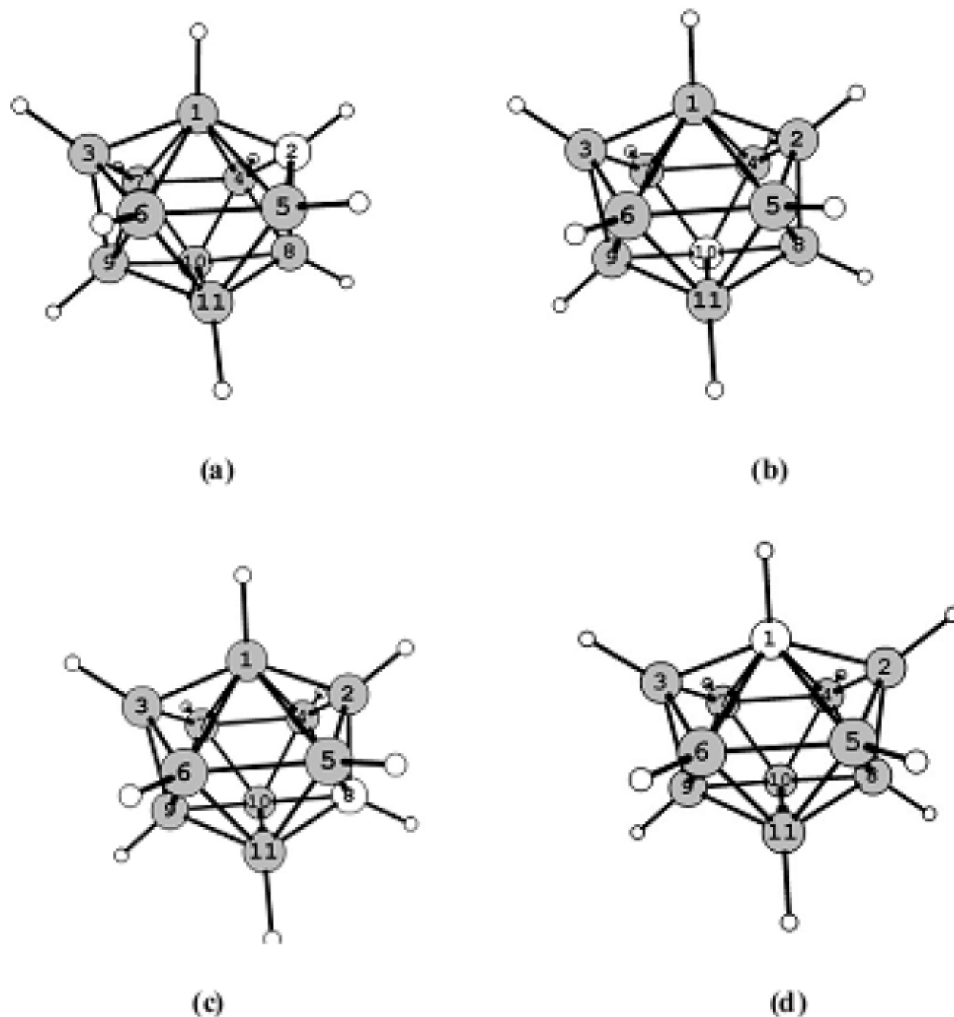

Figure 1 : Structures of stable forms of $CB_{10}H_{11}{}^{-}$ (a) 2-$CB_{10}H_{11}{}^{-}$ (b) 10-$CB_{10}H_{11}{}^{-}$ (c) 8-$CB_{10}H_{11}{}^{-}$ (d) 1-$CB_{10}H_{11}{}^{-}$

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carbons corresponding to the formula $CB_{10}H_{11}^-$ and $C_2B_9H_{11}$, but in this work we studied two more isoelectronic species of $B_{11}H_{11}^{2-}$, containing three and four carbons, with the formula $C_3B_8H_{10}$ and $C_4B_7H_9$ and previously studied $CB_{10}H_{11}^-$ and $C_2B_9H_{11}$ were also reinvestigated.

$CB_{10}H_{11}^-$

All of five positional isomers possible for the above monocarborane i.e., isomers in which the carbon occupies the position 1, position 2, position 4, position 8 and position 10 (reference frame structure (a) Figure 1) were optimized.

According to the empirical valence rule of Williams[11] the carbon prefers the site with lower connectivity, according to which the order of stability should follow the trend $2\text{-}CB_{10}H_{11}^- > 10\text{-}CB_{10}H_{11}^- > 8\text{-}CB_{10}H_{11}^- > 5\text{-}CB_{10}H_{11}^- > 1\text{-}CB_{10}H_{11}^-$. Our calculations on the different possible isomers of $CB_{10}H_{11}^-$ gave the following order of stability

TABLE 1 : Energies of different forms of $CB_{10}H_{11}^-$ in kcal/mol using different basis sets at Hartree-Fock level

Isomer	Relative energies (kcal/mol) at 6-31G*	Relative energies (kcal/mol) at D95V**
$2\text{-}CB_{10}H_{11}^-$	0.00	0.00
$10\text{-}CB_{10}H_{11}^-$	22.12	22.64
$8\text{-}CB_{10}H_{11}^-$	24.05	41.05
$1\text{-}CB_{10}H_{11}^-$	46.02	45.87

TABLE 2 : Energies of different forms of $CB_{10}H_{11}^-$ in kcal/mol using different basis sets at B3LYP level

Isomer	Relative energies (kcal/mol) at 6-31G*	Relative energies (kcal/mol) at 6-31G*
$2\text{-}CB_{10}H_{11}^-$	0.00	0.00
$10\text{-}CB_{10}H_{11}^-$	19.10	19.31
$8\text{-}CB_{10}H_{11}^-$	20.77	24.07
$1\text{-}CB_{10}H_{11}^-$	38.47	38.15

$2\text{-}CB_{10}H_{11}^- > 10\text{-}CB_{10}H_{11}^- > 8\text{-}CB_{10}H_{11}^- > 1\text{-} CB_{10}H_{11}^-$

This order is same as predicted by empirical valence rule of Williams. In this work we obtained four

positional isomers of the monocarborane $CB_{10}H_{11}^-$ out of which the carborane $1\text{-}CB_{10}H_{11}^-$ corresponded to C_{2v} symmetry and possesses one imaginary frequency at Hartree-Fock level and is also least stable; however on 6-31G*/B3LYP level it is seen to be a true minimum on the PES. All other isomers of $CB_{10}H_{11}^-$ are true minima on all the basis sets and levels studied and corresponds to C_s symmetry. Figure 1 shows all the stable

TABLE 2.1 : Single point energies of different forms of $CB_{10}H_{11}^-$ in kcal/mol using different basis sets at geometry optimized at B3LYP level

	$2\text{-}CB_{10}H_{11}^-$	$10\text{-}CB_{10}H_{11}^-$	$8\text{-}CB_{10}H_{11}^-$	$1\text{-}CB_{10}H_{11}^-$
MP4D/6-31G*	0.00	0.00	0.00	0.00
MP4SDQ/6-31G*	12.90	12.93	12.80	12.90
MP2/6-31G*	40.06	39.24	39.78	40.06

TABLE 3 : Energies of different forms of $C_2B_9H_{11}$ in kcal/mol using different basis sets at RHF level

Isomer	Relative energies (kcal/mol) at 6-31G*	Relative energies (kcal/mol) at D95V**
$2,3\text{-}C_2B_9H_{11}$	0.00	0.00
$2,9\text{-}C_2B_9H_{11}$	20.09	20.72
$2,10\text{-}C_2B_9H_{11}$	21.98	23.00
$2,4\text{-}C_2B_9H_{11}$	38.42	39.52
$8,9\text{-}C_2B_9H_{11}$	45.26	46.85
$5,6\text{-}C_2B_9H_{11}$	45.75	46.12
$2,6\text{-}C_2B_9H_{11}$	56.78	50.31
$10,11\text{-}C_2B_9H_{11}$	57.55	59.49

TABLE 4 : Energies of different forms of $C_2B_9H_{11}$ in kcal/mol using different basis sets at B3LYP level

Isomer	Relative energies (kcal/mol) at 6-1G*	Relative energies (kcal/mol) D95V**
$2,3\text{-}C_2B_9H_{11}$	0.00	0.00
$2,9\text{-}C_2B_9H_{11}$	17.32	17.79
$2,10\text{-}C_2B_9H_{11}$	18.89	19.58
$2,4\text{-}C_2B_9H_{11}$	31.70	33.87
$8,9\text{-}C_2B_9H_{11}$	39.83	41.15
$5,6\text{-}C_2B_9H_{11}$	40.96	42.34
$2,6\text{-}C_2B_9H_{11}$	23.57	12.92
$10,11\text{-}C_2B_9H_{11}$	50.96	52.50

TABLE 4.1 : Energies of different forms of $C_2B_9H_{11}$ in kcal/mol using different basis sets at RHF level

	$2,3\text{-}C_2B_9H_{11}$	$2,9\text{-}C_2B_9H_{11}$	$2,10\text{-}C_2B_9H_{11}$	$2,4\text{-}C_2B_9H_{11}$	$8,9\text{-}C_2B_9H_{11}$	$5,6\text{-}C_2B_9H_{11}$	$2,6\text{-}C_2B_9H_{11}$	$10,11\text{-}C_2B_9H_{11}$
MP4D/6-31G*	6.14	12.93	0.00	0.00	0.00	0.00	0.00	0.00
MP4SDQ/6-31G*	0.00	0.00	13.15	1352	12.51	12.57	12.77	12.97
MP2/6-31G*	26.82	27.43	39.68	39.51	40.16	40.38	40.45	38.42

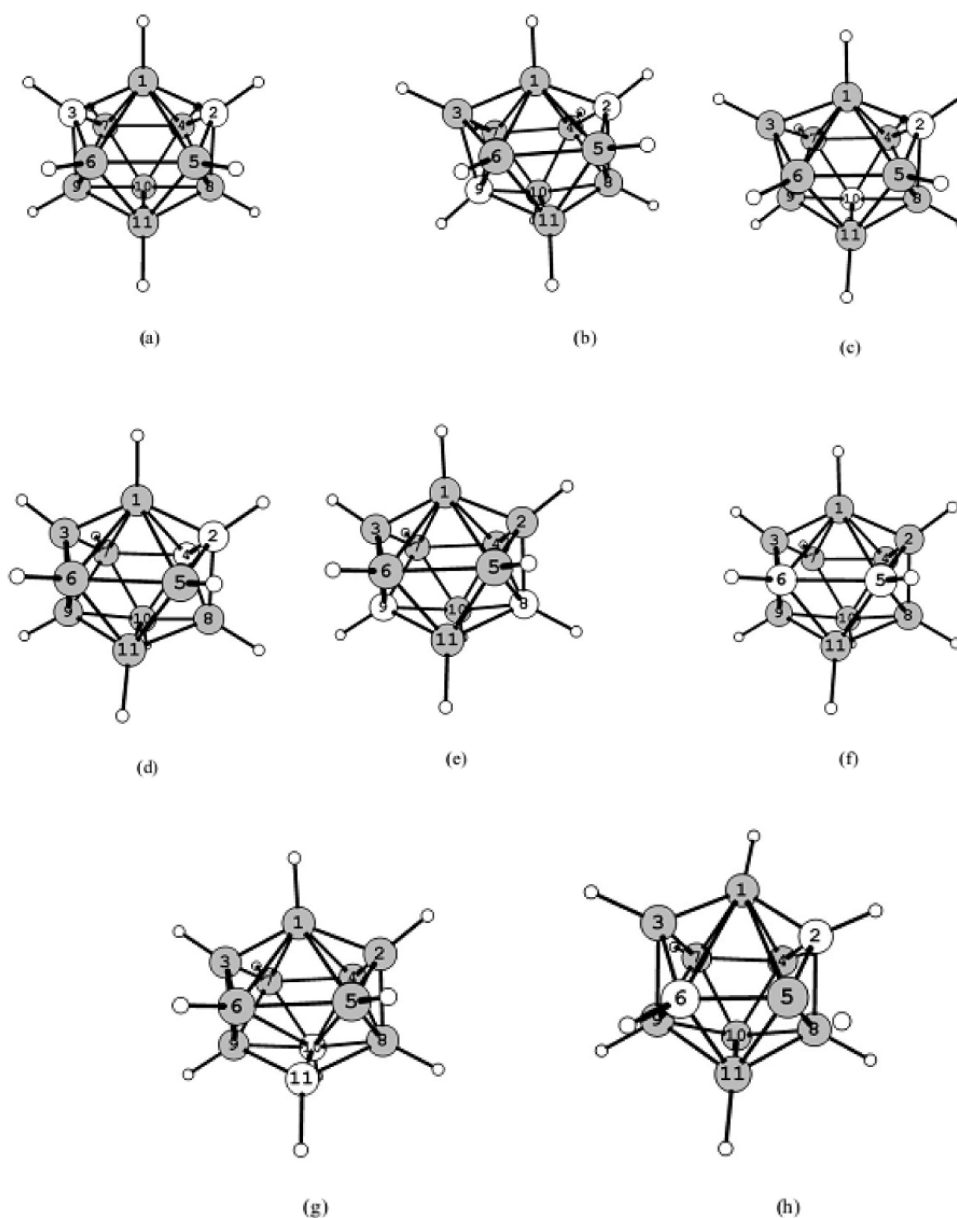*Vibha Kumar and Pompozhi Protasis Thankachan*

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Figure 2 : Structures of stable forms of $C_2B_9H_{11}$ (a) 2,3-$C_2B_9H_{11}$ (b) 2,9-$C_2B_9H_{11}$ (c) 2,10-$C_2B_9H_{11}$ (d) 2,4-$C_2B_9H_{11}$ (e) 8,9-$C_2B_9H_{11}$ (f) 5,6-$C_2B_9H_{11}$ (g) 10,11-$C_2B_9H_{11}$ (h) 2,6-$C_2B_9H_{11}$

isomers of $CB_{10}H_{11}^-$. The isomer 4-$CB_{10}H_{11}^-$ when optimized converged to the most stable form i.e., 2-$CB_{10}H_{11}^-$. The energies of all the isomers obtained are reported in the TABLES 1 and 2 respectively at RHF

and B3LYP levels, number of imaginary frequencies shown in parenthesis. It is observed that the choice of basis set or the level does not alter the stability of the different forms of the molecule $CB_{10}H_{11}^-$.

TABLE 5 : Energies of different forms of $C_3B_8H_{10}$ in kcal/mol using different basis sets at RHF level

Isomer	Relative energies (kcal/mol)	Relative energies (kcal/mol)
1,2,6- $C_3B_8H_{10}$	0.00	0.00
2,3,10-$C_3B_8H_{10}$	0.01	1.84
1,2,9-$C_3B_8H_{10}$	30.54	30.88
6,5,10-$C_3B_8H_{10}$	30.32	31.80

TABLE 6 : Energies of different forms of $C_3B_8H_{10}$ in kcal/mol using different basis sets at B3LYP level

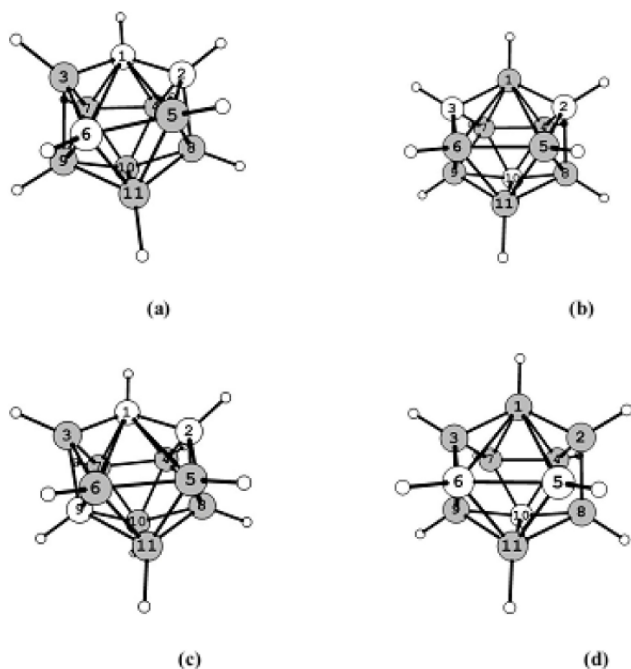| Isomer	Relative energies (kcal/mol)	Relative energies (kcal/mol)
1,2,6-$C_3B_8H_{10}$	0.00	0.00
2,3,10-$C_3B_8H_{10}$	2.72	1.63
1,2,9-$C_3B_8H_{10}$	30.74	30.63
6,5,10-$C_3B_8H_{10}$	31.44	31.54

(a)   (b)

(c)   (d)

Figure 3 : Structures of stable forms of C3B8H10 (a) 1,2,6-C3B8H10 (c) 1,2,9-C3B8H10 (d) 6,5,10-C3B8H10

$C_2B_9H_{11}$

There are twenty possible isomers possible for the dicarborane $C_2B_9H_{11}$, but only 2,3-$C_2B_9H_{11}$ has been isolated and synthesized. According to the rule of topological charge stabilization[17] the four most stable isomers of $C_2B_9H_{11}$ are the 2,3-$C_2B_9H_{11}$ 2,10-$C_2B_9H_{11}$ 2,6-$C_2B_9H_{11}$ and 2,9-$C_2B_9H_{11}$ and these isomers have the following order of stability

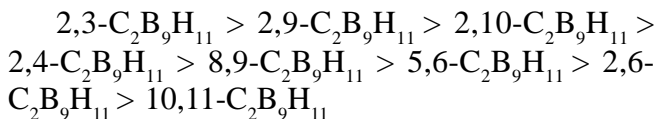**2,3-$C_2B_9H_{11}$ > 2,10-$C_2B_9H_{11}$ > 2,6-$C_2B_9H_{11}$ > 2,9-$C_2B_9H_{11}$**
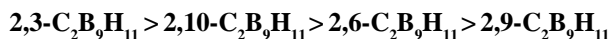
Gimarc and Ott[18] reported the energies of the above four isomers of $C_2B_9H_{11}$ using STO-3G basis set. We reinvestigated these four isomers along with the other possible isomers of $C_2B_9H_{11}$ and found eight stable forms, other forms having either converged to one of these stable forms or were found to be unstable on the PES and are not reported here.
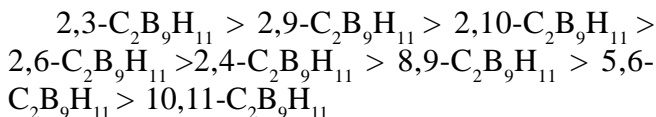
The energies of stable forms are reported in the TABLE 3 and 4 respectively at the RHF and B3LYP level. In our calculations we found the isomer 2,3-$C_2B_9H_{11}$ to be most stable in accord to that found by Gimarc and Ott. Regarding the isomer 2,6-$C_2B_9H_{11}$ both the levels gives different results, according to RHF it is of quite high energy and comes second last in the stability ordering, but at B3LYP levels both the basis sets shows this isomer to be on different position in stability order. At D95V** this isomer is most stable

after 2,3-$C_2B_9H_{11}$, but at 6-31G* it comes at fourth position after 2,10-$C_2B_9H_{11}$ in stability. Figure 2 shows the stable isomers of $C_2B_9H_{11}$. The stability order at two levels is as follows
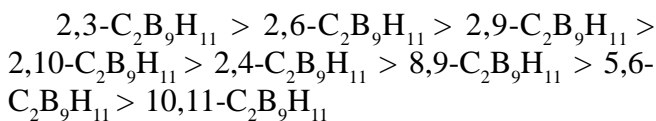
At RHF level

2,3-$C_2B_9H_{11}$ > 2,9-$C_2B_9H_{11}$ > 2,10-$C_2B_9H_{11}$ > 2,4-$C_2B_9H_{11}$ > 8,9-$C_2B_9H_{11}$ > 5,6-$C_2B_9H_{11}$ > 2,6-$C_2B_9H_{11}$ > 10,11-$C_2B_9H_{11}$

At B3LYP/6-31G* level

2,3-$C_2B_9H_{11}$ > 2,9-$C_2B_9H_{11}$ > 2,10-$C_2B_9H_{11}$ > 2,6-$C_2B_9H_{11}$ > 2,4-$C_2B_9H_{11}$ > 8,9-$C_2B_9H_{11}$ > 5,6-$C_2B_9H_{11}$ > 10,11-$C_2B_9H_{11}$

At B3LYP/D95V** level

2,3-$C_2B_9H_{11}$ > 2,6-$C_2B_9H_{11}$ > 2,9-$C_2B_9H_{11}$ > 2,10-$C_2B_9H_{11}$ > 2,4-$C_2B_9H_{11}$ > 8,9-$C_2B_9H_{11}$ > 5,6-$C_2B_9H_{11}$ > 10,11-$C_2B_9H_{11}$
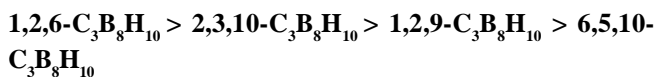
$C_3B_8H_{10}$

In literature work only two carboranes i.e., the monocarboranes and the dicarboranes of $B_{11}H_{11}^{2-}$ have been reported. In the present work we tried to investigate the carboranes isoelectronic with $B_{11}H_{11}^{2-}$ and having three and four carbons. Among various possible isomers of $C_3B_8H_{10}$ only four were found to be minima on the potential energy surface. All other had one or more imaginary frequencies. The isomer 2,3,5-$C_3B_8H_{10}$ on optimization converged to more stable form i.e., 1,2,6-$C_3B_8H_{10}$.

The energies of the stable isomers obtained at RHF and B3LYP levels are reported in the TABLES 5 and 6 respectively.

The observed order of stability is as follows:

1,2,6-$C_3B_8H_{10}$ > 2,3,10-$C_3B_8H_{10}$ > 1,2,9-$C_3B_8H_{10}$ > 6,5,10-$C_3B_8H_{10}$

The isomer 1,2,6-$C_3B_8H_{10}$ is the most stable among all the four stable isomers found for this carborane. This sequence remains unchanged by the choice of basis set and the level. Figure 3 shows the four stable isomers.

TABLE 7 : Energies of different forms of $C_4B_7H_9$ in kcal/mol using different basis sets at RHF level

Isomer	Relative energies at 6-31G* (kcal/mol)	Relative energies at D95V** (kcal/mol)
2,3,4,10-$C_4B_7H_9$	0.00	0.00
1,3,7,10-$C_4B_7H_9$	38.60	38.87

TABLE 8 : Energies of different forms of $C_4B_7H_9$ in kcal/mol using different basis sets at B3LYP level

Isomer	Relative energies at 6-31G* (kcal/mol)	Relative energies (kcal/mol) at D95V**
2,3,4,10-$C_4B_7H_9$	0.00	0.00
2,7,10,11-$C_4B_7H_9$	36.33	35.92

TABLE 8.1 : Single point calculated energies of different forms of $C_3B_8H_{10}$ in kcal/mol using different basis sets at geometry optimized at B3LYP level

	2,3,4,10-$C_4B_7H_9$	2,7,10,11-$C_4B_7H_9$
MP4D/6-31G*	0.88	0.00
MP4SDQ/6-31G*	11.65	11.91
MP2/6-31G*	37.88	35.83
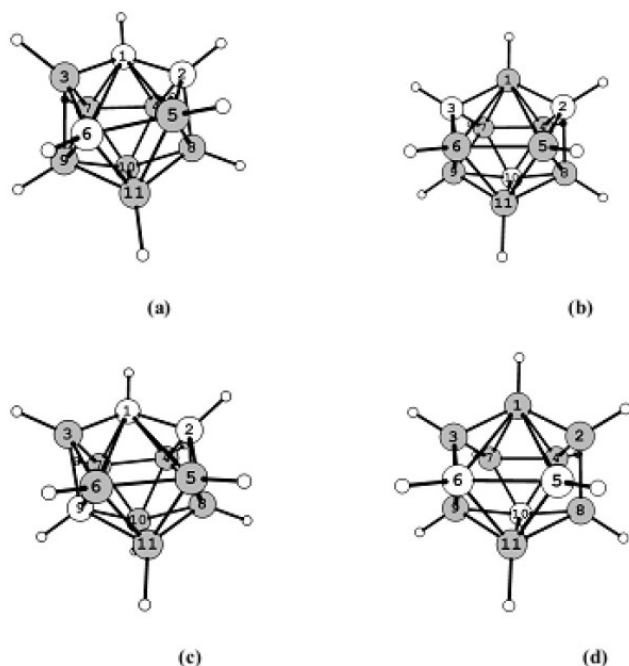
Figure 4 : Structures of stable forms of $C_4B_7H_9$ (a) 2,3,4,10-$C_4B_7H_9$ (b) 2,7,10,11-$C_4B_7H_9$

$C_4B_7H_9$

The tetra carborane $C_4B_7H_9$ is also being studied for the first time as no earlier calculations or experimental work has been reported on this system. Only two stable forms of this isomer have been found, whose energies at the RHF and B3LYP levels are reported in the TABLES 7 and 8. Figure 4 represents the geometries of these isomers. Isomer 2,3,4,10-$C_4B_7H_9$ is the stable one and the other i.e, 1,3,7,10-$C_4B_7H_9$ is higher in energy. Choice of basis sets and the level does not alter the stability of the isomers.

Single point calculations at MP4D, MP4SDQ and MP2 levels have also been done for all structures optimized at the B3LYP level using the 6-31G** basis set. The relative energies (in kcal mol^{-1}) obtained are summarized for all the structures.

CONCLUSION

Four different closo- carboranes isoelectronic with $B_{11}H_{11}^{2-}$ were investigated. Four stable positional isomers were obtained for the monocarborane, the energy sequence remained the same at both RHF and DFT level. While for the dicarborane earlier studies shows only four stable isomers at STO-3G level, on reinvestigation eight stable isomers of the same were obtained but the energy sequence differs at the RHF and DFT levels. The carboranes having three and four carbons were also investigated and four and two stable isomers respectively were obtained for them.

HIGHLIGHTS

In this piece of work, investigation has been performed on four different carboranes of $B_{11}H_{11}^{2-}$ closo borane and the findings shows some new isomers other than those found in earlier studies. Out of the four carboranes studied in this work two (i.e., $C_3B_8H_{10}$ and $C_4B_7H_9$) are studied for the first time. New stable isomers have been found for the carboranes studied earlier i.e., the monocarborane $CB_{10}H_{11}^-$ and dicarborane $C_2B_9H_{11}$.

ACKNOWLEDGMENT

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