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STUDIES ON THE STRUCTURES OF $B_8H_8^{2-}$

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INTRODUCTION

Of all the closo-boranes studied only $B_8H_8^{2-}$ and $B_{11}H_{11}^{2-}$ are found to be fluxional [1]. King [2] in his review defined the criteria for fluxionality in boranes according to which a fluxional borane is one, one or more edges of which are degenerate. This is also experimentally verified by the temperature dependent B^{11} NMR spectra which at low temperature, show several peaks but at higher temperature the peaks coalesce into a single one [3]. $B_8H_8^{2-}$ fits into these criteria and is therefore fluxional.

After the synthesis of neutral boranes by stock [4], many boranes have been found to be stable by theoretical studies. The molecule $B_8H_8^{2-}$ is of interest as it exists in different forms under different conditions. It is a slightly distorted dodecahedron (D_{2d}) in solid state as shown by X-ray diffraction studies of tetraammine Zn-salt [5,6], while in polar solvents it exists in square antiprismatic form (D_{2d}) as suggested by the single signal in B^{11} NMR [7], and in less polar solvents it exists as a bicapped trigonal prism (C_{2v}), as seen by the presence of three peaks (in the ratio 2:4:2) in NMR.

Earlier it was thought that structures of symmetries C_{2v} and D_{4d} were stable and the D_{2d} structure is a high energy form [8], but recent theoretical studies showed only two stable low energy forms of $B_8H_8^{2-}$ namely of C_{2v} and D_{2d} symmetries, which are also experimentally observed and the existence of a D_{4d} form was put in doubt [9]. Kleier and Lipscomb optimized the D_{2d} structure and their calculations yielded a slightly more compact geometry for $B_8H_8^{2-}$ than predicted by X-Ray structure [8], and C_{2v} and D_{2d} structures were predicted not to be thermodynamically stable. Bausch et al optimized the three different structures at HF level and found the stability order $D_{2d} > C_{2v} > D_{4d}$ in agreement with earlier PRDDO results [10,11]. The D_{4d} structure was found not to be the true minima due to the presence of imaginary frequencies in vibrational analysis [12]. Frequency calculations showed D_{2d} and C_{2v} symmetry structures to be true minima as they have no imaginary frequencies. These workers also found the D_{4d} structure to have two imaginary frequencies. Studies at DFT level by King [13]

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predicted only C_{2v} and D_{2d} structures to be stable with low energies and no imaginary frequencies. Two other structures of higher energies were also found, one of D_{6h} symmetry and other of the shape of "kite".

COMPUTATIONAL METHODS

The geometries were optimized at Hartree Fock and DFT (B3LYP) levels using 6-31G, 6-31G**, 6-31++G**, D95V and D95V** basis sets. The calculations were carried out using Gaussian 98. Frequencies calculations were also done along with the structure optimization. The optimized structures for $B_8H_8^{2-}$ are given in fig. 1, and the energies of the different forms of $B_8H_8^{2-}$ at RHF level using different basis sets are given in table 1, and at B3LYP level are given in table 2. The relative energies of different forms of $B_8H_8^{2-}$ in kCal/mol at RHF and B3LYP level are given in table 3 and 4 respectively.

RESULT AND DISCUSSION

We optimized different forms of $B_8H_8^{2-}$ so as to confirm the sequence of energies of different forms. The different forms were optimized at Hartree-Fock and then at DFT level, using 6-31G, 6-31G(dp), 631++G(dp), D95V, D95V(dp) and frequency calculation at optimum geometry were performed to verify that the structure corresponds to a true minima and showed that of the low energy forms the D_{2d} structure is more stable than the C_{2v} form. In earlier calculations by Bausch[12] a structure of D_{4d} symmetry was found to have two imaginary frequencies, but in the present work we have obtained D_{4d} structure different from Busch geometry which corresponds to a true minima, with all positive frequencies. Another form of D_{6h} symmetry was obtained to be a true local minimum, lower than D_{4d} symmetry and geometry with two fused pentagons of C_i symmetry was also found but is of higher energy, a kite like structure with no symmetry was also found, and all the above mentioned structures were true minima. In our work the D_{6h} structure is more stable than D_{4d} form. Earlier results of Kleier and Lipscomb at PRDDO level gave the reverse order. The various structures are shown in fig. 1. The energies obtained at RHF and DFT/B3LYP levels are shown in table 1. The overall order of stability is unaffected by choice of level basis sets and may be given as:

$$D_{2d} > C_{2v} > D_{6h} > C_1(\text{kite}) > D_{4d} > C_i\,(\text{butterfly}).$$

The molecule $B_8H_8^{2-}$ is fluxional and exists in different forms as predicted earlier[1], our calculations also gave the same results. Our work shows that the two forms D_{2d} and C_{2v} of $B_8H_8^{2-}$ molecule are interconvertable into each other. The calculations were done at two different levels, HF and DFT using the basis sets 6-31G, 6-31G** and D95V.

CONCLUSION

A stable form of $B_8H_8^{2-}$ of D_{4d} symmetry has been identified for the first time. The energy barrier for the inter-conversion of the fluxional forms of C_{2v} and D_{2d} symmetries is seen to be very low. Several structures of high energies are also characterized. D_{6h} is also found to be a stable form of $B_8H_8^{2-}$ with no imaginary frequency. Structures of the symmetries D_{3d}, D_{3h} and O_h are highly unstable. A structure with no symmetry is also found to be stable, we have given it the name "kite".

Table 1: Energies of different forms of $B_8H_8^{2-}$ at RHF level in Hartrees using different basis sets

Basis sets	C2V	D2D	D6H	Kite (C1)	D4d
6-31G	-201.9022764	-201.9052915	-201.8227304	-201.7582111	-201.7432877
6-31G**	-202.0035219	-202.0082699	-201.9158529	-201.8755596	-201.8067114
6-31++G**	-202.0229784	-202.0273609	-201.9362855		-201.8554081
D95V	-201.9168973	-201.9200326	-201.8385213	-201.7809082	-201.7756415
D95V**	-202.0212798	-202.0267125	-201.9360498	-201.8986911	-201.8459113

Table 2: Energies of different forms of $B_8H_8^{2-}$ at RHF level in Hartree using different basis sets

Basis sets	C2V	D2D	D6H	Kite (C1)	D4d
6-31G	-203.5572085	-203.5603055	-203.479188	-203.4344876	-203.3824336
6-31G**	-203.6244624	-203.6288553	-203.5416683	-203.4999347	-203.4210516
6-31++G**	-203.657881	-203.6624621	-203.5772482		-203.4684194
D95V	-203.560321	-203.5642894	-203.4859837	-203.4433195	-203.3910838
D95V**	-203.6282943	-203.6334534	-203.5500747	-203.5115122	-203.4360556

Table 3: Energies of different forms of $B_8H_8^{2-}$ at RHF level in kCal/mol using different basis sets

Structures	6-31G	6-31G**	6-31++G**	D95V	D95V**
D_{2d}	0	0	0	0	0
C_{2v}	1.89	2.98	2.75	1.96	3.41
D_{6h}	51.80	57.99	57.15	51.15	56.89
C_1(kite)	92.29	83.27		87.30	80.33
D_{4d}	101.66	126.48	105.90	90.60	113.45

Table 4: Energies of different forms of $B_8H_8^{2-}$ at B3LYP level in kCal/mol using different basis sets

Structures	6-31G	6-31G**	6-31++G**	D95V	D95V**
D_{2d}	0	0	0	0	0
C_{2v}	1.94	2.75	2.87	2.49	3.23
D_{6h}	50.90	54.71	53.47	49.14	52.32
C_1(kite)	78.95	80.89		75.91	76.52
D_{4d}	111.61	130.39	121.76	108.68	123.87

Table 5: Energies barriers of $B_8H_8^{2-}$ at RHF level

Structures	6-31G	6-31G**	D95V
D_{2d} – T.S.	2.04	3.03	1.99
C_{2v}– T.S.	0.15	0.05	0.03

Table 6: Energies barriers of $B_8H_8^{2-}$ at B3LYP level

Structures	6-31G	6-31G**
D_{2d} – T.S.	2.14	2.82
C_{2v}– T.S.	0.20	0.07

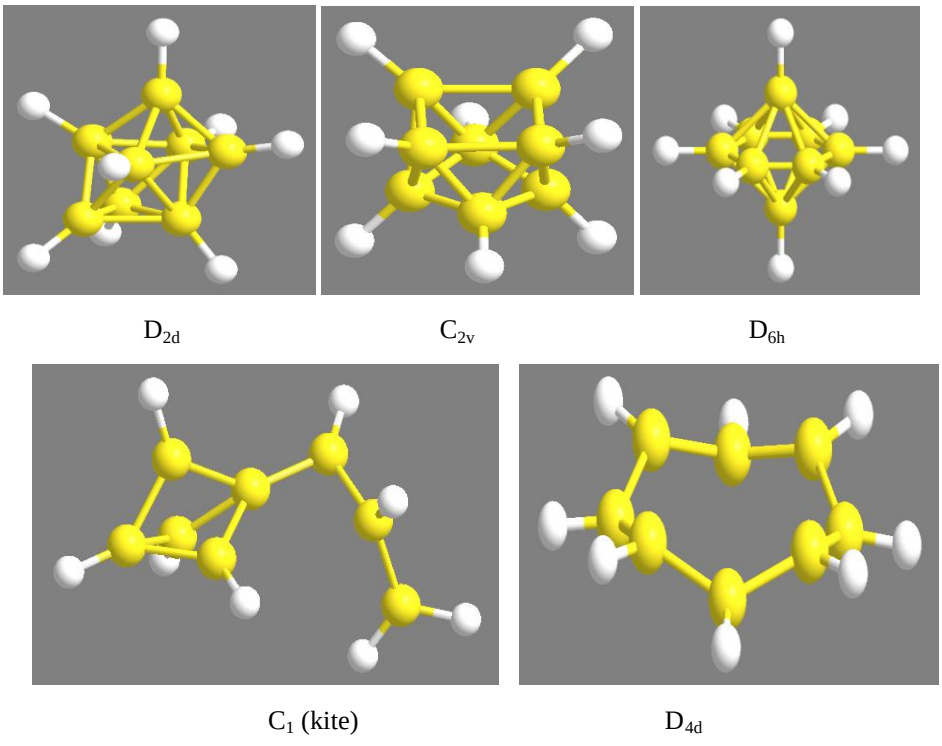

Fig. 1

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