Structural studies on $B_8H_8^{2-}$

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Abstract

Several structures of $B_8H_8^{2-}$ species have been characterized at the Hartree-Fock and Density functional (B3LYP) levels of calculation, using several basis sets in each case. Some of the previously suggested structures (D_{4d}, D_{3h}, and D_{3d} symmetries) are seen not to correspond to true energy minima on the potential energy surface and some previously unreported stable structures are identified.

Keywords: Fluxional, Closo-boranes, Boranes, Frequencies

Introduction

Amongst 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 the 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.

Many boranes have been found to be stable by theoretical studies, after the synthesis of neutral boranes by stock [4]. 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] 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 Gaussian98. 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.

Results 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:

$$D_{2d} > C_{2v} > D_{6h} > C_1(kite) > D_{4d} > C_i(butterfly).$$
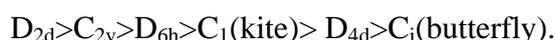
The molecule $B_8H_8^{2-}$ is fluxional and exists in different forms as predicted earlier[1], our calculations also gave the same results. Our work shows that the two forms D_{2d} and C_{2v} of $B_8H_8^{2-}$ molecule are interconvertable into each other. The calculations were done at two different levels, HF and DFT using the basis sets 6-31G, 6-31G** and D95V.

Energy barriers in the structure of symmetry C_{2v} and D_{2d} is also calculated at both the levels RHF and B3LYP, the barrier among the structure and the transition state is found to be low. The energy barriers at RHF and B3LYP are shown in table 5 and 6 respectively.

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

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 2: Energies of different forms of $B_8H_8^{2-}$ at B3LYP 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

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 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

D$_{2d}$ C$_{2v}$ D$_{6h}$
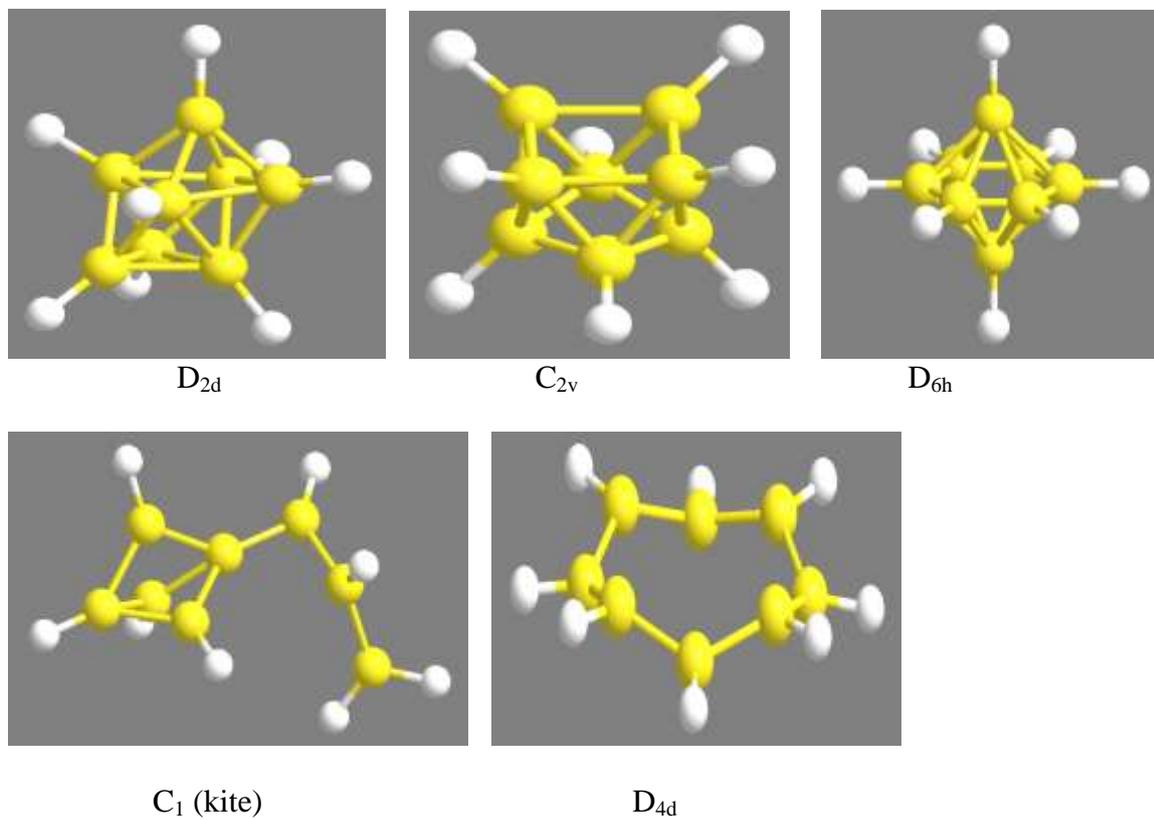
C$_1$ (kite)   D$_{4d}$

Fig. 1

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