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Molecular Structure, Vibrational Assignments and Nonlinear Optical Properties of Borazine by DFT Calculations

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ABSTRACT

In this work, density functional theory (DFT) combined with the finite field (FF) method has been adopted to study the molecular structure, vibrational assignments and nonlinear optical (NLO) properties of borazine. The geometrical parameters, vibrational frequencies and NLO properties have been obtained at B3LYP/6-311++G** level of theory. The optimized geometries and vibrational frequencies for borazine are in excellent agreement with the available experimental determinations. The B-N stretching mode observed is the most intense vibrational mode for borazine. The NLO properties of borazine have been investigated by using finite field method. The β and γ values are calculated at field strength of 0.006 a.u. for borazine using different methods and different basis sets.

Keywords : Borazine, Vibrational spectra, Finite field method, NLO properties.

I. INTRODUCTION

Molecules are the promising materials for the development of photonic devices. This is due to the fact that they have large nonlinear optical (NLO) response with an applied field [1-3]. First and second hyperpolorizabilkies of molecules are the origin of macroscopic second and third nonlinear optical response of molecules to the applied field. The possible applications of the NLO materials are in the development of photonic devices, optical processing, optical storage of data/images, optically based computers and telecommunication systems etc. [4-13]. Extensive efforts have been made to understand the NLO properties of donor-acceptor type molecules with conjugated chain in between [14-20]. Theoretical prediction of NLO properties of molecules and their suitability for the photonic applications can be tested with the help of quantum chemical methods. Once a suitable material is found with high NLO properties, one can go for its synthesis.

Borazine, the inorganic analogue of benzene, can be obtained by replacing each carbon with alternating boron and nitrogen atom. Borazine has been known for more than 30 years.

The inorganic analogue of benzene is the borazine which can be obtained by replacing each carbon with alternating boron and nitrogen atom. Borazine is more reactive than the prototype of aromatic systems. The vibrational spectrum of borazine was examined by Niedenzu et al. using isotropically labeled

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derivatives and identified the two B-N ring vibrations at 1465 and 1406 cm^{-1}.[21] Johnson and Zoellner have investigated the novel conformers of smallest possible borazine-fused Cyclacenes, Cyclo-BN-anthracene and Cyclo-BN-tetracene using Hartree-Fock and density functional theory and determined their structure and properties.[22] Erkoc has used the semiempirical molecular orbital self consistent field calculations at AM1 level within RHF formulation for the investigation of structure and electronic properties of borazine cyclacenes and found that the structure becomes more exothermic with an increase in number of borazine rings in the areniod belt.[23] The evidence for the ionic nature of B-N bond has been provided by Shen et.al. by studying the electronic structure, geometries and aromacity of borazine and its fused ring derivatives using density functional theory.[24] The substituent effect on molecular geometry and aromacity of the symmetric B-trisubstituted borazine was studied by Miao et.al. and found that the electron withdrawing substituents have shortened the B-N bonds, decrease the ∠B-N-B and increases ∠N-B-N whereas for the electron donating substituents the opposite is true.[25] Ab initio and SCF calculations have been performed by Byod et.al. for benzene, s-triazine, borazine and boraxine.[26] They found that the delocalization of the Π-electrons decreased and the polarity of ring bonds increased by substantially as the atoms in the ring become more dissimilar. The aromacities between the carbon cyclacene and borazine cyclacene have been compared by Yang te.al. using ab initio and density functional theory calculations.[27]

The aim of this work is to study the molecular structure, vibrational assignment and nonlinear optical properties of borazine using density functional theory method.

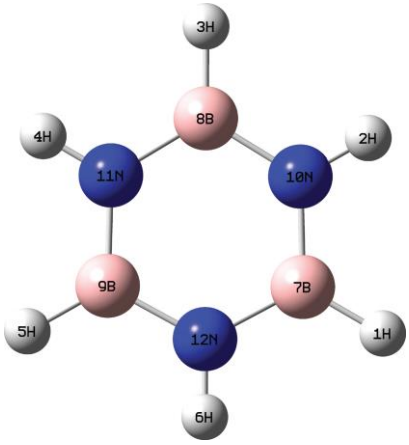
II. METHODS

The Density Functional Theory (DFT) with B3LYP exchange and correlation functional has been used for the optimization of borazine. We have used amino groups as a donor and $-NO_2$, -C≡N, -COCl and $-NMe_2$ groups as acceptors. These molecules are optimized at B3LYP/6-311++G** level of theory. The geometrical parameters of borazine at this level are compared with the available experimental determinations.[41] The vibrational frequencies are also obtained at the same level of theory. A scaling factor of 0.97 has been used for the vibrational frequencies. The vibrational frequencies of borazine are compared with the available experimental determinations.[36] The static hyperpolarizabilities β and γ are calculated using the Finite–Field method.[45] The field is applied either in X, Y or Z direction. The stable hyperpolarizabilities are obtained using different field strengths to avoid numerical instability. The static hyperpolarizabilities β and γ are also obtained for various methods and basis sets for the fixed field strength. Time dependent density functional theory (TDDFT) method has been used to obtain the absorption spectra of the molecules. All the calculations are carried out using Gaussian 03 suit of programme.[28]

III.RESULTS AND DISCUSSION

The optimized structures of borazine at B3LYP/6-311++G** level are shown in fig.1 and their geometrical parameters are represented in Table 1 alongwith the available experimental values for borazine. All the calculated geometrical parameters for borazine are in excellent agreement with the available experimental determinations.[26] The calculated bond length of B-N is elongated by 0.009, 0.009, 0.011 and 0.005 Å for NO_2, C≡N, COCl and NMe_2 as acceptor groups respectively in borazine with NH_2 as donor. The B-H bond length is shortened by 0.011, 0.006, 0.01 and 0.002 Å for NO_2, C≡N, COCl and NMe_2 as acceptors in borazine with NH_2 as donor. There is almost no change in the N-H bond length in

borazine upon donor and acceptor substitution. The C≡N bond length in NH_2-B-CN is 1.15 Å whereas C-Cl, C-O bond lengths are 1.82, 1.18 Å respectively in NH_2-B-COCl. As can be seen N-B-N angle is decreased by 1.1 and 0.3° in NH_2-B-NO_2 and NH_2-B-CN respectively than the borazine. B-N-B angle is increased by 1.1 and 0.3° in NH_2-B-NO_2 and NH_2-B-CN respectively than the borazine. H-B-N angle is increased by 0.4° in NH_2-B-NO_2 and decreased by 0.2, 0.5 and 0.4° in NH_2-B-CN, NH_2-B-COCl and NH_2-B-NMe_2 respectively than the borazine. All H-N-B angles are decreased by 0.9, 0.7, 0.8 and 0.2° respectively in NO_2, C≡N, COCl and NMe_2 as acceptors in borazines than the borazine. The calculated dipole moments are listed in Table 1. The dipole moment of borazine is close to zero whereas the substituted borazines have large dipole moment.



Infrared spectra

The calculated and experimental vibrational frequencies for borazine are in excellent agreement. Comparative vibrational spectra of borazine is shown in fig. 2. As can be seen from Fig. 2, the vibrational spectra of borazine has three vibrational modes of significant IR intensity. The most intense mode is the B-N stretching mode observed at 1435 cm^{-1} which is in close agreement with the experimental value of 1456 cm^{-1}. Other than this, the B-H stretching and N-H & B-H out-of-plane stretching modes are the second and third intense modes respectively appeared at 2533 and 905 cm^{-1}. These two modes are also in close agreement with the experimental determination of 2520 and 927 cm^{-1} respectively. Also, the N-H out-of-plane stretching and N-H stretching modes are also intense and appeared at 703 and 3521 cm^{-1} respectively.

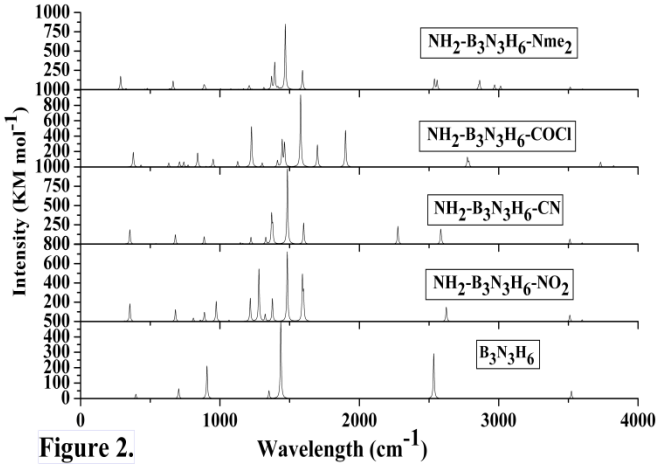


Figure 2.

Table 1 Optimized geometries for borazine at B3LYP/6-311++G** level alongwith experimental values. Bond lengths in Å, angle in degrees and dipole moment in debye.

Parameters	Expt.*	Borazine (B3N3H6)
B-N	1.436 ±0.004	1.431
B-H	1.258 ±0.020	1.191
N-H	1.050 ±0.020	1.008
<N-B-N	117.7 ±2.0	117.0
<B-N-B	121.1 ±2.0	122.9
<H-B-N	----	121.4
<H-N-B	----	118.5
Dipole moment	----	0.01D

Abbreviation: B- $B_3N_3H_6$ * Experimental values from ref [26].

Nonlinear Optical Properties

The static hyperpolarizabilities (β and γ) have been calculated by using energy based equations. We have used the finite field method, for obtaining the hyperpolarizabilities. First we applied different field strengths to calculate β and γ and to avoid numerical instability. Since the finite field equations are

sensitive to the precision in the energy calculations. We have also used β and γ for various methods and basis sets. The optimized structures at B3LYP/6-311++G** level of theory is used for β and γ calculations since at this level of theory, the geometrical parameters and vibrational frequencies for borazine are in excellent agreement with the available experimental determinations. To obtain β and γ using various basis sets and methods, the field strength is kept fixed. We have applied field either in X, Y or Z direction to study the hyperpolarizabilities by applying the field in different direction.

Figure 3 shows the variation of β and γ with field strengths for borazine. Borazine show numerically stable hyperpolarizability about field strength of 0.006 a.u. applied either in X, Y or Z direction. Therefore for the calculation of β and γ using various methods and basis sets, the field strength of 0.006 a.u. is used applied in X direction since application of field in X direction gives higher β and γ than Y or Z direction.

Figure 4 shows the variation of β and γ for borazine obtained using different methods and basis sets with the field of 0.006 a.u. applied in X-direction. In the Fig. 4 when diffuse function are added to the 6-311G basis set, the magnitude of β and γ obtained using different methods changes significantly. The magnitude of β is higher where there is no inclusion of diffuse function in the basis set. The values of β obtained using MP2 are slightly higher than the DFT method. The correlation effect by the MP2 method increases the β at the HF level. The β values using DFT with different exchange and correlation functional viz. PBE1PBE, PBEPBE, B3PW91 and BLYP are nearly equal for all the basis sets with the same method. As seen in Fig. 4(b) when diffuse functions are added to the split valence triple zeta basis set (6-311G), the magnitude of γ obtained using different methods changes significantly. The γ obtained by adding diffuse and polarization functions to the 6-311G basis sets are found to be higher than those with the 6-311G basis set for all the methods used here. The correlation effect by the MP2 and DFT method increases the γ at the HF level. For both β as well as γ, the basis set effects are more than the methods.

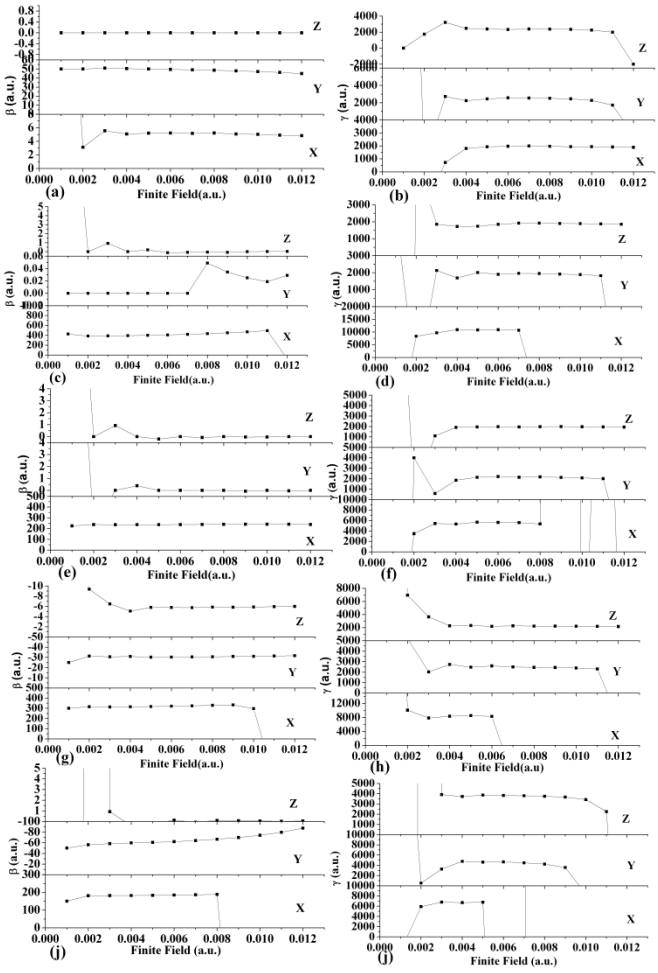
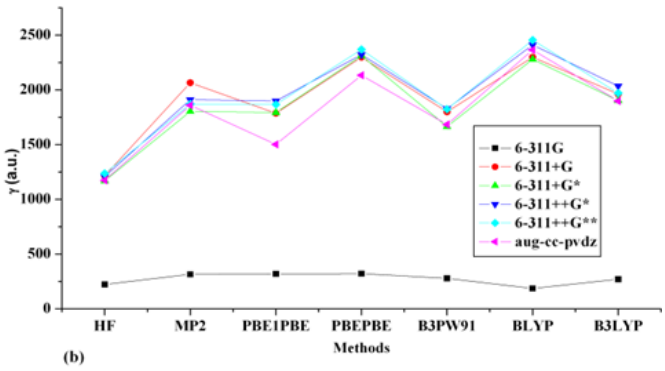


Figure 3.



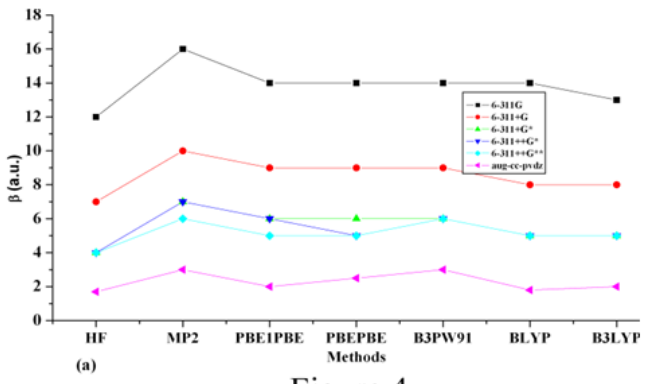


Figure 4.

IV. CONCLUSION

We have performed DFT calculations for the study of first and second hyperpolarizabilities (β and γ) of borazine. The optimized geometries and vibrational frequencies for borazine are in excellent agreement with the available experimental determinations. The B-N stretching mode observed is the most intense vibrational mode for borazine molecule and is in the excellent agreement with the experimental determinations. The substituent effect on NLO properties of borazine has been investigated by using finite field method. The β and γ values are calculated at field strength of 0.006 a.u. for borazine using different methods and different basis sets. The NO_2 as acceptor and NH_2 as donor gives highest β and γ values among the substituents used here at B3LYP/aug-cc-pvdz level of theory. A large change in dipole moment is observed upon donor-acceptor substitution in borazine.

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