

SPECTRAL ANALYSIS AND DFT STUDY ON 3,5-BIS(TRIFLUOROMETHYL) PHENYLBORONIC ACID

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Abstract : The molecular structure and vibrational spectra of 3,5-Bis(trifluoromethyl) phenylboronic acid (BTPA) is calculated with the help of B3LYP density functional theory (DFT) using 6-311G (d,p) basis set. The solid phase FT-IR spectra of BTPA have been recorded in the range 4000-400 cm⁻¹. On the basis of B3LYP calculations, the normal coordinate analysis is performed to assign the vibrational fundamental frequencies according to potential energy distribution. The over estimations of the calculated wave numbers are corrected by the aid of scaled quantum mechanical force field methodology. The computational frequencies are in good agreement with the observed results. The stability of the molecule is analyzed using NBO analysis. The calculated HOMO and LUMO energies show that the charge transfer occurs within the molecule.

Keywords – FT-IR, DFT,NBO, HOMO-LUMO

I. Introduction

Nonlinear optical (NLO) materials have recently attracted a lot of attention due to their potential use in the fields like laser technology, optical communication, optical data storage and optical signal processing [1-3]. Boron and boronic acid containing organic compounds have become an object of recent increasing interest due to their extensive application potentials in the field of material science, supermolecular chemistry, analytical chemistry, medicine, biology, catalysis organic synthesis, crystal engineering, and Non linear optics (NLO) [4]. The calculated value of HOMO-LUMO energy gap used to interpret the NLO activity of the molecule. The optimized structure of 3,5-Bis(trifluoromethyl)phenyl boronic acid is given in figure.1

II. Experimental

3,5-Bis(trifluoromethyl)phenylboronic acid was purchased from Sigma–Aldrich (St. Louis, MO, USA) and used without further purification. The FT- IR spectrum of the compound was recorded using a PerkinElmer Spectrum One FTIR spectrometer in the region 400–4000 cm⁻¹, using a KBr sample pellet, the spectrum was recorded with scanning speed of 10cm⁻¹min⁻¹ and the spectral resolution of 4.0cm⁻¹.

III. Computational details

The quantum chemical calculation of 3,5-Bis(trifluoromethyl)phenyl boronic acid has been performed using Gaussian 09 program package[5] at the B3LYP level with standard 6-311G (d,p) basis set. This has been successfully applied in order to derive the optimized geometry and vibrational wave number of the normal modes.

IV. Result and Discussion

A. Optimized Geometry

The calculated data of 3,5-Bis(trifluoromethyl)phenylboronic acid are in close agreement with the experimental values (Table1). The calculated values were compared with experimental values. The bond length of C₂-C₃ (1.413Å) in the BTMBA has been increased due to the presence of boronic acid group. The bond length of C₄-H₈ (1.086 Å) is increased due to the presence of intramolecular hydrogen bonding. The shortening of the endocyclic angle C₂-C₃-C₄ (118°) at the benzene ring and the increase in the exocyclic angle around the ring C₂-C₃-B₁₀ (122.3°) resulting from the charge transfer interaction of the benzene ring and the boronic acid group in the electron donor side of the NLO compound.

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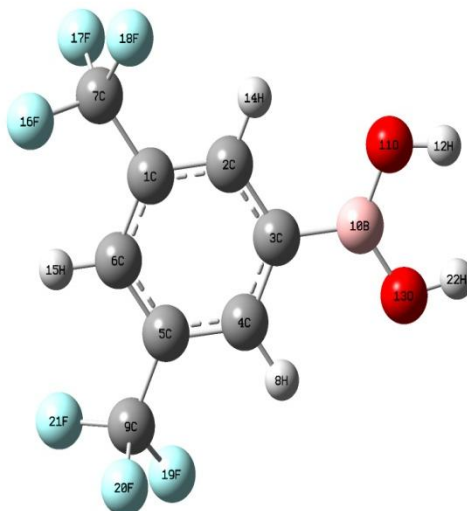


Figure1, shows the optimized structure of 3,5-Bis(trifluoromethyl)phenylboronic acid

Optimized parameters	Exp value	Cal value
C ₂ -C ₃	0.981 Å	1.413 Å
C ₄ -H ₈	0.976 Å	1.086 Å
C ₁ -C ₃ -C ₄	117.9°	118.1°
C ₂ -C ₃ -B ₁₀	121.9°	122.3°

Table 1 .Optimized bond length and bond angle

B. Vibrational Spectral analysis

The hydroxyl stretching vibrations are generally observed around 3500 cm⁻¹ [6]. In BTMBA a strong band is observed in IR at 3357cm⁻¹, which corresponds to the O-H stretching Vibration. The corresponding calculated value is found to be at 3689 cm⁻¹ with a PED of (100%). This shows that there is a red shift in the O-H stretching wave number. The band observed over a wide frequency range 1360-1000 cm⁻¹ may be due to C-F stretching vibrations[7]. The strong band observed at 1057 cm⁻¹ corresponds C-F stretching vibrations. The corresponding calculated value is 1050 cm⁻¹.

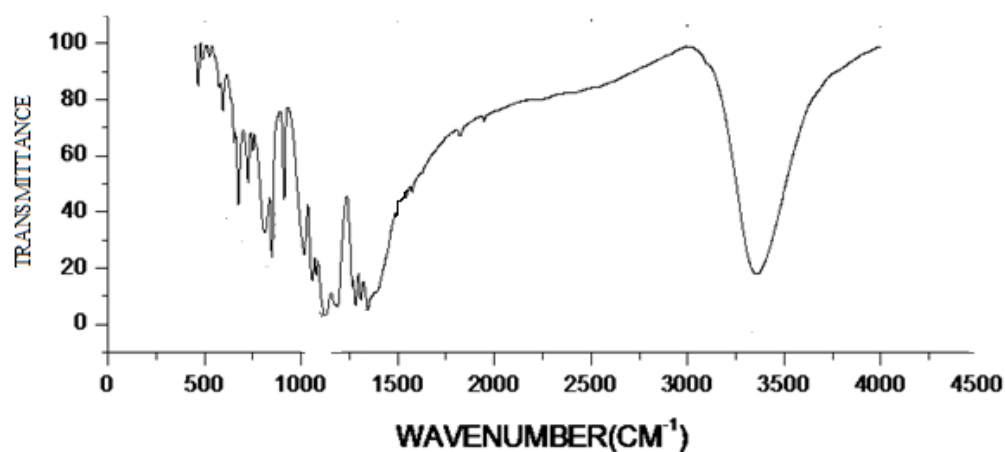


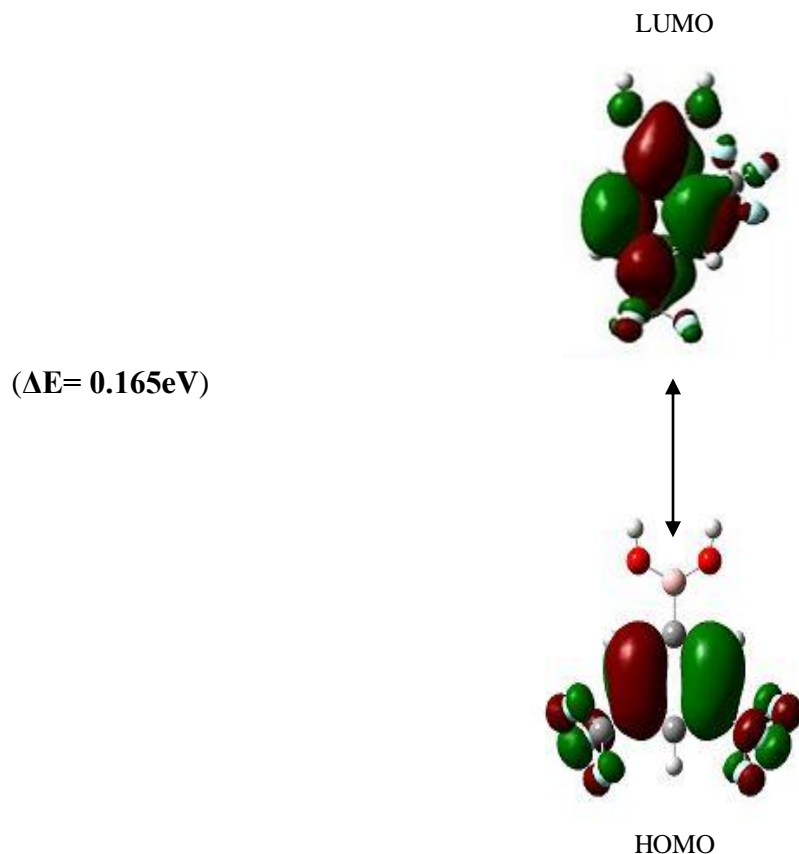
FIGURE:2 FT-IR SPECTRUM OF 3,5-Bis(trifluoromethyl)phenylboronic acid

C. NBO ANALYSIS

The stabilization energy contribution from the bond σ (C_1-C_2) \rightarrow σ^* (C_1-C_6) and σ (C_1-C_2) \rightarrow σ^* (C_3-B_{10}) interaction are 15.22, 13.26 kJ/mol respectively. This highest stabilization energy contribution occurred due to the presence of fluorine group. The intra molecular interaction is formed by the orbital overlap between bonding (σ and π ($C-C$, $C-H$, and $C-F$)) and antibonding σ^* and π^* ($C-C$, $C-H$ and $C-F$) bond orbital which results in intra molecular charge transfer (ICT) causing stabilization of the system. These interactions are observed as an increase in electron density (ED) in $C-C$ antibonding orbital that weakens the respective bonds[8].

Table 2. Second order perturbation theory.

Donar NBO(i)	E.D(e)	Acceptor NBO(j)	E.D(e)	$E^{(2)}$ KJ Mol ⁻¹
$\sigma(c_1-c_2)$	1.974 -0.739	$\sigma^*(c_1-c_6)$	0.024 0.524	15.229
$\sigma(c_1-c_2)$	1.974 -0.739	$\sigma^*(c_3-B_{10})$	0.031 0.425	13.26

HOMO-LUMO

The energies of the HOMO and LUMO based on the optimized structure are computed as 0.357 and 0.192eV respectively. The HOMO-LUMO energy gap is 0.165eV. The calculated HOMO and LUMO energies clearly show that charge transfer occurs within the molecules. The lowering of HOMO-LUMO energy gap shows the NLO activity of the molecule.

V. CONCLUSION

In the present work the complete molecular structural analysis and vibrational frequencies of the fundamental modes of the optimized geometry has been determined using DFT calculations. The highest stabilization energy contribution of the NBO analysis shows the stability of the molecule. The lowering of HOMO-LUMO energy gap shows the NLO activity of the molecule.

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