Conformational and FTIR analyses of 2,3-dimethoxyphenylboronic acid

2,3-dimethoxyphenylboronic acid isomer molekülünün konformasyonu ve FTIR analizi

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Abstract

The experimental and theoretical investigations of solvent effect on conformational structure and the hydroxyl stretching vibration of 2,3-dimethoxyphenylboronic acid (2,3-dmpba; C_{12}H_{10}O_{3}:B(OH):) molecule were studied by Fourier transform infrared (FTIR) spectroscopy and density functional theory (DFT). Calculations were performed by four conformational isomers of the title compound in eighteen different organic solvents by the polarizable continuum model (PCM). Scaled quantum mechanical (SQM) method was performed for the vibrational analysis. Most stable conformational isomer of the compound is independent of the solvent effect. Results of SQM method are very successful in determining the solvent effect on vibrational frequency. Experimental and theoretical findings from the present search will be useful to understand structural characteristics of phenylboronic acid derivatives.

Keywords: Phenylboronic acid derivatives, FTIR, DFT, SQM, Solvent effect

1 Introduction

Boronic acid is a compound related to boronic acid in which one of the three hydroxyl groups is replaced by an alkyl or aryl group. Boron and boronic acid-based include large number of potentials of related application in medicine, biology, material science and supramolecular or analytical chemistry [1-2]. A variety of typical properties of boronic acids enable them to be well suitable for practices in biomedicine [2]. Polymers including boronic acid have a wide range of uses in various biomedical applications such as management of HIV, obesity, diabetes, and cancer [3].

Phenylboronic acid (PBA) containing a phenyl substituent is an example of boronic acid. PBA and its derivatives have also attracted much attention as modifier of layer by layer films or microcapsules [4]. Molecular characteristics of PBA and its some derivatives have been studied for years. Crystal and molecular structures or some spectroscopic properties of PBA [5] and its dimer [6], diphenyl phenolboronate [7], 3-fluorophenylboronic acid [8], 4-chloro-or-bromo-phenylboronic acid [9], 2- and 4-iodo-phenylboronic acid [9], 2,4-difluorophenylboronic acid [10], 3-formylphenylboronic acid [11], 3-aminophenylboronic acid [12] were investigated.

There are many theoretical and experimental structural investigations on boronic acid derivatives such as 4-pyridineboronic acid [13], methylboronic acid [14], acenaphthene-5-boronic acid [15] and 2-thienylboronic acid [16]. Furthermore, conformational, vibrational or electronic properties of phenylboronic acid derivatives such as 4-chloro-or -bromo-phenylboronic acid [17], 3,4-dichlorophenylboronic acid [18], 2,4- or 2,6-dimethoxy phenylboronic acids [19],[20], 2,3-difluorophenylboronic acid [21], 3-bromophenylboronic acid [22], 3,5-difluorophenylboronic acid [23], 3-fluorophenylboronic acid [24], 4-mercaptophenylboronic acid [25], 4-carboxy phenylboronic acid [26], 3-(acrylamido)phenylboronic acid [27], 5-bromo-2-ethoxyphenylboronic acid [28] and pentafluorophenylboronic acid [29] were reported by combining both experimental and theoretical works. This research is a continuation of these previous studies [17]-[29] and according to the detailed literature survey there is no any theoretical or experimental studies on the structural and vibrational properties of 2,3-dmpba. The detailed analysis was performed to examine the solvent effect on conformational isomerism of 2,3-dmpba.

Further, the frequencies of hydroxyl stretch vibrations of the compound were reported by FTIR and DFT studies.

2 Experimental

2,3-dmpba was commercially obtained from Sigma Aldrich and chloroform, methanol, ethanol and dichloromethane solvents were procured from Merck. FTIR spectrum of free and solid 2,3-dmpba were optimi reported via Potassium Bromide (KBr) pellet technique by Perkin Elmer Frontier FT-IR spectrophotometer at a resolution of 2 cm⁻¹. Infrared spectra of 2,3-dmpba in the pure solvents ranged from 0.28 to 0.31 mol/L. Solvents of 25 μL were placed between CaF₂ windows whose cell thickness was 12 μm.
3 Calculational details

Many possible conformational isomers could be proposed for 2,3-dmmpba molecule. However, the discussion in this research is limited to cis-cis (CC), cis-trans (CT), trans-cis (TC) and trans-trans (TT) forms (Figure 1). Gaussian 09 was used for all calculations [30]. The optimized molecular structures were viewed with the GaussView program [31]. Calculations were performed by DFT method at B3LYP/6-31++G** in the gas phase and solutions. PCM model was employed to assess the solvent effect[32]. After, optimization processes were repeated with no geometric constraints until imaginary frequencies were not seen, calculations were performed for vibrational frequency under the same theory. Harmonic vibrational frequencies were scaled according to 0.955 [33] and SQM [34],[35]. Mole fractions for the isomers were calculated as given before [36],[37].

4 Results and discussion

Optimization energies of four isomers of the compound in eighteen different solvents are given in Table 1. Optimization energy vs. solvent dielectric constant plot of 2,3-dmmpba in CT form are also depicted in Figure 2.

Solvation is the process of interaction between solvent and solute molecules and is in part due to the attraction of a charge for a dipole. If the solute has polarity, solvent molecules will be thus drawn to the solute molecules. The greater the polarity of the solvent, the more the attraction is and therefore the more close attraction of the solvent molecules to the solute molecules is. Thus more electrostatic work is performed and so is more energy lost by the system, which inevitably turns more stable [38]. As seen from Table 1 and Figure 2, since dielectric constant of the solvent increases for the all forms, the molecule becomes more stable.

According to direction of various substituents in the gas phase, 3,4-dichloro [18], 2,4-dimethoxy [19], 2,3-difluoro [21] and 3,5-difluorophenylboronic acid [23] prefer to CT form whereas the CC conformer is the most stable for 2,6-dimethoxyphenylboronic acid [20]. Optimized relative energies and mole fractions for all forms of 2,3-dmmpba in different medium are listed in Table 2. Computed optimize energies indicate that the CT form is more stable than CC, TC and TT forms by 7.77-9.57 kcal/mol, 9.11-10.63 kcal/mol and 10.10-13.97 kcal/mol correspondingly. According to results of mole fraction computations of isomers, the title molecule prefers to CT conformational isomer with the probability of 100% for all medium (Table 2).

Table 3 presents the calculated lengths of hydroxyl bond and dipole moments of 2,3-dmmpba, from which the OH bond lengths in CT form are seen to exhibit a linear correlations with the hydroxyl stretching frequencies of the compound as $R^2=0.99484$ (C) and 0.99554 (T). Dipole moment of the compound increases gradually by solvent polarity. It is in agreement with the literature. However, it is inversely proportional with the hydroxyl stretching frequencies. As seen from Figure 3, there is good and linear correlation between OH stretching frequencies and dipole moments ($R^2=0.99466$).

Length of OH bond increases as the polarity of the solvent does. Hydroxyl stretching frequency should therefore decrease. It follows from Table 3 that this requirement is significantly fulfilled for the compound and OH frequencies decreases by increases in the bond lengths ($R^2=0.99956$). Hydroxyl stretching frequencies are inversely proportional to the polarity of the solvent (Figure 2).

OH stretching vibrations of the investigated molecule needs to special attention. Once these bands of some PBA derivatives are investigated, they are comprehensible and this suggests that the intramolecular hydrogen bondings occur in different environments of boronic acids [25]. The hydroxyl stretching bands in the infrared spectra of free 3,4-dichlorophenylboronic acid [18], 2,4- and 2,6-dimethoxyphenylboronic acid [19],[20], 2,3-difluorophenylboronic acid [21] and 5-bromo-2-ethoxyphenylboronic acid [28] were observed at 3465/3425, 3480/3339, 3335 and 3400/3332 and 3371 cm$^{-1}$ correspondingly. However, there is no any peak for 3,5-difluorophenylboronic acid [14]. OH stretching band of free 2,3-dmmpba is shown at 3368 cm$^{-1}$ for the solid phase. This observation is consistent with previously reported paper.
As seen from Table 4, they are observed at 3468 cm$^{-1}$, 3351 cm$^{-1}$, 3350 cm$^{-1}$ and 3351 cm$^{-1}$ in chloroform, dichloromethane, ethanol and methanol, respectively, as one strong and broad band. These experimental OH stretching frequencies also decrease by increasing of the dielectric constant of the solvent. In Table 4, theoretical OH stretching vibrations scaled by literature coefficient and SQM are also given together with their experimental values. Correlation values between the experimental and computed vibrational frequencies are found to be 0.76684 for scaling factor and 0.99872 for SQM. The biggest difference between the experimental and theoretical frequencies is 133 cm$^{-1}$ for scaling factor in literature and 29 cm$^{-1}$ for SQM. Hence, there is a poor agreement between the theoretically scaled frequencies by scaling factor of the B3LYP/6-31**G** and those obtained experimentally. However, the predicted values by SQM show a good correlation with experimental data and this method constitutes a reliable complement the understanding of vibrational bands of the investigated compound.

![Table 1: Optimization energy (Hartree) of 2,3-dmmba in various medium.](image)

| Medium                  | CC                           | TT                           | CT                           | TC                           |
|-------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|
| Gas phase               | -637.34875320                | -637.34173799                | -637.36400100                | -637.34706046                |
| n-hexane                | -637.35319394                | -637.34696008                | -637.36720199                | -637.35111167                |
| n-heptane               | -637.35329185                | -637.34707820                | -637.36769830                | -637.35120243                |
| Cyclohexane             | -637.35362546                | -637.34748170                | -637.36796394                | -637.35151230                |
| 1,4-dioxane             | -637.35417813                | -637.34815308                | -637.36840238                | -637.35207277                |
| Tetrachloromethane      | -637.35422626                | -637.34821172                | -637.36844044                | -637.35207277                |
| Benzene                 | -637.35433731                | -637.34834717                | -637.36852819                | -637.35217673                |
| Toluene                 | -637.35459477                | -637.34866174                | -637.36873128                | -637.35241822                |
| Diethylether            | -637.35473615                | -637.35253059                | -637.37094067                | -637.35514797                |
| Chloroform              | -637.35785270                | -637.35288547                | -637.37125964                | -637.35556333                |
| Tetrahydrofuran         | -637.35933333                | -637.35480220                | -637.37238275                | -637.35706528                |
| Dichloromethane         | -637.35980249                | -637.35541587                | -637.37273492                | -637.35755450                |
| 2-butanol               | -637.36088794                | -637.35684683                | -637.37354195                | -637.35868563                |
| 2-propanol              | -637.3613953                 | -637.35718054                | -637.37372740                | -637.35895230                |
| Acetone                 | -637.3612195                 | -637.35727806                | -637.37373184                | -637.35903041                |
| Ethanol                 | -637.36141711                | -637.35754951                | -637.37393128                | -637.35924822                |
| Methanol                | -637.36164963                | -637.35785914                | -637.37410146                | -637.35949737                |
| Acetonitrile            | -637.36171457                | -637.35794572                | -637.37414888                | -637.35956717                |
| Dimethylsulfoxide       | -637.36187993                | -637.35816643                | -637.37426945                | -637.35974535                |

![Table 2: Relative energy and mole fraction for 2,3-dmmba in various medium.](image)

| Medium                    | Relative energy (kcal/mol) | Mole fraction (%) |
|---------------------------|----------------------------|-------------------|
|                           | CC                         | TT               | CT               | TC               | CC                         | TT               | CT               | TC               |
| Gas phase                 | 9.57                       | 13.97            | -                | 10.63           | 0                          | 0                | 100              | 0                |
| n-hexane                  | 9.05                       | 12.96            | -                | 10.36           | 0                          | 0                | 100              | 0                |
| n-heptane                 | 9.04                       | 12.94            | -                | 10.35           | 0                          | 0                | 100              | 0                |
| Cyclohexane               | 9.00                       | 12.85            | -                | 10.32           | 0                          | 0                | 100              | 0                |
| 1,4-dioxane               | 8.93                       | 12.71            | -                | 10.28           | 0                          | 0                | 100              | 0                |
| Tetrachloromethane        | 8.92                       | 12.70            | -                | 10.27           | 0                          | 0                | 100              | 0                |
| Benzene                   | 8.90                       | 12.66            | -                | 10.26           | 0                          | 0                | 100              | 0                |
| Toluene                   | 8.87                       | 12.59            | -                | 10.24           | 0                          | 0                | 100              | 0                |
| Diethylether              | 8.47                       | 11.67            | -                | 9.91            | 0                          | 0                | 100              | 0                |
| Chloroform                | 8.41                       | 11.53            | -                | 9.85            | 0                          | 0                | 100              | 0                |
| Tetrahydrofuran           | 8.19                       | 11.03            | -                | 9.61            | 0                          | 0                | 100              | 0                |
| Dichloromethane           | 8.12                       | 10.87            | -                | 9.53            | 0                          | 0                | 100              | 0                |
| 2-butanol                 | 7.94                       | 10.48            | -                | 9.32            | 0                          | 0                | 100              | 0                |
| 2-propanol                | 7.90                       | 10.38            | -                | 9.27            | 0                          | 0                | 100              | 0                |
| Acetone                   | 7.89                       | 10.36            | -                | 9.26            | 0                          | 0                | 100              | 0                |
| Ethanol                   | 7.85                       | 10.28            | -                | 9.21            | 0                          | 0                | 100              | 0                |
| Methanol                  | 7.81                       | 10.19            | -                | 9.16            | 0                          | 0                | 100              | 0                |
| Acetonitrile              | 7.80                       | 10.17            | -                | 9.15            | 0                          | 0                | 100              | 0                |
| Dimethylsulfoxide         | 7.77                       | 10.10            | -                | 9.11            | 0                          | 0                | 100              | 0                |
5 Conclusions

Theoretical and experimental works have been performed by using DFT and FTIR to investigate solvent effect on the structure and hydroxyl stretching vibration of 2,3-dmpba as phenylboronic acid derivatives. There is no solvent effect on conformational isomers of the compound. Solvent induced OH frequencies are inversely proportional with the dipole moment, bond length and dielectric constant. Unscaled and scaled frequencies by B3LYP/6-31++G** have poor correlations with experimental data whereas SQM results are in excellent agreement and it is very successful in revealing the dielectric-induced solvent effect on the vibrational frequency.

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7 References

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