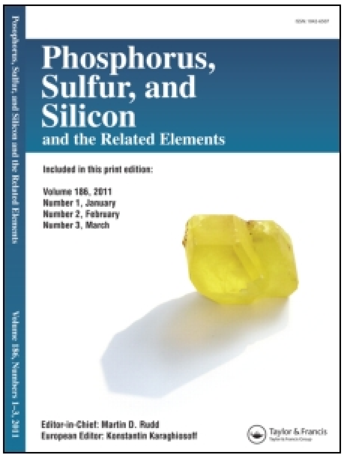

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Theoretical Study of the Interactions Between Borthiin and Fluorinated Borthiins with Difluorine

Reza Ghiasi[a]; Ali Moghimi[a]
[a] Department of Chemistry, East Tehran Branch (Qiam Dasht), Islamic Azad University, Tehran, Iran

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THEORETICAL STUDY OF THE INTERACTIONS BETWEEN BORTHIIN AND FLUORINATED BORTHIINS WITH DIFLUORINE

Reza Ghiasi and Ali Moghimi
Department of Chemistry, East Tehran Branch (Qiam Dasht), Islamic Azad University, Tehran, Iran

The nature of borthiin and fluorinated borthiin interactions with difluorine was studied with ab initio calculations. The interaction energies were calculated at the B3LYP/6-311+G(d,p) level. Vibrational and AIM analyses of the complexes indicate that the variation of densities correlates well with the obtained interaction energies. Also, the nucleus independent chemical shift (NICS) values have been used for studying aromaticity in species. These values suggest that aromaticity increases in complexes.

Keywords Atoms in molecules analysis (AIM); borthiin; borthiin complexes; fluorinated borthiins; interaction energy; nucleus independent chemical shift (NICS)

INTRODUCTION

Boron and sulfur combine to form an extensive series of molecular and solid state substances. $B_3S_3(NMe_2)_3$ was synthesized by Forstner and Muetterties.[1] The electronic structure of the borthiin has raised many questions about the potential aromaticity of these compounds. Aromaticity in borthiin and other derivatives has been studied extensively by diverse theoretical methods.[2–5]

Noncovalent interactions of unsaturated hydrocarbons involving π bond (R) with homo- or heteronuclear halogens (XY) are under active exploration, particularly through the last two decades.[6–11] A few studies have been reported on the complexes of sulfur compounds with halogen molecules.[12]

In the present study, the interactions between borthiin and fluorinated borthiins with difluorine are theoretically studied. Also, the structure, properties, and aromaticity of the borthiins and their complexes are investigated.

RESULT AND DISCUSSION

Energetic Aspects

Figure 1 shows the complexes we investigate in this article. Table I presents the computed energies, relative energies, interaction energies (IE), basis set superposition

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Address correspondence to Reza Ghiasi, Department of Chemistry, East Tehran Branch (Qiam Dasht), Islamic Azad University, Tehran, Iran. E-mail: rezaghiasi1353@yahoo.com

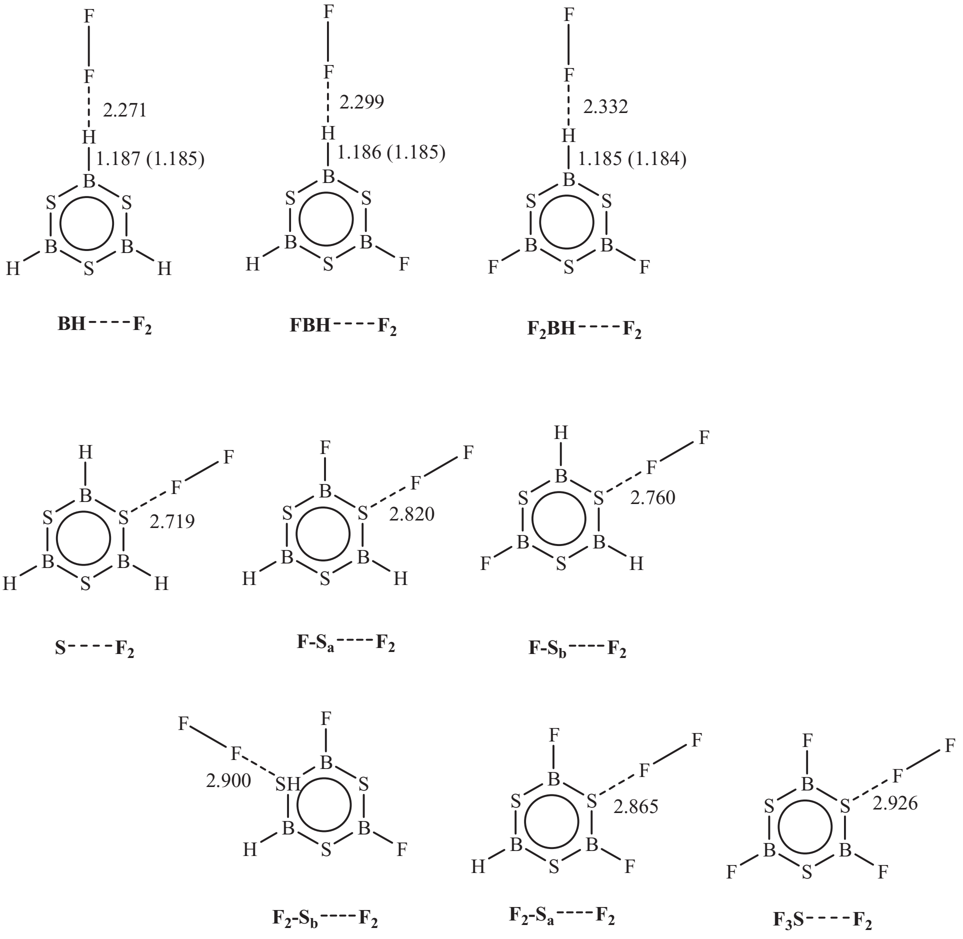

Figure 1 B3LYP/6-311+G(d,p) optimized structures of the complexes between borthiin and fluorinated borthiins with F_2. The values in parentheses correspond to the monomer.

Table I Calculated energy (Hartree), relative energy (ΔE, kcal/mol), interaction energy (kcal/mol), BSSE (kcal/mol), and corrected interaction energy (kcal/mol) for the borthiin and fluorinated borthiin complexes with F_2 by the method B3LYP and MP2 with 6-311+G(d,p) basis set

	MP2		B3LYP				
Complex	**E**	**I.E**	**E**	**ΔE**[a]	**I.E**	**BSSE**	**I.E^{corr}**
BH . . . F_2	−1468.3970	−0.908	−1470.7501	0.000	−0.502	0.432	−0.070
F-BH . . . F_2	−1567.5481	−0.907	−1570.0867	0.000	−0.473	0.412	−0.061
F_2-BH . . . F_2	−1666.6989	−0.918	−1669.4230	0.000	−0.438	0.417	−0.021
S . . . F_2	−1468.3979	−1.440	−1470.7513	0.753	−1.266	0.639	−0.627
F-S_a . . . F_2	−1567.5490[b]	−1.500[b]	−1570.0876	0.565	−1.020	0.602	−0.418
F-S_b . . . F_2	−1567.5498	−2.000	−1570.0878	0.690	−1.148	0.616	−0.532
F_2-S_a . . . F_2	−1666.6997	−1.406	−1669.4238	0.502	−0.922	0.583	−0.339
F_2-S_b . . . F_2	−1666.6997	−1.405	−1669.4237	0.439	−0.836	0.563	−0.273
F_3-S . . . F_2	−1765.8496	−1.392	−1768.7590	–	−0.792	0.546	−0.246

error (BSSE), and corrected interaction energies for the complexes of $B_3S_3H_nF_{3\text{-}n}$ (n = 0–3) with F_2. The relative energies show that the $S\cdots F_2$ isomer is more stable than the B-$H\cdots F_2$ isomer in all species. This is compatible with differences in electronegativity between hydrogen with sulfur.

It can be seen that IE and IE^{corr} values decrease with an increase of F. Also, these values show that $S\cdots F_2$ interactions are stronger than B-$H\cdots F_2$ interactions.

Geometry of the Complex

Figure 1 presents the structures and B-$H\cdots F_2$ and $S\cdots F_2$ interactions of the borthiin and fluorinated borthiin complexes.

From Figure 1, for B-$H\cdots F_2$ interactions, it can be seen that the increment of the B-H bond length is lower for fluorinated species, which suggests that the interaction in the B-$H\cdots F_2$ is weaker in fluorinated species. This is compatible with the electron withdrawing ability of F-subsituents.

As can be seen from Table I, the distance of $S\cdots F_2$ increases in fluorinated species. These values show that the strength of $S\cdots F_2$ in borthiin$\cdots F_2$ interactions is greatest, while it is poorest in F_3-$S\cdots F_2$ complexes. It can be observed that these variations have the same trend as the interaction energy. When this bond is shorter, there is the stronger interaction.

Vibrational Frequencies

The most important vibrational frequency of the proton donor, υ_1, can be approximately described as the stretching of B-$H\cdots F_2$. See Table II.

From our calculations, it can be seen that the υ_1 decreases (red shifts) and the IR intensity increases greatly in complexes in comparison with those of the isolated monomers, showing the formation of the B-$H\cdots F_2$ interaction. Also, the complex $BH\cdots F_2$ is the most stable one since there is the largest frequency shift in it (23.59 cm^{-1}), while $F_2BH\cdots F_2$ is the least stable one with the least frequency shift (only 18.39 cm^{-1}), as is consistent with the analyses of geometries and interaction energies.

Nucleus-Independent Chemical Shift

Nucleus independent chemical shift (NICS) values of borthiin, fluorinated borthiin, and the complexes of $B_3S_3H_nF_{3\text{-}n}$ (n = 0–3) with F_2 are listed in Table III. These values show that NICS values of species are all negative, which supports the existence of delocalization and aromaticity in these complexes. In order to further analyze the aromaticity, we calculated the NICS (0.5), NICS (1.0), NICS (1.5), and NICS (2.0) values by placing a ghost atom

Table II Calculated υ(B-H) (cm^{-1}) and IR intensity (KM/mol) for the borthiin and fluorinated borthiins and their complexes with F_2 by the method B3LYP with 6-311+G(d,p) basis set

Complex	υ(B-H) in complex	υ(B-H) in monomer	IR intensity in complex	IR intensity in monomer
$BH\cdots F_2$	2641.88	2665.47	332.1	124.0
F-$BH\cdots F_2$	2646.39	2667.18	278.1	120.2
F_2-$BH\cdots F_2$	2655.82	2674.21	224.8	71.7

Table III Calculated NICS (0.0), NICS (0.5), NICS (1.5), NICS $(1.5)_{zz}$, and NICS (2.0) (ppm) for the borthiin and fluorinated borthiins and their complexes with F_2 by the method B3LYP with 6-311+G(d,p) basis set

Complex	NICS (0.0)	NICS (0.5)	NICS (1.0)	NICS (1.5)	NICS $(1.5)_{zz}$	NICS (2.0)
$B_3S_3H_3$	−1.16	−2.08	−3.21	−2.54	−7.67	−2.54
$B_3S_3FH_2$	−1.56	−2.19	−2.93	−2.78	−6.16	−2.14
$B_3S_3F_2H$	−2.99	−3.20	−3.25	−2.71	−5.75	−1.96
$B_3S_3F_3$	−4.09	−3.97	−3.46	−2.61	−5.19	−1.78
$BH\cdots F_2$	−1.31	−2.21	−3.31	−3.28	−7.65	−2.60
$F\text{-}BH\cdots F_2$	−1.87	−2.49	−3.15	−2.92	−6.37	−2.24
$F_2\text{-}BH\cdots F_2$	−3.30	−3.46	−3.40	−2.80	−5.78	−2.02
$S\cdots F_2$	−1.22	−2.10	−3.21	−3.21	−7.34	−2.55
$F\text{-}S_a\cdots F_2$	−2.16	−2.65	−3.14	−2.85	−6.13	−2.16
$F\text{-}S_b\cdots F_2$	−1.71	−2.28	−2.97	−2.82	−5.91	−2.18
$F_2\text{-}S_a\cdots F_2$	−3.30	−3.48	−3.43	−2.83	−5.88	−2.05
$F_2\text{-}S_b\cdots F_2$	−3.54	−3.62	−3.44	−2.79	−5.79	−2.00
$F_3\text{-}S\cdots F_2$	−4.12	−3.99	−3.49	−2.65	−5.01	−1.82

above (by 0.5, 1.0, 1.5, 2.0 Å) the center of the six-membered ring. It is worth noting that the maximum negative value of NICS is found at the about 1.5 Å above the center of the ring (NICS, 1.5). For this reason, NICS (1.5) may be more appropriate for these systems with more important π-aromatic character.[13] The NICS (1.5) values show that all complexes are less aromatic than borthiin. Also, these values show that aromaticity increases in the complexes. On the other hand, aromaticity of $S\cdots F_2$ complexes is more than $BH\cdots F_2$ complexes.

The correlation between NICS (1.5) and NICS $(1.5)_{zz}$ is good (Figure 2). There is not a good correlation between the NICS (0.0) and NICS $(1.5)_{zz}$ values ($R^2 = 0.7405$, Figure 2). This indicates that these two NICS values measure rather different effects. It is likely that the NICS $(1.5)_{zz}$ better explains the π aromaticity effects, whereas NICS (0.0) results better reveal both the σ and π aromaticity or antiaromaticity effects. Therefore, the correlation between these two NICS values is rather low.

Atoms in Molecules Analysis

Table IV lists the values of ρ and $\nabla^2\rho$ of the complexes at the B3LYP/6-311+G(d,p) level. It contains the electron densities at the bond critical points of $B\text{-}H\cdots F_2$ and $S\cdots F_2$ interactions. Different features of the electron densities analysis that were obtained in the AIM framework are summarized as follows:

1. All the bond critical points (BCP) of $B\text{-}H\cdots F_2$ and $S\cdots F_2$ interactions are characterized by small $\rho(r)$ values and positive Laplacian of the electron density. The sign of the Laplacian is determined by the positive curvature of $\rho(r)$ along the interaction line, as the Pauli Exclusion Principle leads to a relative depletion of charge density in the interatomic surface. These interactions are dominated by the contraction of charge density away from interatomic surface toward each of the interacting species. It has been confirmed that the electron density at the BCP can be used as a measure of the binding strength. The Laplacians $\nabla^2\rho$ are all positive, indicating the typical closed-shell interactions in the complexes. Figure 3 represents the plot of calculated interaction

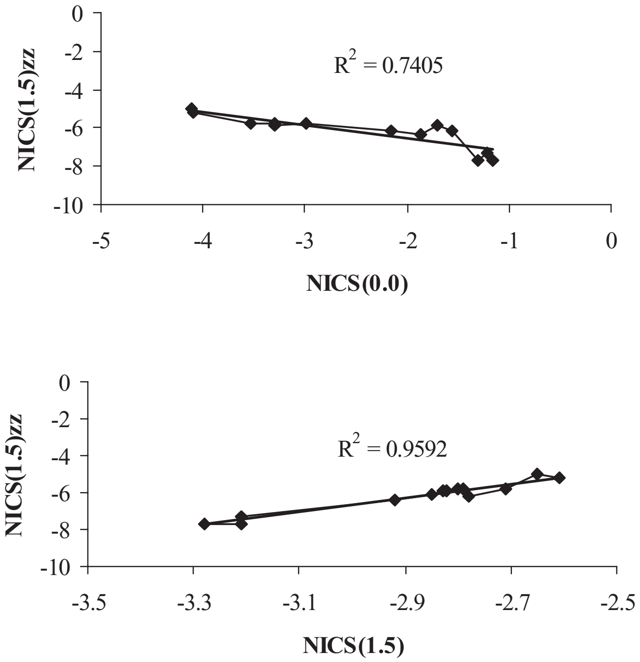

Figure 2 Correlation between the NICS (1.5)zz with NICS (0.0) and NICS (1.5)zz with NICS (1.5) for the complexes.

energies of borthiin$\cdots F_2$ complexes versus their electron density at the BCP($S\cdots F_2$) and BCP($B\text{-}H\cdots F_2$), which indicates the regression coefficient of 0.9512.

2. Figure 4 shows the bond length of $B\text{-}H\cdots F_2$ and $S\cdots F_2$ versus the density at the BCP of $B\text{-}H\cdots F_2$ and $S\cdots F_2$ of borthiin$\cdots F_2$ complexes, which indicates the regression coefficient of 0.9988 and 0.9913, respectively.
3. Figure 5 indicates the correlation between the interaction energy versus the Laplacian at the BCP of $B\text{-}H\cdots F_2$ and $S\cdots F_2$ for the complexes. This diagram shows the regression coefficient of 0.9747.

Table IV Electron densities ρ (e/a_0^3) and Laplacians $\nabla^2\rho$ (e/a_0^5) for borthiin and fluorinated borthiin complexes with F_2 by the method B3LYP with 6-311+G(d,p) basis set within the AIM theory

Complex	ρ(F$\cdots$H or S)	∇^2(F$\cdots$H or S)	ρ(3,+1)	∇^2(3,+1)
$B\text{-}H\cdots F_2$	0.0100	0.0378	0.0104	0.0476
$F\text{-}BH\cdots F_2$	0.0094	0.0355	0.0102	0.0462
$F_2\text{-}BH\cdots F_2$	0.0086	0.0325	0.0100	0.0448
$S\cdots F_2$	0.0187	0.0698	0.0103	0.0476
$F\text{-}S_a\cdots F_2$	0.0147	0.0561	0.0102	0.0460
$F\text{-}S_b\cdots F_2$	0.0169	0.0639	0.0102	0.0460
$F_2\text{-}S_a\cdots F_2$	0.0132	0.0510	0.0100	0.0447
$F_2\text{-}S_b\cdots F_2$	0.0121	0.0472	0.0100	0.0447
$F_3\text{-}S\cdots F_2$	0.0113	0.0447	0.0098	0.0435

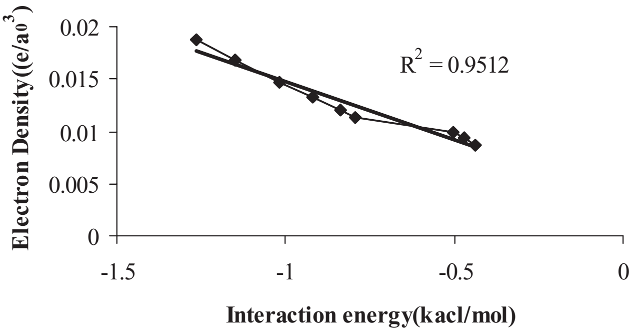

Figure 3 Correlation between the interaction energies and the density at the BCP of B-H$\cdots$F$_2$ and S$\cdots$F$_2$ for the complexes.

4. Among all complexes, the obtained value for electron density is larger for the S$\cdots$F$_2$ interactions. This is compatible with interaction and relative energies results. These values decrease with the number of F.
5. Figure 6 shows NICS(1.5) versus the Laplacian at the ring center [$\nabla^2(3,+1)$] for the complexes, which indicates the regression coefficient of 0.9036.

COMPUTATIONAL METHODS

Becke's hybrid three-parameter exchange functional methods and the nonlocal correlation functional methods of Lee, Yang, and Parr (B3LYP)[14] in combination with

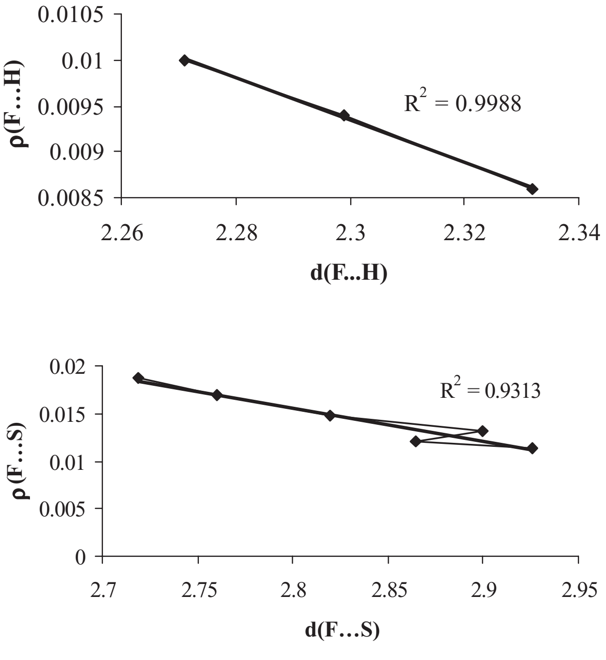

Figure 4 Correlation between the bond length of B-H$\cdots$F$_2$ and S$\cdots$F$_2$ versus the density at the BCP of B-H$\cdots$F$_2$ and S$\cdots$F$_2$ for the complexes.

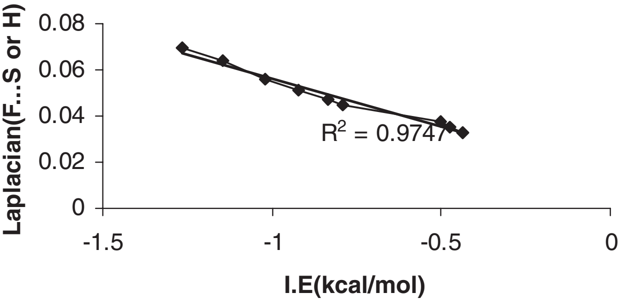

Figure 5 Correlation between the interaction energy versus the Laplacian at the BCP of BH$\cdots$F$_2$ and S$\cdots$F$_2$ for the complexes.

6-311+G(d, p)[15] basis sets for B, O, S, H, F have been used for searching the most stable structures. In all cases, the steady-state nature (minimum on the potential energy surface) of the optimized structures has been confirmed by calculating the corresponding frequencies at the same computational level. All the calculations have been performed using the GAUSSIAN 2003 quantum chemical package.[16]

The nucleus independent chemical shift (NICS) was used as a descriptor of aromaticity from the magnetic point of view. The index is defined as the negative value of the absolute magnetic shielding computed at ring centers[17] or another interesting point of the system.[18] The NICS denoted as NICS(2) is calculated 2 Å above the ring center and is expected to better reflect the π-electron structure details.[19] Rings with highly negative values of NICS are quantified as aromatic by definition, whereas those with positive values are antiaromatic.

Interaction energies have been corrected for basis set superposition error (BSSE) using the counterpoise correction method of Boys and Bernardi.[20]

Wave function files were generated from the Gaussian output files at the B3LYP/6-311+ G(d,p) level of theory to perform AIM calculations.[21] Here, the topological properties of the electronic charge density have been characterized using the AIM methodology with the AIM2000 program package.[22–24] on the wave functions obtained at the B3LYP/6-311+ G(d,p) level.

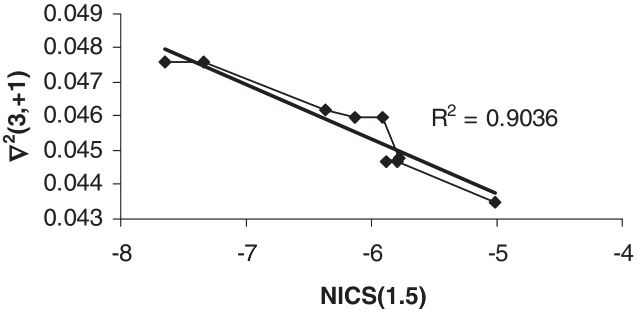

Figure 6 Correlation between the NICS (1.5) and the Laplacian at the ring center [∇^2(3,+1)] for the complexes.

CONCLUSION

In the present theoretical study, the interactions of borthiin and fluorinated borthiins with difluorine have been investigated. The calculations suggest that the interactions are weaker in fluorinated borthiin$\cdots F_2$ complexes. The results also show that $S\cdots F_2$ interactions are stronger than B-H$\cdots F_2$ interactions. The NICS values show that aromaticity increases in the complexes. Also, aromaticity of $S\cdots F_2$ complexes is more than B-H$\cdots F_2$ complexes. In addition, the results of AIM analyses show that the density at the $S\cdots F_2$ and B-H$\cdots F_2$ critical points is a useful measurement for the interaction strength.

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