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## Theoretical insights into the properties of the borazine...X<sup>-</sup> complexes (X<sup>-</sup> = H, F, Cl, CN, NC or NCO)

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**Abstract:** The character of the NH...X<sup>-</sup> (X<sup>-</sup> = H, F, Cl, CN, NC or NCO) interactions of borazine with anions was studied using *ab initio* method. The interaction energies were calculated at the B3LYP/6-311++G(d,p) level. The energetic and geometric characteristics of the complexes were compared. The “atoms in molecules” methodology was used to analyze the electron density and to obtain atomic contributions to the total energy and charge of the systems. Natural bond orbital (NBO) analysis demonstrated the charge transfer in the study of the nature of the intermolecular interactions. The aromaticity of these compounds was predicted in light of the nucleus-independent chemical shift (NICS).

**Keywords:** borazine; borazine complexes; interaction energy; NBO; AIM methodology.

### INTRODUCTION

Inorganic cyclic ring systems that are isoelectronic with benzene, of which borazine is a textbook example of a six- $\pi$ -electron six-membered ring, have been known for many years.<sup>1</sup> Many derivatives of borazine have been synthesized and well characterized.<sup>2</sup> Theoretical studies showed that the six  $\pi$ -electrons are significantly localized on the nitrogen atoms, due to the large electronegativity difference between boron and nitrogen.<sup>3</sup> Whether borazine is aromatic remains a controversy,<sup>4</sup> but it is a fact that borazine is considerably less aromatic than benzene.

This paper studies the complex formed by interaction between borazine and X<sup>-</sup> anions (X<sup>-</sup> = H, F, Cl, CN, NC or NCO). The optimized structures, the interaction energies and natural population analysis (NPA) are discussed.

The “atom in molecules” (AIM) methodology of Bader was also applied to study the properties of the bond critical point of the X<sup>-</sup> and borazine contacts to

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analyze the dependencies between topological, energetic, and geometrical parameters of the complexes.

#### CALCULATION METHODS

The structures of borazine and  $X^-$  ( $X^- = H, F, Cl, CN, NC$  or  $NCO$ ) were optimized by the B3LYP method and 6-311++G(d,p) was chosen as the basis set.

The optimization was realized together with a frequency calculation for each complex to verify that the geometry was the real minimum without any imaginary frequency.

The interaction energy,  $IE$ , can be evaluated from the difference between the energy of the complex and the sum of the energies of borazine and  $X^-$ :

$$IE = E(\text{complex}) - (E(\text{borazine}) + E(X^-))$$

The calculated interaction energies were corrected for basis set superposition errors (BSSE), which were computed for all calculations using the counterpoise correction method of Boys and Bernardi.<sup>5</sup>

All electronic structure calculations were performed using the Gaussian 98 program.<sup>6</sup>

Population analysis was also performed by the natural bond orbital method<sup>7</sup> at the B3LYP/6-311++G(d, p) level of the theory using the NBO program<sup>8</sup> under the Gaussian 98 program package.

AIM Methodology was applied to analyze the electron density and its corresponding Laplacian at the critical point of the  $B_3N_3H_6 \cdots X^-$  contact from the structures of  $B_3N_3H_6 \cdots X^-$  optimized at the B3LYP/6-311++G(d, p) level. Topological analyses was performed with the AIM 2000 program<sup>9</sup> using B3LYP/6-311++G(d, p) wave functions as the input.

#### RESULTS AND DISCUSSION

##### *Energetic*

The computed interaction energies ( $IE$ ) and the corrected interaction energies ( $IE^{\text{corrected}}$ ) for the  $B_3N_3H_6 \cdots X^-$  complexes ( $X = H, F, Cl, NC, CN$  or  $NCO$ ) (Fig. 1) are presented in Table I. For a given complex,  $IE$  was the largest for  $X = F$ , which is in agreement with analyses from the distance  $r(H \cdots X)$ .

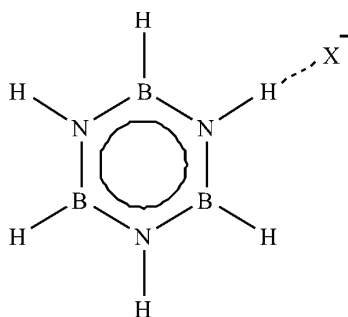


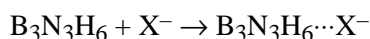
Fig. 1. Geometry of the borazine $\cdots X^-$  complexes ( $X^- = H, F, Cl, CN, NC$  or  $NCO$ ).

##### *Thermochemical analysis*

Thermochemical analysis was performed for all the complexes. The values of  $\Delta H$ ,  $\Delta S$  and  $\Delta G$  are reported in Table II, whereby the individual terms refer to a temperature of 298 K. The reaction can be considered as:

TABLE I. Calculated energy (Hartree), interaction energy (*IE*), *BSSE*, corrected interaction energy, *r*(H...X) for borazine...X<sup>-</sup> complexes by the B3LYP method with the 6-311++G(d,p) basis set

X <sup>-</sup>	<i>E</i> Hartree	<i>IE</i> kcal mol <sup>-1</sup>	<i>BSSE</i> ×10 <sup>3</sup> Hartree	<i>IE</i> <sup>corrected</sup> kcal mol <sup>-1</sup>	<i>r</i> (H...X) Å
H	-243.3064214	-14.8644	1.264305116	-14.0710	1.45814
F	-342.6796508	-26.5987	3.227830862	-24.5732	1.34335
Cl	-703.0702164	-11.2445	0.682776676	-10.8161	2.19947
CN	-335.6559382	-11.8542	0.271105435	-11.6841	2.00025
NC	-335.6566621	-12.3085	0.337451621	-12.0967	1.86189
NCO	-410.9556042	-12.8988	0.452088312	-12.6151	1.82806



As can be seen, the  $\Delta S$  values are similar for all complexes. Since in this reaction two particles form one,  $\Delta S$  should have a negative value, although the relative difference of  $\Delta G$  is almost the same as that for the  $\Delta H$ . The equilibrium constants of the all complexes are also given in Table II, from which it can be seen that the equilibrium constant is the largest for X<sup>-</sup> = F.

TABLE II. Calculated thermodynamic parameters for the for the borazine...X<sup>-</sup> (X<sup>-</sup> = H, F, Cl, CN, NC or NCO) complexes by the B3LYP method with the 6-311++G(d,p) basis set

X <sup>-</sup>	$\Delta G$ / kcal mol <sup>-1</sup>	$\Delta H$ / kcal mol <sup>-1</sup>	$\Delta S$ / kcal mol <sup>-1</sup> K <sup>-1</sup>	<i>K</i>
H	-9.45657	-15.908	-0.02165	8.6×10 <sup>6</sup>
F	-21.4715	-28.5925	-0.0239	5.6×10 <sup>15</sup>
Cl	-5.27171	-11.4615	-0.02077	7.3×10 <sup>3</sup>
CN	-4.31789	-11.4044	-0.02378	1.5×10 <sup>6</sup>
NC	-4.49171	-11.7777	-0.02445	2.0×10 <sup>3</sup>
NCO	-5.97828	-12.3343	-0.02133	2.4×10 <sup>4</sup>

#### Atoms in molecules analysis

Analysis of the electron density by means of the Bader atoms in molecules (AIM) methodology provides useful tools to confirm the presence of NH...X<sup>-</sup> interactions between borazine and X<sup>-</sup>.

The values of  $\rho$ , eigenvalues of the Hessian matrix of density ( $\lambda_1$ ,  $\lambda_2$  and  $\lambda_3$ ), and  $\nabla^2\rho$  of the complexes at the B3LYP/6-311++G(d,p) level are listed in Table III. It contains the electron densities at the bond critical points of the NH...X<sup>-</sup> interactions. Different features of the electron densities analysis obtained in the AIM framework are summarized as follows:

1. All the BCPs of NH...X<sup>-</sup> interactions are characterized by small  $\rho(r)$  values and a 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 the charge density in the interatomic surface. These interactions are dominated by a contraction of the char-

TABLE III. Electron densities  $\rho(e/a_0^3)$ , eigenvalues of the Hessian matrix of density ( $\lambda_1$ ,  $\lambda_2$  and  $\lambda_3$ ) and Laplacians  $\nabla^2\rho(e/a_0^5)$  at the intermolecular bond critical points of borazine... $X^-$  ( $X^- = \text{H, F, Cl, CN, NC or NCO}$ ), calculated at the B3LYP/6-311++G(d,p) level within the AIM theory

$X^-$	$\rho$	$\lambda_1$	$\lambda_2$	$\lambda_3$	$\nabla^2\rho$
H	0.046	-0.069	-0.068	0.160	0.023
F	0.104	-0.261	-0.260	0.701	0.180
Cl	0.026	-0.030	-0.030	0.123	0.062
CN	0.031	-0.041	-0.040	0.141	0.060
NC	0.035	-0.051	-0.050	0.196	0.094
NCO	0.036	-0.053	-0.053	0.208	0.102

ge density away from the interatomic surface toward each of interacting species. It was confirmed that the electron density at the bond critical point can be used as a measure of the binding strength. The Laplacians  $\nabla^2\rho$  are all positive, indicating a typical closed-shell kind of interactions in the complexes. A plot of the calculated interaction energies of the borazine... $X^-$  interaction of the complexes vs. their electron density at the BCP(NH... $X^-$ ) is presented in Fig. 2, which indicates a regression coefficient of 0.9984.

2. Among all the complexes, the obtained value for electron density was the highest for the interaction  $\text{NH}\cdots\text{F}^-$ .

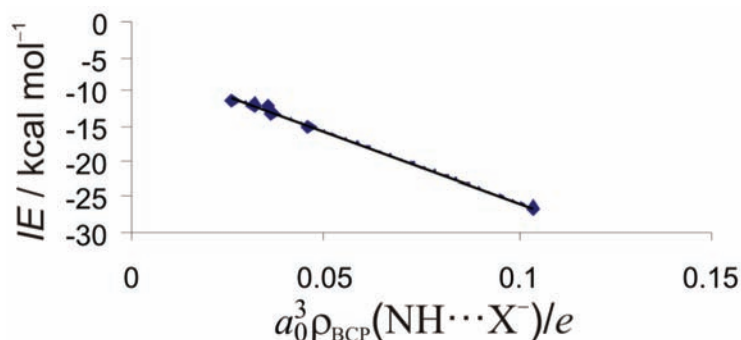


Fig. 2. A plot of the calculated interaction energies ( $IE = -201.56\rho_{\text{BCP}} - 5.6114$ ;  $R^2 = 0.9984$ ) of borazine... $X^-$  ( $X^- = \text{H, F, Cl, CN, NC or NCO}$ ) interaction complexes vs. their electron density at the BCP(NH... $X^-$ ).

#### Natural population analysis

Natural bond orbital analysis stresses the role of intermolecular orbital interactions in a complex, particularly charge transfer ones. This analysis is carried out by considering all possible interactions between filled donor and empty acceptor NBOs and estimating their energetic importance by a second-order perturbation theory. For each donor NBO ( $i$ ) and acceptor NBO ( $j$ ), the stabilization

energy  $E^{(2)}$  associated with electron delocalization between donor and acceptor is estimated as:

$$E^{(2)} = -q_i \frac{(F_{i,j})^2}{\epsilon_j \epsilon_i}$$

where  $q_i$  is the orbital occupancy,  $\epsilon_i$  and  $\epsilon_j$  are diagonal elements and  $F_{i,j}$  is the off-diagonal NBO Fock matrix element.

The results of the second-order perturbation theory analysis of the Fock matrix at the B3LYP/6-311++G(d,p) level of theory are collected in Table IV. For the borazine...X<sup>-</sup> complexes, most of the charge transfer energies reported in Table IV are related to the dominant interaction, which is between donor species and acceptor species.

TABLE IV. The results of second-order perturbation theory analysis of the Fock matrix within the NBO basis

X <sup>-</sup>	Donor	Acceptor	$E^{(2)}$ / kcal mol <sup>-1</sup>	$\epsilon_j - \epsilon_i$	$F_{ij}$
H	LP (1) H	$\sigma^*(\text{N-H})$	58.05	0.51	0.154
F	LP (4) F	$\sigma^*(\text{N-H})$	82.38	0.81	0.230
Cl	LP (4) Cl	$\sigma^*(\text{N-H})$	15.43	0.71	0.093
CN	LP (1) C	$\sigma^*(\text{N-H})$	27.90	0.78	0.132
NC	LP (1) N	$\sigma^*(\text{N-H})$	21.43	0.91	0.125
NCO	LP (1) N	$\sigma^*(\text{N-H})$	22.12	0.94	0.129

Interaction of NH...X<sup>-</sup> in borazine has an attractive aspect. The strongest interaction is between the LP(4) F donor and the  $\sigma^*(\text{NH})$  acceptor.

It is interesting to note that the obtained results based on the NBO are completely accordant with the results obtained within the AIM framework.

A comparison between the results of the  $IE^{\text{corrected}}$  in Table I and the  $E^{(2)}$  in Table IV showed that, from all the considered anions, the interaction energy is the greatest when the borazine interacts with F<sup>-</sup>.

The natural population analysis (NPA) shows that the charge on X<sup>-</sup> decreases in the order H, F, Cl, CN (Table V). These results are compatible with charge transfer from X<sup>-</sup> to borazine.

TABLE V. Natural population analysis (NPA) for the borazine...X<sup>-</sup> (X<sup>-</sup> = H, F, Cl, CN, NC or NCO) complexes by the method B3LYP with 6-311++G(d,p) basis set

X <sup>-</sup>	X	X(monomer)	H	H(borazine)
H	-0.74268	-1.00	0.40502	0.39928
F	-0.83744	-1.00	0.48555	0.39928
Cl	-0.93896	-1.00	0.46306	0.39928
CN	-0.20834	-1.00	0.45176	0.39928
NC	-0.94379	-1.00	0.47455	0.39928
NCO	-0.94288	-1.00	0.47771	0.39928

*Nucleus independent chemical shifts (NICS)*

In order to further study the aromaticity of borazine complexes, the nucleus independent chemical shifts (NICS) of the optimized structures were calculated at the ring center and at 0.5 and 1.0 Å perpendicularly away from the successions of points of the plane, as listed in Table VI.

TABLE VI. NICS(0.0), NICS(0.5) and NICS(1.0) values for borazine...X<sup>-</sup> (X<sup>-</sup> = H, F, Cl, CN, NC or NCO) complexes by the B3LYP method with the 6-311++G(d,p) basis set

Species	NICS(0.0)	NICS(0.5)	NICS(1.0)
Borazine	-1.5844	-2.2813	-2.6670
H	-1.7779	-2.6086	-3.0760
F	-1.8756	-2.5839	-2.9570
Cl	-1.8172	-2.5660	-2.9647
CN	-2.0349	-2.8114	-3.1570
NC	-1.8252	-2.5911	-3.0052
NCO	-2.1471	-2.9309	-3.2172

In this study, first the values of NICS(0.0) at the geometrical centers of the planar six-membered ring, which provide a direct measure of the ring current effects, were calculated. The calculated results are listed in Table VI. The NICS values of borazine and the other species are all negative. It can be seen that all complexes are more aromatic than borazine. In order to further analyze the aromaticity, the values of NICS(0.5), NICS(1.0) were calculated by placing a ghost atom 0.5 and 1.0 Å, respectively, above the center of the six-membered ring. The values of NICS(0.5) and NICS(1.0) for all species were negative, supporting the existence of delocalization and aromaticity in these complexes. The most negative values of NICS(0.0), NICS(0.5) and NICS(1.0) were obtained for X<sup>-</sup> = NCO.

## CONCLUSIONS

Calculations on borazine...X<sup>-</sup> (X<sup>-</sup> = H, F, Cl, CN, NC or NCO) complexes were performed at the B3LYP level with the 6-311++G(d,p) basis set. A good correlation between  $\rho_{\text{BCP}}(\text{NH}\cdots\text{X}^-)$  and the interaction energy was found for the complexes.

The aromaticity of these compounds was predicted in light of the nucleus-independent chemical shift (NICS). All of the molecules were found to be highly  $\pi$ -aromatic in nature.

## ИЗВОД

ТЕОРИЈСКО САГЛЕДАВАЊЕ СВОЈСТАВА БОРАЗИН...X<sup>-</sup>  
КОМПЛЕКСА (X<sup>-</sup> = H, F, Cl, CN, NC ИЛИ NCO)

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Карактер интеракција NH...X<sup>-</sup> (X<sup>-</sup> = H, F, Cl, CN, NC or NCO) између боразина и ањона испитиван је *ab initio* методом. Енергије интеракције израчунате су на V3LYP/6-311++G(d,p) нивоу. Упоређене су енергетске и геометријске карактеристике комплекса. Коришћена је методологија „атома у молекулима“ за анализу густине и атомског доприноса укупној енергији и наелектрисању система. Анализа орбитале природне везе (NBO) показала је пренос наелектрисања при испитивању природе међумолекулских интеракција. Ароматичност једињења претпостављена је на основу хемијског помераја који не зависи од типа језгра (NICS).

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