Behavior of the Local Reactivity Descriptors during Complexation: A Case Study of $BXX'X''NH_3$ (X, X′, X″ = H, F)

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Received: September 9, 2004; In Final Form: October 12, 2004

The behavior of local reactivity descriptors such as condensed fukui functions, “relative electrophilicity”, and “relative nucleophilicity” was studied as the complexation reaction of BH_3 or fluoroboranes and NH_3 proceeds. This study reveals the change of these descriptors of different atoms during the reaction. The case study indicates the general properties of descriptors in a reactive surface.

I. Introduction

The prediction and interpretation of the preferred direction of a reaction and the product formation is the major question that is associated with the problem of reactivity of molecules under different environmental conditions.[1,2] The study of molecular interactions has been a great challenge from the experimental and theoretical point of view.[3] Theoretical models in correlating the reactivity of molecular systems based on different quantities, such as molecular orbital density, charge on atoms, bond order, etc., have been used extensively.[4] These models provide simpler theoretical perspectives, compared to the more rigorous quantitative calculation of interaction energies and reactivity. In particular, the correlation between the frontier molecular orbitals and reactivity was examined in the seminal works of Fukui and co-workers.

In this context, the concepts of density-based descriptors, such as chemical potential, hardness, and softness, have been used to provide a simple model. The global hardness and softness, along with the concept of the hard−soft acid−base (HSAB) principle[5] and the principle of maximum hardness have been studied to describe the reactivity of acids and bases and the stability of chemical systems. The HSAB principle has systematized the reactivity of the acids and bases, in terms of softness and hardness indices, based on the experimental observations. The nature of these basic chemical concepts (hardness and softness, which are called global reactivity descriptors (GRD)), has been theoretically justified within the framework of density functional theory (DFT).[6,7] Many groups have attempted to validate and prove the HSAB principle, using the GRDs and local reactivity descriptors (LRDs).[8] These studies have led to some important insights about the nature of the reactivity and the stability of molecular systems, in terms of the global hardness (η) and the global softness (S).[9−19]

However, these global descriptors are unable to give information about the reactivity of a particular site in a molecule. LRDs such as Fukui function (FF) and local softness were proposed to rationalize the problem and identify reactive sites in molecules.[20−22] Electrophilic and nucleophilic FFs have been used as indicators of reactivity to nucleophilic and electrophilic reagents, respectively.[23−25]

Roy and co-workers[26,27] used the local softness, as well as the local hardness, to probe both the intramolecular and intermolecular reactivity of a nucleophilic attack on carbonyl compounds and introduced concepts of relative electrophilicity and relative nucleophilicity, which have been shown to be reliable descriptors for intramolecular reactivity.

LRDs and GRDs have been used to formulate the local HSAB principle for interaction energy between two molecules.[9,14−17,22] Different forms of the local HSAB principle have been used successfully recently. It is well-known that an atom or site with the highest condensed FF is the most-reactive atom. There are three different types of FFs, for electrophilic, nucleophilic, and radical attack. In this respect, it was shown that relative electrophilicity and nucleophilicity are more reliable to characterize the most-reactive atom in a molecule. For example, in BH_3, it is shown that the B atom is the most electrophilic in character, either from the point of view of the relative electrophilicity of the B atom or by simply examining the electrophilic FF of atoms in the BH_3 molecule. Similarly, the N atom behaves as the most nucleophilic atom in ammonia. However, it is important to know what happens to these descriptors of atoms as the reaction occurs. The objective of this paper is to study the relative change of different descriptors as the reaction happens, using the example of the interaction of BH_3 or fluorine-substituted boranes and NH_3. It is not clear a priori if descriptors undergo monotonic change or go through an extremum during the reaction paths. In our example, we vary the distance between the B and N atoms as the BH_3 or fluoroboranes and NH_3 approach each other. The possible implications of these changes in the interaction energy obtained through the local HSAB principle are also discussed.

The paper has been organized as follows. In section II, we give a brief theoretical background of GRDs and LRDs. In section III, the methodology and computational details are presented. In section IV, we will present our results and discuss the reactivity behavior of atomic sites for electrophilic and nucleophilic attacks.

II. Theoretical Background

According to the Hohenberg−Kohn (HK) theorem, the ground-state energy of an atom or molecule is written as a function of electron density (ρ):[28]

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10.1021/jp045924d CCC: $27.50

$$E[\rho] = \int \rho(r)\upsilon(r)\,\mathrm{d}r + F_{\mathrm{HK}}[\rho] \tag{1}$$

with

$$F_{\mathrm{HK}}[\rho] = T[\rho] + V_{\mathrm{ee}}[\rho] \tag{2}$$

where $\upsilon(r)$ is the external potential and F_{HK} is the universal Hohenberg−Kohn functional, which is comprised of the electronic kinetic energy functional ($T[\rho]$) and the electron−electron interaction functional ($V[\rho]$).

The first and second partial derivatives of $E[\rho]$, with respect to the number of electrons N under the constant external potential $\upsilon(r)$, are defined as the chemical potential (μ) and the global hardness (η) of the system, respectively.[5c,7,29,30] The global softness (S) is the half inverse of the hardness. The global descriptor of hardness has been known as an indicator of the overall stability of the system.[5b,31] It has been customary to use a finite difference approximation for the computation of μ and η: [6]

$$\mu = -\frac{I + A}{2} \tag{3}$$

$$\eta = \frac{1}{2}(I - A) \tag{4}$$

However, the site selectivity of a chemical system cannot be studied using the global descriptors of reactivity. For this, appropriate local descriptors need be defined. An appropriate definition of the local softness $s(r)$ is given by[32]

$$\begin{aligned} s(r) &= \left(\frac{\partial\rho(r)}{\partial N}\right)_{\upsilon(r)}\left(\frac{\partial N}{\partial\mu}\right)_{\upsilon(r)} \\ &= f(r)S \end{aligned} \tag{5}$$

such that

$$\int s(r)\,\mathrm{d}(r) = S \tag{6}$$

where $f(r)$ is defined as the Fukui function.[32] It can be interpreted (cf. the use of Maxwell's relation in this scheme) either as the change of the electron density $\rho(r)$ at each point r when the total number of electrons is changed or as the sensitivity of chemical potential of a system to an external perturbation at a particular point r.

$$f(r) = \left(\frac{\partial\rho(r)}{\partial N}\right)_{\upsilon(r)} = \left(\frac{\partial\mu}{\partial\upsilon(r)}\right)_{N} \tag{7}$$

The latter point of view, which is, by far, the most prominent in the literature, faces the N discontinuity problem of atoms and molecules,[33,34] leading to the introduction[20a] of both right- and left-hand-side derivatives, both to be considered at a given number of electrons, $N = N_0$:

$$f^{+}(r) = \left(\frac{\partial\rho(r)}{\partial N}\right)^{+}_{\upsilon(r)} \tag{8}$$

for a nucleophilic attack, provoking an electron increase in the system, and

$$f^{-}(r) = \left(\frac{\partial\rho(r)}{\partial N}\right)^{-}_{\upsilon(r)} \tag{9}$$

for an electrophilic attack, provoking an electron decrease in the system.

By the finite difference method, using the electron densities of N_0, $N_0 + 1$, and $N_0 - 1$, one can define

$$f^{+}(r) \approx \rho_{N_0+1}(r) - \rho_{N_0}(r) \tag{10}$$

and

$$f^{-}(r) \approx \rho_{N_0}(r) - \rho_{N_0-1}(r) \tag{11}$$

A third function, which describes radical attack ($f^{0}(r)$), is then obtained as the arithmetic average of $f^{+}(r)$ and $f^{-}(r)$.

Atom-condensed Fukui functions were first introduced by Yang et al., based on the idea of electronic population over atomic regions,[23] similar to the procedure followed in population analysis technique.[35] Combined with finite difference approximation, this yields working equations of the type

$$f_{\mathrm{A}}^{+} = q_{\mathrm{A},N_0+1} - q_{\mathrm{A},N_0} \tag{12}$$

$$f_{\mathrm{A}}^{-} = q_{\mathrm{A},N_0} - q_{\mathrm{A},N_0-1} \tag{13}$$

where q_{A,N_0} denotes the electronic population of atom A of the reference system.

Several other reactivity descriptors have been proposed. Parr et al.[10f] proposed a global philicity (W) as μ^2/η. Taking from this Chattaraj et al.[36] proposed the existence of a local electrophilicity index $w(r)$, such that $w(r)$ integrates to the global (W). The condensed philicity w_k^{+} in the definition is given by

$$w_k^{+} = Wf_k^{+} \tag{14}$$

To determine the most preferable site for attack by a nucleophile or electrophile, Roy et al. proposed new descriptors: "relative electrophilicity" and "relative nucleophilicity", which are defined as (s_k^{+}/s_k^{-}) and (s_k^{-}/s_k^{+}), respectively. These can also be written as ratios of respective FFs. These relative philicities have been shown to be very reliable candidates for intramolecular reactivity.

Relative electrophilicity and relative nucleophilicity are given by (f^{+}/f^{-}) and (f^{-}/f^{+}), respectively.

III. Methodology and Computational Details

Geometry optimization of individual BH_3 and NH_3, as well as constrained optimization of BH_3NH_3, BH_2FNH_3, BHF_2NH_3, and BF_3NH_3 complexes were performed with ab initio Møller−Plesset perturbation (MP2) quantum chemical calculations, using the 6-31++G(d,p) basis set. Chemical potential and global softness were calculated via eqs 3 and 4. Condensed FFs were calculated via eqs 12 and 13, using Lowdin population analysis (LPA).[37a,b] We have also computed the local descriptors for fluorine and hydrogen that is connected to boron (H^B) and for hydrogen that is connected to nitrogen (H^N), and their average values are reported.

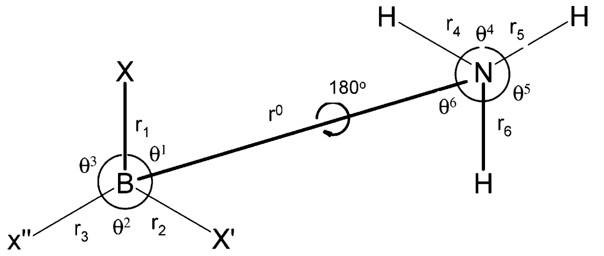

Figure 1. Basic geometry of complexes studied. (X, X′, X″ = H or F.)

TABLE 1: Structural Parameters for Equilibrium Geometry for the $BXX'X''NH_3$ Complexes

parameter	BH_3NH_3; $X = X' = X'' = H$	BH_2FNH_3; $X = F$ and $X' = X'' = H$	BHF_2NH_3; $X = H$ and $X' = X'' = F$	BF_3NH_3; $X = X' = X'' = F$
		Bond Distance (Å)		
r^0	1.6604	1.6644	1.6691	1.6612
r_1	1.2053	1.4260	1.2005	1.3878
r_2	1.2053	1.2051	1.4033	1.3878
r_3	1.2053	1.2051	1.4033	1.3878
r_4	1.0157	1.0167	1.0163	1.0169
r_5	1.0157	1.0167	1.0163	1.0169
r_6	1.0157	1.0163	1.0181	1.0169
		Bond Angle (deg)		
θ^1	113.90	113.70	115.02	114.18
θ^2	113.90	115.92	112.93	114.18
θ^3	113.90	113.70	115.02	114.18
θ^4	107.78	107.94	108.97	108.56
θ^5	107.78	108.54	108.45	108.56
θ^6	107.78	108.54	108.45	108.56

TABLE 2: Variation of Global Softness and Chemical Potential with B−N Distance

	Global Softness, *S*				Chemical Potential, μ			
distance (Å)	BH_3NH_3	BH_2FNH_3	BHF_2NH_3	BF_3NH_3	BH_3NH_3	BH_2FNH_3	BHF_2NH_3	BF_3NH_3
0.9	2.95705	2.88920	2.49534	2.01477	−0.16138	−0.17135	−0.20328	−0.25649
1.2	2.70404	2.66700	2.37529	1.95210	−0.17501	−0.18011	−0.20612	−0.25661
1.5	2.54695	2.54766	2.31296	1.94838	−0.18387	−0.18507	−0.20696	−0.25165
r^0[a]	2.47461	2.48737	2.27714	1.93676	−0.18767	−0.18729	−0.20718	−0.24979
1.8	2.41330	2.43532	2.24891	1.96423	−0.19077	−0.18910	−0.20711	−0.24288
2.0	2.33267	2.35801	2.16949	2.04210	−0.19473	−0.19188	−0.21063	−0.22807
2.3	2.22860	2.23065	2.21316	2.15301	−0.20024	−0.19853	−0.19986	−0.20863
2.6	2.28374	2.27293	2.25608	2.22239	−0.19155	−0.19070	−0.19165	−0.19729
3.0	2.32128	2.30506	2.29203	2.27598	−0.18568	−0.18517	−0.18585	−0.18968
3.5	2.34625	2.32886	2.31985	2.31445	−0.18237	−0.18179	−0.18233	−0.18499
4.0	2.36137	2.34290	2.33616	2.33619	−0.18107	−0.18025	−0.18072	−0.18253
4.5	2.37343	2.35166	2.34594	2.34879	−0.18071	−0.17984	−0.18022	−0.18108
5.5	2.41997	2.36178	2.35748	2.36171	−0.18316	−0.17891	−0.17915	−0.17945
6.0	2.42986	2.36470	2.36082	2.36515	−0.18351	−0.17860	−0.17880	−0.17894
7.0	2.44398	2.36760	2.36439	2.36812	−0.18406	−0.17790	−0.17825	−0.17819
noninteracting	2.47853	2.35959	2.35959	2.35959	−0.18604	−0.17587	−0.17587	−0.17587

[a] r^0 is the B−N distance at the fully optimized geometries of the complexes.

TABLE 3: Condensed Fukui Functions at the Noninteracting Limit

	f^+					f^-				
atom	BH_3	BH_2F	BHF_2	BF_3	NH_3	BH_3	BH_2F	BHF_2	BF_3	NH_3
B	0.86542	0.82868	0.85197	0.88859		0.38263	0.22888	0.17784	0.04782	
H^B	0.04487	0.03588	0.01866			0.20579	0.23688	0.31274		
F		0.09956	0.06468	0.03714			0.29737	0.25471	0.31739	
N					0.06214					0.76410
H^N					0.31262					0.07863

To obtain the limiting values of the FF of atoms of the complex, calculations were performed on isolated BH_3, BH_2F, BHF_2, BF_3, and NH_3 molecules. The calculations were performed using the GAMESS system of programs.[38]

IV. Results and Discussions

Figure 1 represents basic geometries of the complexes used for the calculations. The geometries used were in staggered conformations, and various structural parameters for equilibrium geometry are shown in Table 1. The equilibrium geometries of the complexes corresponding to r^0 are unconstrained optimized geometries. The geometries for different B−N bond lengths were optimized by freezing B and N atoms while the optimum coordinates of other atoms were calculated. As the B−N distance increases, $BXX'X''$ flattens to a planar geometry while NH_3 approaches its tetrahedron geometry. At small B−N distances, B−X and N−H bonds elongate and the XBX' and HNH angles decrease.

Table 2 presents the variation of the global softness *S* and chemical potential μ with B−N distance in complexes. *S* first decreases as the distance increases from 0.9 Å and then increases again. Although it is not minimum at the equilibrium geometry, it cannot be considered to be a violation of the principle of maximum hardness,[5b,32] because the μ value of the complex is not constant as the complexes are dissociated along the B−N bond. Similar behavior of the monotonic change of hardness/softness along a large part of the potential energy surface was observed for diatomic molecules.[39]

Table 3 presents condensed FFs values of different atoms of isolated BH_3 or fluoroboranes and NH_3. Because the complex is formed by a donation of electrons from the N atom of NH_3 to the B atom of BH_3 or fluoroboranes, the electrophilic descriptor of the B atom and the nucleophilic descriptor of the N atom are expected to be the highest in the isolated case. This is evidenced by the highest value for $f^+$of boron among f^+ of atoms of BH_3 (B and H^B) and fluoroboranes (B, H^B, and F) and f^- for the N atom among f^- of atoms of NH_3 (N and H^N).

TABLE 4: Relative Electrophilicity and Relative Nucleophilicity at Noninteracting Limit

	Relative Electrophilicity					Relative Nucleophilicity				
atom	BH_3	BH_2F	BHF_2	BF_3	NH_3	BH_3	BH_2F	BHF_2	BF_3	NH_3
B	2.26177	3.62059	4.79065	18.58197		0.44213	0.27620	0.20874	0.05382	
H^B	0.21803	0.15147	0.05967			4.58663	6.60201	16.75991		
F		0.33480	0.25394	0.11703			2.98684	3.93800	8.54492	
N					0.08132					12.29643
H^N					3.97563					0.25153

TABLE 5: Energies of Complexes at Noninteracting Limits, According to Different Fragmentation Schemes

	Energy (hartree)			
	$(BXX'X'')^- + NH_3$	$(BXX'X'') + NH_3{}^-$	$(BXX'X'')^+ + NH_3$	$(BXX'X'') + NH_3{}^+$
BH_3NH_3	−82.864125	−82.843787	−82.398364	−82.492054
BH_2FNH_3	−181.949566	−181.949998	−181.519133	−181.598264
BHF_2NH_3	−281.043453	−281.061437	−280.568188	−280.709704
BF_3NH_3	−380.131436	−380.161476	−379.580880	−379.809742

Recently, the relative electrophilicity (f^+/f^-) and relative nucleophilicity (f^-/f^+) of atomic centers have been shown to be better indicators of intramolecular reactivity. Table 4 presents the relative electrophilicity and relative nucleophilicity values of different atoms of isolated BH_3, fluoroboranes, and NH_3. In fact, the trend of the most-reactive atom, being associated with the highest value of reactivity descriptor, is visible even more clearly with these descriptors, with values of 12.29643 for the relative nucleophilicity of the N atom and 2.26177, 3.62059, 4.79065, and 18.58197 for the relative electrophilicity of the B atom in BH_3, BH_2F, BHF_2, and BF_3, respectively.

Local softness is not a reliable index for comparing reactivity, because the B−N distance changes, because of the artifact of change in global softness with the change of B−N distance. However, f^+ and f^- values can be used for comparison, because the sum of these descriptors of all atoms of the complex are normalized to unity. Similarly, the relative electrophilicity and relative nucleophilicity can also serve as appropriate indices for comparison of reactivity, because these are also independent of global softness.

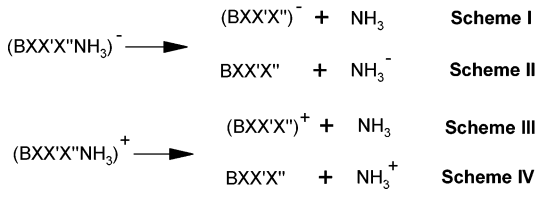

Figure 2. Possible fragmentation schemes for fission of complexes along the B−N bond. (X, X′, X″ = H or F.)

However, the noninteracting values of f^+ or f^- are correct approaches only for atoms of fragmented species for the complex anion or cation, respectively. The possible schemes for fission of $N_0 + 1$ and $N_0 - 1$ electronic states of the $BXX'X''NH_3$ complex along the B−N bond are shown in Figure 2. For example, $(BH_3NH_3)^-$ dissociates as $BH_3{}^-$ and NH_3 (scheme 1 in Figure 2); this dissociation, as Table 5 shows, is the energetically favorable route, which presents energies of complexes at noninteracting limits, according to different fragmentation schemes. Hence, f^+ of atoms of BH_3 in a BH_3NH_3 complex reach the isolated limit values. On the other hand, f^+ of the atoms of NH_3 remain zero. For the systems $(BHF_2NH_3)^-$, $(BHF_2NH_3)^-$, and $(BF_3NH_3)^-$, the dissociation products are neutral BH_2F, BHF_2, BF_3 in the planar geometry of fluoroboranes, which are required for compatibility with the dissociation process and $NH_3{}^-$ (scheme 2 in Figure 2), which is as expected. It is well-known that, in fluoroboranes, boron is less electron-deficient, compared to BH_3, because of back-donation of the *p*-electrons of the F atom into the vacant *p*-orbital on the B atom. The acceptance of an extra electron would be facilitated by pyramidalization, which is not appropriate for the dissociation limit considered here, because the calculations are to be made under constant external potential. Hence, for these fluoroborane−NH_3 complexes, f^+ values of atoms of the NH_3 molecule go to the isolated limit of NH_3 and the f^+ values of B and H^B or F atoms go to zero. In the case of all $(BXX'X''NH_3)^+$ systems, the dissociation leads to $BXX'X''$ and $NH_3{}^+$ (scheme 4 of Figure 2). Hence, f^- of all atoms of NH_3 leads to the isolated case at noninteracting limits and f^- of B and H^B or F

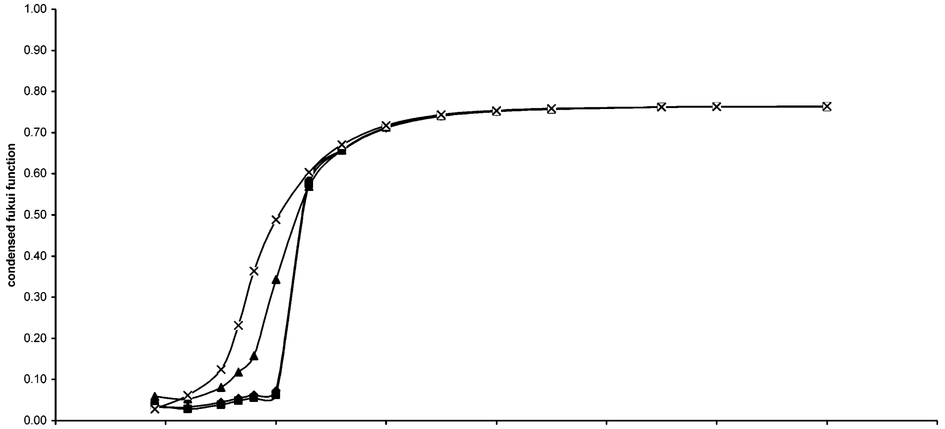

Figure 3. Variation of condensed nucleophilic fukui functions for the N atom of different complexes, relative to B−N distance: (−◆−) BH_3NH_3, (−■−) BH_2FNH_3, (−▲−) BHF_2NH_3, and (−×−) BF_3NH_3.

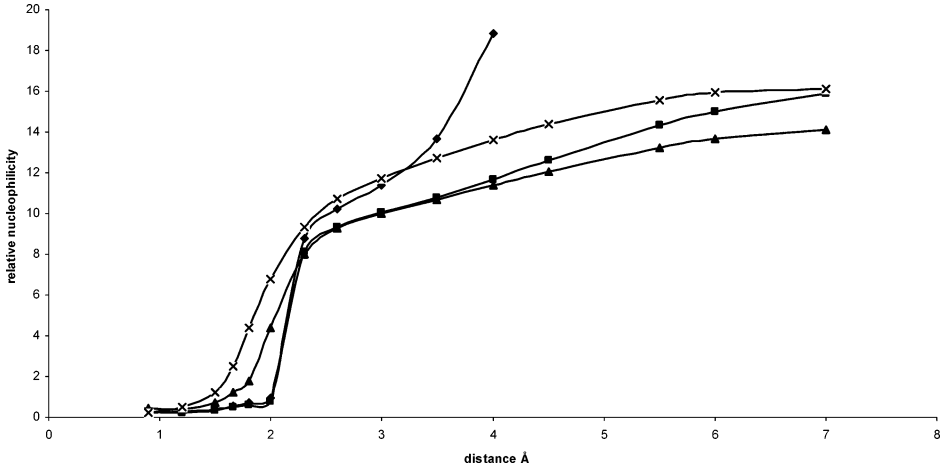

Figure 4. Variation of "relative nucleophilicity" of a N atom of different complexes, relative to B−N distance: (−◆−) BH_3NH_3, (−■−) BH_2FNH_3, (−▲−) BHF_2NH_3, and (−×−) BF_3NH_3.

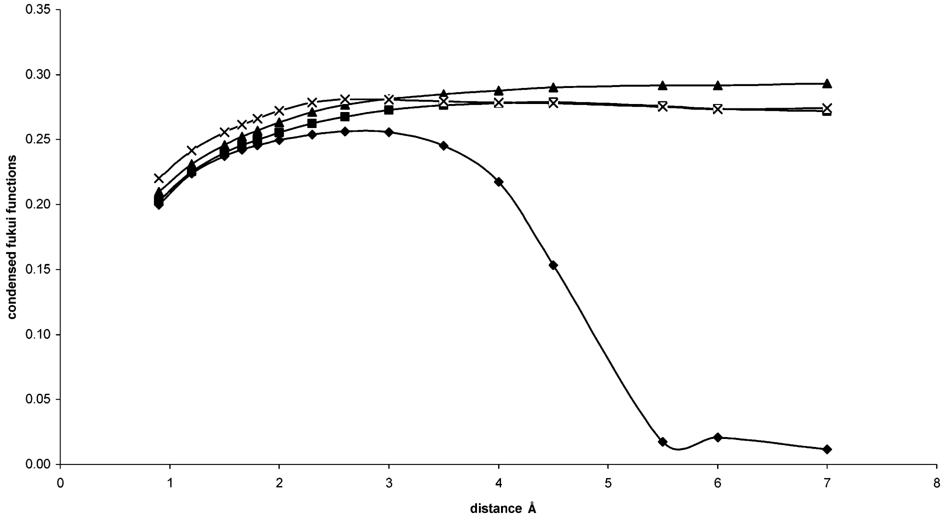

Figure 5. Variation of condensed electrophilic fukui functions for H^N of different complexes, relative to B−N distance: (−◆−) BH_3NH_3, (−■−) BH_2FNH_3, (−▲−) BHF_2NH_3, and (−×−) BF_3NH_3. (H^N is a hydrogen connected to a nitrogen.)

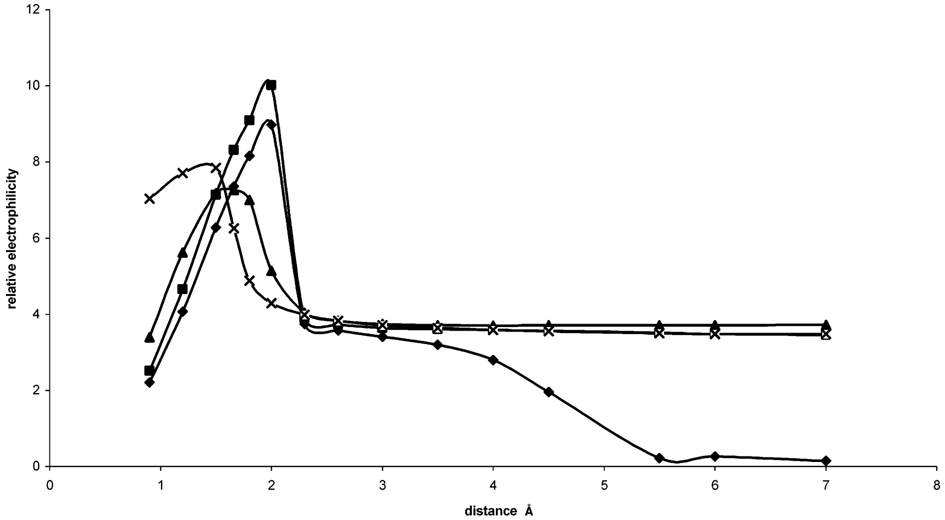

Figure 6. Variation of "relative electrophilicity" of H^N of different complexes, relative to B−N distance: (−◆−) BH_3NH_3, (−■−) BH_2FNH_3, (−▲−) BHF_2NH_3, and (−×−) BF_3NH_3. (H^N is a hydrogen connected to a nitrogen.)

attached to boron becomes zero. Hence, isolated limit results are obtained at the noninteracting limit preferentially only for one fragment, depending on the fragmentation of the anion or cation, as the case may be. The noninteracting limit values for the other fragment approach zero. This manifests in very large relative electrophilicity or relative nucleophilicity values of that fragment, which is due to the artifact of separation limit values of the FF of that particular fragment.

In addition to the previous discussion, the condensed FFs of atoms often become negative, when computed using the Lowdin/

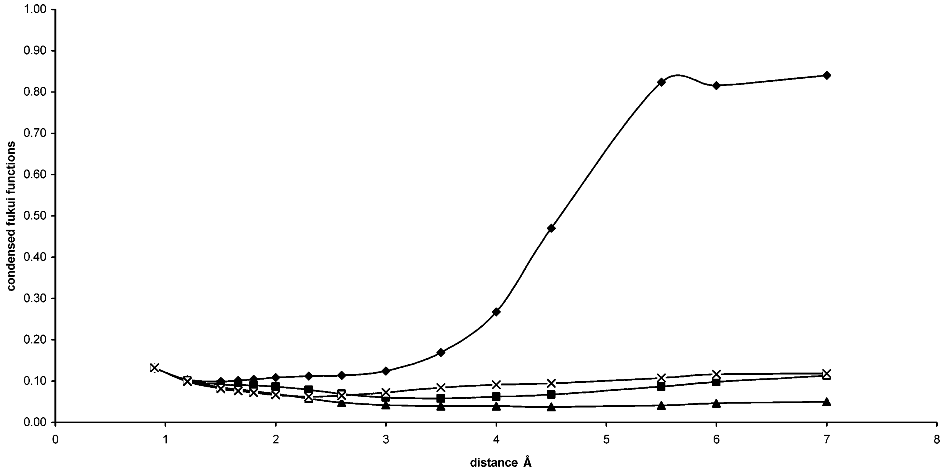

Figure 7. Variation of condensed electrophilic fukui functions for the B atom of different complexes, relative to B−N distance: (−◆−) BH_3NH_3, (−■−) BH_2FNH_3, and (−▲−) BHF_2NH_3.

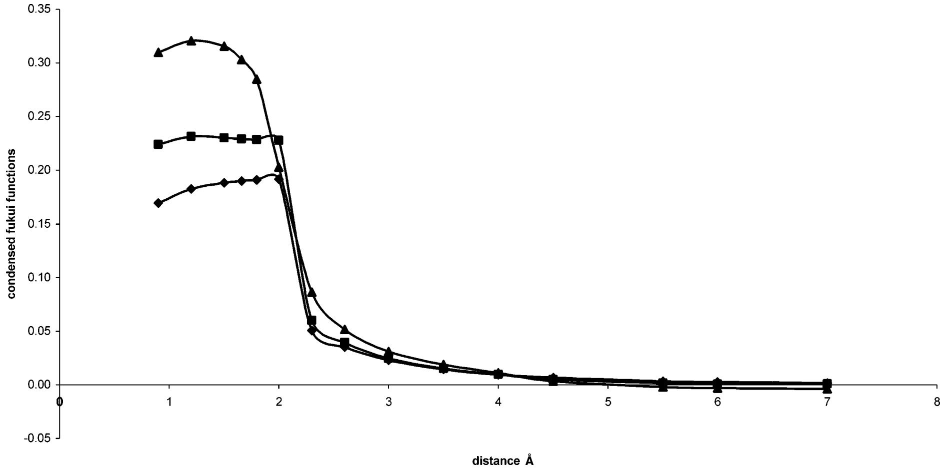

Figure 8. Variation of condensed nucleophilic fukui functions for H^B of different complexes, relative to B−N distance: (−◆−) BH_3NH_3, (−■−) BH_2FNH_3, and (−▲−) BHF_2NH_3. H^B is a hydrogen connected to a boron.

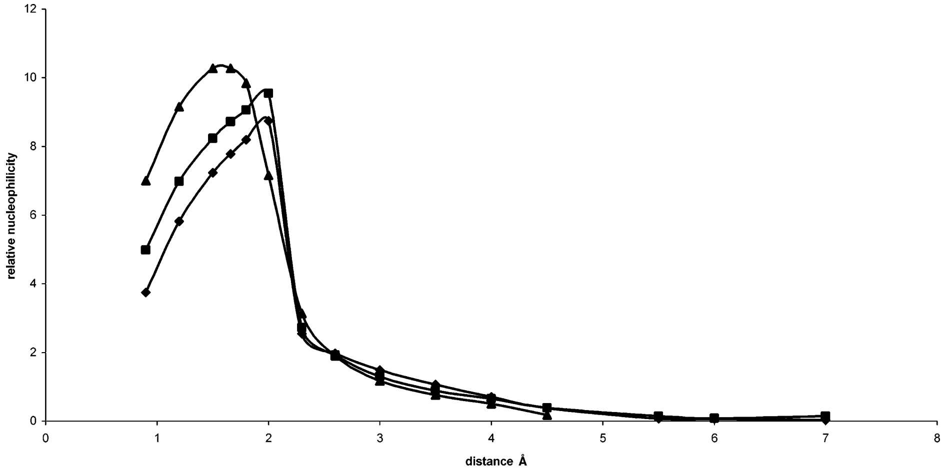

Figure 9. Variation of "relative nucleophilicity" of H^B of different complexes, relative to B−N distance: (−◆−) BH_3NH_3, (−■−) BH_2FNH_3, and (−▲−) BHF_2NH_3. H^B is a hydrogen connected to a boron.

Mulliken population analysis[37] technique. The problem of negative condensed FFs has been analyzed in detail,[40] and it has been realized that the problem originates from the population analysis used. While the aforementioned analyses are quite standard, they lead to negative FF values in some cases, as has been observed by many workers.[27,40,41] However, among these two, LPA is more reliable and, hence, has been used in this paper.

Figure 3 presents the variation of condensed nucleophilic FFs for the N atom of different complexes, relative to B−N distance. The value of f^-(N) falls to much-lower values at interacting distances. The results reveal the loss of nucleophilicity of N as the reaction proceeds. This is due to the electron donation from the N atom to BH_3 or fluoroboranes. Nitrogen, which has a surplus lone pair of electrons in isolated NH_3, is no longer electron-rich as it reaches a near-equilibrium geometry. Figure

4 presents the variation of the relative-nucleophilicity of the N atom, relative to B−N distance, which also shows a similar trend. Variation of condensed electrophilic FFs and relative electrophilicity for the N atom, relative to B−N distance, are shown in the Supporting Information (see Figures S1 and S2). The electrophilic descriptors of N atoms increase monotonically as the reaction proceeds. This is an artifact of donation of electrons by the N atom and, as a result, the electron density around the N atom decreases and the nucleus is somewhat less shielded and thereby marginally increases its affinity for electrons.

Electrophilic descriptors for any H atom that is connected to a N atom should show increasing values as the reaction proceeds, because nitrogen becomes more electronegative at interacting distances as a consequence of its loss of electrons to boron, thereby reducing electron density on hydrogen. Figure 5 presents variation of condensed electrophilic FF for H^N, relative to B−N distance. Although the expected trend is not observed with these values, except for BH_3NH_3, the trend is clearly visible in Figure 6, which presents the variation of the relative electrophilicity of H^N, relative to the B−N distances. The variation of condensed nucleophilic FF and relative nucleophilicity values for H^N, relative to B−N distance, is shown in the Supporting Information (Figure S3 and S4), which shows the expected trend of losing nucleophilicity as reaction proceeds, because of the same reason previously given.

Figure 7 presents the variation of condensed electrophilic FFs for the B atom, relative to B−N distance. Results show how a loss of electrophilicity accompanies the reaction, starting from its limiting value, which was initially very high (>0.8) and now falling to very low values (~ 0.1) at equilibrium geometry. This is attributed to gain of electron by boron atom. The variation of the condensed nucleophilic FF and relative nucleophilicity of B, relative to the B−N distance, are shown in the Supporting Information (Figures S5 and S6). The nucleophilic descriptors of B atoms increase considerably as the reaction proceeds.

The variation of condensed nucleophilic FF for H^B, relative to B−N distance, is shown in Figure 8. As the reaction proceeds, the f^- of the H atom that is connected to the B atom should increase as the B atom, after gaining an electron from the N atom, becomes less electronegative and thereby H^B and F have more electron density around them. This is evidenced by the increased values of f^- of H^B. The same trend is observed in Figure 9, which presents the variation of the relative nucleophilicity of H^B, relative to the B−N distance. The variation of the electrophilic descriptors of H^B, relative to the B−N distance, is shown in the Supporting Information (see Figures S7 and S8). As expected, the electrophilic descriptors of H^B show a monotonic decrease as the complex is formed, because of similar reasons.

The variation of reactivity descriptors of *F* are shown in the Supporting Information (see Figures S9−S12). The fluorine atom behaves in a similar fashion as that of H^B, which is quite expected.

A H atom that is connected to a N atom (H^N) and a H atom connected to a B atom (H^B) which do not have good affinity at noninteracting limits are having larger values of $f^+(H^N)$ and $f^-(H^B)$ (see Figures 5 and 8)) at the equilibrium geometry. Also, the relative electrophilicity of H^N and the relative nucleophilicity of H^B are maximum (see Figures 6 and 9) among all atoms at equilibrium geometry, which clearly justifies the formation of the dihydrogen bond ($N{-}H{\cdots}H{-}B$) in BH_3NH_3 dimer.[42] It also justifies H^N as the site for nucleophilic attack by oxygen in the adduct between 2,3,11,12-tetra-anisyl-18-crown-6 and ammonia borane.[43]

Acknowledgment. A.T. acknowledges the Council of Scientific and Industrial Research, New Delhi, for Research Fellowship. The authors acknowledge Mr. Y. Sajeev for fruitful discussions. The authors also acknowledge one of the reviewers for useful suggestions, which helped in improvement of the manuscript.

Supporting Information Available: Variation of the condensed FF and relative electrophilicity/relative nucleophilicity for the different atoms of the complexes with B−N distance (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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