
Dipole-Bound Anions Supported by Charge–Transfer Interaction: Anionic States of $H_nF_{3-n}N \rightarrow BH_3$ and $H_3N \rightarrow BH_nF_{3-n}$ ($n = 0, 1, 2, 3$)

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ABSTRACT: The possibility of electron binding to five molecules (i.e., $F_3N \rightarrow BH_3$, $H_2FN \rightarrow BH_3$, $HF_2N \rightarrow BH_3$, $H_3N \rightarrow BH_2F$, $H_3N \rightarrow BHF_2$) was studied at the coupled cluster level of theory with single, double, and noniterative triple excitations and compared to earlier results for $H_3N \rightarrow BH_3$ and $H_3N \rightarrow BF_3$. All these neutral complexes involve dative bonds that are responsible for significant polarization of these species that generates large dipole moments. As a consequence, all of the neutral systems studied, except $F_3N \rightarrow BH_3$, support electronically stable dipole-bound anionic states whose calculated vertical electron detachment energies are 648 cm^{-1} ($[H_2FN \rightarrow BH_3]^-$), 234 cm^{-1} ($[HF_2N \rightarrow BH_3]^-$), 1207 cm^{-1} ($[H_3N \rightarrow BH_2F]^-$), and 1484 cm^{-1} ($[H_3N \rightarrow BHF_2]^-$). In addition, we present numerical results for a model designed to mimic charge–transfer (CT) and show that the electron binding energy correlates with the magnitude of the charge flow in the CT complex. © 2003 Wiley Periodicals, Inc. *Int J Quantum Chem* 92: 367–375, 2003

Key words: charge–transfer interaction; electron binding; anionic states; charge flow

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1. Introduction

1.1. ANIONIC STATES SUPPORTED BY NEUTRAL PARENTS INVOLVING DATIVE BONDS

1.1.1. Previous Findings

This is the third article in which we describe the study of excess electron binding to polar molecules involving dative bonds. Because in this contribution we are not only discussing new results but also summarizing those obtained earlier, we begin with a discussion of our previous findings.

In 2000, we became intrigued by the *ab initio* report published by Jagielska et al. [1], who studied structural and energetic properties of the $\text{H}_3\text{N} \rightarrow \text{BH}_3$ complex (involving a strong dative bond) using *ab initio* methods [i.e., Møller–Plesset (MP) perturbation theory and the coupled cluster (CC) method]. They also employed symmetry-adapted perturbation theory to calculate the interaction energy between NH_3 and BH_3 . In particular, it was shown [1] that:

1. The dipole moment of the two noninteracting fragments (NH_3 and BH_3) is 1.65 Debye.
2. If one allows for charge-transfer (CT) interaction manifested by the nitrogen lone-pair donation to the boron atom, the BH_3 molecule is deformed (i.e., becomes nonplanar) and its dipole moment increases, as does the total dipole moment of the complex.
3. As a consequence, the total dipole moment for the equilibrium neutral H_3NBH_3 complex is 5.31 Debye.

These findings motivated us to undertake further studies to investigate the possibility of forming a stable anionic state based on that complex. Indeed, we found that it binds an excess electron by 984 cm^{-1} , forming a dipole-bound anion [2]. In addition, we concluded that this dipole-bound anionic state would not be electronically stable if the CT interaction between NH_3 and BH_3 were “turned off.” Therefore, we believe the CT interaction is responsible for binding an extra electron to H_3NBH_3 [2].

Because such a complex was the first species (described in the literature thus far) involving a dative bond to support a stable dipole-bound anion, we became intrigued about whether this phe-

nomenon is common for other CT molecules and how the electron binding energy of the anion depends on the magnitude of the charge flow in the parent neutral host.

In 2002, we studied H_3NBF_3 [3] and found that this neutral CT complex possesses a dipole moment of 6.53 Debye and supports a dipole-bound anionic state whose electron binding energy we estimated as 2039 cm^{-1} . In addition, a potential energy surface scan of $(\text{H}_3\text{NBH}_3)^-$ indicated (for large separations between NH_3 and BF_3) the existence of a stable valence anion in which the excess electron is localized on the BF_3 unit. We concluded that these two anionic states (i.e., dipole- and valence-bound) could coexist in some regions of the potential energy surface and that the dipole-bound state is more stable at the equilibrium geometry of the complex, while the valence anion is lower in energy at larger interfragment separation [3]. Moreover, we stated that the valence-bound anionic state (which is electronically stable when the distance between NH_3 and BF_3 is larger than ca. 4.3 \AA) should be considered as a valence BF_3^- anion perturbed by the presence of the ammonia molecule.

1.1.2. Goal and Contents of This Contribution

To complete our studies on supporting dipole-bound anionic states by neutral systems whose polarity is caused mainly by CT interaction, we decided to present results for five new molecules (i.e., $\text{F}_3\text{N} \rightarrow \text{BH}_3$, $\text{H}_2\text{FN} \rightarrow \text{BH}_3$, $\text{HF}_2\text{N} \rightarrow \text{BH}_3$, $\text{H}_3\text{N} \rightarrow \text{BH}_2\text{F}$, $\text{H}_3\text{N} \rightarrow \text{BHF}_2$) whose abilities of excess electron binding have not been investigated thus far. It is important to note that these molecules may in fact be considered as derived from the same system (i.e., H_3NBH_3) but with a number of hydrogen atoms replaced with fluorine atoms, which offers a convenient possibility of studying such species and comparing their quantities. In particular, in this contribution we provide the analysis of the electron binding energies for all system studied (at their lowest-energy neutral and anionic geometries). We compare these results to those obtained earlier for H_3NBH_3 and H_3NBF_3 and discuss the role the CT interaction plays in binding an extra electron. In addition, we construct a model system that consists of two molecular fragments (i.e., lone-pair donor and acceptor— NH_3 and BF_3 , respectively) modified by adding $+q$ and $-q$ point charges on the N and B nuclei, respectively, to examine the role of lone-pair donation (see Section 3.3 for details). Such a model system we use to study the dependence of

the charge flow (which is an effect of the interfragment CT interaction) on the total electron binding energy of the anion supported by that system.

1.2. DIPOLE-BOUND ANIONS

The binding of electrons to polar molecules has been addressed in many theoretical studies [4–20]. It has been shown that, within the Born–Oppenheimer (BO) approximation, a dipole moment greater than 1.625 Debye possesses an infinite number of bound anionic states [6], although the more practical critical value to experimentally observe a dipole-bound anion bound by at least 1 cm^{-1} was found to be slightly larger, ca. 2.5 Debye [9]. In fact, it seems that this “practical” value depends strongly on the size and chemical structure of a molecule. For example, we found recently that BOH (whose dipole moment is 2.803 Debye) binds an excess electron by ca. 40 cm^{-1} while its isomer HBO (possessing a similar dipole moment of 2.796 Debye) binds by only $0\text{--}1\text{ cm}^{-1}$ and is not stable when rotational energies are included [21]. In 1976, Jordan and Luken demonstrated that the loosely bound electron in a dipole-bound anionic state occupies a diffuse orbital localized on the positive side of the molecular dipole [7]. This finding was confirmed by many more recent studies [9]. The role of non-BO coupling has been studied by Garrett, who concluded that such couplings are negligible for dipole-bound states with electron binding energies much larger than the molecular rotational constants [8].

It has been shown that the correct estimate of the electron binding energy of a dipole-bound anion requires the use of highly correlated methods [9–13]. In fact, in many cases the electron binding energy of a dipole-bound anion is dominated by the contribution from electron correlation. In particular, the dispersion interaction of the excess electron with the electrons of the neutral parent molecule has proven to be crucial for the stability of many dipole-bound anions [9–13] even though the binding at the self-consistent field (SCF) electrostatic-exchange level was present.

As described in the previous section, because the CT complexes are strongly polar they are potential candidates for systems that may support electronically stable anionic states of dipole-bound nature. In this contribution we present our results for several dipole-bound anions whose existence is a result of such interfragment CT interaction (i.e., $[\text{H}_n\text{F}_{3-n}\text{N} \rightarrow \text{BH}_3]^-$ and $[\text{H}_3\text{N} \rightarrow \text{BH}_n\text{F}_{3-n}]^-$, ($n = 0, 1, 2, 3$)).

2. Methods

We studied the potential energy surface of the neutral and anionic systems at the MP2 level of theory [22] and calculated the values of the electron binding energy (D) by subtracting the energies of the anion from those of the neutral, which favors the use of size-extensive methods. Thereafter, we employed MP perturbation theory up to the fourth order (MP n , $n = 2\text{--}4$) as well as the coupled cluster method with single and double excitations (CCSD) supplemented with a perturbational treatment of triple excitations (CCSD(T)) [23]. In addition, D was analyzed within the perturbation framework designed for dipole-bound anions and solvated electrons (described previously by Gutowski and Skurski [24]).

The simplest theoretical approach to estimate D is based on Koopmans’ theorem (KT) [25]. The KT binding energy (D^{KT}) is the negative of the energy of the relevant unfilled orbital obtained from a Hartree–Fock SCF calculation on the neutral molecule. This is a static approximation to the electron binding energy, which neglects both orbital relaxation and electron correlation effects. These effects were taken into account by performing SCF and CCSD(T) calculations for the neutral and the anion.

The polarization of the neutral host (N) by the excess electron and the effect of backpolarization are taken into account when the SCF calculation is performed for the anion (A), and the accompanying induction effects on D are given by

$$\Delta D_{\text{ind}}^{\text{SCF}} = D^{\text{SCF}} - D^{\text{KT}}, \quad (1)$$

where D^{SCF} is the electron binding energy calculated at the SCF level.

The dispersion interaction between the loosely bound electron and N was extracted from the MP2 contribution to D and approximated here by $\Delta D_{\text{disp}}^{\text{MP2}}$ (see Ref. [24] for details). The total MP2 contribution to D is defined as the difference between D s calculated at the MP2 (D^{MP2}) and SCF (D^{SCF}) levels, and it is naturally split into dispersion and nondispersion terms ($\Delta D^{\text{MP2}} = \Delta D_{\text{disp}}^{\text{MP2}} + \Delta D_{\text{no-disp}}^{\text{MP2}}$).

The higher-order MP contributions to D are defined as

$$\Delta D^{\text{MP}n} = D^{\text{MP}n} - D^{\text{MP}(n-1)}, \quad n = 3, 4. \quad (2)$$

Finally, the contributions beyond the fourth order are estimated by subtracting MP4 results from those obtained at the coupled-cluster SD(T) level

$$\Delta D^{\text{CCSD(T)}} = D^{\text{CCSD(T)}} - D^{\text{MP4}}. \quad (3)$$

Description of the loosely bound electron demands the use of extra diffuse basis functions having low exponents [26]. In addition, the basis set chosen to describe the neutral molecule should be flexible enough to accurately describe the static charge distribution of the neutral and allow for polarization and dispersion stabilization of the anion upon electron attachment [26]. All the calculations presented here were performed with the aug-cc-pVDZ basis set [27] supplemented with a $5s5p4d$ set of diffuse functions centered on the nitrogen atom (because this is the centroid of the positive end of the dipole). The aug-cc-pVDZ basis set was chosen because we earlier showed its usefulness in describing dipole-bound anions compared to other available one-electron basis sets [26]. The extra diffuse functions do not share exponent values and we used even-tempered [28] five-term s , five-term p , and four-term d basis sets. The geometric progression ratio was equal to 3.2 [29], and for each symmetry we started to build up the exponents of the extra diffuse functions from the lowest exponent of the same symmetry included in the aug-cc-pVDZ basis set designed for nitrogen. As a consequence, we achieved lowest exponents of 1.825×10^{-4} , 1.672×10^{-4} , and 2.193×10^{-3} a.u., for the s , p , and d symmetries, respectively. Our final basis set, denoted here as aug-cc-pVDZ+ $5s5p4d$, was used for the optimization of geometries, calculating frequencies, and evaluating the electron binding energies.

In computing correlation energies, all orbitals except the $1s$ orbitals of boron, nitrogen, and fluorine were included. The partial atomic charges were fitted to the electrostatic potential according to the Merz–Singh–Kollman scheme [30]. All calculations were performed with the Gaussian 98 program [31] on the Utah Center for High Performance Computing's Compaq ES40 Sierra Cluster numerical server and our group's AMD Athlon 2.0-GHz computers. The 3-D plots of molecular orbitals presented in this work were generated with the MOLDEEN program [32].

3. Results

3.1. MP2 GEOMETRIES OF NEUTRAL AND ANIONIC SPECIES

The C_{3v} symmetry (for H_3NBH_3 , F_3NBH_3 , and H_3NBF_3) and C_s symmetry (for H_2FNBH_3 ,

HF_2NBH_3 , $\text{H}_3\text{NBH}_2\text{F}$, and H_3NBHF_2) minima on the MP2 potential energy surfaces of the neutral and anionic molecule are characterized in Table I, where we also report the values of the neutral's dipole moments calculated using the SCF and MP2 densities at the neutral and anion equilibrium geometries.* It should be noted that we performed unconstrained geometry optimizations of both neutral and anionic species and these structures turned out to possess C_{3v} or C_s symmetry. Our calculations indicate that the geometries of the neutral and anion differ only slightly. In particular, electron attachment leads to a shortening of the B—N bond length by ca. 0.001–0.005 Å for systems whose electron binding energies are small (i.e., H_2FNBH_3 and HF_2NBH_3) and by ca. 0.02–0.03 Å for more strongly bound anions (i.e., $\text{H}_3\text{NBH}_2\text{F}$, H_3NBHF_2 , and H_3NBF_3); see Table I. The other bonds are even less affected (less than 0.01 Å) and the changes are usually in the 0.001- to 0.003-Å range. The valence angles change by less than 2° upon electron attachment (see Table I) and the largest change (1.992°) corresponds to the $\alpha(\text{B2N1H5})$ angle in H_3NBHF_2 (see Table I and Fig. 1). These relatively small distortions indicate that molecules studied in this work are more rigid than complexes bound by a hydrogen bond [e.g., $(\text{HF})_2$ or $\text{H}_2\text{O}/\text{NH}_3$] [12, 13] but more flexible than covalently bound molecules, which also form dipole-bound anions, such as CH_3CN [9, 10]. Although the reported geometric changes upon electron attachment are not significant, they cause a substantial increase of the dipole moment of the neutral; the largest increase (by 0.502 Debye at the SCF level and 0.460 Debye at the MP2 level) we observed for H_3NBF_3 (see Table II). This reflects the fact that the geometry changes upon attachment of an extra electron lead to a structure for which the CT from the nitrogen-containing unit to $\text{BH}_n\text{F}_{3-n}$ ($n = 0, 1, 2, 3$) is more effective as manifested by the increased polarity of the complexes.

3.2. ELECTRON BINDING ENERGIES

The existence of the dipole-bound anions can be anticipated knowing that the calculated dipole moments of the neutral species are larger than 3.3 Debye for all systems studied but F_3NBH_3 (see Table I). The dipole moment calculated for F_3NBH_3 is

*For F_3NBH_3 we report only the neutral MP2 equilibrium geometry because this molecule does not support a stable anionic state (see Section 3.2).

TABLE I

Geometric parameters of the C_{3v} and C_s symmetry minimum energy structures studied in this work and their anions calculated at the MP2 level with the aug-cc-pVDZ+5s5p4d basis set.

	H_2FNBH_3		HF_2NBH_3		F_3NBH_3		H_3NBH_2F		H_3NBHF_2		H_3NBF_3		H_3NBH_3	
	Neutral	Anion	Neutral	Anion	Neutral	Anion	Neutral	Anion	Neutral	Anion	Neutral	Anion	Neutral	Anion
$r(N1B2)$	1.615	1.610	1.612	1.611	1.665	1.666	1.646	1.666	1.666	1.641	1.654	1.625	1.667	1.653
$r(N1X3)$	1.025	1.027	1.391	1.390	1.367	1.021	1.024	1.021	1.021	1.024	1.021	1.025	1.021	1.023
$r(N1X5)$	1.424	1.423	1.030	1.033	1.367	1.021	1.024	1.021	1.023	1.025	1.021	1.025	1.021	1.023
$r(B2X6)$	1.213	1.216	1.217	1.216	1.209	1.219	1.222	1.219	1.416	1.424	1.398	1.406	1.220	1.223
$r(B2X8)$	1.229	1.227	1.208	1.209	1.209	1.440	1.449	1.440	1.214	1.216	1.398	1.406	1.220	1.223
$\alpha(B2N1X3)$	112.747	113.763	114.639	114.222	115.078	109.887	111.335	111.512	112.673	111.962	110.267	111.962	111.190	112.160
$\alpha(B2N1X5)$	115.620	114.276	116.204	116.867	115.078	112.206	112.921	108.001	109.993	111.962	110.267	111.962	111.190	112.160
$\alpha(X4N1X5)$	109.028	108.002	102.964	103.039	103.328	107.810	106.876	108.389	107.081	106.664	108.664	106.870	107.700	106.651
$\alpha(N1B2X6)$	106.173	106.325	100.099	100.562	100.189	104.939	105.866	102.277	103.795	104.313	105.971	105.971	104.490	105.360
$\alpha(N1B2X8)$	97.348	98.884	105.548	105.353	100.189	101.581	102.997	107.548	108.478	104.313	105.971	105.971	104.490	105.360
$\alpha(X6B2X8)$	113.851	113.598	116.699	116.449	116.940	113.649	112.797	115.173	114.137	112.733	114.100	112.733	113.960	113.251

Bond lengths (r) in Å, valence angles (α) in degrees, dipole moments (μ) in Debyes. For atom numbering see Fig. 1. X, either H or F.

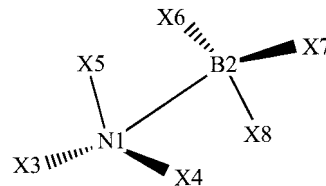


FIGURE 1. Schematic representation of $H_nF_{3-n}N \rightarrow BH_3$ and $H_3N \rightarrow BH_nF_{3-n}$ ($n = 0, 1, 2, 3$) molecular structures showing the atom numbering used in this work.

2.004 Debye (SCF result), so we do not expect this system to support (by $>1 \text{ cm}^{-1}$) an electronically stable anion of dipole-bound nature. In this section we present detailed results for dipole-bound anions formed by the seven remaining molecules[†] and discuss the contributions to the electron binding energy at anion equilibrium geometries. The relevant rotational energy level spacings for all species are much larger than the calculated values of D . Therefore, the non-BO coupling between the electronic and rotational degrees of freedom is expected to be of secondary importance and is not considered in this study.

The electron binding energies were partitioned into incremental contributions calculated at the “successive” levels of theory [KT, SCF, MP n ($n = 2, 3, 4$), and CCSD(T)], and the results for the optimal structures of the neutrals and anions are presented in Table II.

In the KT approximation, the electron binding energy results from the electrostatic and exchange interactions of the excess electron with the SCF charge distribution of the neutral molecule. The value of D^{KT} increases from 35 cm^{-1} (for HF_2NBH_3) to 1110 cm^{-1} (for H_3NBF_3), consistent with an increase of the SCF dipole moment (see Table II). It is worth noting that the KT contribution to the electron binding energy represents ca. 45–54% of the total value of D for the more strongly bound anions (i.e., $[H_3NBH_2F]^-$, $[H_3NBHF_2]^-$, and $[H_3NBF_3]^-$) whose neutral parents’ dipole moments are larger than 6 Debye and about 15–36% of D for the weakly bound anions (i.e., $[H_2FNBH_3]^-$, $[HF_2NBH_3]^-$, and $[H_3NBH_3]^-$) whose neutral parents’ dipole moments are smaller than 5.5 Debye (see Table II).

The SCF binding energies include orbital relaxation and thus take into account static polarization of the neutral molecule by an extra electron and the

[†]The results for $[H_3NBH_3]^-$ and $[H_3NBF_3]^-$ have been previously reported in Refs. [2] and [3]; however, we decided to include them in this work for completeness.

TABLE II
Electron binding energies (cm^{-1}) for the anionic states of $\text{H}_n\text{F}_{3-n}\text{N} \rightarrow \text{BH}_3$ and $\text{H}_3\text{N} \rightarrow \text{BH}_n\text{F}_{3-n}$ ($n = 0, 1, 2, 3$).

	$\text{H}_2\text{FN} \rightarrow \text{BH}_3$		$\text{HF}_2\text{N} \rightarrow \text{BH}_3$		$\text{H}_3\text{N} \rightarrow \text{BH}_2\text{F}$		$\text{H}_3\text{N} \rightarrow \text{BHF}_2$		$\text{H}_3\text{N} \rightarrow \text{BH}_3$		$\text{H}_3\text{N} \rightarrow \text{BF}_3$	
	Neutral geometry	Anionic geometry	Neutral geometry	Anionic geometry	Neutral geometry	Anionic geometry	Neutral geometry	Anionic geometry	Neutral geometry	Anionic geometry	Neutral geometry	Anionic geometry
D^{KT}	167	198	31	35	441	540	582	753	309	356	814	1100
$\Delta D_{\text{ind}}^{\text{SCF}}$	25	31	3	5	55	69	68	91	40	46	94	129
$\Delta D_{\text{disp}}^{\text{MP2}}$	249	286	78	86	384	452	457	560	315	353	603	754
$\Delta D_{\text{no-disp}}^{\text{MP2}}$	-78	-92	-26	-29	-94	-117	-139	-180	-45	-55	-186	-250
ΔD_{MP3}	6	6	1	1	18	20	24	27	10	11	23	28
ΔD_{MP4}	52	58	21	23	53	59	52	59	57	62	71	78
$\Delta D^{\text{CCSD(T)}}$	160	161	109	113	178	184	167	174	208	212	195	200
Sum	581	648	217	234	1035	1207	1211	1484	894	984	1614	2039
μ_{SCF}	4.434	4.556	3.477	3.527	5.857	6.102	6.190	6.552	5.356	5.484	6.530	7.032
μ_{MP2}	4.309	4.418	3.371	3.416	5.704	5.929	5.986	6.320	5.299	5.414	6.308	6.768

All results were obtained with the aug-cc-pVDZ basis supplemented with the 5s5p4d diffuse functions. The SCF and MP2 dipole moments (in Debye) for the corresponding neutral systems are also shown.

secondary effect of backpolarization. The orbital relaxation correction to D^{KT} , denoted $\Delta D_{\text{ind}}^{\text{SCF}}$ in Table II, represents 5–6% of the total D for all systems except HF_2NBH_3 , for which it is even less important (2% of D). The contribution denoted $\Delta D_{\text{disp}}^{\text{MP2}}$ results from dynamic correlation between the loosely bound electron and the electrons of the neutral molecule. This term is always stabilizing and amounts to 36–38% of the total value of D for all systems excluding H_2FNBH_3 , for which it is larger (44% of D); see Table II. This finding is consistent with our earlier results for other dipole-bound anions [4, 5, 9].

Because the MP2 electron correlation effects reduce the dipole moment of the neutral by 0.1–0.3 Debye in comparison with the SCF value (see Table I), the values of $\Delta D_{\text{no-disp}}^{\text{MP2}}$ are destabilizing because they describe other electron correlation factors affecting the charge distribution (and the dipole moment) of the neutral molecule and thus its electrostatic interaction with the extra electron. However, the total MP2 contribution to D remains stabilizing due to the dominant role of the dispersion component.

The contributions from ΔD^{MP3} are stabilizing but responsible for less than 2% of D in all cases and thus relatively unimportant. The contributions calculated at the MP4 level (denoted ΔD^{MP4} in Table II) are larger, stabilizing and responsible for 4–6% of the total value of the electron binding energy for the more strongly bound anions (i.e., $[\text{H}_3\text{NBH}_2\text{F}]^-$, $[\text{H}_3\text{NBHF}_2]^-$, and $[\text{H}_3\text{NBF}_3]^-$) while for the weakly bound species the ΔD^{MP4} term is more important and represents ca. 10–20% of D . Higher-order correlation effects, approximated here by $\Delta D^{\text{CCSD(T)}}$, are stabilizing and amount to 10–15% of the total value of D for systems possessing larger (greater than 6 Debye) dipole moments and are even more important for less polar species (i.e., H_2FNBH_3 , HF_2NBH_3 , and H_3NBH_3) for which $\Delta D^{\text{CCSD(T)}}$ terms represent ca. 22–48% of the total D . They produce our final prediction for the vertical electron detachment energies of 984 cm^{-1} for $[\text{H}_3\text{NBH}_3]^-$, 648 cm^{-1} for $[\text{H}_2\text{FNBH}_3]^-$, 234 cm^{-1} for $[\text{HF}_2\text{NBH}_3]^-$, 1207 cm^{-1} for $[\text{H}_3\text{NBH}_2\text{F}]^-$, 1484 cm^{-1} for $[\text{H}_3\text{NBHF}_2]^-$, and 2039 cm^{-1} for $[\text{H}_3\text{NBF}_3]^-$.

3.3. MODEL CALCULATIONS

Because many polar molecules are known to form electronically stable anionic states of dipole-bound nature (if their dipole moments are large

enough), it seems intuitive that molecular complexes that involve dative bonds should exhibit strong tendency to excess electron binding. This is due to the significant polarity of such species, which is an effect of charge flow (between two interacting fragments of the complex) accompanying dative bond formation. We have recently shown for $\text{H}_3\text{N}\cdot\text{BH}_3$ that it is indeed the dative bond that is responsible for significant polarization of the neutral species. In particular, in the case of $\text{H}_3\text{N}\cdot\text{BH}_3$ it generates a significant dipole moment of 5.3 Debye. We have also shown that this dipole moment would be much smaller (2.26 Debye) and thus not capable of ($>1\text{ cm}^{-1}$) excess electron binding if the interfragment CT interaction were “forbidden” [2].

Considering $\text{H}_3\text{N} \rightarrow \text{BH}_3$ as the reference system, one can replace one or more hydrogen atoms in its NH_3 unit (which donates electron density while forming the dative bond) with fluorine atoms and thus achieve neutral molecules that are less polar. Replacing hydrogen atoms in BH_3 (which acts as an electron density acceptor) with fluorine atoms results in more polar species. Indeed, our calculations indicate that the dipole moment of the neutral complex at its equilibrium geometry is the smallest for $\text{F}_3\text{N} \rightarrow \text{BH}_3$ (2.004 Debye) and increases when fluorine atoms are consecutively replaced with hydrogen atoms (3.477 Debye for $\text{HF}_2\text{N} \rightarrow \text{BH}_3$ and 4.434 Debye for $\text{H}_2\text{FN} \rightarrow \text{BH}_3$), achieving 5.356 Debye for $\text{H}_3\text{N} \rightarrow \text{BH}_3$ (see Table II). Further increase of the dipole moment is observed when hydrogen atoms in BH_3 are consecutively replaced with fluorines (5.857 Debye for $\text{H}_3\text{N} \rightarrow \text{BH}_2\text{F}$ and 6.190 Debye for $\text{H}_3\text{N} \rightarrow \text{BHF}_2$) and the largest value of dipole moment we found for $\text{H}_3\text{N} \rightarrow \text{BF}_3$ (6.530 Debye); see Table II.

The increase in polarity is related to the extent of the lone-pair donation (from N to B) so one might expect that the strength of the dative bond in the complexes studied changes in the same direction as their dipole moments (i.e., the weakest N \rightarrow B bond is formed for $\text{F}_3\text{N} \rightarrow \text{BH}_3$ and the strongest for $\text{H}_3\text{N} \rightarrow \text{BF}_3$). However, it is not confirmed by the population analysis (according to the Merz–Singh–Kollman scheme [30]) we performed for each of these complexes and it does not correlate with the dative N \rightarrow B bond length, which changes only slightly (see Table I). Thus, there are likely other than simple electrostatic reasons for why the extent of the charge flow is not directly related to the polarity of the system (it may also be that the population analysis itself is one of them). In addition, one has to recall that the series of complexes $\text{H}_n\text{F}_{3-n}\text{N} \rightarrow \text{BH}_3$

and $\text{H}_3\text{N} \rightarrow \text{BH}_n\text{F}_{3-n}$ ($n = 0, 1, 2, 3$) de facto consists of completely different molecules from the chemical point of view, so such simple attempts of correlating their N \rightarrow B bond lengths or their lone-pair-donation extent with their polarity are likely to fail.

Therefore, we decided to construct a relatively simple model that would allow us to study the dependence of the electron binding energy (in the anion) on the strength of the interfragment CT interaction (in the neutral parent). We arbitrarily picked one of our systems ($\text{H}_3\text{N}\cdot\text{BF}_3$) and modified it by adding $+n \times 0.1$ a.u. and $-n \times 0.1$ a.u. partial charges on the N and B nuclei, respectively, with n varying from 0–10. Because we view $\text{H}_3\text{N}\cdot\text{BF}_3$ as a system that consists of two molecular fragments (i.e., lone-pair donor and acceptor— NH_3 and BF_3 , respectively), the extra charges we added can only increase the extent of the N \rightarrow B lone-pair donation (because they increase the polarity of the complex). Therefore, we were able to change the extent of the lone-pair donation by using different values of n . We estimated the extent of that interfragment CT by summing all the partial atomic charges separately for NH_3 and BF_3 and labeling the excess charge (positive for NH_3 and negative for BF_3) as the charge flow. The $\text{H}_3\text{N}\cdot\text{BF}_3$ reference system ($n = 0$) has a charge flow of ca. 0.3 a.u., while that for $n = 10$, which is $\text{H}_3\text{O}^+/\text{BeF}_3^-$, has a charge flow of ca. 0.8 a.u. The charge flow (between two fragments) for each of these neutral complexes and the calculated electron binding energies for the corresponding anions appear in Table III and Figure 2 and indicate that:

1. The electron binding energies calculated at the KT and SCF levels depend almost linearly on the charge flow (see Fig. 2). This is consistent with the observation that the KT binding energies include only electrostatic and exchange interaction of the excess electron with the neutral parent so the charge flow between two fragments should change the polarity of the complex and thus the D^{KT} . The SCF electron binding energies (which include static polarization of the neutral molecule by an extra electron and the secondary effect of backpolarization) are not significantly larger than the KT binding energies (by ca. 10%) so the dependence of D^{SCF} vs. charge flow is similar to that obtained for D^{KT} .
2. The MP2 electron binding energy is larger the larger charge flow is and increases faster than

TABLE III
Numerical data used in Figs. 2 and 3.

Charge flow (a.u.)	D^{KT}	D^{SCF}	D^{MP2}	ΔD_{disp}^{MP2}	$\Delta D_{no-disp}^{MP2}$
0.296	726	811	1340	603	-186
0.314	1181	1318	1874	808	-252
0.342	1657	1847	2560	1044	-331
0.371	2256	2512	3399	1310	-423
0.407	2996	3327	4403	1602	-526
0.450	3887	4306	5580	1911	-637
0.502	4940	5460	6936	2229	-753
0.562	6165	6796	8471	2547	-873
0.631	7565	8316	10,181	2856	-991
0.707	9143	10,020	12,062	3145	-1103
0.793	10,897	11,904	14,103	3410	-1211

Charge flow (in a.u.) is defined as the excess positive charge on the NH_3 unit of the $\text{H}_3\text{N} \rightarrow \text{BF}_3$ complex obtained by summing partial atomic charges on the nitrogen and three hydrogen atoms. The partial atomic charges were fitted to the electrostatic potential according to the Merz–Singh–Kollman scheme (all the charges were calculated for the neutral species).

D^{SCF} or D^{KT} (see Fig. 2). Because this is simply caused by the ΔD^{MP2}_{disp} contribution, which becomes more important for larger qs , we decided to plot the ΔD^{MP2}_{disp} and $\Delta D^{MP2}_{no-disp}$ vs. the charge flow to see which of these two terms is responsible for changes in ΔD^{MP2} .

- The magnitude of both ΔD^{MP2}_{disp} and $\Delta D^{MP2}_{no-disp}$ terms is larger (see Fig. 3) when the charge flow is larger. These two contributions are of opposite sign (i.e., the former is stabilizing while the latter is destabilizing) but the ΔD^{MP2}_{disp}

dominates, so the ΔD^{MP2} term (which is defined as $\Delta D^{MP2} = \Delta D^{MP2}_{disp} + \Delta D^{MP2}_{no-disp}$) is always positive. The dependence of ΔD^{MP2} , ΔD^{MP2}_{disp} , and $\Delta D^{MP2}_{no-disp}$ on the charge flow is monotonic although not linear.

4. Conclusions

On the basis of CCSD(T)/aug-cc-pVDZ+5s5p4d calculations we conclude that:

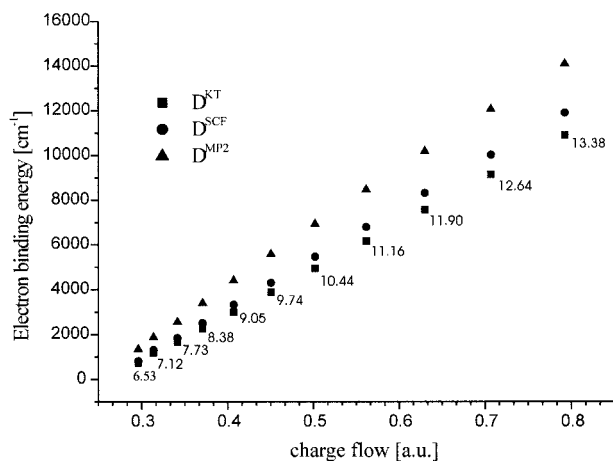


FIGURE 2. Electron binding energy D [KT (squares), SCF (circles), and MP2 (triangles)] vs. charge flow between two interacting fragments of the $\text{H}_3\text{N} \rightarrow \text{BF}_3$ modified by $+n \times 0.1$ a.u. and $-n \times 0.1$ a.u. charges on N and B, respectively (see text for how charge flow is calculated). For numerical values see Table III.

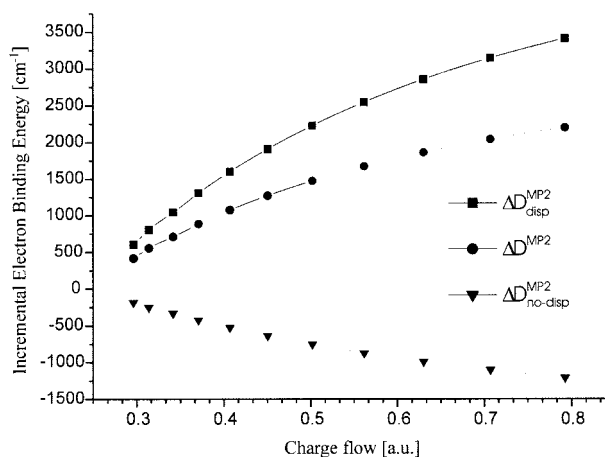


FIGURE 3. Dependence of the *incremental* electron binding energy ΔD^{MP2} (circles) and the ΔD^{MP2}_{disp} (squares) and $\Delta D^{MP2}_{no-disp}$ (triangles) contributions to the ΔD^{MP2} on the charge flow between two interacting fragments of the $\text{H}_3\text{N} \rightarrow \text{BF}_3$ complex. For numerical values see Table III.

1. $H_nF_{3-n}N \rightarrow BH_3$ and $H_3N \rightarrow BH_nF_{3-n}$ ($n = 0, 1, 2, 3$) bind an extra electron to form electronically stable dipole-bound anions (excluding F_3NBH_3).
2. Our best estimates of the vertical electron detachment energies are 648 cm^{-1} ($[H_2FN \rightarrow BH_3]^-$), 234 cm^{-1} ($[HF_2N \rightarrow BH_3]^-$), 1207 cm^{-1} ($[H_3N \rightarrow BH_2F]^-$), and 1484 cm^{-1} ($[H_3N \rightarrow BHF_2]^-$).
3. The electron binding energy of the dipole-bound anion strongly depends on the extent of the lone-pair donation in the neutral parent involving the dative bond.

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