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Theoretical investigation on electrophilicity indexes and proton affinities of some boron-nitrogen open-chain species

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Abstract: Some neutral boron-nitrogen open-chain compounds were optimized at Hartree-Fock (HF) methods with cc-pvdz basis set in the gas phase. Atomic charges were determined by the natural bond orbital (NBO) analysis. HOMO composition was calculated from the atomic orbital coefficients. The compounds were protonated from the atom supplying the highest contribution to HOMO and deprotonated from the most positive charged atom. Electrophilicity indexes of all the species were determined from the optimized structures. A parabolic curve was obtained from the graph of nucleophilicity parameters against electrophilicity indexes of all the chemical species. Electrophilicity indexes of the cationic species were found to be higher than the neutral and anionic species. Electrophilicity indexes increased with increasing of boron/nitrogen ratio for the neutral and cationic species and decreased with increasing of boron/nitrogen ratio for the anionic species. Proton affinities of the neutral and anionic species were calculated to determine their basicities. Proton affinities of the neutral species increased with decreasing of electrophilicity and boron/nitrogen ratio. Whereas proton affinities of the anionic species increased with increasing of electrophilicity.

Keywords: *Theoretical study, Electrophilicity index, Proton affinity, Boron-nitrogen open-chain species*

1. Introduction

Recently, the boron-nitrogen compounds have drawn the attention of scientist due to their promising future in many applications, such as in the field of conducting polymers, the chemical vapor deposition, the fuel cell and the hydrogen storage [1]. The electrophilicity and nucleophilicity are important parameters in the understanding of molecular properties. Quantum chemical calculations have introduced two new important concepts in chemistry. These concepts are chemical potential (μ) [2] and chemical hardness (η) [3]. These quantities are used to predict the acidity and reactivity of chemical species. The definition of these concepts is

$$\mu = -\frac{I + A}{2} \quad (1)$$

$$\eta = \frac{I - A}{2} \quad (2)$$

where I is the ionization potential and A is the electron affinity. (I+A)/2 is the Mulliken electronegativity (χ) for chemical species [2]. Softness (σ) is the inverse of the hardness. According to Koopman's theorem [4,5], I and A depend on frontier molecular orbital energies.

$$I = -E_{HOMO} \quad (3)$$

$$A = -E_{LUMO} \quad (4)$$

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Although Pearson's chemical hardness definition is $\eta=(E_{LUMO}–E_{HOMO})/2$, recently, Pearson has used to eq. (5) for calculation of the chemical hardness [6].

$$\eta = E_{LUMO} - E_{HOMO} \quad (5)$$

One way of predicting the interaction between chemical species is to take into consideration of electrophilicity indexes (ω). Parr et al. have defined the electrophilicity index as a measure of energy lowering due to maximal electron flow between donor and acceptor [7]. Electrophilicity index depending on the chemical hardness and chemical potential is given as follows.

$$\omega = \frac{\mu^2}{2\eta} \quad (6)$$

Kiyooka et al. have detected that the ω is a function of μ/η in the second-order parabola for various neutral, cationic and anionic species [8] and they have proposed the ε parameter related to nucleophilicity.

$$\varepsilon = \mu\eta \quad (7)$$

Proton affinity (PA) is very important thermodynamic parameter for determination of gas phase acidities of organic and inorganic compounds. Lewis proposed a definition of acid-base behavior in terms of electron-pair donation and acceptance [9]. According to Lewis definition, electron-pair donation species are considered as Lewis bases and electron-pair acceptances are regarded as Lewis acids. The boron-nitrogen open-chain compounds can be considered as both Lewis acid and Lewis base. Because these compounds have LUMO on the boron atom and HOMO on the nitrogen atom. Acid or base behaviors of these compounds can be determined by calculating PA values. PA can be computed from the energy differences between the interested molecule and the same molecule with one additional proton.

In this study, ω and ε values were calculated for the compounds (H_2BNH_2, H_2BNHBH_2, H_2NBHNH_2, $H_2BNHBHNH_2$, $H_2BNHBHNHBH_2$, $H_2NBHNHBHNH_2$), their geometric isomers, their cationic and anionic species. The ε-ω and boron/nitrogen ratio-ω correlations were investigated for all the species. PA values were obtained for neutral and anionic boron-nitrogen species. The PA-ω and PA-boron/nitrogen ratio relations were determined for the neutral and anionic species.

2. Computational Method

The structures of neutral boron-nitrogen open-chain compounds were drawn in Gaussview 5.0.8 [10]. Geometry optimizations and frequency calculations were made in the gas phase by using Gaussian 09 Revision-A.02 [11]. HF theory [12], density functional theory (DFT) [13], Becke-style three-parameter functional with Lee-Yang-Parr exchange-correlation functional (B3LYP) method [14] and second order Møller-Plesset perturbation (MP2) method [15,16] were used to optimize the structure of the neutral boron-nitrogen open-chain compounds. Dunning's correlation consistent polarized valance double zeta (cc-pvdz) basis set [17-19] was used to represent the atomic orbitals of boron, nitrogen and hydrogen. Geometry optimizations were followed by frequency calculations and no imaginary frequency was found for restricted spin neutral boron-nitrogen compound [20]. The same procedures were applied for the cationic and anionic boron-nitrogen species. Frontier molecular orbital energies (E_{HOMO} and E_{LUMO}) were obtained from HF, B3LYP and MP2 methods with cc-pvdz basis set. But HF molecular orbital theory provides more reliable data on molecular orbital energy levels than DFT method [8]. Therefore, HF results were used to calculate the ω, ε and PA values. The results of DFT and MP2 methods were given in supplementary data.

3. Results and Discussion

3.1 Electronic structures

The electronic structures of some neutral, cationic and anionic boron-nitrogen compounds and their isomers were optimized at HF, B3LYP and MP2 methods with cc-pvdz basis set. The optimized structures at HF/cc-pvdz level of the neutral species and atomic numbering scheme were given in Fig. 1. BH_2NH_2, BH_2NHBH_2 and NH_2BHNH_2 molecules were labeled as **1a**, **2a** and **3a**, respectively. The molecules labeling with **4a-4b, 5a-5c** and **6a-6c** are the geometric isomers of $NH_2BHNHBH_2$, $NH_2BHNHBHNH_2$ and $BH_2NHBHNHBH_2$, respectively. All the molecules are almost planar. Both nitrogen and boron atoms have sp^2 hybridization in all neutral molecules. The

molecular structures support sp^2 hybridization. Nitrogen atoms p orbitals which is perpendicular to the plane of the molecule form π-bonds between boron and nitrogen atoms.

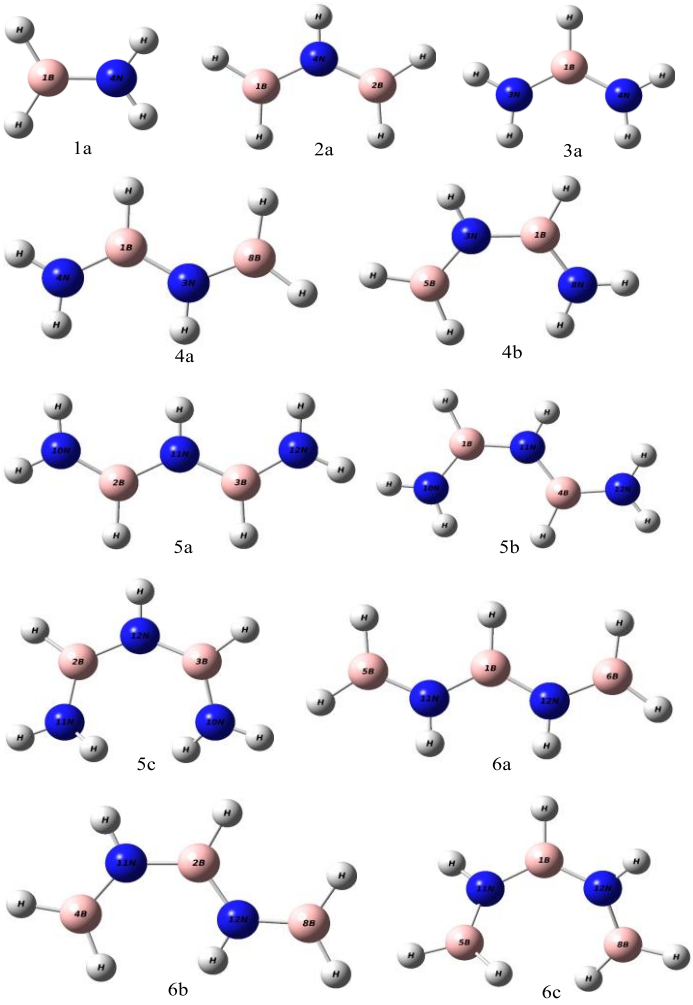

Fig. 1. Molecular structures of some neutral boron-nitrogen compounds optimized at HF/cc-pvdz level and atomic numbering scheme.

3.2 Protonation and deprotonation

The neutral species coordinate with proton by giving HOMO electrons. Therefore, HOMO composition was taken into account for protonation of the neutral species. The compounds given in Fig. 1 were protonated from the atom supplying the highest contribution to HOMO. HOMO composition of boron and nitrogen atoms were calculated from eq. (8) [21] and given in Table 1.

$$\%\,HOMO\ composition = \frac{n^2}{\sum n^2} x100 \qquad (8)$$

where n is the coefficients of atomic orbitals for a certain atom in a molecule and $\sum n^2$ is the sum of the squares of all atomic orbital coefficients in a specific molecular orbital.

Table 1. % HOMO composition of boron and nitrogen atoms calculated at HF/cc-pvdz level

Molecules	% HOMO composition
1a	8.5(1B), 91.5(4N)
2a	5.0(1B), 5.0(2B), 90.0(4N)
3a	0.4(1B), 49.8(3N), 49.8(4N)
4a	1.0(1B), 37.2(3N), 57.7(4N), 4.1(8B)
4b	1.2(1B), 35.7(3N), 1.2(5B), 59.4(8N)
5a	0.3(2B), 0.3(3B), 29.1(10N), 41.2(11N), 29.1(12N)
5b	0.3(1B), 0.3(4B), 32.1(10N), 42.0(11N), 25.2(12N)
5c	1.2(2B), 1.2(3B), 25.9(10N), 26.0(11N), 45.7(12N)
6a	0.4(1B), 4.3(5B), 4.3(6B), 45.5(11N), 45.5(12N)
6b	0.4(2B), 3.8(4B), 4.6(8B), 43.2(11N), 47.9(12N)
6c	2.8(1B), 4.3(5B), 4.3(8B), 44.2(11N), 44.3(12N)

NBO atomic charges were considered to remove the proton from the neutral species. The more positive charged atom is the more electron-withdrawing from X-H (X=B or N) bond. Therefore, separation of H^+ from the positive charged atom is easier than the negative charged atom. NBO charges of boron and nitrogen atoms were calculated at HF/cc-pvdz level for deprotonation. NBO charges were given in Table 2.

Table 2. NBO charges of boron and nitrogen atoms calculated at HF/cc-pvdz level

Molecules	NBO charges
1a	0.601(1B), -1.111(4N)
2a	0.679(1B), 0.679(2B), -1.227(4N)
3a	0.919(1B), -1.154(3N), -1.154(4N)
4a	0.957(1B), -1.226(3N), -1.142(4N), 0.648(8B)
4b	0.956(1B), -1.233(3N), 0.650(5B), -1.141(8N)
5a	0.949(2B), 0.949(3B), -1.147(10N), -1.144(11N), -1.147(12N)
5b	0.948(1B), 0.951(4B), -1.147(10N), -1.250(11N), -1.144(12N)
5c	0.950(2B), 0.950(3B), -1.155(10N), -1.155(11N), -1.259(12N)
6a	1.007(1B), 0.663(5B), 0.663(6B), -1.231(11N), -1.231(12N)
6b	1.010(2B), 0.661(4B), 0.661(8B), -1.236(11N), -1.234(12N)
6c	1.026(1B), 0.663(5B), 0.664(8B), -1.241(11N), -1.241(12N)

3.3 Electrophilicity indexes

HOMO and LUMO energies of the cationic, neutral and anionic boron-nitrogen compounds were obtained from the optimized structure at HF/cc-pvdz level of theory. μ, η, ε and ω were calculated from eq. (1), (5), (6) and (7), respectively. These values were given in Table 3.

As can be seen from Table 3, HOMO and LUMO energy rankings for a certain compound are in the form cationic < neutral < anionic. For example, HOMO and LUMO energy diagrams of $H_2BNH_3^+$, H_2BNH_2 and $HBNH_2^-$ species were given in Fig. 2. The cationic species have lower HOMO and LUMO energy levels than the neutral and anionic species. There is almost the same tendency in the other species.

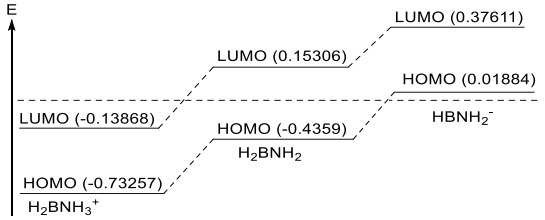

Fig. 2. HOMO and LUMO energy diagrams of $H_2BNH_3^+$, H_2BNH_2 and $HBNH_2^-$ species calculated at HF/cc-pvdz level.

Table 3 Some quantum chemical parameters (a.u.) obtained at HF/cc-pvdz level for neutral, cationic and anionic boron-nitrogen species

Compounds	B/N ratio	HOMO	LUMO	η	μ	ε	ω
1a	1/1	-0.43590	0.15306	0.58896	-0.14142	-0.08329	0.005889
2a	2/1	-0.46400	0.09341	0.55741	-0.18530	-0.10329	0.009569
3a	1/2	-0.36976	0.19188	0.56164	-0.08894	-0.04995	0.002221
4a	1/1	-0.40114	0.13551	0.53665	-0.13282	-0.07128	0.004733
4b	1/1	-0.39828	0.12432	0.52260	-0.13698	-0.07159	0.004903
5a	2/3	-0.36500	0.18545	0.55045	-0.08978	-0.04942	0.002218
5b	2/3	-0.36446	0.18490	0.54936	-0.08978	-0.04932	0.002214
5c	2/3	-0.36757	0.17255	0.54012	-0.09751	-0.05267	0.002568
6a	3/2	-0.42768	0.10297	0.53065	-0.16236	-0.08615	0.006994
6b	3/2	-0.42550	0.09885	0.52435	-0.16333	-0.08564	0.006994
6c	3/2	-0.41975	0.10073	0.52048	-0.15951	-0.08302	0.006621
$1a^+$	1/1	-0.73257	-0.13868	0.59389	-0.43563	-0.25871	0.056351
$2a^+$	2/1	-0.71763	-0.15698	0.56065	-0.43731	-0.24518	0.053608
$3a^+$	1/2	-0.64178	-0.04748	0.59430	-0.34463	-0.20481	0.035292
$4a^+$	1/1	-0.63086	-0.07497	0.55589	-0.35292	-0.19618	0.034618
$4b^+$	1/1	-0.64864	-0.08839	0.56025	-0.36852	-0.20646	0.038042
$5a^+$	2/3	-0.61817	-0.04420	0.57397	-0.33119	-0.19009	0.031478
$5b^+$	2/3	-0.61817	-0.04420	0.57397	-0.33119	-0.19009	0.031478
$5c^+$	2/3	-0.61955	-0.02987	0.58968	-0.32471	-0.19147	0.031087
$6a^+$	3/2	-0.62446	-0.11778	0.50668	-0.37112	-0.18804	0.034893
$6b^+$	3/2	-0.64124	-0.11729	0.52395	-0.37927	-0.19872	0.037683
$6c^+$	3/2	-0.66432	-0.10231	0.56201	-0.38332	-0.21543	0.041288
$1a^-$	1/1	0.01884	0.37611	0.35727	0.197475	0.070552	0.006966
$2a^-$	2/1	-0.01199	0.29194	0.30393	0.139975	0.042543	0.002977
$3a^-$	1/2	0.01581	0.38003	0.36422	0.197920	0.072086	0.007134
$4a^-$	1/1	-0.00918	0.31602	0.32520	0.153420	0.049892	0.003827
$4b^-$	1/1	-0.00943	0.30833	0.31776	0.149450	0.047489	0.003549
$5a^-$	2/3	0.00174	0.32366	0.32192	0.162700	0.052376	0.004261
$5b^-$	2/3	-0.00461	0.35552	0.36013	0.175455	0.063187	0.005543
$5c^-$	2/3	-0.00253	0.34363	0.34616	0.170550	0.059038	0.005034
$6a^-$	3/2	-0.03246	0.27927	0.31173	0.123405	0.038469	0.002374
$6b^-$	3/2	-0.03292	0.27591	0.30883	0.121495	0.037521	0.002279
$6c^-$	3/2	-0.03022	0.29167	0.32189	0.130725	0.042079	0.002750

The chemical hardness rankings are inversely proportional with HOMO and LUMO energy rankings for a certain compound (Table 3). Namely, the cationic species have higher chemical hardness than the neutral and anionic species. This is expected situation. Because, the chemical hardness is related to molar volume. The chemical hardness increases with the decreasing of the molar volume. The ω and ε values were calculated for the 33-chemical species by using their η and μ values. The correlation between the ε and ω values of the 33-chemical species was presented in Fig. 3.

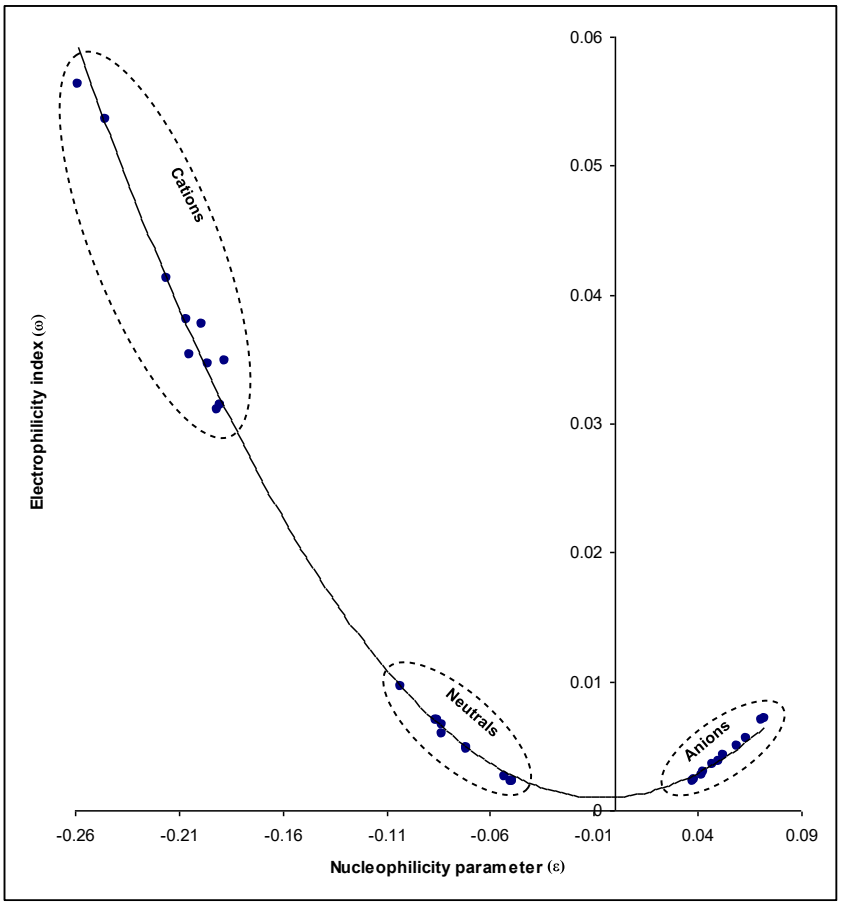

Fig. 3. The ω-ε correlation for the 33-chemical species.

Fig. 3 shows that the cationic and neutral species have negative ε values, whereas the anionic species have positive ε values. The ω values of the cationic species are higher than the neutral and anionic species. Regression analysis of the ω-ε correlation gave a second order parabolic curve. The equation of this parabolic curve is

$$\omega = 0.9077\varepsilon^2 + 0.0103\varepsilon + 0.001 \quad (R^2=0.996)$$

The correlation coefficient (R^2) of the ω-ε relation is very close to 1. This result showed that there is a good correlation between the ω and ε values in the second order parabolic curve. If the ε values of any other boron-nitrogen open-chain compounds are known, the ω values can be calculated from this parabolic curve equation. As can be seen from Fig. 3, the ω values of the cationic and neutral species are in the same tendency. Therefore, B/N ratio-ω correlation was investigated for the neutral and anionic species. This correlation was given in Fig.4.

As can be seen from Fig. 4, generally the ω values of the neutral compounds are increasing with increasing of B/N ratio. The higher B/N ratio means that the number of acceptor boron atoms are increased. The ω values are increasing with increasing the number of acceptor boron atoms for the neutral species. whereas the ω values of the anionic species are decreasing with increasing of B/N ratio. This situation can be explained by separation of the proton from the most positively charged boron atom. The boron atom would thus have negative formal charge. Having more negative formal charge species will have lower ω values.

3.4 Proton affinities of neutral and anionic species

PA values were calculated from the energy differences between the interested molecule and the same molecule with one additional proton. For example, the PA values of the BH_2NH_2 and

$BHNH_2^-$ species can be calculated from the following equations.

$$PA_{(BH_2NH_2)} = E_{(BH_2NH_2)} - E_{(BH_2NH_3^+)} \quad (9)$$

$$PA_{(BHNH_2^-)} = E_{(BHNH_2^-)} - E_{(BH_2NH_2)} \quad (10)$$

where E is the sum of the electronic and thermal energies of the related species. The PA values of the neutral and anionic boron-nitrogen open chain were given in Table 4.

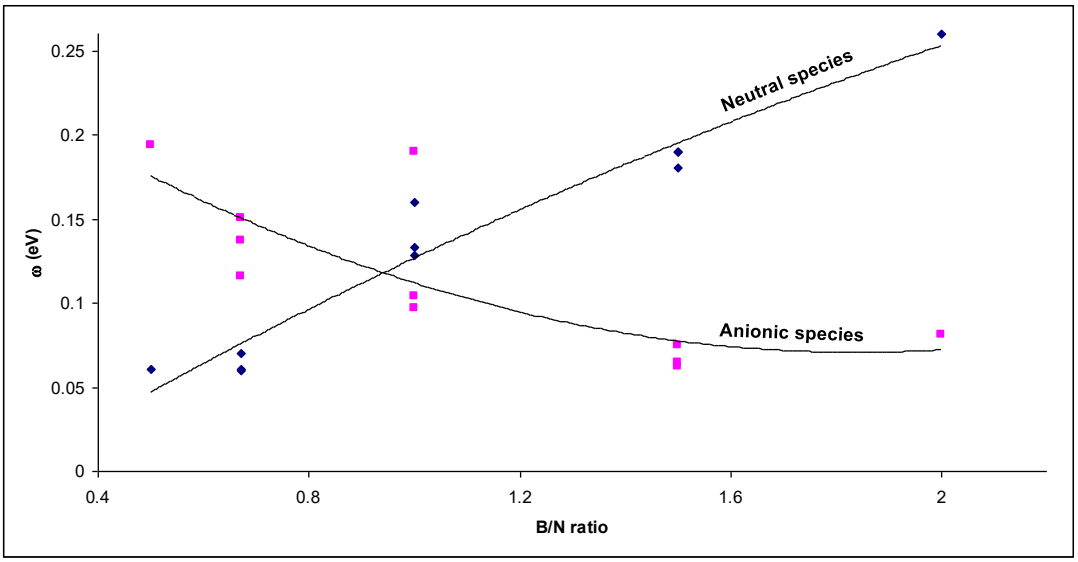

Fig. 4. B/N ratio-ω correlation for the neutral and anionic species.

As can be seen from Table 4, The PA values of the anionic species are higher than the neutral species. The PA values of the neutral species vary from 7 to 10 eV while the PA values of the anionic species are within the range 18-20 eV. These findings indicate that the anionic species have the more basic character than the neutral species. These values are also compatible with HOMO-LUMO energy rankings given in Fig 2. The rankings of PA values for the neutral or anionic species should be associated with B/N ratio or ω values. The PA-B/N ratio and PA-ω relations were investigated for the neutral and anionic species. These relations were given in Fig. 5.

The PA values for the neutral species increase with decreasing of B/N ratio and ω values (Fig 5). The lower B/N ratio means the higher nitrogen number. Nitrogen atoms are electron donor due to the lone pair on the nitrogen atoms. Therefore, PA values and alkalinity of neutral species increase with decreasing of B/N ratio. The PA-ω relation for the neutral species are the same tendency with the relation of PA-B/N ratio. Namely, PA values and alkalinity increase with decreasing of the ω values. This is expected situation. Because, proton is an electrophile and it interacts more strongly with high nucleophilic species. High nucleophilic species have lower ω values. Thus, PA values increase with decreasing of the ω values.

Generally, PA values for the anionic species increase with decreasing of B/N ratio, whereas PA values for anionic species increase with increasing of the ω values (Fig. 5). The PA-B/N ratio relation can be explained as in the neutral species. The PA-ω relationship for anionic species is opposite to those in the neutral species. This is due to increase in the number of electrons per the nucleus. Thus, PA values and alkalinity increase with increasing of the ω values.

Table 4. ω (eV) and PA (eV) values for the neutral and anionic species

Neutral				Anionic			
Species	B/N ratio	ω	PA	Species	B/N ratio	ω	PA
1a	1/1	0.160218	8.134377	$1a^-$	1/1	0.189506	19.20151
2a	2/1	0.260318	7.537820	$2a^-$	2/1	0.080999	18.64219
3a	1/2	0.060430	9.142367	$3a^-$	1/2	0.194064	19.41060
4a	1/1	0.128762	8.725493	$4a^-$	1/1	0.104116	18.90564
4b	1/1	0.133379	8.825277	$4b^-$	1/1	0.096537	18.95343
5a	2/3	0.060344	8.967935	$5a^-$	2/3	0.115911	19.24046
5b	2/3	0.060231	9.004334	$5b^-$	2/3	0.150797	19.02343
5c	2/3	0.069854	9.092611	$5c^-$	2/3	0.136957	19.14890
6a	3/2	0.190258	7.874470	$6a^-$	3/2	0.064572	18.48816
6b	3/2	0.190252	7.955919	$6b^-$	3/2	0.062007	18.50821
6c	3/2	0.180129	8.327008	$6c^-$	3/2	0.074822	18.48914

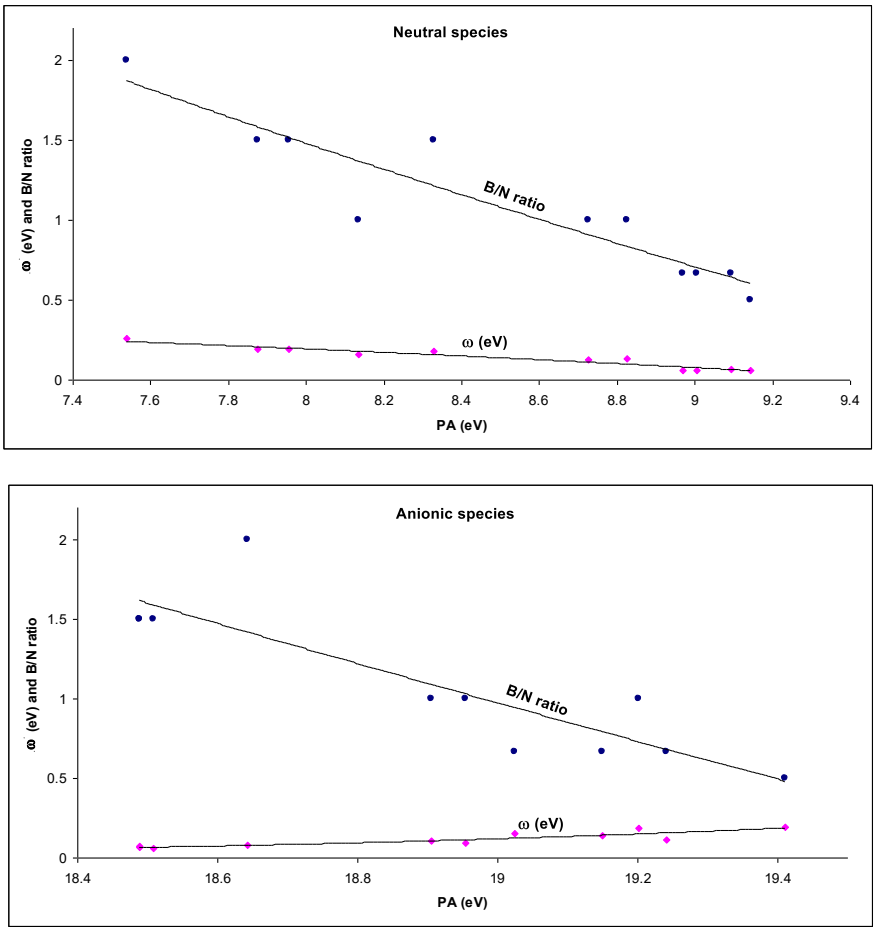

Fig. 5. The PA-B/N ratio and PA-ω relations for the neutral and anionic species.

4. Conclusion

Electrophilicity indexes (ω) and nucleophilicity parameters (ε) were calculated for the 33 boron-nitrogen open-chain species. A parabolic curve was obtained from the graph of the ε against to ω. An equation was derived to calculate the ω values of the boron-nitrogen open-chain species. The correlation ω-B/N ratio was examined. It was found that the ω values of the neutral species increased with increasing of B/N ratio, and the ω values of the anionic species decreased with increasing of B/N ratio. Proton affinities (PA) were calculated for the

comparison of the basicity of the neutral and anionic species. PA values of the anionic species are higher than the neutral species. The PA-B/N ratio and PA-ω relations were investigated. It was found that the PA values of neutral and anionic species increased with decreasing of B/N ratio. PA values of the neutral species increased with decreasing of the ω values, whereas PA values for the anionic species increased with increasing of the ω values.

Acknowledgments

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