Density Functional Theory Analysis of Borazyne Complexes of Ni(B$_3$N$_3$H$_n$F$_{2-n}$) (CO)$_2$ (*n* = 0-2)

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Abstract. The electronic structure and properties of Ni(B$_3$N$_3$H$_n$F$_{2-n}$) (CO)$_2$ (*n* = 0-2) complexes have been explored using hybrid density functional B3LYP theory. Calculations indicate B-fluorinated isomers are more stable, less polarizable, and harder than N-fluorinated isomers. The aromatic nature of the borazyne rings have been analyzed by nucleus independent chemical shift (NICS). The atoms in molecules (AIM) analysis indicates that Ni-C$_{carbonyl}$ bonds distance is well correlated with the electron density of critical point (ρ_{rcp}) in all species.
Key words: Borazyne, borazyne complexes, aromaticity, nucleus-independent chemical shift (NICS), quantum theory atoms in molecules methodology (QTAIM).

Resumen. La estructura electrónica y propiedades de los complejos Ni (B$_3$N$_3$H$_n$F$_{2-n}$)(CO$_2$)(*n* = 0-2) han sido explorados usando la teoría de funcionales de la densidad de híbridos B3LYP. Los cálculos indican que los isómeros B-fluorados son más estables, menos polarizables, y más duros que los isómeros N-fluorados. La naturaleza aromática de los anillos de borazina ha sido analizada por desplazamiento químico independiente del núcleo. El análisis de átomos en moléculas indica que las distancias de enlace Ni-C$_{carbonilo}$ correlaciona bien con la densidad electrónica del punto crítico (ρ_{prep}) en todas las especies.
Palabras clave: Borazina, complejos de borazina, aromaticidad, desplazamiento químico independiente del núcleo, átomos y moléculas.

Introduction

The structure and properties of benzyne have been studied theoretically and experimentally for many years [1-4]. The replacement of CC by BN is known to lead to Borazyne that suggested as an intermediate in the formation of borazanaphthalene and diborazine, during the photolysis of borazine [5]. Borazyne has been not isolated and characterized. A few investigations have been reported about it [6]. Because of the considerable difference between the electronegativity of boron and nitrogen, the ring delocalization of electrons in the borazyne ring is weakened.

Since the first attempt for making metal complexes using benzyne by Wittig and Bickelhaupt in 1958 [7], many benzyne complexes have been successfully prepared [8-11]; for example, M. A. Bennett *et al.* [12] synthesized organometallic compounds, NiL$_2$(C$_6$H$_4$)(L = PCy$_3$, P^{i}Pr$_3$, Cy = cyclohexyl, ^{i}Pr = isopropyl). Deaton and Gin studied the reactions of nickel(0)-benzyne complexes with symmetrically substituted 1,3-diynes in the presence of triethylphosphine, which lead to the regioselective formation of 2,3-dialkynyl naphthalenes [13].

In the present study, the quantum chemical methods were used in order to gain a deeper insight into the structure and bonding of Ni(B$_3$N$_3$H$_n$F$_{2-n}$) (CO)$_2$ (*n* = 0-2) complexes and phenomena of the substituent effect in a benzyne ring.

Computational Methods

All calculations were carried out with the Gaussian 03 suite of program [14]. All molecules were described by the standard 6-31G(d,p) basis set [15-17]. Geometry optimization was performed using Becke's hybrid three-parameter exchange functional and the nonlocal correlation functional of Lee, Yang, and Parr (B3LYP) [18]. A vibrational analysis was performed at each stationary point which corresponds to an energy minimum.

The nucleus-independent chemical shift (NICS) [19-20] has been defined as the absolute magnetic shielding computed at the center of a ring in a molecule. NICS(0.0), NICS(0.5), NICS(1.0), NICS(1.5) and NICS(2.0) were calculated at 0 (center), 0.5, 1.0, 1.5, and 2.0 Å above the ring, respectively.

The AIM2000 program [21] was used for the topological analysis of electron density, and the characteristics of ring critical points (RCPs) were taken into account: density at RCP ($\rho(r_c)$), and its Laplacian ($\nabla^2\rho(r_c)$).

The two-center delocalization index, δ(A, B), was originally defined by Bader as a measure of the extent of the correlative interaction between electrons into different regions [22]. The term δ(A, B), gives a quantitative idea of the number of electrons delocalized or shared between atoms A and B. For a closed shell system the delocalization index can be expressed as

$$\delta(A, B) = \sum_{i,j} 4 S_{ij}^A S_{ji}^B$$

where S^A_{ij} is the overlap between doubly occupied orbitals i and j over the basin of atom A. Using the delocalization index, the average two center indices (ATI) is defined as [23]

$$ATI = \frac{1}{n} \sum_{A-B}^{n} \delta(A, B)$$

where the summation runs over all adjacent pairs of atoms around 6-membered ring.

Results and discussion

Isomers stability

Relative energies (ΔE), polarizability (α), and HOMO-LUMO gaps energies of all species are summarized in Table 1. Calcu-

Table 1. Relative energies (kcal/mol), frontier orbital energies (Hartree), HOMO-LUMO gap energy ($\Delta\varepsilon$, eV) and polarizability of Ni(B$_3$N$_3$H$_n$F$_{2-n}$)(CO)$_2$ (n = 0-2) complexes in the B3LYP/6-31G(d, p) level of theory.

	R.E	E(HOMO)	E(LUMO)	$\Delta\varepsilon$	$<\alpha>$
H4	—	−0.24739	−0.08046	4.54	107.71
NFa	100.23	−0.25793	−0.09001	4.57	110.08
NFb	98.64	−0.25442	−0.08939	4.49	109.95
BFa	0.00	−0.25052	−0.08215	4.58	105.32
BFb	2.20	−0.24868	−0.08285	4.51	105.90
NF2	197.43	−0.26588	−0.09874	4.55	112.43
B$_a$FN$_b$F	98.48	−0.25868	−0.09097	4.56	107.67
B$_b$FN$_b$F	100.79	−0.2553	−0.09137	4.46	108.46
B$_a$FN$_a$F	98.69	−0.25983	−0.09148	4.58	107.66
B$_b$FN$_a$F	102.57	−0.25853	−0.09218	4.53	108.46
BF2	0.00	−0.25215	−0.08468	4.56	103.45

Table 2. Thermochemical parameters of Ni(B$_3$N$_3$H$_n$F$_{2-n}$)(CO)$_2$ (n = 0-2) complexes in the B3LYP/6-31G(d, p) level of theory.

	ΔG (kcal/mol)	ΔH (kcal/mol)	ΔS (kcal/mol.K)	K
H4	−68.59	−56.50	0.04	2.01×10^{50}
NFa	−75.69	−64.16	0.04	3.21×10^{55}
NFb	−69.34	−57.38	0.04	7.14×10^{50}
BFa	−68.21	−56.12	0.04	1.06×10^{50}
BFb	−69.64	−69.44	0.00	1.18×10^{51}
NF2	−80.85	−58.38	0.08	1.97×10^{59}
B$_a$FN$_b$F	−78.64	−56.40	0.07	4.68×10^{57}
B$_b$FN$_b$F	−68.29	−59.67	0.03	1.21×10^{50}
B$_a$FN$_a$F	−71.25	−57.69	0.04	1.81×10^{52}
B$_b$FN$_a$F	−76.54	−65.03	0.04	1.35×10^{56}
BF2	−69.52	−57.56	0.04	9.74×10^{50}

lations indicate the B-fluorinated isomers are more stable, less polarizable, and harder than N-fluorinated isomers. As expected from the principles of minimum energy, minimum polarizability, and maximum HOMO-LUMO gaps, that is, when an isomer changes from the most stable to other less stable species in most cases, the energy increases, the HOMO-LUMO gaps decreases, and the polarizability increases [24]. The increased stability of the B-fluorinated molecules is due to lone pair/lone pair electron repulsion in the N-F bond.

Thermochemical Analysis

Thermochemical analysis is done for borazyne complexes with the following reaction:

$$Ni(CO)_4 + N_3B_3H_4 \rightarrow Ni(CO)_2(N_3B_3H_4) + 2\ CO$$

The values of ΔH, ΔS and ΔG are reported in Table 2 in which the individual terms are referred to a temperature of 298 K. As can be verified, the ΔS values are quite similar for all complexes. Also, it is obvious that ΔS should be positive, since in this reaction three particles formed. Although the relative difference of the ΔG are almost the same as the ΔH. The equilibrium constants of the all complexes are given in Table 2. This shows that the equilibrium constant is more for the fluorinated complexes. This trend is compatible with the decreasing of Ni-b and Ni-N bonding length in fluorinated complexes (Figure 1).

Geometries

The main parameters of geometric structures optimized are indicated in Figure 1. The B1-N1 bond distances of borazyne and fluorinated borazynes becomes elongated when benzyne forms a complex with Ni(CO)$_2$.

The Ni-CO (trans to B) bond lengths in all complexes are slightly longer than the Ni-CO (trans to N). The N atom is

more weakly bonded than B (Figure 1), and thus, they induce stronger Ni-CO$_{trans}$ bonds in complexes. The M-CO σ-bond is formed by the donation of a lone pair of carbon atom into the d orbital of the metal. Overlapping if filled d orbital of metal with the empty CO π* orbital results in the back bonding. The geometrical parameters show the increasing of Ni-CO bond distances in fluorinated borazynes. This increasing is compatible with back bonding decreasing in Ni-CO bond.

Nucleus Independent Chemical Shift analysis (NICS)

NICS is an easy and efficient criterion to identify aromatic nature. A large negative NICS at the ring center (or inside and above the molecular plane) implies the presence of diamagnetic ring currents.

As shown in Table 3, all the negative computed NICS(0.0) values at the geometrical centers of ring suggests that these rings are obviously aromatic. In order to further identify the aromaticity, we calculated the NICS values (including NICS(0.5), NICS(1.0), NICS(1.5), and NICS(2.0)) by placing a series of ghost atoms above (by 0.5, 1.0, 1.5, 2.0 Å) the geometrical centers. All these NICS values are mainly attribute to the delocalized π electrons current. They are shown in Table 3 in detail and are all negative. Also, all NICS(0.0), NICS(0.5), and NICS(1.0) values are most negative of di, mono, and non-fluorinated species, respectively. The negative values inside and above the rings adequately prove that the diamagnetic ring current effect, characteristic for aromaticity, exists in these ground states. It is likely that induced magnetic fields generated by the σ aromaticity are particularly large in the center of the ring, whereas systems having π aromaticity show a minimum NICS at certain distances from the center of the ring, like in benzene.

On the other hand, the NICS values present the increasing of aromaticity in fluorinated rings. Furthermore, aromaticity of N-fluorinated rings is more than B- fluorinated ones. The comparison of NICS values of free borazyne and borazyne complexes show that coordination of Ni(CO)$_2$ decreases aro-

Table 3. The NICS(0.0), NICS(0.5), NICS(1.0), NIS(1.5), and NICS(2.0) values for $Ni(B_3N_3H_nF_{2-n})(CO)_2$ (n = 0-2) complexes in the B3LYP/6-31G(d, p) level of theory.

	NICS(0.0)	NICS(0.5)	NICS(1.0)	NICS(1.5)	NICS(2.0)
H4	−2.76	−3.54	−3.76	−2.90	−1.95
NFa	−5.42	−5.52	−4.78	−3.40	−2.19
NFb	−5.08	−5.13	−4.43	−3.15	−2.02
BFa	−3.47	−3.71	−3.40	−2.53	−1.70
BFb	−2.87	−3.30	−3.21	−2.44	−1.65
NF2	−8.10	−7.45	−5.67	−3.78	−2.34
B_aFN_bF	−5.75	−5.37	−4.20	−2.86	−1.81
B_bFN_bF	−5.06	−4.78	−3.85	−2.71	−1.75
B_aFN_aF	−5.97	−5.59	−4.40	−3.02	−1.93
B_bFN_aF	−5.21	−5.05	−4.15	−2.91	−1.87
BF2	−3.72	−3.51	−2.82	−2.04	−1.38

borazyne					
	NICS(0.0)	NICS(0.5)	NICS(1.0)	NICS(1.5)	NICS(2.0)
H	−5.97	−5.09	−3.48	−2.23	−1.35
NFa	−9.67	−7.64	−4.58	−2.66	−1.51
NFb	−8.51	−6.63	−3.93	−2.33	−1.35
BFa	−6.98	−5.68	−3.55	−2.14	−1.27
BFb	7.04	−5.60	−3.37	−1.98	−1.15
NF2	−11.97	−9.32	−5.38	−2.97	−1.60
B_bFN_aF	−9.76	−7.43	−4.11	−2.25	−1.23
B_aFN_bF	−10.07	−7.65	−4.25	−2.35	−1.31
B_aFN_aF	−9.96	−7.70	−4.40	−2.48	−1.39
B_bFN_bF	−9.64	−7.20	−3.90	−2.17	−1.21
BF2	−7.34	−5.45	−2.87	−1.60	−0.92

maticity of ring. The HOMO-LUMO gap values present the similar result. Therefore, magnetic criteria of aromaticity is compatible with the electronic aromaticity criteria.

QTAIM analysis

As it is difficult to separate the σ and π contributions to the electron density at the bond critical point, the ρ(r) values can be used to evaluate bond strength for different types of bonds (Table 4). The comparison of electron density in the bond critical points of B1N1 shows that ρ(B1N1) decreases in fluorinated rings. This trend is well-matched with the results of the geometrical analysis.

The different values of ρ(r) and $\nabla^2\rho(r)$ for the $Ni-C_{carbonyl}$ bonds evidently indicate the relative Ni-C bond strengths. This result is in agreement with the geometrical analysis, showing that the Ni-C bonds of $\mathbf{H_4}$ are shorter than other species.

The value of electron density and its Laplacian estimated at bond critical point of $Ni-C_{carbonyl}$ correlate very well with the strength of the bond, as well as with its length, since, as it is well known, both the strength and length of a bond are mutually dependent. A good relationship is present between

ρ($Ni-C_{carbonyl}$) values and r($NiC_{carbonyl}$) (R^2 = 0.990 for Ni-C trans to B, and R^2 = 0.999, for Ni-C trans to N).

Interestingly, in the case of all the $Ni-C_{carbonyl}$ bonds, $\nabla^2\rho$ values at corresponding BCPs are positive, as it was found for closed-shell interactions, but with H(ρ) < 0, as found for shared interactions. This is in agreement with observations made for the Ti-C bonds in titanium complexes [25] and similar complexes [26], in the case when the metal-ligand bonding has a characteristic that represents a mix of the closed-shell and shared parameters.

Additionally, the H(ρ) values are more negative for $Ni-C_{carbonyl}$ (trans to N) bonds, which is directly connected with relative greater predominance of lV(ρ)l magnitude over the G(ρ) magnitude. This suggests a more covalent character of the $Ni-C_{carbonyl}$ (*trans* to N) bonds as compared with the trans to B ones.

Generally, the greater value of lH(q)l (with negative sign), the more covalent character of the bond. It seems therefore that the covalent character of the Ni-CO bonds increases in bonds that are *trans* to N.

Table 5 shows the delocalization indexes (DI) and the average two center indices (ATI) for all species. It has to be noticed,
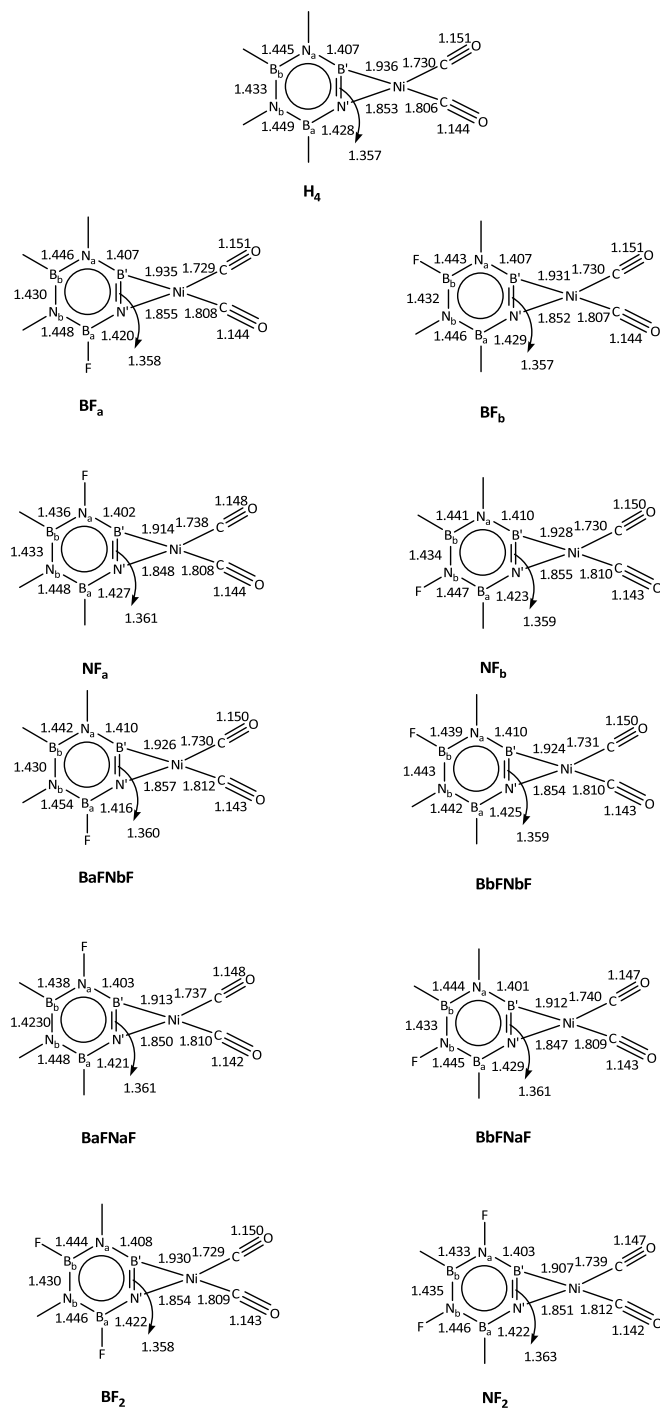
Fig. 1. Structures of the Ni(B$_3$N$_3$H$_n$F$_{2-n}$)Ni(CO)$_2$ (*n* = 0-2) complexes compounds are displayed with bonds distances.

the ATI values in N-fluorinated rings are more than B-fluorinated ones. The similar trend has been found in NICS values.

Conclusion

In this paper were investigated the structures and bonding of the Ni(B$_3$N$_3$H$_n$F$_{2-n}$)Ni(CO)$_2$ (*n* = 0-2) complexes. The ener-

Table 4. Selected AIM based parameters for (a)B'N', (b) Ni-CO(trans to B), and (c)Ni-CO(trans to N)NiC(O) bonds: Electron density (ρ), laplacian of electron density ($\nabla^2\rho$), kinetic electron energy density , G(ρ), the total electron energy density, H(ρ),potential electron energy density, V(ρ), Ni(B$_3$N$_3$H$_n$F$_{2-n}$)(CO)$_2$ (*n* = 0-2) complexes in the B3LYP/6-31G(d, p) level of theory.

(a)BN		
	ρ	$\nabla^2\rho$
H4	0.23964	0.81589
NFa	0.23581	0.80728
NFb	0.23739	0.81878
BFa	0.23769	0.81507
BFb	0.23927	0.81507
NF2	0.23345	0.81177
B$_a$FN$_b$F	0.23505	0.82241
B$_b$FN$_b$F	0.23722	0.81673
B$_a$FN$_a$F	0.23465	0.81600
B$_b$FN$_a$F	0.23554	0.80272
BF2	0.23739	0.82078

(b)Ni-CO(trans to B)					
	ρ	$\nabla^2\rho$	G	H	V
H4	0.13754	0.54398	0.19670	−0.06071	−0.25741
NFa	0.13698	0.53910	0.19498	−0.06020	−0.25518
NFb	0.13635	0.53780	0.19442	−0.05997	−0.25439
BFa	0.13693	0.54106	0.19563	−0.06037	−0.25600
BFb	0.13710	0.54166	0.19582	−0.06040	−0.25622
NF2	0.13587	0.53143	0.19245	−0.05959	−0.25205
B$_a$FN$_b$F	0.13572	0.53471	0.19331	−0.05963	−0.25295
B$_b$FN$_b$F	0.13613	0.53671	0.19398	−0.05981	−0.25379
B$_a$FN$_a$F	0.13620	0.53611	0.19375	−0.05973	−0.25348
B$_b$FN$_a$F	0.13673	0.53771	0.19444	−0.06001	−0.25444
BF2	0.13646	0.53875	0.19473	−0.06004	−0.25477

(c)Ni-CO(trans to N)					
	ρ	$\nabla^2\rho$	G	H	V
H4	0.16509	0.62482	0.23538	−0.07917	−0.31454
NFa	0.16195	0.61385	0.22998	−0.07652	−0.30650
NFb	0.16489	0.62402	0.23489	−0.07888	−0.31377
BFa	0.16546	0.62673	0.23605	−0.07936	−0.31541
BFb	0.16489	0.62422	0.23501	−0.07895	−0.31396
NF2	0.16190	0.61115	0.22922	−0.07643	−0.30565
B$_a$FN$_b$F	0.16536	0.62642	0.23576	0.07915	0.31491
B$_b$FN$_b$F	0.16476	0.62372	0.23467	0.07874	0.31340
B$_a$FN$_a$F	0.16263	0.61665	0.23109	0.07693	0.30801
B$_b$FN$_a$F	0.16172	0.61381	0.22972	0.07627	0.30599
BF2	0.16534	0.62635	0.23578	−0.07920	−0.31498

Table 5. Delocalization index and the average two center indices (ATI) of BN bonds in bond critical point of borazynes calculated at the B3LYP level of theory and with 6-31G(d, p) basis set.

	B1N1	N1B2	B2N2	N2B3	B3N3	N3B1	<DI>
H4	0.69817	0.61262	0.48579	0.50786	0.47623	0.46918	0.54164
NFa	0.70490	0.59349	0.47340	0.51536	0.48692	0.47959	0.54228
NFb	0.69421	0.60992	0.60992	0.48803	0.46656	0.48918	0.55964
BFa	0.69606	0.61193	0.48235	0.50736	0.43013	0.43214	0.52666
BFb	0.69805	0.60887	0.43265	0.45137	0.48567	0.47611	0.52545
NF2	0.69960	0.59171	0.48386	0.49445	0.46851	0.48979	0.53799
B_aFN_bF	0.69374	0.61039	0.49432	0.49022	0.40953	0.43952	0.52295
B_bFN_bF	0.69697	0.60755	0.44225	0.43033	0.46902	0.48584	0.52199
B_aFN_aF	0.70482	0.59182	0.46863	0.51409	0.43045	0.43135	0.52353
B_bFN_aF	0.70452	0.59291	0.41841	0.45606	0.48618	0.47615	0.52237
BF2	0.69703	0.60750	0.43010	0.45163	0.42867	0.42960	0.50742

getic results suggest that B-fluorinated isomers are most stable among the mono-, di-fluorinated complexes. The NICS calculations confirmed the aromaticity in the borazyne rings of the compounds. Using the analyses of both electron densities and energy densities, we could explain the characters of the Ni-C bonds in complexes.

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