

A: Spectroscopy, Molecular Structure, and Quantum Chemistry

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Spectroscopic Studies on Hydrazine-Boranes, Key Compounds for Chemical Hydrogen Storage

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Abstract

Hydrazine-boranes (H₂NNH₂·BH₃ and H₃B·NH₂NH₂·BH₃) have been proposed for the storage of hydrogen but these compounds have not generated extensive researches as ammonia- and methylamine-boranes have made these last decades. In the exciting research devoted to energy storage with environmentally friendly processes, hydrazineborane, hydrazine-bisborane and their simply substituted derivatives, could provide a satisfactory response for hydrogen production and recyclability of the formed products. To date, knowledge of the physical and chemical properties of these compounds is still scarce. In this paper, the electronic structure of various hydrazine-boranes complexes is studied by the UV-photoelectron spectroscopy, which is the experimental technique giving direct access to the energy of occupied molecular orbitals. Thus, the UV-PE spectra were registered and the first ionization energies determined. Understanding of different types of interactions between nitrogen lone pairs and their variations by complexation has been our essential goal in these studies. In particular, a clear stabilization of all molecular orbitals energies is noted when complexation with borane takes place. Evolution of the σ_{BN} bond during the hydrogen release process upon thermal activation has been also studied experimentally by UV-PES and supported by quantum chemical calculations.

INTRODUCTION

Equilibrium between technological development and conservation of our environment is one of the principal challenges in research. Many studies are devoted to the so-called "energies of the future" since actual reserves are reducing while the demand for fuel is increasing. One of the most attractive option in actual research is a fuel cell in combination with hydrogen.¹ Nevertheless, efficient processes for hydrogen production and hydrogen storage need to be developed.

In this field, ammonia-borane has a huge gravimetric-hydrogen storage potential (19.6 wt% of H₂).² During the reaction between ammonia and borane molecules, the nitrogen atom becomes less negative and the boron atom becomes less positive. Haaland studied the nature of the BN bond concluding that the electron pair in this σ bond is closer to the nitrogen atom than to the boron one.³ The substitution of ammonia-borane on the nitrogen atom by organic chains with an electron donating inductive effect rises up the negative charge on the hydrogen atoms located on boron atom.⁴ However, such substitution strongly decreases the hydrogen percentage stored in the molecule. The electronic structures of ammonia-borane⁵ and N-substituted-amine-boranes⁶ have been determined by UV-photoelectron spectroscopy (UV-PES). The formation of the BN covalent sigma bond (σ_{BN}) by the reaction between the BH₃ and NH₃ can be interpreted using the experimental ionization energy (IE) of the σ_{BN} (13.92 eV)⁶ and the nitrogen lone pair (n_N) IE in NH₃ (10.84 eV).⁷ Nguyen et al.^{8,9} on the basis of calculations at the CCSD(T)/CBS level showed how BH_3 can act as a catalyst in the hydrogen release process.¹⁰ On the other hand, in a particularly efficient approach, ammonia-borane gave an extent of hydrogen release (>2.5 equiv. or 18 wt%) per mole of H₃N-BH₃ with a nickel complex as catalyst.¹¹ The hydrogen release reaction enthalpies for NH₃·BH₃, MeNH₂·BH₃ and Me₂NH·BH₃ at 25 °C studied by quantum chemical calculations at the coupled cluster methods at the CCSD(T) level gave -5.1 kcal/mol,¹² -3.5 kcal/mol¹³ and -1.8 kcal/mol¹³, respectively. Dehydrogenation experiments of amine-borane by thermogravimetric analysis (TGA), differential thermal analysis (DTA) and thermomanometry were carried out noting the first hydrogen release at 120 °C.14,15 Dihydrogen released from ammoniaborane has been also evidenced by UV-PES.¹⁶ It should be potentially possible to regenerate the dehydrogenated products.¹⁷

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Hydrazine-boranes can be considered for the same goal that amine-boranes since a great hydrogen percentage is stored in hydrazine-bisborane: 16.9 wt%.¹⁹⁻²¹ H₃B·NH₂NH₂·BH₃ has four protic hydrogen atoms ($H^{\delta+}$) bonded to the nitrogen atoms and six hydridic hydrogen atoms (H^{δ}) bonded to the boron atoms. The capacity for hydrogen storage of a molecule is related with the gas-phase acidity and basicity properties. Adamson et al.²⁰ have studied the dehydrogenation of hydrazine-borane and hydrazine-bisborane, allowing to understand that the dehydrogenation will start more probably at the N-H than the B-H moiety and to conclude that hydrazine complexes can produce hydrogen more easily than amine-boranes. In hydrazine-borane, there is an electron-donor effect from NH₂ to NH₂·BH₃, following to the stabilization the BN bond, but the experimental study of the electronic structure of the BN bond and its nature have not been fully explored.²²⁻²⁶ The characteristic bond between nitrogen and boron atom has been however the principal topic of several studies.²⁷⁻³¹ Hydrazine-bisborane was characterized by XRD, NMR, FTIR, Raman, TGA, and DSC by Demirci et al.³² Recent studies have been carried out at different temperatures for hydrogen release from hydrazine-boranes and also from lithium hydrazinoborohydride.²¹ The reaction enthalpies between hydrazine-borane and LiH, NaH and KH were measured by Pylypko et al.³³ showing very exothermic reactions, but the lack of boron containing compounds was noticed in the volatile by-products.^{21,32,34} For monosubstituted hydrazine-boranes, only some information can be found, and sometimes contradictions of which nitrogen atom shares its electron lone pair for the formation of 1:1 adducts with borane are noted.^{35,36} Understanding interactions between both lone pairs³⁷ and their changes caused by complexation have been our essential goal in these studies. UV-photoelectron spectroscopy assisted by theoretical calculations was used to fully clarify these effects. Evolution of the σ_{BN} bond during the hydrogen release process has been also studied experimentally by UV-PES and supported by quantum chemical calculations. The studied compounds are drawn on Chart 1.



Chart 1

EXPERIMENTAL AND COMPUTATIONAL METHODS

UltraViolet-PhotoElectron Spectroscopy (UV-PES). The UV-PES spectra were recorded on a home-built (IPREM/ECP), three part spectrometer equipped with: i) main body device, ii) He–I radiation source (21.21 and/or 48 eV) and iii) a 127° cylindrical analyzer. The spectrometer works at constant analyzer energy under 5 \times 10⁻⁶ hPa working pressure and $\leq 10^{-7}$ hPa for channeltron (X914L) pressure. The monitoring is done by a microcomputer supplemented by a digital-analogue converter (AEI spectrum). The spectra resulting from a single scan are built from resolution and accuracy of 2048 points and 0.05 eV, respectively. The internal calibration of spectrum is done with helium (peak at 4.99 eV). Spectra are calibrated also with lines of xenon (12.13 and 13.44 eV) and of argon (15.76 and 15.94 eV). The accuracy of the IEs is ±0.03 eV for sharp peaks and ±0.05 eV for broad and overlapping signals. The samples were slowly vaporized under low pressure $(10^{-6} hPa)$ inside a handmade three-valve injector (3/4 in. diameter; 10 cm)length; working temperature: $-190 \le T \le +300$ °C), and the gaseous flow was then continuously analyzed by UV-photoelectron. UV-Photoelectron spectroscopy measures the binding energies of electrons in molecules in the gas phase upon irradiation with monoenergetic He (I) photons of 21.21 eV energy. Valence electrons are ejected and the PE spectra are displayed as plots of the number of ionized electrons versus their

ionization energies (IEs). Thus, PE bands correspond to direct measurement of the accessible energy states of the molecular ion, that is, the energy of occupied molecular orbitals.

Flash Vacuum Thermolysis (FVT): FVT experiments were performed in a temperature gradient range from 30 °C to 300 °C with high vacuum conditions (10⁻³ hPa) with a heating device (furnace) inside the UV-photoelectron (PE) spectrometer. FVT experiments were carried out in tandem with the UV-PES, measuring the molecular orbitals energies and following the release of hydrogen while high temperatures are applied. A supporting study by quantum chemical calculations for hydrogen release is included to the experimental results.

Computational Methods. All calculations of compound structures have been optimized using the Gaussian 09³⁸ software at the CAM-B3LYP/6-311G(d,p) level. A conformational search was made to obtain the global minima for each structure and was followed by frequency calculations in order to verify that the stationary points obtained were true energy minima. For the reliable assignment of PE bands, density functional theory $[\Delta$ SCF+TD-DFT (CAM-B3LYP)]³⁹⁻⁴⁴ and *ab initio* (OVGF,⁴⁵⁻⁵⁰ P3⁴⁹ and SAC-CI⁵⁰) calculations of ionization energies using the 6-311G(d,p) basis set⁵¹ on the ground state have been carried out on optimized geometrical structures of all studied compounds. The advantages of the most frequently employed Δ SCF-DFT method of calculations of the first IEs have been demonstrated previously.^{30,52,53} The TD-DFT approach provides a firstprincipal method for the calculation of excitation energies within a density functional context taking into account the low-lying ion calculated by the Δ SCF method. The vertical IEs were also calculated at the *ab initio* level according to OVGF (in this case the effects of electron correlation and reorganization are included beyond the Hartree-Fock approximation and the self-energy part was expanded up to third order) and SAC-CI (symmetry adapted cluster/configuration interaction methods of Nakatsuji and coworkers which describes accurately and efficiently the electronic structures of the excited, ionized and electron-attached states of molecules) methods. Avogadro software⁵⁴ was used as a visualization tool for all MOs.

A NBO study was performed for hydrazine derivatives. To study the dehydrogenation reaction, the transition state approach was applied; a scan mode was used, finding just

one imaginary frequency (between -1300 cm⁻¹ and -1500 cm⁻¹), checking that this vibration mode corresponds to the hydrogen release.

RESULTS AND DISCUSSION

Synthesis. Unsubstituted **1a** and methyl substituted hydrazines **1b**,**1c** as well as borane (BH₃) and borane-dimethylsulfide are low boiling compounds while complexes are high boiling compounds. Hydrazine-monoboranes **2a-2c** were simply synthesized by slow addition of borane complex on an excess of hydrazine in dichloromethane. Purification was performed by evaporation of low boiling compounds in vacuo and compounds **2a-2c** were obtained in very good yields based on borane. Similarly, hydrazine-bis-boranes **3a-3c** were prepared in very good yields by slow addition of more than 2 equiv. of borane complex on hydrazine followed by the removing of the low boiling compounds. In the particular case of the phenyl derivative, stoichiometric amounts of hydrazine and borane complex were used to obtain a product with a purity higher than 97%. (see the Supporting Information section). On the basis of the ¹H NMR spectra, the presence of the BH₃ group on the nitrogen bearing one or two methyl groups (compounds **2b** and **2c**, respectively) is clearly evidenced as well as the selective complexation of the NH₂ group by BH₃ for phenylhydrazine **2d** (Scheme 1 and NMR data in the Supporting Information).

$$H_{2}N-NRR' (in excess) + BH_{3} \longrightarrow H, N-N-R, N-R, BH_{3} BH_{3}$$

$$1a-1c R, R' = H, Me \qquad \qquad \downarrow (in excess)$$

$$H_{2}N-NRR' + BH_{3}(in excess) \longrightarrow H_{3}B, R', H-N-N-R, 3' BH_{3}$$

$$1a-1c 3a-3c$$

$$H_{2}N-NHPh + BH_{3} \longrightarrow H_{3}B, Ph, H-N-N, H, 2d$$

Scheme 1

UV-photoelectron spectroscopy. The experimental UV-photoelectron spectra (UV-PES) of the monoborane and bisborane derivatives of hydrazine, methylhydrazine and 1,1-

dimethylhydrazine were recorded (Figures 1-3), as well as UV-PES of the free systems which have been already reported^{55,56,57} (see Figures S1,S2 in the Supporting Information Section). Phenylhydrazine and phenylhydrazine-monoborane UV-PES are also illustrated in Figures S3 and 4 respectively. To optimize the spectrum, complexes were progressively heated from 90 to 150 °C to be vaporized and the PE spectra were continuously registered. Only the intensity of the spectrum changes with the increase of the temperature whereas decomposition would have modified the spectrum.



Figure 1: Photoelectron spectra of **a)** hydrazine-borane **2a** (90 °C) and **b)** hydrazine-bisborane **3a** (140 °C), all values in eV.



Figure 2: Photoelectron spectra of **a)** methylhydrazine-borane **2b** (90 °C) and **b)** methylhydrazine-bisborane **3b** (110 °C), all values in eV.



Figure 3: Photoelectron spectra of **a)** 1,1-dimethylhydrazine-borane **2c** (120 °C) and **b)** 1,1-dimethylhydrazine-bisborane **3c** (150 °C), all values in eV.



Figure 4: Photoelectron spectrum of phenylhydrazineborane **2d** (115 °C), all values in eV.

The comparison of the theoretically predicted IEs and experimental data are summarized in Tables 1-5. It appears that the DFT calculations (CAM-B3LYP) best model the experimentally determined IEs. ^{58,59}

In all cases, the first PE band of non complexed hydrazines corresponds to the nitrogen lone pair (n_N) and appears at 9.91 eV for NH₂-NH₂, at 9.36 eV for CH₃NH-NH₂, at 8.85 eV for (CH₃)₂N-NH₂ and at 7.86 eV for C₆H₅NH-NH₂, but, in the last case, the contribution of the aromatic ring is also noteworthy (n_N ⁻ - π_1). The donor inductive effect of methyl substituent is experimentally evidenced and corresponds to 0.55 eV destabilization for one methyl group and to 1.06 eV destabilization if two methyl substituents are present on the substituted nitrogen atom. Additional mesomeric effects of π -electron conjugation in the case of phenylhydrazine decrease the first IE of 2.05 eV.

The first IE of $H_3B\cdot NH_2NH_2$ is located at 10.7 eV, for $CH_3NH(BH_3)NH_2$ at 10.15 eV, for $(CH_3)_2N(BH_3)-NH_2$ at 10.05 eV and at 8.4 eV for $C_6H_5NH-NH_2\cdot BH_3$. The second PE bands range respectively as follow: $H_3B\cdot NH_2-NH_2$ at 11.0 eV, $CH_3NH(BH_3)NH_2$ at 10.5 eV, $(CH_3)_2N(BH_3)-NH_2$ at 10.35 eV and $C_6H_5NH-NH_2\cdot BH_3$ at 9.7 eV. For bisborane derivatives the two first PE bands are located at 11.1 and 11.5 eV for $H_3B\cdot NH_2-NH_2\cdot BH_3$, 10.95 and 11.3 eV for $CH_3NH(BH_3)-NH_2\cdot BH_3$ and at 10.85 and 11.5 eV, for $(CH_3)_2N(BH_3)-NH_2\cdot BH_3$.

The HOMO (9.91 eV) and the HOMO-1 (10.64 eV) in hydrazine **1a** (Table 2) correspond to the two lone pairs of electrons (n_N^+ , and n_N^- , respectively). ⁵⁵ The HOMO-2 (15.61 eV) is the σ_{NN} and HOMO-3 (16.66 eV) is the pseudo $\pi_{NH_2}^-$, while the IE of HOMO-4, which has not been reported before, but our calculations estimate it at 16.97 eV, should correspond to the pseudo $\pi_{NH_2}^+$.

The UV-PES of hydrazine-borane **2a** shows a first band (HOMO) at 10.7 eV attributed to the totally antibonding combination of nitrogen lone pair and σ_{NN} , σ_{BN} and σ_{BH} bonds (σ_{BH} $-\sigma_{BN} - \sigma_{NN} - n_N$). The second band (HOMO-1) at 11.0 eV is attributed to the σ_{BH} bond off-plane ionization. The third band at 11.3 eV (HOMO-2) is mainly due to the newly formed BN bond, as a result of the delocalization of the HOMO-1 (10.64 eV) from the hydrazine molecule (n_N^-) to the boron $2p_z$ vacant orbital. The HOMO-3 at 13.0 eV and HOMO-4 at 15.9 eV are the σ_{NN}, σ_{BH} and π_{NH}^- orbitals, respectively.

In the UV-PES of hydrazine-bisborane **3a** the first band at 11.1 eV contains two ionizations and is attributed to the HOMO and HOMO-1. The HOMO (11.1 eV) and the HOMO-3 (11.8 eV) correspond to the bonding and antibonding interactions of sigma BH bonds (σ_{BH}^+ and σ_{BH}^- , respectively). The HOMO-1 (11.1 eV) is attributed to the antibonding interaction of σ_{BH} and σ_{BN} , while the HOMO-2 (11.3 eV) is more localized on σ_{BH} part of the molecule. When the first reaction takes place, the non-complexed lone pair is stabilized by 0.79 eV (from 9.91 eV to 10.7 eV). When the second borane moiety is added,-the first BN bond is stabilized by 1.8 eV (from 11.3 eV to 13.1 eV).

The interpretations of these results supported by theoretical evaluation of ionization energies are presented below in Tables 1-5.

Table 1: Molecular orbital energies for hydrazine **1a** and borane: experimental and calculated by Kohn-Sham energies of MOs (ϵ^{K-S}) and Δ SCF+TD-DFT at the CAM-B3LYP/6-311G(d,p) level, OVGF, P3 and SAC-CI. Δ (HOMO – LUMO) = $\epsilon^{K-S}_{LUMO} - \epsilon^{K-S}_{HOMO}$. All values in eV. MO's visualizations from Avogadro software.

		Hydrazine (*)		E	Borane (*)
	Method	· •	C ₂		D _{3h}
гимо	CAM-B3LYP 6-311g(d,p)		çá		
		Δ(ΗΟΜΟ	-LUMO) = 10.615	Δ(ΗΟΜΟ	-LUMO) = 10.705
	-E ^{K-S}	8.375		11.466	
	∆SCF+TD-DFT	9.902		13.237	
Β	OVGF	9.766		13.209	
우	P3	9.649		12.993	
-	SAC-CI	9.683	n_N^+	13.210	σ_{BH}
	EXP.	9.91	а	12.24	e'
	-ε ^{κ-S}	8.514		11.466	
10-1	∆SCF+TD-DFT	10.273		13.237	
	OVGF	9.970		13.209	
l S	P3	9.841		12.993	
I	SAC-CI	9.875	n_N^-	13.210	σ_{BH}
	EXP.	10.64	b	12.24	e'

*: Experimental values from references 60,61

Table 2: Molecular orbital energies for hydrazine **1a**, hydrazine-borane **2a** and hydrazine-bisborane **3a**: experimental and calculated by Kohn-Sham energies of MOs ($-\epsilon^{K-S}$) and Δ SCF+TD-DFT at the CAM-B3LYP/6-311G(d,p) level, OVGF, P3 and SAC-CI. All values in eV. MO's visualizations from Avogadro software.

		Ну	drazine (*)	H	Hydrazine monoborane		Hydrazine bisborane	
	Method	4	C2			C _{2h}		
	-ε ^{K-S}	8.375		9.390		10.101		
	∆SCF+TD-DFT	9.902		10.601		11.046		
ð	OVGF	9.766		10.785		11.462		
ЮН	P3	9.649	n_N^+	10.529	$\sigma_{BH} - \sigma_{BN} - \sigma_{NN} - n_N$	11.201		
	SAC-CI	9.683		10.634		11.486	σ^+_{BH}	
	EXP.	9.91	а	10.7	a'	11.1	a _u	
	-ε ^{K-S}	8.514		9.465	~	10.183		
	∆SCF+TD-DFT	10.273		10.670		11.092		
10-1	OVGF	9.970		10.835		11.491		
HON	P3	9.841		10.594	σ_{BH}	11.254		
	SAC-CI	9.875	n_N	10.731	DII	11.505	$o_{BH} - o_{BN}$, o_{NN}	
	EXP.	10.64	b	11.0	a"	11.1	a _g	
HOMO-2	-ε ^{K-S}	14.034		10.007		10.350		
	∆SCF+TD-DFT	15.660		11.203		11.312		
	OVGF	15.556		11.322		11.692		
	P3	15.645	σνν	11.159	σ_{RN}	11.440		
	SAC-CI	15.666	UNIN CININ	11.223	- 1011	11.717	$\sigma_{BH} - \sigma_{BN}$	
	EXP.	15.61	а	11.3	a'	11.5	b _u	
	-ε ^{K-S}	15.073		11.508		10.422		
_	∆SCF+TD-DFT	16.800		12.630		11.733		
0	OVGF	16.841		12.756		11.793		
HON	P3	16.784		12.602		11.527		
	SAC-CI	16.911	π_{NH_2} (pseudo)	12.676	σ_{NN} , σ_{BH}	11.838	σ_{BH}^{-}	
	EXP.	16.66	b	13.0	a'	11.8	b _g	
	-ε ^{κ-s}	15.438		14.640		12.048		
HOMO-4	∆SCF+TD-DFT	17.088		15.810		12.947		
	OVGF	17.143		16.298		13.158		
	P3	17.111	π_{hu}^+ (pseudo)	16.196	π_{NH}^{-}	13.016		
	SAC-CI	17.241	mn ₂ (r)	16.327		13.271	σ_{BN}	
	EXP.	(16.66)	а	15.9	a"	13.1	a _g	

*: Experimental values from reference ⁶¹

Table 3: Molecular orbital energies for methylhydrazine **1b**, methylhydrazine-borane **2b** and methylhydrazine bisborane **3b**: experimental and calculated by Kohn-Sham energies of MOs ($-\epsilon^{K-S}$) and Δ SCF+TD-DFT at the CAM-B3LYP/6-311G(d,p) level, OVGF, P3 and SAC-CI. All values in eV. MO's visualizations from Avogadro software.

		Methylhydrazine (*)		Methylhydrazine borane		Methylh	nydrazine bisborane
	Method						
	KS		€ C ₁		Γ C ₁		<u>к</u> С ₁
	-~ ³ -	8.005		9.079		10.006	
	∆SCF+TD-DFT	9.259		10.166		10.927	
Β	OVGF	9.168		10.368		11.287	
오	P3	9.023		10.151		11.031	
	SAC-CI	8.983	n_N^{π}	10.107	$o_{BH} - o_{BN} - o_{NN} - n_N$	11.033	σ_{BH}
	EXP.	9.36	а	10.15	а	10.95	а
	-ε ^{K-S}	8.516		9.444		10.039	
	∆SCF+TD-DFT	9.639		10.414		11.023	e. 🔽
6	OVGF	9.753		10.751		11.332	
₽ N	P3	9.621	n_N^σ	10.499		11.070	
1	SAC-CI	9.623	14	10.641	σ_{BH}	11.136	σ_{BH}
	EXP.	10.28	а	10.5	а	10.95	а
	-ε ^{K-S}	12.118		9.949		10.180	
	∆SCF+TD-DFT	13.213		11.078		11.148	40 7
0-7	OVGF	13.635		11.017		11.475	
₽	P3	13.483	σ_{NN}, π_{CH_2}	10.870		11.213	
1	SAC-CI	13.582		11.022	σ_{BN}	11.261	σ_{BH}
	EXP.	13.38	а	11.2	а	11.3	а
	-ε ^{K-S}	12.920		12.097		10.251	
	∆SCF+TD-DFT	14.150		13.209		11.440	📡
0-3	OVGF	14.501		13.439		11.540	
NO NO	P3	14.322		13.224		11.279	
1	SAC-CI	14.437	π_{CH_2}	13.302	σ_{NN} , σ_{BH}	11.335	σ_{BN}
	EXP.	14.32	а	13.0	а	11.8	а
	-ε ^{K-S}	14.387		13.218		11.618	
4	∆SCF+TD-DFT	15.583		13.882		12.415	
	OVGF	15.644		14.670		12.615	
MO	P3	15.690		14.494	-	12.480	
	SAC-CI	15.737	π_{NN}^{*} , π_{CN}^{*}	14.552	σ_{NN} , π_{CH_2}	12.338	σ_{BN}
1	EXP.	15.87	а	13.2	а	13.0	а

*: Experimental values from reference ⁶¹

Compared to the unsubstituted hydrazine, in methylhydrazine, (Table 3) the inductive donor effect of methyl substituent is experimentally evidenced by the lower IE (higher HOMO) of methylhydrazine (9.36 eV) versus hydrazine (9.91 eV). HOMO-1 energies of 1a and 1b are located at 10.64 eV and 10.28 eV respectively, HOMO-2 (13.38 eV) in methylhydrazine **1b** is the σ_{NN} , π_{CH_2} as it is σ_{NN} (15.61 eV) in the hydrazine molecule, but due to the presence of the methyl substituent, the contribution of a pseudo π_{CH_2} is also noticed. HOMO-3 (14.32 eV) corresponds to the $\pi_{{\it CH}_2}$ and HOMO-4 (15.87 eV) to the antibonding MOs (π_{NN}^* and π_{CN}^*), as described by Mayer et al.⁶² When a borane molecule reacts with **1b**, the HOMO of methylhydrazine-borane appears at 10.15 eV (σ_{BH} $-\sigma_{BN} - \sigma_{NN} - n_N$). HOMO-1 in **2b** (10.5 eV) corresponds to the σ_{BH} (off-plane), while HOMO-2 (11.2 eV) is mainly due to the σ_{BN} bond. HOMO-3 (13.0 eV) and HOMO-4 (13.2 eV) are attributed to the σ_{NN} , σ_{BH} and σ_{NN} , π_{CH_2} , respectively. In the UV-PES of hydrazine bisborane **3b** the first and the second bands correspond to the HOMO (10.95 eV), HOMO-1 (10.95 eV) and HOMO-2 (11.3 eV), and have a σ_{BH} nature. The HOMO-3 (11.8 eV) and the HOMO-4 (13.0 eV) are attributed to the two σ_{BN} bonds. When the reaction between methylhydrazine and borane takes place, the new BN bond appears at 11.2 eV, and the lone pair on the other nitrogen is stabilized by 0.79 eV (from 9.36 eV to 10.15 eV). When methylhydrazine monoborane reacts with another borane molecule, the new BN bond appears at 11.8 eV and the firstly formed BN bond is stabilized by 1.8 eV (from 11.2 eV to 13.0 eV).

Table 4: Molecular orbital energies for 1,1-dimethylhydrazine **1c**, 1,1-dimethylhydrazineborane **2c** and 1,1-dimethylhydrazine-bisborane **3c**: experimental and calculated by Kohn-Sham energies of MOs ($-\epsilon^{K-S}$) and Δ SCF+TD-DFT at the CAM-B3LYP/6-311G(d,p) level, OVGF, P3 and SAC-CI. All values in eV. MO's visualizations from Avogadro software.

		1,1-Din	nethylhydrazine (*)	1,1-Dimethylhydrazine borane		1,1-Dimethylhydrazine bisborane	
	Method	ľ	C1				
Q	-ε ^{κ-S}	7.688		8.947		9.858	
	∆SCF+TD-DFT	8.675		9.960		10.791	
	OVGF	8.652		10.166		11.095	
ЮН	P3	8.510		9.948	$\sigma_{BH} - \sigma_{BN} - \sigma_{NN} - n_N$	10.838	
	SAC-CI	8.328	n_N^π	9.889		10.966	σ_{BH}
	EXP.	8.85	а	10.05	a'	10.85	a'
	-ε ^{K-S}	8.622		9.356	Č	9.865	
	∆SCF+TD-DFT	9.625		10.239		10.813	
IO-1	OVGF	9.744		10.614		11.158	\rightarrow
10N	P3	9.583	n_{σ}^{σ}	10.359		10.876	
-	SAC-CI	9.550		10.449	σ_{BH}	11.043	σ_{BH}
	EXP.	10.07	а	10.35	a"	10.85	a"
10-2	-ε ^{K-S}	11.696		9.878		10.102	
	∆SCF+TD-DFT	12.604		10.851		10.873	
	OVGF	13.045		10.844		11.345	
NOF	P3	12.883		10.707	бли	11.082	
-	SAC-CI	12.912	σ_{NC}	10.829	• OBN	11.211	σ_{BH}
	EXP.	12.65	а	10.75	a'	10.85	a"
	-ε ^{κ-s}	12.134		11.843		10.145	
~	∆SCF+TD-DFT	13.047		12.865	Лсн.	11.222	$\prec \geq$
<u>ا</u> 0-3	OVGF	13.470		13.070		11.381	
ИОН	P3	13.318	σ_{NN}	12.853		11.121	C av
_	SAC-CI	13.315	1111	12.958		11.263	o_{BN}
	EXP.	13.00	а	12.9	a'	11.5	a'
	-ε ^{K-S}	12.501		12.683		11.168	
_ [∆SCF+TD-DFT	13.561		13.213		11.797	
νΟ	OVGF	13.980		13.944		12.026	
ЮH	P3	13.786	π_{CH_2}	13.793	$\prec \sigma_{NC}$	11.930	σρη
- [SAC-CI	13.898	5112	13.876	-	11.856	⊂BN
	EXP.	13.50	а	13.5	a"	12.05	a'

*: Experimental values from reference ⁵⁶

As previously described for hydrazines, the HOMO (8.85 eV) and HOMO-1 (10.07 eV) of 1,1-dimethylhydrazine **1c** (Table 4) correspond to the two nitrogen lone pairs π and σ interactions (n_N^{π} and n_N^{σ} , respectively).⁵⁶ The HOMO-2 (12.65 eV) is the σ_{NC} , while the

HOMO-3 (13.0 eV) in **1c** is linked with the σ_{NN} . Finally, the HOMO-4 (13.5 eV) corresponds to the π_{CH_2} molecular orbital ionization. The HOMO in 1,1-dimethylhydrazine-borane **2c** (10.05 eV) corresponds to the totally antibonding combination of nitrogen lone pair (n_N) and the sigma BH, BN and NN MOs ($\sigma_{BH} - \sigma_{BN} - \sigma_{NN} - n_N$). The HOMO-1 (10.35 eV) comes from the off-plane σ_{BH} orbital of borane molecule. The HOMO-2 (10.75 eV) is attributed to the ionization of the σ_{BN} bond formed from the n_N^σ orbital in **1c** (HOMO-1) and the empty 2p_z boron orbital. The HOMO-3 and HOMO-4 (12.9 and 13.5 eV) in **2c** correspond to the π_{CH_2} and σ_{NC} orbital ionizations, respectively. For the 1,1dimethylhydrazine-bisborane **3c** the first PE intense band at 10.85 eV contains three ionizations: the HOMO, HOMO-1 and HOMO-2; all are attributed to the σ_{BH} orbitals. The σ_{BN} bond ionization corresponds to the HOMO-3 (11.5 eV) and HOMO-4 (12.05 eV).



Figure 5: Diagram of selected molecular orbital interactions of hydrazine, **1a-1c** and their mono and bisborane derivatives. All values in eV. Figure 5 shows the energetic evolution of the MO energy corresponding to the nitrogen lone pair before complexation and how this energy is lowered after interaction with p empty B orbital. Beyond, the second complexation allows another energetic stabilization.

To summarize these studies, a general diagram (Figure 5) of molecular orbital interactions of hydrazines **1a-1c** and their mono and bisborane derivatives is presented, showing how the inductive effects [+I] of the substituents destabilize the n_N^+ orbital. The energies of molecular orbitals corresponding to the lone pairs of nitrogen atoms in 1,1dimethylhydrazine⁵⁶ are 8.85 eV (n_N) and 10.07 eV (n_N), respectively, and they have an energetic gap between them of 1.22 eV. This difference is less important in the cases of methylhydrazine⁶¹ (0.92 eV; n_N 9.36 eV and n_N 10.28 eV) and hydrazine⁶¹ (0.73 eV; n_{N^+} 9.91 eV and n_N^- 10.64 eV). The experimental measures of the inductive effects of two 1,1-dimethylhydrazine (1.06)eV) methyl groups in or one methyl group in methylhydrazine (0.55 eV), respectively, in comparison with the corresponding orbitals in hydrazine are thus nicely evidenced (destabilization of the HOMO and HOMO-1 orbitals). The sigma BN bond ionization is located at 11.3 eV for hydrazine-monoborane, at 11.2 eV for methylhydrazine-monoborane and at 10.75 eV for dimethylhydrazine-monoborane. The second complexation by BH₃ shifts the first sigma BN bonds IEs to 13.1 eV for hydrazine bisborane, to 13.0 eV for methylhydrazine bisborane and to 12.05 eV for 1,1dimethylhydrazine bisborane. Furthermore, we can observe how for all hydrazine systems the molecular orbitals are stabilized when one or two molecules of borane are complexed to the systems with the σ_{BN} bond formation (figure 5). We should notice that the complexation in these systems occurs on the nitrogen with more methyl substituents, but when the substituent is a phenyl group, the complexation take place on the less substituted nitrogen because of the mesomeric effects from the aromatic ring, which strongly decrease the nucleophilicity of the lone pair of the NH group. This effect is opposite of that we observed with methyl substituents. Table 5 shows the experimental IE's values obtained for phenylhydrazine by Streets et al.⁵⁷ and reported for HOMO to HOMO-3. For the sake of consistency of all our results we also recorded the phenylhydrazine photoelectron spectrum and have complemented by values of HOMO-4 and HOMO-5.

Table 5: Molecular orbital energies for phenylhydrazine **1d** and phenylhydrazine monoborane **2d**: experimental and calculated by Kohn-Sham energies of MOs ($-\varepsilon^{K-S}$) and Δ SCF+TD-DFT at the CAM-B3LYP/6-311G(d,p) level, OVGF, P3 and SAC-CI. All values in eV. MO's visualizations from Avogadro software.

		Phenylhydrazine (*)		Phenylbydrazine monoborane		
	Method		$\langle \gamma \rangle$			
			\sim	\sim	\sim	
	Corrected	X _{exp} =0.823		X _{exp} =0.459		
	Conected	7.860		8.400		
OMO	-ε ^{κ-S}	7.037		7.941		
	∆SCF+TD-DFT	7.766		8.609		
	OVGF	7.540		8.438		
-	P3	7.798	l	8.687	1	
	SAC-CI	7.146	$n_N^~\pi_1$	7.929	$n_N - \pi_1$	
	EXP.	7.86	а	8.4	а	
	Corrected	9.233		9.477		
	-ε ^{κ-S}	8.410		9.018		
	∆SCF+TD-DFT	9.237	\sim \sim \sim	9.808		
MC	OVGF	9.006		9,608		
IO	P3	9.137		9.724		
-	SAC-CI	8,717	π_2	9.235	π_2	
	FXP.	9.19	a	9.7	a	
	Corrected	9 951		9 984		
	-£ ^{K-S}	9 128		9.525		
-2		9 954		10 103		
ģ	OVGE	10 182		10.823		
ō	P3	10.004	$\gamma \sim$	10.528	\sim	
I		0.836	n_N^+	10.615		
	FXP	10.00	2	10.010	0 <u>8H</u>	
	Corrected	10.868		10 104	ŭ	
ę		10.000		9.645		
		10.040		10 276		
Q	OVGE	10.700		10.270		
ō	0	10.500		10.510	$\gamma \gamma \gamma$	
Т	SAC-CI	10.337	$\sigma_{av} = \pi_{a}$	10.740	σρμ	
	FXP	10.200	<u> </u>	10.7 40	- <u>511</u> 2	
	Corrected	11 845	a	11,336		
	-£ ^{K-S}	11 022		10.877		
4	ASCE+TD-DET	11.853		11 468		
Q	OVGE	11.852		11 401		
ō	P3	12 011		11 346		
Т	54C-CI	11 664	π^*	10.975	$\sigma_{CN} = \pi_2$	
	EXP	11.85	^ ⁿ⁴	11 1	a	
HOMO-5	Corrected	12,361	<u>u</u>	12 088	u	
	-5 ^{K-S}	11.538		11 629		
	ASCE+TD-DET	12 377		12 228		
		12 368		12.220		
	P3	12.000		12.022	γ	
		12.777	π_{ς}^{*}	12.101		
		12.170	, ,	12.191	$o_{BN} - \pi_{CC}$	
	EAF.	12.4	d	12.2	d	

 \ast Experimental values from reference 57 . HOMO-4 and HOMO-5 IEs experimental from this work.

The lone pair of the NH₂ group in the phenylhydrazine molecule corresponds to the HOMO-2 (10.09 eV), while the HOMO of phenylhydrazine (7.86 eV) is the $n_N^- - \pi_1$ antibonding combination. The π aromatic ring matches with HOMO-1, HOMO-3, HOMO-4 and HOMO-5 at 9.19 eV, 10.64 eV, 11.85 eV and 12.4 eV. In phenylhydrazine-borane, the BN bond appears as the HOMO-5 (12.2 eV), while the HOMO ($n_N - \pi_1$) and HOMO-1 (π_2) are located at 8.4 eV and 9.7 eV, respectively.

The HOMO ($n_N^- - \pi_1$;7.86 eV) and HOMO-1 (π_2 ;9.19 eV) of **1d** are shifted by 0.54 eV and 0.51 eV, respectively upon complexation and appears at 8.4 eV and 9.7 eV in **2d**, respectively. HOMO-2 and HOMO-3 are σ_{BH} orbitals (10.8 eV) and HOMO-4 ($\sigma_{CN} - \pi_3$) at 11.1 eV in **2d** corresponds to the stabilization of HOMO-3 of **1d** (10.64 eV).

NBO Analysis. The theoretical studies of the electronic structure of hydrazines **1a-1d** and their corresponding borane **2a-2d** and bisborane derivatives **3a-3c** were carried out applying the NBO analysis⁶² (Figure 6). (We have identified by theoretical calculation the regioisomers of all hydrazine derivatives. Computational details on optimized geometry of the thermodynamically most stable isomers are reported in the Supporting Information). The BN and NN bonds contain almost two electrons (single bond); the boron contribution to the BN bond (%B), not exceeding the 20% and decreasing when a second borane moiety or more methyl groups are present, with discrepancies noticed for tetramethylated derivatives certainly due to the steric hindrance. The pyramidal shape of nitrogen atom can be correlated with the sigma parameter (Σ), which is the sum of α , β and γ angles as shown in Figure 7, describing a planar (sp²) nitrogen when Σ =360°. In order to compare the monoborane and bisborane hydrazine complexes, the most substituted nitrogen atom N₁ and the attached boron atom B₁ are taken into account.

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Figure 6: Natural bonding orbital (NBO) analysis of hydrazine derivatives when complexed by one or two borane moieties. Numbers on bonds correspond to NBO's occupation (single bond close to 2). Contribution of boron atom to the BN bond (%B) and pyramidal geometry of nitrogen atom (Σ) are also given.



Figure 7: Representation of considered angles for hydrazine derivatives. R₁, R₂, R₃ and R₄ = H or CH₃.

The Σ parameter increases when more methyl groups are present and decreases when the first borane molecule reacts with the more substituted nitrogen atom in hydrazine. After complexation, the boron atom is less positively charged (and nitrogen less negatively), corresponding to the charge transfer into the $2p_z$ originally empty boron orbital. The consequences of this charge transfer are related to the BN bond length elongation when more methyl or borane substituents are present as shown in Figure 8. The presence of methyl groups in the structure creates interactions of $CH_3\cdots CH_3$, $CH_3\cdots BH_3$ and $BH_3\cdots BH_3$, the $CH_3\cdots BH_3$ being the favored ones, giving the gauche-like conformers.



Figure 8: Hydrazine **1a-1c**, hydrazine-monoborane **2a-2c** and hydrazine-bisborane **3a-3c** derivatives. Bond length in angstroms (Å) and angles in degrees.

Dehydrogenation. The capacity of these complexes to store and release hydrogen should be considered. The hydrogen elimination reaction has been studied by the transition state of a four membered ring as presented on Figure 9. Reaction pathway for 1,2-elimination of H_2 from hydrazine-borane (Figure 10) and methylhydrazine-borane (Figure 11) show the dehydrogenation product formation considering a more exergonic reaction, and the hydrogen release carried out with a negative Gibbs free energy, meaning that it is a more spontaneous process when a higher temperature is applied. Computational details of optimized geometry of the dehydrogenated compounds are reported in the Supporting Information.



Figure 9: Transition states of hydrazine-bisborane for **a)** 1,2-elimination and **b)** for 1,3-elimination reactions.



Figure 10: Calculated (CAM-B3LYP/6-311G(d,p) reaction pathway for hydrogen release of hydrazine-monoborane **2a** at 25 °C (pink) and 200 °C (red). All ΔG values in kcal/mol.



Figure 11: Calculated (CAM-B3LYP/6-311G(d,p) reaction pathway for hydrogen release of methylhydrazine-monoborane **2b** at 25 °C (light blue) and 200 °C (dark blue). All Δ G values in kcal/mol.

When the hydrogen is released from hydrazine-borane derivatives, the electronic structure of molecules changes and, subsequently, the IE of σ_{BN} bond is modified. The study of the evolution of the ionization energy of the σ_{BN} bonds is difficult to follow by UV-PES due to the considerable overlapping of the bands in this area, also the very narrow temperature zone for selective elimination limits our experimental set-up for that purpose. The UV-PE spectra are so complex due to the mixture of formed products that the reliable bands attribution is risky. However, the presence of IE = 15.98 eV with the vibrational progression corresponding to dihydrogen (PE spectrum in Figure 12) demonstrates the formation of dihydrogen as shown in Figures 13-15, with the exception of 1,1-dimethylhydrazine-borane **2c** for which a 1,2-dehydrogenation cannot occur.



Figure 13: FVT photoelectron spectra of **a**) hydrazine-borane **2a** at 120 °C, **b**) hydrazine-bisborane **3a** at 190 °C, **c) 3a** at 190 °C, corrected baseline; all values in eV.



Figure 14: FVT photoelectron spectra of **a**) methylhydrazine-borane **2b** at 233 °C, **b**) methylhydrazine-bisborane **3b** at 150 °C; all values in eV.



Figure 15: FVT photoelectron spectra of **a**) 1,1-dimethylhydrazine-borane **2c** at 300 °C, **b**) 1,1-dimethylhydrazine-bisborane **3c** at 290 °C; all values in eV.

The theoretical values of IEs issues of Δ SCF+TD-DFT calculations have been used to track the evolution of σ_{BN} bonds to double or triple BN bonds during the dihydrogen release process. Hereafter the diagrams (Figure 16) with the energetic variation of σ_{BN} bonds are showed when one, two, three or four moles of dihydrogen are released from hydrazinebisborane **3a** and for hydrazine-borane **2a** (Tables S1-S3 in the Supporting Information).

 It should be noted that formation of more conjugated systems follows to bigger general IE values of σ_{BN} i.e. its energy lowering (stabilization).



Figure 16: MO energy diagrams for hydrazine mono (red) and bisborane (brown) for hydrogen release. TD-DFT values extracted from Tables S1-S3. All values in eV.

Similar studies were performed with methylhydrazine (Table S4) and 1,1dimethylhydrazine-borane (Table S6) and -bisborane derivatives (Tables S5,S7), leading to the energetic stabilization of BN bond when one, two, three or four dehydrogenation reactions occur. For 1,1-dimethylhydrazine-borane -2c) the BN bond is destabilized after 1,3-elimination reaction, while for 1,1-dimethylhydrazine-bisborane (3c) as for the other derivatives (2a, 3a, 2b and 3b) the 1,2-elimination stabilizes the BN bond. These results support the reason why the PE spectrum of dihydrogen was not observed in the

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experimental measurements of **2c**, corroborating that dihydrogen is released by 1,2elimination reaction.

CONCLUSION

Syntheses of complexes between hydrazines and borane have been performed and products were characterized by NMR and UV-PES spectroscopies. The complexation occurs by the lone pair of the more alkyl substituted nitrogen atom (as methyl with a donor inductive effect). In the case of phenylhydrazine, the complexation occurs with the lone pair of the less substituted nitrogen atom because of the presence of a mesomeric effect (nitrogen lone pair directly involved in the electronic delocalization with the phenyl substituent). UV-PE spectra of complexes have been recorded and the analysis was supported by theoretical calculations of IEs. Results show a general stabilization of molecular orbitals when complexation with borane takes place. Presence of inductive effect when a methyl group is attached to the hydrazine structure has been highlighted by the higher energies of HOMO and HOMO-1 (lower IEs).

FVT experiments have evidenced for the first time by UV-PES the presence of hydrogen (15.98 eV) released from hydrazine-borane derivatives. However, the process of dihydrogen elimination was not selective enough to allow direct characterization of dehydrogenated products (too complex mixture of present compounds) and a reliable attribution of PE bands present. The experimentally measured theoretically evaluated IEs provided unique information about σ_{BN} bond stabilization when dihydrogen is released from complexes and stabilization increase by conjugation effects when double or triple bonds are formed.

Optimization of hydrogen release conditions and regeneration processes of these compounds should be continued with the aim to demonstrate the potentiality related to these compounds as a regenerative spent fuel.

ASSOCIATED CONTENT

The Supporting Information is available free of charge on the ACS Publications website at DOI: ***

List of compounds; Experimental details on hydrazine-borane, hydrazinebisborane derivatives; NMR data; Computational details of optimized geometry of hydrazines, hydrazine-borane and hydrazine-borane derivatives; Transition states; Calculated MO energies (Tables).

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Note

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