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The nature of the chemical bond in borazine (B₃N₃H₆), boroxine (B₃O₃H₃), carborazine (B₂N₂C₂H₆), and related species

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Abstract

The bonding problem in borazine ($B_3N_3H_6$), boroxine ($B_3O_3H_3$), and carborazine ($B_2N_2C_2H_6$) is successfully addressed through the consideration of the excited states of the constituent fragments, namely BH($a^3\Pi$), NH($A^3\Pi$), and CH($a^4\Sigma^-$). We propose the participation of resonant structures for all three species that help to explain the experimental findings. A discussion on the chemical pattern of the parental molecule benzene (C_6H_6) helps to make coherent the whole bonding analysis on the titled species.

KEYWORDS

ab initio, borazine, boroxine, carborazine, chemical bonding

1 | INTRODUCTION

Chemistry is traditionally subdivided into several branches, two of which are inorganic and organic chemistry. Although the border lines between different subfields are nowadays blurry organic chemistry is mainly concerned with only one element of the periodic table, carbon, and the species it can form, while inorganic chemistry with all the rest. The richness of carbon chemistry is phenomenal and due to its third excited $^5S(2s^12p^3)$ state just 4.18 eV[1] above its ground $^3P(2s^22p^2)$ one. It suffices to mention that the ground state of simple organic species like, for example, CH_2 ($\tilde{X}^3B_1$)[2] and consequently $CH_4(\tilde{X}^1A_1)[\leftarrow CH_2(\tilde{X}^3B_1)+2H(^2S)]$ are due to this C(^5S) state.[3] The above point of view or way of interpreting the chemical bond is founded on our belief that molecules are made of atoms that may participate in a variety of quantum states beyond their ground ones. This was already known to the "old" masters (see e.g., Ref. [3] and references therein) of quantum chemistry but unfortunately it is largely forgotten nowadays. We strongly believe that the atoms in molecules[4] "hypothesis" provides the shortest path to reach a deep understanding of how molecules are formed.

The most archetypal species of all of organic chemistry is benzene (C_6H_6), a planar arrangement of six CH units in a D_{6h} structure. Since 1865, when Kekulé[5] first conjectured a ring shaped structure with alternating single (σ) and double (π) bonds, benzene has been extensively studied from any imaginable point of view and perspective. Its most characteristic property, although not so clearly defined, is aromaticity, a rather strange[6,7] enhanced stability of ring shaped flat molecules with resonant bonds as compared to any other geometrical arrangement of the same collection of atoms. The above stability is largely attributed to the delocalization of the π electrons (e⁻) theoretically delineated by Hückel[8] in 1930.

In the world of inorganic chemistry a molecule of a comparable status is borazine ($B_3N_3H_6$) known also as "inorganic benzene" since B—N is isoelectronic to C—C. Although both species share similar physical properties[9,10] borazine is classified as a nonaromatic compound deficient of any ring current based on the diamagnetic susceptibility exaltation method, nucleus independent chemical shift calculations, and ¹H chemical shifts of both H(B) and H(N) hydrogen atoms.[11–28] And this is indeed strange since borazine features a regular plane hexagonal ring structure while it is possible to write down Kekulé-type structures with N→B π bonding superimposed on the σ frame.[10]

One of the first electronic structure studies on borazine is the ab initio work by Cooper et al.[11] Based on spin coupled (SC) calculations it was found that the π structure of borazine is different from that of benzene albeit the same number of 6 π e⁻, in particular there are three pairs of electrons associated with each N atom. There are two distinct SC orbitals centered on each N atom, one of fairly localized but slightly distorted $2p_\pi(N)$ character and the other showing considerable delocalization into the neighboring B centers. Although this work is important, it is not explicitly said how three BH and three NH units bind together to form a quasi D_{3h} structure[29,30] and what is the origin of the N lone π pairs.

SCHEME 1

$$2sp_z \quad 2p_y$$

$$= CH(a\,{}^4\Sigma^-)$$

$$C({}^5S) \quad H({}^2S)$$
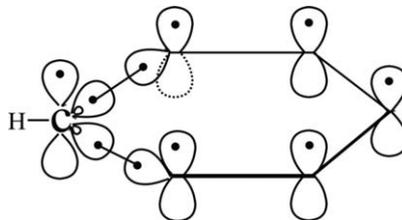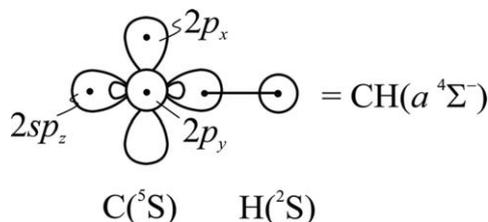
SCHEME 2

Our sole goal in the present work is to address the bonding problem in borazine, and in some related species like boroxine ($B_3O_3H_3$) and carborazine ($B_2N_2C_2H_6$); both of them are related to both benzene and borazine in too many interesting ways. To this end we shall firstly present the bonding situation in benzene, being the prototypical molecule for all the titled species, then the intermediate systems borabenzene (C_5H_5B) and pyridine (C_5H_5N), and finally the titled ones. Our findings and analysis are based on the restricted coupled cluster singles and doubles and perturbative triples (RCCSD(T)) method coupled with correlation consistent polarized valence triple zeta (cc – pVTZ) basis set[31] for all atoms. All of our calculations were done with the help of MOLPRO[32] under C_s or C_1 symmetry conditions.

2 | RESULTS AND DISCUSSION

The emblematic character of benzene has attracted the vivid interest of various theoretical chemists since the pioneering study by Pauling and Wheland.[33] Benzene is usually represented by a resonating combination of five, but unequally contributing, highly localized or valence bond (VB) structures, two of which are known as Kekulé and the rest as Dewar structures. Conversely, aromaticity is heavily based on the delocalized or molecular orbital (MO) picture of the π electronic system and this is clearly evident from the canonical Hartree–Fock (HF) orbitals being drawn in every chemistry textbook. The two points of view seem rather incompatible although it is always possible, albeit not unambiguously, to transform the canonical HF orbitals to more localized ones. Disputing the universally accepted belief that the 6 $\pi\,e^-$ are delocalized around the ring may sound heretical but these electrons are substantially localized on the six carbon atoms in essentially deformed $C(2p_\pi)$ orbitals slightly distorted symmetrically toward the neighboring carbon atoms.[34] The 6 $\pi\,e^-$ are coupled into a singlet through five spin functions that in the Rumer representation are known as Kekulé and Dewar structures.[35]

But what about the bonding in benzene? How do six CH units bind together to form the famous benzene ring? Although this is not stated explicitly in previous studies, not even in the most recent work by Cardozo et al.[36] it is alluded in the form of the π skeleton SC orbitals.[34,35] Six CH units initially in their $X^2\Pi$ state approach each other in a D_{6h} arrangement and are gradually getting promoted to their first excited $a^4\Sigma^-$ state ($\Delta E = 17.2$ kcal/mol),[37] or in other words, the carbon atom gets excited from ${}^3P(2s^22p^2)$ to ${}^5S(2s^12p^3)$ to form four bonds.[3] This is also corroborated by the HF Mulliken population analysis of the carbon atom $2s^{1.25}2p_z^{0.98}2p_y^{0.87}2p_x^{0.96}/_C$. The benzene wavefunction can be visually transcribed in the following valence bond Lewis (vbL) diagram (see Scheme 1) featuring six CH units in their $a^4\Sigma^-$ state (see vbL Scheme 2)

$$2s2p_y2p_z$$
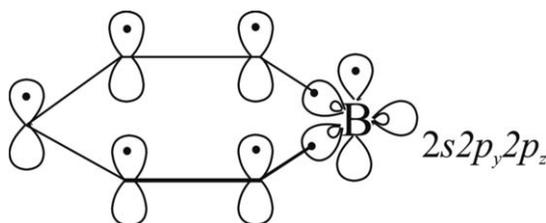
SCHEME 3

TABLE 1 Optimized geometries and energies of BH, CH, NH, O, borazine ($B_3N_3H_6$), boroxine ($B_3O_3H_6$), and carborazine ($B_2N_2C_2H_6$) at the RCCSD(T)/cc – pVTZ computational level

Species	r_{XY}(Å)	$\angle_{XYZ}$(°)	$-E$(hartree)	ΔE(kcal/mol)
BH($X^1\Sigma^+$)	1.235(1.2324)[a]		25.230 615	
BH($a^3\Pi$)	1.193(1.2006)[a]		25.182 158	30.4[b]
CH($X^2\Pi$)	1.122(1.1199)[a]		38.410 237	
CH($a^4\Sigma^-$)	1.090(1.085)[a]		38.385 073	15.8[b] (17.11 ± 0.18)[c]
NH($X^3\Sigma^-$)	1.039(1.0362_1)[a]		55.140 363	
NH($A^3\Pi$)	1.035(1.0369_8)[a]		55.000 223	87.9[b] (85.2)[a]
O(^3P)			74.973 688	
$B_3N_3H_6$	1.433(1.4355_{21})$^d_{BN}$, 1.195(1.258_{14})$^d_{BH}$, 1.007(1.050_{12})$^d_{NH}$	117.0($117.7_{1.2}$)$^d_{NBN}$, 123.0($121.1_{1.2}$)$^d_{BNB}$	242.227 126	699[e], 1054[f]
$B_3O_3H_6$	1.379_{BO}, 1.187_{BH}	120.0	301.839 911	770[e], 861[f]
$B_2N_2C_2H_6$	1.440_{BN}, 1.354_{NC}, 1.509_{BC}, 1.192_{BH}, 1.012_{NH}, 1.085_{CH}	123.7_{BNC}, 120.6_{NCB}, 115.8_{CBN}	238.640 205	676[e], 945[f]

Experimental Results in Parenthesis.
[a]Reference [40].
[b]T_e value.
[c]T_0 value, see Ref. [41].
[d]Reference [29].
Stabilization energies with respect to the adiabatic[e] (diabatic)[f] fragments, see text for details.

The two yz-plane e^- form two sigma bonds with the two neighboring CH units while the third ($\sim 2)p_x$ e^- is highly localized on its parental center. One can add six H atoms approaching perpendicularly to the molecular plane creating cyclohexane, subsequently stabilized in a chair conformation; its building units are now six CH_2 ($\tilde{X}^3B_1$) species.[2]

When we replace one CH unit with boron (B), we get borabenzene (C_5H_5B). C_6H_6 and C_5H_5B show striking structural and electronic similarities; see for example, Ref. [38]. On the basis of SC calculations it was concluded that the π space in borabenzene is very similar to that in benzene involving two dominating Kekulé and three less important Dewar-type Rumer spin functions classifying borabenzene as aromatic. An important feature is that C_5H_5B is a strong Lewis acid due to a "hole" located on B.[38] All of the above become evident when we consider its bonding motif. The B atom finds itself in its excited $^4P(2s2p_y2p_z)$ state thus being isomorphic to CH($a^4\Sigma^-$) (see Scheme 2) and ready to form a benzene like σ– and π– frames; see vbL Scheme 3.

Once again the HF Mulliken population analysis reflects the B($2s^12p^2$; ^4P) character, $2s^{1.1}2p_z^{0.13}2p_y^{0.77}2p_x^{0.77}/_B$. There are three in plane ($2s2p_y2p_z$) hybrids two of which host one e^- each and they form two sigma bonds with the two neighboring CH($a^4\Sigma^-$) units while the third one is an "empty hole" at the back of the molecule, the third electron, partially delocalized, "sits" on a boron $\sim 2p_x$ orbital.

The situation is similar in pyridine (C_5H_5N), where a CH unit is replaced by a N atom. But now, nitrogen, in its ground $^4S(2s^22p^3)$ state, is ready to form a benzene like structure. SCVB calculations[39] show that only small changes occur in the form of the orbitals and in the relative importance of the different spin couplings of the π electrons when a CH unit is replaced by N. The addition of six H atoms to both C_5H_5B and C_5H_5N results in the complete analog of cyclohexane, borinane ($C_5H_{10}BH$), and piperidine ($C_5H_{10}NH$), respectively.

All of the above molecules, namely C_6H_6, C_5H_5B, C_5H_5N, and their fully hydrogenated products exist because the C, B, and N atoms are or can be found in the chemically ready $^5S(2s^12p^3)$, $^4P(2s^12p^2)$, and $^4S(2s^22p^3)$ atomic states, respectively.
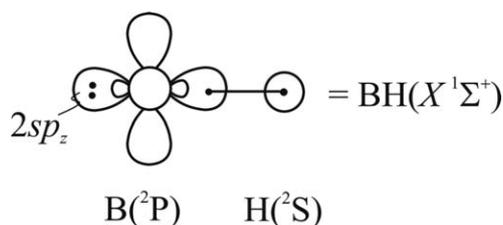
SCHEME 4
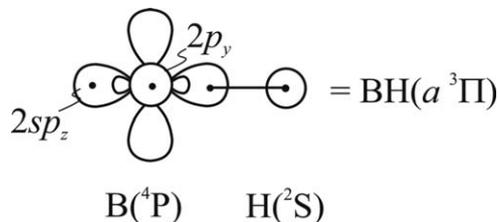
SCHEME 5
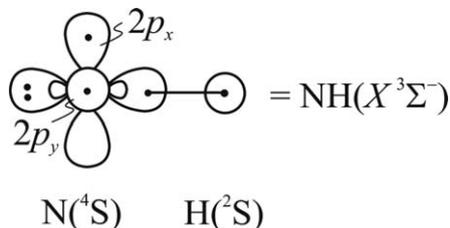
SCHEME 6

Now, let us consider borazine. What is important to understand is its bonding pattern, how three BH units bind to three NH units. To this end, we shall discuss in some detail the electronic structure of its constituent fragments, namely BH and NH.

The ground state of BH is of $X^1\Sigma^+$ symmetry while its first excited state is of $a^3\Pi$ symmetry (with an excitation energy T_e= 30.4 kcal/mol at the RCCSD(T)/cc – pVTZ computational level; see Table 1). An electronic structure analysis[42] reveals that in the $X^1\Sigma^+$ state the boron atom is found in its ground $^2P(2s^22p^1)$ state while in the $a^3\Pi$ state in its first excited $^4P(2s^12p^2)$ state. The HF Mulliken population analysis leaves no doubt about it, $2s^{1.69}2p_z^{1.05}2p_x^{0.06}2p_y^{0.06}/_B(X^1\Sigma^+)$ versus $2s^{1.27}2p_z^{0.72}2p_x^{0.98}2p_y^{0.02}/_B(a^3\Pi)$. The pictorial representation of their wavefunctions is depicted in Schemes 4 and 5, respectively.

Conversely, the ground NH state is of $X^3\Sigma^-$ symmetry with corresponding HF Mulliken distributions $2s^{1.88}2p_z^{1.28}2p_x^{1.0}2p_y^{1.0}/_N$ represented adequately by the vbL Scheme 6.

From all the above we understand that to form a stable molecular species the BH unit cannot be in the $X^1\Sigma^+$ state but rather in its first excited $a^3\Pi$ one. And this is to be expected since in borabenzene the B atom is in situ in its excited ^4P state. So, how can one combine three BH($a^3\Pi$) and three NH($X^3\Sigma^-$) fragments in a chemically meaningful way? The only way to do it is nicely displayed in the following vbL Scheme 7.

There are six BN sigma bonds, three in plane BH bonds, and three perpendicular NH bonds. The above structure is stabilized by 575(666) kcal/mol with respect to $3 \times BH[X^1\Sigma^+(a^3\Pi)] + 3 \times NH(X^3\Sigma^-)$ at the CCSD(T) computational level currently employed.
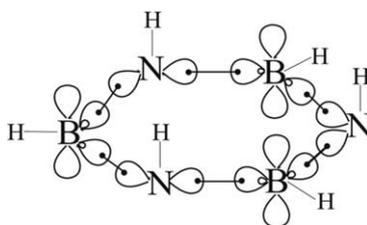
SCHEME 7
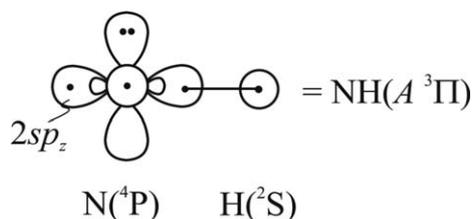
SCHEME 8
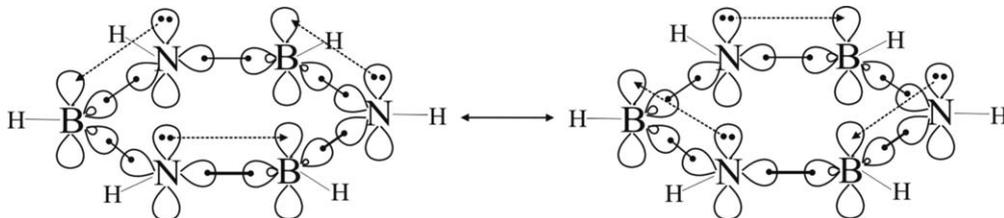
SCHEME 9
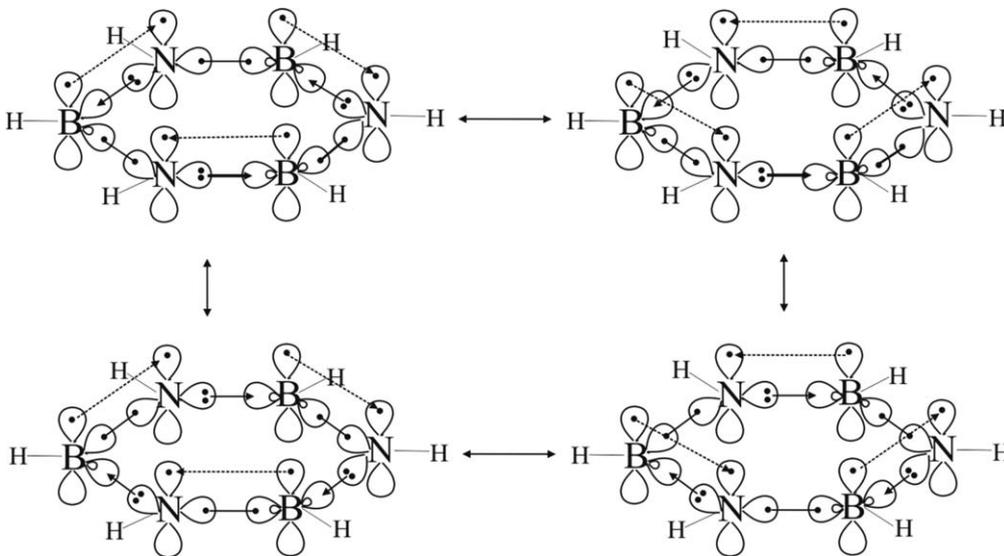
SCHEME 10

But it is clear that the $(BHNH)_3$ configuration of Scheme 7 is not borazine.[29,30] The only way to comply with borazine's characteristics, that is, six in plane H atoms and three lone pairs on every N atom, is through the promotion of the NH unit to its $A^3\Pi$ ($2s^{1.63}2p_z^{0.74}2p_x^{1.0}2p_y^{2.0}/_N$) excited state ($T_e = 87.9$ kcal/mol; Table 1) schematically given by the vbL Scheme 8.

The N atom is now found in its valence $^4P(2s^12p^4)$ atomic state, 10.93 eV[1] above the ground $^4S(2s^22p^3)$ one. Three BH($a^3\Pi$) and three NH ($A^3\Pi$) fragments can be combined in two ways so that all H atoms lie in a plane and there are $6\ \pi\ e^-$. These are shown in Schemes 9 and 10.

In Scheme 9, there are three electron pairs centered on N but delocalized into the empty $2p_\pi$ boron orbitals. In Scheme 10, there are six singly occupied $2p_\pi$ orbitals centered on both the B and N atoms but there is a charge migration from B – to – N. The Mulliken population analysis $2s^{1.0}2p_z^{0.79}2p_y^{0.62}2p_x^{0.31}/_B 2s^{1.36}2p_z^{1.13}2p_y^{1.10}2p_x^{1.57}/_N$ shows the average situation of both structures. So, it is better to describe borazine as a resonance of the structures shown in Schemes 9 and 10. This is indeed necessary if one wants to explain both the experimental observation that elecrophiles attack the N atoms[43,44] and the existence of cyclotriborazane $(H_2BNH_2)_3$,[45,46] the analog of cyclohexane. We can also combine the Lewis acid centers (B) and Lewis base centers (N) of two borazine molecules (Scheme 9) to form a dimer. Theoretical calculations establish low dimerization energies of ∼3.0 kcal/mol; see for example, Refs. [47–49]. Finally, borazine is bound by 699(1054) kcal/mol with respect to $3 \times BH[X^1\Sigma^+(a^3\Pi)] + 3 \times NH[X^3\Sigma^-(A^3\Pi)]$.

At this point, we should ask ourselves why the ground state of borazine is planar (see Schemes 9 and 10) and not that depicted in Scheme 7 where the NH units are found in their ground $X^3\Sigma^-$ state and not excited by as much as ∼ 88 kcal/mol to their $A^3\Pi$ one. The profound reason is on the delocalization of the N π lone pairs (see Scheme 9) or to the B–to–N charge migration (see Scheme 10). Both of them are absent in Scheme 7
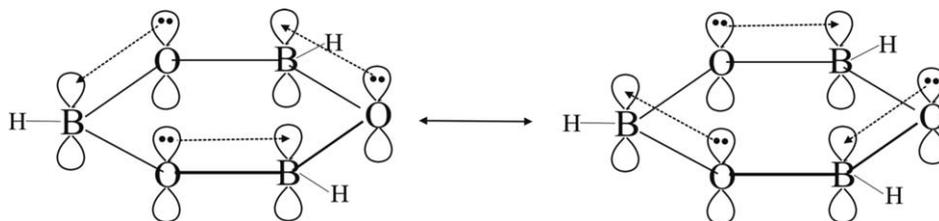
SCHEME 11
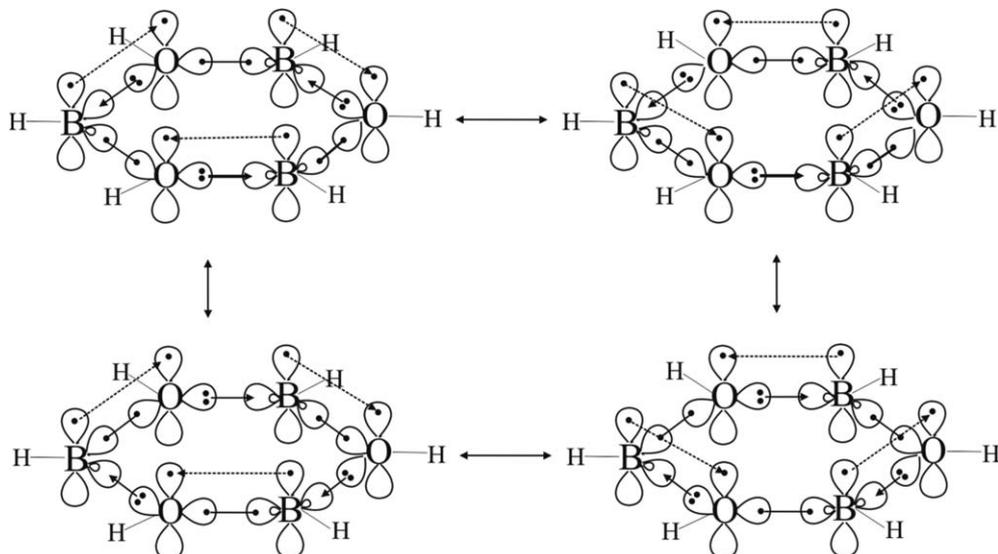
SCHEME 12
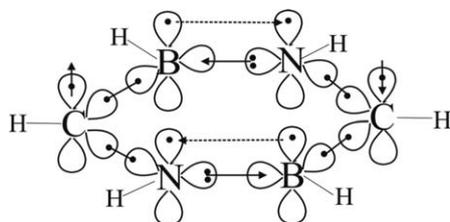
SCHEME 13

since the NH bond, perpendicular to the molecular plane, is highly localized between the N and H centers and certainly the associated electronic density cannot delocalize into the empty B $2p_\pi$ orbitals. The configuration of Scheme 7 can be viewed as an isomer of borazine that lays 124 kcal/mol higher.

In boroxine the bonding situation is similar to that in borazine. Our guide will be the vbL Scheme 7. The NH unit is isoelectronic to oxygen while the 2 e$^-$ sigma N—H bond is isomorphic to the lone pair of the $^3P(2s^2 2p_z^1 2p_y^1 2p_x^2)$ oxygen state. So, when we replace the three $NH(X^3\Sigma^-)$ units with three $O(^3P)$ atoms we get boroxine. Its optimized geometry appears in Table 1. The molecule is bound by 770(861) kcal/mol with respect to $3 \times BH$ $[X^1\Sigma^+(a^3\Pi)] + 3 \times O(^3P)$. Boroxine appears to be more stabilized than the configuration shown in Scheme 7, with respect to their respective constituents, and that may be attributed to the partial delocalization of the O $\sim 2p_x$ electron pairs (see below) that is absent in the species of Scheme 7.

Its vbL diagram appears in Scheme 11 where three pairs of electrons appear to be fairly localized on the three O atoms with some degree of delocalization into the neighboring B centers. The HF Mulliken population analysis is quite informative, $2s^{0.89} 2p_z^{0.75} 2p_y^{0.53} 2p_x^{0.24}/B2s^{1.65} 2p_z^{1.38} 2p_y^{1.57} 2p_x^{1.65}/_O$. There are six 2 electron – 2 center (2e$^-$ – 2c) sigma bonds between B and O while it seems that ~ 0.25 electrons migrate to the B $2p_x$ orbitals from the two neighboring O atoms. The latter is equivalent to say that there are three partial π bonds from O to its neighboring B atoms.

But there is another symmetry allowed way we can combine three $BH(a^3\Pi)$ and three $O(^3P)$ atoms, the one shown in Scheme 12.

Now, there are three 2e$^-$ – 2c bonds alternating with three putative sigma bonds between the B and O atoms while six singly occupied $2p_x$ orbitals make up the π frame.
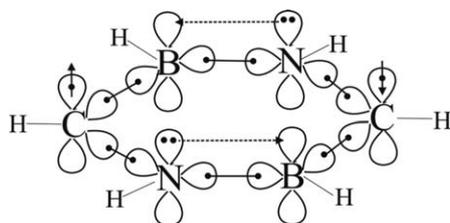
SCHEME 14

The six π electrons are coupled into a singlet but there is a charge migration from $2p_x(B)$ to $2p_x(O)$ that makes the perfect pairing spin function the most dominant. The net result is that a quasi pair of electrons seems to be associated with each O atom.

The last molecule to be considered is carborazine $(BHNHCH)_2$, a molecular system intermediate to benzene and borazine and isoelectronic to both of them. A recent theoretical study establishes the aromaticity of carborazine based on nucleus-independent chemical shift calculations.[50] The only way to have six in plane H atoms and $6\ \pi\ e^-$ is to consider that its constituent fragments BH, CH, and NH should be in situ in their $a^3\Pi$, $a^4\Sigma^-$, and $A^3\Pi$ states, respectively. As we have already seen in both boroxine and borazine, there are two ways to combine these six diatomic species, see Schemes 13 and 14.

The bonding similarities with borazine are evident and should not be repeated here. In both vbL Schemes 13 and 14 the two C $2p_\pi$ electrons are singlet coupled and localized on their parental centers. We can even say that the two carbon centers "isolate" the electronic migration between the B and N atoms into two well separated regions of the ring instead of being everywhere around it as in borazine or boroxine. The HF Mulliken populations of the π skeleton, $2p_x^{0.57}/_B 2p_x^{1.39}/_N 2p_x^{0.92}/_C$, are consistent with both ways to represent the chemical species. The atomic distributions of the σ frame, $2s^{1.0}/_B 2s^{1.37}/_N 2s^{1.27}/_C$, show truly that BH, NH, and CH are indeed in their $a^3\Pi$, $A^3\Pi$, and $a^4\Sigma^-$ states, respectively. So, carborazine, as boroxine and borazine, is a resonance of two different configurations that each one grants a distinctive feature. Carborazine is bound by 676(945) kcal/mol with respect to $2 \times BH[X^1\Sigma^+(a^3\Pi)] + 2\times NH[X^3\Sigma^-(A^3\Pi)] + 2 \times CH[X^2\Pi(a^4\Sigma^-)]$.

It is clear that when we add six H atoms to form the analog of cyclohexane, it is the structure of Scheme 13 that leads to this hydrogenated product. This product was recently synthesized and hailed as an "... unusually kinetically stable chemical hydrogen storage material (compound H, Figure 1) with a H_2 storage capacity of 4.7 wt%."[51] It was also reported that two cage compounds were produced by the dimerization of two carborazine molecules (with the two carbons being saturated). And for that dimerization to happen the vbL structure of Scheme 14 is the most suitable because it combines a Lewis acid center (B atom) and a Lewis base center (N atom) the one next to the other. The two monomers are actually buttoned to each other through putative bonds between the N and B centers of the two monomers.

3 | CONCLUSIONS

In the present work, we have addressed the question of how three molecular systems, borazine, boroxine, and carborazine, isoelectronic to benzene are formed or in other words how their constituent fragments, BH, CH, and NH bind together. We have shown that the above units are in their $a^3\Pi$, $a^4\Sigma^-$, and $A^3\Pi$ excited states, respectively, to form the ground states of the titled species. We have also proposed that these ground states are resonances of VB structures that primarily differ in the way the $6\ \pi\ e^-$ are initially placed on the parental centers. The importance of the resonant structures is reflected on the existence of their hydrogenated species similar to cyclohexane and to the possibility of adding nucleophiles and/or electrophiles. We have also shown that the chemical elucidation and chemistry of such systems of mixed organic–inorganic interest may be understood once one considers the excited states of their parental units when these are wisely chosen provided that we do believe that atoms make molecules and not orbitals.

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