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# Dihydrogen Bond Cooperativity in Aza-borane Derivatives

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A theoretical study of the dihydrogen-bonded clusters of three aza-borane derivatives,  $\text{H}-\text{N}\cdots\text{B}-\text{H}$ , has been carried out using DFT, M05-2X, computational methods. Clusters consisting of up to 10 monomers have been considered. The energetic results show an increment of the average interaction energy per monomer as the size of the cluster increases. Similarly, a shortening of the intermolecular distances up to 0.1 Å is observed. Among the electrostatic properties, an increment of the dipole moment and the absolute values of the molecular electrostatic potential at the interacting point of the cluster are observed. Finally, the orbital interaction responsible for the dihydrogen bond follows the same pattern observed for the bond distances. Thus, it can be concluded that these systems show behavior, with respect to cooperativity, similar to those observed in standard hydrogen bonds.

## Introduction

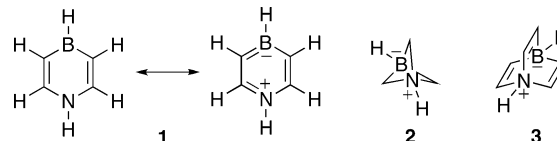
Hydrogen bond (HB) formation induces changes within the molecules that are involved in it. In many cases, these changes facilitate the aggregation of additional molecules to the initially formed complex. This phenomenon is known as cooperativity or nonpairwise effects. It greatly influences the properties of the molecules and those of the formed clusters. Thus, for instance, the water trimer shows basicity comparable to ammonia.<sup>1–3</sup> A number of theoretical studies have been devoted to analyzing the cooperativity effects in hydrogen-bonded systems.<sup>4</sup>

One of the most recent incorporations into the field of hydrogen bonds corresponds to those cases where the HB acceptor is a negatively charged hydrogen atom. These interactions have been named as dihydrogen bonds (DHB). They were first reported in 1968,<sup>5</sup> then developed by Crabtree,<sup>6</sup> and reviewed several times.<sup>6–9</sup> The DHB characteristics from a theoretical point of view were described by Liu and Hoffman<sup>10</sup> in 1995, Popelier<sup>11</sup> in 1998, Sadlej and co-workers<sup>12</sup> in 2003, by Grabowski, Sokalski, and Leszczynski in 2004<sup>13</sup> and 2007,<sup>14</sup> Sing and Patwari in 2007,<sup>15</sup> Rangel et al. in 2009,<sup>16</sup> and by some of us.<sup>17–22</sup> The spin–spin coupling constants of  $\text{H}_3\text{BNH}_3$  head–tail dimer that present bifurcated DHBs have been studied by Cybulski and Sadlej.<sup>23</sup>

A few articles have been devoted to the cooperativity in complexes that show a dihydrogen bond interaction. In general, those studies consider clusters where different interaction types are present, one of them being a dihydrogen bond.<sup>24–27</sup> Our group has described that  $\text{HCCBeH}$  clusters could adopt a head–tail DHB configuration with modest cooperativity effect.<sup>28</sup> More recent studies have shown the possibility of negative cooperativity in DHB cluster of ammonia and  $\text{BeH}_4^{(2-)}$ .<sup>29</sup>

In recent years an increasing interest has been generated in the aza-borane derivatives because of their potential uses in hydrogen storage.<sup>30–33</sup> One of these molecules has been the 1,2-azaborazine, which is the analog of benzene with a B–N moiety.

## SCHEME 1: Systems Considered in the Present Study



Its synthesis,<sup>34</sup> microwave structure,<sup>35</sup> and spectroscopic properties<sup>36</sup> have been described.

In the present article, the cluster formed by molecules with NH and BH moieties along symmetry axes has been investigated (Scheme 1). Thus, it is possible to obtain head–tail interactions along linear chains of molecules. The 1,4-dihydro-1,4-azaborine, **1**, has already been theoretically studied, proving to be 23 kcal/mol less stable than the 1,2-dihydro-1,2-azaborine isomer.<sup>37–39</sup> However, derivatives of **1** have been experimentally described in the literature.<sup>40</sup> No previous theoretical reports have been found for the azaborabicyclo[1.1.1]pentane, **2**, and azaborabicyclo[2.2.2]octa-2,5,7-triene, **3**.

## Methods

The geometry of the isolated monomers and dimers has been fully optimized at the M05-2X/6-311++G(d,p) computational level<sup>41,42</sup> within the Gaussian 03 program.<sup>43</sup> The M05-2X functional has been shown to be very adequate for the description of noncovalent interaction as hydrogen bonds.<sup>41</sup> The geometry of the clusters has been optimized using a  $C_{3v}$  symmetry for **2** and **3** ( $C_{3v}$ ) while for the cluster of **1**, the  $C_{2v}$  symmetry has been adopted. More stable clusters are obtained without the symmetry restrictions mentioned before but with no linear DHB interactions, making difficult the possibility of using them in cooperativity studies.

The interaction energy of the clusters has been calculated as the difference between the total energy of the cluster and the corresponding times of the monomers. The use of ab initio supermolecule calculations is known to be susceptible to basis set superposition error (BSSE) when finite basis sets are used. The most common way to correct the BSSE is with the full counterpoise method.<sup>44</sup> Systematic studies at the Restricted

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**TABLE 1: Charges on the Hydrogen Atoms (e) and Dipole Moment (Debye)**

system	AIM		NBO		dipole moment
	BH	NH	BH	NH	
<b>1</b>	−0.630	0.408	−0.047	0.401	4.12
<b>2</b>	−0.635	0.368	−0.034	0.384	3.62
<b>3</b>	−0.621	0.398	−0.003	0.416	4.89

Hartree-Fock (RHF) level have indicated that the counterpoise-corrected interaction energies are no more reliable than the uncorrected ones.<sup>45</sup> Alternatively, the results can be checked with an almost saturated basis set. Thus, we have reoptimized the clusters of **1** and **3** up to tetramer with the M05-2X/6-311++G(3df,2pd) computational level and the BSSE has been corrected using the full counterpoise method. The uncorrected interaction energies obtained at such level differ in less than 1% to those obtained at the M05-2X/6-311++G(d,p) and about 1% in the dipole moment (the results of these calculations are included in the Supporting Information, Table S1). The BSSE correction at the M05-2X/6-311++G(3df,2pd) represents less than 4% of the interaction energy and its inclusion does not change the energetic profile without the correction (Table S1).

The molecular electrostatic potential of the systems has been calculated and their minima have been located at the M05-2X/6-311++G(d,p) computational level using the facilities of the Gaussian 03 program.

The electron density of the systems has been analyzed within the “atoms in molecules” (AIM) methodology<sup>46,47</sup> with the AIMPAC,<sup>48</sup> MORPHY98,<sup>49</sup> and AIM2000 programs.<sup>50</sup> The atomic integrations have been carried trying to obtain small values of the integrated Laplacian for all the atoms. Ideally, a perfect integration within an atomic basin should provide a null integrated Laplacian. We have shown that values of the integrated values smaller than  $1 \times 10^{-3}$  for all the atoms of a given system provide small energetic and charge errors when the sum of the atomic contributions are compared to those obtained with the ab initio methods for the whole system.<sup>51</sup> The 0.001 e/bohr<sup>3</sup> isosurface has been used to evaluate the Molecular Electrostatic Potential (MEP)<sup>52</sup> since this isosurface has been shown to resemble the experimental van der Waals surface.<sup>53</sup>

The “natural bond orbital” (NBO) method<sup>54</sup> has been used to analyze the intermolecular interaction between the occupied and the empty orbitals. These interactions are of main importance in the formation of hydrogen-bonded clusters.

## Results and Discussion

**Monomers.** The electronic properties of the chosen molecules show an important separation of the charge as indicated by a large dipole moment and the charges of the hydrogen atoms in the extreme of the symmetry axis (Table 1). The calculated charges with the NBO and AIM method provide similar values at the positive end of the molecule while they are very different in the hydrogen atom attached to the boron atom. These results are in line with previous reports that have indicated that the AIM charges are overestimated.<sup>55</sup>

The calculated radius of the molecule along the symmetry axis shows that the hydric hydrogen atom is larger than the protic one (Table 2). The molecular electrostatic potential of the isolated monomers shows the presence of a negative region associated to the B–H moiety and a positive one in the N–H one (Figure 1). The values of the electrostatic potential along the symmetry axis of the molecule show that the bigger hydric hydrogens are those with more negative values of the MEP while in the case of the protic hydrogen a similar relationship is not

**TABLE 2: Radius (Å) and MEP (au) in the Axial Directions**

axial direction	1		2		3	
	radius	MEP	radius	MEP	radius	MEP
N–H	1.220	0.087	1.280	0.070	1.228	0.097
B–H	1.474	−0.024	1.478	−0.032	1.503	−0.038

so clear. **3** is the system that presents the larger absolute values at both extremes of the molecule.

**Clusters.** The present study has focused only on the possible DHB interactions of the proposed molecules. Thus, and for simplicity, a  $C_{2v}$  symmetry has been adopted for the cluster of **1** and the  $C_{3v}$  symmetry for those of **2** and **3** (Figure 2). In these dispositions, a linear BH...HN is adopted, which have been shown to be the most stable one for a DHB interaction.

The total interaction energy and the average interaction energy per DHB interaction in the cluster studied are gathered in Table 3. The interaction energies obtained for the clusters of **3** are almost twice those of **1** and **2**, in good agreement with the analysis of the electronic properties of the monomers. The values of the interaction energies in the three systems for a given number of monomers show an almost perfect linear correlation, as can be observed in eqs 1 and 2.

$$\begin{aligned} \text{Ei}(\text{cluster of } \mathbf{1}) &= 0.95 \times \text{Ei}(\text{cluster of } \mathbf{2}), \\ n = 9, r^2 &= 0.999 \quad (1) \end{aligned}$$

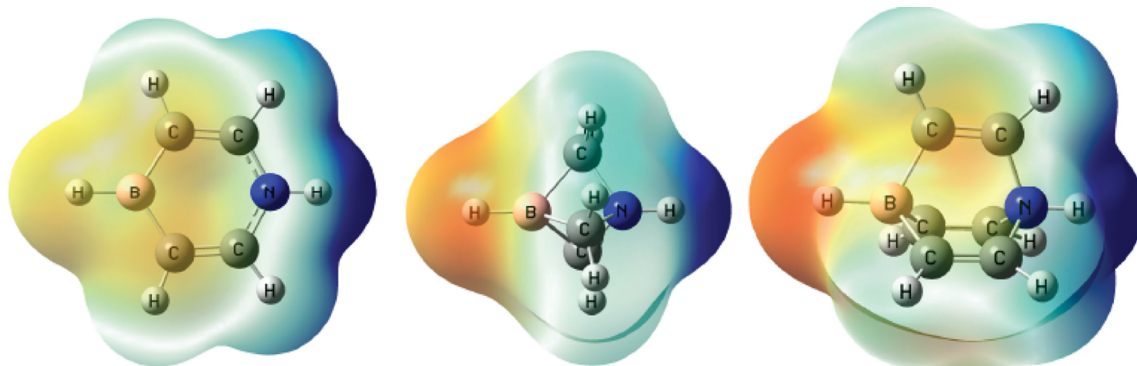
$$\begin{aligned} \text{Ei}(\text{cluster of } \mathbf{1}) &= 0.51 \times \text{Ei}(\text{cluster of } \mathbf{3}), \\ n = 9, r^2 &= 0.999 \quad (2) \end{aligned}$$

The evolution of the average interaction energy per DHB interaction (Figure 3) shows the typical shape observed in other HB clusters that show cooperativity effect. Thus, a continuous increment of the average interaction energy with the number of monomers involved in the cluster is observed. It is interesting to notice that the average interaction energy per DHB interaction in the decamer is between 23% and 25% larger than the one observed in the corresponding dimer for the systems considered here. The data in Figure 3 have been fitted with a second-order polynomial equation, and from the value of the intercept, the value of the interaction energy at infinite length chain can be extrapolated. The values obtained are −15.3, −16.1, and −30.4 kJ mol<sup>−1</sup> for the average interaction energy per DHB interaction in infinite chains of **1**, **2**, and **3**, respectively.

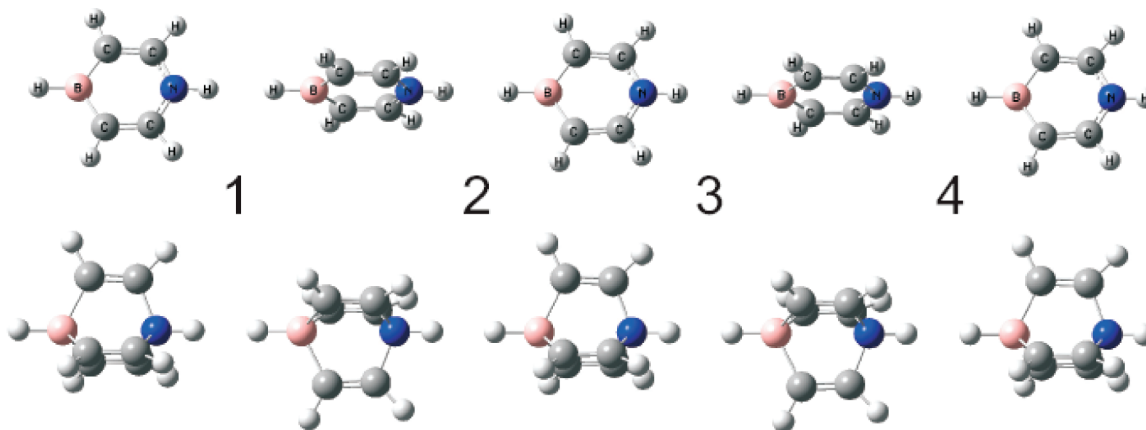
Another way to analyze the cooperativity effect is by looking at the change in the interaction energy upon addition of an additional molecule to the DH-bonding chain (Figure 4). This figure clearly shows that the change in the interaction energy is maintained approximately constant for clusters larger than 6 units. The increment of the interaction energy going from the nonamer to the decamer is between 28% and 31% more than the interaction energy of the corresponding dimer.

**Geometry.** The interatomic distances of the hydrogens involved in the interactions are gathered in the Supporting Information (Table S2). The shortest intermolecular distances are obtained for the clusters of **3** ranging between 1.70 and 1.80 Å while those of **1** and **2** range between 1.89 and 1.99 Å. These results are in agreement with the energetic results that show much larger interaction energies for the cluster of **3** than those of **1** and **2**.

The evolution of the intermolecular distances along the cluster chain for molecule **3** is represented in Figure 5. A similar profile is obtained for the other two molecules considered, as can be



**Figure 1.** Molecular electrostatic potential on the 0.001 e/bohr<sup>3</sup> electron density isosurface. Negative and positive regions are shown in red and blue colors, respectively.



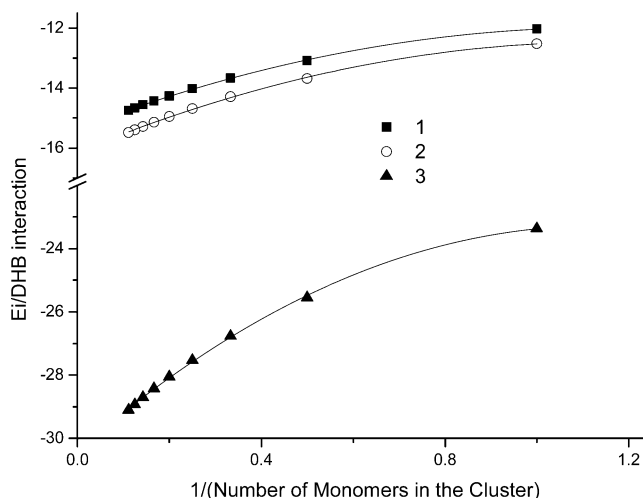
**Figure 2.** Optimized geometries of the pentamers of **1** and **3**. The numbering used for the DHB interactions along the article is shown.

**TABLE 3: Total Interaction Energy and Average Interaction Energy per DHB Interaction (kJ mol<sup>-1</sup>)**

no. of molecules cluster	<b>1</b>		<b>2</b>		<b>3</b>	
	Ei	Ei/DHB	Ei	Ei/DHB	Ei	Ei/DHB
2	-12.03	-12.03	-12.52	-12.52	-23.37	-23.37
3	-26.18	-13.09	-27.37	-13.69	-51.10	-25.55
4	-41.00	-13.67	-42.88	-14.29	-80.31	-26.77
5	-56.09	-14.02	-58.76	-14.69	-110.13	-27.53
6	-71.31	-14.26	-74.77	-14.95	-140.25	-28.05
7	-86.61	-14.43	-90.84	-15.14	-170.54	-28.42
8	-101.95	-14.56	-106.99	-15.28	-200.93	-28.70
9	-117.32	-14.67	-123.20	-15.40	-231.39	-28.92
10	-132.69	-14.74	-139.40	-15.49	-261.89	-29.10

observed in the Supporting Information (Figures S1 and S2). It clearly shows an important reduction of the interatomic distances (up to 0.1 Å) from the one obtained in the dimer to that in the larger cluster. In addition, the effect of the intermolecular reduction is more important in the central interactions, where the minima for each cluster is located, while larger distances are obtained at both ends of the chain. Similar behavior have been described in the study on the cooperativity effect of H-bonding chains of 4-pyridone<sup>56</sup> and DHB chains of HC-CBeH.<sup>28</sup>

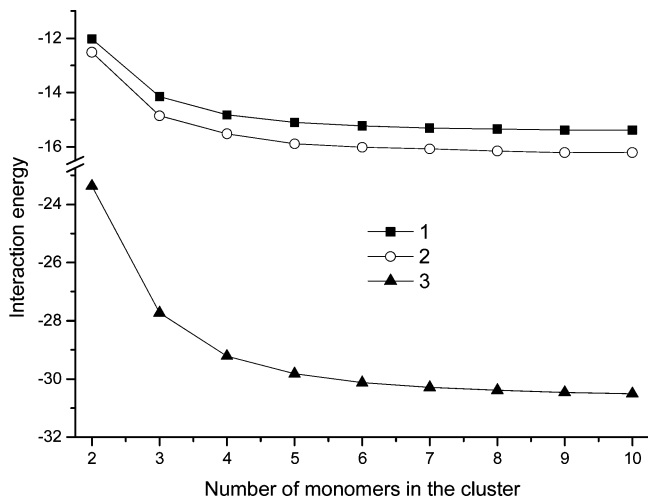
**Electronic Properties.** The hydrogen bond formation is usually associated with a dipole moment enhancement due to the charge transfer and electron polarization of the molecules involved in the interaction. In linear hydrogen-bonded complexes where cooperative effects have been observed, it has been shown that the dipole moment enhancement increases with the size of the cluster<sup>56,57</sup> up to a maximum value. In the present case, such behavior is observed for the average dipole moment per molecule with the size of the cluster (Figure 6). The average



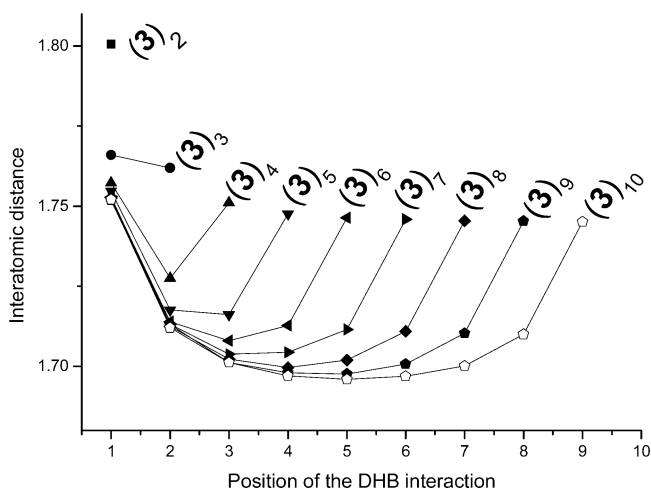
**Figure 3.** Average interaction energy per DHB interaction (kJ mol<sup>-1</sup>) vs inverse of the number of monomers in the cluster at the M05-2X/6-311++G(d,p) computational level. The three second-order polynomial fitted curves present square correlation coefficients larger than 0.999.

dipole moment increases up to a 43% of the value of the isolated monomers for the decamer of **3**.

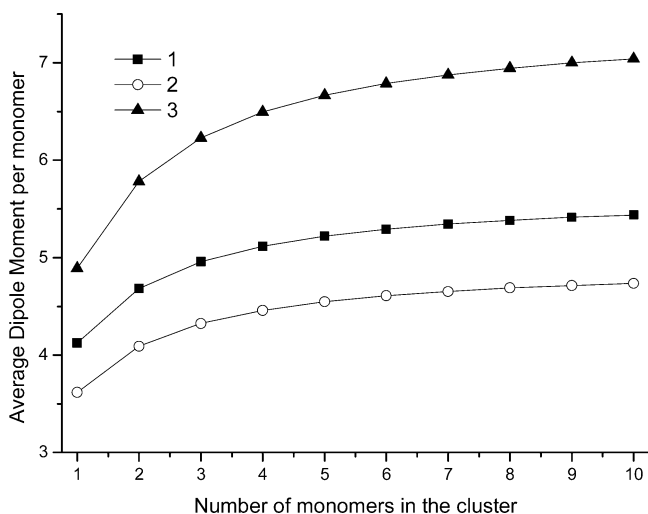
The analysis of the van der Waals radii along the symmetry axes of the clusters, using the 0.001 e/bohr<sup>3</sup> isosurface, shows that in the hydric side it became larger and the protic one smaller as the size of the cluster increases (Table S3), indication of a larger electron population in the first case and smaller in the second. However, the values of the radii rapidly converge with a small number of monomers. In the same way, the values of



**Figure 4.** Change in interaction energy upon addition of a molecule to the DH-bonding chain calculated at the M05-2X/6-311++G(d,p) computational level.

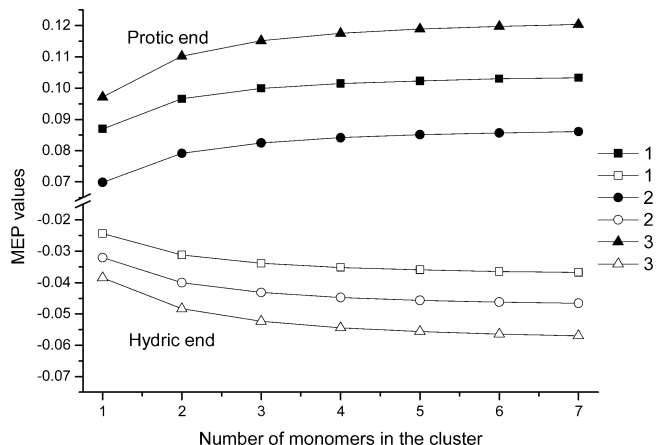


**Figure 5.** Evolution of the HB distance (Å) along the chains in the cluster of **3** studied at the M05-2X/6-311++G(d,p) computational level.



**Figure 6.** Dipole moment per monomer vs number of monomers in the cluster at the M05-2X/6-311++G(d,p) computational level.

the MEP at the van der Waals extremes show an increasing tendency, in absolute value, with the size of the cluster (Figure 7).



**Figure 7.** Evolution of the MEP values (au) at the van der Waals surface along the symmetry axes with the number of monomers of the cluster at the M05-2X/6-311++G(d,p) computational level.

The topological analysis of the electron density shows the presence of an intermolecular bond critical point, bcp, for each DHB interaction. The location of the bcp is always closer to the protic hydrogen atom, on average to a fractional distance of 0.45, than to the hydric one. This result is a clear indication of the smaller overall electronic population of the protic hydrogen vs the hydric one.

The values of the electron density in the bcp range between 0.019 and 0.009 au and those of the Laplacian between 0.050 and 0.024 au. In all the cases, these values correspond to closed shell interactions and have been associated to weak hydrogen bonds.<sup>58</sup> The representation of the electron density and Laplacian at the bcp vs the interatomic distance (Figure S3) shows exponential relationships, as already have been shown to be a general trend in hydrogen bonds.<sup>59–61</sup>

The extent of charge transfer between the occupied orbital of the HB acceptor and the empty one of the HB donor, as evaluated by the NBO methodology, has been shown to be a good measure of the strength of a hydrogen bond interaction.<sup>62</sup> In the systems studied in this article, the most important intermolecular orbital corresponds to the interaction of the B–H occupied  $\sigma$  orbital with the empty  $\sigma^* \text{N–H}$  one. With use of the second-order perturbation methodology, an estimate of the stabilization due to this interaction can be obtained. The representation of the values obtained along the cluster chain (Figure 8) resembles the figure previously shown for the intermolecular distances (Figure 5). The stronger interactions are obtained in those individual interactions with the shorter distances, which corresponds to the central interactions for each cluster, in agreement with the general belief that an energy–distance relationship exists in HB interactions. A similar profile has been described for the orbital interaction energies in HCN clusters.<sup>63</sup>

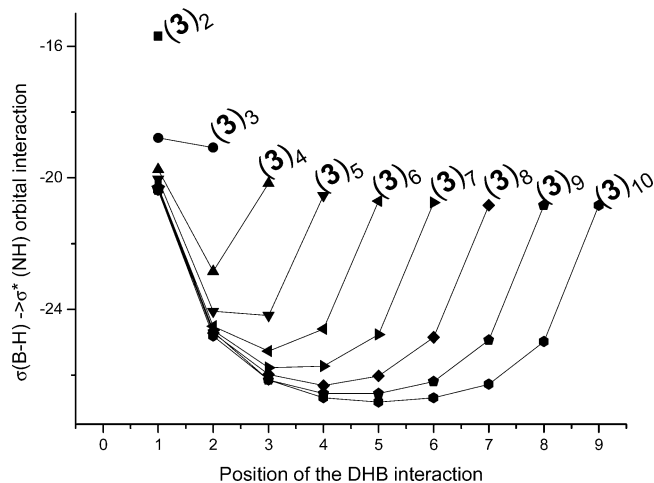
In addition, when the individual interactions are represented vs the corresponding intermolecular interaction (Figure 9), they show good linear correlation for the cluster of each compound but it is obvious that in some cases the results of two families cannot be mixed as in those of **1** and **2**.

The total sum of the  $\sigma \text{B–H} \rightarrow \sigma^* \text{NH}$  orbital interactions in each cluster correspond up to 85% of the interaction energy of the largest cluster studied of **3**, 70% in the case of **2** and 54% in **1**.

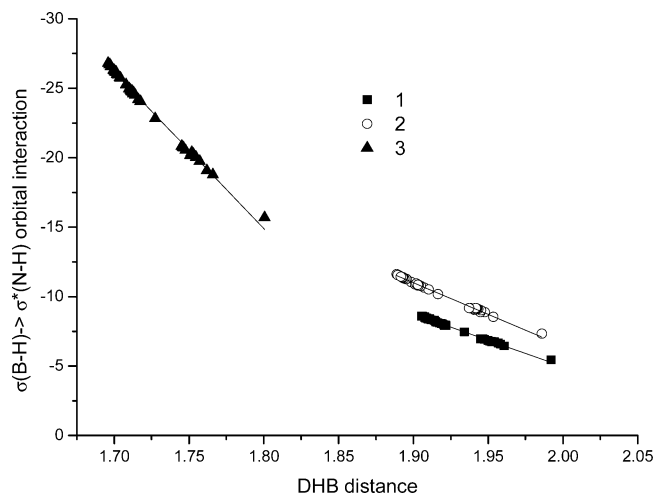
## Conclusions

A theoretical study of the DHB complexes of three molecules that present a BH and NH in a symmetry axis has been carried





**Figure 8.** Evolution of the NBO second-order perturbation energy ( $\text{kJ mol}^{-1}$ ) of the  $\sigma \text{ B-H} \rightarrow \sigma^* \text{ N-H}$  charge transfer with the position of the DHB interaction in the clusters of **3**. (Those of **1** and **2** are included in the Supporting Information, Figures S3 and S4).



**Figure 9.** Relationship between the  $\sigma \text{ B-H} \rightarrow \sigma^* \text{ N-H}$  orbital interaction energy ( $\text{kJ mol}^{-1}$ ) and the DHB distance ( $\text{\AA}$ ).

out by means of DFT computational methods, M05-2X/6-311++G(d,p). Clusters up to 10 monomers have been considered.

The electronic characteristics of the monomers show regions of different electronic signs at the two ends of the symmetry axis of the molecule. Electron deficiency is associated with the hydrogen atom attached to the nitrogen and positive ones to the hydrogen bonded to the boron atom.

The average interaction energy per DHB in the clusters shows increasing absolute values with the size of the cluster, in the three cases studied. The intermolecular distances become shorter as the size of the cluster increases. In addition, they depend on the position along the chain. Those interactions in the extremes are longer than the ones in the intermediate positions.

An increasing dipole moment enhancement is observed as the number of monomers increases in the clusters. In the same sense, the values of the MEP at the axial ends of the cluster become more positive in the protic side and more negative in the hydric one as the number of monomers involved in the cluster increases.

The NBO analysis shows a stabilizing  $\sigma \text{ B-H} \rightarrow \sigma^* \text{ N-H}$  intermolecular orbital interaction. The energy value of this interaction is larger in those DHB contacts with shorter distances. The overall value of these interactions along the cluster can account for up to 88% of the interaction energy.

All these results show that the clusters studied behave similarly to other systems with standard hydrogen bonds where cooperativity effects have been observed.

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**Supporting Information Available:** Comparison of the optimized systems with the M05-2X/6-311++G(d,p) and M05-2X/6-311++G(3df,2pd) computational levels of a selection of systems. BSSE correction of selected clusters at M05-2X/6-311++G(3df,2pd) computational level. Intermolecular distances, van der Waals radii ( $\text{\AA}$ ) along the symmetry axes, MEP values (au), electron density and its Laplacian (au) at the bcp vs the DHB distance, and NBO second-order perturbation energy ( $\text{kJ mol}^{-1}$ ) of the  $\sigma \text{ B-H} \rightarrow \sigma^* \text{ NH}$  charge transfer of all the systems studied. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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