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Characterization of a Dihydrogen Bond on the Basis of the Electron Density

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A new type of hydrogen bond, called a *dihydrogen bond*, has recently been introduced. In this bond a hydrogen is donated to another (hydridic) hydrogen. We apply a set of criteria developed in the context of the theory of “atoms in molecules” that were previously successfully used to study conventional hydrogen bonds. This method enables one to characterize the dihydrogen bond on the basis of the electron density only. We investigated a dimer structure of BH_3NH_3 at the ab initio level which contains two dihydrogen bonds that differ in strength. The combination of a theoretical density with our hydrogen-bonding criteria turns out to be a valuable new and independent source of information complementary to techniques such as NMR, IR, and structural crystallography.

1. Introduction

Very recently the new term *dihydrogen bond*¹ was coined to describe an interaction of the type $\text{D}\cdots\text{H}\cdots\text{E}$, where D is a typical hydrogen donor such as N or O and E is an element to be specified below. What makes this hydrogen bond so unusual is that the acceptor atom is a hydrogen. For this bond to be intuitively acceptable, one correctly infers that the accepting hydrogen atom must be negatively charged. Transition metals and boron are typical elements (E) that can accommodate this hydridic hydrogen, which is why at present dihydrogen bonds have been observed in those systems.

All examples of dihydrogen bonds involving metals date from the 1990s and were found in Ir complexes² and in an Fe complex.³ An intermolecular version of this interaction was characterized by neutron diffraction on a Re complex,⁴ and a stringent search of the Cambridge Structural Database (CSD) even revealed the existence of $\text{M}\cdots\text{H}\cdots\text{C}$ bonds.⁵

In this contribution we focus on a boron-containing complex: the dimer $(\text{BH}_3\text{NH}_3)_2$ which was the subject of an interesting study by Crabtree, Siegbahn, and co-workers.¹ They showed that as many as 26 $\text{N}\cdots\text{H}\cdots\text{B}$ intermolecular dihydrogen bonds were lurking in the CSD, some data going back to the 1960s. Although their conclusion was based on purely geometrical observations mainly involving X-ray crystal structures, a concomitant calculation showed that a $\text{H}\cdots\text{H}$ bond could be associated with an energy of 25 kJ/mol. This number falls within the range of $\text{H}\cdots\text{H}$ bond strengths of 12–28 kJ/mol established by NMR and IR applied on metal-containing complexes.⁶

Just as conventional hydrogen bonds cause deviations in simple properties such as the boiling point, dihydrogen bonds demonstrate their existence by a striking melting point difference. Indeed, the difference in melting point between BH_3NH_3 and the isoelectronic ethane molecule is as large as 285 K. This formidable anomaly clearly suggests the presence of intermolecular bonds. Of course one may argue that BH_3NH_3 has a considerable dipole moment unlike ethane, but then CH_3F and methane have practically the same melting point despite a large difference in dipole moment.

The main question we want to address here is whether dihydrogen bonds can be confirmed and characterized by a

method independent from crystallographic, spectroscopic, or physicochemical methods.

For that purpose we need a method that provides a rigorous and unambiguous criterion to determine which atoms are bonded in a molecule. The theory of “atoms in molecules” (AIM)⁷ is an excellent candidate, for it has already been successfully applied to understand conventional hydrogen bonds⁸ and $\text{C}\cdots\text{H}\cdots\text{O}$ bonds.⁹ The AIM method uses the electron density as its starting point, which is a real object that can be obtained computationally or experimentally. Based on the topology of the electron density ρ , it then provides quantities and concepts for a researcher to extract chemical information from ρ .

After a brief but comprehensive review of the necessary AIM concepts, we give some details on how the results have been obtained. We then confirm and independently prove the existence of the $\text{H}\cdots\text{H}$ bond and characterize it by means of AIM quantities. Integrated properties are also discussed in light of the discussion of charge transfer and energy densities.

2. Topological Properties of the Electron Density

The key to reveal the topology of the electron density ρ is the gradient vector $\nabla\rho$. It is everywhere perpendicular to a constant-electron-density surface (or envelope) and points in the direction of steepest ascent. A sequence of infinitesimal gradient vectors—the next one evaluated at the end point of the current one—traces a *gradient path*. Because gradient vectors have a direction, gradient paths also have a direction: they can go uphill or downhill. Typically they are attracted to a point in space, called an *attractor*. So gradient paths have an end point and a starting point, which can be infinity or some special point in the molecule.

All nuclei are attractors, and the collection of gradient paths each nucleus attracts is called an *atomic basin*, denoted by Ω . This result is one of the cornerstones of the theory of “atoms in molecules” because this atomic basin constitutes the portion of space allocated to an *atom*. It is over this volume that properties are integrated to yield atomic properties; for example the integration of ρ yields the atom’s population. Note that in a manner of speaking the electron density slices itself up into atoms in a simple and unbiased way.

The second cornerstone of the AIM theory is the definition

of a bond. As shown below defining a bond within the context of gradient paths is straightforward. Some gradient paths do not start from infinity but from a special point appearing somewhere in between two nuclei, called a *bond critical point* (BCP). Critical points (CPs) are extrema in the electron density or points in space where $\nabla\rho$ vanishes. The two gradient paths, each starting at the BCP and terminating at a nucleus, are called the *atomic interaction line*. If all forces on all the nuclei vanish, the atomic interaction line becomes a *bond path* (BP). Practically this is a line linking two nuclei, which we consequently call bonded.

In summary AIM provides a simple but powerful definition of an atom and a bond, two concepts of paramount importance in chemistry. It has been shown before that these atomic basins can be regarded as true quantum subspaces¹⁰ adding to their rigorous and compelling character. As a result the atomic subspace adopts an important property from the total system: the virial theorem. This theorem justifies the concept of the energy of an atom in a molecule, a quantity that we will compute and discuss in the results. For the sake of completeness a few more terms need proper introduction.

In three-dimensional space there are four types of CPs (rank 3, i.e. nondegenerate) which are denoted as (3,-3), (3,-1), (3,+1), and (3,+3). The first and last type are a maximum (e.g. nuclear position) or a minimum, respectively, and the two middle ones are saddle points, called the *bond critical point* (BCP) and the *ring critical point* (RCP), respectively. The minimum (3,+3) is also known as a *cage critical point* (CCP).

There is a second set of special gradient paths, which we can think of as conjugated to the bond paths. They start at infinity and terminate at the BCP instead of being attracted to a nucleus. This bundle of paths does therefore not belong to any atom and forms a surface, which is appropriately called the *interatomic surface* (IAS).

3. Computational Details

All ab initio geometry optimizations of BH_3NH_3 and the dimer $(\text{BH}_3\text{NH}_3)_2$ were executed by the program CADPAC¹¹ at the restricted Hartree-Fock (HF) and second-order Møller-Plesset perturbation theory (MP2) level using the 6-31G** basis set.¹² Reliable and consistent data for hydrogen bonding have been obtained before with this basis set.^{8,9,13} The topological analysis was performed using the program MORPHY97,¹⁴ and some atomic integrations were carried out by PROAIM.¹⁵ The positions of the critical points were detected using the eigenvector following method.¹⁶ The charges of the monomer's atoms add up to 0.0005, and the sum of the atomic energies differs by approximately 0.5 kJ/mol from the total energy. The integration of the dimer proved to be more challenging and leaves a net total charge of just under $0.01e$ and an average energy discrepancy on the order of 5 kJ/mol, errors that are acceptable for our purposes.

4. Results and Discussion

4.1. Geometries. The geometry of the monomer BH_3NH_3 (C_{3v} symmetry) is given in Table 1. It is clear that the effect of correlation is negligible, the most pronounced difference being a shorter B-N bond. Previous ab initio calculations¹ using a different level of theory on the dimer reported five different optimized structures, one of which turned out to be a transition state. Since it is not the purpose of this paper to systematically explore the potential energy surface of the dimer, we concentrate on one particular minimum. The structure we

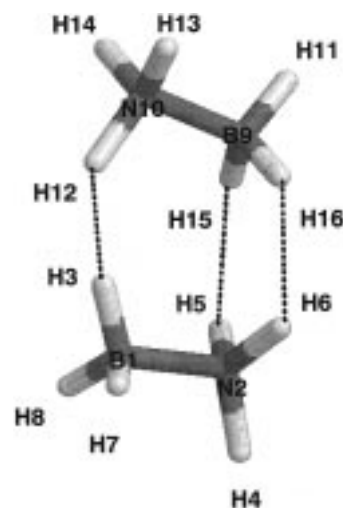


Figure 1. Numbering scheme for the dimer $(\text{BH}_3\text{NH}_3)_2$. The plane of the paper is the mirror plane.

TABLE 1: Selected Geometrical Parameters (Å and deg) and Energies (au) of BH_3NH_3

	HF/6-31G**	MP2/6-31G**
B-N	1.687	1.657
B-H	1.208	1.202
N-H	1.003	1.014
H-B-N	104.38	104.46
B-N-H	110.64	111.03
H-B-H	114.05	113.98
H-N-H	108.28	107.87
H-B-N-H	180.00	180.00
H-B-N-H'	60.00	60.00
energy	-82.624 97	-82.932 29

have selected shows three dihydrogen bonds, two of which are identical due to the presence of a mirror plane (C_s symmetry).

A numbering scheme for the dimer is given in Figure 1, and details of its geometry can be found in Table 2. Again the geometries computed at the HF and MP2 level are virtually the same. The main effect of electron correlation is to shorten the B-N bonds. The next question is how the monomer's geometry changes when bound in the dimer. All B-H and N-H bonds involved in the dihydrogen bonds lengthen, the B-H bonds more so than the N-H bonds. All bonds not directly participating in the $\text{B-H}\cdots\text{H-N}$ bond shrink slightly. The valence angles all remain stable within two degrees. Finally when considering the newly formed bond distances and angles, the $\text{H}\cdots\text{H}$ bonds both shrink considerably (by almost 0.2 Å) under the influence of correlation and the discrepancy for the $\text{N-H}\cdots\text{H}$ and the $\text{B-H}\cdots\text{H}$ angles can amount to five degrees.

The recent CSD investigation¹ mentioned in the Introduction proposed the range of $\text{H}\cdots\text{H}$ distances (d_{HH}) to be 1.7–2.2 Å, with an average value μ of 1.96 Å and a standard deviation σ of 0.13 Å. Only the HF value for the $\text{H5}\cdots\text{H15}$ value does not fall in this range. However, very few neutron diffraction structures of boron compounds have been carried out, so the proposed experimental range has been subject to corrections typical for hydrogen positions determined by X-ray diffraction. Experimental ranges have also been proposed for the $\text{N-H}\cdots\text{H}$ angle (117–171°, $\mu = 149^\circ$, $\sigma = 17^\circ$) and for the $\text{B-H}\cdots\text{H}$ angle (90–171°, $\mu = 120^\circ$, $\sigma = 26^\circ$). Including metal dihydrogen bonds into this set of observations corroborates the conclusion that the $\text{E-H}\cdots\text{H-N}$ bond is strongly bent at both ends. It follows from Table 2 that all computed dihydrogen bond angles fall in their respective range, the average of the two $\text{N-H}\cdots\text{H}$ angles (MP2 level) coinciding with the experi-

TABLE 2: Selected Geometrical Parameters (Å and deg) and Energies (au) of (BH₃NH₃)₂

	HF/6-31G**	MP2/6-31G**		HF/6-31G**	MP2/6-31G**
B1–N2	1.659	1.635	H3–B1–N2	105.8	106.5
B1–H3	1.219	1.213	H7–B1–N2	105.7	105.9
B1–H7	1.207	1.201	H3–B1–H7	112.3	111.8
N2–H4	1.003	1.014	H7–B1–H8	114.2	114.4
N2–H5	1.004	1.016	H4–N2–B1	110.2	110.2
B9–N10	1.659	1.634	H5–N2–B1	111.8	112.6
B9–H11	1.206	1.194	H4–N2–H5	108.4	108.1
B9–H15	1.215	1.209	H5–N2–H6	106.1	104.9
N10–H12	1.007	1.022	H11–B9–N10	106.2	106.6
N10–H13	1.003	1.015	H15–B9–N10	105.2	105.2
H3···H12	1.914	1.726	H11–B9–H15	113.1	112.8
H5···H15	2.324	2.149	H15–B9–H16	113.3	113.3
			B9–N10–H12	110.8	111.0
H3–B1–N2–H4	180.0	180.0	B9–N10–H13	110.9	111.2
H7–B1–N2–H5	–178.7	–178.3	H12–N10–H13	108.2	107.9
H7–B1–N2–H4	60.7	60.9	H13–N10–H14	107.9	107.5
H11–B9–N10–H12	180.0	180.0	N10–H12···H3	163.5	168.7
H15–B9–N10–H13	180.0	–179.9	B1–H3···H12	144.6	139.2
H15–B9–N10–H14	–60.2	–60.2	N2–H5···H15	128.7	130.0
			B9–H15···H5	113.8	112.6
energy	–165.265 10	–165.885 50			

TABLE 3: Summary of Eight Criteria Based on the Theory of “Atoms in Molecules” Used To Characterize a D–H···A Hydrogen Bond

- (1) Topological pattern of the electron density: a BCP, IAS, and BP for the H···A bond accompanied by a typical shape of the atomic basins of H and A
- (2) The electron density at the bond critical point: range 0.002–0.035 au
- (3) The Laplacian of the electron density at the bond critical point: range 0.024–0.139 au
- (4) Mutual penetration of the hydrogen and the acceptor atom
- (5) Increased net charge of the hydrogen atom
- (6) Energetic destabilization of the hydrogen atom
- (7) Decrease of dipolar polarization of the hydrogen atom
- (8) Decrease of the hydrogen atomic volume

mental average and the calculated average of the two B–H···H angles being two-tenths of a standard deviation off the corresponding experimental average. In summary we may conclude that our computed dihydrogen bonds share the purely geometrical characteristics previously determined.¹ However it should be emphasized that the following topological analysis provides a novel and independent set of criteria to characterize the dihydrogen bond.

4.1. Fulfillment of Hydrogen Bond Criteria. Eight AIM criteria have been proposed before⁹ to study and characterize hydrogen bonds whether they are of a conventional type^{8,13} or rarer⁹ such as the C–H···O bond. They are given in Table 3 and will be systematically applied to the current two dihydrogen bonds, which can actually be viewed as special types of hydrogen bonds.

Topology. Figure 2 clearly demonstrates the existence of a BCP for every dihydrogen bond, roughly lying in the middle. A glance at Figure 3 reveals the expected bond path and interatomic surface associated with the H···H BCP. The atomic basin of H3 is strikingly similar to an (accepting) oxygen in a typical hydrogen bond. This resemblance suggests that H3 is hydridic and takes on the role of hydrogen bond acceptor. This remarkable action of hydrogen is due to the low electronegativity of boron, a fact that is reflected in its atomic population discussed below.

The total topology of the dimer is consistent since the Poincaré–Hopf relationship holds. This equation says that the number of nuclei minus the number of BCPs plus the number of RCPs minus the number of CCPs equals one. Note that this



Figure 2. Schematic drawing of the dimer (BH₃NH₃)₂ showing the geometry of all its critical points. The small light spheres represent the hydrogen atoms, and the small dark spheres are the bond critical points (BCPs). Note that the B–H BCPs lie close to the hydrogens. The ring critical points are marked by two large spheres. A dotted line denotes the dihydrogen bond's bond path. Note that the bond paths of the two dihydrogen bonds on the right are curved, signifying structural instability.

type of double-ring topology may also occur in bicyclic hydrocarbons, for example norbornane (bicyclo[2.2.1]heptane).

The Electron Density of the Bond Critical Point. This quantity is denoted by ρ_b and is listed in Table 4 for the monomer bonds and Table 5 for the dimer bonds. It has been shown that ρ_b is related to the bond order and thus to the bond strength.¹⁷ As a result the value for ρ_b is much lower for the H···H bond compared to a typically covalent N–H bond for example. Again the effect of correlation is marginal. Given that ρ_b is not very basis-dependent, its values for the H···H bonds do fall within the proposed range of 0.002–0.035 au.⁹ Since $\rho_b(\text{H5} \cdots \text{H15})$ is about half $\rho_b(\text{H3} \cdots \text{H12})$, we expect the former bond to be weaker than the latter, which is in agreement with the following consideration.

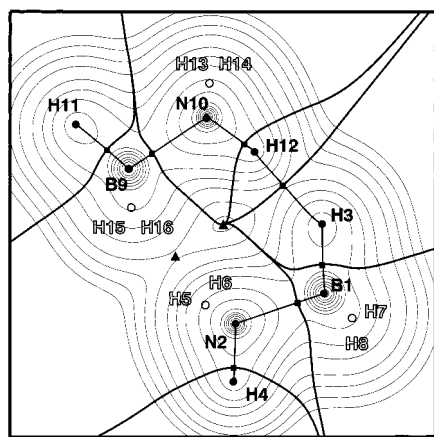


Figure 3. Superposition of the contour lines (thin) of the electron density and the molecular graph (bold) and interatomic surfaces (bold) of the dimer $(\text{BH}_3\text{NH}_3)_2$ at the MP2/6-31G** level. Bond critical points are denoted by squares, and the ring critical points by triangles. The plane of the paper is the dimer's mirror plane. The labels of the nuclei that lie in the mirror plane are bold, and those that do not lie in this plane are open.

TABLE 4: Analysis^a of the Bond Critical Points (BCPs) in BH_3NH_3

level	BCP	ρ_b	$\nabla^2\rho_b$	λ_1	λ_2	λ_3	ϵ
HF	B–N	0.0894	0.5081	−0.0983	−0.0983	0.7046	0.0000
	B–H	0.1659	−0.0608	−0.3726	−0.3174	0.6291	0.1739
	N–H	0.3605	−2.0306	−1.4164	−1.3875	0.7734	0.0208
MP2	B–N	0.0993	0.4906	−0.1141	−0.1141	0.7187	0.0000
	B–H	0.1683	−0.1099	−0.3615	−0.3113	0.5629	0.1613
	N–H	0.3439	−1.8496	−1.3101	−1.2859	0.7465	0.0189

^a Symbols are explained in the text.

Diagonalization of the Hessian of the electron density $\nabla\nabla\rho$ yields three (ordered) eigenvalues, $\lambda_1 < \lambda_2 < \lambda_3$. The ellipticity ϵ is defined as $\lambda_1/\lambda_2 - 1$ and measures the extent to which charge is preferentially accumulated. For example, the C–C bond shows an increasing ellipticity in going from ethane over benzene to ethene. The ellipticity provide a measure for not only the π character of a bond but also its structural stability.

TABLE 5: Analysis^a of the Bond Critical Points (BCPs) in $(\text{BH}_3\text{NH}_3)_2$

level	BCP	ρ_b	$\nabla^2\rho_b$	λ_1	λ_2	λ_3	ϵ
HF	B1–N2	0.0992	0.5185	−0.1394	−0.1306	0.7884	0.0668
	B9–N10	0.0991	0.5199	−0.1355	−0.1322	0.7876	0.0253
	B1–H3	0.1560	−0.0007	−0.3397	−0.2876	0.6266	0.1810
	B1–H7	0.1668	−0.0669	−0.3699	−0.3235	0.6265	0.1434
	B9–H11	0.1676	−0.0707	−0.3724	−0.3251	0.6267	0.1456
	B9–H15	0.1614	−0.0324	−0.3546	−0.3044	0.6266	0.1648
	N2–H4	0.3606	−2.0291	−1.4100	−1.3854	0.7663	0.0178
	N2–H5	0.3594	−2.0395	−1.4373	−1.4131	0.8109	0.0172
	N10–H12	0.3557	−2.0272	−1.4509	−1.4272	0.8509	0.0166
	N10–H13	0.3600	−2.0270	−1.4103	−1.3855	0.7687	0.0179
	H3...H12	0.0126	0.0353	−0.0144	−0.0142	0.0639	0.0149
	H5...H15	0.0067	0.0247	−0.0061	−0.0040	0.0349	0.5511
	H5...H15	0.0067	0.0247	−0.0061	−0.0040	0.0349	0.5511
MP2	B1–N2	0.1055	0.5574	−0.1619	−0.1511	0.8703	0.0718
	B9–N10	0.1057	0.5597	−0.1578	−0.1538	0.8713	0.0261
	B1–H3	0.1560	0.0221	−0.3390	−0.2881	0.6492	0.1769
	B1–H7	0.1685	−0.0572	−0.3743	−0.3302	0.6474	0.1335
	B9–H11	0.1692	−0.0617	−0.3767	−0.3320	0.6470	0.1345
	B9–H15	0.1622	−0.0136	−0.3560	−0.3080	0.6504	0.1560
	N2–H4	0.3510	−1.9609	−1.3505	−1.3290	0.7186	0.0161
	N2–H5	0.3495	−1.9720	−1.3799	−1.3588	0.7667	0.0155
	N10–H12	0.3429	−1.9398	−1.3878	−1.3673	0.8152	0.0150
	N10–H13	0.3506	−1.9586	−1.3492	−1.3273	0.7179	0.0164
	H3...H12	0.0190	0.0464	−0.0239	−0.0235	0.0938	0.0183
	H5...H15	0.0096	0.0347	−0.0096	−0.0066	0.0509	0.4544
	H5...H15	0.0096	0.0347	−0.0096	−0.0066	0.0509	0.4544

^a Symbols are explained in the text.

Substantial bond ellipticities reflect structural instability; that is, the bond can easily be ruptured.¹⁸ In Table 5 we see that $\epsilon(\text{H5}\cdots\text{H15})$ is much larger than $\epsilon(\text{H3}\cdots\text{H12})$, confirming that the former bond is weaker. Another criterion for structural stability is the distance between a BCP and a RCP. If these two critical points coalesce, they annihilate corresponding to bond rupture and concomitant ring opening. Again the distance between BCP(H5...H15) and the nearest RCP is 0.7 Å, whereas the distance between BCP(H3...H12) to its nearest RCP is 1.2 Å, rendering the latter as the more stable dihydrogen bond.

The Laplacian of the Electron Density of the Bond Critical Point. The Laplacian $\nabla^2\rho_b$ is simply the sum of the eigenvalues λ_i . It has been observed that for ionic bonds, hydrogen bonds, and van der Waals interactions (so-called *closed-shell interactions*) the Laplacian is positive. For covalent bonds (*shared interactions*) the Laplacian is negative. According to Table 5, the N–H bond is clearly covalent, but the B–N bond is ionic in both monomer and dimer regardless of the inclusion of correlation. The ionicity of B–N is confirmed by its low ρ_b value. Both dihydrogen bonds are typical closed-shell interactions, the values for $\nabla^2\rho_b$ lying in the proposed range of 0.014–0.139 au.⁹

Mutual Penetration of Hydrogen and Acceptor Atom. We define the nonbonded radius of an atom A [$r_0(\text{A})$] as the distance of its nucleus to a given electron density contour in the monomer. This distance is measured in the direction of hydrogen bond formation as seen from the nucleus. Usually a value of 0.001 au for the contour is taken because this yields molecular sizes and atomic diameters in good agreement with gas-phase van der Waals radii. The bonded radius [$r_b(\text{A})$] is then simply the distance from the nucleus to the BCP in question (in the dimer), a concept unique to AIM. The penetration $\Delta r(\text{A})$ is defined as the nonbonded radius minus the bonded radius, or $\Delta r(\text{A}) = r_b(\text{A}) - r_0(\text{A})$. It should be realized that AIM enables one to mutually compare each atom's *individual* penetration caused by complex formation; in other words it is possible to assess which atom penetrates more into the other to account for the total penetration of the monomers into each other.

The nonbonded radius of the hydridic hydrogen (attached to boron) varies little with direction and is about 1.53 Å, which is

TABLE 6: Atomic Properties (in au) for Atoms in the Monomer BH₃NH₃

level	atom	$q(\Omega)$	$M(\Omega)$	$\nu(\Omega)$	$-E(\Omega)$
HF	B	2.1560	0.033	16.6	23.6968
	N	-1.2556	0.178	102.9	54.9557
	H(B)	-0.7460	0.325	87.0	0.8870
	H(N)	0.4460	0.169	27.2	0.4374
	Σ	0.0005			82.6252
	E^a				82.6250
MP2	B	2.0329	0.043	19.7	23.8287
	N	-1.1812	0.189	100.3	55.0879
	H(B)	-0.7103	0.285	85.2	0.8896
	H(N)	0.4266	0.175	29.0	0.4490
	Σ	0.0006			82.9324
	E^a				82.9323

^a This is the (original) total energy of the molecule associated with the analyzed wave function.

TABLE 7: Atomic Properties^a for Atoms in the Dimer (BH₃NH₃)₂

level	atom	$q(\Omega)$	$M(\Omega)$	$\nu(\Omega)$	$-E(\Omega)$
HF	B1	2.1604	0.035	16.2	23.6902
	N2	-1.3025	0.213	101.9	54.9988
	H3	-0.7445	0.294	84.1	0.8821
	H4	0.4424	0.169	27.1	0.4394
	H5	0.4662	0.166	26.0	0.4246
	H7	-0.7415	0.325	86.1	0.8860
	B9	2.1637	0.045	15.7	23.6934
	N10	-1.3096	0.207	103.7	55.0018
	H11	-0.7385	0.328	86.3	0.8855
	H12	0.4871	0.161	23.9	0.4088
	H13	0.4453	0.169	27.1	0.4377
	H15	-0.7459	0.308	84.9	0.8846
	Σ	0.0067			165.2671
	E^a				165.2671
MP2	B1	2.1683	0.042	15.7	23.7890
	N2	-1.3109	0.213	100.5	55.1902
	H3	-0.7403	0.288	79.9	0.8938
	H4	0.4404	0.168	27.7	0.4376
	H5	0.4671	0.164	25.5	0.4209
	H7	-0.7407	0.317	85.9	0.8945
	B9	2.1681	0.042	15.3	23.7930
	N10	-1.3195	0.208	103.2	55.1889
	H11	-0.7380	0.320	85.8	0.8938
	H12	0.4955	0.153	22.1	0.4005
	H13	0.4413	0.167	27.7	0.4369
	H15	-0.7452	0.299	82.5	0.8953
	Σ	0.0086			165.8820
	E^a				165.8859

^a This is the (original) total energy of the molecule associated with the analyzed wave function.

larger than the accepted van der Waals radius of 1.2 Å. The protic hydrogen (attached to nitrogen) has a nonbonded radius of 1.27 Å. For the stronger dihydrogen bond H3...H12 the penetration of H3(-B) and H12(-N) is 0.48 and 0.41 Å, respectively, whereas for H5...H15 the penetration of H15(-B) and H5(-N) is 0.25 and 0.19 Å, respectively. So the hydridic hydrogen is penetrated most, an effect that is more pronounced for the weaker dihydrogen bond.

A link between the HSAB (hard and soft acid and base) principle and the degree of penetration has been suggested before.^{8,9} It was established that if a hydrogen is penetrated considerably, it belongs to a soft group. On this basis it was previously concluded that C-H is a soft acidic group,⁹ which was independently confirmed by Desiraju.¹⁹ Accordingly, we conclude that N-H is moderately hard.

Increased Net Charge of the Hydrogen Atom. All integrated properties can be found in Tables 6 and 7 for the monomer and the dimer, respectively. In this subsection we focus on the net

charge on an atom $q(\Omega)$, which is given by the sum of the nuclear charge and the electron population of the atom. For example, if the atomic basin of carbon contains 5.5 electrons, then its net charge is +0.5. From Tables 6 and 7 it is obvious that boron is stable as an electron-deficient atom in any system and at any level. This is at variance with a Mulliken population analysis published before¹ for a slightly different complex (and at a marginally different level) in which the boron is believed to carry a charge of -0.26.

Upon dimerization the charge of the donor hydrogen H12 increases from 0.43 to 0.50 (MP2), which corresponds to a loss of 0.07e. Similarly the charge on the H5 atom (in the weak dihydrogen bond) goes up from 0.43 to 0.47, which is a loss of only 0.04e. Comparable electron losses were found in a set of four C-H...O containing van der Waals complexes,⁹ where again the smallest loss coincided with the energetically weaker complex.

Energetic Destabilization of the Hydrogen Atom. This criterion requires that the protic hydrogen atom be destabilized upon complex formation; that is, its energy should rise. The energy of atom H12 indeed rises by 127 kJ/mol (MP2) and that of atom H5 by 74 kJ/mol. Again the strength of the dihydrogen bonds is reflected in these values. The destabilization observed here is in line with numbers computed before for conventional hydrogen bonds. Note that energy changes on other hydrogen atoms are typically in the other direction and 5–10 times smaller. So the energetic destabilization of the donor hydrogen is a dramatic and dominant effect.

Decrease of Dipolar Polarization of the Hydrogen Atom. Atomic integration of a position vector times the electron density yields the first moment, $M(\Omega)$. It provides a measure of the extent and direction of the dipolar polarization of the atom's electron density by determining the displacement of the atom's centroid of negative charge from the position of the nucleus. Here we are only concerned with this vector's magnitude, $M(\Omega)$, which is listed in Tables 6 and 7. The value for the hydrogen attached to the nitrogen in the monomer is 0.175 au and decreases to 0.153 and 0.164 au for the strong and weak hydrogen bond, respectively.

Decrease of the Hydrogen Atom's Volume. Note first of all that the hydridic hydrogen is about 3 times larger than the protic one. The protic hydrogen does indeed shrink from 29.0 au to 22.1 au (H12) and 25.5 au (H5). Even this property leaves a track of the difference in bond strength.

A final comment about overall charge transfer is appropriate here. Adding the net charges of all the atoms belonging to one monomer being part of the dimer yields 0.005, which means that within the integration error there is no overall charge transfer from one monomer to the other. This is not surprising. What is remarkable though is that the BH₃ and NH₃ moieties are essentially neutral.

5. Conclusion

That hydrogen is a "creative" element in terms of bonding will not be contradicted by those researchers that first came across the hydrogen bond, the agostic bond,²⁰ or the binding of hydrogen on metal surfaces during catalysis.²¹ It has even been reported that very high pressures induce ionic character in the hydrogen molecule (formation of the protonium hydride H⁺H⁻).²² Now hydrogen continues to surprise us by *accepting* its own hydrogen bonds, forming the so-called dihydrogen bond. We have proven that this new type of bond can be classified as a hydrogen bond using a set of criteria developed in the study of conventional hydrogen bonds. For that purpose we have used

the theory of "atoms in molecules". The $(\text{BH}_3\text{NH}_3)_2$ dimer can adopt a structure containing a weak and a strong dihydrogen bond at the same time. Some of the proposed criteria enable the characterization of these bonds in terms of their strength.

This investigation is solely based on the electron density and therefore provides an interesting complement, or even alternative, to NMR, IR, and structural crystallography.

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