Modulating the Strength of Hydrogen Bonds through Beryllium Bonds

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ⓈSupporting Information

ABSTRACT: The mutual influence between beryllium bonds and inter- or intramolecular hydrogen bonds (HBs) has been investigated at the B3LYP/6-311++G(3df,2p) level of theory, using the complexes between imidazole dimer and malonaldehyde with BeH_2 and BeF_2 as suitable model systems. Imidazole and its dimer form very strong beryllium bonds with both BeH_2 and BeF_2, accompanied by a significant geometry distortion of the Lewis acid. More importantly, we have found a clear cooperativity between these two noncovalent interactions, since the intermolecular HB between the two imidazole molecules in the dimer−BeX_2 complex becomes much stronger than in the isolated dimer, whereas the beryllium bond becomes also stronger in the dimer−BeX_2 complex, with respect to that found in the imidazole−BeX_2 complex. The effects of beryllium bonds are also dramatic on the strength of intramolecular HBs. Depending on to which center the BeX_2 is attached, the intramolecular HB becomes much stronger or much weaker. The first situation is found when the beryllium derivative is attached to the HB donor, whereas the second occurs if it is attached to the HB acceptor. The first effect can be so strong as to produce a spontaneous proton transfer, as it is actually the case of the malonaldehyde−BeF_2 complex.

■ INTRODUCTION

In general, the name "noncovalent interactions" is used to design weak interactions, typically between closed-shell systems with no electron sharing between the interacting subunits.[1] There is, however a great variety of noncovalent interactions attending both to their energy and to their nature, and some of them are almost as strong as conventional covalent linkages,[1] because even if closed-shell interactions may be involved, a substantial amount of charge transfer might take place. Noncovalent interactions play a crucial role in nature, because they are responsible for the organization of practically all molecular assemblies, either of natural origin like DNA or of artificial origin as the so-called metal−organic frameworks (MOFs)[2] or "soft matter",[3] a term usually employed to describe materials that are held together by noncovalent interactions involving energies of the order of the thermal energy, kT.[3,4] Hence, not surprising, a good knowledge of the noncovalent interactions turned out to be essential for the development of new molecular materials. Among them conventional[5−7] and nonconventional[8−10] hydrogen bonds (HBs) have received particular attention. In this case, the interaction is leaded by a hydrogen atom which interacts with two moieties, one of which behaves as a Lewis base, the HB acceptor, and the other as a Lewis acid, the HB donor.

This interaction scheme is not necessarily exclusive of HBs and could be found whenever an element, not very electronegative with low-lying empty orbitals, is covalently bound to a more electronegative one. One of the elements, which initially fulfills these conditions, is beryllium. Hence, not surprisingly it has been found that beryllium derivatives, BeX_2, starting from beryllium hydride, interact rather strongly with different Lewis bases, B, leading to the formation of what have been called beryllium bonds.[11] These linkages are characterized by the existence of a bond critical point (BCP) between the Be atom and the active site of B,[11,12] its electron density being usually larger than the one typically associated with conventional HBs.[11] It has been also shown that beryllium bonds share many of the characteristics of conventional HBs. As a matter of fact, both linkages have a dominant electrostatic character, and in both a non-negligible charge transfer takes place from one of the interacting subunits to the other.[11] For the particular case of a HB, this transfer takes place from the HB acceptor lone-pairs toward the $\sigma_{YH}*$ antibonding orbital of the HB donor. In beryllium bonds the transfer is from the lone pairs of the Lewis base B, toward the $\sigma_{BeX}*$ antibonding orbital of BeX_2 and the empty p orbital of Be as well. Also importantly, the formation of a beryllium bond is followed by a significant distortion of the BeX_2 subunit, which as suggested in ref 13 should alter its electron-acceptor capacity.

One of the signatures of HBs is the existence of cooperativity effects,[14−47] manifested by a strengthening of the HB between the HB donor and the HB acceptor, when one of them, or both, interacts with a third HB donor or acceptor. These effects are actually rather important in clusters involving water,[15,16,20,22,25,26,33,36,40,47−49] alcohol clusters,[19,23,26,27,29,50−52] and other complexes.[28,32−34,39,41−43,45,53,54] The possibility of having cooperative effects among HB and other different noncovalent interactions have been reviewed recently.[55] The question we wish to address in this paper is whether we can also modulate the strength of a HB, through the formation of a beryllium

bond involving either the HB donor or the HB acceptor. For this purpose we have chosen as a suitable model system the imidazole dimer. Imidazole has the advantage of having within the same aromatic system a basic site, the imino nitrogen, able to act as a good proton acceptor or yield strong beryllium bonds and at the same time an acidic site, the amino nitrogen, able to act as an efficient HB donor. On the top of that imidazole is a good model of biochemical bases. Also interesting would be to investigate whether beryllium bonds can compete and displace HBs. In fact it has been shown that Be can displace H^+ in many strong HBs, in processes in which Be behaves as a "tetrahedral proton".[56−58] Also important will be to know the effect that the presence of a beryllium may have on the characteristics of intramolecular HBs (IMHBs). A rather good model to investigate this question is provided by malonaldehyde, where both the carbonyl or the hydroxyl group may act as beryllium-bond acceptors, and because Be usually shows preference to be bound to O atoms.[56,59]

COMPUTATIONAL DETAILS

For our theoretical survey we have used the B3LYP density functional approach, which combines the three-parameter hybrid exchange functional of Becke[60] with the nonlocal LYP correlation functional.[61] For the geometry optimizations a 6-31+G(d,p) basis set has been used, whereas to obtain more reliable final energies a larger 6-311++G(3df,2p) basis set expansion was employed. This theoretical model has been shown to adequately reproduce the characteristic of conventional inter- and intramolecular HBs.[24,62,63] Our results for the imidazol dimer slightly underestimate very recent values obtained at the CCSD(T)/CBS level[64] and with the values calculated at the G4 level (see Table S1, Supporting Information). When other functionals recently proposed as good methods to describe HBs, namely X3LYP, M05-2X, M06-2X, or B97-D, are used, the values obtained underestimate the CCSD(T) and the G4 ones but differ very little from the B3LYP value with the only exception of the M05-2X functional (see Table S1, Supporting Information). However, while B3LYP also underestimates the G4 values for the dissociation energy of the beryllium bonds, the other functionals, with the only exception of X3LYP, overestimate it, so B3LYP turns out to be a better option when the simultaneous description of both HBs and beryllium bonds is required. Harmonic vibrational frequencies, obtained at the B3LYP/6-31+G(d,p) level, were used to classify the stationary points found as local minima of the potential energy surface, to estimate the zero point energy corrections and to analyze the vibrational shifting of relevant stretching frequencies as a measure of cooperative or anticooperative effects due to the mutual interaction between HBs and beryllium bonds.

The dissociation energies of both the HBs or the beryllium bonds, D_0, will be obtained as the difference between the energy of the complex and those of the two interacting subunits in their equilibrium conformation. The reported values for D_0 will include the ZPE corrections. The basis set superposition error (BSSE), estimated using the counterpoise method, is not significant, ~0.5 kJ mol^{-1} for the imidazol dimer and ~1.0 kJ mol^{-1} for the imidazol−BeH$_2$ complex. A more realistic measure of the strength of these bonds is given by the interaction energy, E_{int}, defined as the difference between the energy of the complex and those of the two interacting subunits in the distorted conformation they have in the complex.[13]

There are different procedures to analyze the strength of noncovalent interactions, most of them based on an analysis of the electron density. In this study we will use three complementary approaches, namely the atoms in molecules (AIM) theory,[65,66] the noncovalent interaction (NCI) index,[67,68] and the natural bond orbital (NBO) approach.[69] AIM permits to define the molecular graph of the investigated systems as the ensemble of maxima of the electron density, ρ, associated with the position of the nuclei, saddle points, in which ρ has two negative and one positive curvatures, the so-called BCPs and the zero gradient lines connecting them, or bond paths. The value of the electron density at the BCP, ρ_b, for inter- and intramolecular HBs[46,70−80] and for beryllium bonds as well is a good quantitative measure of the strength of the bond.

The characterization of noncovalent interactions is however not always a trivial matter, but it has been recently shown that they can be revealed solely from the electron density,[67] through the definition of the NCI index, which is based on the reduced density gradient, s, and the electron density, ρ, where

$$s = \frac{1}{2(3\pi^2)^{1/3}} \frac{|\nabla\rho|}{\rho^{4/3}}$$

and which permits to highlight interactions characterized by a low-density regime. The bonding interactions can then be identified by the negative sign of the λ_2 eigenvalue of the electron density Hessian.[67,68]

The NBO method is based on the use of localized atomic hybrids, obtained as block eigenvectors of the one-particle density matrix, which are characterized by their occupation numbers. Once these molecular orbitals are obtained, it is possible to evaluate the second order interaction energies between occupied and empty orbitals, which would be a measure of the charge transfer from the former to the latter, and to calculate the Wiberg bond order,[81] which is another useful way of quantitatively define the strength of a linkage.

The molecular electrostatic potential (MEP) of the isolated monomers have been calculated on the electron density isosurface of 0.001 au. This isosurface has been shown to resemble the van der Waals (vdW) surface.[82] These calculations have been carried out with the facilities of the Gaussian 09 program and numerical results depicted using the WFA program.[83]

RESULTS AND DISCUSSION

Beryllium Bonds and IMHBs. As indicated in the Introduction Section, we have used the imidazole dimer as a probe of the effect of beryllium bonds on intermolecular HBs. As Lewis acids able to form the beryllium bonds with the basic site of imidazole dimer, we have considered beryllium hydride and beryllium difluoride, since the latter should yield stronger beryllium bonds than the former.

The BeX$_2$ Lewis acid may interact with the imidazole dimer, by behaving as an electron acceptor of the imino N which does not participate in the intermolecular HB.

The corresponding dissociation, D_0, and interacting, E_{int}, energies characterizing the HB of the imidazole dimer and the beryllium bonds in imidazole−BeH$_2$ and imidazole−BeF$_2$ complexes are summarized in Table 1. For the complexes formed by the interaction of the imidazole dimer with the two Lewis acids under consideration, the dissociation and

Table 1. B3LYP/6-311++G(3df,2p) Dissociation (D_0) and Interaction Energies (E_{int}) for the Complexes Included in This Study[a]

complex	Be bond		HB	
	D_0	E_{int}	D_0	E_{int}
imidazole dimer			30.0	35.5
imidazole−BeH$_2$	111.0	166.0		
imidazole−BeF$_2$	132.0	205.0		
imidazole dimer−BeH$_2$	126.2	181.7	45.6	52.3
imidazole dimer−BeF$_2$	149.3	221.8	47.0	54.2

[a]All values in kJ mol^{-1}.

interaction energies for both and the hydrogen and the beryllium bonds are reported.

The optimized structures of the aforementioned complexes are given in Figure 1.

The first conspicuous fact is that imidazole forms rather strong beryllium bonds with both BeH$_2$ and BeF$_2$, since the length of the corresponding Be···N beryllium bonds is almost 2.0 Å shorter than the sum of the corresponding vdW radii (3.55 Å), with dissociation and interaction energies (see Table 1) which are about four times the energy of the HB in the imidazole dimer. This is actually consistent with the essential characteristics of the Be bonds, which involve a strong donation from the lone-pairs of the Lewis base to the empty p orbital of Be and to the σ_{BeX}^* antibonding orbital. The former charge transfer leads to a large deformation of the BeH$_2$ molecule which departs significantly from linearity. The latter charge transfer is responsible of the elongation of the BeH bond the BeH$_2$ moiety, which goes from 1.331 Å in the isolated molecule to 1.374 Å in the imidazole−BeH$_2$ complex. All these effects are actually so strong in the case of imidazole−BeH$_2$ and imidazole dimer−BeH$_2$ complexes that the NBO analysis actually predicts the formation of a very polar Be−N bonding orbital, with a strong participation of the N hybrids (90%), the Wiberg bond index being 0.30. This description is consistent with that obtained when applying the NCI index which shows the existence of a rather strong noncovalent interaction between the two imidazole molecules (see Figure 2) but a covalent bond between Be and N. Also, the AIM analysis (see Figure 2) shows the existence of a N−Be BCP in the imidazole−BeH$_2$ complex, with an electron density almost three times larger than that associated with the N−H···N HB of the imidazole dimer,

whereas the electron density at the Be−H BCP is 0.012 au smaller in the imidazole−BeH$_2$ complex than in the isolated BeH$_2$ molecule.

As expected the Be bonds become stronger when the Lewis acid is BeF$_2$, because the high electronegativity of the fluorine atom enhances the electron-acceptor capacity of beryllium.

The most interesting changes however are observed when looking at the complexes between imidazole dimer and BeH$_2$ or BeF$_2$, in which both noncovalent interactions are present. As it is evident from Figures 1 and 2 and from the values in Table 1 as well, there is a mutual influence between both types of interactions, which become simultaneously reinforced. Indeed, not only the NH···N HB becomes shorter on going from imidazole dimer to its complexes with BeH$_2$ and BeF$_2$, but the Be···N beryllium bonds become shorter too on going from the imidazole−BeX$_2$ complexes to the imidazole dimer−BeX$_2$ complexes. Consistently, the electron densities at the corresponding BCPs become greater (see Figure 2) as well as the Wiberg bond orders, which change from 0.30 to 0.34, and the NCI index also shows stronger bonding interactions reflected in greater absolute values of λ_2. The energetic effects are also significant, on going from the imidazole to the imidazole dimer complexes with BeX$_2$, the beryllium bond dissociation energy becomes 13% larger. Similarly, the dissociation energy of the N−H···N HB becomes 50% larger than in the isolated imidazole dimer.

The reinforcement of the HB of the imidazole dimer when it interacts with BeX$_2$ derivatives is actually triggered by the significant charge transfer from the imino N of the imidazole acting as HB donor to the BeX$_2$ molecule to form the beryllium bond. This leads to a global decrease of the natural electron population of this imidazole ring of 0.2 e$^-$, which results in an enhancement of the acidity of its N−H group, which behaves accordingly as a better HB donor. In fact, whereas the NBO second-order interaction energy between the N lone-pair and the σ_{NH}^* antibonding orbital in the imidazole dimer is 75 kJ mol^{-1}, for the imidazole dimer−BeH$_2$ and −BeF$_2$ complexes, this energy increases up to 105 and 109 kJ mol^{-1}, respectively. Consistently, the lengthening of the NH bond is larger in the latter complexes, the electron density at the NH BCP smaller. A typical signature of these effects will be the red-shifting undergone by the NH stretching frequency. As a matter of fact, on going from imidazole to its dimer, there is a red-shifting of the NH stretching frequency of 326 cm^{-1}, but upon BeH$_2$ and BeF$_2$ association, the shifting increases by 182 and 203
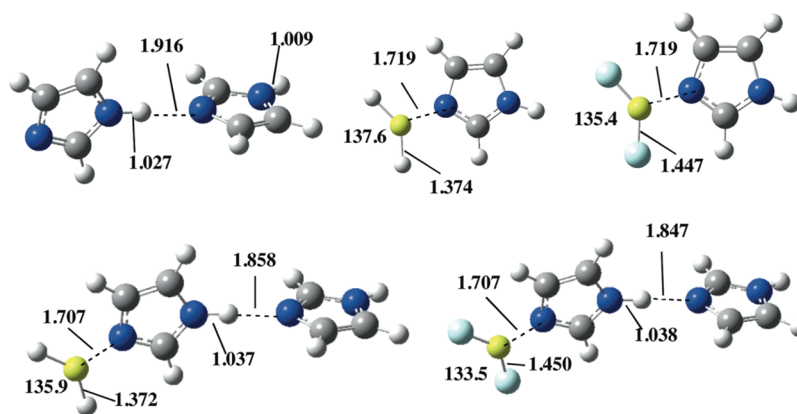
Figure 1. B3LYP/6-31+G(d,p) optimized geometries for the imidazole dimer, imidazole−BeH$_2$, imidazole−BeF$_2$, and the complexes formed by the interaction of imidazole dimer with BeH$_2$ and BeF$_2$. Bond lengths in Å and bond angles in degrees.
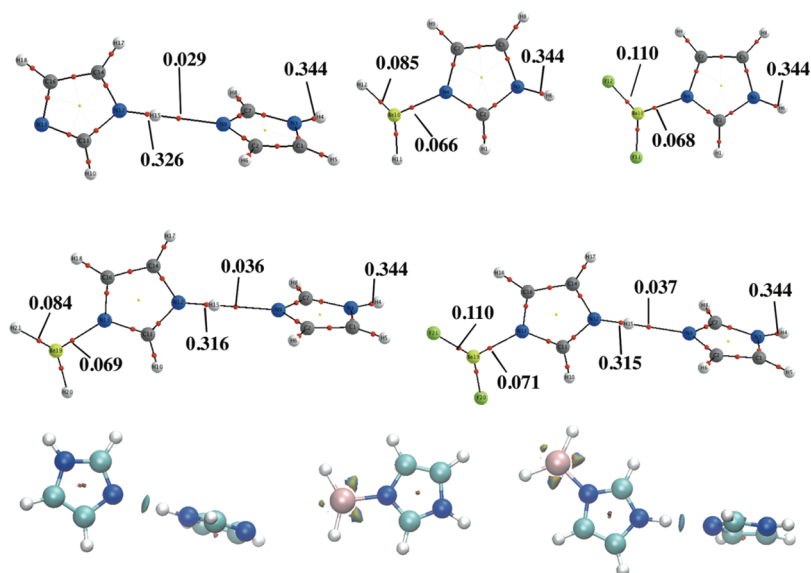
Figure 2. Molecular graphs of for the imidazole dimer, imidazole−BeH$_2$, imidazole−BeF$_2$, and the complexes formed by the interaction of imidazole dimer with BeH$_2$ and BeF$_2$. The red dots correspond to BCPs. The electron densities are in au. The lower file represents the NCI surfaces for imidazole dimer, imidazole−BeH$_2$ complex and imidazole dimer−BeH$_2$ complex for $s = 0.5$.
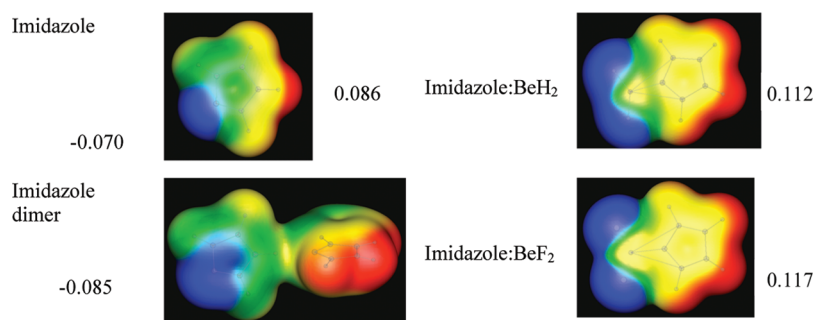

Figure 3. MEP on the vdW surface with indication of some of the minima and maxima values for the systems studied. The color code used is: red > 0.04 > yellow > 0.0 > green > −0.03 au > blue.
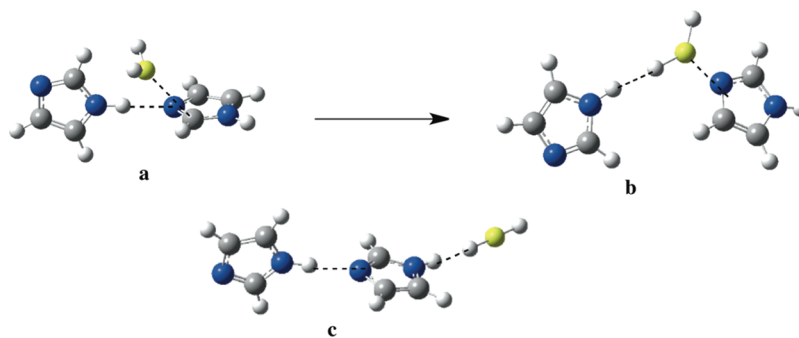

Figure 4. Structures **b** and **c** are local minima of the PES for imidazole dimer−BeH$_2$ complexes, when the BeH$_2$ molecule interacts with the imino nitrogen involved in the intermolecular HD of the imidazole dimer or with the NH group not involved in that HB. Structure a was the initial geometry used in the first case and which collapses to structure **b**.

cm^{-1}, respectively, so the total red-shifting with respect to the isolated imidazole is enormous, 508 and 529 cm^{-1}, respectively.

Similarly, the imino nitrogen of the imidazole, which acts as a HB donor in the imidazole dimer, is a better electron donor than that of the isolated imidazole, since the partial transfer of the proton toward the HB acceptor moiety enhances the basicity of the system. Not surprisingly, the second-order NBO interaction energy between the lone-pair of the imino nitrogen of HB donor and the empty p orbital of Be and the $\sigma_{BeX}*$

antibonding orbital, which in the imidazole−BeH$_2$ is 376 and 16 kJ mol^{-1}, respectively, in the imidazole dimer−BeH$_2$ complex results in the formation of a very polar N−Be covalent linkage.

The MEP for isolated imidazole and imidazole dimer and for the complexes imidazole−BeH$_2$ and imidazole−BeF$_2$ have been plotted on the vdW surface (see Figure 3) in order to analyze whether the MEP adequately reflects the cooperativity effects discussed above. The MEP minimum associated to the N3,
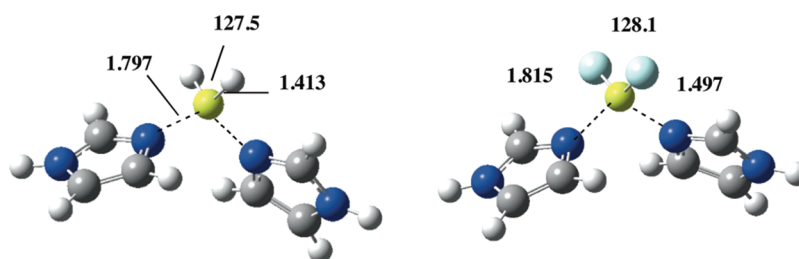
Figure 5. Structure of the complex formed by BeX$_2$ (X = H, F) and two imidazole molecules, when the former is allowed to interact with the two basic sites of the two imidazole monomers. A similar structure is found for BeF$_2$.

which in the isolated monomer has a value of −0.070 au, becomes deeper (up to −0.085 au) in the dimer. This clearly indicates that N3 atom should be expected to interact strongly with a positive charge in the dimer, in agreement with the reinforcement observed in the beryllium bond on going from the imidazole−BeX$_2$ to the imidazole dimer−BeX$_2$ complex.

Similarly, the maximum of the MEP associated to the N1H group in the isolated imidazole (0.086 au) increases (to 0.112 and 0.117 au) in the complexes with BeH$_2$ and BeF$_2$, respectively, indicating that in the latter, this group should be a better HB donor. Hence, we can conclude that the variations in the MEP, when either a HB or a beryllium bond is formed, may be a good index to predict the appearance of cooperative effects.

Competition between Beryllium Bonds and HBs. The complexes between imidazole dimer and BeH$_2$ can be a good model to investigate the competition between both types of non-covalent interactions. For this purpose we have considered the complex which can be eventually formed when the imino nitrogen which participates in the intermolecular HB also interacts with the BeH$_2$ molecule to form a beryllium bond, which would correspond to structure **a** in Figure 4. When this initial structure is fully optimized it evolves to yield structure **b**, in which the imidazole subunit, that behaved as a HB acceptor in the imidazole dimer, now electrodonates to the BeH$_2$ molecule forming the corresponding beryllium bond. Interestingly, the BeH$_2$ molecule forms also a dihydrogen bond with the imidazole dimer that behaved as the HB donor. In summary the initial HB was replaced by a beryllium bond and a dihydrogen bond. This new structure is however 21.6 kJ/mol higher in energy than the imidazole dimer−BeH$_2$ complex shown in Figure 2.

We have considered also of interest to investigate what would be the structure of the complex if the BeH$_2$ molecule interacts with the NH group of the imidazole dimer not involved in the intermolecular HB. In this situation, since the NH group is a very poor electron donor, with the N lone-pair implicated in the conjugation of the ring, the structure found (**c** in Figure 4) corresponds to the formation of a dihydrogen bond between this NH group and the BeH$_2$ molecule.

There is another finding which ratifies the prevalence of beryllium bonds over HBs, at least for the systems investigated. When the BeH$_2$ (or BeF$_2$) molecule is allowed to interact with the basic sites of both imidazole molecules, the structure shown in Figure 5, in which two beryllium bonds are formed, is found. This structure is not only a local minimum of the PES but is almost degenerate in energy, 2.0 (BeH$_2$) and 3.0 (BeF$_2$) kJ mol^{-1}, respectively, above the complex shown in Figure 1, which is stabilized by one HB and one beryllium bond.

This is an important finding which may shed some light into one of the fascinating properties of Be, which has been called a

"tetrahedral proton",[84] because Be displaces H$^+$ in many strong HBs, behaving as a "tetrahedral proton",[56−58,84] very much in the same way as it behaves in the structures shown in Figure 5.

Beryllium Bonds and IMHBs Interactions. The IMHB in malonaldehyde may be perturbed by beryllium bonds in two ways, by association of the BeX$_2$ derivative either to the carbonyl oxygen atom, which acts as the HB acceptor, or to the hydroxyl group, which acts as HB donor. The complexes so formed when the Lewis acid is BeH$_2$ are shown in Figure 6.
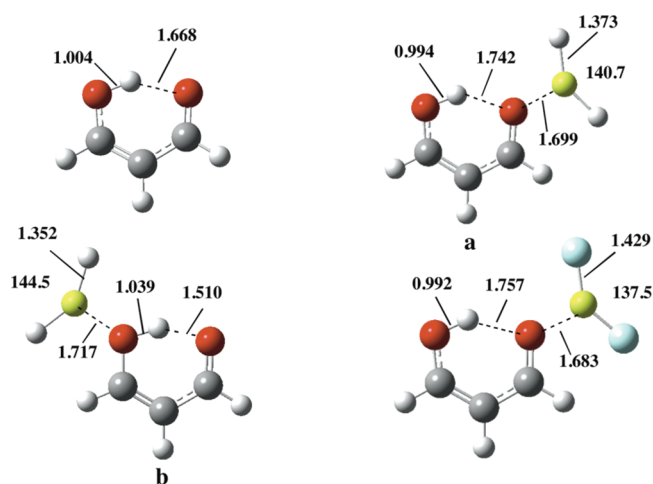

Figure 6. B3LYP/6-31+G(d,p) optimized geometries for malonaldehyde and its complexes with BeH$_2$ and BeF$_2$. Bond lengths in Å.

It is apparent that, as in the case of imidazole and its dimer, malonaldehyde forms also significantly strong beryllium bonds with both Lewis acid, as reflected by the Be···O distances, again much shorter than the sum of the vdW radii of the two atoms and by the dissociation and interaction energies (See Table 2). Note that these energies are however about a 30% smaller than those found for complexes involving imidazole, because the intrinsic basicity of both the C=O and the OH groups is much lower than that of the imino N of imidazole. It can be also

Table 2. B3LYP/-6-311++G(3df,2p) Dissociation (D_0) and Interaction Energies (E_{int}) for the Beryllium Bonds Formed between Malonaldehyde and BeH$_2$ and BeF$_2$[a]

	Be bond	
complex	D_0	E_{int}
malonaldehyde−BeH$_2$ (**a**)	69.0	120.2
malonaldehyde−BeH$_2$ (**b**)	49.0	90.8
malonaldehyde−BeF$_2$	90.2	156.6

[a]All values in kJ mol^{-1}.

observed that, as expected, the beryllium bond involving the OH group (complex **b** in Figure 6) is significantly weaker than that involving the carbonyl group (complex **a** in Figure 6), as the former is a much poorer electron donor than the latter.

These differences are also reflected in the electron density at the O····Be BCP, which is larger in complex **a** than in complex **b** (see Figure 7). The weaker beryllium bond formed in the latter case is also mirrored in a smaller lengthening of the BeH bond and in a larger electron density at the Be−H BCP.
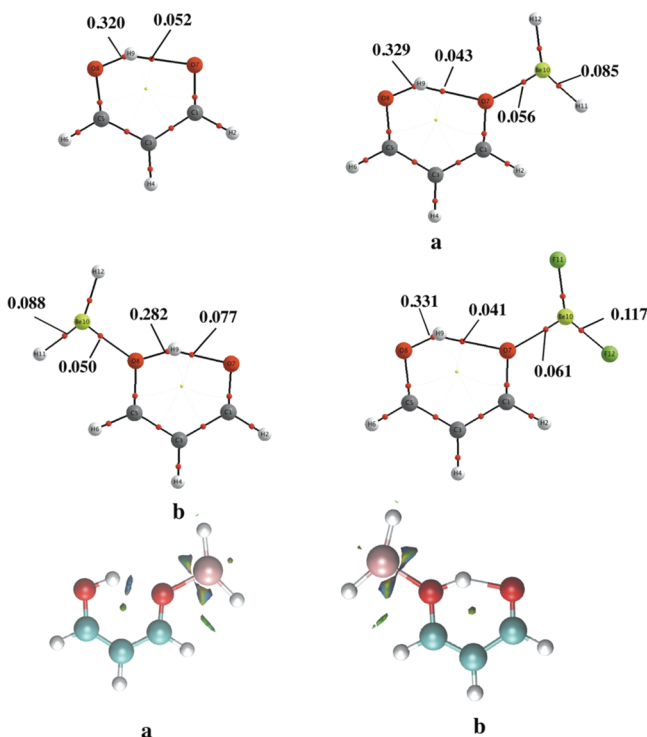

Figure 7. Molecular graphs for malonaldehyde and its complexes with BeH$_2$ and BeF$_2$. The red dots correspond to BCPs. The electron densities are in au. The lower file represents the NCI surfaces for complexes **a** and **b** involving BeH$_2$, for *s* = 0.5.

Very importantly, the effects of the beryllium bonds on the strength of the IMHB are really significant. Although it is not possible to give a reliable energetic measure of this effect, it can be traced by looking at the HB length, the electron densities at the IMHB, and the red-shifting of the OH stretching frequency.

It is apparent from the molecular graphs shown in Figure 7 that the IMHB of malonaldehyde becomes much weaker when BeH$_2$ interacts with the carbonyl oxygen. This basic site donates a significant amount of charge to the BeH$_2$ subunit, through the interaction of the oxygen lone-pairs with the empty p orbitals of Be, measured by a second-order interaction energy of 355 kJ mol^{-1}, and the σ_{BeH}* antibonding orbital, with a second-order interaction energy of 29 kJ mol^{-1}. The obvious consequence is a significant decrease in the HB acceptor capacity of the carbonyl group. Indeed, whereas the second-order interaction energy between the lone-pair of the carbonyl oxygen and the σ_{OH}* antibonding orbital in the isolated malonaldehyde molecule is 129 kJ mol^{-1}, in the aforementioned complex with BeH$_2$, it reduces to 76 kJ mol^{-1}. Consistently, the electron density at the HB BCP decreases 0.009 au, whereas that at the OH BCP increases by the same amount. Accordingly the OH stretching frequency shifts to the blue by 220 cm^{-1}.

The effects are the opposite when the BeH$_2$ molecule interacts with the OH group of the aldehyde. The charge transfer to Be leads necessarily to a large increment of the intrinsic acidity of the OH group and therefore of its HB donor capacity. Hence, the second-order interaction energy between the lone-pairs of the carbonyl and the σ_{OH}* antibonding orbital, which as indicated above was 129 kJ mol^{-1} for the isolated malonaldehyde molecule, becomes in the complex 242 kJ mol^{-1}. Consistently, the electron density at the IMHB BCP increases by 0.034 au, whereas that at the OH BCP decreases by 0.038 au, its stretching frequency being red-shifted by 547 cm^{-1}, and the NCI index classifies the interaction as a bond (see Figure 7).

It should be noted that complex **a** is 24 kJ mol^{-1} more stable than complex **b** in which the IMHB is much stronger. This is a clear indication that similarly to what was found for intermolecular HBs, where there is a prevalence of the beryllium bonds, this prevalence is also observed when dealing with IMHBs.

Interestingly, when the Lewis acid is BeF$_2$ only complex **a** is found to be a stationary point on the PES. Actually, when the BeF$_2$ is attached to the hydroxyl group, a spontaneous proton transfer takes place. In other words, the acidity enhancement of the OH group produced by BeF$_2$, which, as commented already above, is a stronger Lewis acid than BeH$_2$, is so strong that the proton is spontaneously transferred to the carbonyl group, to yield a structure formally identical to the one obtained when BeF$_2$ interacts with the carbonyl group. Also coherently with our previous arguments, the IMHB in this complex is even weaker than in the complex with BeH$_2$, as indicated by a smaller electron density at the IMHB and a larger blue-shifting (257 cm^{-1}) of the OH stretching frequency.

These modulation effects on the strength of inter- and IMHBs by beryllium bonds can be viewed also under the perspective of the positive charge-assisted hydrogen bonding,[85,86] which reflects the close relationship between hydrogen bonding and protonation.[87] It is known for instance, both experimentally[88−90] and theoretically[87,91,92] that upon protonation the HB in both imidazole dimer and malonaldehyde becomes significantly reinforced, the proton sitting near the midpoint of the two heteroatoms. The formation of the beryllium bond implies a similar mechanism in which the charge transfer goes to the Be system rather than to an incoming proton.

■ CONCLUDING REMARKS

Imidazole and its dimer yield very strong beryllium bonds with both BeH$_2$ and BeF$_2$, the latter being as expected stronger than the former. As it has been found before for other beryllium bonds reported in the literature, the formation of this linkage involves a significant geometry distortion of the Lewis acid, which significantly departs from linearity, whereas the Be−X bonds lengthen.

The most important conclusion of this theoretical survey is however the significant mutual interactions between HBs and beryllium bonds when they are present in the same molecular system. Using as a model imidazole dimer and BeX$_2$ (X = H, F), we have found a clear cooperativity between these two noncovalent interactions, with the result that both become reinforced with respect to the systems in which only one of them is present. Hence, the intermolecular HB between the

two imidazole molecules in the dimer becomes much stronger when the dimer interacts with the BeX_2 derivative, whereas the beryllium bond becomes also stronger in the complex imidazole dimer–BeX_2 with respect to that found in the imidazole–BeX_2 complex.

The effects of beryllium bonds are also dramatic on the strength of IMHBs. Depending on to which center the BeX_2 is attached, the IMHB becomes much stronger or much weaker. The first situation is found when the beryllium derivative is attached to the HB donor, whereas the second occurs if it is attached to the HB acceptor. The first effect can be actually so strong as to produce a spontaneous proton transfer as is actually the case of the malonaldehyde–BeF_2 complex.

Beryllium bonds compete and even replace HBs, yielding complexes in which Be behaves as a "tetrahedral proton".[56–58,84]

■ ASSOCIATED CONTENT

ⓢ Supporting Information

Calculated D0 values for the HB in imidazole dimer and for the beryllium bond in imidazole-BeH2 adducts, using different DFT functionals and G4 theory. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
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