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On the existence and characteristics of π-beryllium bonds

Estefanía Fernández Villanueva, Otilia Mó and Manuel Yáñez*

The existence of π-beryllium bonds explains the stability of the complexes between ethylene and acetylene and BeX_2 (X = H, F, and Cl) derivatives. These linkers involve a significant charge transfer from the π_{CC} bonding orbitals into the empty p orbitals of Be and to a much smaller degree into the σ_{BeH}* antibonding orbitals. The significant deformation of the BeX_2 moiety and the slight deformation of the unsaturated hydrocarbon result in distortion energies as high as the dissociation energy of the complex. The π-beryllium bonds are about four times stronger than conventional π-hydrogen bonds and even stronger than the strongest π-hydrogen bond reported to date in the literature. The topology of their electron density is characterized as being very flat in the bonding region between the π-system and Be, which leads to topologically unstable structures close to catastrophe points. Among the functionals considered in our study M06 is the one that leads to values in better agreement with CCSD(T)/aug-cc-pVTZ calculations used as a reference. B3LYP underestimates some interactions, whereas M06-2X overestimates all of them. MP2 also yields good agreement with the CCSD(T) method.

Introduction

Beryllium bonds are recently described linkers in which a Lewis base interacts with a beryllium derivative acting as a strong Lewis acid.[1,2] These non-covalent interactions share many common characteristics with other non-covalent interactions, in particular, with hydrogen bonds,[1] and actually may compete with them.[3,4] One of the signatures of $X_2Be\cdots$Lewis base beryllium bonds is the significant charge transfer from the Lewis base into the empty p orbitals of Be and into the σ_{BeX}* antibonding orbitals of the X_2Be molecule. These charge transfer processes result in a significant distortion of the X_2Be Lewis acid, whose structure significantly deviates from linearity and whose Be–X bond significantly lengthens.[1] But not only the Lewis acid becomes significantly distorted, since significant, sometimes dramatic changes are also induced in the intrinsic properties of the Lewis base interacting with the X_2Be derivative.[5] Actually it has been shown how the interaction of conventional bases, such as aniline, can be changed into a Bronsted acid stronger than phosphoric acid.[6–10] These acidity enhancements are also behind the spontaneous H_2 loss from acids such as squaric acids and their S and Se containing analogues when they interact with beryllium dihydride.[11] The aforementioned charge transfers are also responsible for the significant cooperative and anti-cooperative effects in complexes which are stabilized by the simultaneous presence of beryllium bonds and other non-covalent interactions, such as hydrogen bonds, dihydrogen bonds or halogen bonds.[12–14]

The aim of this paper is to investigate the characteristics of the possible beryllium bonds when the Lewis acid is an unsaturated compound, in order to establish whether we can actually define π-beryllium bonds very much in the same way as we define π-hydrogen bonds,[15–22] and in that case what are their basic characteristics. For this purpose we have chosen, as suitable model systems, ethylene and acetylene interacting with X_2Be (X = H, F, Cl).

Computational details

Since there are no previous studies on the interactions between π-systems and beryllium derivatives, we have considered it necessary to carry out the assessment of different theoretical models based on the use of density functional theory approaches or on *ab initio* molecular orbital methods. Within the first set we have included the B3LYP,[23,24] M06 and M06-2X functionals.[25] The former is used because it was found to describe reasonably well other non-covalent interactions such as inter- and intra-molecular hydrogen bonds[26–28] and also shows a good performance when dealing with conventional beryllium bonds not including π-interactions. The other two can be considered functionals of the new generation and, in particular, the latter has been claimed to be well suited to describe non-covalent interactions.[29] Since correlation effects are critical in all these kinds of interactions, the *ab initio* calculations were carried out by using the

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MP2 method. In all cases the 6-311+G(d,p) basis set was used for the geometry optimizations. In all cases the harmonic vibrational frequencies have been calculated in order to evaluate the zero point energy (ZPE) corrections, and to ensure that the stationary points found actually correspond to local minima on the potential energy surface (PES). In order to check the sensibility of the optimized geometries to the quality of the basis set all the previous geometries were refined by using a more flexible aug-cc-pVTZ basis set expansion. Since there are no experimental information to compare with, in our assessment, we have taken as a reference the results obtained in CCSD(T)/aug-cc-pVTZ calculations carried out on CCSD optimized geometries by using the same basis set. To verify that the values obtained at the CCSD(T)/aug-cc-pVTZ level can be considered converged, for the particular cases of the complexes with BeH$_2$, the dissociation and interaction energies were reevaluated at the CCSD(T)/aug-ccpVQZ level.

The bonding in the complexes under scrutiny was analyzed using four different and complementary procedures, the quantum theory of atoms in molecules (QTAIM),[30,31] the natural bond orbital (NBO) method,[32] the Localized Molecular orbital Energy Decomposition analysis (LMOEDA)[33] and the Natural Orbitals for Chemical Valence (NOCV).[34] In the framework of the QTAIM approach we have calculated the molecular graphs for the different complexes. The molecular graph is defined by the ensemble of critical points of the electron density and the gradient paths of the electron density that originate and terminate at these points. Within the former, maxima correspond to the position of the nuclei and first order saddle points, in which one of the curvatures of the electron density is positive, are usually known as bond critical points (BCPs). The lines of maximum density connecting two maxima and containing one BCP are usually named bond paths.[35] The density and its Laplacian at the BCPs provide useful information on both the nature and the strength of the interaction between two bonded atoms of the systems. The NBO approach describes the bonding in terms of localized natural hybrids centered on the different nuclei of the system, and allows a clear identification of dative bonds and back-donation effects through the calculation of second order perturbation energies[32] involving occupied and empty orbitals of the system investigated.

The LMOEDA approach is an extension of previous decomposition methods,[36–39] in which the total interaction energy is decomposed into four components (see eqn (1)), namely, the electrostatic term, ΔE_{elstat}, that describes the classical Coulomb interaction of the occupied orbitals of one of the interacting units with those of the other, the ΔE_{ex+rep}, which measures the repulsive exchange component resulting from the Pauli exclusion principle, the polarization term, ΔE_{pol}, which is defined as the orbital relaxation energy on going from each subunit to the complex; and the dispersion one, ΔE_{disp}, which is the only one not accounted for at the HF level. The LMOEDA analysis has been carried out, at the CCSD(T)/aug-cc-pVTZ level, by using the GAMESS program (version 2013-R1).[40]

$$\Delta E_{int} = \Delta E_{elstat} + \Delta E_{ex+rep} + \Delta E_{pol} + \Delta E_{disp} \qquad (1)$$

The NOCV approach is based on the use of the eigenvectors of the deformation density matrix,[34] and combined with the Extended Transition State (ETS) approach[37] permits us to obtain the orbital interaction term in terms of the NOCV eigenvalues. In the ETS-NOCV approach, the interaction energy is decomposed as,

$$\Delta E_{int} = \Delta E_{elstat} + \Delta E_{pauli} + \Delta E_{orb} \qquad (2)$$

where the first two terms, ΔE_{elstat} and ΔE_{Pauli}, have similar meanings as in eqn (1), and are usually named steric interaction. The term ΔE_{orb} accounts for the interactions between the occupied molecular orbitals of one subunit with the empty orbitals of the other, and within the same subunit. The ETS-NOCV calculations have been carried out by means of the ADF-2013.01 suite of programs.[41]

Results and discussion

The complexes between ethylene or acetylene and BeX$_2$ (X = H, F, and Cl) may adopt two different C_{2v} conformations depending on the relative orientation of the BeX$_2$ subunit with respect to the unsaturated molecule. In conformation (I), the BeX$_2$ molecule lies in a plane perpendicular to the plane of the unsaturated molecule, which bisects the C–C bond. In the other conformation (II), this plane contains the C=C or the C≡C bond and for the particular case of the ethylene containing complexes it bisects the HCH angles of the ethylene molecule (see Scheme 1).
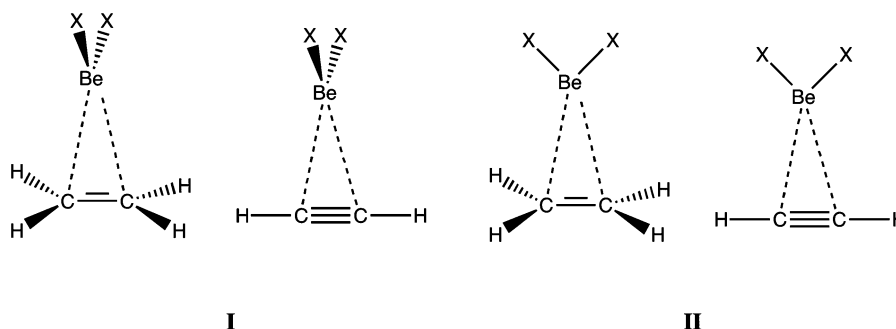
Scheme 1 Possible conformations of the complexes between ethylene and acetylene with BeX$_2$ derivatives.

Geometrical distortions

A detailed analysis of the optimized structures for both kinds of complexes revealed, in agreement with similar findings reported in the literature as mentioned in the introduction, that both the Lewis acid and the Lewis base become distorted, though such distortion is more significant for the Lewis acid. Indeed, in all the complexes the BeX_2 subunit, which for the isolated molecule is perfectly linear, is not linear anymore, with X–Be–X angles between $138°$ and $149°$ at the CCSD level, whereas at the same time the Be–X bonds become longer. For instance, whereas the CCSD bond length of the Be–H bond for the isolated beryllium dihydride is found to be 1.331 Å, in the complexes with ethylene and acetylene, the Be–H bond length becomes 1.348 and 1.352 Å, respectively. Similar bond lengthening is found when the Lewis acid is BeF_2 (*ca.* 0.025 Å) and $BeCl_2$ (*ca.* 0.045 Å). Simultaneously, the unsaturated moiety is also distorted, so that the acetylene molecule within the complex is not linear either, and the ethylene molecule is not strictly planar since the sum of the angles around the two carbon atoms differs, although very slightly, from $360°$. The most significant change, however, in both kinds of complexes is the lengthening of the C=C (*ca.* 0.013 Å) and C≡C (*ca.* 0.005 Å) bonds, respectively.

These geometrical changes are coherent with the orbital interactions involved in the formation of the beryllium bonds. As shown by NBO analysis the largest second order interaction energies involved the π_{CC} bonding orbital and the empty p orbital of the Be atom, as well as the σ_{BeX}^* antibonding orbital of the BeX_2 subunit, although the former are clearly dominant (see Table 1). It should be noted that, as expected, no back-donation is found between the occupied orbitals of the BeX_2 subunit and the empty orbitals of the unsaturated hydrocarbon. This feature will be important, as we will discuss later, when analyzing the energy involved in this interaction.

One important consequence of the deformation undergone by the interacting systems, in particular that of the Lewis acid, is that the dissociation energy of the complex, D_0, obtained as the energy difference between the energy of the complex and the sum of the energies of the two interacting compounds in their equilibrium conformation may significantly underestimate the strength of the interaction, because of the relaxation energy gained when the interacting systems go from the structure they have in the complex to the more stable equilibrium conformation. In such cases a more meaningful measurement of the strength of the interaction is given by the interaction energy, E_{int}, calculated as the difference between the energy of the complex

and the energy of the two interacting systems keeping the structure they have in the complex.

Preferred conformations

No matter the theoretical model used for the geometry optimizations we have found that for acetylene complexes the global minimum of the PES corresponds to conformation I, conformation II being a transition state. Conversely, all the complexes of ethylene, with the only exception of the one formed with BeH_2, adopt conformation II. As far as the geometrical details are concerned, it must be emphasized that the differences between the values of the optimized geometrical parameters are very small not only between the three functionals considered in our survey, but also when these geometries are compared with the *ab initio* ones obtained either at the MP2 or at the CCSD level. Indeed, the averaged deviations for bond lengths are 0.6% and for bond angles 1.8%. It should also be emphasized that the changes found when changing the 6-311+G(d,p) basis set by the aug-cc-pVTZ in the optimization processes for all the methods considered are even smaller than the one found between the different methods when the small basis set is used. More importantly, the effect of these slight geometrical differences on the CCSD(T)/aug-cc-pVTZ final energies is in most cases negligibly small, yielding typically energy differences smaller than 1 kJ mol^{-1} and never larger than 2.5 kJ mol^{-1}. These results allow us to conclude that a 6-311+G(d,p) basis set is flexible enough to describe complexes stabilized by π-beryllium bonds, and that any of the DFT approaches analyzed provide very similar structures to those obtained by the much more costly CCSD approach.

Energetics and bonding

The D_0 dissociation enthalpies of the ethylene$\cdots$$BeX_2$ and acetylene$\cdots$$BeX_2$ complexes into the two interacting subunits obtained using the different theoretical models considered in this study are summarized in Table 2. This table also contains the corresponding interaction enthalpies, ΔH_{int}, as defined above.

The first conspicuous fact is that the interaction enthalpies, ΔH_{int}, are at least twice as large as the dissociation enthalpies, D_0, showing that the deformation energies of the interacting subunits are rather high, although dominated by those of the BeX_2 molecules. Also, the π-beryllium bonds characterized here

Table 1 Second order interaction energies (kJ mol^{-1}) between the occupied and empty orbitals for the complexes between ethylene and acetylene and BeX_2 (X = H, F, and Cl) derivatives

Complex	$\pi_{CC} \rightarrow p(Be)$	$\pi_{CC} \rightarrow \sigma_{BeX}^*$
$C_2H_2\cdots BeH_2$	467	4
$C_2H_2\cdots BeF_2$	222	3
$C_2H_2\cdots BeCl_2$	416	8
$C_2H_4\cdots BeH_2$	345	2
$C_2H_4\cdots BeF_2$	141	5
$C_2H_4\cdots BeCl_2$	222	7

Table 2 Dissociation and interaction enthalpies (values within brackets) for the complexes between ethylene and acetylene and BeX_2 (X = H, F, and Cl) derivatives. All values are in kJ mol^{-1}

Complex	B3LYP	M06	M06-2X	MP2	CCSD	CCSD(T)
$C_2H_2\cdots BeH_2$	33 [78]	36 [77]	47 [88]	28 [51]	19 [42]	31 [62]
					27 [50][a]	31 [62][a]
$C_2H_2\cdots BeF_2$	23 [50]	34 [61]	46 [75]	30 [49]	28 [49]	34 [59]
$C_2H_2\cdots BeCl_2$	11 [58]	27 [72]	35 [84]	33 [79]	14 [53]	28 [68]
$C_2H_4\cdots BeH_2$	19 [59]	23 [58]	33 [71]	20 [46]	9 [33]	21 [50]
					16 [40][a]	20 [49][a]
$C_2H_4\cdots BeF_2$	18 [41]	35 [57]	41 [67]	29 [50]	26 [49]	31 [55]
$C_2H_4\cdots BeCl_2$	9 [43]	26 [58]	34 [70]	34 [63]	19 [52]	30 [61]

[a] Values obtained at the CCSD(T)/aug-cc-pVQZ level of theory.

are even stronger than the strongest π-hydrogen bonds reported to date,[42] but more than four times stronger than most of the conventional π-hydrogen bonds.[18,19,43] However, both the dissociation enthalpy and the interaction enthalpy are about five times smaller than the values calculated, at the same level of theory, for the complexes between ethylene and acetylene with CuF.[44] As we have mentioned above, BeX_2 compounds are very good electron acceptors as reflected in the NBO second order interaction energies between the π_{CC} occupied orbital and the $2p(Be)$ empty orbital, which are actually larger than those between the same occupied orbital and the empty 4s orbital of Cu in CuF.[44] However, the BeX_2 systems are not able to back-donate, as Cu does through the electron pairs in its d orbitals, explaining the smaller strength of the π-beryllium bonds. It is also worth noting that the calculated values do not change significantly with the nature of the substituent X, although the interaction enthalpies are systematically larger when X = Cl than in the other two cases. It should also be emphasized that the trends found for the dissociation enthalpies do not follow those of the interaction enthalpies, showing the importance of the deformation in the energetic description of these complexes. Also, in agreement with what was found for the interactions with CuF,[44] the interaction energies for ethylene are slightly lower than those for acetylene.

The LMOEDA analysis indicates that the largest stabilizing contribution, in all cases, comes from the electrostatic term (see Table 3), which on average accounts for 53% of the total binding energy. This is not surprising if one takes into account that the Be atom bears a rather high positive natural charge (*ca.* +0.7). In agreement with the NBO description discussed above polarization is also a significant contributor to the stabilization of these complexes accounting for 39% of the total binding energy, whereas the dispersion contributions are somewhat marginal, being on average only 7% of the total binding energy.

This description is in harmony with the one obtained by means of the ETS-NOCV approach (see Table 4). It is worth noting that the orbital interaction energy (as it is the polarization energy) is minimum for the BeF_2 complexes, whereas the maximum value is systematically observed for the BeH_2 complexes. These differences can be easily understood by looking at the dominant deformation channels that contribute to the orbital energy. Whereas for the ethylene H_2CCH_2:BeH_2 complex there is strong stabilization (-83 kJ mol^{-1}) arising from the charge transfer between the highest π-occupied orbital of the unsaturated moiety and the lowest unoccupied p_{Be} orbital of the BeH_2 moiety, the same interaction is weaker (-51 kJ mol^{-1}) for the H_2CCH_2:BeF_2 complex.

Table 3 LMO-EDA partition terms (kJ mol^{-1}) for the complexes between ethylene and acetylene and BeX_2 (X = H, F, and Cl) obtained at the CCSD(T)/aug-cc-pVTZ level of theory

Complex	ΔE_{elstat}	ΔE_{ex+rep}	ΔE_{pol}	ΔE_{disp}
HCCH:BeH$_2$	-151	224	-115	-20
HCCH:BeF$_2$	-97	108	-62	-7
HCCH:BeCl$_2$	-124	172	-91	-17
H$_2$CCH$_2$:BeH$_2$	-121	186	-94	-21
H$_2$CCH$_2$:BeF$_2$	-86	105	-62	-11
H$_2$CCH$_2$:BeCl$_2$	106	149	-83	-21

Table 4 ETS-NOCV orbital interaction energies (kJ mol^{-1}) for the complexes between ethylene and acetylene and BeX_2 (X = H, F, and Cl)

Complex	ΔE_{steric}	ΔE_{orb}
HCCH:BeH$_2$	77	-144
HCCH:BeF$_2$	19	-72
HCCH:BeCl$_2$	51	-106
H$_2$CCH$_2$:BeH$_2$	72	-125
H$_2$CCH$_2$:BeF$_2$	23	-69
H$_2$CCH$_2$:BeCl$_2$	46	-95

On top of that for the H_2CCH_2:BeH_2 system there is a back-donation from the BeH occupied orbital of the BeH_2 molecule into the empty π* antibonding orbital of ethylene which further stabilizes the system by -28 kJ mol^{-1}, and which for the H_2CCH_2:BeF_2 system is negligible small. A similar pattern is observed for the corresponding acetylene-containing analogues. It is worth noting however that for the HCCH:BeH_2 complex, besides the two interactions described above for the ethylene analogue, which contribute -87 and -34 kJ mol^{-1} to the stabilization of the system, there is a third deformation channel which involves the charge transfer from the HOMO $-$ 1 π-orbital of the C_2H_2 system into a second empty p_{Be} orbital which further contributes 12 kJ mol^{-1} to stabilize the system and which does not occur for the ethylene-containing analogue, in agreement with the larger value of the orbital interaction energy calculated for HCCH:BeH_2 as compared with H_2CCH_2:BeH_2.

As mentioned before, the interaction energy increases again on going from BeF_2 to the $BeCl_2$ complexes. This is essentially due to the fact that both deformation channels associated with the charge transfer between the highest π-occupied orbitals of the unsaturated moiety and the lowest unoccupied p_{Be} orbitals of the BeH_2 moiety which for BeF_2 account for -51 and -7 kJ mol^{-1}, respectively, and for $BeCl_2$ become -74 kJ mol^{-1} and -12 kJ mol^{-1}, respectively.

The calculated values obtained at the CCSD(T)/aug-cc-pVTZ level of theory can be considered converged, because when the basis set is enlarged to the aug-cc-pVQZ level, the variation in the calculated dissociation and interaction enthalpies for the complexes $C_2H_2\cdots BeH_2$ and $C_2H_4\cdots BeH_2$, is less than 0.3 and 0.6 kJ mol^{-1}, respectively. M06 is the DFT method which provides dissociation and interaction enthalpies closer to the CCSD(T) ones. B3LYP, however, yields too low interaction energies for complexes with BeF_2 and, in particular, with $BeCl_2$. The M06-2X method overbinds all the complexes. In some cases, this overestimation is as large as 16 kJ mol^{-1}. The MP2 values are in very good agreement with the CCSD(T) results, if obtained with the aug-cc-pVTZ basis set. It cannot be discarded that the good performance of M06 and MP2 calculations could be due to error cancellations, since the interaction energies are obtained as differences between total energies affected by the same kind of limitations. There are some differences between CCSD and CCSD(T) indicating the importance of including triple excitations to get a reliable description of the bonding in these complexes. These differences become much smaller when the aug-cc-pVQZ basis set is used, indicating that whereas CCSD(T) can be considered converged at the aug-cc-pVTZ level, this seems not to be the case when triple excitations are not included.
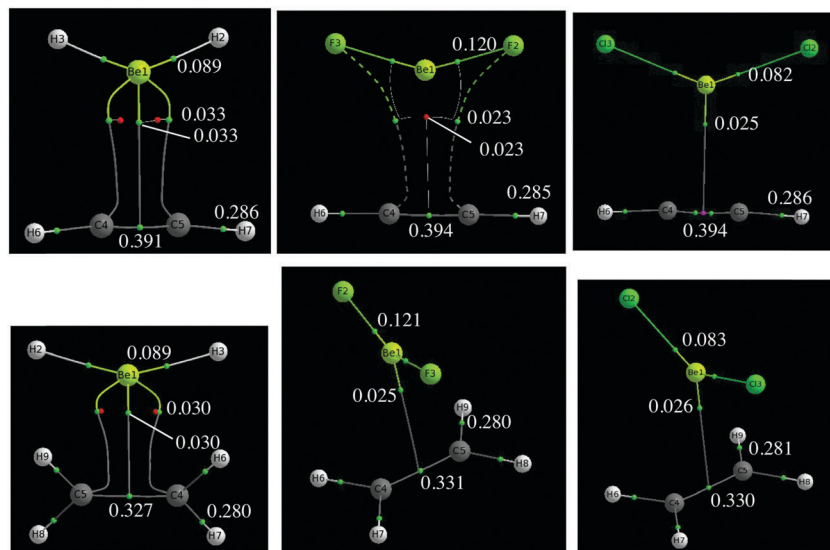
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Fig. 1 Molecular graphs of the complexes between acetylene and ethylene with BeH$_2$, BeF$_2$ and BeCl$_2$. Green and red dots denote bond and ring critical points respectively. Electron densities are in a.u.

The molecular graphs of the C$_2$H$_2\cdots$BeX$_2$ (X = H, F, and Cl) complexes are apparently very different (see Fig. 1). For beryllium dihydride a bond path is found between Be and the two carbon atoms of acetylene and a third one between Be and the C–C BCP, containing the corresponding ring critical point, whereas for BeCl$_2$ only the latter is found. For BeF$_2$ the situation is more complex, because the bond path is found between the two F atoms and the two carbon atoms of the unsaturated system. It should be noticed however, that when the density is obtained by using the B3LYP method instead of the CCSD the molecular graph obtained for the C$_2$H$_2\cdots$BeF$_2$ complex is the same as the one shown in Fig. 1 for the C$_2$H$_2\cdots$BeH$_2$ system. These apparent anomalies indicate that a very flat and small density in the area between the C–C bond and the Be nucleus is formed, which leads to topologically unstable structures close to catastrophe points. This is corroborated by the fact that, for example, for the C$_2$H$_2\cdots$BeH$_2$ complex the electron densities at the three critical points are practically identical, showing that actually the electron density is very flat within the CC$\cdots$Be region so it remains almost constant between the Be atom and the C–C bond. This is actually consistent with the very high values of the ellipticity at these critical points. Similar situations have been reported in the literature for the bonding between transition metals and carbocyclic rings[45] as well as in complexes of Co with alkynes,[46] and metal–metal interactions.[47] Accordingly, the three situations can be considered homomorphic, and the fact that we locate three or only one critical point has no special meaning because the values of the densities are practically undistinguishable, and one may go from one situation to the other by a simple catastrophe. The molecular graph for the C$_2$H$_4\cdots$BeH$_2$ complex is similar to the one obtained for the acetylene analogue, although if the method is changed, for instance, to B3LYP the molecular graph obtained is similar to the one found at the CCSD level for the C$_2$H$_2\cdots$BeCl$_2$ complex. The small values of the densities and the fact that the Laplacian of the density at the BCPs is positive indicate that the interactions are essentially closed shell.

Conclusions

The complexes between ethylene and acetylene and BeX$_2$ (X = H, F, and Cl) derivatives are stabilized by a significant charge transfer from the π_{CC} bonding orbitals of the unsaturated hydrocarbon into the empty p orbitals of Be and to a much smaller degree into the σ_{BeH}* antibonding orbitals. These kinds of charge transfers are the signature of the so-called beryllium bonds, and therefore we can talk of π-beryllium bonds. As in conventional beryllium bonds the formation of these complexes is accompanied by a significant deformation of the BeX$_2$ moiety and a slight deformation of the unsaturated hydrocarbon. As a consequence, the sum of the distortion energies of the two interacting monomers is in many cases as large as the dissociation energy of the complex. Hence, very often the interaction enthalpy is twice as large as the dissociation enthalpy. The π-beryllium bonds are about four times stronger than conventional π-hydrogen bonds and even stronger than the strongest π-hydrogen bond reported to date in the literature. The topology of the electron density of these new linkers is characterized as being very flat in the bonding region between the π-system and Be, which leads to topologically unstable structures close to catastrophe points. Among the functionals considered in our study M06 is the one that leads to values in better agreement with CCSD(T)/aug-cc-pVTZ calculations used as a reference. B3LYP underestimates some interactions, whereas M06-2X overestimates all of them. MP2 also yields good agreement with the CCSD(T) method.

Acknowledgements

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