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Relationship between the Critical Points Found by the Electron Localization Function and Atoms in Molecules Approaches in Adducts with Hydrogen Bonds

Alejandra M. Navarrete-López, Jorge Garza,* and Rubicelia Vargas

Departamento de Química, División de Ciencias Básicas e Ingeniería, Universidad Autónoma Metropolitana-Iztapalapa, San Rafael Atlixco 186, Col. Vicentina, Iztapalapa, C. P. 09340, México D. F., México

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In this work, 11 adducts with hydrogen bonds were studied by using the B3LYP exchange-correlation functional of the Kohn−Sham approach and the Møller−Plesset second-order perturbation theory MP2. With both approaches, the geometry of each adduct was optimized with the aug-cc-pVTZ basis set. The binding energies of the considered systems, found by the MP2 method, range from 1.2 to 8.3 kcal/mol. By using the atoms in molecules (AIM) analysis and the electron localization function (ELF) we found that the critical points positions characteristic of hydrogen bonds obtained by AIM and ELF are very similar each other. Besides, we found a linear correlation between the critical points positions found by AIM and those obtained by ELF with the B3LYP method and also with the MP2 method. The slope of such a linear relationship was close to 1 and the *y*-intercept close to 0.

Introduction

The hydrogen bond (HB) is an important topic in several branches of the sciences, and chemistry is no exception. Experimental and theoretical chemists have been working for many years to elucidate and understand the nature of this kind of interaction from macroscopic and microscopic points of view.[1−5] From the quantum chemistry point of view, chemists have used mainly quantum chemistry codes based on Gaussian functions[6] and have obtained several observations that are in agreement with experimental data.[7−13] Structural information has been determined, mainly in the gas phase, with quantum chemistry codes for HBs; many of them are in good agreement with experimental information.[14−17] For example, for the contact D−H···A, where D and A are the donor and acceptor atoms of the H atom, respectively, it is known that the strong hydrogen bonds present short distances, *d*(H···A). This observation allows to establish a relationship between the *d*(H···A) and the binding energy involved in the HB; such a relationship has been obtained from theoretical methods for many systems in the gas phase.[18−21] Also some spectroscopy properties computed with quantum chemistry codes have been correlated with the strength of the HB.[5,22−24]

Additionally to the energetic and structural information obtained by the quantum chemistry methods for the HBs, there are other quantities that are useful to understand the HBs' behavior. For example, some scalar fields properties have been studied as a function of the HB strength and they have served to establish the possible HB presence in many systems. The electronic density is the scalar field used by the atoms in molecules (AIM) theory,[25−27] developed by Bader and coworkers. With the AIM approach, one can determine if there is or not a bond involved in a system by using criteria based on the electron density, which is a scalar field obtained by several quantum chemistry methods or by experimental techniques. Additionally to the electron density, the AIM approach uses first and second derivatives of it to indicate if a chemical bond is present to divide a system in atomic regions.[25,28−30] For the HBs, some criteria have been established to characterize these contacts. By inspecting several HBs, Popelier and Koch[31] found some values where the electron density falls when it is evaluated at a point where its gradient is zero (critical point). Almost in each work where the AIM is used to identify critical points in HBs, the Popelier and Koch criteria have been used;[32−34] evidently, this is an important theoretical tool to study HBs, because in many cases one may determine if such a contact is present or not.

The electron localization function (ELF)[35,36] is another scalar field that has been used in the last years to characterize HBs.[19,37−46] The framework of this methodology is totally different than that used in the AIM approach, since it is based in the first-order density matrix and is defined such that its values range between 0 and 1. As with the AIM approach to study the chemical bond, the critical points in the ELF are useful, but zeros at the gradient of the ELF does not necessarily imply bonds, since core and valence are separate by these points.[47] The usefulness of this function has been probed in many systems to localize electron pairs,[48] delocalized electrons,[49] shell structure in atoms,[35,50] and other applications.[51−54] The HBs are not the exception, but there are fewer reported works on this topic,[19,37−46] compared with the AIM approach. One can see that AIM and ELF complement each other and then perform both studies in a particular system to see if there is or not a HB or to characterize it.

In this work, we show that AIM and ELF give similar answers in the critical points found in 11 systems linked by HBs; these systems exhibit binding energies in a range of 1.2−8.3 kcal/mol, and in this way we have a representative set of strengths of the HB.

Methodology

The systems considered in this work are depicted in the Figure 1; they are $FH\cdots OH_2$ (**1a**), $HCONH_2\cdots OCHNH_2$ (**1b**),

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* Corresponding author. E-mail:jgo@xanum.uam.mx.

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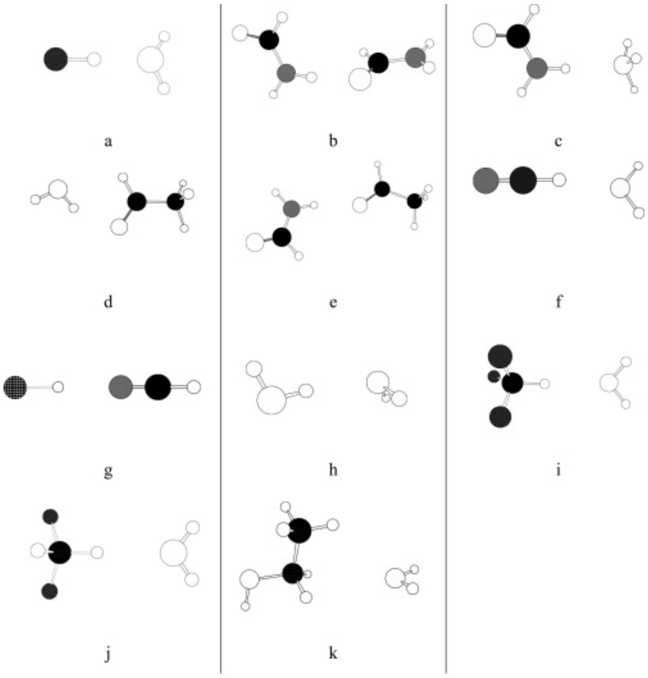

Figure 1. Geometries of the 11 conformers linked by hydrogen bonds and optimized with the MP2/aug-cc-pVTZ method: black circles, carbon; big white circles, oxygen; gray circles, nitrogen; small white circles, hydrogen; striped circle, fluorine; checked circle, chlorine.

TABLE 1: Binding Energies Obtained with the aug-cc-pVTZ Basis Set, with and without BSSE[a]

	B3LYP		MP2		
system	with BSSE	without BSSE	with BSSE	without BSSE	error[b]
$FH\cdots OH_2$	−8.8	−8.8	−8.9	−8.3	0.5 (6.0)
$HCONH_2\cdots OCHNH_2$	−6.0	−5.9	−7.4	−6.6	0.7 (10.6)
$HCONH_2\cdots NH_3$	−5.8	−5.7	−6.9	−6.3	0.6 (9.5)
$OH_2\cdots OCHCH_3$	−4.9	−4.9	−6.1	−5.7	0.8 (14.0)
$HCONH_2\cdots OCHCH_3$	−4.6	−4.5	−5.7	−5.1	0.6 (11.8)
$NCH\cdots OH_2$	−4.8	−4.7	−5.4	−4.9	0.2 (4.1)
$ClH\cdots NCH$	−4.1	−4.0	−5.4	−4.9	0.9 (18.4)
$OH_2\cdots OH_2$	−4.6	−4.5	−5.2	−4.7	0.2 (4.3)
$F_3CH\cdots OH_2$	−3.0	−2.9	−3.7	−3.3	0.4 (12.1)
$F_2CH_2\cdots OH_2$	−2.1	−2.0	−2.7	−2.4	0.4 (16.7)
$HOCH_2CH_3\cdots OH_2$	−1.5	−1.4	−1.5	−1.2	0.2 (16.7)

[a] All quantities are in kcal/mol. [b] ERROR is the absolute error between B3LYP and MP2 results without the BSSE. The percent relative error is reported in parenthesis.

$HCONH_2\cdots NH_3$ (**1c**), $OH_2\cdots OCHCH_3$ (**1d**), $HCONH_2\cdots OCHCH_3$ (**1e**), $NCH\cdots OH_2$ (**1f**), $ClH\cdots NCH$ (**1g**), $OH_2\cdots OH_2$ (**1h**), $F_3CH\cdots OH_2$ (**1i**), $F_2CH_2\cdots OH_2$ (**1j**), and $HOCH_2CH_3\cdots OH_2$ (**1k**). All of them were fully optimized, without symmetry restrictions, with the B3LYP[55−57] exchange-correlation functional of the Kohn−Sham model and with the Moller−Plesset second-order perturbation theory (MP2).[58,59] Both methods used the aug-cc-pVTZ basis set.[60] The starting points were geometries obtained with the 6-311++G** basis set;[61] this basis set also was used for a frequencies analysis coupled with the B3LYP method. The frequencies analysis shown that all conformations considered in this work are at a minimum of the potential energy surface (PES), except for the **1b** adduct. Even when this conformation of the **1b** adduct is not at a minimum of the PES, it will be considered and discussed later. In this work, we considered just the largest basis set (aug-cc-pVTZ), and with this basis set we corrected the interaction energies with the basis superposition error (BSSE) correction as proposed by Boys and Bernardi.[62] Geometry optimization, frequencies analysis, and binding energies were obtained with the NWChem v5.0 code.[63]

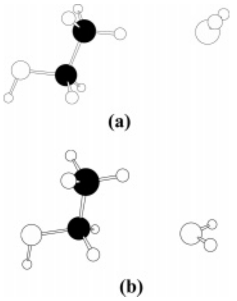

Figure 2. Geometries for the ethanol−water adduct optimized with the (a) B3LYP and (b) MP2 methods. In both cases, the aug-cc-pVTZ basis set was used.

The topological analysis was done with the ToPMoD code.[64] The input electron densities were obtained with the Gaussian 98 code,[65] for B3LYP and MP2 methods. For convenience, we translated and rotated each adduct such that the hydrogen participating in the HB was at the origin, the acceptor atom along the z-axis, and the donor atom in the $x-z$ plane.

Results and Discussion

A. Binding Energies. The binding energies, determined for the systems of this study by using the aug-cc-pVTZ basis set, are reported in the Table 1. The ordering of these systems is according to the binding energies predicted by the MP2 method. In this way, the strongest contact is present in the $F-H\cdots O$ adduct and the weakest in the $C-H\cdots O$. As it has been reported previously, the BSSE has a bigger impact in the MP2 method than in the B3LYP method.[66] Clearly the BSSE does not affect the ordering of binding energies for both methods. However, the B3LYP method predicts different ordering for the binding energies, principally for weak HBs; thus, whereas this method predicts that the water−water system has a stronger interaction than the $ClH\cdots NCH$ system, the MP2 predicts a contrary behavior. The same observation is found for the systems $HCONH_2\cdots OCHCH_3$ and $NCH\cdots OH_2$.

Considering just the binding energies corrected by the BSSE, we can see that the difference between B3LYP and MP2 does not exceed 1 kcal/mol; however, if we compute the percent relative error, we can obtain a difference that represent more than 10%. This difference can be important in systems containing several similar contacts. Particularly for the $HOCH_2CH_3\cdots OH_2$, the binding energy predicted by both methods differs by just 0.2 kcal/mol, but it represents an error of 16.7%.

B. Geometrical Parameters. The distances $H\cdots A$ [$d(H\cdots A)$] and $D-A$ [$d(D-A)$] and the angle $D-H\cdots A$ [$\alpha(D-H\cdots A)$] are reported in the Table 2. From this table we can see that the shortest $d(H\cdots A)$ is presented for the adduct with the strongest HB and the largest $d(H\cdots A)$ corresponds to the weakest one. It is worth to note that there are small differences in the distances $d(H\cdots A)$ predicted by B3LYP and MP2 methods, since the biggest difference is of 0.12 Å (for the **1i** adduct). Even for this similar prediction with both methods, the MP2 method predicts the shortest distances. Bigger differences are found for the distance $d(D-A)$, in particular, for the **1k** adduct corresponding to a $C-H\cdots O$ contact; in this adduct we found a difference between the methods that represents 9.4%, by using the MP2 value as a reference. The geometry predicted for the **1k** adduct is very different when the $\alpha(D-H\cdots A)$ angle is compared. We see a difference of 49.6°; whereas the B3LYP method predicts an almost a linear contact, the MP2 method

TABLE 2: Geometrical Parameters Related with the Contact D−H···A

method	**1a**	**1b**	**1c**	**1d**	**1e**	**1f**	**1g**	**1h**	**1i**	**1j**	**1k**
					d(H···A), Å						
B3LYP	1.70	1.98	2.10	1.94	2.05	2.06	2.01	1.95	2.24	2.38	2.77
MP2	1.70	1.93	2.06	1.93	2.01	2.05	2.00	1.95	2.12	2.33	2.77
					d(D−A), Å						
B3LYP	2.64	2.99	3.11	2.87	3.06	3.13	3.31	2.92	3.33	3.47	3.85
MP2	2.64	2.92	3.07	2.83	3.01	3.12	3.29	2.91	3.29	3.42	3.52
					α(D−H···A), deg						
B3LYP	176.9	177.2	178.4	159.7	175.4	179.3	179.6	172.1	176.2	179.2	175.8
MP2	176.9	164.3	176.2	153.1	170.2	179.2	179.6	171.7	175.1	179.6	126.2

TABLE 3: AIM Analysis for the Eleven Adducts Considered in This Work

	d(H···bcp), Å		ρ(bcp), au		$L = -\nabla^2\rho$(bcp), au	
adduct	B3LYP	MP2	B3LYP	MP2	B3LYP	MP2
1a	0.54	0.54	0.045	0.043	−0.097	−0.103
1b	0.71	0.68	0.023	0.027	−0.079	−0.088
1c	0.73	0.71	0.023	0.025	−0.060	−0.065
1d	0.76	0.73	0.019	0.020	−0.071	−0.078
1e	0.68	0.67	0.026	0.027	−0.082	−0.087
1f	0.76	0.75	0.019	0.019	−0.072	−0.075
1g	0.71	0.70	0.025	0.025	−0.070	−0.071
1h	0.69	0.68	0.025	0.025	−0.079	−0.082
1i	0.87	0.86	0.013	0.014	−0.051	−0.056
1j	0.94	0.92	0.010	0.011	−0.038	−0.043
1k	1.14	1.18	0.005	0.005	−0.016	−0.019

predicts an adduct with almost a stacked conformation. In Figure 2, we present the **1k** adduct geometry obtained with both methods. From this figure one may suspect that there are additional contacts, when the MP2 method is used, although the possible C−H···O contacts exhibit very long H···O distances (3.01 Å). It may be a consequence of the fact that the dispersion forces are more pronounced in the MP2 method and for that reason such a conformation is predicted by this method.[67] It is interesting to note that even when the MP2 method predicts more contacts in this adduct its binding energy is less than that predicted by the B3LYP method.

The **1b** adduct is another system where the α(D−H···A) angle shows an important difference. We must remember that such an adduct is not at a minimum of the PES. There are several works where this adduct is reported.[68−71] In ref 70, the authors considered the five most stable conformers of the formamide dimer, and they found that the **1b** adduct is a minimum. However, in this work, we found that at least with the B3LYP/6-311++G** method this conformation exhibits some imaginary frequencies. This result with another published previously suggests that the formamide dimer does not form adducts with just one HB.[72]

For the systems considered in this work, we can conclude that even when the B3LYP method predicts almost linear HBs, the MP2 method could give a different prediction, particularly when there is a very weak HB.

C. Topological Analysis. Additionally to the energetic and geometrical analysis, we performed a topological study in order to confirm the presence of the HBs and to characterize them. By using the AIM analysis, in the Table 3 we are reporting the distance of the bonding critical point (bcp) found between the hydrogen atom and the corresponding acceptor. In our case, we are reporting the distance between the bcp and the H atom, d(H···bcp). In the same table, we are also including the electron density and the Laplacian evaluated at the bcp. Clearly, the methods considered in this work give similar bcp positions, with the shortest d(H···bcp) for the FH···OH_2 adduct and the longest for the $HOCH_2CH_3$···OH_2. Such an observation has motivated works where the bcp position is correlated with the strength of the HB.[18−20] Also the electron density evaluated on the bcp, ρ(bcp), as a fuction of the d(H···bcp) has been shown in other theoretical and experimental studies.[73] We have validated our methodology by plotting the ln(ρ(bcp)) vs d(H···bcp), and such a plot is depicted in Figure 3. Clearly our methodology coincides with the expected behavior, since big ρ(bcp) values correspond to small d(H···bcp) values, or a big ρ(bcp) corresponds to a big interaction energy.

It is worth noting, from the Table 3, that the value of the electron density at the bcp is very similar between both methods; in fact, for the adduct that is not at a minimum, **1b**, we found the biggest difference (14.8%). We must remember that this quantity evaluated on bcps, corresponding to HBs, shows small values. It is important to note that, even when B3LYP and MP2 predict different binding energies for the **1f**, **1g**, **1h**, and **1k** adducts, these methods give the same electronic density evaluated on the bcp. We may conclude from these results that the B3LYP electron density, in our systems linked by HB, is similar to that obtained by the MP2 method. However, there are appreciable differences when second derivatives of the electron density are considered between both methods, as can be seen in Table 3.

According our results, independently of the used method, the Popelier and Koch criteria are satisfied to establish the presence of a HB. We want to do additional comments related with the **1b** and **1k** adducts. Even when the **1b** adduct is not at a minimum on the PES, we found a bcp; this observation is in accord with the work of Pacios,[74] where HBs are studied along several paths. Although such paths do not correspond to minima of PES, this author found bcps. For the **1k** adduct, we performed the AIM analysis with the MP2 and B3LYP electron densities, and we found for the MP2 geometry three bcps corresponding to a C−H···O contact with the methyl group and two C−H···O contacts corresponding to the CH_2 group. For

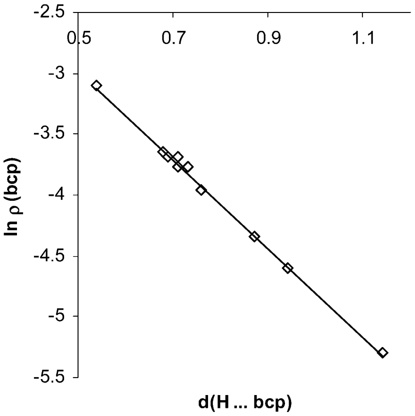

Figure 3. Relationship between ρ(bcp) and d(H···bcp). For B3LYP, ln(ρ(bcp)) = −3.6674d(H···bcp) − 1.1421 with R^2 = 0.9970 and for MP2, ln(ρ(bcp)) = −3.3774d(H···bcp) − 1.3593 with R^2 = 0.9918.

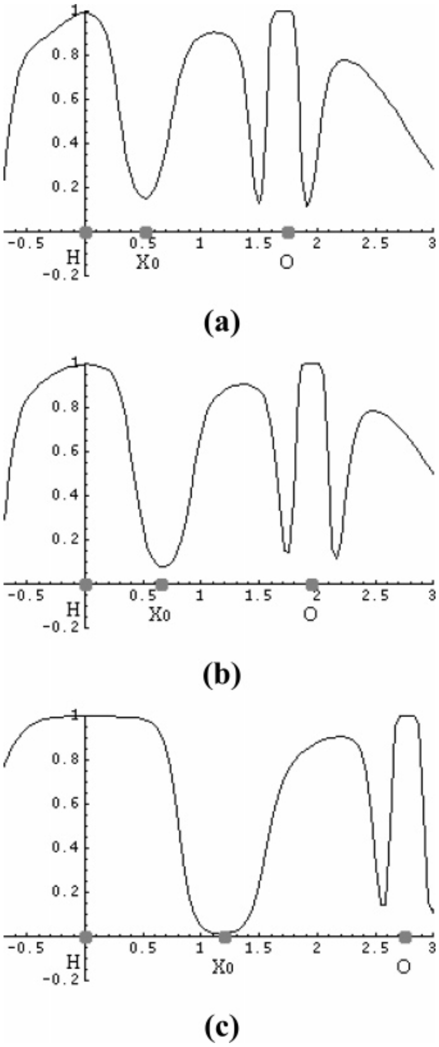

Figure 4. ELF along the H⋯O contact line for the adducts: (a) $FH\cdots OH_2$, (b) $OH_2\cdots OH_2$, and (c) $OHCH_2CH_3\cdots OH_2$. X_0 represents the position of the minimum of the ELF.

these last two critical points, the distance between the bcp and the participating H atom is 1.54 Å and the electron density at each bcp is 0.004 au. For the B3LYP method, we found just one C−H⋯O contact corresponding to the methyl group. This result confirms that, whereas the B3LYP predicts an adduct with one HB, the MP2 method predicts an adduct with three HBs. However, the additional contact predicted by the MP2 method does not contribute to the binding energy, since it is less stable than that predicted by the B3LYP method.

The previous topological analysis is almost standard in works related with HBs where many people search the presence of HBs. Less common are those works where the ELF analysis is carried out in systems presenting such interactions. The ELF behavior along the HB contact for three systems, where the D−H⋯O contact is present, is depicted in the Figure 4. In this figure, the solid points in the extremes of each plot represent the positions of the hydrogen and oxygen atoms. As it has been discussed elsewhere, the ELF can give the core zones in an atom according to the basins found in it.[35,47] We can see in this figure the core region of the oxygen atom. Furthermore, between H⋯O and out of the core region there is clearly a point, X_0, where this function exhibits a minimum, ELF(X_0); precisely this point can be associated with the presence of a HB.[37,38,74] Evidently, the Figure 4 suggests a dependence of X_0, and ELF(X_0), with the strength of the HB, since for a strong HB the ELF(X_0) exhibits a big value (and a small X_0), and contrary to this behavior, the ELF(X_0) shows a small value (large X_0) in a weak HB.

TABLE 4: Critical Point, X_0, Found between the Hydrogen and Its Respective Acceptor Atoms

	X_0, Å		ELF,[a] au	
adduct	B3LYP	MP2	B3LYP	MP2
1a	0.52	0.52	0.182	0.152
1b	0.72	0.68	0.074	0.089
1c	0.71	0.69	0.109	0.104
1d	0.76	0.74	0.054	0.054
1e	0.68	0.67	0.094	0.088
1f	0.76	0.75	0.056	0.051
1g	0.70	0.69	0.106	0.095
1h	0.69	0.68	0.086	0.077
1i	0.87	0.86	0.039	0.036
1j	0.95	0.92	0.032	0.032
1k	1.14	1.17	0.015	0.014

[a] The ELF function is evaluated at X_0.

In the Table 4, we report the distance between the critical point X_0 found for the ELF and the H atom. It is important to mention that the X_0 reported in the Table 4 is the distance between the participating H atom and the critical point in the ELF. These points do not necessarily correspond with those plotted in Figure 4, since many bcps corresponding to HBs do not lie on the H⋯A line. We can see that the X_0 values predicted by B3LYP and MP2 are very similar each other, but the most important observation we want to remark on is the similar behavior shown by X_0 and the d(H⋯bcp). For this reason, we correlate both quantities, X_0 and d(H⋯bcp), and we found a linear relationship with both methods; such relationships are depicted in Figure 5. It is impressive how the linear fitting gives a slope close to 1 and a y-intercept close to 0 for both methods. These fitting parameters show that the critical points position with AIM and ELF in a HB is very similar.

In a previous work, Berski and Latajka[40] presented profiles of the electron density and ELF in $(X\cdots Y\cdots X)^-$ complexes, with X = F, Cl, Br and Y = H, Li. In that study, the authors do not correlate the minima of both scalar fields, since they use only the ELF, but we can see that even in the systems studied by these authors the linear correlation between both distances could be obtained.

This linear relationship is interesting, since the framework of each method is different. By using the definition of the ELF, we obtained its gradient, and the resulting expression was evaluated at a point where $\nabla\rho = 0$; by using this procedure we could not find the reason why $\nabla ELF = 0$. However, we can rationalize this relationship in terms of the kinetic energy density (KED). It is known that the KED exhibit minima close to the bcps obtained with the AIM approach, and also it is known that the ELF has a dependence on the KED; in fact, this function is build in terms of the KED. Thus, the empirical relationship obtained for AIM and KED is mapped to the ELF.[18,75]

We must mention that the linear relationship reported in this work cannot be applied to bonds where the hydrogen is bound with a covalent bond, since for such a case $\nabla ELF \neq 0$ when $\nabla\rho = 0$. This asseveration can be confirmed in works where hydrogen bonds have been studied. For example, in ref 38 the F−H⋯N−N system has been studied with the ELF. In that work a minimum along the contact line of H⋯N is observed, while in the same plot, we can see that there is no minimum in the bond F−H. According to AIM, we should find a minimum in the electron density. Thus, whereas the electron density exhibits a minimum, the ELF does not.

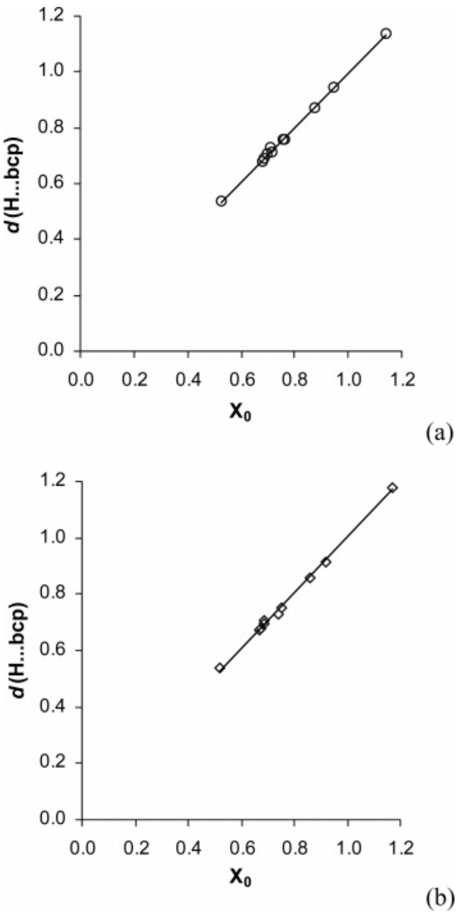

Figure 5. Relationship between the critical points of the electron density and the ELF in the hydrogen bonds. (a) For B3LYP, $d(\mathrm{H}\cdots\mathrm{bcp}) = 0.9935X_0 + 0.0111$ with $R^2 = 0.9976$. (b) For MP2, $d(\mathrm{H}\cdots\mathrm{bcp}) = 0.9803X_0 + 0.0187$ with $R^2 = 0.9975$.

Finally, in the **1k** adduct we found two minima in the ELF, with the MP2 method, corresponding to the oxygen of the water and the two hydrogen atoms of the CH_2 group of the alcohol, confirming the C−H···O interactions in this system. For this case, ELF = 0.007, with a distance from X_0 to H of 1.565 Å. Evidently this conformation deserves more attention, since although there are three interactions the conformation is not more stable than when there is just one, suggesting anticooperative interactions.[2b] A deeper study of this kind of interaction is out of the scope of this report, but we are working on it in our laboratory.

Conclusions

Eleven adducts linked by HBs were characterized by AIM and ELF models. Geometrical structures, binding energies, and electron densities were obtained with the B3LYP and MP2 methods. We found that, even when these adducts show different binding energies, the B3LYP method gives similar geometrical information for the adducts, except for one conformer, where the binding energy competes with the accuracy of the methods considered here. In this case, the B3LYP method predicts an adduct with one HB, and the MP2 method predicts an adduct stabilized with three HBs. Even with this difference, we found that the position of the critical points found by ELF is very similar to that obtained by the analysis of AIM independent of the level of theory used, B3LYP or MP2. This fact is interesting, because both methods have a different nature. Currently, we are looking for such a relationship in bonds with different strength than hydrogen bonds.

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