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REVIEW

The topology of $\pi \cdots H$ hydrogen bonds

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Abstract Unsaturated hydrocarbons are routinely used as proton acceptors because their π clouds possess a capacity to interact with Lewis acids and cationic species. Thus, in order to understand the formation of π hydrogen-bonded complexes, which in many cases are considered as weakly bound systems, the topological quantification of the charge density ruled by quantum mechanic theorems is very useful. Although elaborated by Richard Bader 40 years ago, the Quantum Theory of Atoms in Molecules (QTAIM) has only recently become widely known, and it has been applied in several scientific fields, allowing great insights in chemical bonding studies of intermolecular systems, in particular those formed by $\pi \cdots H$ hydrogen bonds.

Keywords QTAIM · Unsaturated hydrocarbons · Hydrogen bonds

Introduction

The hydrogen bond: a worldwide chemistry topic

Developing a real comprehension of the nature of the hydrogen bond is seen as one of the most coveted research topics in physical and organic chemistry, quantum mechanics, materials science, biology, and other related areas. In the book entitled “Hydrogen Bond in Biological Structures” [1], Jeffrey and Saenger stated that “The discovery of the hydrogen bond could have won someone the Nobel prize, but it didn’t.” In a quantum study published very recently, Michaelides and co-authors affirmed that “hydrogen bonds are essential to life on earth” [2]. In a short comment, Arunan [3] expressed the importance of the hydrogen bond as a “fascination forever.” Surely, these acclamations are motivated by the hydrogen bond’s grandiosity, whose importance reaches many branches of science, thus providing a topic of great interest for research in chemical and biochemical processes [4–6], or even in macromolecule investigations [7], such as for pharmacologic drugs [8], for instance.

Hydrogen bonds exhibit a broad range of phenomena, which are intensely studied in virtually all states of matter by a large number of experimental and theoretical methods [9–11]. Since the first investigations of Lewis [12], Pauling [13], and Huggins [14], after all these years the hydrogen bond’s brightness has led us to consider it as a chapter apart in chemistry [15–32]. Therefore, the preeminence of the theme “the hydrogen bond” [33] is discussed every 2 years at the international conference “Horizons in Hydrogen Bond Researches” [34], an event that brings together experts in phenomena derived from hydrogen bond formation in a wide range of systems [35, 36].

Regarding the historical background, the classical nature of the hydrogen bond based in van der Waals interactions was published by Pimentel and McClellan [37] in a book entitled “The Hydrogen Bond.” Moreover, albeit elaborated many times in the past, a modern concept of the hydrogen bond was developed by Pauling [38] in his remarkable book “The Nature of the Chemical Bond,” in which he said that a hydrogen bond can be formed as follows:

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$$B\cdots H-A \qquad (1)$$

where A has fairly high electronegativity in comparison with the hydrogen atom, whereas B is a region with elevated charge density, which can be essentially lone-electron pairs or π electrons [39]. If B is designed as lone-electron pairs, more generally from oxygen, nitrogen, and sulfur, the hydrogen bonds O···H [40], N···H [41], and S···H [42] are modeled as strongest because their energetic strength varies between 5 and 45 kJ mol^{-1} [43, 44].

The modern hydrogen bond

Nevertheless, the fascination of scientists with hydrogen bonds as a central point in chemistry is recognized by the International Union of Pure and Applied Chemistry (IUPAC) [45]. Nowadays, the IUPAC assumes that the electrostatic effect rules the formation of hydrogen bonds, which is totally in accordance with Pauling's theory [38]. Recently, a selected group of scientists, including Alkorta [46], Hobza [47], Arunan [48], Dannenberg [49], Desiraju [50], Legon [51], Clary [52], and others, reunited in Pisa, Italy, in 2005, and later in Bangalore, India, in 2006, with the purpose of elaborating a re-organization and/or modernization statement related to "hydrogen bond conception" [53]. After several critiques and discussions, besides the electronegative parameter highlighted above, it was concluded that A should be bound to an atom or a group of atoms (Y) in same molecule or in another one in which there is evidence of hydrogen bond formation, but in the sense of an uncertain interaction named by Desiraju [54] as "A Bond by Any Other Name." Anyway, the hydrogen bond is well featured as an interaction of four bound elements: Y, B, H, and A.

$$Y-B\cdots H-A \qquad (2)$$

Of course by depending of the proton acceptor B, often the hydrogen bond strength can be energetically dispersed [55]. Ideally, if π electrons are acting as proton acceptors, the veracity of the stacking $\pi\cdots\pi$ [56] in sandwich systems and hydrogen bonds $\pi\cdots$H [57] is demonstrated from experimental and theoretical perspectives with medium and/or weak energetic strengths in the range of 3–18 kJ mol^{-1} [58, 59]. However, nowadays many hydrogen bonds can be found in several system types, but the nature of the proton acceptor is condensed in n-electron pairs [60] and π centers [61], albeit the capacity of the π bonds as proton acceptors is well known [62].

Recently, Pejov, Solimannejad, and Stefov [63] reported a theoretical analysis regarding the quadrupole moment of acetylene (see Fig. 1). This investigation served as the basis to interpret the orientation of the isolated species in the potential energy surface when they bind each other upon the formation of the intermolecular complex. Regarding the $\pi\cdots$H hydrogen bonds [64, 65], many studies are still being developed to elucidate whether individual atoms or π-electrons should be considered as proton acceptors [66], albeit neutron diffraction analysis shows that the $\pi\cdots$H hydrogen bonds are aligned directly in the midpoint of the π bond [67]. This feature also has been proven theoretically by means of ab initio [68] and density functional calculations [69]. According to this insight, the complexes derived from benzene are often routinely examined in cases where water, ammonia, or haloacids are the proton donors [70]. In classical comparisons of hydrogen complexes [71], the capacity of benzene and ethylene to function as proton acceptors is well recognized, and in some cases quite similar to acetylene [72].

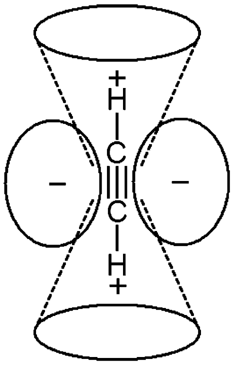

Fig. 1 Illustration of the quadrupole moment of acetylene

Unsaturated systems stabilized by hydrogen bonds

In organic chemistry, it is becoming increasingly established that examinations for reaction intermediaries are carefully done if the formation of hydrogen bonds is taken into account, such as, for instance, electrophilic addition to π bonds rather than the conventional lone-electron pairs [73]. In this sense and in conformity with Pejov et al. [63], Wojtulewski and Grabowski [74], and Ren et al. [75], it is admitted that π bonds are proton acceptors, whereas monoprotic acids ideally are the donors upon the formation of the bimolecular hydrogen-bonded complex $C_2H_2\cdots HF$ [76], whose structure is characterized by a T-shape geometry discriminated by a C_{2v} point group symmetry with the hydrogen bond $\pi\cdots$H linked exactly in the midpoint of the π bond of the acetylene, either as mentioned above [58, 59] or according to the works of Pople et al. [77, 78] as well as Sapse et al. [79]. Furthermore, according to studies reported by van der Veken et al. [80, 81], which discuss that unsaturated hydrocarbons such as ethylene are able to act as proton acceptors, their trimolecular π hydrogen complexes grant extra stability because of the presence of the second halide molecule. In other words, a catalytic reaction provoked by acid excess is conceived [82, 83]. The verification of this statement was endorsed by Jursic [84], who showed in a concerted mechanism study of ethylene and haloacids that a double acid attack is energetically more favorable by 38 kJ mol^{-1}.

Beyond the neutral hydrogen bonds

In terms of the isolated species, it is well known that their molecular properties are drastically affected by the formation of the hydrogen complexes [85]. Among the most important properties, of course, are the bond length enhancement of the proton donor and the change in the infrared spectrum, with frequency shifting either to the red [86] or blue [87] region, accompanied by the hydrogen bond strength, which compose the set of parameters routinely analyzed in studies of intermolecular systems [88]. In comparison, naturally the $\pi\cdots$H hydrogen bond is weaker than those formed by n lone-electron pairs as proton acceptor, n$\cdots$H with n = oxygen, and nitrogen, and sulfur [89], and thus it becomes established that π complexes are slightly bound, which leads us to use robust theoretical approaches in the investigations of these π complexes that are formed basically by unsaturated hydrocarbons, e.g., acetylene and ethylene [90], and pseudo-π proton donor cyclopropane [91]. By using high level calculations, the π nature of acetylene was examined by Grabowski [92], albeit in an overview; the $\pi\cdots$H hydrogen bond has gained several designations, such as "uncommon" [93], "unusual" [94], "improper" [95], "non-conventional" [96], or "unconventional" [97].

Besides the n lone-electron pairs of halogens and chalcogens or π bonds as proton acceptors [98], the different faces of the hydrogen bonds also have ramifications on its structure [99], such as, for instance, the multicenter hydrogen bonds that occur in carbocations, carbanions, and metallic clusters [100]. By acting as a Lewis basis, the π center of the acetylene was able to interact with cationic species, such as those derived from lithium, sodium, and hydrogen, and due to this formed the hydrogen bonds $\pi\cdots H^+$ and $\pi\cdots$H in the complexes $C_2H_2\cdots Li^+$ and $C_2H_2\cdots Na^+$ and $C_2H_2\cdots H^+$, or, moreover, the formation of three centers and two electrons in the following system: $C_2H_2\cdots H^+\cdots C_2H_2$ [101]. Multicenter hydrogen bonds are observed in systems formed by three center and two electrons (3c-2e), such as $C_2H_3{}^+$ and $C_2H_5{}^+$ [102], by which originate the complexes $C_2H_2\cdots H^+\cdots C_2H_2$ and $C_2H_4\cdots H^+\cdots C_2H_2$. Note that $\pi\cdots H^+$ hydrogen bonds govern the structure of these systems, and certainly for each of these complexes there are two $\pi\cdots H^+$ interactions. One of them is covalent, and the other has hydrogen bond characteristics [103]. For both of them, the $\pi\cdots H^+$ interactions were classified as unique, wherein the π electrons act either as donor or receptor of protons, whose applicability can be useful in biological research, such as in evaluation of protein structures, for instance [104].

A theoretical view of the hydrogen bonds

Throughout modern physical chemistry, hydrogen bond detection has been taken into account importantly as one of the crucial procedures in the research of intermolecular systems [105]. In the midst of many works [106, 107], the theoretical studies of Humbel [108] and Sandler [109] are examples of hydrogen bond examinations related to the application of classical methods, such as valence bond analysis and molecular orbit theory. Nevertheless, it is by means of the chemical concept of "bonded and non-bonded" that bound centers and interactive systems should be classified [110]. In this context, some time ago Gruschus and Kuki [111] presented evidence on whether σ, π, and n lone-electron pairs are capable of forming interactions between pairs of ethane and formaldehyde molecules. Historically, the first theoretical hydrogen bond studies were developed in 1954 by Coulson, Danielson, and Tsubomura [112, 113], and in accordance with the evolution of the ab initio methods; thereby hydrogen bond studies have been performed with more accuracy and criteria [114, 115], often through the application of the Møller-Plesset Perturbation Theory of Second Order (MP2) [116] and/or calculations derived from the Density Functional Theory (DFT) [117].

Methodology

The theoretical topology of the QTAIM approach

Furthermore, it is important to mention that the theoretical description of the hydrogen bond is not unique. As said before, ab initio and DFT calculations are widely used in accuracy examinations of molecular properties [118], either in ground states or excited states [119], or in addition in gas phase or under the influence of the solvent [120]. Independently, the scientific community long felt the need for a theoretical method by which the chemical bond content could be elucidated in its essence. Indeed, this theoretical method emerged 40 years ago through an insight of Bader based on catching information computed directly from the electronic density [121]. Baptized as the Quantum Theory of Atoms in Molecules (QTAIM), this method models all points of the molecular surface through the integration of the electronic density by taking into account the formalism of quantum mechanics for subspace [122]. Thus, the principle adopted by Bader [123, 124] was purely based on quantum mechanics, but with the purpose of describing the atomic behavior within the molecular environment. By revisiting the trajectory of the QTAIM development, Bader simply took into account the atomistic cooperative activity [125, 126], by which atoms were defined in a molecule as open systems able to exchange charge and momentum with their neighbors.

To set out the QTAIM formalism, the math masterpieces of Dirac, Feynman, and Schwinger [127–129] were used to describe the principle of least action for particle motion in subspace conditions. The principle of least action states that a quantity (q) derived from wave function is minimized in space and time (t_1 and t_2), and the atomic surface of a open system is modeled as a zero-flux surface, by which the time variation in end points is zero, and the surface also is zero in the extreme of functions, which can be summarized as:

$$\delta \mathrm{W}_{12}(\psi) = \int_{t_1}^{t_2} \left(\frac{\partial L}{\partial \psi} - \frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial L}{\partial \dot{\psi}} \right) \delta\psi \, \mathrm{d}t = 0 \qquad (1)$$

In this equation, L symbolizes the Lagrangian defined by the kinetic (K) and potential (U) energies. In surface, $\delta \mathrm{W}_{12}$ vanishes according to the Euler-Lagrange equation [130], and therefore, the Schrödinger equation for normalized wave function can be determined as $\hat{\mathrm{H}}\psi^* - E\psi^* = 0$ and $\hat{\mathrm{H}}\psi - E\psi = 0$ with $\hat{H} = -\left(\frac{i\hbar}{2m}\right)\sum\nabla^2 - \hat{\mathrm{U}}$. Ruled by Gauss's surface theorem, integrating the Schrödinger equation over a spatial region S(Ω) obtains:

$$\begin{aligned} K(\Omega) - G(\Omega) &= -\left(\frac{\hbar}{4m}\right)\int_{\Omega} \nabla^2 \rho d\tau \\ &= -\left(\frac{\hbar}{4m}\right)\oint \mathrm{d}S(\Omega)\nabla\rho \cdot n \end{aligned} \qquad (2)$$

where $K(\Omega)$ and $G(\Omega)$ represent the kinetic energy densities [131], which are equivalent to the Laplacian of the charge density, $\nabla^2\rho(r)$. If the surface $S(\Omega)$ is one of zero flux at any point r where n is a normal vector [132], $K(\Omega) = G(\Omega)$, and the condition becomes established:

$$\nabla\rho(r) \cdot n = 0 \text{ for all points on surface } S(\Omega) \qquad (3)$$

This equation defines the surface by which the atom is delimited as zero flux of charge density [133]. In other words, the value of the first electronic density derivative is zero, whereas the second derivatives go to a minimum or maximum of charge concentration. The relationship between surface conditions and high and low electronic density sites is ruled by the virial theorem [134].

QTAIM foundations and stability of intermolecular systems

By assuming the contributions of the kinetic and potential energies, elevated and depressive charge density regions are modeled by the positive (kinetic energy density G is positive) and negative (electronic potential energy density U is negative) Laplacian values [135], as demonstrated by Eq. (4):

$$2G(\Omega) - U(\Omega) = -\left(\frac{\hbar^2}{4m}\right)\nabla^2\rho(r) \qquad (4)$$

By the action of the kinetic (G) and potential (U) energy operators [136], QTAIM identifies the maximum and minimum electronic density in the molecular surface, and the chemical bonds are classified as closed shell if $\nabla^2\rho(r) > 0$ or shared interactions when $\nabla^2\rho(r) < 0$ [137]. Figure 2 illustrates a real description of the charge concentration and its relationship with Laplacian profiles [138]. As said before, the negative Laplacian indicates a high concentration of charge density (uphill), whereas depletion of charge density is motivated by the positive Laplacian (downhill). The Laplacian $\nabla^2\rho(r)$ is defined by the sum of the eigenvalues of the Hessian matrix ($\nabla^2\rho(r) = \lambda_i + \lambda_1 + \lambda_2 + \lambda_3$) [139], whereas the electronic density $\rho(r)$ is described as a set of critical points, such as cage critical points (CCP), ring critical points (RCP), bond critical points (BCP), and nuclear attractor (NA) [140]. All these critical points are specific, and their internal formalisms are ruled either by the sum of the eigenvalue signs ($\lambda_i = \lambda_1 + \lambda_2 + \lambda_3$) or by the number of non-zero eigenvalues. Therefore, a coordinate pair (r, s) is obtained, which can be used to classify the critical points cited above. For instance, the coordinates of CCP, RCP, BCP, and NA are (3,+3), (3,+1), (3,−1), and (3,−3). As explained above, r is a coordinate where a normal vector is aligned perpendicularly to the molecular surface, but now r is interpreted as an intermediary point wherein two gradient paths of electronic density emerge from two bonded nuclei [141]. Actually, this analysis is routinely applied in many investigations [142], but as Fig. 2 highlights, the application in systems formed by hydrogen bonds must be worthwhile [143]. As has been widely established, these arguments have also been applied

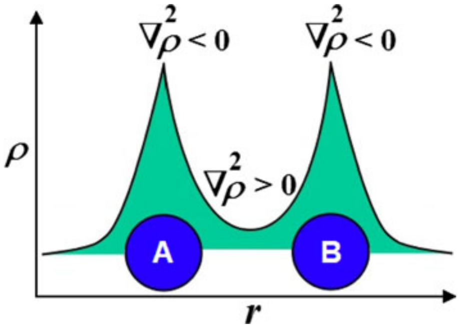

Fig. 2 Design of the charge density relief and the Laplacian ($\nabla^2\rho$) interpretation

successfully to study π-systems [144] and hydrogen-bonded complexes [145], surely including those formed by acetylene and hydrofluoric acid [146].

In terms of hydrogen bonds [54], we can see critical points as extremes of electronic density, that is, the maximum or minimum in each particular case. For instance, the BCP coordinates (3,−1) imply that the tridimensional (x, y, z) electronic density is extreme, whereas −1 is the summed result of two maximum (two −1 signs) and one minimum (one +1 sign) of electronic density. According to the nature of the π···H hydrogen bonds, the proton donor is aligned perpendicularly to the π cloud, but in regard to QTAIM critical points, the BCP (3,−1) between the above-mentioned carbon atoms is the attractor for the bond path linking the hydrogen to the C≡C, C=C, and C–C interacting bonds. In this context, it is assumed that (3,−1) along the CC bonds is a QTAIM source able to accept protons. Figure 3 (**1**) presents an example of contour plots of electronic density, showing the respective concentrations and depletions of charge density on the C≡C (acetylene) bond as well as on the π···H hydrogen bond of the complex $C_2H_2\cdots HF$ [147]. In this figure the small black points represent BCP.

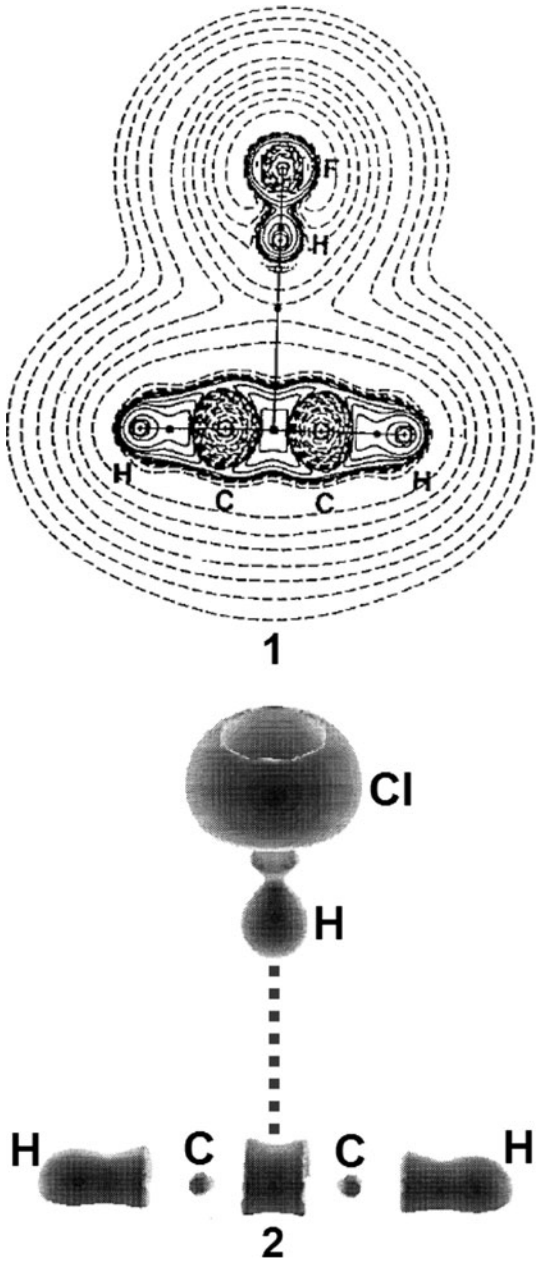

Fig. 3 The contour map of the Laplacian of the electron density for the complexes $C_2H_2\cdots HF$ (**1**) and $C_2H_2\cdots HCl$ (**2**)

Discussion

Within the content of the π···H hydrogen bonds, specifically the QTAIM calculations take all BCPs to integrate the electronic density and thereby model the molecular surface topologically [see Fig. 3 (**2**) with Laplacian mapping of the complex $C_2H_2\cdots HCl$] [91], of course by obeying the gradient of the electronic density and the virial theorem. Thus, the topologies of π bonds also have been studied through the application of QTAIM computations, whose values of electronic density and its Laplacian are presented in Table 1 [46]. As can be seen, all $\rho(r)$ values are very small, accompanied by positive results of $\nabla^2\rho(r)$, which is an indistinguishable characterization of hydrogen bonds as closed-shell interactions, i.e., the total charge density is almost concentrated on the separated centers, in this case, hydrogen atoms and π clouds. Note that all electronic density values vary on the scale of $10^{-2}\ e/\alpha_o^3$, which is important because very weakly bound systems such as van der Waals interactions present smaller results of $\rho(r)$, varying between $10^{-3}\ e/\alpha_o^3$ [46]. According to this scenerio, it cannot be said that all π complexes depicted in Table 1 interact only weakly, once there are other weakest bonded ones. Although the results collected in Table 1 were calculated at the B3LYP/6-311++G(d,p) level of theory, the smallest electronic density values can be obtained through the application of more sophisticated levels of theory, such as MP2/6-311++G(d,p) and MP2(FULL)/6-311++G(d,p), whose respective results are 0.0158 and 0.011 e/α_o^3 for the complex $C_2H_2\cdots HF$ [46], for instance.

Nevertheless, the electronic condition of the π bonds after complexation cannot be forgotten. As a foregoing insight, it seems to be natural that if a quantity of charge density is transferred to the proton donor, of course the electronic density on the C≡C and C=C bonds tends to diminish. In Table 1, all $\rho(r)$-CC values can be seen to have decreased upon the formation of the π···H hydrogen bonds. However, the most elegant QTAIM procedure to evaluate elevation and depletion of charge density in π and

Table 1 Values of the electronic densities and Laplacians of the $\pi \cdots H$ hydrogen bonds of the complexes $C_2H_2 \cdots HF$ (acetylene), $C_2H_4 \cdots HF$ (ethylene), $C_3H_4 \cdots HF$ (cyclopropene), $C_3H_6 \cdots HF$ (cyclopropane), $C_4H_4 \cdots HF^c$ (cyclobutadiene), $C_4H_4 \cdots HF^d$ (tetrahedrane), and $C_6H_6 \cdots HF$ (benzene)

Complexes	QTAIM topological parameters			
	$\rho_{(\pi \cdots H)}$	$\nabla^2\rho_{(\pi \cdots H)}$	$\rho_{(CC)}$	$BO_{(CC)}$
$C_2H_2 \cdots HF$	0.0181	0.054	0.411 (0.412)	3.0 (3.0)
$C_2H_4 \cdots HF$	0.0176	0.046	0.341 (0.344)	1.9 (2.0)
$C_3H_4 \cdots HF$	0.0189	0.052	0.348 (0.352)	2.0 (2.1)
$C_3H_6 \cdots HF$	0.0175	0.057	0.222 (0.234)	0.9 (1.0)
$C_4H_4 \cdots HF^c$	0.0201	0.049	0.341 (0.344)	1.9 (2.0)
$C_4H_4 \cdots HF^d$	0.0195	0.053	0.227 (0.239)	0.9 (1.0)
$C_6H_6 \cdots HF$	0.0123	0.036	0.306 (0.308)	1.5 (1.6)

Electronic densities = $\rho(r)$. Laplacians = $\nabla^2\rho(r)$. Values of $\rho(r)$ and $\nabla^2\rho(r)$ are given in e/α_o^3 and e/a_o^5. Values were calculated at the B3LYP/6-311++G(d,p) level of theory. Values in parentheses are related to the acetylene, ethylene, cyclopropene, cyclopropane, cyclobutadiene, tetrahedrane, and benzene isolated molecules

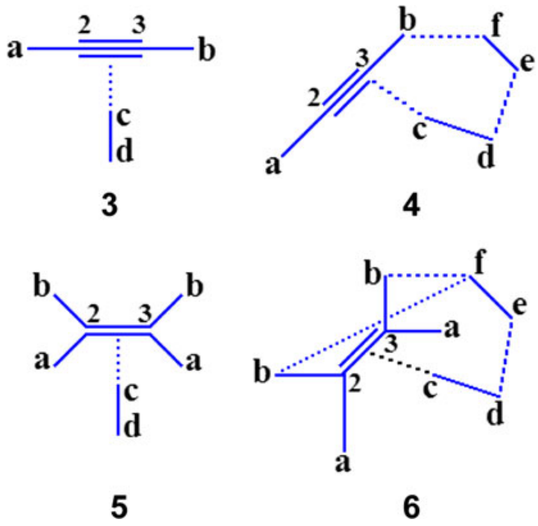

Fig. 4 Geometries of the bimolecular and trimolecular π hydrogen-bonded complexes formed by acetylene (**3** and **4**) and ethylene (**5** and **6**)

σ bonds is by means of the bond order (BO) analysis [148, 149]. In fact, multiple BO emerges along the charge density accumulation at each BCP between nuclei. Thus, QTAIM defines BO for CC bonds as follows:

$$BO = e^{\{A(\rho - B)\}} \tag{5}$$

where A and B symbolize constants that should be adjusted exponentially for the case where $B = \rho(r)$ of ethane, whereas $A = 1.0$, 1.6, 2.0, and 3.0 for ethane, benzene, ethylene, and acetylene [136]. By analyzing the values organized in Table 1, all values show a decrease of BO, which indicates an apparent loss of π character. Of course, due to the charge transfer from the π bond to the hydrofluoric acid molecule, the π character is altered. With the exception of acetylene, all complexes present reduction of BO, such as 2.0 for ethylene monomeric and 1.9 for the complex $C_2H_4 \cdots HF$.

However, apparently there are a limited number of topological works related to ternary hydrogen complexes [150, 151], since structural and energetic results are the only routine parameters studied theoretically [90]. Using all the inherent capabilities of the QTAIM method, we have reported that its application to identify the hydrogen bonds in the complex $C_2H_2 \cdots 2(HF)$ must be timely and worthwhile because according to Rozas et al. [46], the $\pi \cdots H$ hydrogen bond is defined as interactions formed between the $C \equiv C$ of the acetylene and only one hydrofluoric acid molecule. Subsequently, the parameters obtained from $C_2H_2 \cdots HF$ were taken into account as a starting point for a theoretical discussion about the $\pi \cdots H$ interaction in the trimolecular hydrogen-bonded complex $C_2H_2 \cdots 2(HF)$, but also in other similar systems, such as $C_2H_4 \cdots HF$ and $C_2H_4 \cdots 2(HF)$, which are also featured in Fig. 4 [152].

Verifying the bond paths and relief maps documented recently, a QTAIM analysis was performed in terms of topological parameters, such as the electronic density and its Laplacian field, whose values for the π complexes $C_2H_2 \cdots HF$, $C_2H_2 \cdots 2(HF)$, $C_2H_4 \cdots HF$, and $C_2H_4 \cdots 2(HF)$ are presented in Table 2. As explained above, the Laplacian is defined as the sum of the eigenvalues from diagonalization of the Hessian matrix of the electronic density, such as in the covalent bonds $\nabla^2\rho(r) < 0$. In this manner, in conformity with the values of $\nabla^2\rho(r)$ shown in Table 2, the H–F bonds are entirely characterized as shared interactions in 2(HF) dimer, as well as in the hydrogen-bonded complexes $C_2H_2 \cdots HF$ and $C_2H_2 \cdots 2(HF)$. Regarding the hydrogen bonds, these interactions are defined as closed shells because the results of the Laplacian are positive, whose values are in the range of $0.026\ e/a_o^5 < \nabla^2\rho(r) < 0.119\ e/a_o^5$

Concerning the electronic density, the values obtained for all hydrogen bonds are justly very low. For instance, in the hydrogen complex $C_2H_2 \cdots 2(HF)$, their interactions $H^c \cdots C^3$ and $F^d \cdots H^e$ present electronic density values of 0.023 and 0.029 e/α_o^3. However, the $\pi \cdots H$ interaction in the hydrogen complex $C_2H_2 \cdots HF$ presents the lower electronic density amount, whose value is 0.018 e/α_o^3. Comparing the electronic density among $\pi \cdots H$, $F^d \cdots H^e$, and $F^f \cdots H^b$, in fact the lowest value of 0.007 e/α_o^3 for $F^f \cdots H^b$ is described as a closed-shell interaction. Moreover, it should be highlighted that the typical condition of the Laplacian field guarantees the formation of $F^f \cdots H^b$, in other words, $\nabla^2\rho(r) > 0$. In the formation of the hydrogen complex C_2H_2 2(HF), the QTAIM calculations furnish essential information about the $\pi \cdots H$ interaction, requiring then special attention.

Table 2 Values of electronic densities and Laplacians of the hydrogen-bonded complexes $C_2H_4\cdots HF$, $C_2H_4\cdots 2HF$, $C_2H_2\cdots HF$, and $C_2H_2\cdots 2HF$

Topology	Hydrogen-bonded complexes			
	$C_2H_4\cdots HF$	$C_2H_4\cdots 2HF$	$C_2H_2\cdots HF$	$C_2H_2\cdots 2HF$
$\rho_{(H^c-F^d)}$	0.353	0.336	0.354	0.339
$\rho_{(H^e-F^f)}$	–	0.345	–	0.349
$\rho_{(C^2-C^3)}$	0.342	0.343	0.411	0.410
$\rho_{(\pi\cdots H)}$	0.017	0.024	0.018	–
$\rho_{(H^c\cdots C^3)}$	–	–	–	0.023
$\rho_{(F^d\cdots H^e)}$	–	0.040	–	0.029
$\rho_{(F^f\cdots H^b)}$	–	0.021	–	0.007
$\nabla^2\rho_{(H^c-F^d)}$	−2.63	−2.30	−2.65	−2.51
$\nabla^2\rho_{(H^e-F^f)}$	–	−2.43	–	−2.64
$\nabla^2\rho_{(C^2C^3)}$	−1.02	−1.00	−1.24	−1.23
$\nabla^2\rho_{(\pi\cdots H)}$	0.050	0.019	0.053	–
$\nabla^2\rho_{(H^c\cdots C^3)}$	–	–	–	0.061
$\nabla^2\rho_{(F^d\cdots H^e)}$	–	0.137	–	0.119
$\nabla^2\rho_{(F^f\cdots H^b)}$	–	0.141	–	0.026

Electronic densities = $\rho(r)$. Laplacians = $\nabla^2\rho(r)$. Values of $\rho(r)$ and $\nabla^2\rho(r)$ are given in e/α_o^3 and e/a_o^5. Values are calculated at the B3LYP/6-311++G(d,p) level of theory. Values of $\rho(r)$ and $\nabla^2\rho(r)$ for the hydrofluoric acid monomer are 0.369 e/α_o^3 and −2.890 e/a_o^5. Values of $\rho_{(C^2C^3)}$on the monomers: C_2H_4 = 0.344 e/α_o^3 and C_2H_2 = 0.411 e/α_o^3. Values of $\nabla^2\rho_{(C^2C^3)}$on the monomers: C_2H_4 = −1.03 e/a_o^5 and C_2H_2 = −1.24 e/a_o^5

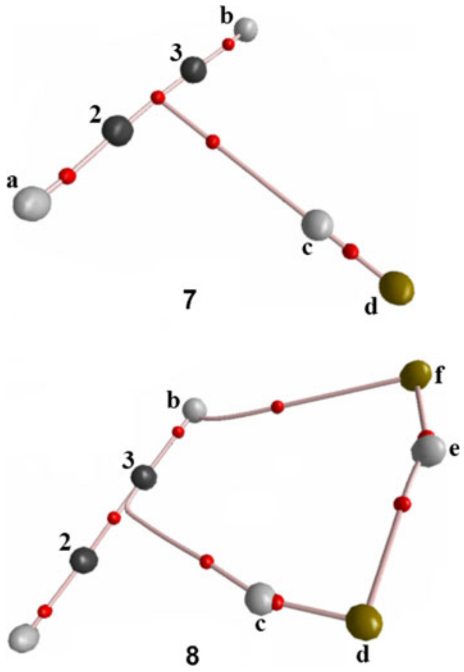

Fig. 5 Bond paths and BCP localized through the QTAIM calculations for the hydrogen complexes $C_2H_2\cdots HF$ (**7**) and $C_2H_2\cdots 2(HF)$ (**8**)

Throughout this study, we have mentioned that the $\pi\cdots$H interaction in the hydrogen complex $C_2H_2\cdots HF$ is formed exactly at the middle point of the C≡C bond of the acetylene; see Fig. 5 (**7**) [153]. However, the QTAIM calculations for the hydrogen complex C_2H_2 2(HF) show that the well-defined $\pi\cdots$H interaction is not observed. On the contrary, an unusual $\pi\cdots$H hydrogen bond was found, up to now symbolized as $H^c\cdots C^3$, but it is characterized with an electronic density amount of 0.023 e/α_o^3 and a Laplacian field of 0.061 e/a_o^5, however, formed by the interaction between the H^c hydrogen and the C^3 atom, as seen in the Fig. 5 (**8**). Henceforth, the possibility of the traditional charge transference from π center to the σ^* anti-bonding orbital of the HF molecule in the hydrogen complex $C_2H_2\cdots 2(HF)$ is practically discarded. Prominently, a redistribution of the electronic density along the cyclic hydrogen complex $C_2H_2\cdots 2(HF)$ is witnessed under the following conditions, $\sigma \rightarrow \sigma^*$ (C^3–H^c), $\sigma \rightarrow \sigma^*$ (F^d–H^e), and $\sigma \rightarrow \sigma^*$ (F^f–H^b) [135, 136], in a similar way to systems formed by resonance-assisted hydrogen bonds (RAHB) [154].

Concerning the complexes formed by ethylene, $C_2H_4\cdots HF$ (**4**), and $C_2H_4\cdots 2HF$ (**6**), by consulting Tables 1 and 2, it is clearly perceived that the electronic densities on C=C bonds are slightly unchanged, e.g., values of 0.342 and 0.343 e/α_o^3 for the bimolecular $C_2H_4\cdots HF$ and trimolecular $C_2H_4\cdots 2HF$ π hydrogen-bonded complexes. In opposition to this, a sensitive variation in the electronic density on the hydrofluoric acid was seen, whose values are 0.353 and 0.336 e/α_o^3 for H^c–F^d from $C_2H_4\cdots HF$ to $C_2H_4\cdots 2HF$, as well as 0.336 e/α_o^3 (H^c–F^d) and 0.345 e/α_o^3 (H^e–F^f) only in the trimolecular complex. Once again charge density depletions in the intermolecular interactions are computed, in which the values vary in 0.017–0.024e/α_o^3. In conjunction with positive Laplacian values, these electronic densities indicate the formation of hydrogen bonds within each intermolecular BCP. Notwithstanding that the possibility of a ternary interaction between the second hydrofluoric acid H^e–F^f and hydrogen atoms (H^b) of ethylene could be a real event, in fact the positive Laplacian value of 0.141 e/α_o^3 indicates a characterization for both ternary interactions $F^f\cdots H^b$ as bifurcated hydrogen bonds. In overview, such a profile is in line with the framework of Bader's QTAIM approach on a natural atomic basis, which says that the hydrogen bonds possess charge density concentrated in separated nuclei (donors and acceptors of protons) [155, 156].

According to Grabowski [157, 158], the interpretation of the topology of the $\pi\cdots$H hydrogen bond can be governed by the essence of the QTAIM approach. In Table 3 the values of QTAIM parameters are organized, such as the already known electronic density and Laplacians, and two novels: kinetic (G) and potential (U) energies. These two physical operators are included in the QTAIM foundationalism by means of the local energy density, $H\rho(r)$, which was proposed by Cremer and Kraka [159].

Table 3 Values of electronic densities, Laplacians, kinetic, and potential energies/a.u. for the complexes formed by acetylene and ethylene as proton acceptors

Systems	Topology			
	$\rho_{(\pi \cdots \mathrm{H})}$	$\nabla^2\rho_{(\pi \cdots \mathrm{H})}$	G	U
$C_2H_2 \cdots HF^a$	0.0176	0.053	0.0104	−0.0076
$C_2H_2 \cdots HCl^a$	0.0116	0.0300	0.0058	−0.0041
$C_2H_2 \cdots HCF_3{}^a$	0.0055	0.0140	0.0027	−0.0021
$C_2H_2 \cdots C_2H_2{}^a$	0.0049	0.0120	0.0025	−0.0019
$C_2H_2 \cdots 2(HF)^b$	0.0220	0.0601	0.0131	−0.0112
$C_2H_2 \cdots 3(HF)^b$	0.0262	0.0647	0.0153	−0.0144
$C_2H_2 \cdots 4(HF)^b$	0.0282	0.0664	0.0164	−0.0162
$C_2H_4 \cdots HF^b$	0.0165	0.0390	0.0086	−0.0062
$C_2H_4 \cdots 2(HF)^b$	0.0227	0.0536	0.0119	−0.0103
$C_2H_4 \cdots 3(HF)^b$	0.0263	0.0562	0.0135	−0.0130
$C_2H_4 \cdots 4(HF)^b$	0.0239	0.0539	0.0124	−0.0113

Electronic densities = $\rho(r)$. Laplacians = $\nabla^2\rho(r)$. Kinetic energy = G. Potential energy = U. Values of $\rho(r)$ and $\nabla^2\rho(r)$ are given in e/α_o^3 and e/a_o^5

[a] Values calculated at the B3LYP/6-311++G(d,p) level of theory

[b] Values calculated at the MP2/6-311++G(d,p) level of theory

$$\mathrm{H}\rho(r) = \mathrm{G}\rho(r) + \mathrm{U}\rho(r) \tag{6}$$

Note that this relationship is a consequence of Eq. (4), and for this reason we can affirm the QTAIM applicability, whose interpretation leads us to comprehend the profile of the chemical bonds. If $H\rho(r)$ is negative, this means that the potential operator is dominant in the internuclear region, which indicates then "covalence" [160]. In opposition to this, if $H\rho(r)$ becomes positive and is the kinetic operator that provides the major contribution, this is indicative of shared electronic density. Actually, this is a classical QTAIM procedure to characterize hydrogen bonds [161], and in agreement with all values listed in Table 3, these systems are well recognized as hydrogen-bonded complexes with their hydrogen bonds formed exactly in the middle of the π bond of acetylene and ethylene. It is worthwhile to remember that the exact computation of $G\rho(r)$ and $U\rho(r)$ requires the execution of the first order matrix of electronic density [162]. The low electronic density of 0.0649 has been computed as e/α_o^3 accompanied by a positive Laplacian of 0.0149 e/a_o^5 for the complex $C_2H_3{}^+ \cdots C_2H_2$, the results yielded by the sums of the kinetic and potential energy results of 0.0286 and −0.0534 a.u. represent the electronic energy density $H(\rho)$, whose value is −0.0248 a.u. In spite of this, this same trend was also verified for the complex $C_2H_3{}^+ \cdots C_2F_2$ and other very similar ones [103].

Derived from acetylene, the ethyl cation is an intermediary whose stabilization is ruled by means of the hyperconjugation effect [163, 164]. Interestingly, a large number of theoretical studies of the ethyl cation and its hyperconjugation effect have been reported, including the classic work done by Pople [165] and others [166]. However, Zuilhof et al. [167] and Carneiro et al. [168] analyzed the molecular geometry of the ethyl cation using the MP2(FULL)/6-31G(d,p) and B3LYP/6-311G(d,p) calculations. At these two levels of theory, the structure of the ethyl cation was characterized by a C_{2v} point group, although two distinct results for the distance between C^1 and C^2 carbons (see Fig. 6) were computed, whose values were 1.386 and 1.381 Å. These $R^{1\ 2}_{(C-C)}$ distances align midway between the experimental data of 1.34 and 1.53 Å for ethylene and ethane [169]. On the basis of these results [170], we have assumed that a $R^{1\ 2}_{(C-C)}$ bond length of 1.38 Å is an appropriate parameter for evaluating the hyperconjugation effect of the ethyl cation (**11**).

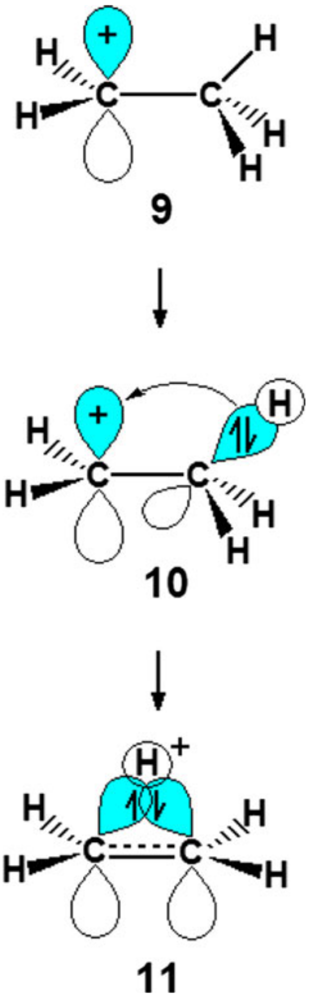

Fig. 6 Schematic drawing of the delocalized electronic distribution on the ethyl cation. The hyperconjugation effect can be visualized in **10**

In the case of the hydrogen-bonded complexes derived from the ethyl cation, the representations of the contour

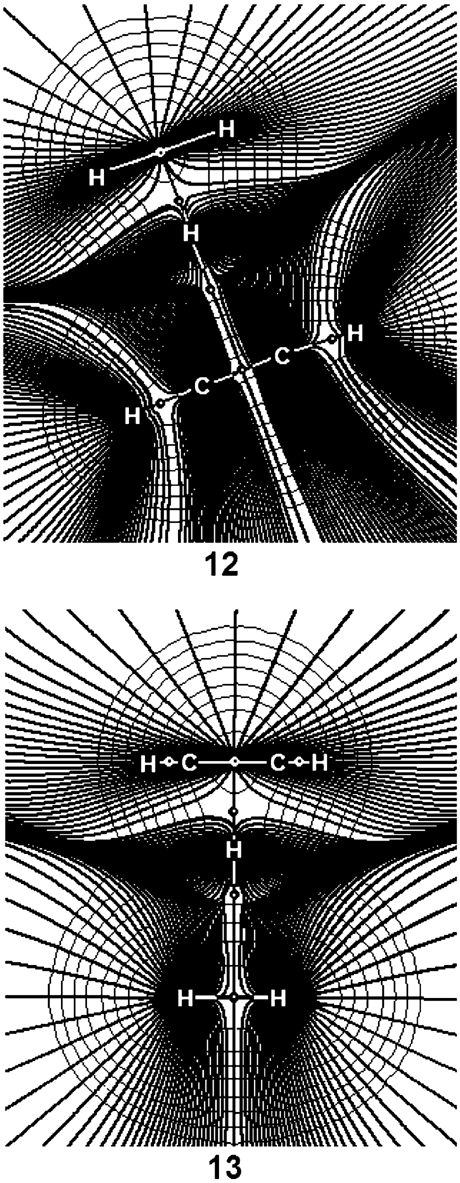

Fig. 7 *Contour lines* of the electronic densities of hydrogen-bonded complexes $C_2H_5{}^{+} \cdots C_2H_2$ (**12**) and $C_2H_5{}^{+} \cdots C_2H_4$ (**13**) using QTAIM default integrations

lines of the electronic densities for these systems are illustrated in Fig. 7 (**12**, **13**). It is through the analysis of these charge density diagrams that all QTAIM topological parameters, such as the electronic density $\rho(r)$ and its Laplacian $\nabla^2\rho(r)$, are computed, whose values for the above-presented complexes are listed in Table 4. Firstly, the electronic densities of 0.028 and 0.027 e/α_o^3 for the $\pi \cdots H^+$ hydrogen bonds of the hydrogen-bonded complexes **12** and **13** were determined. Using the QTAIM protocol, we can characterize the interaction between two neighboring atoms by means of analysis of the Laplacian, $\nabla^2\rho(r)$. Thus, the Laplacians of the $\pi \cdots H^+$ hydrogen bonds are positives, whose results range from 0.013 to 0.010 e/a_o^5. It is worth mentioning that the interaction between the ethyl cation and acetylene and ethylene is governed by a concentration of charge density in separate centers, i.e., the H^+ and π sites. Before the calculation of $\rho(r)$ and $\nabla^2\rho(r)$, QTAIM searches BCP at each chemical bond, whose purpose is to build electronic density pathways between neighboring atoms. In essence, BCP is an intrinsic region of the chemical bond, within which the interactomic frontier is estimated. In other words, BCP calculation is a suitable proposal for answering an old question in chemistry: "Where is the atomic frontier within a chemical bond?"

Taking the BCP localized on all chemical bonds, the QTAIM approach performs a numeric integration of the electronic density on the molecular surface. Because of this, in addition to electronic depletions, concentrations of charge density are also quantified, and these are identified by the Laplacian as being $\nabla^2\rho(r) < 0$. Bearing in mind these conditions, covalent and unsaturated bonds are characterized quantum chemically, although our interest here is restricted to the $C \equiv C$ and $C{=}C$ bonds. According to results grouped together in Table 4, the negative Laplacian values of -1.235 and -1.009 e/a_o^5 indicate that the π bonds cited above have been identified as shared charge density concentrations. Note that these values are quite similar for acetylene and ethylene monomers (see footnote to Table 4), which leads us to the conclusion that the hyperconjugation effect of the ethyl cation is preserved after the formation of the hydrogen-bonded complexes **12** and **13**. If we analyze the electronic density values of 0.411 and 0.340 e/α_o^3, it can be clearly seen that insignificant variations in $\rho(r)$ are to be observed on the $C \equiv C$ and $C{=}C$ bonds when compared with the data for monomers.

A great deal of attention is always dedicated to acetylene and its capability to form hydrogen bonds either with neutral or cationic species [92]. In other studies, Grabowski [100] investigated the complexes' T-shape derived from the ethyl cation where the presence of three centers and two electrons is a notorious phenomenon. However, the veracity of the ethyl cation structure was also investigated and whether the delocalized hydrogen is able to interact with π centers. Systems such as $C_2H_2 \cdots H^+ \cdots C_2H_2$ and $C_2H_4 \cdots H^+ \cdots C_2H_2$ were proposed in order to discuss the reliable affirmation: "Is a $\pi \cdots H^+ \cdots \pi$ complex hydrogen bonded?" [98]. Figure 8 illustrates the bond path and BCP of the complexes $C_2H_2 \cdots H^+ \cdots C_2H_2$ (**14**) and $C_2H_4 \cdots H^+ \cdots C_2H_2$ (**15**). If we look carefully, these systems do not present the hyperconjugation effect inherent to ethyl cation, which is not substantial in this current context since only the characterization of the $\pi \cdots H^+ \cdots \pi$ is important. Moreover, acetylene is also perceived to align orthogonally to olefin. The BCPs corresponding to the donor (**d**) and to the acceptor (**a**) are indicated (Fig. 8), and one can see that

Table 4 Values of electronic densities and Laplacians of the main bonds of the hydrogen-bonded complexes $C_2H_5^+\cdots C_2H_2$, $C_2H_5^+\cdots C_2H_4$, $C_2H_2\cdots H^+\cdots C_2H_2$, and $C_2H_4\cdots H^+\cdots C_2H_2$

Systems	Topology							
	$\rho^+_{(\pi\cdots H)}$	$\nabla^2\rho^+_{(\pi\cdots H)}$	$\rho_{(C\equiv C)}$	$\nabla^2\rho_{(C\equiv C)}$	$\rho_{(C=C)}$	$\nabla^2\rho_{(C=C)}$	$\rho_{(HX)}$	$\nabla^2\rho_{(HX)}$
$C_2H_5^+\cdots C_2H_2$[a]	0.028	0.013	0.411	−1.235	–	–	–	–
$C_2H_5^+\cdots C_2H_4$[a]	0.027	0.010	–	–	0.340	−1.009	–	–
$C_2H_2\cdots H^+\cdots C_2H_2$[b]	0.064	0.026	–	–	–	–	0.140	−0.179
$C_2H_4\cdots H^+\cdots C_2H_2$[b]	0.028	0.057	–	–	–	–	0.172	−0.256

Electronic densities = $\rho(r)$. Laplacians = $\nabla^2\rho(r)$. Values of electronic densities obtained from B3LYP/6-311++G(d,p) geometries of the C≡C and C=C bonds of the hydrocarbon monomers are 0.412 and 0.344 e/α_o^3. Values of Laplacian obtained from B3LYP/6-311++G(d,p) geometries of the C≡C and C=C bonds of the hydrocarbon monomers are −1.241 and −1.030 e/a_o^5

[a] Values calculated at the B3LYP/6-311++G(d,p) level of theory

[b] Values calculated at the MP2/6-311++G(d,p) level of theory

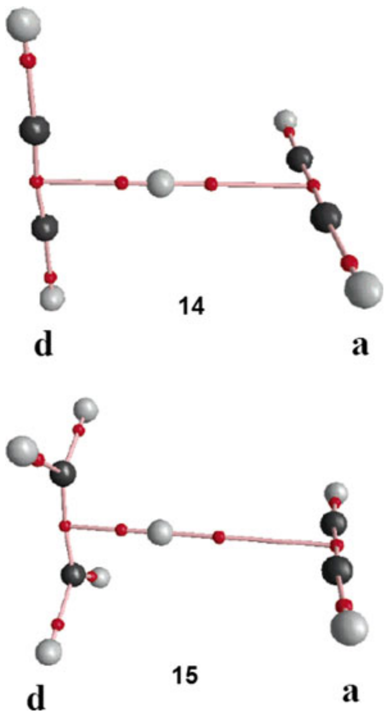

Fig. 8 Bond paths and BCP localized through the QTAIM calculations for the hydrogen complexes $C_2H_2\cdots H^+\cdots C_2H_2$ (**14**) and $C_2H_4\cdots H^+\cdots C_2H_2$ (**15**)

the first one is closer to the hydrogen atom than the second one.

For the $C_2H_4\cdots H^+\cdots C_2H_2$, the proton is closer to the C_2H_4 molecule, and the $C_2H_4\cdots H^+$ is the proton donating system, which presents features of covalence [171, 172] because their Laplacian values are negative, i.e., −0.179 and −0.256 e/a_o^5 for the complexes $C_2H_2\cdots H^+\cdots C_2H_2$ and $C_2H_4\cdots H^+\cdots C_2H_2$. Despite this, a covalent character within the intermolecular contact where π centers are functioning as proton acceptors was also evidenced [98], wherein the local energy $H(\rho)$ reveals a dominant contribution of the potential energy (U) upon the formation of the complex $C_2H_3^+\cdots C_2H_2$. By the foundations of the hydrogen bond theory, by means of the Morokuma's [173] decomposition analysis or symmetry-adapted perturbation theory [174], the dominance of the electrostatic potential, followed by charge transfer, polarizability, and London dispersion forces in cases of blue-shifting hydrogen bonds is well known [47].

Conclusions

The applicability of the QTAIM theory to the electronic density partition attained a complexity level with merit and prospects. Chemical systems ruled by unclear phenomena regarding the chemical bonds have been unraveled by the QTAIM topological vision. Intermolecular complexes formed by $\pi\cdots H^+$ hydrogen bonds are one of the examples whose physical-chemical content has been gradually elucidated after theoretical analysis based on topological parameters, such as electronic density and its Laplacian, as well as obtained from physical operators, such as kinetic and potential energies. In advance, the topological cornerstone of the $\pi\cdots H^+$ hydrogen bonds is revealed by the depletion of electron density and the dominant contribution of the kinetic energy, accompanied by the positive Laplacian field. This is arguable because there are systems stabilized through the $\pi\cdots H^+$ hydrogen bonds with high covalent character. However, by taking into account the current definition of the hydrogen bonds, Y–B···H–A, Y–B is quoted to represent the π center of the hydrocarbons, but due to the charge transfer from the π center to the H–A proton donor, significant alterations of charge density of the C≡C and C=C bonds are observed.

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