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Non-covalent interactions – QTAIM and NBO analysis

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Abstract MP2(full)/6-311++G(3df,3pd) calculations were carried out on complexes linked through various non-covalent Lewis acid – Lewis base interactions. These are: hydrogen bond, dihydrogen bond, hydride bond and halogen bond. The quantum theory of ′atoms in molecules′ (QTAIM) as well as the natural bond orbitals (NBO) method were applied to analyze properties of these interactions. It was found that for the A-H…B hydrogen bond as well as for the A-X…B halogen bond (X designates halogen) the complex formation leads to the increase of s-character in the A-atom hybrid orbital aimed toward the H or X atom. In opposite, for the A…H-B hydride bond, where the H-atom possesses negative charge, the decrease of s-character in the B-atom orbital is observed. All these changes connected with the redistribution of the electron charge being the effect of the complex formation are in line with Bent′s rule. The numerous correlations between energetic, geometrical, NBO and QTAIM parameters were also found.

Keywords Bent′s rule · Dihydrogen bond · Halogen bond · Hydride bond · Hydrogen bond · Non-covalent interaction · Natural bond orbitals method · Quantum theory of ′atoms in molecules′ (QTAIM) · The Lewis acid-Lewis base interaction

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Introduction

The role of non-covalent interactions in various chemical and biochemical processes is the subject of numerous investigations [1]. The hydrogen bond is most often analyzed among such interactions and its key role in different reactions and phenomena is very well known [2–5]. However in recent years the significance of other non-covalent interactions is also analyzed extensively [6]. These are, for example, halogen bond [7–10], dihydrogen bond [11–14], hydride bond [15–18] and halogen-hydride bond [6]. There are also other examples of non-covalent interactions, for example, very recently the N…P attractive interaction was analyzed [19, 20] and discussed in terms of ab initio calculations and the natural bond orbitals (NBO) theory [21–23]. For all of them the electrostatic interaction is very important since the positively charged Lewis acid center interacts with the negatively charged Lewis base center [1, 10]. This is in line with the σ-hole concept which was applied to the halogen bond and to other non-covalent interactions [1, 10, 24–29].

The common feature of the interactions mentioned above is the electron charge transfer from the Lewis base to the Lewis acid being the result of complex formation [6]. In other words, the Lewis acid moiety is usually negatively charged in the complex. This is why not only the electrostatic interaction is important for such complexes, but also the charge transfer and polarization contributions usually attributed to the covalency of interaction. The covalent character of hydrogen bond was mainly analyzed and discussed in previous studies [30]. The term Lewis acid – Lewis base interaction seems to be more proper than the term non-covalent interaction for the hydrogen bond, halogen bond and all other interactions where the complex formation is connected with the significant electron charge redistribution. Such a term indicates the character of two interacting moieties, the Lewis acid and the Lewis base, and it shows their electron accepting and electron donating abilities, respectively.

There are common properties of the Lewis acid – Lewis base interactions; they were mainly analyzed for the hydrogen bond [30, 31]. For example, two effects are attributed to the complex linked through the A-H…B hydrogen bond: the hyperconjugative effect of the A-H bond weakening and the rehybridization-promoted A-H bond strengthening [32]. The first effect, the hyperconjugative interaction, is well known and it was analyzed many times before [21–23]. It is connected with the electron charge transfer from the lone pair of B into the antibonding σ* orbital of the A-H bond. The second effect leads to the increase of the s-character in the A-atom hybrid orbital of the A-H bond and it is connected with strengthening this bond [32]. The increase of s-character correlates with the strength of the hydrogen bond interaction; for the stronger hydrogen bond the greater s-character is observed [32–34]. It was also pointed out that the rehybridization effect is in line with Bent´s rule [32]. According to the Bent rule atom maximizes the s-character in hybrid orbital aimed toward electropositive substituent. Atom maximizes its p-character and minimizes its s-character in such orbital aimed toward electronegative substituent [35]. Both effects, the hyperconjugation and rehybridization, are attributed to all hydrogen bonds [32].

According to the previous investigations mentioned above [21–23, 32] the A-H…B hydrogen bond formation may be described in the following way. This is partly electrostatic interaction. However it is also connected with the electron charge transfer from the Lewis acid to the Lewis base, i.e., from the proton acceptor (B) to the proton donating part (A-H). This charge transfer is greater for stronger hydrogen bonds and shorter proton – acceptor distances. It leads to the increase of the polarization of the A-H proton donating bond. In other words the electron charge is further transferred from the H-atom into the electronegative A-atom. This is connected with the increase of s-character in the A-atom hybrid orbital aimed toward the H-atom. The latter effect is in line with Bent´s rule since the H-atom may be treated as the electropositive substituent influencing the A-center. The repolarization of the A-H bond being the result of the hydrogen bond formation is connected with the increase of the positive charge of H-atom. One may say that the H-atom is more electropositive after complex formation what leads to the greater s-character in the A-hybrid orbital according to Bent´s rule. It seems that the electron charge redistribution is connected with an unexpected phenomenon [21] since there is the electron charge transfer from the proton acceptor (B) to the proton donor (A-H) but it leads to the increase of the positive charge of the H-atom in the A-H bond.

Other properties of hydrogen bonded complexes may be mentioned. For example, the decrease of the volume of H-atom of the A-H…B system [36, 37] or more recently found property of the increase of the radius of A-atom and the decrease of the radius of H-atom [38]. The latter radii may be treated as a result of the partitioning of the A-H bond. If the H-radius decrease outweighs the increase of the A-atom radius then the blue shift hydrogen bond connected with the decrease of the A-H bond length is observed [38] as a result of compelxation. These consequences of the hydrogen bond formation are observable for other Lewis acid – Lewis base interactions [39, 40]. For example, the A-X…B halogen bond formation (X designates Cl, Br or I atom) is connected with the increase of the X-atom positive charge and consequently with the increase of the s-character in the A-atom hybrid orbital aimed toward X and with the decrease of the X-volume [39, 40].

The aim of this study is to show that one can observe common properties for all Lewis acid – Lewis base interactions. It is proved here that the same mechanism occurs for the formation of hydrogen, halogen, hydride and dihydrogen bond. This means that for complexes linked through such interactions common processes follow the electron charge transfer from the Lewis base moiety to the Lewis acid one. The processes discussed here for different Lewis acid – Lewis base interactions were analyzed before only for hydrogen bonds.

Computational details

The calculations were carried out with the Gaussian09 set of codes [41]. The complexes linked through various types of Lewis acid – Lewis base interactions were taken into account (see Fig. 1). These are the hydrogen bonded (HB) complexes: H_2O… HOH, F_3CH…OH_2, FH…C_2H_4, two complexes with dihydrogen bonds (DHBs): NH_4^+…HBeH and NH_4^+…HMgH, the complex with halogen bond (XB) F_3CCl…OCH_2 and two complexes where the hydride bond (HyB) exists: Na^+…HBeH and Na^+…HMgH. Such a choice allows to consider and to compare different kinds of interactions. Even for hydrogen bonded systems there is a variety of interactions since one can see the typical O-H…O hydrogen bond for the H_2O… HOH, the C-H…O blue shift hydrogen bond for the F_3CH…OH_2 complex since the shortening of the C-H bond as a result of complex formation was observed here [42], and the FH…π hydrogen bond with π-electrons as the proton acceptor for the FH…C_2H_4 complex.

The complexes were optimized at the MP2(full)/6-311++G (3df,3pd) level, they are in energetic minima since no imaginary frequencies were observed for them. The binding energies for the mentioned above complexes were calculated. These are the differences between the total energy of the complex and the energies of monomers. These energies were corrected for the basis set superposition error (BSSE) by the counterpoise

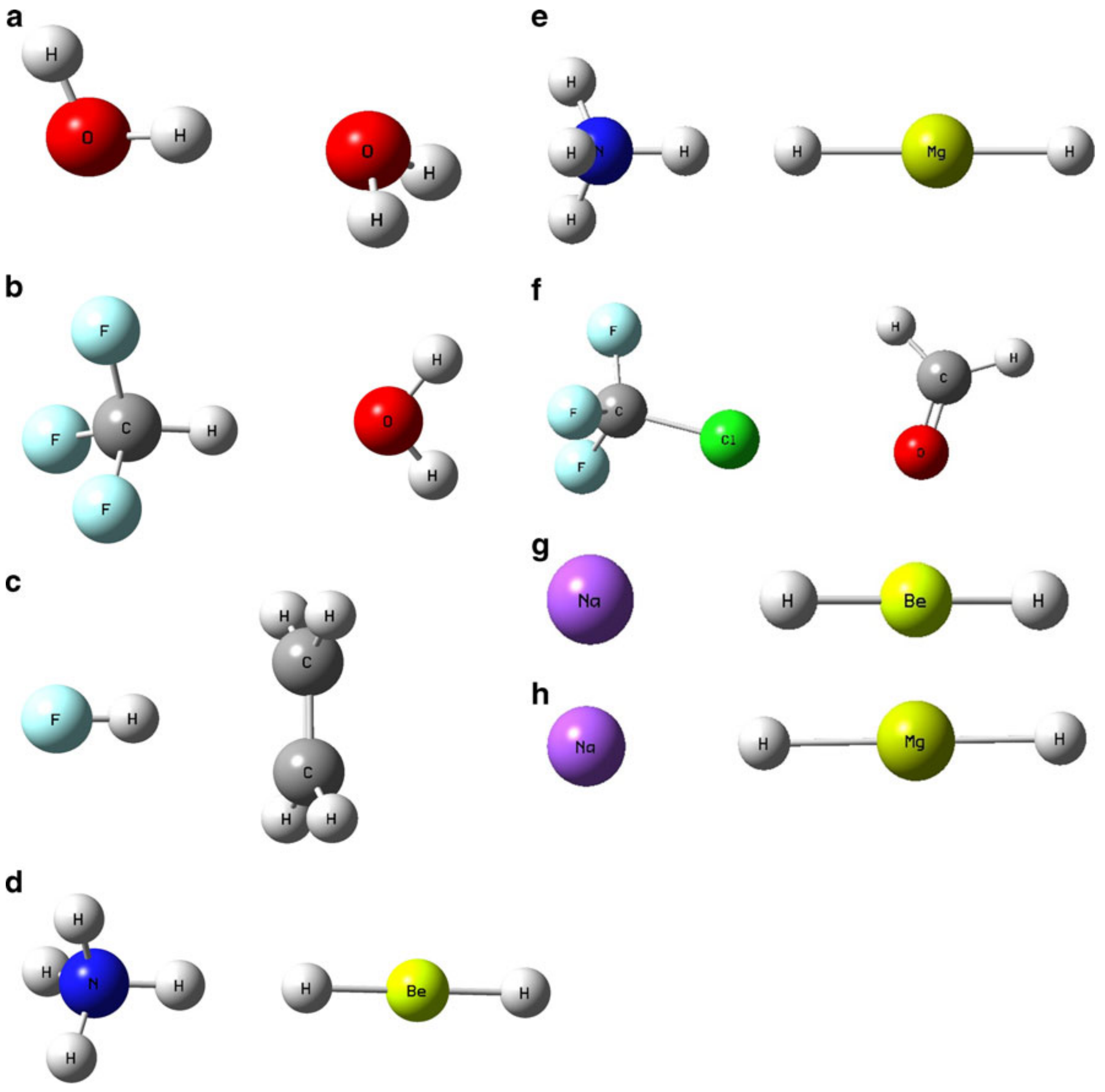

Fig. 1 The complexes analyzed in this study; the hydrogen bonded ones: (a) H_2O… HOH, (b) F_3CH…OH_2, (c) FH…C_2H_4, with dihydrogen bonds: (d) NH_4^+…HBeH and (e) NH_4^+…HMgH, the complex with halogen bond – (f) F_3CCl…OCH_2 and two complexes with the hydride bond (g) Na^+…HBeH and (h) Na^+…HMgH

method [43]. The energies of optimized geometries of isolated monomers were taken for the calculation of binding energies. Hence the deformation of monomers as a result of the complex formation is included. In other words, the binding energies contain the deformation energy term [44, 45].

The quantum theory of 'atoms in molecules' (QTAIM) [46–49] was applied to find the bond paths and the corresponding critical points (BCPs). The QTAIM calculations were carried out with the use of the AIMAll program [50]. There are the following characteristics of BCP usually considered: the electron density at BCP (ρ_{BCP}), its Laplacian ($\nabla^2\rho_{BCP}$), the total electron energy density at BCP (H_{BCP}), the potential electron energy density (V_{BCP}) and the kinetic electron energy density (G_{BCP}). There are the relationships between the characteristics mentioned above (in atomic units).

$$1/4\nabla^2\rho_{BCP} = 2G_{BCP} + V_{BCP} \ and \ H_{BCP} = G_{BCP} + V_{BCP} \qquad (1)$$

The natural bond orbitals (NBO) method [21–23] was also applied. For the A-H…B hydrogen bond, the $n_B \rightarrow \sigma_{AH}$* interaction is one of its main characteristics. It is connected with the maximum $n_B \rightarrow \sigma_{AH}$* overlapping, n_B designates the lone electron pair of the proton acceptor and σ_{AH} is an antibonding orbital of the proton donating bond. The $n_B \rightarrow \sigma_{AH}$* interaction energy is calculated (Eq. 2) as the second-order perturbation theory energy.

$$\Delta E(n_B \rightarrow \sigma_{AH}{}^*) = -2\langle n_B|F|\sigma_{AH}{}^*\rangle^2/\left(\varepsilon\left(\sigma_{AH}{}^*\right) - \varepsilon(n_B)\right) \qquad (2)$$

$\langle n_B|F|\sigma_{AH}{}^*\rangle$ designates the Fock matrix element and $(\varepsilon(\sigma_{AH}{}^*) - \varepsilon(n_B))$ is the orbital energy difference. For the

H_2O…HOH and F_3CH…OH_2 complexes there are the $n_O \rightarrow \sigma_{OH}^*$ and $n_O \rightarrow \sigma_{CH}^*$ interactions, respectively. Equation 2 is slightly modified for other interactions considered here. The A-H…H-B dihydrogen bond may be treated as a special type of the A-H…B hydrogen bond [30, 51]. However for two dihydrogen bonded complexes considered here, NH_4^+…HBeH and NH_4^+…HMgH, there are the $\sigma_{BeH} \rightarrow \sigma_{NH}^*$ and $\sigma_{MgH} \rightarrow \sigma_{NH}^*$ interactions, respectively. The maximum $n_O \rightarrow \sigma_{CCl}^*$ overlapping is considered for the C-Cl…O halogen bond. For hydride bonds it is the $\sigma_{Be\text{-}H} \rightarrow n_{Na}^*$ or $\sigma_{Mg\text{-}H} \rightarrow n_{Na}^*$ interaction. In the case of the hydrogen bond with π-electrons as the proton acceptor this is the $\pi_{CC} \rightarrow \sigma_{FH}^*$ interaction. The E_{NBO} designation for the $n_B \rightarrow \sigma_{AH}^*$ interaction energy (Eq. 2) and all the other related and mentioned above is further applied here.

Results and discussion

Energies and NBO parameters

Table 1 presents energetic and NBO parameters for the complexes considered in this study. These are the binding and NBO energies, ΔE and E_{NBO}, respectively. The latter energies are expressed by Eq. 2 or its modifications described in the previous section. The s-character in the A or B hybrid orbital aimed toward the H-atom is included, in the case of the halogen bond it is the Cl-atom instead of the H-atom. Table 1 also presents the polarization of the A-H (or A-Cl) and of the B-H bond (% at A or B atom). The latter two terms are named further here shortly as the s-character and the bond polarization. A and B correspond to the designations proposed previously for the Lewis acid – Lewis base interactions [39]. For example, the hydrogen bond is designated as A-H…B since the positively charged H-atom is connected with the A-center. The A-H bond belongs to the Lewis acid sub-unit of the complex while B is the Lewis base center; the O-H…O, C-H…O and F-H…π hydrogen bonds are considered here. The hydride bond where the negatively charged H-atom is situated between two electropositive centers is designated as A…H-B. Two interactions of this type, Na^+…H-Be and Na^+…H-Mg, are analyzed in this study. Two A-H…H-B dihydrogen bonds, N-H…H-Be and N-H…H-Mg are included in the sample analyzed and one complex with the A-X…B halogen bond, i.e., C-Cl…O. One can see that A and B designate the centers of the Lewis acid and Lewis base moieties, respectively. If the H-atom is connected with the A-center then it is positively charged and it acts as the electron acceptor center. Such a case is observed for hydrogen bonds and for one of H-atoms in dihydrogen bonds. The negatively charged H-atom is connected with B for the A…H-B hydride bond and for the A-H…H-B dihydrogen bond.

Table 1 The parameters of complexes analyzed in this study; the binding energy, ΔE (kcal mol^{-1}), the E_{NBO} defined by Eq. 2 (kcal mol^{-1}) or its modifications, the s-character in the hybrid A or B orbital, the polarization of A-H(Cl) or B-H bond (% at A or B) corresponding to the A or B atom indicated in column with s-character. The values given in parentheses correspond to the monomers not involved in intermolecular interactions

Complex	ΔE	E_{NBO}	s-character – A/B	Polarization
Lewis acid properties				
NH_4^+…HBeH	−9.9	15.4	28.6(25.0) – N	75.0(72.9)
NH_4^+…HMgH	−18.9	37.6	30.2(25.0) – N	76.9(72.9)
F_3CH…OH_2	−3.2	4.0	31.7(30.4) – C	58.5(56.6)
F_3CCl…OCH_2	−1.9	1.7	27.0(26.4) – C	47.3(46.7)
FH…C_2H_4	−4.2	7.3	24.5(21.1) – F	79.0(77.8)
H_2O…HOH	−4.6	7.8	26.2(23.4) – O	74.9(73.2)
Lewis base properties				
NH_4^+…HBeH	−9.9	15.4	47.8(49.9) – Be	20.5(28.1)
NH_4^+…HMgH	−18.9	37.6	46.5(49.8) – Mg	11.5(19.9)
MgH_2…Na^+	−21.9	2.4	43.2(49.8) – Mg	10.7(19.9)
BeH_2…Na^+	−12.2	1.3	46.7(49.9) – Be	19.9(28.1)

Table 1 shows the strongest interactions for the Na^+…HMgH and NH_4^+…HMgH complexes, i.e., for the hydride and dihydrogen bond, −21.9 and −18.9 kcal mol^{-1}, respectively. The halogen bond presented here is the weakest interaction among the systems considered here, i.e., −1.9 kcal mol^{-1}. This is connected with the choice of CF_3Cl sub-unit. The most positive electrostatic potential for the Cl atom (on the 0.001 au surface) for the latter moiety amounts to 16.3 au (B3PW91/6-31G** level calculations – ref. [24]) while for the Br atom of CF_3Br and the Cl atom of HCCCl it is equal to 21.3 and 20.6 au, respectively [24]. It was pointed out that the strength of halogen bond increase in the order Cl < Br < I. For example, for CF_3Cl…NH_3, CF_3Br…NH_3 and CF_3I…NH_3, the binding energies are equal to −2.3, −4.7 and −6.4 kcal mol^{-1}, respectively [24]. Generally halogen bonds are not the weakest Lewis acid – Lewis base interactions. Very often their strength is comparable with the strength of hydrogen bonds [7]. However it was pointed out [18] that hydride bonds are very strong with energies often outweighing 20 kcal mol^{-1} (if the modulus of the binding energy value is considered). The E_{NBO} energy connected with the electron charge transfer from the Lewis base to the Lewis acid is very low for the hydride bonds and for the halogen bond. And it is the greatest one for the dihydrogen bonds and next for the hydrogen bonds. It is worth mentioning that the hydride and dihydrogen bonds considered here are assisted by charge and this is the reason why such interactions may be stronger than the other ones. It was found that for the charge assisted hydrogen and dihydrogen bonds the delocalization interaction energy term is the most important attractive term [52]. The delocalization energy is approximately the sum of polarization and charge transfer energy terms. This is why the greatest charge transfer energy expressed by Eq. 2 is observed for the charge assisted dihydrogen bonds analyzed here. The greater values of binding energies for the hydride bonds are connected with the meaningful polarization and electrostatic interaction energy terms.

The s-character for the Lewis acids concerns N, C, F and O atoms connected with the hydrogen or chlorine (Table 1). One can see that it increases for complexes in comparison with corresponding monomers not involved in interactions. This effect was observed previously for the hydrogen bonded complexes [32–34] and it has been pointed out that the increase of the s-character is one of the main characteristics of hydrogen bond formation [32]. Such increase of the s-character was also observed recently for the A-X…B halogen bonds [39]. This is observed here for the hydrogen bond, halogen bond and dihydrogen bond. The increase of the s-character is accompanied by the increase of the polarization of the A-H (or A-Cl) bond (% at A). It seems that this is the common characteristic of the Lewis acid moiety in the Lewis acid – Lewis base interactions.

The reverse trends are observed for the Lewis base subunit (Table 1). The complex formation leads to the decrease of s-character (B hybrid orbital) and of the B-H bond polarization (% at B = Be, Mg). Figure 2 shows the dependence between the change of s-character and the strength of interaction. The clear relationship is not observed here; especially the C_2H_4…HF complex is out of the hardly accepted trend. The latter is probably connected with the special features of the hydrogen bonds where π-electrons play the role of the proton acceptor [53]. For example, one can observe the large delocalization energy contribution in comparison with the other attractive interaction energy terms for such interactions [52]. The other reason for the lack of correlation between the change of s-character and the strength of interaction is connected with the diversity of the sample, various complexes and different interactions are considered. However one can see that the complex formation for any interaction analyzed is connected with the increase or decrease of s-character, it depends if the Lewis acid or Lewis base moiety is considered. The correlations between the change in s-character and the parameters related to the strength of interaction were observed for the samples of complexes linked through the same kind of interactions [32–34].

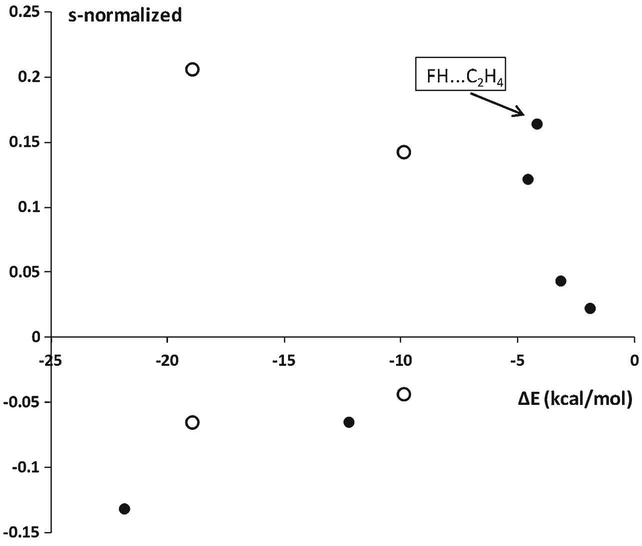

Fig. 2 The relationship between the binding energy, ΔE (kcal mol^{-1}), and the s-normalized parameter (see Eq. 3), open circles correspond to the dihydrogen bonded systems

The s-character in the A or B hybrid orbital in the complex presented in Fig. 2 is normalized in relation to the s-character for the isolated Lewis acid or Lewis base not involved in any interaction (Eq. 3).

$$s - normalized = \left(s_{complex} - s_{monomer}\right)/s_{monomer} \qquad (3)$$

The latter value is negative for the B hybrid orbital and it is positive for the A hybrid orbital (Fig. 2).

QTAIM characteristics

Table 2 presents selected QTAIM parameters for the complexes analyzed here. The electron density at the bond critical point (BCP), ρ_{BCP}, the total electron energy density at BCP, H_{BCP}, the charges of the Lewis acid and Lewis base sub-units, ΔQ, and the atomic integrated charges, q. The atomic charges concern atoms directly involved in intermolecular interactions (H and Cl atoms) and the atoms connected with the latter ones, i.e., the A and B atoms. The ρ_{BCP} and H_{BCP} characteristics concern the BCP of intermolecular contact; H…B for hydrogen bonds, H…H for dihydrogen bonds, Cl…B for halogen bond and H…A for hydride bonds. One can observe that ΔQ is negative for the Lewis acid moieties and it is positive for the Lewis bases for all complexes considered. This is connected with the common characteristic of the Lewis acid – Lewis base interaction, the electron charge transfer from the Lewis base to the Lewis acid [6]. The greatest transfer occurs for DHBs while it is meaningless for the halogen bond. There are similar observations for ρ_{BCP}, the greatest values for DHBs are observed and the smallest one for halogen bonding. This is interesting that ρ_{BCP}´s are rather low for the hydride bonds which are characterized by the large binding energies. For DHBs considered here the negative values of H_{BCP} are observed which means that these interactions are partly covalent in nature [54, 55], H_{BCP}´s for stronger hydride bonds are positive. Hence, according to the QTAIM characteristics, the hydride bonds are not covalent in nature. Figure 3 presents the relationship between the s-normalized parameter and the charge of the Lewis acid or Lewis base sub-unit, ΔQ. White circles correspond to DHBs for which the greatest ΔQ

Table 2 The selected QTAIM parameters (in au) of the complexes analyzed here; the electron density at the BCP corresponding to the intermolecular contact, ρ_{BCP}, the total electron energy density at this BCP, H_{BCP}, the charge of Lewis acid or Lewis base sub-unit, ΔQ, the charges of A or B atom q (A, B) and of H or Cl atom, q(H,Cl). The values given in parentheses correspond to the monomers not involved in intermolecular interactions

Complex	ρ_{BCP}	H_{BCP}	ΔQ	q(A,B)	q(H,Cl)
Lewis acid properties					
NH_4^+…HBeH	0.030	−0.004	−0.057	−1.063(−1.035)	0.528(0.509)
NH_4^+…HMgH	0.046	−0.014	−0.107	−1.069(−1.035)	0.528(0.509)
F_3CH…OH_2	0.014	0.002	−0.006	1.915(1.960)	0.134(0.079)
F_3CCl…OCH_2	0.013	0.001	−0.004	2.102(2.126)	−0.105(−0.129)
FH…C_2H_4	0.020	0.000*	−0.045	−0.789(−0.757)	0.744(0.757)
H_2O…HOH	0.025	0.000*	−0.018	−1.258(−1.207)	0.645(0.604)
Lewis base properties					
NH_4^+…HBeH	0.030	−0.004	0.057	1.713(1.705)	−0.825(−0.852)
NH_4^+…HMgH	0.046	−0.014	0.107	1.595(1.572)	−0.759(−0.786)
MgH_2…Na^+	0.020	0.002	0.053	1.595(1.572)	−0.815(−0.786)
BeH_2…Na^+	0.016	0.002	0.034	1.714(1.705)	−0.852(−0.852)

* positive and much smaller than +0.001 au

are observed. Additionally the dihydrogen bonds may be treated as the sub-class of hydrogen bonds and as the sub-class of hydride bonds since they possess the characteristics of both latter interactions [15, 18]. For the remaining interactions (after the exclusion of DHBs) the excellent correlation is observed. This seems to be an important finding since the complexes considered are linked through different kinds of interactions (Fig. 3).

There are other interesting results collected in Table 2. One can see that for the Lewis acid moiety, the complex formation leads to the increase of the positive charge of the atom connected with A, i.e., hydrogen or chlorine atom, q(H) or q(Cl). The only exception is the H-atom of the F-H…π hydrogen bond. The latter is probably connected with the enormous electron charge transfer as a result of complex formation into HF molecule in spite of a rather weak interaction for FH…C_2H_4 complex. It is worth mentioning that the increase of the positive charge of the H-atom in the A-H…B hydrogen bond is one of the main signatures of the existence of such an interaction [21, 37]. One can also observe (Table 2) the negative A-atom charge increase. It is connected with the increase of the polarization of the A-H (A-Cl) bond mentioned earlier here. These changes are in line with Bent´s rule [35] since the increase of the positive charge of the H or Cl atom is connected with the increase of s-character. In other words, the complex formation leads to the increase of the electropositive character of the H or Cl atom.

The changes within the Lewis base sub-unit are not as clear as for the Lewis acid. However one can see the increase of the positive charge of the B-atom. The latter observation is connected with the hydride and dihydrogen bonds where the single B-H bond plays the role of the Lewis base center. The changes of the H-atom charge of B-H bond are meaningless (Table 2).

Figure 4 presents the relationship between the s-normalized value and the integrated charge of A or B atom. The latter is normalized in the following way:

$$q(A,B) - normalized = \left[q(A,B)_{complex} - q(A,B)_{monomer}\right] / \left|q(A,B)_{monomer}\right| \tag{4}$$

q(A,B)-normalized is negative if the atomic charge decreases and it is positive if it increases in the complex in relation to the monomer. It decreases (the negative charge increases) with the increase of the s-value for the A-H (A-Cl) Lewis acid bond. For the B-H Lewis base bond the positive atomic charge of B increases with the decrease of s-character. The correlation between the q(A,B)-normalized and the s-normalized values is good, the linear correlation coefficient amounts to 0.97, if DHBs are excluded from the sample considered (Fig. 4).

Table 3 presents the geometrical QTAIM parameters; the volumes of A and B atoms of the Lewis acid and Lewis base sub-units, respectively. The volumes of H atoms connected with A and B are also included as well as the volume of the Cl atom connected with the carbon atom for the halogen bond considered here. The QTAIM volume is defined [49] as the space bounded by the intersection of the zero-flux surface or surfaces bounding the atom from the remaining part of the molecule and a chosen outer isodensity envelope (0.001 au was chosen here). Table 3 also contains the atomic radii of the atoms mentioned above for which the volumes were calculated. For example, for the A-H (A-Cl) or B-H bond there is the bond critical point which divides the bond into two radii being the distances between that BCP and the attractor corresponding to the atomic position (Chart 1). Table 3 shows that the complex formation always leads to the decrease of r(H,Cl) radius and the increase of r(A) radius. It was found previously that for hydrogen bonds such a tendency is observed [38]. If the first effect of the decrease of r(H) outweighs the second one of the increase of

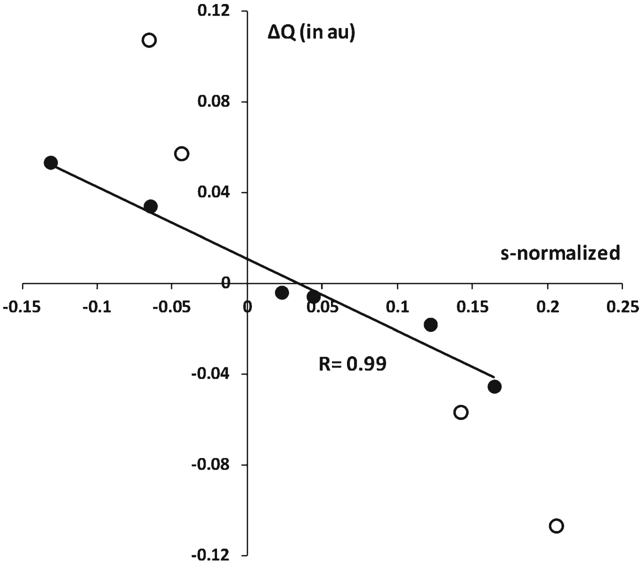

Fig. 3 The correlation between s-normalized parameter (Eq.3) and the charge (in au) of the Lewis acid (negative) or of the Lewis base (positive) sub-unit, ΔQ, open circles correspond to the dihydrogen bonded systems

r(A) then the blue-shift hydrogen bond occurs where there is the proton donating bond shortening as a result of the hydrogen bond formation. It seems that this is the general property of the A-H, A-Cl or any other Lewis acid bond participating in the Lewis acid – Lewis base interaction, i.e., the increase of A-radius and the decrease of the radius of an atom connected with A. The clear tendencies are also observed for the atomic volumes of the A-H (Cl) bond, the increase of A-volume, V(A), and the decrease of H(Cl)-volume, V(H,Cl).

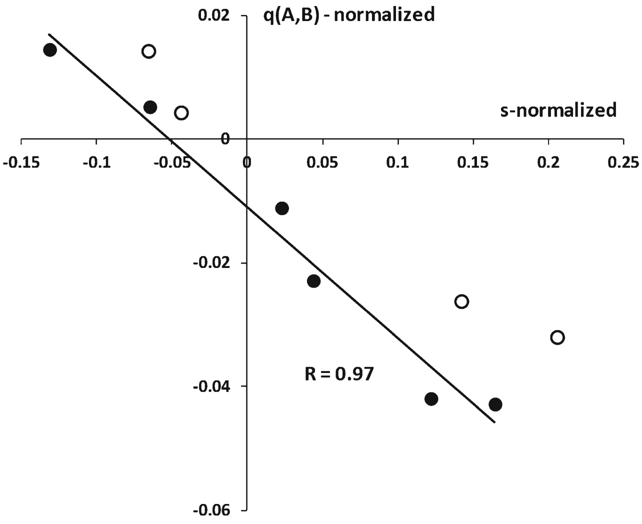

Fig. 4 The correlation between s-normalized parameter (Eq. 3) and the normalized charge, q(A,B)-normalized (see Eq. 4), of the A Lewis acid atom or the B Lewis base atom, open circles correspond to the dihydrogen bonded systems

Similarly, clear changes are observed for the atomic volumes and radii of the Lewis base B-H bond (Table 3). The increase of both B and H radii, r(B) and r(H), the increase of B-atom volume, V(B), and the decrease of H-atom volume, V(H), are observed. Approximately, the above mentioned changes are greater for stronger interactions. Figure 5 presents the relationship between the binding energy and the normalized r(A,B) radius. The normalization was performed according to Eq. 5.

$$r(A,B) - normalized = \left[r(A,B)_{complex} - r(A,B)_{monomer}\right] / r(A,B)_{monomer} \tag{5}$$

One can see that there is linear correlation between the two above mentioned parameters if only A-radius is considered, i.e., the radii of O, F and C atoms for the corresponding O-H, F-H and C-H proton donating bonds in hydrogen bonds, the N-radius for N-H bond of the dihydrogen bond and the C-radius of C-Cl bond in halogen bond. The B-radius also increases if the complex is formed (Fig. 5). It concerns Be and Mg radii for hydride and dihydrogen bonds. However, in this case, the scattering of points connected with the B-radii and the small number of complexes considered do not allow to perform a valuable statistical analysis.

Conclusions

The hyperconjugative effect of the A-H bond weakening and the rehybridization-promoted bond A-H strengthening [32] were proposed as two factors which are responsible for the electron charge redistribution in the A-H…B system. For example the increase of the negative charge of A-atom and the increase of the positive charge of H-atom are observed. The other parameters follow the above changes, the increase of the polarization of the A-H bond and the increase of s-character in A-hybrid orbital. The latter changes are in line with Bent´s rule [35]. The A-H bond length, i.e., the bond shortening or lengthening in the hydrogen bond, is controlled by a balance of these two effects. According to the other mechanism proposed [56] the withdrawal of the electron charge by A is manifested in the increase of the negative charge of A and the increase of the positive charge of H when B approaches H. In consequence, there are two factors influencing the A-H bond length, the electrostatic attractions between A and H and between H and B. The first effect is responsible for the shortening of A-H bond, the second one for its lengthening. The observations concerning the electron charge distribution in the hydrogen bonded system for this model [56] are similar to those of the concept of hyperconjugative and rehybridization effects. However it seems to be controversial to explain the complexity of the

Table 3 The geometrical QTAIM parameters (radii in Å, volumes in Å^3) of the complexes analyzed here; the radius of A or B atom, r(A,B), the radius of H or Cl atom, r(H,Cl), the corresponding volumes are presented, V(A,B) and V(H,Cl), respectively. The radii collected in this table are defined in the text and Chart 1. The values given in parentheses correspond to the monomers not involved in intermolecular interactions

Complex	r(A,B)	r(H,Cl)	V(A,B)	V(H,Cl)
Lewis acid properties				
NH_4^+…HBeH	0.803(0.776)	0.211(0.219)	16.3(16.1)	2.9(3.6)
NH_4^+…HMgH	0.827(0.776)	0.217(0.219)	16.4(16.1)	2.8(3.6)
F_3CH…OH_2	0.724(0.715)	0.339(0.350)	4.0(3.8)	5.4(6.4)
F_3CCl…OCH_2	0.782(0.778)	0.955(0.961)	2.8(2.7)	30.0(30.9)
FH…C_2H_4	0.791(0.781)	0.100(0.100)	20.6(20.2)	1.5(2.0)
H_2O…HOH	0.793(0.778)	0.142(0.151)	23.3(22.8)	2.0(3.2)
Lewis base properties				
NH_4^+…HBeH	0.580(0.571)	0.759(0.744)	3.1(3.0)	18.1(20.5)
NH_4^+…HMgH	0.893(0.870)	0.850(0.819)	12.0(12.1)	19.2(22.8)
MgH_2…Na^+	0.893(0.870)	0.850(0.819)	12.0(12.1)	21.4(22.8)
BeH_2…Na^+	0.580(0.571)	0.762(0.744)	3.1(3.0)	19.2(20.5)

hydrogen bond formation in terms of purely electrostatic model, especially to explain the changes of the charge distribution of the A-H covalent bond. There are other numerous concepts concerning the blue and red shift hydrogen bonds. For example H-index was introduced defined as the ratio between the change of electron density in the σ* antibonding A-H orbital and the total electron charge transfer from the Lewis base to the Lewis acid [57]. It was found that H-index is smaller than 0.3 for blue shift hydrogen bonds, for red shift interactions it is greater than the latter value and often close to 1. The concept of H-index allows to diversify the blue and red shift hydrogen bonds but it does not deepen the mechanisms of the electron charge distribution. The low value of H-index, below 0.3 or even close to zero, signifies that the greater part of the electron charge transferred from the Lewis base to the Lewis acid is further transferred from the A-H bond to other parts of the proton donating moiety [57, 58].

The findings presented here are in agreement with the σ-hole concept [1, 10, 24–29] and with the concept of hyperconjugative and rehybridization effects [21–23]. The first one explains why the non-covalent interaction is initiated and the second concept explains further processes of the electron charge redistribution for hydrogen bonded complex. The results presented in this study show that both concepts may be applied for all Lewis acid – Lewis base interactions. All of them are partly electrostatic interactions according to the σ-hole concept [1, 10, 24–29]. Additionally the common feature of them is the electron charge transfer from the Lewis base sub-unit to the Lewis acid sub-unit. Such an electron charge transfer influences the other parameters of complexes. For example, for the bond of the Lewis acid participating directly in the interaction, the A-H bond for the hydrogen bond or the A-Cl bond for the halogen bond, there is the increase of the positive charge of terminating atom (H or Cl). Hence the H-atom or the Cl-atom may be treated as more electropositive than it was before the complex formation. In such a way the Lewis acid – Lewis base interaction follows the Bent rule since the complex formation

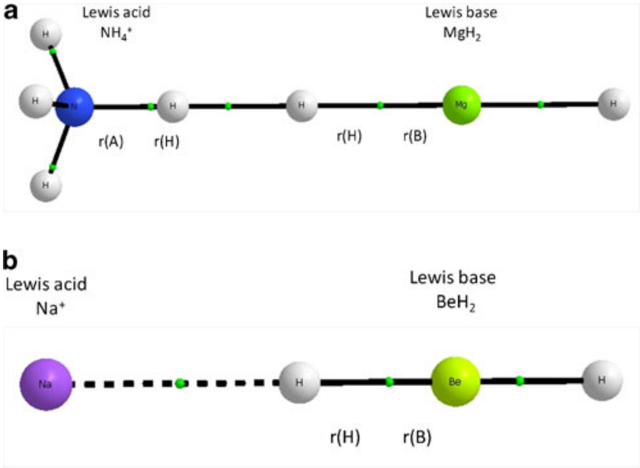

Chart 1 QTAIM atomic radii for NH_4^+…HMgH (**a**) and Na^+…HBeH (**b**) complexes

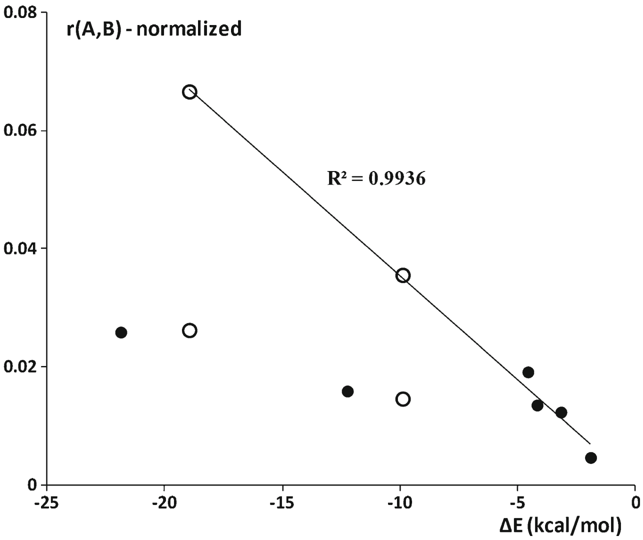

Fig. 5 The relationship between the binding energy, ΔE (kcal mol^{-1}), and the radius of A or B atom - r(A,B)-normalized parameter (see Eq. 5), open circles correspond to the dihydrogen bonded systems

leads to the increase of the s-character in the A hybrid orbital aimed to the H or Cl atom.

For the B-H Lewis base bond the complex formation is connected with the decrease in the s-character. According to Bent´s rule it should also be connected with the increase of the electronegative character of H-atom. However the changes of H-charges for the B-H bonds are not so clear (see Table 2).

There are the other changes of parameters of complexes considered. For the A-H(Cl) bond there is the decrease of H(Cl) radius and the increase of A-radius. For B-H bonds there is the increase of both B and H radii. The numerous regularities and tendencies concerning the other parameters are observed in this study.

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