



Article [FHF]⁻—The Strongest Hydrogen Bond under the Influence of External Interactions

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Abstract: A search through the Cambridge Structural Database (CSD) for crystal structures containing the [FHF]⁻ anion was carried out. Forty five hydrogen bifluoride structures were found mainly with the H-atom moved from the mid-point of the F ... F distance. However several [FHF]⁻ systems characterized by $D_{\infty h}$ symmetry were found, the same as this anion possesses in the gas phase. The analysis of CSD results as well as the analysis of results of *ab initio* calculations on the complexes of [FHF]⁻ with Lewis acid moieties show that the movement of the H-atom from the central position depends on the strength of interaction of this anion with external species. The analysis of the electron charge density distribution in complexes of [FHF]⁻ was performed with the use of the Quantum Theory of Atoms in Molecules (QTAIM) approach and the Natural Bond Orbitals (NBO) method.

Keywords: [FHF]⁻ anion; crystal structures; hydrogen bond; electron charge transfer; Quantum Theory of Atoms in Molecules; Natural Bond Orbitals method

1. Introduction

The [FHF]⁻ system has been the subject of numerous studies [1–3] since it is an example of one of the strongest hydrogen bonds (if not the strongest known) [4–7]; it is often classified as a short strong hydrogen bond (SSHB) [5,8]. The electronic structure of the [FHF]⁻ anion and of other hydrogen bihalides, [XHX]⁻, is often interpreted in terms of a three-center four-electron bond [9]; these bihalides are linear with a symmetrically shared proton [10]. In numerous studies the bond dissociation energy, D_0 , of the reaction [FHF]⁻ \rightarrow F⁻ + HF was evaluated and is located over a broad range between 35 and 60 kcal/mol [3,10]. Recent benchmark fc-CCSD(T) calculations with aug-cc-pVnZ basis sets up to cardinal number n = 7 and followed by extrapolation to the complete basis set limit, with the consideration of zero point vibration energy and contribution of the mass-dependent diagonal Born-Oppenheimer correction, results in D₀ value of 43.39 kcal/mol [3].

It seems that the hydrogen bihalides, $[XHX]^-$, described briefly here, are the only well documented systems with a symmetrical position of the H-atom, exactly in the middle of X ... X distance. The $H_5O_2^+$ and $(N_2)H^+(N_2)$ species, or others often known as proton-bound homodimers [11], were analyzed and the high level calculations show that the H-atom is slightly moved from the mid-point of the distance between the neighboring heavier centers [12]. It is situated closer to one of the neighboring electronegative centers but the potential barrier height for the proton transfer process is very low, even negligible [12]. This explains why studies on the symmetrical and unsymmetrical [FHF]⁻ systems are very interesting. The latter anion is characterized by the $D_{\infty h}$ symmetry in a gas phase [1–3] but in crystal structures shifts of the proton from the mid-point are often observed [4,13].

A brief survey of the properties of the [FHF]⁻ anion and the corresponding deuterated species, [FDF]⁻, was performed by Jeffrey [4]—these anions possess $D_{\infty h}$ symmetry in crystal structures

containing Na⁺ and K⁺ cations. However for the crystal structure with the pCH₃C₆H₅NH₂⁺ cation the H-atom is shifted from the centric position which results in the F-H distances for the [FHF]⁻ ion amounting 1.025 and 1.235 Å. Analysis on the NMR and neutron diffraction data for the [FHF]⁻ anion was performed by Panich [13]. The shorter fluorine-hydrogen distance in this species is designated as F-H, the longer one as H . . . F while the distance between fluorine atoms as F-F. These designations are retained for the results discussed by Panich as well as for the results of this study discussed herein. The relationship between the F-H and F-F distances was found and discussed [13]; one can observe shortening of the F-H distance with elongation of the F-F distance; *i.e.*, a greater H-atom shift from the central position for longer F-F distances is observed. It is worth mentioning that systems containing [FHF]⁻ ions of the D_{∞h} symmetry have been observed in LiHF₂, NaHF₂, KHF₂, CsHF₂, and Ca(HF₂)₂ structures [13].

The similar relationships between the A-H bond length and the A ... B distance were found in numerous samples of the A-H ... B hydrogen bonds analyzed both experimentally and theoretically [4]. Such relationships were described early for the O-H ... O hydrogen bonded systems in crystal structures [14–17]. It is interesting that the correlations between A-H and H ... B (or A ... B) distances are often in agreement with the simple model known as the bond number conservation rule [18,19] which is based on adaptation for triatomic systems of the concept of bond number introduced early by Pauling [20]. Numerous studies on the interrelation between this rule for triatomic A-H ... B hydrogen bonded systems and experimental or theoretical dependencies have been reported [21–25]. The rule may be briefly described for hydrogen bonds in the following way; for the A-H single bond not involved in any interaction the bond number of A-H is equal to unity; for the A-H ... B systems, the A-H bond is elongated and its bond number decreases. However the latter is compensated by H ... B contact because the sum of the A-H and H ... B bond number conservation rule was also applied to systems which are the subject of this study, *i.e.*, for the FHF hydrogen bonds [26]; the dependence derived from this rule is in excellent agreement with the geometrical experimental parameters [26].

Numerous other important studies on the [FHF]⁻ systems may be mentioned. For example, liquid state ¹H and ¹⁹F NMR studies were performed at different temperatures for hydrogen bonded complexes of the fluoride anion, F^- , with HF molecules (from one to four HF molecules) [27]. At low concentration of the HF species the bifluoride ion, [FHF]⁻, was observed, while at higher concentration of HF, [F(HF)_n]⁻ complexes (n = 2, 3, 4), are formed [27]. The low-temperature (the temperature range 94–170 K) ¹H, ¹⁹F, and ¹⁵N NMR spectra were also measured for collidine-HF mixtures in CDF₃/CDF₂Cl solvent [26]. The chemical shifts and scalar coupling constants were measured for the analyzed species which led to the determination of their composition [26]; one can mention that collidinium hydrogen difluoride is an ionic salt linked through a strong hydrogen bond [26].

The FHF hydrogen bonds were also analyzed in clusters of $[F(HF)_n]^-$, $[RF(HF)_n]$, and $[XF(HF)_n]$ where R is alkyl while X = H, Br, Cl, and F [28]. The MP2/6-31++G(d,p) calculations were performed on twenty five such complexes and it was found that the bonding character in the complexes changes from covalent to van der Waals interaction [28]. Of note is the study on the H/D isotope effects on the hydrogen bond geometries of $[F(HF)_n]^-$ complexes [29], or the studies on the significance of the hydrogenic zero-point vibrations which give rise to structural changes and to geometric H/D isotope effects in the $[FHF]^-$ ion [30,31], the latter effects were analyzed also for the low barrier N-H ... N hydrogen bonds [25]. In the study mentioned earlier [27] one-bond couplings between a hydrogen bond proton and two heavy atoms (fluorine atoms) of a hydrogen bridge were observed in the $[F(HF)_n]^-$ clusters. Further analyses of spin-spin coupling constants were performed for the $[F(HF)_n]^-$ species [32] as well as for the $[FHF]^-$ and $[FDF]^-$ ions [33].

It can be seen that there are numerous experimental and theoretical studies on the [FHF]⁻ ion and the related complexes and clusters. For the purposes of this study the most interesting are those where changes of the geometry of the hydrogen bifluoride are considered; related studies were mentioned earlier here [26–31]. The other example concerns the CID level calculations with a [3s2pld/2slp] basis

set where the transition from a centrosymmetric single minimum to a pair of equivalent minima as the inter-fluorine distance increases was observed; this transition occurs at the F-F distance approximately equal to 2.4 Å [34]. Similar conclusions were stated in the other study where the proton transfer process was also analyzed [35]. More recently the $(ROH)_n \dots [FHF]^-$ clusters (n = 1, 2 and $R = H, CH_3$, C_2H_5) were analyzed theoretically and the influence of the external O-H ... F hydrogen bonds on the position of H-atom in $[FHF]^-$ was observed [36]. The other recent and interesting theoretical study is concerned with the interrelations between the $[FHF]^-$ system and the pnicogen bonded complex [37].

The aim of this study is to analyze the geometry of the [FHF]⁻ anion, particularly the factors influencing the asymmetry of the H-atom position are considered. There have been earlier studies where the symmetric and asymmetric hydrogen bifluoride anions were considered [26–37]. However in this study the emphasis is put on electron charge redistribution being the result of complexation. That is why the Quantum Theory of Atoms in Molecules (QTAIM) [38] and the Natural Bond Orbitals (NBO) method [39,40] have been applied here. The parameters which may be treated as indicators of the hydrogen bifluoride anion asymmetry are also discussed and the examples of the crystal structures containing [FHF]⁻ anion are presented for comment. However the main topic not analyzed previously which concerns this study, is the decomposition of the [FHF]⁻ anion due to its strong, covalent in nature interactions with Lewis acid centers.

2. Experimental and Computational Section

The Cambridge Structural Database (CSD) [41] search was performed to find structures containing the [FHF]⁻ anion. The following search criteria were used: no disordered structures, no structures with unresolved errors, no powder structures, no polymeric structures, e.s.d.'s ≤ 0.005 Å, R $\leq 7.5\%$ and geometrical restrictions of F-F distance less than 2.6 Å and the F-H-F angle in the range (140°–180°). Thirty four crystal structures containing 45 unique [FHF]⁻ geometries were found. Additionally the search was performed for the sample mentioned above of crystal structures to find the Lewis acid—fluorine (F-atom belongs to the [FHF]⁻ anion) contacts, shorter than the corresponding sum of the van der Waals radii. Two hundred and ninety H ... F contacts were found corresponding to the hydrogen bond interactions and 34 other contacts (for details see the next section).

MP2/aug-cc-pVTZ calculations were performed with the Gaussian09 set of codes [42] on the $[FHF]^-$ anion and its complexes with the HF, HCl, H₂O, C₂H₂, HCN, and H₂S species. The complexes with the NH₄⁺, PH₄⁺, H₃O⁺, and H₃S⁺ cations were also calculated since strong hydrogen bonds between them and $[FHF]^-$ are expected. Additionally interactions with Li⁺ and Na⁺ cations are considered for comparison with the sample of the H-bonded systems. Figure 1 presents the molecular graphs (based on the electron charge distributions derived from the Bader theory [38]) of selected complexes considered in this study; the molecular graph of the $[FHF]^-$ ion not involved in any interaction is included for comparison.

The geometry optimizations performed on these moieties as well as on the monomeric Lewis acids led to energetic minima since no imaginary frequencies were observed for them. The interaction energies and binding energies were calculated for the complexes analyzed. The interaction energy, E_{int} , of the A ... B complex is usually defined according to the supermolecular approach [43] by the following expression—Equation (1).

$$E_{int} = E_{A \dots B} (A \dots B)^{A \cup B} - E_{A \dots B} (A)^A - E_{A \dots B} (B)^B$$

$$\tag{1}$$

The designations in parentheses correspond to systems for which energies are calculated, the superscripts correspond to the basis sets used and the subscripts relate to the optimized geometry. Thus the interaction energy is the difference between the energy of the A ... B complex and the energies of the A and B monomers. The geometry for the complex was optimized with the use of the complex $A \cup B$ basis set. The monomers are characterized by geometries taken from the complex—energies for them were calculated with the A and B monomers' basis sets.



Figure 1. Molecular graphs of selected systems analyzed here, big circles correspond to atoms, continuous and broken lines to bond paths while small, green circles to bond critical points.

The binding energy, E_{bin} , takes into account the deformation energy (E_{def}) being the result of complexation.

$$E_{bin} = E_{int} + E_{def} = E_{A...B}(A...B)^{A\cup B} - E_A(A)^A - E_B(B)^B$$
(2)

For the binding energy (Equation (2)) the energies of separately optimized monomers are considered (see the appropriate subscripts). The deformation energy defined by Equation (3) is positive since the separate molecules having geometries taken from the complex are not in energetic minima.

$$E_{def} = E_{A...B}(A)^{A} + E_{A...B}(B)^{B} - E_{A}(A)^{A} - E_{B}(B)^{B}$$
(3)

The Counterpoise (CP) correction is applied here to calculate the basis set superposition errors (BSSE) [44]. Hence the BSSE corrected interaction and binding energies, E_{int}BSSE and E_{bin}BSSE, for complexes analyzed here are also presented.

The Natural Bond Orbitals (NBO) method [39,40] implemented in the NBO 5.0 program [45] and incorporated into GAMESS set of codes [46] was applied. The NBO method was used to calculate the atomic charges of the systems considered. The Quantum Theory of "Atoms in Molecules" (QTAIM) [38] was applied for the localization of bond paths and corresponding critical points in the species analyzed. The following characteristics of BCPs corresponding to the intermolecular interactions are considered here; the electron density at BCP (ρ_{BCP}), its Laplacian ($\nabla^2 \rho_{BCP}$) and the total electron energy density at BCP (H_{BCP}). The QTAIM calculations were carried out with the use of the AIMAII program [47].

3. Results and Discussion

3.1. [FHF]⁻ Anion in Crystal Structures

Figure 2 presents two crystal structures of bis(tetramethylammonium) di-fluoro-dioxoiodide hydrogen difluoride, and tetramethylammonium hydrogen difluoride (refcodes: FAJHAA and KELRIC01, respectively) where the $D_{\infty h}$ symmetry of the [FHF]⁻ anion results from the crystal symmetry. It means that the symmetrical environment of the fluorine atoms of the hydrogen difluoride does not enforce the change of the $D_{\infty h}$ anion symmetry. Another situation is observed in the crystal structure of diphenylguanidinium hydrogen difluoride (Figure 3, refcode: IBOWOL) where the non-symmetrical environment of the [FHF]⁻ anion results in the break of the $D_{\infty h}$ symmetry since the F-H and H . . . F distances are equal to 1.14 and 1.17 Å, respectively, and the F-H-F angle amounts to 165.9°.



Figure 2. The fragments of the crystal structures of (**a**) bis(tetramethylammonium) di-fluoro-dioxoiodide (FAJHAA); (**b**) tetramethylammonium hydrogen difluoride (KELRIC01).



Figure 3. The fragment of the crystal structure of diphenylguanidinium hydrogen difluoride (IBOWOL).

Deviations from the above-mentioned $D_{\infty h}$ symmetry are observed for other crystal structures; Forty five different hydrogen bifluoride structures in 34 crystal structures were found through the Cambridge Structural Database (CSD) [41] search (see details in the former section). For example, for tetramethylammonium dihydrogen trifluoride (Figure 4, refcode: GIBGOB01) the F-H and H ... F distances are equal to 0.89 and 1.43 Å, respectively, and the F-H-F angle amounts to 177.9°. X-ray crystal structures are considered here since only one structure of the search used results from neutron diffraction measurement. For the X-ray crystal structures the positions of the H-atoms are not as accurate as the positions of heavier atoms. It is worth mentioning that several neutron diffraction [FHF]⁻ structures [4,13] discussed briefly in the introduction are usually not classified as organic or organometallic structures and thus not inserted in the CSD [41].

One can see that for the GIBGOB01 structure (Figure 4) one of the F-centers of the $[FHF]^-$ anion is strongly affected by the proximity of the HF molecule. In principle the $[FHF]^-$... HF system may

be treated as an $F_3H_2^-$ anion since it is characterized by C_{2v} symmetry with symmetry equivalent positions of the H-atoms.



Figure 4. The fragment of the crystal structure of tetramethylammonium dihydrogen trifluoride (GIBGOB01).

For the 45 hydrogen bifluoride anions found in the crystal structures the F-centers' intermolecular contacts were analyzed here; the rough criterion for contacts to be shorter than the sum of the corresponding van der Waals radii was applied. It is interesting that 290 F ... H contacts were found and only 34 contacts between fluorine centers and the other non-hydrogen atoms (Z-atoms). However for the latter F ... Z contacts, Z is mainly nitrogen or oxygen belonging to O-H or N-H proton donating bond or a cation of a transition metal. Only in one case, an F ... S interaction with a positively charged sulfur atom is observed. The contacts with the N or O centers result from the N-H ... F and O-H ... F hydrogen bonds being far from linearity thus they correspond to the sample of 290 F ... H interactions mentioned earlier. One can see that all short intermolecular contacts of the [FHF]⁻ ions concern interactions with the Lewis acid centers, mainly with H-atoms. It means that in crystal structures the [FHF]⁻ anion forms mainly hydrogen bonds with proton donating moieties and interactions with other Lewis acid centers are rather rare. The strong Lewis base properties of the [FHF]⁻ anion may be explained by the negative electrostatic potential of the whole isosurface of this anion (0.001 au electron density isosurface is considered). A minimum electrostatic potential for this isosurface is equal to -0.234 hartrees, *i.e.*, -614.4 kJ/mol (calculated at MP2/aug-cc-pVTZ level).

3.2. The Geometry of the [FHF]⁻ Anion

The results of the CSD search presented in the former section show that in the crystal structures the $[FHF]^-$ anion interacts with the Lewis acid centers, in particular through the hydrogen bonds since F ... H contacts are most often observed. This is why the MP2/aug-cc-pVTZ calculations were performed here on the $[FHF]^-$ complexes with the proton donating species; the interactions with the Li⁺ and Na⁺ cations are also considered for comparison (Figure 1). If in the complexes only the geometry of the hydrogen bifluoride is considered, one can consequently divide them into three groups. Equal distances between the H-atom and the fluorine atoms are observed for the first group containing the isolated $[FHF]^-$ anion and its two complexes with Li⁺ and Na⁺ (Figure 1). It was mentioned earlier that free $[FHF]^-$ is characterized by the $D_{\infty h}$ symmetry; however in the complexes with lithium and sodium cations this anion is not linear and it possesses C_{2v} symmetry, the same as for the whole corresponding complexes.

For the second group of complexes the hydrogen bifluoride anion preserves its identity since it may be treated as an integral unit. These are the complexes with H_2O , C_2H_2 , HCN, and HF which

act as Lewis acids but particularly they may be considered here as Brønsted acids since they are the proton donating species in the hydrogen bonds formed. The [FHF]⁻ structure for the latter complexes is not destroyed since interactions between the hydrogen bifluoride and the Brønsted acid moieties occurring here are not so strong—discussed in the next sections. One can see that the [FHF]⁻ ... HF complex of the C_{2V} symmetry (Figures 1 and 4) may be also treated as interaction of two HF molecules with the central F^- anion.

The strong $[FHF]^-$ –Brønsted acid interactions enforce great structural changes of the $[FHF]^$ moiety for the third group of complexes. These are complexes with HCl, H₂S, NH₄⁺, PH₄⁺ H₃O⁺ and H₃S⁺ which may be also considered as clusters where the HF ... HF dimer interacts with the Cl⁻, SH⁻, NH₃, PH₃, H₂O, and H₂S species, respectively (Figure 1 presents the complexes with H₃O⁺ and HCl). In this group of complexes the $[FHF]^-$ ion does not preserve its identity.

Table 1 presents the geometrical parameters of the [FHF]⁻ anion in the analyzed complexes. The linearity of the hydrogen bifluoride is only slightly disturbed by external interactions with neutral species; in the case of interactions with cations there are greater deviations from linearity because the F-H-F angle amounts here to $\sim 151-167^{\circ}$. Figure 5 presents the relation between the F-H and H ... F distances; there is a second order polynomial regression for the theoretical results ($R^2 = 0.983$). The experimental results taken from CSD are included for comparison (the geometrical parameters of [FHF]⁻ anion in the crystal structures are collated in the Supplementary Material, Table S1). In general, the experimental results are in agreement with the results of the calculations. One can see that a greater disagreement between experimental and theoretical results occurs for greater F ... H distances. It may be an effect of packing forces; intermolecular distances in crystals are usually shorter than in a gas phase [48,49] and this effect may result in the compression of the [FHF]⁻ anion. Additionally the X-ray results are analyzed here and the X-ray bonds containing H-atoms are shorter than the neutron diffraction counterparts [50]. In the former case the bond length is determined as the distance between electron density maxima while in the latter case as the distance between nuclei [50], thus these experimental techniques present different physical properties of the structures analyzed. One can see that the neutron diffraction bond length is in accordance with the accepted understanding of the chemical bond length. However the X-ray results are presented in Figure 5 only to show that the experimental tendency is roughly in agreement with the theoretical relationship. Figure 5 presents also the continuous line passing through the points corresponding to the hydrogen bifluoride anions possessing $D_{\infty h}$ and C_{2v} symmetries; theoretical results are presented (free [FHF]⁻ anion and its complexes with Na⁺, Li⁺ cations) as well as species found in the crystal structures.

Complex	F-H	$H \dots F$	F-F	F-H-F	F H(Li ⁺ , Na ⁺)
[FHF] ⁻	1.143	1.143	2.286	180.0	-
[FHF] ⁻ H ₂ O	1.036	1.284	2.320	179.1	1.565
$[FHF]^{-} \dots C_2H_2$	1.049	1.263	2.311	179.7	1.672
[FHF] ⁻ HCN	1.013	1.333	2.345	179.5	1.469
[FHF] ⁻ HF	1.008	1.343	2.351	178.4	1.343
[FHF] ⁻ HCl	0.956	1.535	2.488	174.6	1.026
[FHF] [−] H ₂ S	0.963	1.499	2.460	176.2	1.077
$[FHF]^{-} \dots NH_4^{+}$	0.943	1.648	2.555	160.2	0.995
[FHF] ⁻ H ₃ O ⁺	0.939	1.721	2.593	152.9	0.959
$[FHF]^- \dots PH_4^+$	0.933	1.734	2.651	167.0	0.947
$[FHF]^{-} \dots H_3S^{+}$	0.935	1.744	2.641	159.7	0.947
[FHF] ⁻ Li ⁺	1.148	1.148	2.224	151.2	1.801
[FHF] ⁻ Na ⁺	1.151	1.151	2.274	162.4	2.289

Table 1. The geometrical parameters (Å, degrees), F-H and H . . . F are distances within $[FHF]^-$ anion, F-H-F is the angle of this anion, F . . . $H(Li^+, Na^+)$ is the distance between the F-center of the anion and the external Lewis acid center.

Table 1 shows the F ... H contacts corresponding to the interactions of the [FHF]⁻ anion with Brønsted acids. The cation ... F distances for complexes with Li⁺ and Na⁺ are also presented, they are equal to 1.80 and 2.29 Å, respectively and are greater than the F ... H distances. This may be connected with the greater radii of these cations than of the H-atom. However it may also result from the nature of interactions; for complexes with Li⁺ and Na⁺ cations electrostatic interactions are the most important attractive ones while for the remaining complexes charge transfer and polarization interactions play the major role.

The external F ... H distance is situated between 0.95 Å and 1.67 Å. For the third sub-group of complexes mentioned earlier the F ... H distances are close to 1 Å (or even less). It means that for this group two HF molecules are formed—the hydrogen bifluoride does not preserve its identity. It also means that for this group of complexes the F ... H external distance is just the H-F bond length for the newly formed hydrogen fluoride molecule. Such short distances were not detected for 290 F ... H contacts found here in the crystal structures. Only in four cases were the F ... H distances situated in the (1.20 Å; 1.43 Å) range. However these distances are observed in the [FHF]⁻ ... HF complex. This complex was observed in earlier studies [27–29] and is also analyzed here; it possesses C_{2v} symmetry and may be considered as the $F_3H_2^-$ anion. The (MP2/aug-cc-pVTZ level) F-H and H ... F distances calculated here for this complex are equal to 1.008 and 1.343 Å, respectively (Table 1) which is in agreement with the previous MP2/6-31+G** calculations where 1.012 and 1.349 Å distances were found [27].



Figure 5. The dependence between the F-H and H...F distances in the $[FHF]^-$ species interacting with Lewis acid centers; open circles—theoretical results, full circles—experimental data taken from the Cambridge Structural Database (CSD); R² is the squared correlation coefficient (for this figure and other ones presented in this study). The solid line passing through the structures of the D_{∞h} and C_{2v} symmetries is presented.

3.3. Interactions of the [FHF]⁻ Anion

Table 2 presents the binding energies and interaction energies, defined earlier, for the analyzed complexes; these energies corrected for BSSE are also included as well as the deformation energies. The deformation energy is the loss of energy from the result of the change of geometries of the interacting species after complexation [51,52]. This loss of energy is compensated by the stabilizing, attractive interaction in the complex which as a whole is in the energetic minimum.

One can see (Table 2) that the strongest interactions (characterized by "the most negative values") exist for the mentioned earlier third group of complexes as well as for complexes with Li^+ and Na^+ cations. However for the former complexes the interactions correspond to the F ... H contacts which possess characteristics of covalent bonds (the F ... H distances of ~1Å); the [FHF]⁻ anions are

destroyed here followed by the formation of two HF molecules. This formation is connected with the large deformation energies between 137 and 355 kJ/mol (Table 2). The structural changes observed are connected with large electron density redistributions which usually correspond to large attractive charge transfer and polarization interactions. The latter interactions are often attributed in the literature to covalency [53]. For complexes with sodium and lithium cations much lower deformation energies are observed, 9.6 and 26.8 kJ/mol, respectively, and the structure of hydrogen bifluoride is preserved; it may be connected with much lower contributions to the interaction energies coming from the polarization and charge transfer effects. Hence for the two latter complexes, with Li⁺ and Na⁺ cations, electrostatic interactions should be dominant. For the remaining complexes the interaction energy (corrected for BSSE) is situated approximately in the range between -57 kJ/mol to -144 kJ/mol; thus these interactions are not so weak. One can see (Table 2) that the binding energies are "less negative" than the corresponding interaction energies. The latter results from the positive deformation energies' contributions included in the binding energies.

Table 2. The interaction and binding energies, E_{int} 's and E_{bin} 's, for complexes analyzed here, the basis set superposition errors (BSSE) corrected values are also given, E_{int} BSSE's and E_{bin} BSSE's, respectively; the deformation energies, E_{def} 's, are included (all energies in kJ/mol).

Complex	Eint	E _{int} BSSE	E _{bin}	E _{bin} BSSE	E _{def}
[FHF] ⁻ H ₂ O	-80.8	-77.4	-72.4	-69.0	8.8
$[FHF]^- \dots C_2H_2$	-60.7	-57.3	-54.4	-50.6	6.7
[FHF] ⁻ HCN	-124.7	-120.1	-106.3	-101.7	18.4
[FHF] ⁻ HF	-148.1	-143.5	-121.8	-117.2	26.4
[FHF] ⁻ HCl	-332.2	-324.3	-146.9	-139.3	184.9
$[FHF]^{-} \dots H_2S$	-212.1	-204.6	-74.9	-67.4	137.2
$[FHF]^{-} \dots NH_4^{+}$	-860.6	-852.3	-592.9	-584.5	267.8
[FHF] ⁻ H ₃ O ⁺	-1077.4	-1068.6	-741.8	-733.0	335.6
$[FHF]^- \dots PH_4^+$	-975.8	-967.4	-620.7	-612.4	355.1
$[FHF]^{-} \dots H_3S^{+}$	-1021.7	-1012.9	-708.6	-699.7	313.2
[FHF] ⁻ Li ⁺	-701.7	-698.7	-674.9	-672.0	26.8
[FHF] ⁻ Na ⁺	-566.5	-564.8	-556.9	-554.8	9.6



Figure 6. The second order polynomial relationship between the F-H distance and the deformation energy. Two cases of [FHF]⁻ ... Li⁺ and [FHF]⁻ ... Na⁺ are not included in this relation, however they are presented in the figure (squares).

Figure 6 presents the second order polynomial relationship between the F-H length in the [FHF]⁻ anion and the deformation energy. The F-H geometrical parameter shows the movement of the H-atom from its central position, this distance is shorter for stronger interactions of the hydrogen bifluoride

ion with the Brønsted acids (Table 1). The greater H-atom movement, *i.e.*, the shorter F-H distance, is connected with the greater deformation of this anion. In extreme cases of very strong hydrogen bonds, such as complexes with HCl, NH_4^+ or other complexes of this group, this movement leads to the destruction of the anion and to the formation of two HF molecules. Extremely short F-H distances in the latter complexes are typical for covalent bonds. Hence the relationship presented in Figure 6 illustrates the nature of the above mentioned deformation in that it is connected mainly with the position of the H-atom within the [FHF]⁻ anion. Two complexes with Na⁺ and Li⁺ are presented in Figure 6 for comparison with the H-bonded systems. They are characterized by the central position of the H-atom (only the F-H-F angle is slightly out of linearity) thus the deformation energy is low as was described earlier.

3.4. The Electron Charge Redistribution

Table 3 presents the Natural Bond Orbitals (NBO) [39,40] atomic charges as well as the NBO electron charge, El_{trans} , transferred in complexes from the [FHF]⁻ anion to the Lewis acid. One can see that the lowest El_{trans} values occur for complexes with lithium and sodium cations, values of 22 and 9 milielectrons, respectively. It means that the charge transfer and polarizations effects for these complexes are not as important as for the remaining complexes; the latter confirms the conclusions from the previous sections. The greatest El_{trans} values, between 230 and 380 milielectrons, are observed for those complexes where the hydrogen bifluoride structure is not preserved.

Table 3 shows that for the [FHF]⁻ anion the fluorine atom being in contact with the Lewis acid is "more negative" than the further placed F-atom. The greater differences between F-atom charges occur for the group of complexes with weaker interactions where the structure of [FHF]⁻ is preserved; the greatest difference of 100 milielectrons occurs for the complex with water. For the group of complexes with stronger interactions, there the fluorine being in contact with the H-atom Brønsted acid center practically belongs to the new HF molecule, formed as a result of complexation. The symmetrical distribution of the electron density is observed for complexes with Li⁺ and Na⁺ thus the F-atoms' charges are equal to each other, and there is only a slight electron charge shift, El_{trans}, from [FHF]⁻ thus the Li⁺ and Na⁺ ions possess charges very close to unity, +0.978 au and +0.991 au, respectively. Hence for the latter complexes the interactions may be classified as those between ions: between the [FHF]⁻ anion and the sodium or lithium cation. It is worth mentioning that for all [FHF]⁻ species (Table 3) the H-atom charge is situated in the range between +0.572 and +0.602 au, this means that the hydrogen bifluoride does not have the composition of two fluorine anions and a proton since within this species the large electron charge density shift is observed; from the terminal F-atoms to the H-atom center.

Table 3. The Natural Bond Orbitals (NBO) atomic charges (in au) in the $[FHF]^-$ anion, Q_{F1} , Q_H and Q_{F2} (free anion and its complexes are presented); Q_{F2} designates the charge of fluorine being in contact with external Lewis acid, Q_{Hext} is the charge of the external H-atom (or the charge of the Li⁺, Na⁺ ion), El_{trans} is the electron charge transfer from $[FHF]^-$ to the Lewis acid (in au).

Complex	Q _{F1}	Q _H Q _{F2}		Q _{Hext}	El _{trans}	
[FHF] ⁻	-0.790	0.581	-0.790	-	0.000	
[FHF] ⁻ H ₂ O	-0.725	0.595	-0.825	0.544	0.045	
$[FHF]^{-} \dots C_2H_2$	-0.733	0.593	-0.820	0.323	0.040	
[FHF] ⁻ HCN	-0.706	0.598	-0.805	0.341	0.088	
[FHF] ⁻ HF	-0.702	0.599	-0.794	0.599	0.103	
[FHF] ⁻ HCl	-0.644	0.601	-0.688	0.533	0.269	
$[FHF]^- \dots H_2S$	-0.654	0.602	-0.711	0.492	0.237	
$[FHF]^{-} \dots NH_4^+$	-0.617	0.590	-0.657	0.574	0.316	
[FHF] ⁻ H ₃ O ⁺	-0.608	0.591	-0.626	0.596	0.357	
$[FHF]^{-} \dots PH_4^+$	-0.598	0.581	-0.616	0.569	0.367	
$[FHF]^{-} \dots H_3S^{+}$	-0.599	0.583	-0.608	0.575	0.377	
[FHF] ⁻ Li ⁺	-0.775	0.572	-0.775	0.978	0.022	
[FHF] ⁻ Na ⁺	-0.782	0.573	-0.782	0.991	0.009	

3.5. The Analysis of QTAIM Parameters

The Quantum Theory of Atoms in Molecules (QTAIM) [38] calculations were performed here. Table 4 presents characteristics of the bond critical points of the analyzed complexes. The bond critical points (BCPs) within the [FHF]⁻ anion are analyzed; for the F-H and H ... F interactions, as well as the critical point corresponding to the interaction with the Lewis acid, *i.e.*, corresponding to the F ... H contact (or to the contacts with Na⁺ and Li⁺). All F-H interactions within anions, that is those which concern the shorter fluorine-hydrogen distances, may be treated as covalent bonds. The latter is supported by the characteristics of the F-H BCP; large values of the electron density at BCP, ρ_{BCP} , as well as negative values of the laplacian of the electron density at BCP, $\nabla^2 \rho_{BCP}$. The negative value of $\nabla^2 \rho_{BCP}$ is connected with the concentration of the electron density in the interatomic region [38] thus it is often treated as a signature of the covalent character of interaction. In the case of free [FHF]⁻ and complexes with monatomic cations the same characteristics of the second interaction are observed due to the symmetry of the anion. For the remaining systems the further H ... F interaction in the anion is characterized by the positive value of $\nabla^2 \rho_{BCP}$; however the total electron energy density at BCP, H_{BCP}, is negative in this case. It means that these interactions may be classified at least as partly covalent in nature [54,55].

Table 4. The Quantum Theory of Atoms in Molecules (QTAIM) characteristics of bond critical points (BCPs) (in au). The ρ , $\nabla^2 \rho$ and H values designate the electron density at the BCP, its laplacian and the total electron energy density at the BCP, respectively. F-H and H ... F subscripts correspond to distances within the [FHF]⁻ anion, F ... H subscript stands for the contact between the F-atom and the external Lewis acid center (H, Li⁺ or Na⁺).

Complex	ρ_{F-H}	$\nabla^2 \rho_{F-H}$	\mathbf{H}_{F-H}	$\rho_{H\ldotsF}$	$ abla^2 ho_{H \dots H}$	H _H F	$\rho_F \ldots {\bf H}$	$ abla^2 ho_F \dots H$	$H_{F \dots H}$
[FHF] ⁻	0.176	-0.572	-0.257	0.176	-0.572	-0.257	-	-	-
[FHF] ⁻ H ₂ O	0.241	-1.537	-0.489	0.116	0.047	-0.086	0.055	0.145	-0.015
$[FHF]^- \dots C_2H_2$	0.232	-1.412	-0.460	0.124	0.000	-0.102	0.043	0.137	-0.006
[FHF] ⁻ HCN	0.261	-1.807	-0.552	0.101	0.112	-0.061	0.074	0.157	-0.026
[FHF] ⁻ HF	0.264	-1.870	-0.567	0.098	0.121	-0.057	0.098	0.121	-0.057
[FHF] ⁻ HCl	0.318	-2.706	-0.767	0.056	0.146	-0.016	0.250	-1.680	-0.516
$[FHF]^{-} \dots H_2S$	0.309	-2.581	-0.737	0.063	0.150	-0.020	0.217	-1.191	-0.400
$[FHF]^{-} \dots NH_4^{+}$	0.335	-2.889	-0.815	0.043	0.129	-0.008	0.280	-2.008	-0.605
[FHF] ⁻ H ₃ O ⁺	0.340	-2.952	-0.829	0.036	0.120	-0.004	0.316	-2.622	-0.749
[FHF] [−] PH ₄ ⁺	0.348	-3.022	-0.850	0.033	0.113	-0.003	0.331	-2.754	-0.783
$[FHF]^{-} \dots H_3S^{+}$	0.346	-3.000	-0.843	0.033	0.113	-0.003	0.332	-2.769	-0.786
[FHF] ⁻ Li ⁺	0.178	-0.540	-0.253	0.178	-0.540	-0.253	0.038	0.340	0.013
[FHF] ⁻ Na ⁺	0.174	-0.539	-0.248	0.174	-0.539	-0.248	0.020	0.153	0.007

It is interesting that for complexes with NH_4^+ , PH_4^+ , H_3S^+ and H_3O^+ cations, the H_{BCP} values for $H \dots F$ are still negative but very close to zero, between -0.008 and -0.003 au. The latter shows the interaction possesses low covalent character. In fact for these complexes the strongest interactions of hydrogen bifluoride with Lewis acid moieties are observed (Table 2) and the $H \dots F$ BCPs discussed here are concerned rather with the intermolecular $H \dots F$ contacts between two HF molecules since the complexation leads to the decomposition of the [FHF]⁻ species.

For the BCPs corresponding to the F ... Li⁺ and F ... Na⁺ interactions in the [FHF]⁻ ... Li⁺ and [FHF]⁻ ... Na⁺ complexes, the H_{BCP} values are positive which indicate interactions between closed-shell systems. The lack of covalency for these interactions (or only its low contribution) and the strong total interactions (see Table 2 where interaction energies corrected for BSSE are equal to -699 and -565 kJ/mol) suggest a great contribution of electrostatic interactions to the stabilization of these systems. For the remaining complexes the H_{BCP} values of F ... H contacts are negative thus these interactions are at least partly covalent in nature. In the case of the [FHF]⁻ ... HCCH complex a rather low 0.043 au value of ρ_{BCP} is observed for the external F ... H interaction. The corresponding H_{BCP} value is very close to zero, -0.006 au which may suggest the weakest interaction occurs here. It is supported by a still strong interaction but the weakest interaction in the sample analyzed; the energy of interaction amounts to -57 kJ/mol (Table 2).

Figure 7 shows how the electron charge transfer, El_{trans}, from the [FHF]⁻ anion to the Brønsted acid influences the electron density at the BCPs discussed above. The complexes with Na⁺ and Li⁺ are excluded from the relationships but the free [FHF]⁻ anion is included in Figure 7 for comparison.



Figure 7. The relationships between the electron shift, El_{trans} (in au), and (**a**) ρ_{FH---} electron density at the BCP of the F-H of [FHF]⁻; (**b**) $\rho_{H...F}$ —electron density at BCP of the H ... F of [FHF]⁻; (**c**) $\rho_{F...H}$ —electron density at BCP of the external [FHF]⁻—Brønsted acid contact.

It was discussed earlier that a greater El_{trans} is connected with a greater deformation of the hydrogen bifluoride structure, thus the greatest El_{trans} values are observed for those systems where the [FHF]⁻ anion structure is destroyed. Figure 7a shows that for the F-H interaction the greater ρ_{BCP} value is observed for greater El_{trans} (second order polynomial correlation); this is connected with the strengthening of the F-H interaction and the shortening of the corresponding F-H distance. The further interaction in the anion, *i.e.*, the H ... F one, is weakened for greater El_{trans} which is reflected by the lower values of ρ_{BCP} (Figure 7b, second order polynomial relationship). Finally greater El_{trans} is connected with stronger F ... H interactions between the [FHF]⁻ anion and the external Brønsted acid, the ρ_{BCP} value increases for such interactions with the increase of El_{trans} (Figure 7c,

linear correlation) up to such cases where F-H covalent bonds are formed (complexes with H_2S , HCl, NH_4^+ , PH_4^+ , H_3O^+ or H_3S^+).

Figure 8 shows the molecular graphs of the selected species analyzed in this study; the isolines of laplacian of electron density are also presented, positive values of laplacian are depicted in solid lines and negative values in broken lines. The negative laplacian values show the regions of concentration of electron density while the positive values of its depletion [38]. It can be seen that for the [FHF]⁻ anion the electron density concentration occurs around the fluorine and hydrogen atoms' nuclei. The concentration of the electron charge close to the H-atom nucleus confirms the earlier observations performed here of the electron charge shifts from F-atoms to the center of the hydrogen bifluoride anion. Besides, both BCPs are situated in the region of negative laplacian which confirms the covalent character of both fluorine-hydrogen interactions in the [FHF]⁻ ion. A similar situation is observed for the [FHF]⁻ ...Li⁺ complex (and [FHF]⁻...Na⁺ not presented in Figure 8). However, as it was mentioned earlier, the [FHF]⁻ anion is not linear in the latter complexes due to electrostatic interactions with the Li⁺ (or Na⁺) cation, and it is characterized by C_{2v} symmetry.



Figure 8. The molecular graphs of [FHF]⁻, [FHF]⁻...Li⁺, [FHF]⁻...HCCH, [FHF]⁻...HF and [FHF]⁻...H₃O⁺. Solid and broken lines correspond to bond paths, big circles to attractors, and small green circles to BCPs, isolines of laplacian of electron density are presented; positive values are depicted in solid lines and negative values in broken lines.

The movement of the H-atom to one of the fluorine centers in the [FHF]⁻ ion is observed for its complex with acetylene (Figure 8). This movement is connected with the strengthening of one of the interactions (F-H) and the weakening of the second one (H...F). The linearity of the [FHF]⁻ ion is preserved in this complex. A slightly different situation is observed for the [FHF]⁻...HF complex. Figure 8 shows that the species may be considered as the symmetrical (C_{2y} symmetry) $F_3H_2^-$ anion; two H-atoms are moved to the terminal fluorines while the central F-atom may be treated as an F⁻ ion; in other words this system may be considered as a F^{-} ...(HF)₂ cluster. A quite different situation is observed for the $[FHF]^- \dots H_3O^+$ complex where the hydrogen bifluoride structure is completely destroyed and the whole system may be considered as a H₂O ... HF ... HF cluster. Even continuous areas of negative laplacian values for H-F bonds of the hydrogen fluoride molecules are observed (Figure 8). A similar situation occurs for complexes with the H₂S, HCl, PH₄⁺, and H₃S⁺ Brønsted acids as well as for the $[FHF]^- \dots NH_4^+$ complex which may be considered as complexes with a separated HF ... HF system. It is worth mentioning that the H₃N ... HF ... HF cluster was analyzed both experimentally by rotational spectroscopy and theoretically by *ab initio* calculations [56]. Two well defined HF molecules were found for this system [56]; additionally this cluster was compared with the $H_3N \dots$ HF complex since the cooperativity effects were analyzed. It was found that the $H_3N \dots$ HF interaction is stronger in the triad than in the corresponding diad [56].

4. Conclusions

It was confirmed in this work that the [FHF]⁻ anion, which is linear and centrosymmetric in the gas phase, is often deformed in crystal structures due to interactions with Lewis acids, mainly from external hydrogen bonds. The asymmetry of the hydrogen bifluoride anion has been observed and discussed in numerous earlier studies. Such deformation is characterized mainly by the movement of the H-atom in the anion towards one of the fluorine atoms situated further from the Lewis acid than the other F-center of the anion. This movement is accompanied by a slight deformation of the F-H-F angle from the linear.

It was found here that in the case of very strong interactions with an external moiety the decomposition of the [FHF]⁻ anion is observed with the creation of two HF molecules interacting with the deprotonated species; the following systems are observed in such a case; FH ... FH ... B, where B designates the Lewis base center (N, P, O or S in this study). The interaction of hydrogen bifluoride with HF leads to system which may be considered as [FHF]⁻ ... HF on the one hand and as a F⁻ ... (HF)₂ cluster on the other hand. Such a system has been analyzed previously both experimentally and theoretically [27–29].

Numerous interrelations between energetic, geometrical, and topological parameters were found for the species considered here. The electron charge distribution, described by the QTAIM and NBO parameters, follows geometrical dependencies.

It is interesting that the decomposition described here of hydrogen bifluoride is typical for some moieties commonly known as super-acids [57,58]. For example HBF₄, HSbF₆, HPF₆ or HB(C₆F₅)₄ acids do not exist because of such decomposition, for the HB(C₆F₅)₄ moiety the cleavage of a B-C bond is observed, similarly HBF₄ should be treated as a HF ... BF₃ complex linked through a strong F ... B interaction. For the complexes analyzed here the decomposition of the hydrogen bifluoride anion followed by the formation of two HF molecules is connected with large electron charge density shifts from this anion to the Lewis acid moiety.

Supplementary Materials: The following are available online at www.mdpi.com/2073-4352/6/1/3/s001, Table S1: Geometrical parameters (Å, degrees) for the [FHF]⁻ anions found in crystal structures through the CSD search; refcodes and R-factors for the crystal structures are included in the table.

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