Unconventional F–H⋯π hydrogen bonds — ab initio and AIM study

Sławomir Wojtulewski, Sławomir J. Grabowski*

Institute of Chemistry, University of Białystok, Al.J. Piłsudskiego 11/4, 15-443 Białystok, Poland

Abstract

Ab initio HF/6-311++G** and MP2/6-311++G** calculations on complexes of hydrogen fluoride with acetylene and its derivatives have been performed to study the unconventional F–H⋯π hydrogen bonding. The results show that topological parameters of the Bader theory correlate better with H-bond strength than geometrical parameters. The changes of proton donating molecule (HF) due to dimerization also reflect well the H-bond strength. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Unconventional H-bonds; The Bader theory; Acetylene complexes; H-bond strength

1. Introduction

An important assumption in many studies of crystal engineering is the dominance of strong H-bonds like O–H⋯O and N–H⋯O interactions in determining stable crystal packing [1]. However more recently, weaker interactions such as unconventional H-bonds: C–H⋯O, C–H⋯π, O–H⋯π and others have been investigated in terms of their influence on the arrangement of molecules in crystals [2–5]. It was also pointed out that the unconventional H-bonds may belong to the strong ones. For example, ab initio MP2/6-311++G(3d,3p) calculations on H_3N^+–CH_2^- complex with acetylene have indicated the C–H⋯C hydrogen bond energy of −8.2 kcal/mol [6]. The MP2/6-311++G** calculations made on the other unconventional H-bonds — dihydrogen bonded systems, show that for some cases the H-bond energy

may be of about −10 kcal/mol or even less, for example for NaH⋯HF complex it amounts to −13.8 kcal/mol [7]. HF/6-31G**, MP2/6-311++G** and B3LYP/6-311++G** calculations have been performed on the complexes formed between hydrogen fluoride and a series of π-systems (acetylene, ethylene, cyclopropene, cyclobutadiene, and benzene) and three-membered-ring derivatives (cyclopropane and tetrahedrane)[8]. The results of this study show that the interaction energies for such systems are around −3 kcal/mol; for the complexes of hydrogen fluoride with ethylene and cyclobutadiene, this energy goes up to −4.1 and −4.4 kcal/mol, respectively at B3LYP level and −3.4 and −3.6 kcal/mol, respectively at MP2 level [8].

It was found that H-bond energy often correlates with different geometrical parameters. For O–H⋯O systems it is the correlation with H⋯O distance or O–H bond length [9]. Recently the nature of hydrogen bonding has been often studied using the atoms-in-molecules (AIM) theory of Bader [10], which is

---

* Corresponding author. Fax: +48-85-745-7581.
  E-mail address: slagra@noc.uwb.edu.pl (S.J. Grabowski).

F
|
H
⋮
X—C≡C—Y
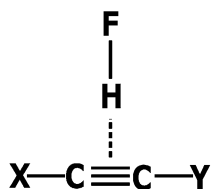
Scheme 1.

based on a topological analysis of the electronic charge density (ρ). For a case of O–H⋯O intermolecular hydrogen bonds in water and methanol clusters, a linear correlation between the charge density at H⋯O bond critical point and the strength of H-bond was reported [11]. The correlations between H-bond energy and geometrical or topological parameters were also found for the other O–H⋯O systems [12] and even for unconventional dihydrogen bonds [13,14]. It seems that a reasonably good correlation may be found for stronger H-bonds but not for weak interactions.

The aim of the present work is to study unconventional H-bonded systems with π-electrons as proton acceptors. Acetylene molecule and its simple derivatives were chosen as Lewis bases and HF molecule as a proton donating system. This study is related to the earlier studies on H⋯π interactions [8]. However, the main aim of the present paper is to investigate the correlations between the geometrical and topological parameters and to show the differences for such correlations between the unconventionally H-bonded systems as those studied here and the conventional H-bridges. Additionally the emphasis is made here on the parameters of HF proton donating molecule within the H-bonded complexes.

2. Computational details

All the computations were performed using GAUSSIAN 98 series of programs [15]. Geometry optimizations of the monomers and complexes reported in this study were carried out at HF/6-311++G** and MP2/6-311++G** levels of theory. The binding energies were calculated as the difference between the dimer energy and the energy of the isolated monomers. The dimerization energies are affected by the basis set superposition error (BSSE). The full counterpoise method of Boys and Bernardi [16] is used here to

correct for BSSE. The topological parameters of the electronic charge density were characterized using the atoms-in-molecules methodology (AIM) within the AIMPAC program package [17].

3. Results and discussion

The binding energies (E_{HB}s) were calculated here for complexes of HF molecule with acetylene and its simple derivatives. The T-shaped configuration of the dimer was taken into account (Scheme 1).

HF molecule is a proton donor and π-electrons of acetylene or its derivative act as the Lewis base. All monomers and complexes were fully optimized during the calculations. For complexes with X=Y, highly symmetric configurations were obtained (HF perpendicular to XCCX molecule); the angle between HF and proton accepting molecule is $81.1°$ and for HCCF + HF and HCCCl + HF complexes for HF/6-311++G** level of theory, the corresponding angles for MP2 method amount to 84.9 and 86.0°, respectively. Table 1 presents the topological, geometrical and energetic parameters of the complexes investigated here. The following results are presented: HF bond lengths, H⋯π distances, the electronic densities at H–F and H⋯π bond critical points — ρ_{HF} and $\rho_{H\cdots\pi}$, respectively, and Laplacians of these densities $\nabla^2\rho_{HF}$ and $\nabla^2\rho_{H\cdots\pi}$, respectively. The results obtained within HF/6-311++G** and MP2/6-311++G** levels of theory are given. One can see that for the complex with FCCF proton accepting molecule the H-bond energy amounts to -0.06 and -0.49 kcal/mol for HF and MP2 methods, respectively. It means that such a complex may not be energetically stable. The greatest binding energies are for LiCCLi⋯HF and NaCCNa⋯HF dimers; for example, the binding energy is equal to -15.4 kcal/mol for LiCCLi⋯HF complex for MP2/6-311++G** level of theory. We see that H-bonds with π electrons as proton acceptors may belong to strong interactions. These results are partly in line with previous investigations [8] where F–H⋯π complexes were taken into account, among them FH⋯C_2H_2 dimer for which the optimized geometrical and topological parameters are also included in Table 1. However in the previous studies [8] it was shown that H-bond energies are around -3 kcal/mol and only for two cases (and only within

Table 1

Geometrical parameters — H–F bond lengths, H$\cdots\pi$ distances (in Å); H-bond energies — E_{HB} (in kcal/mol) and topological parameters (in a.u.) for the complexes of hydrogen fluoride with acetylene and its derivatives. MP2/6-311++G** and HF/6-311++G** (in parentheses) results are given.

Complex	E_{HB}	r_{H-F}	$r_{H\cdots\pi}$	ρ_{HF}	$\rho_{H\cdots\pi}$	$\nabla^2\rho_{HF}$	$\nabla^2\rho_{H\cdots\pi}$
HCCH + HF	−3.11 (−2.69)	0.918 (0.902)	2.186 (2.470)	0.360 (0.388)	0.016 (0.010)	−2.755 (−3.402)	0.053 (0.034)
HCCF + HF	−2.11 (−1.53)	0.922 (0.900)	1.881 (1.843)	0.362 (0.391)	0.015 (0.008)	−2.763 (−3.413)	0.049 (0.028)
HCCCl + HF	−2.48 (−1.77)	0.923 (0.900)	2.248 (2.238)	0.361 (0.390)	0.016 (0.008)	−2.752 (−3.410)	0.053 (0.029)
FCCF + HF	−0.49 (−0.06)	0.920 (0.898)	2.349 (2.809)	0.366 (0.395)	0.011 (0.004)	−2.795 (−3.424)	0.038 (0.012)
ClCCCl + HF	−1.48 (−0.66)	0.922 (0.899)	2.203 (2.624)	0.362 (0.393)	0.015 (0.006)	−2.760 (−3.419)	0.053 (0.021)
NaCCNa + HF	[a] (−17.53)	[a] (0.935)	[a] (1.952)	[a] (0.332)	[a] (0.029)	[a] (−2.856)	[a] (0.066)
LiCCLi + HF	−15.36 (−14.42)	0.970 (0.924)	1.951 (2.029)	0.300 (0.349)	0.044 (0.024)	−2.070 (−3.064)	0.075 (0.063)

[a] This complex was not optimizable at MP2/6-311++G** level of theory.

Table 2
Electron density at the bond critical point of C≡C bond — ρ_{CC} (in a.u.) of the monomers within the complexes with HF and that of the isolated monomers calculated at the MP2/6-311++G** level using AIM methodology.

	ρ_{CC} (within complex)	ρ_{CC} (isolated monomer)
HCCH + HF	0.389	0.389
HCCF + HF	0.371	0.372
HCCCl + HF	0.377	0.378
FCCF + HF	0.367	0.367
ClCCCl + HF	0.367	0.369
LiCCLi + HF	0.381	0.380

B3LYP/6-311++G** level) they are around −4 kcal/mol. For the sample of complexes investigated here, stronger H-bonds were found (Table 1).

Table 2 presents the values of electron densities at C≡C bond critical points (ρ_{CC}s) for isolated XCCY molecules and the same values for these molecules within complexes with hydrogen fluoride. The results show that the differences between ρ_{CC}s for isolated molecules and for complexes are negligible, in line with the previous investigations on related F–H···π systems [8]. Table 2 shows that even for stronger binding energy, for LiCCLi + HF complex, the change in ρ_{CC} is not meaningful but we observe, contrary to the other systems, a small

Table 3
The correlation coefficients for relationships between energetic, geometrical and topological parameters; HF/6-311++G** and MP2/6-311++G** results are given.

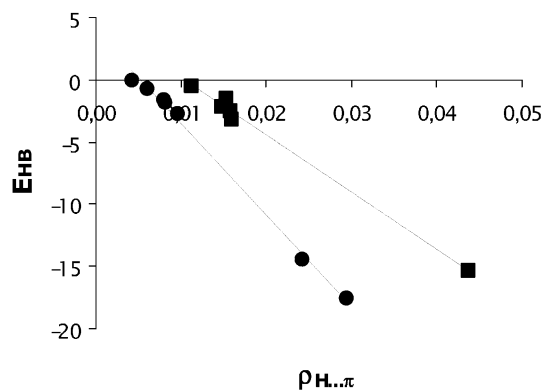|	r_{H-F}	$r_{H \cdots \pi}$	ρ_{HF}	$\rho_{H \cdots \pi}$	$\nabla^2 \rho_{HF}$	$\nabla^2 \rho_{H \cdots \pi}$
HF level						
E_{HB}	0.995	0.591	0.997	0.997	0.986	0.971
r_{H-F}	–	0.574	0.999	0.993	0.998	0.950
$r_{H \cdots \pi}$	–	–	0.572	0.628	0.550	0.688
ρ_{HF}	–	–	–	0.995	0.995	0.958
$\rho_{H \cdots \pi}$	–	–	–	–	0.983	0.981
$\nabla^2 \rho_{HF}$	–	–	–	–	–	0.928
MP2 level						
E_{HB}	0.982	0.547	0.996	0.997	0.993	0.931
r_{H-F}	–	0.523	0.993	0.989	0.996	0.889
$r_{H \cdots \pi}$	–	–	0.527	0.545	0.518	0.580
ρ_{HF}	–	–	–	0.998	0.999	0.914
$\rho_{H \cdots \pi}$	–	–	–	–	0.996	0.939
$\nabla^2 \rho_{HF}$	–	–	–	–	–	0.904

Fig. 1. The relationship between H-bond energy — E_{HB} (in kcal/mol) and the electron density at H···π bond critical point — $\rho_{H \cdots \pi}$ (in a.u.), squares correspond to MP2/6-311++G** results and circles to HF/6-311++G** ones.

concentration of electron density for C≡C bond critical point.

Table 3 shows the linear correlation coefficients for relationships between the parameters presented in Table 1. The correlations for HF and MP2 results are given. One can see that there is no correlation between H···π distance and the binding energy — correlation coefficients are of 0.591 and 0.547 for HF and MP2 results, respectively. It is in contrast to the typical, conventional H-bonds because the correlations between corresponding parameters were observed for such systems. For example, the correlation between H···O distance and H-bond energy for O–H···O systems was often found for homogenous samples [18]. Additionally for O–H···O conventional bonds the relation between O–H bond length and H···O distance is well known [19]. For the sample investigated here the correlation coefficients for the relation between HF bond length and H···π distance amount to 0.574 and 0.523 for HF/6-311++G** and MP2/6-311++G** levels of theory, respectively. These are the main differences between F–H···π unconventional H-bonds investigated here and the typical O–H···O bonds.

Table 3 shows that H-bond energy well correlates with topological parameters. For the relation E_{HB} vs $\rho_{H \cdots \pi}$ (the electronic density at H···π bond critical point) the correlation coefficient amounts to 0.997 for HF and MP2 methods. Fig. 1 shows these relations. For the E_{HB} vs $\nabla^2 \rho_{H \cdots \pi}$ relation the
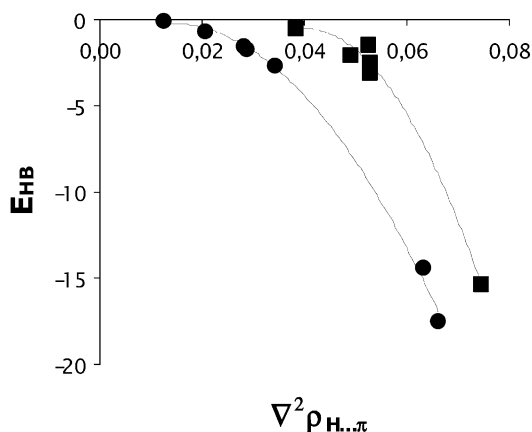
Fig. 2. The relationship between H-bond energy — E_{HB} (in kcal/mol) and the Laplacian of the electronic density at H···π bond critical point —$\nabla^2\rho_{H···\pi}$ (in a.u.), squares correspond to MP2/6-311++G** results and circles to HF/6-311++G** ones.

linear correlation coefficients amount to 0.971 and 0.931 for HF and MP2, respectively. The better correlations for that relation are observed for second order polynomial regression (Fig. 2), correlation coefficients are of 0.999 and 0.995 (HF and MP2, respectively).

The correlations between H-bond energy and topological parameters were observed previously for conventional O–H···O systems [11] and unconventional H-bonds, for example, dihydrogen bonds [7]. For simple modeled dihydrogen bonded systems, correlations between binding energy and topological parameters of HF proton donating bond were observed [14]. Such relations were also found
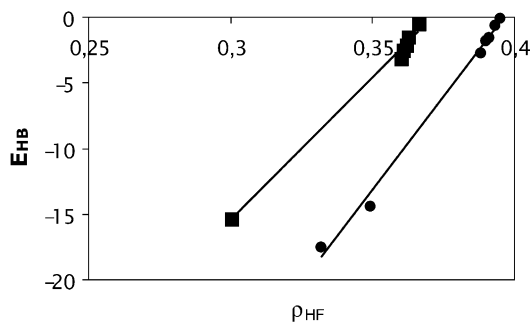

Fig. 3. The dependence between H-bond energy — E_{HB} (in kcal/mol) and the electron density at H–F bond critical point — ρ_{HF} (in a.u.); squares correspond to MP2/6-311++G** results and circles to HF/6-311++G** ones.

here. Table 3 shows the strong correlations between E_{HB} and ρ_{HF} or $\nabla^2\rho_{HF}$ topological parameters and between E_{HB} and HF bond length. Fig. 3 shows the dependence between E_{HB} and ρ_{HF}. Strictly speaking, we observe better correlations between the parameters of HF donating bond and the H-bond energy than between the parameters of H···π contact and this energy. It is in line with recent findings that the modified parameters of the proton donating bond may properly describe the H-bond strength even for heterogeneous samples of complexes [20].

The relation between proton donating bond length and proton-acceptor distance is a simple consequence of the valence sum rule [21]. Such a relation was found for O–H···O bonds [22] and even for F–H···H within dihydrogen bonded systems [7]. Table 3 does not show any such geometrical dependence but we may observe the relation between the corresponding topological parameters: ρ_{HF} vs $\rho_{H···\pi}$ and $\nabla^2\rho_{HF}$ vs $\nabla^2\rho_{H···\pi}$ which may be also treated as a consequence of the valence sum rule [23,24].

4. Summary

The main conclusions of this study concern the characteristics of F–H···π unconventional H-bonds. We do not observe the typical correlation between binding energy and proton-acceptor distance, which is known for conventional systems. Strictly speaking, the topological parameters describe better the H-bond strength than the corresponding geometrical parameters. Additionally, the parameters of proton donating bond (HF in the case of the sample considered here) correlate better with binding energy than the parameters of H···π contact. It is in line with previous findings [14,20,22] that the parameters of Lewis acid within complexes may be good descriptors of H-bond strength. The strength of H-bond for some of F–H···π systems indicates that such interactions may be dominant in determining crystal packing.

References

[1] G.R. Desiraju, Crystal Engineering: the Design of Organic Solids, Elsevier, Amsterdam, 1989.

[2] Z. Berkovitch-Yellin, L. Leiserowitz, Acta Crystallogr. B40 (1984) 159.

[3] G.R. Desiraju, Acc. Chem. Res. 29 (1996) 441.

[4] S.J. Grabowski, J. Chem. Res. (1996) 534.

[5] D. Philp, J.M.A. Robinson, J. Chem. Soc. Perkin Trans. 2 (1998) 1643.

[6] J.A. Platts, S.T. Howard, K. Woźniak, Chem. Commun. (1996) 63.

[7] S.J. Grabowski, Chem. Phys. Lett. 312 (1999) 542.

[8] I. Rozas, I. Alkorta, J. Elguero, J. Phys. Chem. A 101 (1997) 9457.

[9] P. Gilli, V. Bertolasi, V. Ferretti, G. Gilli, J. Am. Chem. Soc. 116 (1994) 909 and references cited therein.

[10] R.F.W. Bader, Atoms in Molecules. A Quantum Theory, Oxford University Press, New York, 1990.

[11] O. Mó, M. Yañez, J. Elguero, J. Mol. Struct. (Theochem) 314 (1994) 73.

[12] E. Espinosa, E. Molins, C. Lecomte, Chem. Phys. Lett. 285 (1998) 170.

[13] S.J. Grabowski, Chem. Phys. Lett. 327 (2000) 203.

[14] S.J. Grabowski, J. Phys. Chem. A 104 (2000) 5551.

[15] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.F., Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery, Jr., R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, B.B. Stefanov, G. Lui, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzales, M. Challa-combe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, J.L. Andres, C. Gonzalez, M. Head-Gordon, E.S. Replogle, J.A. Pople, GAUSSIAN 98, Revision A.6, Gaussian, Inc., Pittsburgh, PA, 1998.

[16] S.F. Boys, F. Bernardi, Mol. Phys. 19 (1970) 553.

[17] F.W. Biegler-König, R.F.W. Bader, T.H. Tang, J. Comput. Chem. 3 (1982) 317.

[18] T. Dziembowska, B. Szczodrowska, T.M. Krygowski, S.J. Grabowski, J. Phys. Org. Chem. 7 (1994) 142.

[19] M. Ichikawa, J. Mol. Struct. 552 (2000) 63 and references cited therein.

[20] S.J. Grabowski, Chem. Phys. Lett. 338 (2001) 361.

[21] I.D. Brown, Acta Crystallogr. B48 (1992) 553 and references cited therein.

[22] S.J. Grabowski, Tetrahedron 54 (1998) 10153.

[23] I. Alkorta, I. Rozas, J. Elguero, J. Mol. Struct. (Theochem) 452 (1998) 227.

[24] I. Alkorta, L. Barrios, I. Rozas, J. Elguero, J. Mol. Struct. (Theochem) 496 (2000) 131.