

ORIGINAL ARTICLE

King Saud University

Arabian Journal of Chemistry

www.ksu.edu.sa





The DFT and MP2 based computational scrutiny on blue-shifted H–F stretching vibrational frequencies in hydrogen-fluoride complexes with nitriles: Insights into the decisive role of intermolecular hydrogen bonding (IMHB) in ground and electronic excited states

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Received 20 October 2014; accepted 3 June 2015 Available online 18 June 2015

KEYWORDS

RCN···HF; Density functional theory (DFT); TD-DFT; AIM; NBO Abstract In the current study, the RCN···HF (R = H, F, Cl, Br, CN, OH, SH, NH₂, NO₂ and CH₃) systems are studied as the interest sample for the consideration of different measures of Hbond strength. The calculations are conducted by means of DFT (B3LYP) and MP2 methods in conjunction with the 6-311 + + G** and aug-cc-pVTZ basis sets for geometry optimization of complexes and monomers and also evaluation of the intermolecular interaction energies. It is found that a blue-shifted hydrogen bonding (HB) in RCN···HF complexes in that N atom of the nitrile molecules acts as a proton-acceptor. The nature of intermolecular hydrogen bond has been investigated by means of the Bader theory of Atoms In Molecules (AIM) and Natural Bond Orbital (NBO) analysis. The calculated highest occupied and lowest unoccupied molecular orbital (HOMO and LUMO, respectively) energies show that charge transfer occurs within the studied complexes. The results obtained from molecular orbital interactions play an important role toward characterization of the chemical reactivity and kinetic stability of the H-bonded systems. Likewise, the strengthening of the intermolecular hydrogen bond and moving the ¹H chemical shift of participating H atom in the hydrogen bridge to up fields are associated with each other. The obtained results indicate a strong influence of the R substituent on the hydrogen bond strength. Moreover, the

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http://dx.doi.org/10.1016/j.arabjc.2015.06.003

1878-5352 © 2015 The Authors. Published by Elsevier B.V. on behalf of King Saud University. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/). excited-state properties of intermolecular hydrogen bonding in the RCN····HF systems have been investigated theoretically using the time-dependent density functional theory (TD-DFT) method. Besides, numerous correlations between topological, geometrical and energetic parameters are also found.

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1. Introduction

The investigation of the hydrogen bond (HB), may be either an intermolecular or intramolecular interaction, is an important subject in old and modern chemistry (Jeffrey, 1997), because it has an essential role in life sciences and is fundamental for molecular recognition and supramolecular synthesis (Jeffrey and Saenger, 1991). Therefore, the understanding of the nature of hydrogen bonds is underpinning any insight into the molecular bases of chemical and biological systems (Desiraju and Steiner, 1999; Malecka, 2010; Pauling, 1960; Steiner, 2002). Both intra- and intermolecular hydrogen bonding play a critical role for the structure and function of molecules (Abraham, 1993; Han and Zhao, 2010). However, it is well-known that intermolecular interactions are very important in understanding organic, organometallic, and biomolecular structures, supramolecular assembly, crystal packing, reaction selectivity specificity and drug-receptor interactions (Hobza and Havlas, 2000; Scheiner, 1997; Thar and Kirchner, 2006; Woo et al., 2005). Moreover, intermolecular hydrogen bonds may strongly influence the geometries of molecules, mainly in the terminal groups of atoms participating in these interactions (Desiraju and Steiner, 1999; Grabowski, 2006). Also, it is noticeable that the formation of the X-H···Y hydrogen bond causes the elongation of the proton-donating covalent (X-H) bond and consequently, X-H stretching vibration mode shifts the red even by hundreds of cm⁻¹ (Desiraju and Steiner, 1999).

In the past few years several pieces of evidence were gathered (Hobza and Havlas, 2000) which showed that the $X-H\cdots Y$ arrangement can be along with opposite geometrical and spectral manifestation. Instead of the elongation of the X-H bond accompanied by a red shift of the X-H stretch vibration, the contraction of this bond and the blue shift of the respective stretch vibration were detected (Hobza and Havlas, 2002). Due to the most important characteristics (the shortening of the CH bond and blue shift of the respective stretch vibration frequency) were opposite to those specifications of the standard H-bond, this bonding type the "improper, blue-shifting" Hbond has been called (Zierkiewicz et al., 2002). Direct evidence of the blue shift in the gas phase had been lost until 1999, when a complex between fluorobenzene and chloroform was examined using the double-resonance infrared ion-depletion spectroscopy (Hobza and Havlas, 2000; Hobza et al., 1999). Theoretical study of the improper, blue-shifting intermolecular H-bond is hard, and the most precise techniques should be applied (Hobza and Havlas, 2000). The improper, blue-shifting concept is of a general nature and stabilizes not only intermolecular complexes but might also appear in intramolecular systems (Hobza and Havlas, 2000). Hobza et al. (Hobza and Havlas, 2000; Li et al., 2002; Mrazkova and Hobza, 2003) proposed that red-shifting includes largely the transfer of electronic charge from the proton acceptor Y to the $\sigma^{*}X$ -H molecular orbital

of the proton donor, which weakens the X-H bond, while blue-shifting results from electronic charge moving from the acceptor to outer portions of the donor (e.g., the fluorines in F3C-H), followed by electronic and structural rearrangements that produce a strengthening of the X-H bond (Murray et al., 2008). Intermolecular hydrogen bonding has a significant effect on chemical behavior, especially on the excited state properties. It is notable that excited-state hydrogen bonding can directly influence the microscopic structures and functions of molecules (Zhao and Han, 2012). Recent time has witnessed the emergence of TD-DFT method as a reliable standard tool for the theoretical treatment of electronic structure. In the last years, the time-dependent density functional theory (TD-DFT) has emerged as a popular scheme able to deliver significant accuracies with "reasonable" computational times for both organic and inorganic species (Jacquemin et al., 2005, 2006). So, in this work, the density functional theory (DFT) and the timedependent density functional theory (TD-DFT) calculations on the RCN···HF (R is substituted, equivalent to H, F, Cl, Br, CN, OH, SH, NH₂, NO₂ and CH₃) systems as convenient model systems are performed to describe their ground and excited-state properties, respectively. Such systems are chosen because of their simplicity; N-atom acts as a proton-accepting center as it is pointed out that such situation is much more probable for the CN group than π -electrons as an acceptor. Although nitriles are important organic compounds, their use is limited and the detailed study of their behavior is a very significant subject. Recently, Raissi et al. (2012) have attempted to elucidate the substitution effects on the intermolecular hydrogen bond strength in nitriles-methanol systems. Since hydrogen-fluoride (HF) is one of the strongest inorganic acids (Hatzifotis et al., 2004), therefore, there is a great interest in the study of the hydrogen fluoride-nitriles interaction.

The aim of this article is to analyze different measures of intermolecular H-bond strength for the simple $RCN \cdots HF$ complexes and investigate the role of the R-substitution on the H-bond strength. Moreover, the intermolecular H-bonds are investigated to get insight into their nature, if they are blue- or red-shifted. Also, for all of the investigated systems, the relationship between the H—F bond length and its stretching vibrational frequency has been discussed in order to show whether the H—F bond length can be preferred as a more rigid and credible criterion for identifying H-bond strength or not. One of the aims of this study is to consider the effect of each substitution group on the HB energy of the studied systems and the synergistic effects of substitutions on the HB energy of RCN…HF complexes will be investigated.

2. Methods and computational aspects

The application of high-level quantum chemical computations with electron correlation in a large basis set is essential in order

to sufficiently depict hydrogen-bonded systems. Furthermore, electron correlation effects are fundamental to be taken into account as dispersion forces that play an important role in describing H-bonds. Also, in order to better depict the nonspherical atomic densities and polarizability effects, diffuse and polarization functions must be included in the basis set (Buckingham et al., 1988). So, in this work, all DFT (density functional theory) calculations are performed by using the B3LYP exchange-correlation functionalities (Becke, 1993; Burke et al., 1998) theoretical level, using $6-311 + + G^{**}$ basis set and since the DFT methods do not reproduce dispersive forces correctly (Ortmann et al., 2006), for the sake of comparison, MP2 calculations are also performed at the same basis function. In order to investigate the effect of basis set and level of theory on the calculated geometries of a series of small molecules having one or two nonhydrogen atoms, a careful study had been conducted by Helgaker et al. (2000) and they found that augmented correlation-consistent polarizedvalence triple-zeta (aug-cc-pVTZ) basis set gave quite good results. Besides, for a relatively small molecule such as ethane, aug-cc-pVTZ uses 230 basis functions: in contrast, 6- $311 + G^{**}$ uses 86 basis functions (Wiberg, 2004). So, in this article, such Dunning correlation consistent basis set (Dunning, 1989), known to adequately describe for the organic molecules and hydrogen-bonded systems, is also applied.

All quantum-chemical calculations have been performed using Gaussian 03 package (Frisch et al., 2003). The geometries of the RCN···HF systems have been displayed using GaussView program. It is worth mentioning that full optimizations are performed for complexes as well as for isolated monomers.

Moreover, the topological parameters that accompany the formation of the intermolecular hydrogen bond have been analyzed by the AIM method (Bader, 1990) using AIMPAC program (Biegler-König et al., 1982) at the B3LYP/6-311++ G**. B3LYP/aug-cc-pVTZ, $MP2/6-311 + + G^{**}$ and MP2/aug-cc-pVTZ levels of theory. Natural Bond Orbital (NBO) analysis is carried out at the same levels of approximation by using the NBO 3.1 (Glendening et al., 1992) program, as implemented in the Gaussian 03 package (Frisch et al., 2003) to understand the orbital interactions and charge delocalization during the course of the H-bond formation. In addition, the population analysis has been performed by the NBO method to obtain the second-order perturbation interaction energy. The contour plot for visualization of the NBO result is constructed on NBOView (Version 1.1) (Glendening et al., 1996; Wendt and Weinhold, 2001) software package using the standard keywords implemented therein. Harmonic vibrational frequencies are computed to evaluate the zero-point vibrational energy (ZPVE) corrections, which have been included in all the obtained energies. It is notable that no imaginary frequencies are found for the all of RCN···HF complexes, which verify that these systems are all minima in the potential energy surfaces (PESs) at all of the theoretical levels. The basis set superposition error (BSSE) (Kestner, 1968), a source of error in supermolecular calculations of intermolecular hydrogen bonding, occurs due to the finite size of the basis set. For very accurate treatments, this error may be approximately accounted for by the counterpoise correction (Boys and Bernardi, 1970). Also, the molecular orbital (MO) calculations such as HOMO (the highest occupied MO) and LUMO (the lowest unoccupied MO) are also performed on the studied systems.

3. Computational results and remarkable discussion

3.1. Monomer properties

In Table 1, the geometric properties, dipole Moment (μ_0) of the HF and HCN monomers are reported. They are compared with the experimental values (Herzberg and Johns, 1969; Laurie and Herschbach, 1962; Legon et al., 1980; Nelson et al., 1967; Hinchliffe, 1981). The results of Table 1 show that in general the results of calculations and experiment ones are in accordance with each other. The HF molecule possesses the relatively good agreement between the experimental and theoretical results of both methods, but for the C=N bond length of HCN molecule, the better agreement with experiment can be recognized at the DFT method. The dipole moment of both molecules shows a good agreement with experimental ones at the DFT (B3LYP/6-311 + $+G^{**}$ level of theory). In Table 1, also, the ab initio calculations of harmonic frequencies are reported, and again compared with the experimental values (Bendtsen and Edwards, 1974; Hüber and Herzberg, 1979; Somasundram et al., 1986). In this case, also, there is a relatively good agreement between the experimental and theoretical results. This indicates the basis sets used in these calculations are large enough to calculate the properties of HF and HCN molecules in both methods. Note that HCN is particularly difficult molecule for the calculation of dipole moment derivatives; see for example the variety of results from correlated wavefunction calculation in (Somasundram et al., 1986).

3.2. Molecular geometry and calculated H-bond energies

In the case of the hydrogen fluoride–nitriles interaction, at the certain distance, $r_{N...H}$, the hydrogen bond is formed, the properties of which depend on the nature of substitutions.

The optimized structural parameters of RCN···HF complexes (R = H, F, Cl, Br, CN, OH, SH, NH₂, NO₂ and CH₃) are listed in Table 2, in accordance with the atom numbering scheme given in Fig. 1. It is worth noticing that in the investigated systems, the N atom of the nitrile molecules acts as a proton-accepting center and hydrogen-fluoride (HF) molecule as a proton-donating molecule. The H-bonding strength is often described by use of the interatomic distance of the proton and its acceptor atom. In the context of the substituent effect on the hydrogen bond strength in the studied systems, the $N \cdots H$ distance is a very important geometric characteristic. In this case, the smaller N···H distance, the stronger H-bond is. Relying on geometrical parameters presented in Table 2 and taking HCN···HF system as a reference, it is notable that at the all of the applied theoretical levels, with only a few exceptions, the N···H distances are increased for substituting systems with the electron-withdrawing groups (F, Cl, Br, CN and NO₂) during complexation while the situation is vice versa for substituted systems with the electrondonating groups (OH, SH, CH₃ and NH₂). Therefore, it can be concluded that stronger intermolecular hydrogen bond belongs to systems with the electron-donating substitutions. Moreover, the NHF bond angle can be an explanation for the HB's strength. Considering the results tabulated in Table 2, it is obvious that with only a few exceptions, this bond angle in the electron-donating substituted complexes is

Table 1 Optimized geometries (in Å), dipole moments (μ° , in Debye), harmonic frequencies (in cm⁻¹) for HF and HCN monomer.

		HF			HCN			<i>v</i> ₁	<i>v</i> ₂	<i>v</i> ₃
		R _H —F	μ_0	ν	R _{H-C}	$R_{C \equiv N}$	μ_0			
DFT	6-311 + + G** aug-cc-PVTZ	0.922 0.924	1.982 1.812	4095.790 4069.940	1.067 1.065	1.149 1.146	3.054 3.040	764.340 757.900	2196.480 2199.100	3456.040 3446.630
MP2	6-311++G** aug-cc-PVTZ	0.917 0.922	2.066 1.935	4198.640 4122.710	1.068 1.065	1.171 1.167	3.319 3.302	729.090 720.020	2016.200 2021.610	3483.140 3463.190
	Experimental ^a	0.917	1.820	4138.000	1.066	1.153	2.979	727.000	2129.000	3442.000

^a Experimental data for bond lengths from references Herzberg and Johns (1969), Laurie and Herschbach (1962), dipole moments from reference Legon et al. (1980), Nelson et al. (1967), Hinchliffe (1981) and harmonic frequencies from references Bendtsen and Edwards (1974), Hüber and Herzberg (1979), Somasundram et al. (1986).

Table 2 The geometrical parameters (*r* and θ is in Å and °) and the intermolecular hydrogen bond energies (in kJ mol⁻¹) for HCN···HF complex and its derivatives at DFT and MP2 methods.

Method	R	6-311++	- G**				aug-cc-pVTZ						
		$N{\cdots}H$	$N{\cdots}F$	H - F	NHF	E _{HB}	$N{\cdots}H$	$N{\cdots}F$	H — F	NHF	E _{HB}		
DFT	Н	1.8363	2.7725	0.9362	179.058	-23.93	1.8217	2.7605	0.9389	179.184	-23.48		
	F	1.8479	2.7828	0.9349	179.939	-20.64	1.8339	2.7713	0.9374	179.942	-20.85		
	Cl	1.8342	2.7704	0.9362	179.985	-22.95	1.8172	2.7561	0.9389	179.989	-23.00		
	Br	1.8289	2.7653	0.9365	179.750	-23.48	1.8146	2.7539	0.9393	179.766	-23.65		
	OH	1.7951	2.7340	0.9392	178.150	-28.50	1.7852	2.7267	0.9418	178.601	-28.20		
	SH	1.8083	2.7464	0.9382	179.124	-26.22	1.7973	2.7380	0.9408	179.352	-25.98		
	CN	1.9057	2.8373	0.9316	179.998	-13.87	1.8912	2.8251	0.9339	180.000	-13.43		
	NH_2	1.7680	2.7099	0.9419	179.270	-33.06	1.7609	2.7053	0.9444	179.271	-32.88		
	CH_3	1.7837	2.7244	0.9406	179.987	-30.19	1.7747	2.7179	0.9432	179.860	-30.25		
	NO_2	1.9275	2.8580	0.9306	179.955	-11.78	1.9048	2.8381	0.9333	179.955	-12.13		
MP2	Н	1.8883	2.8156	0.9273	179.605	-17.27	1.8348	2.7695	0.9348	179.268	-14.89		
	F	1.9018	2.8279	0.9260	179.940	-15.17	1.8497	2.7829	0.9332	179.944	-13.91		
	Cl	1.8823	2.8096	0.9274	179.989	-15.52	1.8347	2.7692	0.9346	179.992	-13.90		
	Br	1.8809	2.8085	0.9276	179.755	-15.61	1.8264	2.7616	0.9351	179.779	-13.23		
	OH	1.8470	2.7761	0.9294	178.178	-20.44	1.8033	2.7401	0.9369	178.679	-19.15		
	SH	1.8551	2.7841	0.9291	179.121	-17.87	1.8137	2.7499	0.9363	179.316	-15.76		
	CN	1.9572	2.8810	0.9238	180.000	-6.75	1.8959	2.8266	0.9307	180.000	-4.73		
	NH_2	1.8224	2.7536	0.9313	179.110	-23.28	1.7818	2.7207	0.9389	179.300	-22.15		
	CH_3	1.8343	2.7649	0.9306	179.938	-21.75	1.7923	2.7305	0.9381	179.964	-20.17		
	NO_2	1.9724	2.8955	0.9231	179.959	-4.28	1.9111	2.8411	0.9301	179.962	-3.56		



Figure 1 The geometry and numbering of RCN···HF complexes.

relatively more than the corresponding value of the HCN···HF complex, which proves that the existence of the stronger hydrogen bond in these systems. Furthermore, investigation of the obtained geometrical values reveals that among all of the studied systems, the least value of the N···H distance is related to the NH₂ substituted system with the strongest intermolecular hydrogen bond. This conclusion can also be

confirmed via the obtained values of the H—F bond length (see Table 2). The N···F distance provides further confirmation. This distance is expected to be decreased as the H-bond becomes stronger. From Table 2, it can be stated that for NH₂CN···HF complex with the strongest HB, the distance between N and F atoms in N···H—F intermolecular HB is the least (2.7099, 2.7053, 2.7536 and 2.7207 Å at the B3LY P/6-311++G**, B3LYP/aug-cc-pVTZ, MP2/6-311++G** and MP2/aug-cc-pVTZ levels of theory, respectively).

The intermolecular H-bond energy provides a measure of the HB strength in the studied complexes. Here, the energy of the intermolecular H-bonds (E_{HB}) is calculated as a difference between the energy of the complexes (using the equation: $E_{\text{Complex}} = E_{\text{Product}+\text{ZPVE}+\text{BSSE}}$) and the energies of isolated monomers. The outcomes are given in Table 2. It can be seen from this table, clearly, the choice of method and basis set has a significant influence on the calculated H-bond energy values. It is interesting to mention that up to now, there is no contradictory hydrogen bond type prediction reported between MP2 and B3LYP calculations. Alabugin et al. have compared the results obtained by MP2 calculation with those obtained by B3LYP computation, for studying C-H···Y hydrogen bond, and concluded that 'the B3LYP results parallel the MP2 data quite closely' (Alabugin et al., 2003). In this paper, it can be seen the agreement between MP2 and B3LYP calculations in predicting the hydrogen bond type of the RCN···HF complexes, too. It is most notable that the calculated values of H-bond energy using B3LYP calculations are more than that obtained ones by applying MP2 methods, which show the stronger HBs are related to the DFT calculations. Significantly, at all of the theoretical levels, the highest value of H-bond energy is obtained for NH₂CN···HF complex, which is further proof on being the strongest HB in this system. The situation is vice versa for $NO_2CN \cdots HF$ complex, which confirms that the existing H-bond in this system is the weakest ones $(-11.78, -12.13, -4.28 \text{ and } -3.56 \text{ kJ mol}^{-1} \text{ at}$ the $B3LYP/6-311 + + G^{**}$, B3LYP/aug-cc-pVTZ, MP2/6- $311 + + G^{**}$ and MP2/aug-cc-pVTZ levels of theory, respectively). Moreover, the obtained $E_{\rm HB}$ values confirm the Hbond strength in systems with the electron-donating substitutions is more than the other substituted systems (see Table 2). Closer inspection of intermolecular H-bond energy denotes that interestingly, with a few exceptions, the HB strength in the three halogenated complexes increases in the following order: $FCN \cdots HF < ClCN \cdots HF < BrCN \cdots HF$, whereas according to the results of Table 2, it is clear that there is the opposite trend for the binding distances. This fact confirms that among three investigated halogen-containing complexes, the strongest H-bond belongs to the BrCN···HF system.

For the investigated systems, there is a good correlation between E_{HB} values versus the N···H distance values. Thus, the E_{HB} can be correlated with N···H distance $(r_{\text{N···H}})$ at the B3LYP/6-311++G**, B3LYP/aug-cc-pVTZ, MP2/6-311++G** and MP2/aug-cc-pVTZ levels of theory, respectively, by the following equations:

$$E_{\rm HB} = 132.01(141.55, 121.53, 141.57)r_{\rm N\cdots H}$$
$$- 265.52(-281.02, -244.79, -273.83)$$

R = 0.995, 0.995, 0.985 and 0.982

Moreover, a linear correlation coefficient for the dependency of the $E_{\rm HB}$ versus N···F interaction is found to be 0.994, 0.994, 0.986 and 0.982 at the B3LYP/6-311 + G**, B3LYP/aug-cc-pVTZ, MP2/6-311 + G** and MP2/aug-ccpVTZ levels of theory, respectively. Therefore, there is a decent correlation between the $E_{\rm HB}$ and the N···F distance as the following equations:

$$y = 141.85(153.02, 128.37, 151.96)$$

× -416.39(-445.61, -376.72, -434.95)

where *y* corresponds to E_{HB} and *x* corresponds to $N \cdots F$ distance.

3.3. Charge density properties

The topological parameters derived from the Bader theory (Bader, 1985) are often used as descriptors of H-bond strength.

Topological criteria are also useful in detecting the existence of H-bond interactions (Koch and Popelier, 1995). Since the geometrical parameters may not be sufficient to have a comprehensive study of the analyzed RCN...HF complexes, the study of charge density properties is performed. Furthermore, in order to have a deeper knowledge about the nature of the hydrogen-bonds in the studied systems, performing such calculations seem to be necessary. The electron density at N···H bond critical point gauges the strength of the intermolecular H-bond interaction, which is manifested by the distance between N and H atoms. As it can be seen, Table 3 encompasses electron density at BCP (ρ_{BCP}), its Laplacian at BCP ($\nabla^2 \rho_{BCP}$) and also energetic AIM parameters (the kinetic electron energy density at BCP (G_C), the potential electron energy density at BCP $(V_{\rm C})$ and the total electron energy density at BCP $(H_{\rm C})$ for the investigated systems. According to this table, with only a few exceptions, the $\rho_{N...H}$ and $\nabla^2 \rho_{N...H}$ values for the electron-withdrawing substitutions are less than the values of the same parameters in HCN···HF, which is another evidence of weaker H-bond in these systems. It is worth mentioning that for the electrondonating substitutions, the situation is reversed. Furthermore, the minimum of N···H contact, associated with the maximum of electron density at N···H BCP and its Laplacian, belongs to NH₂CN···HF complex, a system with the strongest HB. The comparison of the $\rho_{N \cdots H}$ and $\nabla^2 \rho_{N \cdots H}$ values obtained from the two applied computational methods using $6-311 + + G^{**}$ basis set shows that their values at the DFT (B3LYP) method are more than the MP2 ones. This is also the case for the performed calculations using aug-cc-pVTZ basis set. Therefore, it can be confirmed that the evaluated hydrogen bond strength by DFT (B3LYP) method is specifically greater.

The results of AIM calculations also confirm findings based on the geometrical data and as a consequence, increase in the H-bond distance is accompanied by the decrease in electron density of the corresponding H-bond critical point and vice versa; the H-bond distance if decreases, undergoes an increase of the electron density. Besides, for the analyzed systems, there are the substantial correlations between topological and geometrical parameters. For example, the distance-electron density linear relationship for N···H interaction is found with an excellent correlation coefficient (more than 0.9) at all studied levels of theory. Also, there is a good linear correlation coefficient for the electron density Laplacian dependency versus N···H distance (0.999, 0.990, 0.999 and 0.999 at the B3L $YP/6-311 + + G^{**}$, B3LYP/aug-cc-pVTZ, MP2/6-311++G** and MP2/aug-cc-pVTZ levels of theory, respectively). Such correlation may be surprising since the Laplacian is very sensitive to the nature of interaction and varies strongly if any interaction considered is even slightly changed. Meanwhile, $\nabla^2 \rho_{N \cdots H}$ may be evaluated from $r_{N \cdots H}$, as follows:

$$\nabla^2 \rho_{\text{N}\cdots\text{H}} = -0.1491(-0.0477, -0.1885, -0.093)r_{\text{N}\cdots\text{H}} + 0.3801(0.165, 0.4636, 0.2584)$$

According to the results of AIM calculations, it is worth mentioning that the values of the electron density Laplacian $(\nabla^2 \rho_{\rm HF})$ and total electron energy density $(H_{\rm C}^*)$ at the H–F BCP are negative, which confirm that in all of the studied

Table 3 The selected topological parameters of the investigated molecules and the density of the total energy of electrons (H_C) and its two components, the kinetic (G_C) and potential (V_C) electron energy densities (in a.u.), the density of the total energy of electrons related to HF molecule (H_C^*) (in a.u.) and $-G_C/V_C$ ratio^a.

Method	R	$\rho_{\mathbf{N}\cdots\mathbf{H}}$	$\nabla^2 \rho_{\mathbf{N}\cdots\mathbf{H}}$	$G_{\rm C}$	V _C	$H_{\rm C}$	$-G_{\rm C}/V_{\rm C}$	$ ho_{ m HF}$	$ abla^2 ho_{ m HF}$	$H^*_{ m C}$
DFT		6-311++	G**							
	Н	0.03153	0.10667	0.02681	-0.02696	-0.00015	0.99455	0.34798	-2.61354	-0.71211
	F	0.02989	0.10481	0.02574	-0.02527	0.00047	1.01846	0.34987	-2.63371	-0.71827
	Cl	0.03135	0.10685	0.02676	-0.02680	-0.00005	0.99832	0.34802	-2.61394	-0.71223
	Br	0.03189	0.10751	0.02712	-0.02737	-0.00025	0.99098	0.34752	-2.60952	-0.71067
	OH	0.03470	0.11259	0.02936	-0.03058	-0.00122	0.96026	0.34369	-2.56883	-0.69826
	SH	0.03383	0.11057	0.02859	-0.02953	-0.00094	0.96802	0.34502	-2.58326	-0.70258
	CN	0.02594	0.09617	0.02256	-0.02107	0.00149	1.07062	0.35474	-2.68249	-0.73395
	NH_2	0.03758	0.11609	0.03145	-0.03388	-0.00243	0.92824	0.33983	-2.52618	-0.68568
	CH_3	0.03633	0.11386	0.03042	-0.03238	-0.00196	0.93959	0.34164	-2.54593	-0.69155
	NO_2	0.02440	0.09214	0.02125	-0.01946	0.00179	1.09179	0.35634	-2.69693	-0.73899
								(0.36932)	(-2.79770)	(-0.77899)
MP2	Н	0.02487	0.10787	0.02406	-0.02116	0.00291	1.13730	0.35344	-2.98613	-0.75613
	F	0.02337	0.10451	0.02290	-0.01968	0.00323	1.16393	0.35572	-3.00223	-0.76294
	Cl	0.02493	0.10876	0.02423	-0.02128	0.00295	1.13884	0.35355	-2.98378	-0.75620
	Br	0.02512	0.10888	0.02433	-0.02144	0.00289	1.13468	0.35314	-2.98227	-0.75511
	OH	0.02737	0.11520	0.02634	-0.02388	0.00246	1.10312	0.34994	-2.95886	-0.74551
	SH	0.02706	0.11401	0.02601	-0.02351	0.00250	1.10627	0.35054	-2.96388	-0.74737
	CN	0.02032	0.09478	0.02014	-0.01659	0.00355	1.21418	0.35987	-3.02771	-0.77508
	NH_2	0.02952	0.11993	0.02808	-0.02619	0.00190	1.07248	0.34672	-2.93225	-0.73568
	CH ₃	0.02883	0.11778	0.02741	-0.02538	0.00203	1.08005	0.34776	-2.94387	-0.73911
	NO_2	0.01937	0.09160	0.01928	-0.01565	0.00362	1.23145	0.36145	-3.03054	-0.77915
	-							(0.37310)	(-3.06617)	(-0.81070)
DET			777							
DFI	ц	0.02520	12	0.02205	0.02822	0.00438	0.84520	0.34060	2 80215	0 72045
	E E	0.03330	0.07827	0.02393	-0.02855	-0.00438	0.84330	0.34909	-2.89313	-0.73943
		0.03535	0.07870	0.02303	-0.02030	-0.00332	0.80743	0.33102	-2.91432	-0.74380
	D.	0.03555	0.07870	0.02403	-0.02842	-0.00457	0.84014	0.34937	-2.895//	-0.73923
	DI	0.03303	0.07873	0.02421	-0.02873	-0.00433	0.84248	0.34912	-2.88710	-0.73700
	ОП SU	0.03823	0.08010	0.02581	-0.03139	-0.00378	0.81099	0.34302	-2.83282	-0.72043
	SI	0.03739	0.07937	0.02323	-0.03062	-0.00339	0.82404	0.34094	-2.80055	-0.75070
		0.02931	0.07483	0.02047	-0.02223	-0.00176	0.92072	0.33008	-2.96069	-0.701/9
	NH ₂	0.04089	0.08068	0.02/38	-0.03439	-0.00/21	0.79158	0.34199	-2.81317	-0./1463
	CH ₃	0.03982	0.08001	0.02667	-0.03333	-0.00666	0.80009	0.34392	-2.83112	-0./2065
	NO_2	0.02823	0.07379	0.01981	-0.02118	-0.00137	0.93552	(0.35796) (0.37178)	(-3.06249)	(-0.80714)
MP2	н	0.03132	0.08775	0.02356	-0.02518	-0.00162	0.93551	0 34764	_3 41386	_0 77798
1011 2	F	0.02951	0.08678	0.02330	0.02338	0.00000	0.96137	0.35012	3 /3188	0.78536
	C1	0.02951	0.08786	0.02247	0.02338	0.00146	0.90137	0.33012	3 41575	0.78550
	Br	0.03175	0.08730	0.02393	0.02568	0.00175	0.03188	0.34718	3 40743	0.77636
		0.03175	0.08871	0.02393	-0.02308	-0.00173	0.93166	0.34/18	-3.40743	-0.77030
	SH SH	0.03331	0.09077	0.02313	0.02737	0.00244	0.91103	0.34420	3 20541	0.70803
	SI	0.03293	0.08987	0.02470	-0.02093	-0.00223	1.00672	0.34332	-3.39341	-0.77097
	NU	0.02041	0.08231	0.02044	-0.02031	0.00014	0.88757	0.33403	- 3.44810	-0./9/33
	CU	0.03300	0.09277	0.02030	-0.02992	-0.00330	0.00/3/	0.34105	-3.30384	-0.73833
	CH ₃	0.03500	0.09169	0.02603	-0.02915	-0.00311	0.89321	0.34226	-3.3/304	-0.76210
	NO_2	0.02525	0.08063	0.01968	-0.01920	0.00048	1.02499	0.35600	-3.44590	-0.80059
								(0.37032)	(-3.44436)	(-0.83536)

^a Values in the parenthesis are related to free HF molecule.

complexes, the H—F bond is strong with covalent character in nature. Investigation of the changes of the electron density properties in the hydrogen-fluoride (HF) molecule upon HB formation seems to be interesting. The results of our theoretical calculations show that the hydrogen bond formation causes a decrease of electron density at the H—F bond. As can be seen from Table 3, the ρ_{BCP} and H_C^* values at the H—F BCP in N···H—F interaction are smaller than those of free HF

molecule, indicating that the strength of the H–F bond and in turn its covalent nature decrease upon the formation of $N \cdots H$ –F intermolecular HB.

Since the electron density at $N \cdots H$ interaction for analyzed systems here and its Laplacian have been identified as an estimator of hydrogen bonding strength, it can be expected that these parameters correlate well with the hydrogen bond energy. To better highlight this point, the relationship between $\rho_{\rm BCP}$ and $\nabla^2 \rho_{\rm BCP}$ versus $E_{\rm HB}$ is obtained. The correlation coefficients for these dependencies are about 0.97 and it can be stated that the AIM parameters are in agreement with the energetic ones (binding energies).

According to Rozas et al. statements (Rozas et al., 1998a,b) and the $-G_{\rm C}/V_{\rm C}$ ratio, which are used as criteria of the nature of H-bond, it is deduced that the N···H interaction may be classified as follows:

At the B3LYP/6-311 + + G** and MP2/aug-cc-pVTZ levels of theory, with only a few exceptions, the H-bonds are medium with partly covalent nature ($\nabla^2 \rho_{\rm BCP} > 0$, $H_{\rm C} < 0$ and $0.5 < -G_{\rm C}/V_{\rm C} < 1$, see Table 3). Besides, it is obvious that this conclusion for all of the investigated systems at the B3LYP/aug-cc-pVTZ level of theory is true. It is notable that at the MP2/6-311 + + G** level of theory, the weak H-bonds are predicted because of the positive $\nabla^2 \rho_{\rm BCP}$ and $H_{\rm C}$ values (see Table 3).

It has been reported that for closed-shell interactions, including ionic bonds, hydrogen bonds and van der Waals interactions, the $\nabla^2 \rho_{BCP}$ is positive (Koch and Popelier, 1995). With regard to Table 3, it can be seen that the $\nabla^2 \rho$ values at the BCP of the N···H contact are positive (about 0.1 a.u.), suggesting the typical closed-shell kind of interactions and also depletion of electronic charge along the bond path as a characteristic of this type of interaction.

3.4. Population analysis from NBO perspective, NBO atomic charges

Apart from the analyses of geometry and energetic parameters of the systems in this study, a better comprehension of the molecular interactions in the complexes is provided by the Natural Bond Orbital (NBO) analysis. It is important to emphasize that hydrogen bonding causes an increase of the occupancy of the σ_{XH}^* antibond orbital and further the weakening and lengthening of the X-H bond within the X-H···Y hydrogen bridge. But only for the so-called blueshifted hydrogen bonds the complexation leads to slightly different effects (Bader, 1985). The NBO analysis is applied to evaluation of the hydrogen bond strength in RCN···HF complexes studied in this work. In the NBO analysis of hydrogen bonded system, the charge transfer between the lone pairs of proton-acceptor and anti-bond orbital of the proton-donor is the most important. The results of NBO analysis, calculated at the all of the theoretical levels, are given in Table 4. The obtained results illustrate that in the studied systems, lone pairs of nitrogen atom participate as electron-donor and the $\sigma_{\rm HF}$ interaction as electron-acceptor in the intermolecular charge transfer interactions. The charge transfer accomplished between lone pairs of the nitrogen atom and the $\sigma^*_{\rm HF}$ interaction causes an increase of the occupancy of the $\sigma_{\rm HF}$ antibond orbital and further the strengthening of the intermolecular N···H bond. It is worth noticing that in comparison with the HCN···HF molecule, there are stronger H-bonds in the RCN···HF complexes when R is an electron-donating substitution; because of more occupancy of $\sigma_{\rm HF}^*$ orbital, associated with the H-bond strengthening (see Table 4). This behavior is vice versa for the electron-withdrawing substitutions (the $BrCN \cdots HF$ system is an exception), which confirms that with respect to the HCN···HF complex, the existing H-bonds in these systems are weaker. According to NBO analysis, the values of the second-order perturbation stabilization energy $E^{(2)}$ between the lone pair (LP) orbital of N atom and σ antibonding orbital (σ^*) of H-F bond ($E_{LP(N) \to \sigma^*HF}^{(2)}$ in kcal mol⁻¹) for the RCN···HF systems are computed and presented at Table 4. Based on this table, it is obvious that the lowest of the $E_{LP(N) \to \sigma^*HF}^{(2)}$, occupation number (O.N) of $\sigma_{\rm HF}^*$ and $E_{\rm LP}$ values are obtained for NO₂ substitution. Therefore, as a consequence, the weakest HB is related to this substituted system, which is in agreement with $E_{\rm HB}$ values. Besides, the $E_{LP(N) \rightarrow \sigma^* HF}^{(2)}$ value of the OHCN···HF system is approximately more than the corresponding value of the SHCN...HF system, which is in excellent accord with the result from the $E_{\rm HB}$ values. Meanwhile, the comparison between the OH and SH substituted systems depicts that the former has the shorter $N \cdots H$ contact length, the more occupation number (O.N) of $\sigma_{\rm HF}^*$ orbital, the lower O.N_{LP} value and therefore, the higher interaction between lone pairs of the nitrogen atom and the $\sigma_{\rm HF}^*$ orbital (see Tables 2 and 4). According to this fact, it can be concluded that the H-bond in the former is stronger than the latter. In this way, it can be concluded that between the OH and SH substitutions, the more electron-donating property belongs to the OH substituent.

The NBO analysis also describes the bonding in terms of the natural hybrid orbitals. The atomic charge distribution and percentage of the s-character of F3 atom and the pcharacter of N₂ atom are investigated at all of the theoretical levels. Based on given values of these parameters at the $B3LYP/6-311 + + G^{**}$ level of theory, it is obvious that the p-character of the N_2 atom in NH_2 substitution (sp^{0.87}) is lower than the corresponding value of the HCN···HF complex $(sp^{0.91})$, similarly, the N···H contact length in this substitution (1.7680 Å) is also shorter than what that calculated for the HCN···HF system (1.8363 Å). This fact is another proof on being the strongest HB in the NH₂CN···HF system. Besides, our theoretical results show that the proton-accepting bond length is essentially controlled by the p-character of these hybrid orbitals. Furthermore, the percentage of the scharacter of F₃ natural hybrid orbitals of σ_{HF}^* in the HCN···HF system is obtained 24.68%. With respect to this value, it can be seen a 1.05% increase for the NH₂ substitution accompanies with an increase in hydrogen bond formation energy. This is also the case for the other electron-donating substitutions. It can be also mentioned that for the OH, SH and CH3 substituted systems, the N···H contact length has been found to decrease whereas the % s-character found to increase. We have also examined the relation between the H-F bond length and % p-character of the N₂ atom for these complexes. It can be pointed out that the % p-character of N₂ atom decreases with the H-F bond lengthening, reflecting the stronger HB in these systems.

Besides, in comparison with the HCN···HF system, the least s-character of the F₃ natural hybrid orbitals of σ_{HF}^* (23.45%) belongs to NO₂ substituted system, which is another evidence for existence of the weakest H-bond in this compound. Interestingly, closer inspection of the other theoretical levels confirms the conclusions received from the B3LYP/6-311++G** method.

Furthermore, a linear correlation coefficient value for the NBO energy $(E_{LP(N) \rightarrow \sigma^* HF}^{(2)})$ versus the intermolecular Hbonds (E_{HB}) is found to be 0.997, 0.999, 0.977 and 0.984 corresponding to the B3LYP/6-311++G**, B3LYP/aug-cc-

Method	R	6-311++	G**							aug-cc-pVTZ							
		$E_{(LP)}$	$E_{\sigma^*\mathrm{HF}}$	$E^{(2)}_{\rm LP(N)\rightarrow\sigma^*\rm HF}$	O.N _(LP)	$O.N_{\sigma^*HF}$	$v_{\rm HF}$	$\Delta v_{\rm HF}$	γ _{HF}	$E_{(LP)}$	$E_{\sigma^*\mathrm{HF}}$	$E^{(2)}_{\rm LP(N) \rightarrow \sigma^* \rm HF}$	O.N _(LP)	$O.N_{\sigma^*HF}$	$v_{\rm HF}$	$\Delta v_{ m HF}$	$\gamma_{\rm HF}$
DFT	Н	-0.5795	0.4398	12.61	1.9555	0.0271	633.14	0.00	3788.21	-0.5841	0.4501	13.41	1.9520	0.0297	657.44	0.00	3741.88
	F	-0.6069	0.4391	11.63	1.9402	0.0245	606.79	-26.35	3817.29	-0.6196	0.4506	12.08	1.9360	0.0271	625.69	-31.75	3772.77
	Cl	-0.5772	0.4387	12.48	1.9382	0.0266	681.52	48.38	3787.71	-0.5837	0.4503	13.24	1.9347	0.0295	653.18	-4.26	3739.81
	Br	-0.5694	0.4394	12.76	1.9353	0.0273	632.24	-0.90	3779.82	-0.5729	0.4502	13.42	1.9327	0.0300	658.57	1.13	3730.53
	OH	-0.5703	0.4452	15.32	1.9362	0.0325	678.63	45.49	3724.42	-0.5815	0.4565	15.65	1.9320	0.0350	696.46	39.02	3680.83
	SH	-0.5600	0.4413	14.31	1.9374	0.0308	659.16	26.02	3743.40	-0.5648	0.4520	14.85	1.9352	0.0331	689.87	32.43	3699.26
	CN	-0.6172	0.4288	8.53	1.9618	0.0184	519.99	-113.15	3885.89	-0.6236	0.4396	8.94	1.9569	0.0203	573.00	-84.44	3844.69
	NH_2	-0.5463	0.4486	17.61	1.9350	0.0375	705.80	72.66	3666.87	-0.5558	0.4595	17.77	1.9307	0.0398	717.68	60.24	3625.83
	CH_3	-0.5466	0.4444	16.41	1.9399	0.0352	699.45	66.31	3693.62	-0.5519	0.4552	16.90	1.9351	0.0376	717.73	60.29	3650.69
	NO_2	-0.6276	0.4274	7.56	1.9570	0.0163	505.16	-127.98	3908.26	-0.6364	0.4391	8.19	1.9517	0.0189	555.39	-102.05	3859.48
MP2	Н	-0.7871	0.7405	10.09	1.9719	0.0131	596.92	0.00	3958.42	-0.7907	0.7377	13.74	1.9664	0.0182	606.48	0.00	3832.54
	F	-0.8206	0.7389	9.06	1.9632	0.0115	579.58	-17.34	3988.77	-0.8319	0.7379	12.25	1.9573	0.0161	617.68	11.20	3868.42
	Cl	-0.7869	0.7373	10.09	1.9608	0.0131	567.67	-29.25	3957.17	-0.7913	0.7364	13.28	1.9559	0.0177	644.78	38.30	3837.11
	Br	-0.7786	0.7375	10.15	1.9596	0.0132	588.57	-8.35	3951.90	-0.7802	0.7354	13.83	1.9546	0.0185	657.61	51.13	3824.02
	OH	-0.7811	0.7440	12.63	1.9596	0.0162	633.87	36.95	3914.10	-0.7900	0.7425	16.15	1.9531	0.0215	676.79	70.31	3791.23
	SH	-0.7676	0.7392	11.93	1.9595	0.0156	597.01	0.09	3918.00	-0.7705	0.7372	15.15	1.9551	0.0203	678.61	72.13	3798.76
	CN	-0.8327	0.7276	6.23	1.9754	0.0080	427.17	-169.75	4036.41	-0.8384	0.7260	8.97	1.9693	0.0120	571.41	-35.07	3920.65
	NH_2	-0.7550	0.7463	14.63	1.9581	0.0190	668.59	71.67	3870.23	-0.7622	0.7444	18.33	1.9511	0.0245	705.89	99.41	3743.62
	CH ₃	-0.7515	0.7436	13.76	1.9605	0.0181	644.40	47.48	3884.17	-0.7551	0.7411	17.44	1.9533	0.0233	707.09	100.61	3758.53
	NO_2	-0.8505	0.7234	5.54	1.9729	0.0071	479.90	-117.02	4052.30	-0.8580	0.7232	8.06	1.9672	0.0108	550.80	-55.68	3935.72

Table 4 The NBO analysis of the RCN···HF complexes [the second-order perturbation energy (kcal mol⁻¹), occupation number is labeled as O.N. with corresponding energies presented] and the frequencies (in cm⁻¹) of stretching (ν), out-of-plane bending (γ) modes of H–F bond and $\Delta \nu_{\rm HF}$ values.

pVTZ, MP2/6-311 + + G** and MP2/aug-cc-pVTZ levels of theory, respectively. So, the dependency between these energies makes it possible to evaluate $E_{\text{LP(N)}}^{(2)} \rightarrow \sigma^{*}\text{HF}$ value easily from E_{HB} , as follows:

$$E_{\text{LP(N)}\to\sigma^*\text{HF}}^{(2)} = -0.4735(-0.4696, -0.4766, -0.5415)E_{\text{HB}} + 1.8128(2.5279, 2.8843, 6.0607)$$

This implies that the properties of the charge transfer between the lone pairs of proton-acceptor and antibond of protondonor can be useful to estimate the strength of the intermolecular hydrogen bond.

For deeper analysis of the interaction between the electron lone pair of nitrogen (N_2) with an antibonding H_4 — F_3 orbital, the dimensional contour plots of HCN···HF complex and its NO₂ and NH₂ derivatives are drawn in Fig. 2, which fortunately reinforce the correctness of the obtained geometrical and topological conclusions about these derivatives.

In the present work, the NBO charge population analysis is carried out to obtain information regarding the distribution of partial atomic charges of the HCN···HF complex and its NH₂ and NO₂ derivatives. The analysis of NBO charge population of atoms can provide insight into the study of the change of hydrogen bonding interaction. So, the magnitudes of the NBO atomic charge values at the various atoms of the above-mentioned systems are calculated at the B3LYP/6- $311 + + G^{**}$ level of theory and the charge distribution structures are shown in Fig. 3. It is well known that the NBO charge on the H₄ atom reflects the ability of the hydrogen-fluoride molecule to attract electrons. As designated by Fig. 3, the substitution of the HCN···HF system by NH₂ electron-donating group leads to a redistribution of electron density. The charge of N atom is negative in the HCN···HF system, however, because of added NH₂ group, the value of NBO atomic charge of the same atom is bigger for $NH_2CN \cdots HF$ complex. This fact proves that the NH₂CN plays a role as the greatest electron-donating center. Indeed, the negative charges of NH₂CN···HF complex are mainly populated on N₂ atom, which confirms that this atom is potentially active site and can interact with hydrogen bond donor. Also, based on the positive value of NBO atomic charge of the H₄ atom, it is interesting that for NH₂CN···HF complex, the NBO atomic charge of H₄ atom occupies the higher positive values and therefore, this atom becomes more acidic. Hence, it is clear that with respect to the HCN...HF complex, the NH₂ substituted system has the stronger electron-accepting center. So, it may be suggested that the more charge transfer during HB formation and therefore, the presence of the stronger intermolecular H-bonding in the NH₂CN···HF complex. It should be pointed out that as clearly seen from Fig. 3, the situation is vice versa for the substituted system with NO₂ electronwithdrawing group. Therefore, this system has the least value of NBO atomic charge of the H₄ atom and the weakest HB. Consequently, reducing NBO atomic charge value of the H₄ atom, the intermolecular interaction decreases.

3.5. Vibrational frequencies and frequency shifts

In continuation of our studies, in order to better elucidate HB strength, vibrational frequencies for all of RCN...HF complexes are calculated. Hydrogen bond formation is usually accompanied with a red-shift in the stretching frequency of the H-bond donor (Pimentel and McClellan, 1960). However, an increasing number of cases have shown that the stretching frequency of the HB donor is also associated with a blue-shift upon the formation of a hydrogen bond (Hobza and Havlas, 2000). It is clear that the blue-shift magnitude of the proton-donor stretching vibrational frequency can be an explanation for the HB's strength. In this case, the more blue-shifting can be attributed to the stronger HB. According to the results of frequency calculations, displayed in Table 4, it is obvious that with the strengthening of the hydrogen bond, the H-F stretching mode (v_{HF}) shifts to higher frequencies while in-plane ($\delta_{\rm HF}$) and out-of-plane $(\gamma_{\rm HF})$ bending modes of H–F bond shift to lower frequencies. Besides, the calculations performed at all of the theoretical levels demonstrate that the strengthening of the N···H-F bond causes shortening of the proton-acceptor distance with a greater blue-shift of the H-F stretching vibrational frequency (see Tables 2 and 4). It is noteworthy that the shorter proton-acceptor distance, the larger the blue-shift of the proton-donating bond stretching vibrational frequency is. It is notable that the largest N···H distance, the least blue-shift of the H-F stretching vibrational frequency and consequently, the weakest HB are related to NO2 substituted system, whereas the situation is vice versa for NH₂CN···HF complex with a blue-shift of 72.66 and 71.67 at the $B3LYP/6-311 + G^{**}$ and MP2/6-311 + + G^{**} levels of theory, respectively (except calculations at aug-cc-pVTZ basis set). According to the frequency values shown in Table 4, it can be stated that without any exceptions, the proton-donor stretching vibrational



Figure 2 NBO contour plots illustrating the interaction between the electron lone pair of nitrogen (N₂) with an antibonding F_3 -H₄ orbital in the HCN···HF system and its NO₂ and NH₂ derivatives at the B3LYP/6-311 + + G** level of theory.



Figure 3 The NBO charge distribution for the HCN···HF system and its NO₂ and NH₂ derivatives at the B3LYP/6-311 + + G^{**} level of theory.

frequencies for systems with the electron-donating substitution (such as OH, SH, CH₃ and NH₂) are higher than the corresponding values of the HCN···HF complex, which prove that the intermolecular hydrogen bond in these substituted systems is vigorous. From Tables 2 and 4, it is evident that for halogenated complexes, the stretching vibrational frequency of the proton-donor bond follows the same trend of magnitude as the intermolecular H-bond energy (except calculations at $6-311 + + G^{**}$ basis set). This fact confirms that among three investigated halogen-containing complexes, the strongest H-bond belongs to the BrCN···HF system.

It is also expected to be a good relationship between the occupancy of $\sigma_{\rm HF}^*$ anti-bond orbital and the stretching vibrational frequency of the proton-donor bond ($v_{\rm HF}$). So, computational efforts are currently undertaken to investigate this dependency. With regard to Table 4, it is important to emphasize that the most occupancy of $\sigma^*_{\rm HF}$ anti-bond orbital, the greatest blue-shift of the H-F bond stretching frequency is. For more explanation, at all of the theoretical levels, in comparison with the HCN···HF system, more occupancy of $\sigma_{\rm HF}^*$ anti-bond orbital is related to the electron-donating substitutions which is accompanied with the higher blue-shift of the proton-donor bond stretching mode. Regarding SH and OH electron-donating substituted systems, it is obvious that the blue-shift of the H-F stretching vibrational frequency for OHCN...HF system is more than the corresponding value of the SHCN···HF system (45.49, 39.02 and 36.95 cm^{-1} at $B3LYP/6-311 + + G^{**},$ B3LYP/aug-cc-pVTZ and the $MP2/6-311 + + G^{**}$ levels of theory, respectively), indicating that the HB strength in OH substituted system is more than what that obtained for SH substitution.

Also, the influence of computational level and basis set on the predicted trend of the blue-shifted H-bonding systems is investigated, which proves that this trend is dependent on both of them.

Moreover, in examining our data, we come up to a series of good correlations between

- (I) v_{HF} and $r_{\text{N...H}}$ with the correlation coefficient of 0.964 (0.992, 0.947, 0.968 at the B3LYP/6-311++G**, B3LYP/aug-cc-pVTZ, MP2/6-311++G** and MP2/aug-cc-pVTZ levels of theory, respectively) using equation $v_{\text{HF}} = -1338.4(-1188.1, -1415.1, -1244.6)$ $r_{\text{N...H}} + 3086.2(2817, 3244.6, 2924.8).$
- (II) $v_{\rm HF}$ and $E_{\rm HB}$ using equation $v_{\rm HF} = -10.004(-8.3317, -11.644, -8.2709)$ $E_{\rm HB} + 397.48(459.67, 394.47, 524.72)$ with the correlation coefficient of 0.956(0.990, 0.962, 0.927).
- (III) $v_{\rm HF}$ and $\rho_{\rm HF}$ utilizing equation $v_{\rm HF} = -1266(-10,848, -14,359, -10,700)$ $\rho_{\rm HF} + 5031.8(4443.7, 5650.3, 4361.5)$ with the correlation coefficient of 0.949(0.991, 0.936, 0.967).

Furthermore, the relationship between the H–F bond length and its stretching vibrational frequency has been investigated, too. Our theoretical computations show that there is a good linear correlation between above-mentioned parameters with the correlation coefficient of 0.947, 0.933, 0.990 and 0.967 at the B3LYP/6-311++G**, B3LYP/aug-cc-pVTZ, MP2/6-311++G** and MP2/aug-cc-pVTZ levels of theory, respectively, and therefore, it can be concluded that the H–F bond length can be applied as a credible criterion for the expression of the H-bond strength. The $\Delta v_{\rm HF}$ values are also given in Table 4. The $\Delta v_{\rm HF}$ parameter for each substituted system is defined as a difference between its $v_{\rm HF}$ and the related value of the HCN···HF compound. As it is obvious from Table 4, the electron-withdrawing groups such as NO₂ decrease the $\Delta v_{\rm HF}$ (by 127.98 units relative to the HCN···HF at the B3LYP/6-311 + + G** level of theory) whereas electron-donating groups e.g. NH₂ increase this parameter (by 72.66 units at the same level of theory). There is a linear correlation between $\Delta v_{\rm HF}$ and the N···H distance ($r_{\rm N}$ ···_H) at all levels of theory; the linear correlation coefficient is 0.964 (0.992, 0.947 and 0.968), with derived equation as follows:

$$\Delta v_{\rm HF} = -1338.4(-1188.1, -1415.1, -1244.6)r_{\rm N\cdots H} + 2453.1(2159.6, 2647.7, 2318.3)$$

3.6. NMR calculations of chemical shifts and J-couplings

The study of various complexes using NMR approach is an interesting and important scope of both experimental and computational research (Del Bene and Elguero, 2005, 2007; Ebrahimi et al., 2009). As it is well known, ¹H NMR chemical shifts (δ^{1} H) are closely relevant to understanding the electronic structure in a molecule. Besides, Nuclear Magnetic Resonance (NMR) studies are frequently used for examining many interactions, because of their versatility and applicability to molecular systems (Del Bene et al., 2008). Hence, in this work, for more investigation of intermolecular H-bond, the ¹H NMR chemical shifts, a powerful tool in identifying and characterizing hydrogen bonds of RCN···HF structures, are also calculated by employing Gauge Induced Atomic Orbital (GIAO) approach. It is worth mentioning that the calculated chemical shielding is converted into chemical shifts (δ) by subtracting 31.76 and 31.74, the ¹H shielding of tetramethylsilane (TMS) modeled at the B3LYP/6-311++G** and B3LYP/aug-ccpVTZ levels of theory, respectively. The outcomes are given in Table 5. As it is obvious from this table, the strengthening of the intermolecular hydrogen bond causes the ¹H chemical shift of H moves to up fields. Moreover, it is important to emphasize that the highest value of the ¹H chemical shifts, the strongest HB is. So, taking into account of the obtained results, it can be stated that the greatest value of $\delta^1 H_4$ is related to the NH₂CN···HF complex reflecting that the strongest intermolecular hydrogen bond belongs to this system. Obviously, higher values of $\delta^1 H_4$ are obtained for derivatives with the electron-donating substitution in comparison with the HCN···HF system, which prove that in these systems, the hydrogen bond formation has greater influence on H atom movement toward the proton-acceptor atom and also more electronic charge distribution. But the situation is vice versa for RCN···HF systems when R is the electron-withdrawing group. Furthermore, the increase of $\delta^1 H_4$ by the electrondonating substituents is compatible with the decrease in $N \cdots H$ distance (see Tables 2 and 5), which is another evidence for the existence of the stronger H-bonds in these compounds with respect to the HCN···HF complex. The plots of $\delta^1 H_4$ versus intermolecular H-bond energy (E_{HB}) for all of the studied complexes are shown in Fig. 4. As can be seen, the correlation coefficients are equal to 0.978 and 0.982 at the B3LYP/6-311++G** and B3LYP/aug-cc-pVTZ levels of theory, respectively. Likewise, for the investigated compounds, there is also a good polynomial correlation (the polynomial of the second degree) between $\delta^1 H_4$ and $E_{LP(N)}^{(2)} \rightarrow \sigma^{*}HF$. Therefore, $\delta^1 H_4$ can be easily evaluated from $E_{LP(N)}^{(2)} \rightarrow \sigma^{*}HF$ at the B3LYP/6-311++G** and B3LYP/aug-cc-pVTZ levels of theory, respectively, as follows:

$$\begin{split} \delta^{1}\mathbf{H}_{4} &= 0.0057(0.0046) \left[E^{(2)}_{\mathrm{LP(N)} \to \sigma^{*}\mathrm{HF}} \right]^{2} \\ &+ 0.0731(0.1016) E^{(2)}_{\mathrm{LP(N)} \to \sigma^{*}\mathrm{HF}} + 2.2442(3.2476) \end{split}$$

R = 0.989 and 0.980

In order to complement our theoretical studies, we have calculated the spin-spin coupling constants, a new tool which allows representing the electron density shift in those regions where intermolecular H-bonding formation is expected. Indeed, a better understanding of these constants would much benefit for closer study of the H-bonding formation. We used analytical procedure for calculations of spin-spin constants (J)that is available in Gaussian software (Alabugin et al., 2003). Herein, a careful study of the substituent effect on J_{N2-H4} and J_{H4-F3} coupling constants across N···H-F hydrogen bridge is performed by B3LYP method using $6-311 + +G^{**}$ and aug-cc-pVTZ basis sets. The values of these parameters for the investigated RCN···HF systems are listed in Table 5. It must be pointed out that $J_{N^2-H^4}$ coupling constant can be applied for the evaluation of H-bonding strength. According to the results of Table 5, the least value of the J_{N2-H4} belongs to the RCN···HF complex with $R = NO_2$, which has the weakest HB. The deeper analysis of J_{N2-H4} values also shows that in the investigated halogen-containing complexes, J_{N2-H4} value increases in order FCN···HF < ClCN···HF < BrCN···HF, similar to the obtained trend for their E_{HB} values. This fact gives another assurance that among these halogenated complexes, the strongest H-bond belongs to the BrCN···HF system. It is also to note that the J_{H4-F3} coupling constant values support the correctness of the received results from the geometrical and topological studies (see Tables 2, 3 and 5). It is important to point out that the value of the J_{H4-F3} decreases by the electron-donating substituents while this value increases by the electron-withdrawing substituents, whereas this behavior for $O.N_{\sigma^*HF}$ values is vice versa (see Tables 4 and 5). Meanwhile, from Table 5, it is clear that the J_{H4-F3} values for the electron-donating substitutions increase as follows:

NH₂ < CH₃ < OH < SH < H. Besides, this trend for $E_{\rm HB}$ is vice versa. Hence, it can be concluded that in the electron-donating substitutions the $J_{\rm H4-F3}$ value is a more rigid measure for the H-bond strength. The $J_{\rm H4-F3}$ values for the electron-withdrawing substitutions can be arranged in accordance with the trend of H < Cl < Br < F < CN < NO₂, against the $E_{\rm HB}$ trend (except Cl and Br substitutions). To some extent, the $J_{\rm H4-F3}$ values can be a criterion of H-bond strength for this type of substitutions. Since substituents have an effect on both binding energy and coupling constant $J_{\rm H4-F3}$, a logical relationship (the polynomial of the second degree) can be expected between these criteria (with equations: $J_{\rm H4-F3} = -0.0191(-0.0209) [E_{\rm HB}]^2 - 0.5878(-0.5066) E_{\rm HB} + 392.97(412.91)$ with the correlation coefficient of 0.972(0.982)).

Table 5 The selected ¹H chemical shifts (in ppm), spin–spin coupling constants (in Hz), the calculated E_{HOMO} , E_{LUMO} , frontier molecular orbital energy gap (GAP), chemical hardness (η), chemical softness (S), chemical potential (μ) in terms of eV, stability index ($F_{H/L}$), the electronegativity (χ) and electrophilicity (ω) indices for HCN···HF complex and its derivatives performed by DFT method.^a

(11/2)	*	e ;	00	1 2						1		
R	$\delta^1 H_4$	$J(N_2 - H_4)$	$J(H_4 - F_3)$	$E_{\rm HOMO}$	$E_{\rm LUMO}$	GAP	$F_{ m H/L}$	η	S	μ	χ	ω
Н	4.077	-2.465	395.677	-10.254	-1.057	-9.198	9.704	-4.599	-0.217	-5.656	5.656	-3.478
	[5.395]	[-2.459]	[412.739]	[-10.228]	[-1.070]	[-9.158]	[9.561]	[-4.579]	[-0.218]	[-5.649]	[5.649]	[-3.484]
F	4.052	-3.039	397.342	-10.369	-1.566	-8.802	6.619	-4.401	-0.227	-5.968	5.968	-4.046
	[5.386]	[-3.056]	[415.080]	[-10.332]	[-1.528]	[-8.805]	[6.764]	[-4.402]	[-0.227]	[-5.930]	[5.930]	[-3.994]
Cl	3.983	-2.748	396.536	-10.123	-1.542	-8.581	6.565	-4.291	-0.233	-5.832	5.832	-3.964
	[5.344]	[-2.755]	[413.535]	[-10.081]	[-1.517]	[-8.563]	[6.643]	[-4.282]	[-0.234]	[-5.799]	[5.799]	[-3.927]
Br	4.015	-2.690	396.723	-9.717	-2.229	-7.488	4.359	-3.744	-0.267	-5.973	5.973	-4.765
	[5.391]	[-2.701]	[413.846]	[-9.689]	[-2.148]	[-7.542]	[4.512]	[-3.771]	[-0.265]	[-5.919]	[5.919]	[-4.645]
OH	4.789	-2.707	394.662	-9.714	-1.812	-7.902	5.362	-3.951	-0.253	-5.763	5.763	-4.203
	[6.116]	[-2.675]	[410.912]	[-9.677]	[-1.782]	[-7.895]	[5.429]	[-3.947]	[-0.253]	[-5.730]	[5.730]	[-4.158]
SH	4.428	-2.544	394.926	-8.739	-1.907	-6.832	4.582	-3.416	-0.293	-5.323	5.323	-4.148
	[5.715]	[-2.524]	[411.378]	[-8.731]	[-1.917]	[-6.814]	[4.554]	[-3.407]	[-0.294]	[-5.324]	[5.324]	[-4.160]
CN	3.126	-2.655	397.234	-10.711	-3.499	-7.212	3.061	-3.606	-0.277	-7.105	7.105	-6.999
	[4.315]	[-2.706]	[415.782]	[-10.686]	[-3.439]	[-7.247]	[3.107]	[-3.623]	[-0.276]	[-7.063]	[7.063]	[-6.883]
NH_2	5.309	-2.366	392.032	-8.590	-1.340	-7.250	6.409	-3.625	-0.276	-4.965	4.965	-3.401
	[6.586]	[-2.318]	[407.599]	[-8.599]	[-1.350]	[-7.250]	[6.371]	[-3.625]	[-0.276]	[-4.974]	[4.974]	[-3.413]
CH_3	4.911	-2.248	392.439	-9.908	-0.881	-9.027	11.243	-4.513	-0.222	-5.395	5.395	-3.224
	[6.151]	[-2.206]	[408.262]	[-9.884]	[-0.903]	[-8.981]	[10.948]	[-4.490]	[-0.223]	[-5.393]	[5.393]	[-3.239]
NO_2	3.216	-2.759	397.289	-10.540	-4.993	-5.548	2.111	-2.774	-0.361	-7.766	7.766	-10.872
	[4.523]	[-2.841]	[415.960]	[-10.494]	[-4.879]	[-5.615]	[2.151]	[-2.807]	[-0.356]	[-7.687]	[7.687]	[-10.523]
0												

^a The values in brackets refer to calculations at the aug-cc-pVTZ basis set.



Figure 4 Correlation graphic of ¹H NMR chemical shifts (δ^{1} H₄) and intermolecular H-bond energy (E_{HB}) at the B3LYP/6-311 + + G** (\blacklozenge) and B3LYP/aug-cc-pVTZ (\blacksquare) levels of theory.

3.7. Frontier Molecular Orbitals (FMOs)

Comprehensive information about reactivity of specific regions of the molecule can be obtained from molecular orbital energies. Among the molecular orbitals, a fundamental role is played by the frontier orbitals. Indeed, it can be determined the way the molecule interacts with other species considering the highest occupied and the lowest unoccupied molecular orbitals (HOMO and LUMO, respectively); hence, they are called the frontier orbitals. HOMO as an electron-donor represents the ability to donate an electron, while LUMO as an electron-acceptor represents the ability to receive an electron. Moreover, molecules with high HOMO energy values can donate their electrons more easily compared to molecules with low HOMO energy values, and hence are more reactive. Besides, molecules with low LUMO energy values are more able to accept electrons than molecules with high LUMO energy values. Likewise, HOMO energy is a measure of the nucleophilicity of a molecule, whereas the LUMO energy is a measure of the electrophilicity. The calculated energies of the lowest unoccupied and the highest occupied molecular orbital $(E_{LUMO} \text{ and } E_{HOMO}, \text{ respectively})$ and HOMO-LUMO energy gap (GAP) at the $B3LYP/6-311 + G^{**}$ and B3LYP/aug-cc-pVTZ levels of theory, given in Table 5, are the important molecular descriptors. The difference between the HOMO and LUMO energies has been identified as an index of the determining molecular electrical transport properties. Also, it is important to point out that the bond strength is controlled predominately by the HOMO-LUMO gap. Besides, the energy values of LUMO, HOMO and HOMO-LUMO energy gap help to characterize the chemical reactivity and kinetic stability of the molecule (Uesugi et al., 1997). It is well known that a molecule with a small frontier orbital gap is more polarizable and is generally associated with a high chemical reactivity, low kinetic stability and is also termed as soft molecule (Powell et al., 2004; Rauk, 2001; Streitwieser, 1961). Closer inspection of our theoretical results denotes that with regard to $E_{\rm HOMO}$ and $E_{\rm LUMO}$ values, for electron-donating substitutions in comparison with the HCN···HF complex, a low GAP there will be, which reveals in these derivatives, transfer of the proton toward proton-acceptor through Hbond formation leads to more reactivity and less stabilization. This is also the case for the electron-withdrawing substituted systems. It can be clearly seen from Table 5 that at the studied theoretical levels, the NO₂ substituted system with the minimum of energy gap value, acts as the most reactive and the least stable system. On the other hand, it is important to

mention that there are studies (Choi and Kertesz, 1997) which state that the size of the HOMO–LUMO gap and the extent of H-bond length alternation of some compounds are directly related to each other. Therefore, in this study it is interesting to evaluate both the H-bond length involved in the $N \cdots H$ —F hydrogen bridge and the HOMO–LUMO gap value for all of the investigated systems. The obtained results indicate that the most $N \cdots H$ distance, the lowest GAP is (see Tables 2 and 5).

Another descriptor giving the information on the stability of the molecule is stability index defined as the ratio between the HOMO and LUMO energies ($F_{H/L}$). In this work, low values of this parameter are related to the systems with low stability. As it is seen from Table 5, among all of the studied RCN···HF systems, the minimum value of the computed stability index is obtained for the NO₂ substituted system, which reflects this complex as the least stable system. According to our theoretical results in Table 5, it is obvious that the $F_{H/L}$ values in the electron-donating substitutions are small, compared to that in HCN···HF complex, indicating less stabilization in these systems (except CH₃CN···HF system).

In order to perform more investigation about the electronic transition from the ground to the first excited state and also, to understand the bonding scheme of $NH_2CN \cdots HF$ system with the strongest H-bond, the frontier molecular orbital pictures for this complex are drawn in Fig. 5. The positive phase is red and the negative one is green. According to Fig. 5, the HOMO of $NH_2CN \cdots HF$ system shows bonding character at



Figure 5 Frontier molecular orbital (HOMO and LUMO) pictures for the $NH_2CN\cdots HF$ system obtained from the (a) $B3LYP/6-311++G^{**}$ and (b) B3LYP/aug-cc-pVTZ levels of calculation. The computed energies of the frontier MOs are also indicated.

 $N \cdots H$ —F hydrogen bridge. As depicted in Fig. 5, it can be clearly seen that the filled orbital (HOMO) is mostly accumulated on the nitrogen atom of the nitrile molecule. The HOMO presents a charge density localized on all compounds except participating H and F atoms in hydrogen-fluoride molecule. Indeed, there is no electronic projection over this molecule and so on; the antibonding character belongs to the H₄—F₃ bond. Similarly, the LUMO of the investigated complex shows the antibonding character over the same bond. Also, the frontier molecular orbitals determine the way in which the molecule interacts with other species. Furthermore, the frontier molecular orbitals, used to elucidate information regarding charge transfer within the molecule, manifest the low value of the GAP; therefore, the eventual charge transfer (CT) interactions take place within NH₂CN···HF complex.

A deeper understanding of chemical reactivity and kinetic stability can be also gained by chemical hardness (η) and chemical potential (μ) parameters (Pearson, 1990). These parameters can be calculated from the HOMO and LUMO energies using the following approximate expression:

$$\mu = (\varepsilon_{\text{HOMO}} + \varepsilon_{\text{LUMO}})/2, \qquad \eta = (\varepsilon_{\text{HOMO}} - \varepsilon_{\text{LUMO}})/2$$

Chemical hardness is a measure of the resistance of a chemical species to change its electronic configuration, while electronic chemical potential measures the escaping tendency of an electron cloud. The reciprocal of the hardness is the softness, which measures the easiness of charge transfer and it is associated with high polarizability. Besides, the electronegativity (χ) and electrophilicity (ω) indices can be obtained using equations given below (Chattaraj and Giri, 2007; Padmanabhan et al., 2007):

$$\chi = -(\varepsilon_{\rm HOMO} + \varepsilon_{\rm LUMO})/2$$
 $\omega = \mu^2/2\eta$

Herein, chemical hardness and chemical potential parameters, used as complementary tools to describe reactivity and stability of RCN···HF complexes, are computed at the B3LYP/6-311++G** and B3LYP/aug-cc-pVTZ levels of theory and given in Table 5. Based on this table, for NO₂ substituted system, chemical hardness value is the least, indicating that this compound is softer than the others and therefore, the greatest polarizability there will be. Table 5 indicates that chemical hardness values for all of the substituted systems have been decreased, which confirm less stability of these molecules with respect to the HCN...HF molecule. This is in agreement with the order of stability arrived from the HOMO-LUMO energy gaps. Moreover, inspection of Table 5 reveals clearly that the values of chemical potential increase for the electronwithdrawing substituents and decrease for the electrondonating substituents (except OHCN···HF system). According to the results of Table 5, it is notable that the most values of the electronegativity and electrophilicity indices belong to the NO₂ substituted system indicating this compound can be acted as the highest electrophilic system. For NH₂CN···HF molecule, the trend is reversed, which proves this compound can be the least electrophilic system.

3.8. Investigation of dipole moments and Potential energy of dipole–dipole interaction

Knowledge of the dipole moment, a parameter given as a vector in three dimensions, reflects the charge distribution in the molecule. So, it can be applied as descriptor to depict the charge movement across the molecule. Direction of the dipole moment vector in a molecule depends on the centers of positive and negative charges. Dipole moments are strictly determined for neutral molecules. Besides, it is well known that the molecular structure mainly determines the activity of the compound (Rani, 2010), and the insight about this can be obtained from its dipole moment values. Moreover, the dipole moment is a valuable parameter for the description of changes in the geometry of molecule. It was assumed that the lower value of dipole moment provides the higher geometrical fluctuation of molecules and vice versa (Rienstra-Kiracofe et al., 2002). In this work, dipole moment (μ_0) values are calculated for RCN···HF systems and the results are presented in Table 6. Afterward substituent effects on the dipole moments are also examined. Obviously, for the investigated systems with blueshifted intermolecular N···H-F hydrogen bonds, the binding energies are correlated with the dipole moment values. In this case, the obtained results indicate that the higher values of the dipole moment are accompanied by the stronger H-bond (see Tables 2 and 6). It has been pointed out that in comparison with HCN ... HF complex, the electron-donating substitutions increase the μ_0 values, whereas with only a few exceptions, the electron-withdrawing substituents decrease them, showing that the hydrogen bond in the case of electron-donating substituents is relatively stronger than the other substitutions. As it is obvious from Table 6, the smallest value of dipole moment at the MP2 method is noticed for substituted system with NO₂, which reinforces the idea that the weakest intermolecular H-bond belongs to this system. According to the results of μ_0 calculations, it is clear that dipole moment value can be a criterion for the charge transfer character of the molecule. In this case, the more dipole moment values, the higher charge transfer between the lone pairs of proton-acceptor and antibond of proton-donor is (see Tables 4 and 6). Besides, it should also be mentioned that the chemical reactivity of the RCN···HF complexes can be explained by the consideration of the dipole moment values. In this work, a large amount of dipole moment illustrates the low reactivity of the molecule. As a result of our calculations, at the all of the theoretical levels, the highest dipole moment value is observed for NH₂CN···HF system, which reflects this complex as the lowest reactive system. Obtained results from the MP2 calculations reveal that the reverse phenomenon is found for NO₂CN···HF system with the most chemical reactivity. With considering the results of DFT calculations using 6-311++G** and aug-cc-pVTZ basis sets, the correlations between dipole moment and different HB properties (geometrical, topological and energetic parameters) have been checked for the investigated complexes. The correlation matrices for correlations among μ_0 , E_{HB} , H_{C} , G_{C} , v_{HF} , $\delta^1 H_4$ and spin-spin coupling constants have been reported in Table 7. With regard to this table, it is important to emphasize that μ_0 parameter shows the best linear relationship with $r_{N \dots F}$ at the B3LYP/6-311++G** and B3LYP/aug-cc-pVTZ levels of theory, with correlation coefficient of 0.983 and 0.987, respectively. Therefore, dipole moment can be easily evaluated from $r_{N \cdots F}$, as follows:

$$\mu_0 = -34.87(-37.111)r_{\rm N\dots F} + 102.57(108.3)$$

In order to gain more insights into dipole moments, the interaction potential energy (U) between the two polar protondonor (HF) and proton-acceptor (RCN) molecules, existing on RCN \cdots HF systems, has been calculated using the following equation (Atkins, 1992):

$$U = ((\mu_{\rm RCN} \times \mu_{\rm HF})/4\pi\varepsilon_0) \times (f/r^3))$$

where $f = 1 - 3\cos^2\theta$, $\varepsilon_0 = 1$, θ is angle of NHF and r is N···H distance. Here, μ_{RCN} and μ_{HF} are the dipole moments of the corresponding RCN (R = H, F, Cl, Br, CN, OH, SH, NH₂, NO₂ and CH₃) molecules and hydrogen-fluoride molecule, respectively. According to obtained interaction potential energy values, collected in Table 6, it is worth pointing out that the most value of interaction potential energy belongs to the NH₂CN···HF system with the highest stability and the strongest HB. Furthermore, at all of the theoretical levels, less values of U parameter are obtained for all of the substituted systems in comparison with what that calculated for HCN···HF complex (except for the SH and NH₂ substituted systems). This fact reveals that the substitution process causes a reduction in the interaction potential energy between the HF and RCN molecules.

3.9. Thermodynamic parameters perspectives

In order to further investigate and to understand the interaction between the proton-donor and proton-acceptor molecules, during complexation, thermodynamic studies have been carried out in this section. Furthermore, to throw light upon the stability of the RCN...HF complexes, thermodynamic parameters of these systems, i.e. the standard free energy changes (ΔG_{298}^0), the standard enthalpy change (ΔH_{298}^0) and the standard entropy change (ΔS_{298}^0) , are calculated and discussed in detail (see Table 6). The relative standard Gibbs energy of complexation can be an excellent explanation of system stability. So, thermodynamic knowledge of the investigated complexes has fundamental importance and therefore, has been another significant subject in this article. It is worth pointing out that the complexes with lower relative standard Gibbs energy of formation are relatively more unstable, whereas those with the higher relatively standard energy of formation are more stable. According to Table 6, it is noticeable that the lowest ΔG_{298}^0 value is related to the NO₂CN···HF system with the minimum of stability. The thermodynamic data, given in Table 6, reveal that at all studied levels of theory, the sign of the standard enthalpy change (ΔH^0_{298}) values for the formation of RCN···HF complexes are negative and, therefore, the complexation process is enthalpically exothermic (favored). Moreover, the standard free energy changes (ΔG_{298}^0), obtained from the DFT calculations, indicate that the formation of RCN···HF complexes is thermodynamically disfavored ($\Delta G_{298}^0 > 0$). Based on the results from the MP2 method, this conclusion can be manifested, that for the CN and NO₂ electron-withdrawing substituted systems and all of the electron-donating ones (except the SHCN...HF system at the MP2/6-311 + + G** level of theory), the formation of RCN···HF complexes is thermodynamically favored ($\Delta G_{298}^0 < 0$). Besides, the standard entropy change (ΔS_{298}^0) can be evaluated according to the equation $\Delta G_{298}^0 = \Delta H_{298}^0 - T \Delta S_{298}^0$ using the values of the standard free energy changes and the standard enthalpy changes. The values of $T\Delta S_{298}^0$ imply the large entropy changes during the formation of complexes. The thermodynamic parameters, calculated

Method	R	μ_0	$\mu_{\rm RCN}$	U	ΔH^0_{298}	ΔG_{298}^0	$T\Delta S^0_{298}$
DFT	6-311++	G**					
	Н	6.075	3.054(1.982)	-0.156	-27.440	11.717	-39.157
	F	5.214	2.179	-0.014	-27.288	14.681	-41.969
	Cl	6.217	2.953	-0.009	-27.299	16.182	-43.481
	Br	6.646	3.293	-0.069	-27.311	12.108	-39.419
	OH	7.015	3.981	-0.011	-26.576	3.349	-29.925
	SH	6.943	3.630	-0.193	-26.379	3.203	-29.582
	CN	3.143	0.000	0.000	-26.851	18.980	-45.831
	NH_2	8.025	4.657	-0.250	-26.540	3.419	-29.960
	CH_3	7.365	4.054	-0.013	-26.690	1.321	-28.011
	NO_2	3.160	0.090	0.000	-25.690	0.948	-26.638
MP2	Н	6.306	3.320(2.067)	-0.099	-31.074	9.671	-40.745
	F	5.193	2.222	-0.013	-29.741	11.740	-41.480
	Cl	6.237	3.054	-0.008	-31.958	10.244	-42.202
	Br	6.640	3.388	-0.067	-31.938	6.531	-38.469
	OH	6.976	4.063	-0.019	-29.800	-0.909	-28.891
	SH 6.976		3.761	-0.193	-34.013	1.132	-35.145
	CN	3.104	0.000	0.000	-31.508	-4.875	-26.633
	NH_2	7.938	4.739	-0.257	-30.475	-0.980	-29.495
	CH_3	7.527	4.302	-0.029	-30.621	-3.712	-26.909
	NO_2	2.728	0.263	-0.001	-32.548	-6.400	-26.147
	aug-cc-pV	TZ					
DFT	Н	5.954	3.041(1.813)	-0.142	-27.495	11.790	-39.285
	F	5.183	2.258	-0.013	-27.232	15.076	-42.307
	Cl	6.146	2.976	-0.008	-27.306	16.758	-44.064
	Br	6.547	3.295	-0.061	-27.278	12.520	-39.797
	OH	6.939	3.962	-0.139	-26.514	3.813	-30.327
	SH	6.798	3.562	-0.157	-26.418	4.127	-30.545
	CN	3.028	0.000	0.000	-25.869	1.518	-27.387
	NH ₂	7.875	4.613	-0.229	-26.488	3.805	-30.293
	CH ₃	7.252	4.042	-0.051	-26.613	4.253	-30.865
	NO ₂	3.252	0.279	-0.001	-25.746	3.255	-29.001
MP2	Н	6.250	3.302(1.935)	-0.155	-35.935	3.111	-39.046
	F	5.252	2.319	-0.013	-33.618	8.673	-42.292
	Cl	6.285	3.128	-0.008	-35.868	8.128	-43.996
	Br	6.648	3.412	-0.063	-37.082	2.597	-39.679
	OH	7.037	4.096	-0.168	-34.233	-4.039	-30.193
	SH	6.942	3.733	-0.176	-35.914	-5.597	-30.317
	CN	3.072	0.000	0.000	-35.338	-7.904	-27.434
	NH_2	7.936	4.742	-0.238	-35.160	-4.744	-30.416
	CH ₃	7.491	4.295	-0.021	-35.464	-4.882	-30.582
	NO ₂	2.964	0.007	0.000	-35.523	-8.339	-27.184

Table 6 The values of the dipole moments (μ° , in Debye), the potential energy of dipole–dipole interaction (U, in kJ mol⁻¹), enthalpies free Gibbs energies and $T\Delta S_{0.99}^{0.99}$ values (in kJ mol⁻¹) at 298 K^a

^a The values in the parenthesis are related to the dipole moments of the free HF molecule.

using the DFT method with two different basis sets, show that the high negative values of $T\Delta S_{298}^0$ dictate the positive values of ΔG_{298}^0 . The outcome of our theoretical calculations demonstrates that there is a good polynomial correlation (the polynomial of the third degree) between the standard free energy changes of the complexes (ΔG_{298}^0) and the related $E_{\rm HB}$ values with correlation coefficient of 0.930, 0.884, 0.883 and 0.873 at the B3LYP/6-311++G**, B3LYP/aug-cc-pVTZ, MP2/6-311++G** and MP2/aug-cc-pVTZ levels of theory, respectively, giving an equation in the form of $\Delta G_{298}^0 =$ 0.0232(0.0151, -8E-06, 0.0206) $[E_{\rm HB}]^3$ + 1.6695(1.1376, 0.1648, 0.9604) $[E_{\rm HB}]^2$ + 37.311(26.879, 4.6465, 13.018) $E_{\rm HB}$ + 216.66(160.18, -6.8979, 10.907).

3.10. Consideration of hydrogen bonded systems in the excited state

Time-dependent density functional theory (TD-DFT) has been proved to be an efficient theoretical approach to explore the excited state properties of different systems (Runge and Gross, 1984). To depict the intermolecular hydrogen bond in RCN···HF systems at the excited state, S₁, the salient geometric and energetic aspects and also corresponding oscillation strengths, displayed in Table 8, have been calculated at the B $3LYP/6-311++G^{**}$, B3LYP/aug-cc-pVTZ, MP2/6-311+ $+G^{**}$ and MP2/aug-cc-pVTZ levels of theory using the

Index	r _{NH}	r _{N···F}	$\rho_{N\cdots H}$	$\nabla^2 \rho_{\mathbf{N}\cdots\mathbf{H}}$	$E_{\rm HB}$	$G_{\rm C}$	$H_{\rm C}$	$E^{(2)}$	$O.N_{\sigma^*HF}$	$v_{\rm HF}$	γнг	$\delta^1 H_4$	$J_{\rm H4-F3}$	$E_{\rm HOMO}$	$E_{\rm LUMO}$	μ	μ_0
r _{N···H}	1																
	[1]																
r _{N···F}	0.999	1															
	[0.999]	[1]															
$\rho_{\mathbf{N}\cdots\mathbf{H}}$	0.996	0.995	1														
	[0.997]	[0.996]	[1]														
$\nabla^2 \rho_{\mathbf{N}\cdots\mathbf{H}}$	0.999	0.999	0.992	1													
	[0.990]	[0.992]	[0.976]	[1]													
E_{HB}	0.995	0.994	0.998	0.992	1												
-	[0.995]	[0.994]	[0998]	[0.974]	[1]												
$G_{\rm C}$	0.998	0.997	0.999	0.995	0.998	1											
	[0.997]	[0.996]	[0.999]	[0.977]	[0.999]												
$H_{\rm C}$	0.979	0.977	0.993	0.971	0.989	0.990	1										
r (2)	[0.991]	[0.989]	[0.998]	[0.962]	[0.997]	[0.998]	[1]	1									
$E^{(-)}$	0.993	0.991	0.998	0.988	0.997	0.998	0.995	1									
ON	[0.994]	[0.993]	[0.999]	[0.962]	[0.999]	[0.999]	[0.999] 0.007	[1]	1								
$O.N_{\sigma^*HF}$	0.992	0.990	0.999	0.980	0.997	0.998	0.997	0.999	1								
	0.064	0.991	[0.996] 0.052	0.905	[0.999] 0.0 5 6	[0.996] 0.056	0.026	[0.999] 0.045	[1] 0.042	1							
VHF	10.0021	0.905	0.955 10.0051	0.900	0.950	0.950	0.920	10 0021	0.943	1 [1]							
	0.992	0.992	0.995	0.975	0.990	0.994	0.991	0.993	0.990	[1] 0.047	1						
/HF	10.992 10.992	0.330 [A 00A]	[0.999 [0.999]	0.980 [0.964]	0.990 [A 998]	0.990 [0.998]	0.997 [0.000]	0.999 [A 000]	0.999 [0.994]	0.947 [0.001]	[1]						
$\delta^1 \mathbf{H}$	0 987	0.967	0.976	0.960	0.978	0 975	0.081	0.986	0.083	0.008	0 081	1					
0 114	0.907 [0.971]	0.907 10.9701	[0.973]	10.9951	10.9821	0.975	0.9761	IO 9781	10.9811	0.900 10.9561	0.978l	[1]					
Ju4_52	0.828	0.822	0.873	0.810	0.866	0.863	0.921	0.887	0.894	0.750	0.890	0.895	1				
• 114-113	[0.898]	[0.893]	[0.928]	[0.830]	[0.930]	[0.927]	[0.948]	[0.941]	[0.945]	[0.917]	[0.944]	[0.923]	 [1]				
Еномо	0.765	0.764	0.779	0.754	0.768	0.775	0.790	0.777	0.782	0.683	0.785	0.771	0.700	1			
nomo	[0.763]	[0.761]	[0.773]	[0.728]	[0.768]	[0.774]	[0.781]	[0.770]	[0.776]	[0.762]	[0.786]	[0.771]	[0.746]	[1]			
$E_{\rm LUMO}$	0.850	0.853	0.823	0.865	0.833	0.830	0.769	0.808	0.805	0.874	0.801	0.757	0.574	0.431	1		
20110	[0.850]	[0.853]	[0.830]	[0.884]	[0.826]	[0.828]	[0.803]	[0.821]	[0.808]	[0.834]	[0.799]	[0762]	[0.657]	[0.424]	[1]		
μ	0.954	0.956	0.940	0.961	0.943	0.944	0.905	0.928	0.928	0.937	0.926	0.888	0.722	0.742	0.925	1	
	[0.956]	[0.957]	[0.945]	[0.966]	[0.940]	[0.943]	[0.929]	[0.937]	[0.931]	[0.943]	[0.928]	[0.894]	[0.805]	[0.741]	[0.922]	[1]	
μ_0	0.982	0.983	0.977	0.981	0.978	0.978	0.957	0.968	0.968	0.967	0.972	0.936	0.780	0.789	0.824	0.945	1
	[0.987]	[0.987]	[0.983]	[0.977]	[0.979]	[0.982]	[0.975]	[0.975]	[0.973]	[0.979]	[0.977]	[0.953]	[0.865]	[0.788]	[0.815]	[0.941]	[1]

The bolded values correspond to correlation coefficients > 0.9. ^a The values in the brackets refer to calculation at the B3LYP/aug-cc-pVTZ level of theory.

time-dependent (TD) method, a very useful tool to study the hydrogen bonding in the electronic excited states of the hydrogen-bonded systems theoretically (Ahlrichs et al., 1989; Schafer et al., 1994). From the TD results in Table 8, it is noted that in the $\pi\pi^*$ state, the H-bond strength is considerably related to the studied methods. A comparison with the ground state (S_0) manifests that at the DFT calculations, the H-bond strength is increased for the investigated systems. Considering the results of DFT method, with only a few exceptions, the distance between the N and H atoms, i.e. the H-bond length and also the N and F atoms in excited state are shorter than the corresponding values in the ground state, which confirm that the N···H-F intermolecular hydrogen bond is significantly strengthened upon excitation to the S_1 state (see Tables 2 and 8). For example, at the $B3LYP/6-311 + + G^{**}$ level of theory, the distance between N and H atoms in intermolecular hydrogen bonding N···H-F for HCN···HF complex is substantially shortened from 1.8363 Å in the ground state to 1.0794 Å in the excited state. In order to better highlight this point, an effort has been made to explore the NHF bond angle. It is noteworthy that for $HCN \cdots HF$ system, the value of this angle is increased from 179.058° in the ground state to 179.604° in the excited state, which is another reason for existence of stronger HB in this molecule in the excited state. As it is obvious from Table 8, the shortest $N \cdots H$ and $N \cdots F$ distances at the DFT calculations belong to the NO₂CN···HF complex, which confirm that the weakest H-bond in the excited state is related to this system. The obtained results from the MP2 calculations reveal that the N···H and N···F geometrical parameters are drastically enhanced upon excitation and therefore, the weaker H-bond can be expected in comparison with the ground state. Besides, with only a few exceptions, the values of NHF bond angle are reduced during excitation process indicating the weaker H-bond in the RCN...HF complexes. According to the obtained geometrical parameters, as a criterion for H-bond strength, it is worth mentioning that the shortest $N \cdots H$ and $N \cdots F$ distances at the MP2 calculations belong to the NH₂CN···HF complex, which confirm that the strongest H-bond in the excited state is related to this system (see Table 8). It can be noticed that at the all of the studied theoretical levels, in comparison with HCN···HF system, the shorter $N \cdots H$ and $N \cdots F$ distances are obtained for the electron-donating substituted systems and therefore, the stronger HB is related to them (except OH substituted system at the MP2/aug-cc-pVTZ level of theory). Herein, from the TD calculations of the excitation energies (E_{ex}) for the $S_0 \rightarrow S_1$ transition, it can be noticed that in comparison with HCN···HF system, the electronic excitation energy values are decreased for all substituted systems (except NH₂CN···HF and $CH_3CN \cdots HF$ systems at the $MP2/6-311 + + G^{**}$ and MP2/aug-cc-pVTZ levels of theory, respectively). Moreover, based on calculations at the MP2/6-311 + + G^{**} level of theory, the highest E_{ex} value is related to the NH₂ substituted system with the strongest HB. The oscillator strength of the investigated systems in S_1 state, presented in Table 8, is the highest for CNCN···HF system (at all studied levels of theory), which is one of the substituted systems with the weakest H-bond.

3.11. Molecular electrostatic potential map (MEP)

The molecular electrostatic potential (MEP) map is related to the electronic density and is a very useful descriptor in determining sites for electrophilic and nucleophilic reactions as well as hydrogen bonding interactions (Okulik and Jubert, 2005). Indeed, the MEP is a plot of electrostatic potential mapped onto the constant electron density surface, in that the negative regions can be regarded as nucleophilic centers, whereas regions with the positive electrostatic potential are potential

Table 8 The salient geometric parameters (*r* and θ is in Å and °), the electronic excitation energies (E_{ex} , in eV) and also the oscillator strength (*f*) for RCN···HF complexes in the first electronic excited state.

Method	R	6-311+	+G**					aug-cc-pVTZ						
		$N{\cdots}H$	$N{\cdots}F$	H — F	NHF	Eex	f	$N{\cdots}H$	$N{\cdots}F$	H — F	NHF	E _{ex}	f	
DFT	Н	1.0794	2.9851	0.9283	179.604	4.7393	0.0012	1.7554	2.7988	0.9363	176.389	5.8006	0.0019	
	F	1.0975	2.5652	0.9268	177.999	1.7641	0.0010	1.7994	2.5678	1.4758	178.317	2.7798	0.0008	
	Cl	1.0871	2.5886	1.5017	178.784	3.7327	0.0095	1.8188	2.7578	0.9390	179.947	1.9852	0.0010	
	Br	1.0985	2.5460	0.9345	178.401	2.6208	0.0012	1.7957	2.7369	0.9413	179.801	1.8000	0.0009	
	OH	1.0623	2.6558	1.5940	179.776	3.7264	0.0013	1.6652	2.6522	0.9536	179.976	3.3876	0.0010	
	SH	1.0596	2.6746	1.6151	179.889	1.7424	0.0013	1.0621	2.7960	0.9360	179.979	2.2553	0.0011	
	CN	1.0681	2.6630	1.5949	179.992	3.9442	0.0034	1.8856	2.8194	0.9338	180.000	4.3598	0.0024	
	NH_2	1.0346	2.6866	0.9349	179.452	1.5243	0.0008	1.6681	2.6159	0.9552	179.263	1.5982	0.0019	
	CH_3	1.0316	2.8296	1.8013	178.277	4.7343	0.0013	1.7350	2.7253	0.9432	179.989	5.7841	0.0007	
	NO_2	1.9083	2.8396	0.9313	179.961	1.7613	0.0011	1.8912	2.8257	0.9345	179.971	1.7535	0.0014	
MP2	Н	2.0641	2.9664	0.9027	177.694	3.6185	0.0020	2.0273	2.9322	0.9050	179.316	5.2412	0.0017	
	F	2.1422	3.0426	0.9009	177.659	1.8604	0.0014	2.1297	3.0302	0.9029	175.077	1.9649	0.0015	
	Cl	2.1046	3.0057	0.9016	177.716	2.8342	0.0014	2.0999	3.0022	0.9035	176.508	2.8920	0.0012	
	Br	2.1100	3.0115	0.9016	178.628	3.0989	0.0011	2.0135	2.9188	0.9053	179.757	5.1784	0.0011	
	OH	2.0497	2.9528	0.9032	178.764	1.8809	0.0009	2.0365	2.9416	0.9053	178.628	2.0021	0.0010	
	SH	2.0166	2.9203	0.9042	177.810	2.9873	0.0003	2.0107	2.9160	0.9061	177.229	3.0591	0.0002	
	CN	2.1517	3.0522	0.9006	178.899	3.4785	0.0023	2.0644	2.9682	0.9038	180.000	4.4714	0.0019	
	NH_2	1.9463	2.8528	0.9065	179.865	4.7152	0.0000	1.9350	2.8435	0.9085	179.835	4.7610	0.0000	
	CH ₃	2.0092	2.9133	0.9046	177.681	3.5281	0.0019	1.9744	2.8820	0.9077	178.783	5.4406	0.0016	
	NO_2	2.0713	2.9733	0.9020	179.960	3.0406	0.0000	2.0462	2.9504	0.9042	179.963	3.1132	0.0000	



Figure 6 Electron density isosurface mapped with electrostatic potential surface for HCN···HF complex and its NH₂ and NO₂ derivatives at the B3LYP/6-311 + + G** level of theory.

electrophilic sites. MEPs have been employed as a helpful criterion and an informative tool in chemistry to understand and to predict the behavior and reactivity of the molecules. It is mapping potentials created in the space around a molecule by its nuclei and electrons. The importance of MEP lies in the fact that it simultaneously displays molecular size, shape as well as positive, negative and neutral electrostatic potential regions in terms of color grading and is very useful in research of molecular structure with its physiochemical property relationship (Alkorta and Perez, 1996; Murray and Sen, 1996). To predict reactive sites of electrophilic and nucleophilic attacks for the investigated molecules, the MEP is calculated by using the obtained geometries at the B3LYP/6- $311 + + G^{**}$ level of theory. The MEP maps for HCN···HF complex and its NH₂ and NO₂ derivatives, shown in Fig. 6, provide a visual representation of the chemically active sites and comparative reactivity of atoms. There are three important colors: blue, red and green used to indicate the value of the electrostatic potential. The red color surfaces with negative MEP belong to high electron density, indicating a strong attraction between the proton and existing points on the molecular surface. Indeed, negative region is chiefly on the H_4 — F_3 bond. The blue color surfaces correspond to areas of the lowest electron density. The surfaces with green colors indicate zero potential. In MEP map drawn for NH₂ substituted system, the surfaces over the H and F atoms indicate maximum negative electrostatic potential whereas the surfaces over the NH₂ group represent maximum positive electrostatic potential. So, these surfaces may be sites of nucleophilic and electrophilic reactions, respectively. Considering the MEP shown for the NO₂CN···HF system, it can be stated that in comparison with the HCN···HF system, the negative region over the H-F bond is reduced. This fact confirms the weaker HB belongs to NO₂ electron-withdrawing substituted system. Moreover, it is observable the maximum positive electrostatic potential over the C=N and C-N bonds, which expresses these bonds can be sites of electrophilic reaction.

4. Concluding remarks and perspectives

In the present study, the intermolecular HB in RCN···HF $(R = H, F, Cl, Br, CN, OH, SH, NH_2, NO_2 \text{ and } CH_3)$ complexes has been examined by means of ab initio (MP2/aug-cc-pVTZ and MP2/6-311 + + G**) and DFT (B3LYP/aug-

cc-pVTZ and B3LYP/6-311 + + G^{**}) calculations. It can be stated that the topological parameters derived from the theory of Bader can be applied to estimate the H-bond strength. It is detected that the minimum of N···H distance is associated with the maximum of electron density at $N \cdots H$ contact for the investigated systems. Moreover, the $\nabla^2 \rho$ values at the BCP of the $N \cdots H$ contact are positive (about 0.1 a.u.), suggesting the typical closed-shell kind of interactions. Significantly, the highest value of H-bond energy is obtained for NH₂CN···HF complex, whereas the lowest of that is for NO₂CN···HF complex. Besides, the E_{HB} values confirm the geometrical and topological conclusions. It is notable that at all of the applied theoretical levels, with only a few exceptions. the N···H distances are increased for substituted systems with the electron-withdrawing groups (F, Cl, Br, CN and NO₂) during complexation while the situation is vice versa for substituted systems with the electron-donating groups (OH, SH, CH₃ and NH₂). Based on NBO calculations, the lowest of the $E_{\text{LP(N)} \rightarrow \sigma^*\text{HF}}^{(2)}$, occupation number (O.N) of σ_{HF}^* and ELP values are obtained for NO2 substitution. Therefore, as a consequence, the weakest HB is related to this substituted system, which is in agreement with $E_{\rm HB}$ values. With strengthening of H-bond, the H-F stretching mode shifts to higher frequencies while in-plane and out-of-plane bending modes of H-F bond shift to lower frequencies. Furthermore, higher values of $\delta^1 H_4$ are obtained for derivatives with the electrondonating substitution in comparison with the HCN···HF system, which prove that in these systems, the hydrogen bond formation has greater influence on H atom movement toward the proton-acceptor atom and also more electronic charge distribution. But the situation is vice versa for RCN...HF systems when R is the electron-withdrawing group. With regard to $E_{\rm HOMO}$ and $E_{\rm LUMO}$ values, for the electron-donating substitutions in comparison with the HCN···HF complex, a low GAP there will be, which reveals in these derivatives, transfer of the proton toward proton-acceptor through H-bond formation leads to more reactivity and less stabilization. This is also the case for the electron-withdrawing substituted systems. Besides, at the studied levels of theory, the least chemical hardness and the greatest chemical potential belong to the NO₂ substituted complex meaning this substituted system is the softest molecule. A comparison with HCN···HF complex shows that the electron-donating substitutions increase the μ_0 values whereas with only a few exceptions, the electronwithdrawing substituents decrease them. So, the hydrogen bond in the case of electron-donating substituents is relatively stronger than the other substitutions. The thermodynamic data reveal that at all studied levels of theory, the sign of the standard enthalpy change (ΔH_{298}^0) values for the formation of RCN···HF complexes is negative and, therefore, the complexation process is enthalpically exothermic (favored). The electronic excited state properties of the substituted systems have been investigated by time-dependent (TD) method. We are demonstrated that the N···H—F intermolecular hydrogen bond strength is significantly enhanced at the DFT calculations while it is lessened at the MP2 methods for the investigated systems in the electronically excited state.

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