A comparative study of intramolecular hydrogen bond on *N*-formylformamide derivatives in ground and first singlet excited state: a DFT and TD-DFT study

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Abstract

Intramolecular hydrogen bond (IHB) of *N*-formylformamide derivatives in the both ground (GS) and first singlet excited state (S_1) have been investigated by DFT and TD-DFT methods with the standard basis set 6-311++G (d,p), respectively. Also the potential energy density method was used to calculate of the IHB energies in the both GS and S_1 . Our calculations show that IHB energies in the GS are much higher than the S_1 one. In order to explain this energy difference, molecular orbital analysis (MO_s) has been employed. According to the MO_s , it was found that electron density on antibonding orbital (δ_{O-H}^*) increases after excitation, which can be a reason for the weakened IHB in the S_1 . In this work, we evaluated and compared the substitution effects on the IHB strength in the both GS and S_1 by some of the IHB descriptors such as geometrical, topological and orbital charge transfer parameters. The results proved that the substitution effects on the both GS and S_1 are same. As with replacing of the halogen atoms at R_2 position the IHB energies increased while for the R_2 and $R_{1,2}$ decreased. Moreover, for the first time, various geometry—based resonance indices such as Gilli (Q and λ) parameters, original harmonic oscillator model of aromaticity, harmonic oscillator model of electron delocalization and harmonic oscillator model for heterocyclic with π -electrons delocalization were calculated and compared in the both GS and S_1 . Interestingly, it is found from the resonance indices that electron delocalization in the S_1 increased that this result is against the RAHB theory in the studied molecules. Finally, the linear equations of the IHB energies versus the IHB descriptors parameters and resonance indices in the both GS and S_1 indicate that the potential energy density is an inappropriate method for calculation of the IHB energies of the heterocyclic RAHB systems in the S_1 .

Keywords *N*-formylformamide · Intramolecular hydrogen bond · First singlet excited state

1 Introduction

Diamides derivatives play an important role in chemistry of insecticides and pesticides. They selectivity effect on the ryanodine receptors of the insects and release calcium which causes muscle contraction, paralysis and ultimately lead to death [1–3]. *N*-formylformamide (NFF) (Fig. 1), as one of the simplest member of β -diamide compounds display interesting properties such as Amide $\leftrightarrow$ Imidic acid tautomeric equilibrium, intramolecular hydrogen bond

(IHB), amide resonance and proton transfer that have been studied in ground state at previous works [4, 5]. In the Imidic acid form of NFF, the orientation of functional groups in conjugated framework of compound can form an IHB that is resonance assisted hydrogen bond (RAHB) with a heteroatom (N). Concept of RAHB was introduced by Gilli [6]. In the RAHB system of NNF, amide resonance is the most important factor that determines the hydrogen bond strength in this molecule [4]. Thus, the substitution of electron withdrawing and donating groups on the RAHB ring

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Fig. 1 The molecular structures of *N*-formal formylformamide derivatives including Gilli's parameters

lead to change in the resonance and make a great change in some of the IHB descriptor properties such as geometrical parameters, electron density and resonance indices, both in the ground and excited states [7–10].

The estimation of the hydrogen bond strength is important in biological systems. Hence, NFF is an appropriate model for describing the properties of hydrogen bond in biological macromolecules [11]. Generally, the hydrogen bond energy is a useful quantity to assessment of its strength. Although IHB energy is attained by different methods such as Potential energy density of Espinoza (PED), related rotamers method (RRM), open-close method (OCM), Energy–geometry correlation of Musin and Mariani (GCM) and Isodesmic reactions (IRM) [12–16], for the ideal RAHB systems (without heteroatom) but results of previous researches show that more of these methods are not suitable for non-ideal RAHB systems containing heteroatom [10, 17, 18]. Therefore, in this condition, the IHB descriptor parameters that were mentioned above can help us for evaluation of the IHB strength. One way to reach this goal is investigation of the correlations between IHB energies and these parameters. With a good linear correlation between them we can conclude that the IHB energy method is accurate.

In the recent years, many articles about these correlations on the hemicyclic and heterocyclic rings such as malonaldehyde (MA) and 3-imino-propen-1-ol have been published in ground state [8, 19]. Similar to the ground state, some of the systems such as MA and 3-thioxopropanal have theoretically been studied in the excited states [10, 20–22]. But, heretofore, there is no report about the IHB in the NFF derivatives and correlations between the IHB energies and its descriptor parameters both in the ground and excited states. Hence, we decided to choose the NFF and do a theoretical work on its diverse aspects.

In this research, we first calculated the IHB energies by potential energy density of Espinoza [12] on the halogenated NFF in the ground (GS) and first singlet excited states (S_1) (Fig. 1). Then, the geometrical, topological and charge

transfer energies are obtained and also the halogen effects on the structural properties of the NFF are explored. Moreover, the resonance in the NFF derivatives was evaluated for the first time in the S_1 by several indices such as the Gilli (Q and λ) parameters [23, 24], original harmonic oscillator model of aromaticity (oHOMA) [25], harmonic oscillator model of electron delocalization (HOMAED) [26] and harmonic oscillator model for heterocyclic with π -electrons delocalization (HOMAHED) [27]. Ultimately, we investigated and compared the correlation between the Espinoza IHB energies of NFF and the descriptor's IHB parameters to obtain the suitable linear equations both in the GS and S_1 .

2 Computational details

In this work, in order to characterize the electronic properties of the systems, the density functional theory (DFT) and the time-dependent density functional theory (TD-DFT) calculations were performed by GAMESS software ab initio package [28]. The geometry of the single structures was fully optimized at B3LYP and TD-DFT in conjunction with standard basis set 6-311++G (d,p) in the GS and S_1 , respectively [29–32]. Harmonic vibrational frequencies of molecules were considered at the both levels of theory to ensure the existence of the stationary points at potential energy surface. The optimized structures were used to create input files for AIM and NBO analyses by mean of AIM200 software and NBO package included in Gaussian 03 suite of program in the both GS and S_1 [33, 34]. Moreover, we estimated the resonance in the NFF derivatives according to the following indices:

1. *Gilli parameters (Q and λ): These parameters can be shown by the following statements*

$$Q = (d_1 - d_4) + (d_3 - d_2) \quad \lambda = (1 - Q)/0.320$$

where d_1 , d_2 , d_3 , and d_4 were bond lengths that shown in Fig. 1

2. *The original harmonic oscillator model of aromaticity (oHOMA) This index is defined equal zero for a model non-aromatic systems (Kekulé structure of benzene), and equal unit for the full aromatic systems (Benzene). It can be presented by the following equation:*

$$\text{oHOMA} = 1 - 98.89/n \cdot \sum (R_o - R_i)^2 R_o \\ = (R_s + \omega \cdot R_d)/(1 + \omega)$$

where n , R_s , R_d , R_i , R_o and ω are the number of bonds taken into account, the reference single and double bond lengths, the real bond length, the appropriate optimum bond length and the ratio of stretching

force constants for pure double and pure single bonds, Respectively. The R_o was calculated according above equation using the harmonic oscillator method of optimization. In this work, $R_{o\ C-N} = 1.334\ \text{\AA}$ and $R_{o\ C-O} = 1.269\ \text{\AA}$ were taken into account in the GS. The factor of 98.89 is the normalization constant (α) that is same for the CX bonds in heterocycles systems [35].

3. Harmonic Oscillator Model of Electron Delocalization (HOMAED)

This parameter is expressed by the below equation:

$$\text{HOMED} = 1 - \alpha/n \cdot \sum (R_o - R_i)^2$$

$$\alpha = 2 \cdot \left\{ (R_o - R_s)^2 + (R_o - R_d)^2 \right\} - 1 \quad (1)$$

$$\alpha = (2i + 1) \cdot \{ (i + 1) \cdot (R_o - R_s)^2 + i \cdot (R_o - R_d)^2 \} - 1 \quad (2)$$

$$\alpha = (2i + 1) \cdot \{ i \cdot (R_o - R_s)^2 + (i + 1) \cdot (R_o - R_d)^2 \} - 1 \quad (3)$$

In this equation the normalization constant (α) are not the same for all the bond lengths. The Eq. (1) can be used to obtain α for the compounds with the even number of bonds ($2i$) containing the same number of single (i) and double (i) bonds. While, for the systems with ($i + 1$) single bonds, (i) double bonds and (i) single bonds, ($i + 1$) double bonds the Eqs. (2) and (3) are considered, respectively. In this article, $\alpha_{C-N} = 93.52$ and $\alpha_{C-O} = 75.75$ were used in the GS.

4. Harmonic Oscillator Model for Heterocyclic with π -electrons delocalization (HOMAHED)

In this index, the bond lengths R_s , R_d , and R_o are extracted from the X-ray experimental data for the heterocyclic reference systems [27]. Also, the calculations are based on the mentioned equation of HOMAED.

Finally, in order to calculate the HOMA parameters in the S_1 , the methylamine (C–N), methanol (C–O), methylamine (C=N) and formaldehyde (C=O) molecules were selected as pure single (R_s) and double (R_d) bonds Refs. [27, 36]. The parameters of R_s and R_d for obtain of resonance indices are calculate at the TD-DFT/6-311++G (d,p) levels of theory for the S_1 . Then R_o and α obtain based on the mentioned equations. Also, the ω ratio was considered about close to 2 for the involved bonds [27, 37]. The calculated R_o and α for the C–N and C–O bonds in the S_1 are about 1.333 Å, 1.276 Å, 58.84 and 64.73, respectively. However, the experimental X-ray data to calculate the HOMAHED index in the S_1 are unavailable.

Table 1 Hydrogen bond (EHB), excitation energy (E), HOMO to LUMO contributions (H → L) and oscillator strength (f) at DFT and TD-DFT levels for *N*-formylformamide derivatives

R_1, R_2	E_{HB} (kJ/mol)	E^C (ev) (H → L) ^C	f^C	E^O (ev) (H → L) ^O	f^O
H, Br	70.95 (83.28)	2.6452 (99.16%)	0.0012	2.6134 (99.83%)	0.0007
H, Cl	69.92 (82.92)	2.6946 (98.84%)	0.0007	2.5632 (98.91%)	0.0007
H, F	68.97 (82.78)	2.7253 (98.76%)	0.0007	2.4951 (98.79%)	0.0006
H, H	28.19 (65.31)	2.7496 (98.59%)	0.0006	2.5123 (98.61%)	0.0006
F, F	17.20 (63.56)	2.9793 (97.87%)	0.0004	2.9164 (97.04%)	0.0006
Cl, Cl	17.43 (61.62)	2.9965 (97.64%)	0.0007	2.9677 (97.62%)	0.0006
Br, Br	17.57 (62.99)	3.9986 (94.82%)	0.0002	3.8964 (94.67%)	0.0005
Br, Cl	17.32 (63.22)	3.0432 (94.35%)	0.0002	2.9821 (94.26%)	0.0004
Cl, Br	17.58 (62.79)	3.4598 (94.21%)	0.0001	3.4065 (94.16%)	0.0004
F, Br	17.46 (62.54)	3.5318 (91.56%)	0.0005	3.4681 (91.44%)	0.0005
Br, F	17.01 (62.61)	3.5823 (91.38%)	0.0003	3.5489 (91.25%)	0.0003
Cl, H	16.89 (60.96)	4.2531 (90.35%)	0.0007	4.1761 (90.29%)	0.0002
F, H	15.01 (50.08)	4.3652 (90.26%)	0.0006	4.3177 (90.24%)	0.0003
Br, H	15.69 (49.50)	4.4799 (90.11%)	0.0003	4.3929 (90.04%)	0.0003

The values in parenthesis are ground state results

C close forms, O open forms

3 Results and discussion

3.1 IHB in the GS and S_1

As mentioned previous, The IHB energies are the best quantitative descriptors of this non-covalent interaction. In the recently researches, several way to calculation of the IHB were used [12–16]. Also, various linear equations between IHB energies of the RRM, RBM and PED with hydrogen bond descriptor parameters on Malonaldehyde derivatives in S_1 were reported [38]. Conclusions of this research proved that the PED is a trusty method for calculation of the IHB energies of Malonaldehyde derivatives in the GS and S_1 [10]. In the PED method, the estimation of the IHB energy is based on the potential energy density at critical point of the hydrogen bond that can be extracted as the following:

$$E_{PED} = -V_{(BCP)}/2$$

Hence, in this work, the IHB energies of NFF derivatives both in the GS and S_1 are calculated by PED method and collected in Table 1. Furthermore, in order to investigate of the IHB in the S_1 , the electronic transition energy (EE) and corresponding oscillator strength (f) for the closed and open forms of NFF derivatives are obtained from TD-DFT calculations. These results also are listed in Table 1. It is evident from Table 1 that the IHB energies in the GS (49.50–83.28 kJ/mol) are significantly higher than the S_1 (15.01–70.95 kJ/mol). However, it seems that the IHB energies are overestimated, especially in the GS.

Molecular orbitals analysis (MO_s) can be used to investigate the IHB strength in the electronically excited states [38–41]. The MO_s for the S_1 of the NFF derivatives have been studied. Dominant contributions of the orbital transitions HOMO (the highest occupied molecular orbital) to LUMO (the lowest unoccupied molecular orbital) for the S_1 on the close and open forms of NFF derivatives are extracted. The data are gathered in Table 1. The results of MO_s indicate that IHB strengthening in the S_1 will increase HOMO to LUMO ($H \rightarrow L$) contributions in the NFF derivatives. For instance, the values of $H \rightarrow L$ contributions for the weakest IHB energy 1-Bromo (15.69 kJ/mol) and the strongest IHB energy 2-Bromo (70.95 kJ/mol) of the NFF are about 90.11% and 99.16%, respectively.

Furthermore, the MO_s in the parent molecule of NFF shows the molecular orbitals (MO) which contributes to S_1 are HOMO and LUMO (Fig. 2). Since that in the S_1 charge transfer occurs from HOMO to LUMO orbitals, It can easily be concluded from Fig. 2 that electron density on the antibonding orbital (δ_{O-H}^*) increases after excitation. This can be a reason for the weakened IHB in the S_1 of the studied molecules. Also, comparing in the close and open NFF forms, indicate that all of the EE of close forms are increased while its $H \rightarrow L$ contributions are decreased, which is in complete agreement with the formation of excited state IHB weakening in the NFF derivatives (see Table 1).

Also, in order to evaluate the substituted effects, we can classify NFF derivatives in three categories R_1 -substituted,

R_2 -substituted and R_1R_2 -substituted ($R=F, Cl, Br$) (Fig. 1). A deeper looks at the data on the Table 1 indicate that with replacement of halogen atoms in R_1 and R_1R_2 positions, the IHB energies decreased, while for R_2 increased. However, within each category, the IHB energies are very close together. The average IHB energies of R_2 , R_1 and R_1R_2 -substituted are about 82.99, 69.94, 53.51, 15.86 and 62.75, 17.37 kJ/mol in the both GS and S_1 , respectively. According to the average IHB energies in both states it was found that for NFF derivatives there is a following order:

R_2 -substituted > NFF > R_1R_2 -substituted > R_1 -substituted

Previous researches have shown that IHB energies in excited state and electronic transition energy (EE) are inversely proportional [41, 42]. In the other hand, with the strengthening of the IHB in the S_1 , the excitation energy may be reduced, or vice versa. Based on our results from Table 1, the maximum and minimum of the EE values are gained for 1-Bromo (4.4799 eV) and 2-Bromo (2.6452) *N*-formalformamide in the S_1 , respectively. Therefore, these compounds have the lowest and highest the IHB energies. However, contrary to previous studies [10], according to our results the EE are in agreement with the IHB energies very well, and there are the following order of EE for three category of NFF in the S_1 .

R_2 -substituted < NFF < R_1R_2 -substituted < R_1 -substituted

The oscillator strength (f) is a dimensionless quantity that expresses the probability of absorption or emission of electromagnetic radiation in transitions between energy levels of an atom or molecule. It can be defined as the ratio between the quantum mechanical transition rate and the hypothetical strength of a single electron oscillator with the same frequency as the transition. The values of the oscillator strength 0 and 1 are related to the fully allowed and forbidden transitions. Data in Table 1 demonstrate that there is not good relationship among the oscillator strength values and EE in the NFF derivatives. On the other hand, (f) values are very close to zero (0.0003–0.007) that probably attribute to the forbidden transition, and irregularly change with decreasing or increasing of the EE.

Fig. 2 The molecular orbital of *N*-formylformamide in the GS and S_1

3.2 Geometrical parameters in the GS and S_1

The several important geometrical parameters included $R_{O...H}$, R_{O-H} and R_{O-O} in the both GS and S_1 are listed in Table 2 for the NFF derivatives. When the IHB is formed, $R_{O...H}$ increases and R_{O-H} and R_{O-O} decreases. It can be easily deduced from the Table 2 that the structural parameters in the S_1 change significantly with respect to GS. For example, the values of $R_{O...H}$, R_{O-H} and R_{O-O} for the 1-Bromo (the weakest IHB) and 2-Bromo (the strongest IHB) change from 1.60071, 1.01366, 2.50201, 1.69617, 0.99752 and

Table 2 The selected length bonds (Å) of *N*-formylformamide derivatives at DFT and TD-DFT levels

R_1, R_2	$R_{O...H}$	R_{O-H}	$R_{O...O}$
H, Br	1.92054 (1.60071)	0.97176 (1.01366)	2.69842 (2.50201)
H, Cl	1.92582 (1.60483)	0.96382 (1.60483)	2.73067 (2.50505)
H, F	1.93265 (1.60121)	0.95209 (1.01478)	2.66413 (2.49968)
H, H	1.93277 (1.68216)	0.95945 (0.99775)	2.73312 (2.54734)
F, F	2.17561 (1.69953)	0.94983 (0.99919)	2.86589 (2.55467)
Cl, Cl	2.16423 (1.71642)	0.94734 (0.98984)	3.03198 (2.55731)
Br, Br	2.16435 (1.69636)	0.94984 (0.99798)	2.98241 (2.55845)
Br, Cl	2.18214 (1.69617)	0.94179 (0.99752)	2.90853 (2.55904)
Cl, Br	2.22138 (1.68726)	0.94994 (0.99936)	2.98791 (2.56265)
F, Br	2.34765 (1.69343)	0.94951 (0.99987)	2.99682 (2.56921)
Br, F	2.39034 (1.70817)	0.94127 (0.99692)	2.85569 (2.55504)
Cl, H	2.39639 (1.74889)	0.94031 (0.98918)	2.05245 (2.58199)
F, H	2.40458 (1.75166)	0.93652 (0.99019)	2.99823 (2.58715)
Br, H	2.40792 (1.76181)	0.93363 (0.98792)	2.88563 (2.58966)

The values in parenthesis are ground state results

2.58966 to 1.92054, 0.97176, 2.69842, 2.40792, 0.93363 and 2.88563, respectively. These changes confirm that the IHB of the NFF derivatives are largely weekend in the S_1 and strongly are in agreement with the IHB energies. Also, investigation of the structural parameters with more details in three categories of NFF derivatives in comparison with the parent molecule NFF, indicate that the presence halogen in R_2 position causes shortening of the $R_{O...H}$ and R_{O-O} and lengthening of R_{O-H} in the both GS and S_1 . Hence, based on the results in Table 2 we can found the following orders.

$R_{O...H}$ and R_{O-O} : R_2 -substituted < NFF
 < R_1R_2 -substituted < R_1 -substituted R_{O-H} :
 R_2 -substituted > NFF > R_1R_2 -substituted
 > R_1 -substituted

Since that these results strongly support the IHB energies. Hence, in this section, the linear dependence between the geometrical parameters $R_{O...H}$, R_{O-H} and $R_{O...O}$ and IHB energies in the GS and S_1 are studied. The result is graphically shown in the Fig. 3 and its linear equations are presented below:

GS:

$$\begin{aligned} E_{HB} &= -195.07 R_{O...H} + 394.81 \quad R^2 = 0.9420 \\ E_{HB} &= 33.860 R_{O-H} + 30.029 \quad R^2 = 0.2644 \\ E_{HB} &= -349.19 R_{O-O} + 956.47 \quad R^2 = 0.9481 \end{aligned}$$

S_1 :

$$\begin{aligned} E_{HB} &= -92.73 R_{O...H} + 231.54 \quad R^2 = 0.6322 \\ E_{HB} &= 1610.6 R_{O-H} + 149.95 \quad R^2 = 0.5751 \\ E_{HB} &= -2.344 R_{O...O} + 9.5039 \quad R^2 = 0.0694 \end{aligned}$$

The equations clearly show that the IHB energies in the GS have good correlation with $R_{O...H}$ and R_{O-O} , while, for

Fig. 3 Correlation between the IHB energies (kJ/mol) and geometrical parameters (Å) in the GS and S_1

R_{O-H} the regression coefficient is unacceptable. Also, the correlation between the IHB and these geometrical parameters in the S_1 is not good and their regression coefficients (R) are inappropriate for a linear equation.

3.3 Topological parameters in the GS and S_1

In recent years, the quantum theory of atoms in molecules (QTAIM) has been extensively used for study of the IHB [10, 43]. Based on the QTAIM, when the hydrogen bond is formed, the total electronic density (ρ) and its corresponding Laplacian ($\nabla^2\rho$) of bond critical point depict the properties of the IHB and molecular reactivity. These two criteria are related to electron density while others as kinetic $G(r)$ and potential $V(r)$ electronic energy densities, are dependent to the integrated properties of the atoms involved in the bond [44].

Some of the most important AIM parameters including electron density (ρ), its Laplacian ($\nabla^2\rho$), the kinetic $G(r)$ and the potential electron energy $V(r)$ densities, ratio of kinetic

to potential electronic energy densities (G/V) and the total electron density or Hamiltonian $H(r)$ on the bond and ring critical points of NFF derivatives are calculated in the GS and S_1 , and their data are listed in Table 3.

It can be seen from Table 3 that (ρ) values in the GS (0.04916–0.06183 a.u.) are slightly higher than what Popiler has reported for an acceptable IHB (0.002–0.04 a.u.) [45]. While that for the S_1 (0.01956–0.05279 a.u.), these values for more the NFF derivatives, except 2-chloro, 2-bromo and 2-fluoro, almost fall into the Popiler's electron density standard values for the IHB. Hence, these conclusions are in full compliance with the IHB energies and clearly indicate the IHB in the S_1 is weaker than GS. Also, the maximum and minimum (ρ) values in GS and S_1 have seen for R_2 -substituted (2-bromo $\rho = 0.06183$, 0.05279 a.u.) and R_1 -substituted (1-bromo $\rho = 0.04916$, 0.01956 a.u.) with the lowest ($d_{O...H} = 1.60071$, 1.92054 Å) and the greatest ($d_{O...H} = 1.76181$ 2.40792 Å) values of O...H distance that strongly support the previous orders of the IHB energies and geometrical parameters. The values of $\nabla^2\rho$ and $H(r)$ at bond and ring critical point in the Table 3 clearly indicate that the IHB in the NFF derivatives in the GS are strong interactions ($\nabla^2\rho < 0$, $H(r) < 0$, $E_{HB} > 24$ kcal/mol), according

to the Rozas et al conclusion, [46] while in the S_1 , the IHB energies are belong to the intermediate and weak interactions ($\nabla^2\rho > 0$, $H(r) < 0$ or $H(r) > 0$, $E_{HB} < 24$ kcal/mol). However, our results are not in full compliance with the Rozas et al conclusion.

Also, in order to assessment of covalent nature of the IHB, the $-G/V$ values are considered. When $-G/V$ is greater than unity, the IHB has noncovalent nature, while for $0.5 < -G/V < 1$ IHB is partly covalent [47]. It is observed from Table 3 that all of the $-G/V$ values for NFF derivatives in the GS are lower than unity and prove that IHBs have covalent nature ($\nabla^2\rho < 0$), while in the S_1 , this factor for more of the NFF derivatives are greater than unity and for other ones are nearly unit that indicate noncovalent nature of IHB ($\nabla^2\rho > 0$). These results strongly are in line with IHB energies order and geometrical parameters in the both GS and S_1 and support results of other researches [10, 47]. In this paper, also, we explored the correlation of IHB energies with topological parameters in the both GS and S_1 . The linear equations and corresponding regression coefficients at the bond critical point are illustrated below:

GS:	S_1 :
$E_{HB} = 1561 \rho_{O...H} - 9.657 \quad R^2 = 0.9787$	$E_{HB} = 1605 \rho_{O...H} - 1508 \quad R^2 = 0.9458$
$E_{HB} = -8584 \nabla^2 \rho_{O...H} - 232 \quad R^2 = 0.8978$	$E_{HB} = -3443 \nabla^2 \rho - 43.15 \quad R^2 = 0.9476$
$E_{HB} = -225.5 G/V + 258.3 \quad R^2 = 0.8488$	$E_{HB} = -236 G/V + 279.3 \quad R^2 = 0.6936$
$E_{HB} = -3081.8 H + 42.25 \quad R^2 = 0.9690$	$E_{HB} = -114.6 H + 32.27 \quad R^2 = 0.9214$

Table 3 The selected topological parameters in the bond and ring critical points (a. u.) of *N*-formylformamide derivatives at DFT and TD-DFT levels

R_1, R_2	ρ_{BCP}	$\nabla^2\rho_{BCP}$	$-G/V$	ρ_{RCP}	$\nabla^2\rho_{RCP}$	H_{BCP}
H, Br	0.05279 (0.06183)	0.02922 (−0.03654)	0.9554 (0.8157)	0.02361 (0.02416)	0.04145 (−0.03817)	−0.002411 (−0.01169)
H, Cl	0.05184 (0.06082)	0.02916 (−0.03643)	0.9467 (0.7914)	0.02353 (0.02411)	0.04132 (−0.03798)	−0.002839 (−0.01317)
H, F	0.04567 (0.06061)	0.02734 (−0.03626)	0.9276 (0.7795)	0.02298 (0.02409)	0.04067 (−0.03735)	−0.003805 (−0.01391)
H, H	0.02784 (0.05098)	0.02246 (−0.03534)	1.0229 (0.8552)	0.01746 (0.02231)	0.02357 (−0.03447)	0.000492 (−0.00721)
F, F	0.01601 (0.04983)	0.01547 (−0.03473)	1.1182 (0.8668)	0.01339 (0.02214)	0.01831 (−0.03427)	0.001482 (−0.00645)
Cl, Cl	0.01861 (0.04929)	0.01575 (−0.03449)	1.0662 (0.8674)	0.01346 (0.02313)	0.01858 (−0.03508)	0.000888 (−0.00622)
Br, Br	0.01875 (0.04927)	0.01598 (−0.03447)	1.0671 (0.8539)	0.01351 (0.02321)	0.01866 (−0.03515)	0.000898 (−0.00701)
Br, Cl	0.01458 (0.04991)	0.01409 (−0.03484)	1.0931 (0.8493)	0.01267 (0.02293)	0.01693 (−0.03519)	0.000106 (−0.00725)
Cl, Br	0.01956 (0.04916)	0.01674 (−0.03463)	1.1012 (0.8524)	0.01243 (0.02276)	0.01673 (−0.03506)	0.001356 (−0.00705)
F, Br	0.01845 (0.04896)	0.01563 (−0.03488)	1.0773 (0.8521)	0.01228 (0.02252)	0.01544 (−0.03496)	0.001028 (−0.00704)
Br, F	0.01652 (0.04892)	0.01605 (−0.03476)	1.1162 (0.8494)	0.01162 (0.02248)	0.01486 (−0.03489)	0.001543 (−0.00718)
Cl, H	0.01622 (0.04289)	0.01564 (−0.03344)	1.1151 (0.8717)	0.01154 (0.02237)	0.01423 (−0.03483)	0.001491 (−0.00595)
F, H	0.01517 (0.04286)	0.01464 (−0.03298)	1.1914 (0.9482)	0.01116 (0.02217)	0.13881 (−0.03287)	0.002183 (−0.00197)
Br, H	0.01532 (0.04151)	0.01493 (−0.03261)	1.1244 (0.9323)	0.01101 (0.02121)	0.01364 (−0.03194)	0.001488 (−0.00255)

The values in parenthesis are ground state results

We can conclude from the equations that the IHB energies correlate well with $\rho_{O...H}$ and H values ($R^2 > 9$) in the GS. While correlation IHB energies with $\nabla^2\rho$ and G/V values ($9 > R^2 > 8$) is not as good as with other parameters. In the S_1 , the linear dependence with appropriate regression coefficients shows that acceptable correlation between IHB energies and topological parameters is observed. However, the correlation of the IHB energies with the G/V parameter ($R^2 = 6934$) is not well. Similarly, the linear equations can be extracted for the topological parameters in the ring critical point.

3.4 NBO analysis

The natural bond orbital (NBO) theory has been extensively used to evaluate the IHB, especially in recent years [10, 38, 48]. According to the NBO theory, a certain charge is shifted from the proton acceptor lone pairs (Lp) to the proton donor antibonding orbital (σ^*) after IHB formation. Hence, the occupancy numbers and their energies of the involved orbitals changed. The magnitude of these charge transfer interactions (E^2) that called stabilization energy is calculated by second-order perturbation theory.

In this research, the NBO analysis was done by DFT and TD-DFT methods and the stabilization energies (E^2) ($Lp_{(O)} \rightarrow \sigma^*_{O-H}$) for the NFF derivatives in the both GS and S_1 are listed in Table 4. As see in this table, the range of E^2 values for the GS and S_1 are about 36.87–16.02 and 9.21–2.31 kcal/mol, respectively. These results indicate that hydrogen bond is stronger in the GS. These results significantly support the IHB energies. Also, based on the NBO data, the halogen effects of the NFF in the both GS and S_1 are in agreement with the previous sections. Furthermore, according to the other NBO parameters such as

Fig. 4 Correlations between the IHB energies (kJ/mol) and charge transfer energies (E_{CT}) (kcal/mol) in the GS and S_1

occupation numbers (n), their energies (E) and off diagonal Fock matrix elements ($F(i,j)$) the similar results are exist, which for space saving we ignored them here.

The graphical linear correlations between the E^2 and IHB energies in both GS and S_1 are indicated in Fig. 4. The regression coefficients are about 0.9359 and 0.7192,

Table 4 The charge transfer energies (E_{CT}) ($Lp(O) \rightarrow \sigma^*_{O-H}$) (kcal/mol), Gilli's parameters (Δ) and HOMA indices for the studied molecules at DFT and TD-DFT levels

R_1, R_2	E_{CT}	Q	Δ	OHOMA	HOMAED	HOMAHED
H, Br	9.21 (36.87)	0.0856 (0.122)	2.857 (2.744)	0.755 (0.435)	0.927 (0.793)	– (0.891)
H, Cl	9.18 (35.84)	0.0893 (0.145)	2.846 (2.672)	0.821 (0.472)	0.912 (0.788)	– (0.879)
H, F	8.95 (35.04)	0.0873 (0.153)	2.852 (2.647)	0.754 (0.673)	0.901 (0.743)	– (0.873)
H, H	8.97 (24.97)	0.0806 (0.179)	2.873 (2.566)	0.819 (0.195)	0.887 (0.625)	– (0.868)
F, F	5.37 (22.45)	0.103 (0.193)	2.803 (2.522)	0.476 (0.238)	0.843 (0.576)	– (0.784)
Cl, Cl	5.45 (22.08)	0.128 (0.177)	2.725 (2.572)	0.594 (0.186)	0.828 (0.512)	– (0.734)
Br, Br	2.83 (22.74)	0.161 (0.181)	2.622 (2.593)	0.601 (0.382)	0.846 (0.532)	– (0.746)
Br, Cl	2.98 (22.36)	0.0954 (0.165)	2.826 (2.609)	0.532 (0.268)	0.795 (0.545)	– (0.754)
Cl, Br	2.65 (22.25)	0.154 (0.181)	2.643 (2.559)	0.498 (0.243)	0.786 (0.529)	– (0.733)
F, Br	2.53 (21.88)	0.159 (0.182)	2.628 (2.556)	0.457 (0.183)	0.752 (0.522)	– (0.712)
Br, F	2.41 (20.72)	0.163 (0.197)	2.615 (2.509)	0.334 (0.174)	0.738 (0.518)	– (0.705)
Cl, H	2.37 (17.31)	0.166 (0.185)	2.606 (2.546)	0.485 (0.122)	0.726 (0.476)	– (0.693)
F, H	2.33 (17.98)	0.159 (0.194)	2.628 (2.519)	0.319 (0.231)	0.722 (0.434)	– (0.625)
Br, H	2.31 (16.02)	0.151 (0.196)	2.653 (2.512)	0.303 (0.487)	0.754 (0.428)	– (0.621)

The values in parenthesis are ground state results

respectively. Based on these results, the correlation of E^2 with the IHB energies in the GS is better than the S_1 .

3.5 Resonance parameters

The resonance is one of the most important concept in describe molecular structures in the aromatic and quasi-aromatic rings, that extensively studied [9, 37, 49, 50]. In the years ago, the various quantitative parameters of resonance that classified as geometry-based, energy-based and magnetic-based were suggested [37, 50–53]. Among these descriptors, the geometries of molecules are a very available source to provide the principle information about resonance. Hence, the some geometry-based descriptors such as Q , λ , OHOMA, HOMAED and HOMAED for NFF derivatives in the both GS and S_1 were calculated and their results listed in Table 4. It seems that from this table that by excitation of the molecules the Q values decreased, while λ and HOMAs indices are increased. Since which these parameters are related to the bond equalization, it can be concluded that resonance augmented in the S_1 . However, this result is in contrast with the IHB energies.

In this work, we not only re-examine Raczynska's and Frizzo's concepts on the NFF derivatives [26, 27], but also for the first time calculated the HOMAs indices in the S_1 (see Table 4). A deeper looks on the Table 4 readily show that the OHOMA values for the NFF derivatives in the both GS and S_1 are not in line of the IHB energies and are scattered. While, the HOMAED and HOMAED values are more reliable and support pervious results from other IHB descriptors, especially in the GS. However, our results are in accordance with Raczynska et al. about inappropriate OHOMA index for compounds containing heteroatom [26]. Finally, investigation of the linear interdependence between the IHB energies and Q , λ , OHOMA, HOMAED and HOMAED resonance indices in the GS, indicate that the regression coefficients are about 0.7721, 0.7721, 0.2996, 0.9435 and 0.8326, respectively. But in the S_1 , our results proved that linear equations all of the resonance indices with the IHB energies are non-linear and are unsuitable for estimation of the IHB strength in the studied molecules.

4 Conclusions

In this article, the intramolecular hydrogen bond of the NFF derivatives in the both ground and first singlet excited state were compared by DFT and TD-DFT methods with the standard basis set 6-311++G (d,p), respectively. The MO analysis was used to investigate the IHB energies difference between the GS and S_1 . Moreover, some of the IHB descriptors such as geometrical, topological, orbital

charge transfer parameters were extracted from the output files. Then, geometry-based resonance indices such as Q , λ , OHOMA, HOMAED and HOMAED were calculated and compared in the both GS and S_1 . Ultimately, the linear equations of the IHB energies versus mentioned parameters in the both GS and S_1 were obtained and the regression coefficients were compared. The conclusions are as follow:

- The potential energy density method was employed to calculate of the IHB energies in the both GS and S_1 . The results indicated that IHB strength in the GS is much stronger than the S_1 one in the NFF derivatives.
- It is obvious from the results that the substitution effects on the both GS and S_1 are same. As with replacing at R_2 position the IHB energies increased while for the R_2 and $R_{1,2}$ decreased and the below order is predictable:
 R_2 -substituted > NFF > R_1R_2 -substituted > R_1 -substituted
- In the next sections of this study, geometrical, topological and charge transfer parameters are comprehensively evaluated and the results strongly supported the IHB energies and the substitution effects in the both GS and S_1 .
- The regression coefficients shown that geometrical, topological and charge transfer descriptors correlate the IHB energies very well in the GS, while for the S_1 the correlation between the IHB energies and more of its descriptors, except topological parameters, is not acceptable. Hence, we can claim that the potential energy density is not a reliable method for calculation of the IHB energies of the heterocyclic RAHB systems in the S_1 .
- Interestingly, the geometry-based resonance indices proved that electron delocalization in the S_1 is higher than GS that this result is against the RAHB theory in the studied molecules. Moreover, from results of the correlation the IHB and the resonance indices, it can be conclude that HOMAED and HOMAED are more suitable than the other indices in the GS. But in the S_1 , all of the resonance indices don't correlate the IHB energies.

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