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Isomerism and Hydrogen Bonding in the *Cis*-enol Forms of 1-(n-pyridyl)butane-1,3-diones: A Theoretical Study

R. Afzali, M. Vakili*, S.F. Tayyari and H. Eshghi

Ferdowsi University of Mashhad, Masshad, Iran

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Molecular structure, isomerism, conformational stability and intramolecular hydrogen bonding (IHB) of *cis*-enol forms of 1-(n-pyridyl)butane-1,3-diones (nPBD) (n = 2, 3, or 4) have been investigated by means of density functional theory (DFT) calculations. Energy differences for all possible nPBD *cis*-enol forms of isomers with respect to the most stable form of the corresponding isomer have been estimated in the gas phase and solution. AIM results (performed at the B3LYP/6-311++G** level) suggest 75.19-84.77 kJ mol^{-1} for the strength of intramolecular hydrogen bond in these systems, as a medium hydrogen bond strength. Theoretical structure, NBO and intramolecular hydrogen bond strength for the stable *cis*-enol forms of nPBD have been compared with each other and also with those of acetylacetone (AA), benzoylacetone (BA), and triflouroacetylacetone (TFAA) molecules. The hydrogen bond strength and molecular stability are investigated by applying the NBO, topological analysis, geometry calculations, and spectroscopic results. The correlation between IHB and some parameters related to hydrogen bonding have been also investigated.

Keywords: 1-(n-pyridyl)butane 1,3-diones, Intramolecular hydrogen bond, Density functional theory, NBO, Atoms in molecules theory

INTRODUCTION

β-Diketones are widely used in organic and inorganic chemistry [1-5]. The *cis*-enol form of β-diketones is specified by a strong to medium intramolecular hydrogen bond [6-7]. The nature of this intramolecular hydrogen bond, O-H···O, in the cis-enol form of symmetric and asymmetric β-diketones have been the subjects of intensive studies [8-10].

Hydrogen bond formation increases the π-electron resonance conjugation. Formation of this hydrogen bond stabilizes the chelated enol forms of β-diketones. Several experimental and theoretical data suggest that some substituents, such as the trifluoromethyl ($-CF_3$) [11], phenyl ($-C_6H_5$) [12], *t*-But ($-C(CH_3)_3$) [13], thiophene (C_4H_3S) [14], and furan (C_4H_3O) [15] groups in α- or β-positions significantly change the strength of intramolecular hydrogen bond (IHB). Electron-withdrawing groups, such as trifluoromethyl ($-CF_3$), decrease the strength of IHB, whilst trifluoromethyl ($-CF_3$), decrease the strength of IHB, whilst substitution of a π-system and bulky groups, such as phenyl, thiophene (C_4H_3S), furan (C_4H_3O) rings, and *t*-But increase the IHB strength.

In 1-(n-pyridyl)butane-1,3-diones (nPBD) molecules, the N and O atoms situated at one side of these molecules might be effectively designed to form polynuclear complexes with interesting architecture and superior properties. These compounds probably possess electronic triplet levels favoring the luminescent properties and are expected to exhibit photostability [16].

The aim of the present study is to investigate the relative stability, geometrical parameters, IHB strength (IHBs), and barrier to rotation of pyridyl ring relative to chelated ring in the stable *cis*-forms of all three isomers of 1-(n-pyridyl)butane-1,3-diones (1-(2-pyridyl)butane-1,3-dione, 2PBD, 1-(3-pyridyl)butane 1,3-dione, 3PBD, and 1-(4-pyridyl)butane 1,3-dione, 4PBD), as an asymmetric β-diketone that one of the terminal groups is the pyridyl ring

*Corresponding author. E-mail: vakili-m@um.ac.ir

and the other is methyl group. Then, the calculated results of nPBD will be compared with the corresponding values of AA, BA and TFAA.

METHOD OF ANALYSIS

Geometrical calculations were performed using Gaussian 09 [17] program. All possible structures were fully optimized at the B3LYP level [18,19], using 6-311++G** basis set.

The correlations between some calculated parameters and the IHB energies have been also investigated. Graphs were drawn and regression analyses were carried out using the Microsoft Excel 2013 program [20]. Acetonitrile and carbon tetrachloride were selected for studying the tautomerism in solution following the SCRF-PCM method [21], according to which the solute is embedded in the dielectric medium surrounded by a cavity shaped in form of the solute [22,23]. The van der Waals radii suggested by Bondi [24] were adopted for atoms.

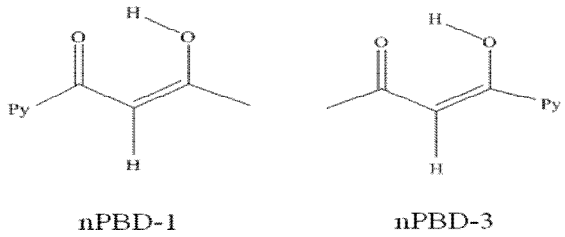
The natural charge distribution, Wiberg bond orders [25], second order interaction energies [26], and steric exchange energies [27] were calculated using NBO 5.0 program [28], based on the wave function information file generated by earlier version of NBO 3.0.

AIM 2000 software [29] was applied to obtain electron density at the hydrogen bond critical points, according to Bader's atoms in molecules (AIM) theory [30], to estimate the intramolecular hydrogen bond strength.

RESULTS AND DISCUSSION

Isomerism and Conformational Analysis

From the theoretical point of view, by considering the position of nitrogen atom in pyridyl ring with respect to the chelated ring of molecule, three isomers 2PBD, 3PBD and 4PBD can be drawn for nPBD molecules. In the case of enolated molecules, for each of these isomers, two possible tautomers characterized by the position of the pyridyl ring, which can be attached to C1 (*i.e.* neighbor the C=O group) or to C3 (*i.e.* neighbor the OH group) are conceivable. They are labeled as nPBD-1 and nPBD-3, respectively (Fig. 1).



nPBD-1 nPBD-3

Fig. 1. Tautomerization in nPBD.

Furthermore, in 2PBD and 3PBD isomers, there are two other conformers which, depending on the position of the nitrogen atom in pyridine ring relative to the oxygen atoms, are designated as gauche (2PBD-1G and 2PBD-3G, 3PBD-1G and 3PBD-3G) and anti (2PBD-1A and 2PBD-3A, 3PBD-1A and 3PBD-3A) forms (see Figs. 2a-b). So, there are four conformers in the case of 2PBD and 3PBD isomers, as shown in Fig. 2a-b, while in the case of 4PBD, there are only two *cis*-enol forms (see Fig. 2c). The relative stabilities of all possible tautomers and conformers of nPBDs with respect to the most stable form of each isomer (in kJ mol^{-1}) and the atom numbering of the system are also given in Fig. 2. The *cis*-enol forms, in which the O-H and C=C bonds are in the *cis* arrangement, are designated as I and their corresponding trans-enol conformers are designated as II. The CH_3 groups in nPBD-1and nPBD-3 are almost staggered and eclipsed with respect to the neighboring oxygen atom, respectively.

The calculated total electronic energies (in Hartrees), relative stabilities with respect to their most stable form (in kJ mol^{-1}), dihedral angle (in degrees) between pyridyl and chelated rings, and dipole moments (in Debye) for all *cis*-enol forms, calculated in the gas phase, are listed in Table 1. According to this table, 2PBD-1A and 3PBD-1A with respect to the other forms in each isomer are the most stable forms.

Table 1 also shows that the relative energies of all species with respect to the most stable enol form of each isomer, 2PBD-1A, 3PBD-1A, and 4PBD-1, are 3.72-26.23, 3.51-6.28, and 2.38 kJ mol^{-1}, respectively. Upon ZPE corrections, these energy differences slightly decreases. As Table 1 shows, the anti-forms of 2PBD and 3PBD are more stable than gauche-forms of the mentioned isomers.

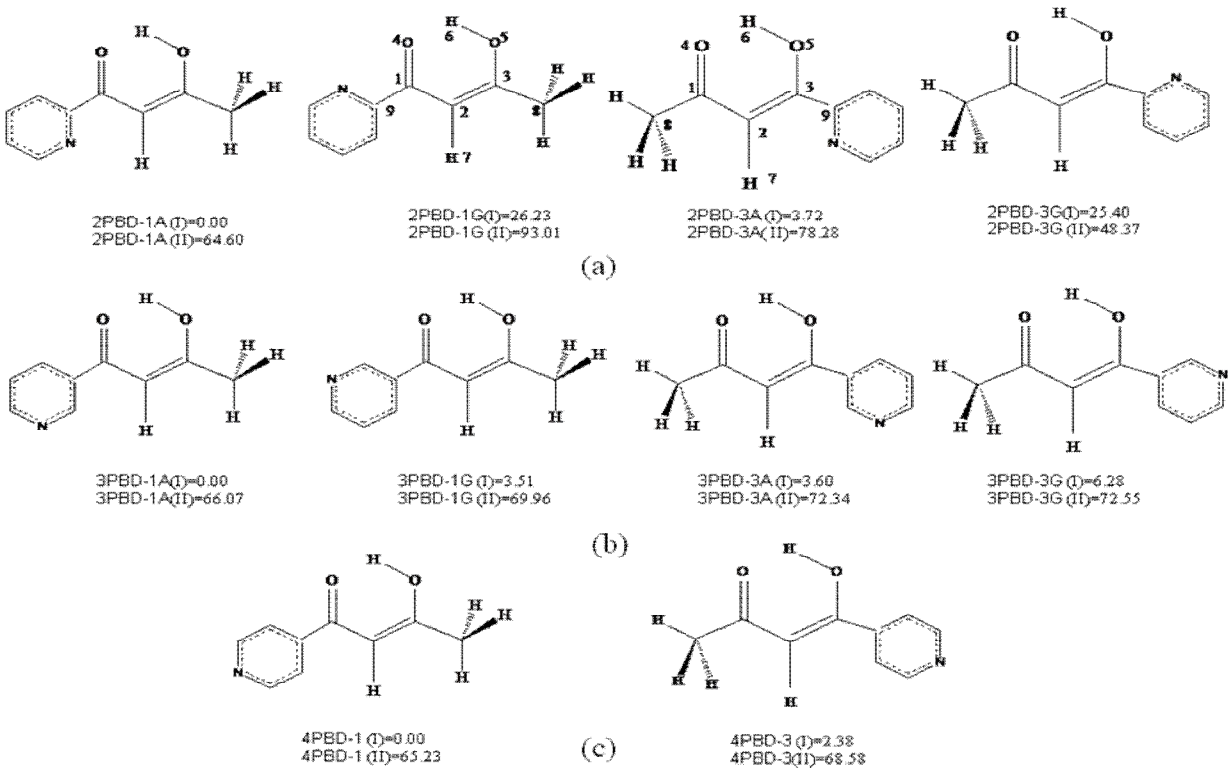


Fig. 2. The possible *cis* enol forms in nPBD, along with their relative stabilities in kJ mol^{-1} for *trans* and *cis* conformers calculated at B3LYP/6-311++G** level, and the atomic numbering system.

According to Table 2, this stability also could be interpreted by resonance increasing between pyridine and chelated rings in the anti-forms (I/IV) in relative to the gauche-forms (II/III) (Tables S1-4), which the resonance can be evaluated by total second order perturbation energy. As shown in Table 2, the total second order perturbation energy for anti-forms (I/IV) of 2PBD-1 and 3PBD-1, 2PBD-3 and 3PBD-3 is more than that in gauche-forms (II/III).

Pyridine Ring Rotational Barriers

To monitor the potential change during anti ↔ gauche interchange, we constrain the pyridyl-enol ring dihedral angle (φ), chosen as the reaction coordinate, at values between 0 and 360° by steps of 10°. The potential energy curves along the reaction path for anti ↔ gauche reaction of 2PBD and 3PBD isomers are shown in Figs. 3-6, respectively. These curves are created in the gas phase by keeping constant the geometrical parameters, except for φ.The total second order perturbation ($E^{(2)}$) and the steric hindrance (ΔE (i,j)) for the conformers obtained due to anti ↔ gauche reaction of both tautomers of 2PBD and 3PBD are collected at Table 2 (see Tables 2, S1-8).

Rotation of the pyridyl group about C1/C3-pyridyl bond produces three barrier heights for the 2PBD and 3PBD isomers, the C1 and C3 atoms stand for nPBD-1 and nPBD-3 tautomers, respectively. The barriers for rotation in both tautomers of 2PBD isomer (2PBD-1 and 2PBD-3) occur at 90°, 180°, and 270° ($\Delta E_{(I'-I)}$ = 31.5, 36.8 and 31.5 kJ mol^{-1}) for 2PBD-1 tautomer, and 28.9, 26.3 and 28.9 kJ mol^{-1} for 2PBD-3 tautomer, respectively). In both 3PBD-1 and 3PBD-3 tautomers, the barriers for rotations occur at 90º, 180º and 270º ($\Delta E_{(I'-I)}$ = 23.6, 10.5 and 23.6 kJ mol^{-1} for 3PBD-1 tautomer, and 17.6, 2.6, and 17.6 kJ mol^{-1} for 3PBD-3 tautomer, respectively).

The first and third barriers in Figs. 3-6 appear due to the stopping of resonance between pyridyl and enol rings.

Table 1. The Absolute Total Electronic Energies (E), the O…O Distances (R), and the Comparative Energies (ΔE) for nPBD Forms of each Isomer with Respect to the most Stable Form of that Isomer, Calculated at B3LYP/6-311++G** Levels of Theory[a]

	2PBD-1A	2PBD-1G	2PBD-3A	2PBD-3G	3PBD-1A	3PBD-1G	3PBD-3A	3PBD-3G	4PBD-1	4PBD-3
R	2.544	2.530	2.534	2.546	2.530	2.528	2.522	2.524	2.530	2.529
E	-553.737830	-553.727845	-553.736409	-553.728163	-553.733794	-553.732456	-553.732426	-553.731397	-553.732363	-553.731460
ΔE	0.00	26.23	3.72	25.40	0.00	3.51	3.60	6.28	0.00	2.38
D.A	-179.99	-33.24	-179.99	29.65	-171.04	15.59	165.96	-16.66	-12.18	13.14
D.M	2.81	5.08	3.47	5.35	1.06	4.92	1.31	4.70	3.39	2.77
ZPE	0.00	25.44	1.55	23.72	0.00	3.47	2.13	4.85	0.00	1.09

[a]R: optimized O…O distance (Å); E: absolute electronic energy (hartrees); ΔE: relative energy related to the most stable form of each isomer, in kJ mol^{-1} at B3LYP/6-311++G**; D.A: dihedral angle between pyridyl and chelated rings; D.M: dipole moment; ZPE: the: relative energy by considering of zero point energy.

Table 2. The Total Second Order Perturbation Energies $E^{(2)}$ and Pairwise Steric Exchange Energies, ΔE (i,j) in kJ mol^{-1}[a]

	2PBD-1	2PBD-3	3PBD-1	3PBD-3
$E^{(2)}$				
(I/IV)	1046.6	1034.7	1080.8	1057.1
(II′)	1086.5	1026.6	1080.7	1061.9
(II/III)	995.2	991.9	1001.0	1035.4
(I′/III′)	952.4	952.9	984.2	997.7
ΔE (i,j)				
(I/IV)	236.1	227.8	233.9	163.9
(II′)	242.1	216.9	234.1	178.2
(II/III)	202.8	202.8	227.5	163.0
(I′/III′)	220.8	211.3	218.9	127.9

[a](I/IV), (II′), (II/III) and (I′/III′) are standed for anti, syn, gauche, and perpendicular forms.

According to Table 2, the total resonance energy ($E^{(2)}$) for anti-forms (I/IV) are higher than those in I′/III′ forms. In Figs. 3-6, these barrier heights indicate that the only possible conformers are (I), so the presence of other conformers in the sample are unlikely. The steric hindrance between pyridyl group and chelated ring is the reason for appearance of the second maximum (II′) in the V(φ) curve. Table 2 shows, the total steric hindrance for II′ of 2PBD and 3PBD forms are higher than that in gauche form (II/III).

In the case of 2PBD-3, the energy difference between I and II′ is 26.3 kJ mol^{-1}, slightly less than that in 2PBD-1 form (36.8 kJ mol^{-1}), as shown in Figs. 3-4, in agreement with the total pairwise steric exchange energies (Table 2). According to Table 2, the total steric energy for (II′) form in

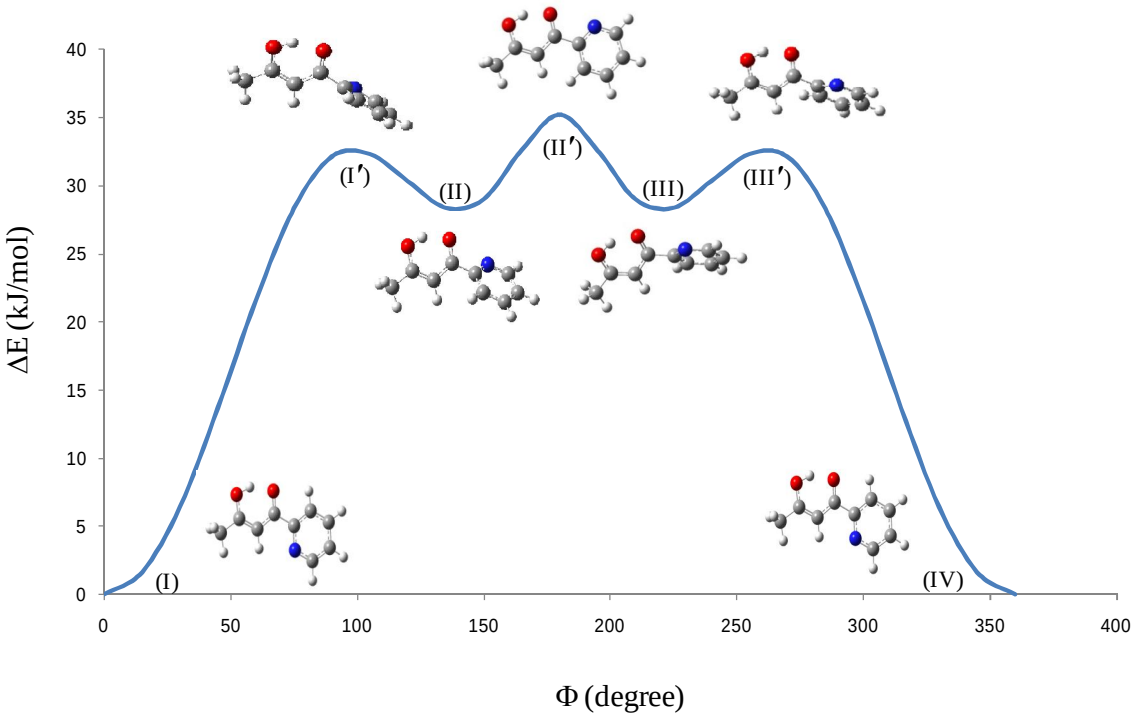


Fig. 3. Potential surface of the pyridine ring torsion in 2PBD-1as a function of dihedral angle (φ), obtained at B3LYP/6-311++G**.

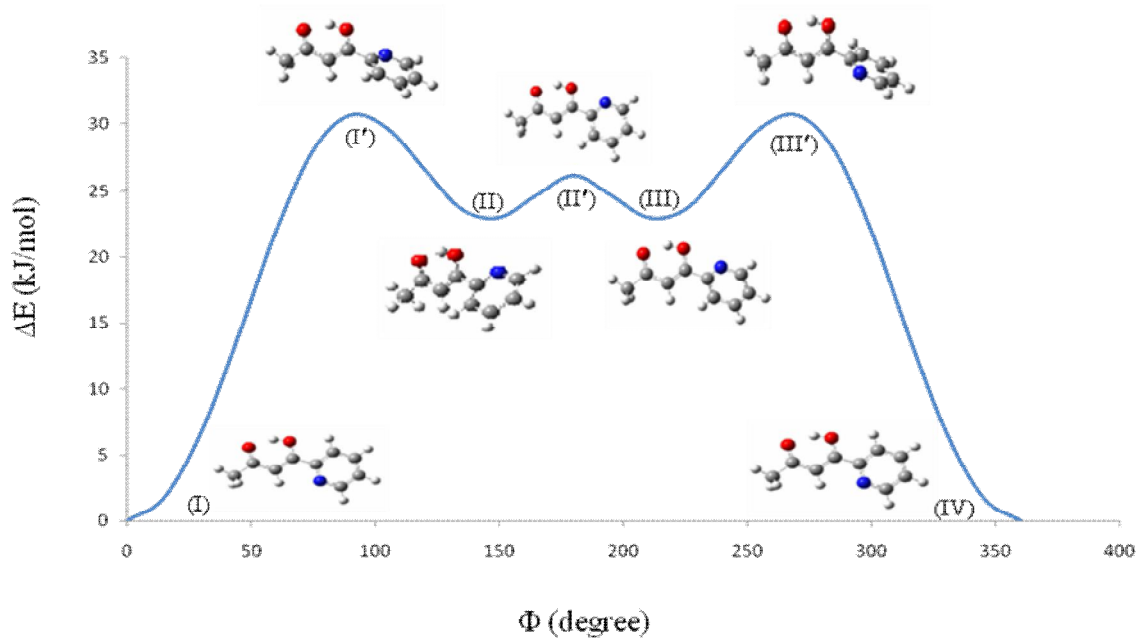


Fig. 4. Potential surface of the pyridine ring torsion in 2PBD-3as a function of dihedral angle (φ), obtained at B3LYP/6-311++G**.

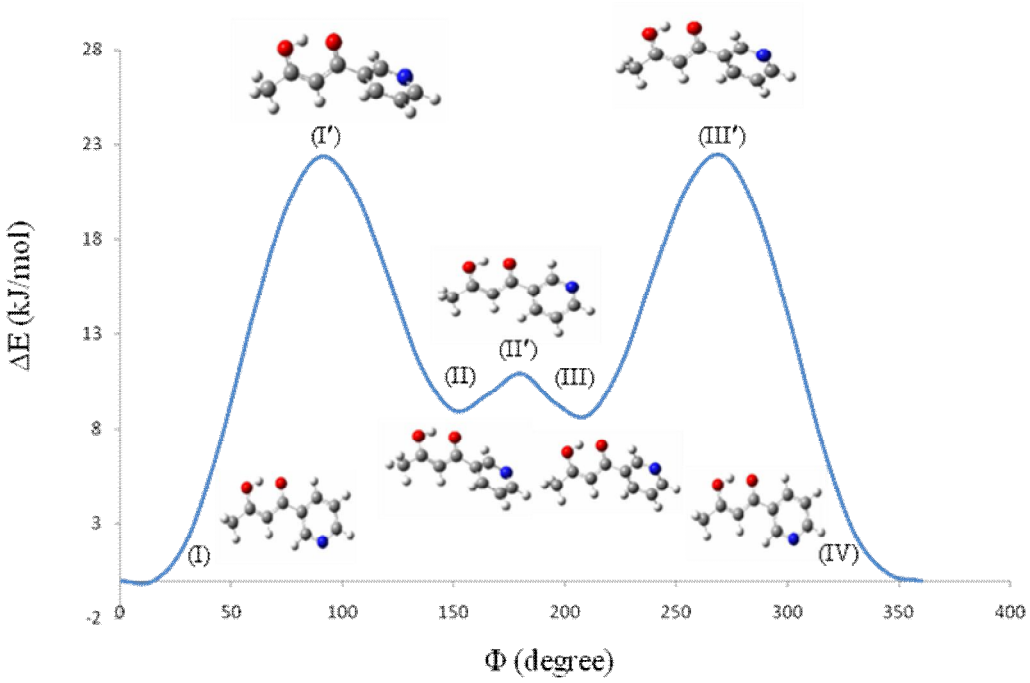


Fig. 5. Potential surface of the pyridine ring torsion in 3PBD-1as a function of dihedral angle (φ), obtained at B3LYP/6-311++G**.

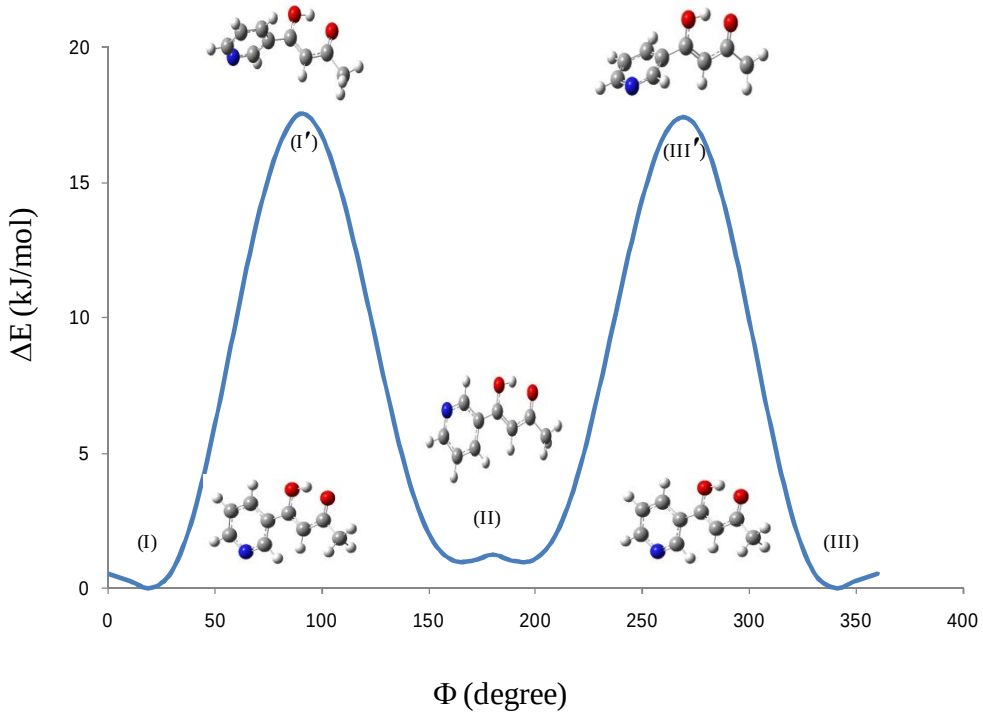


Fig. 6. Potential surface of the pyridine ring torsion in 3PBD-3as a function of dihedral angle (φ), obtained at B3LYP/6-311++G**.

2PBD-3 (216.9 kJ mol^{-1}) is less than 2PBD-1 (242.1 kJ mol^{-1}). The potential surface in 3PBD-1 is similar to that in 2PBD-3 form (with three minima in potential surface, see Fig. 5), while in 3PBD-3 the second barrier is very low (see Fig. 6), confirmed by the results of total steric hindrance at Table 2. As this table indicates, the total steric hindrance of II′ in 3PBD-3 is less than those in the other tautomers. The torsional potential surfaces can be well represented by the Fourier cosine series in the internal rotation angle φ [31]:

$$V(\varphi) = \Sigma (V_i/2)(1-\cos i\varphi)$$

where φ and i are the torsional angle and the foldness of barrier, respectively. The potential function parameters are given in Table 3.

Solvent Effects

Because of significant difference in dipole moments of these species, the given stability order in Table 1 is expected to be changed in solutions. In order to study the solvent influences on the stability of different forms in each isomers of nPBD molecule, the optimization calculations on the chelated forms have been carried out in two solvents, CCl_4 and CH_3CN, characterized by their dielectric permittivity constant (ε) = 2.23 and 36.64, respectively. The electronic energies and the relative stability energies of all forms of nPBD isomers in solution, with respect to the most stable chelated form of each isomer, along with their calculated dipole moments are summarized in Table 4. As shown in Tables 1 and 4, 3PBD-1A and 4PBD-1 are the most stable forms in the corresponding set of their family forms in the gas phase and solutions. While in the case of 2PBD isomer, the energy of 2PBD-1A in the non-polar solvent and gas state is lower than that for the other forms of this isomer, but in polar solvent (CH_3CN), 2PBD-3A is the most stable one.

Structure and Intramolecular Hydrogen Bonding

The fully optimized geometrical parameters of all *cis*-enol forms of 2PBD, 3PBD and 4PBD isomers, the topological parameters including electron density at bond critical points (ρ_{BCP}) and the Laplacian of electron density at the critical points ($\nabla^2\rho_{BCP}$), the ratio of potential electron energy density (V(r)) and kinetic electron energy density (G(r)), [G(r)/V(r)] at the bond critical point, hydrogen bond energy, E_{HB}, (-V(r)/2 in kJ mol^{-1}) according to Rozas *et al.* [32]), for all O···H bonds of all forms are listed in Table 5.

Table 3. Potential Parameters and Barriers of (I) ↔ (II) ↔ (III) Interconversion Obtained at the B3LYP/6-311++G** Level of Theory (in kJ mol^{-1})

	2PBD-1	2PBD-3	3PBD-1	3PBD-3
V1	-0.0539	-0.0373	-0.0923	0.1704
V2	0.1355	0.0792	0.0600	2.0632
V3	-0.4362	-0.3533	-0.5370	-0.0736
V4	0.0000	0.0000	0.0000	0.1067
V5	0.6802	0.6487	0.2533	-0.4977
V6	1.8362	2.1641	2.1100	-0.0251
V7	3.3001	2.3477	0.9719	-0.0716
(I)'s Relative energy	0.0000	3.7200	0.0000	3.6000
(II)'s Relative energy	26.230	25.400	3.5100	6.2800
(I) → (II) Barrier	31.500	28.900	23.600	17.600
(II) → (III) Barrier	36.800	26.300	10.500	2.6000
(III) → (IV) barrier	31.500	28.900	23.600	17.600

Table 4. The Absolute Total Electronic Energies, and the Comparative Energies for nPBD Forms in Solution with Respect to the most Stable Form of each Isomer, Calculated at B3LYP/6-311++G** Levels of Theory[a]

	2PBD-1A	2PBD-1G	2PBD-3A	2PBD-3G	3PBD-1A	3PBD-1G	3PBD-3A	3PBD-3G	4PBD-1	4PBD-3
CCl_4										
ΔE	0.00	21.05	3.35	20.88	0.00	2.59	3.31	5.27	0.00	2.18
E	-553.741209	-553.733187	-553.739934	-553.733252	-553.737707	-553.736725	-553.736446	-553.735693	-553.736386	-553.735555
D.M	3.22	5.93	4.00	6.21	1.23	5.68	1.55	5.43	3.92	3.21
CH_3CN										
ΔE	0.00	0.92	-8.54	1.80	0.00	0.67	2.89	3.26	0.00	1.80
E	-553.741209	-553.740862	-553.744466	-553.740524	-553.742760	-553.742499	-553.741667	-553.741520	-553.741694	-553.741016
D.M	3.76	7.27	4.71	7.56	1.70	6.82	1.91	6.54	4.68	3.88

[a]E: absolute electronic energy (hartrees); ΔE: stability energy related to most stable form of each isomer in solution, in kJ mol^{-1}; D.M: dipole moment.

Table 5. Some Geometrical Parameters, the AIM Results Related to the IHB Strength of *cis*-enol Stable Forms of nPBD Isomers, BA, TFAA and AA[a]

	2PBD-1A	2PBD-1G	2PBD-3A	2PBD-3G	3PBD-1A	3PBD-1G	3PBD-3A	3PBD-3G	4PBD-1	4PBD-3	2BA	4BA	2TFAA	4TFAA	AA
Bond length[b]															
O…O	2.544	2.530	2.534	2.546	2.530	2.528	2.522	2.524	2.530	2.529	2.520[d]	2.513[d]	2.566[e]	2.550[e]	2.544
O…H	1.636	1.615	1.619	1.636	1.618	1.616	1.599	1.603	1.620	1.611	1.604[d]	1.585[d]	1.672[e]	1.654[e]	1.633
O-H	1.002	1.006	1.005	1.002	1.004	1.005	1.007	1.007	1.004	1.005	1.006[d]	1.010[d]	0.997[e]	1.002[e]	1.003
C=O	1.251	1.243	1.247	1.245	1.252	1.251	1.247	1.247	1.250	1.245	1.252[d]	1.250[d]	1.237[e]	1.240[e]	1.246
C-O	1.326	1.323	1.329	1.319	1.323	1.323	1.328	1.327	1.322	1.327	1.324[d]	1.326[d]	1.320[e]	1.318[e]	1.326
C=C	1.372	1.373	1.369	1.374	1.373	1.373	1.375	1.375	1.374	1.372	1.372[d]	1.378[d]	1.378[e]	1.367[e]	1.370
C-C	1.436	1.443	1.444	1.444	1.440	1.441	1.443	1.443	1.439	1.446	1.443[d]	1.439[d]	1.426[e]	1.457[e]	1.444
<OHO	148.4	148.9	149.0	148.7	148.5	148.6	149.8	149.6	148.4	149.3	148.9[d]	150.5[d]	146.8[e]	146.5[e]	148.6
AIM Results[c]															
E_{HB}	75.27	80.63	79.41	75.19	79.83	80.46	84.77	83.64	79.50	81.50	83.76	85.69	61.38	71.38	75.81
ρ_{BCP}	0.0568	0.0600	0.0593	0.0569	0.0593	0.0597	0.0623	0.0616	0.0591	0.0604	0.0615	0.0627	0.0488	0.0548	0.0573
$\nabla^2\rho_{BCP}$	0.1476	0.1484	0.1478	0.1465	0.1500	0.1499	0.1504	0.1501	0.1497	0.1494	0.1518	0.1511	0.1387	0.1427	0.1460
G/V	0.82	0.80	0.81	0.82	0.81	0.81	0.79	0.79	0.81	0.80	0.80	0.79	0.87	0.83	0.82

[a]All calculated at the B3LYP/6-311++G** level. [b]Bond lengths are in Å, bond angle is in degree, and E_{HB} is the IHB energy in kJ mol^{-1}, all calculated at B3LYP/6-311++G**. [c]The units of AIM results are: ρ_{BCP} (e $a.u.^{-3}$), $\nabla^2\rho_{BCP}$ (e $a.u.^{-5}$). [d]Data from Ref. [33]. [e]Data from Ref. [15].

Table 6. Selected Wiberg Bond Orders for nPBD, BA, TFAA and AA Calculated at B3LYP/6-311++G** Level of Theory

Bond	nPBD										BA		TFAA		AA
	2PBD				3PBD				4PBD						
	2PBD-1A	2PBD-1G	2PBD-3A	2PBD-3G	3PBD-1A	3PBD-1G	3PBD-3A	3PBD-3G	4PBD-1	4PBD-3	2BA	4BA	2TFAA	4TFAA	
O-H	0.6239	0.6144	0.6153	0.625	0.6179	0.6163	0.6091	0.6108	0.6178	0.6136	0.6135	0.6096	0.6402	0.5681	0.6211
C=O	1.541	1.5849	1.5829	1.5905	1.5328	1.5381	1.5782	1.5793	1.5424	1.5893	1.5352	1.5702	1.6215	1.1777	1.5883
C-O	1.1632	1.1733	1.1419	1.18	1.1726	1.1741	1.1509	1.1553	1.1765	1.1517	1.1698	1.1556	1.1765	0.9269	1.1627
C=C	1.5381	1.5381	1.5448	1.5311	1.5357	1.5364	1.5225	1.5198	1.5294	1.5345	1.5435	1.5119	1.5128	1.2537	1.5548
C-C	1.2049	1.1909	1.1851	1.1862	1.1949	1.1924	1.1924	1.1933	1.1999	1.1825	1.1894	1.2026	1.2288	0.9939	1.1861

Table 7. Selected Natural Charges (e) for Optimized *cis*-enol nPBD, BA, TFAA and AA

Atom	nPBD										BA		TFAA		AA
	2PBD-1A	2PBD-1G	2PBD-3A	2PBD-3G	3PBD-1A	3PBD-1G	3PBD-3A	3PBD-3G	4PBD-1	4PBD-3	2BA	4BA	2TFAA	4TFAA	
O4	-0.655	-0.613	-0.644	-0.641	-0.657	-0.650	-0.642	-0.643	-0.647	-0.637	-0.656	-0.648	-0.597	-0.621	-0.647
O5	-0.667	-0.664	-0.673	-0.634	-0.663	-0.662	-0.670	-0.664	-0.660	-0.665	-0.666	-0.668	-0.651	-0.640	-0.669
C1	0.489	0.499	0.527	0.526	0.522	0.522	0.527	0.527	0.520	0.529	0.509	0.524	0.438	0.541	0.530
C2	-0.440	-0.455	-0.416	-0.441	-0.450	-0.453	-0.437	-0.441	-0.450	-0.430	-0.444	-0.437	-0.457	-0.416	-0.464
C3	0.470	0.471	0.416	0.436	0.473	0.473	0.457	0.459	0.477	0.452	0.468	0.448	0.488	0.349	0.466
H6	0.507	0.506	0.508	0.505	0.507	0.507	0.508	0.508	0.508	0.508	0.506	0.507	0.508	0.511	0.507

For comparison, the mentioned parameters for BA, TFAA and AA at the same level of theory are collected at Table 5. It should be noted, depending on the position of carbonyl group, the nPBD-1 form of nPBD is compared to the 2BA and 2TFAA forms, and the nPBD-3 form of nPBD compared to 4BA and 4TFAA (see Fig. 7).

As Table 5 shows, the total electronic density is positive in all conformers, which is characteristic of closed shell interactions and also the -G(r)/V(r) values in all cases is close to unit, which partly covalent nature of hydrogen bonds can be concluded. By considering the IHB interactions in all considered forms, they can be classified according to Rozas *et al.* [32], as medium strength hydrogen bonded systems.

As notified by Tayyari *et al.* [33], significant resonance exists between C=O and phenyl groups in 2BA, so that, in comparison with AA, the C=O bond length increases, while the change in other bond lengths in 2BA is negligible. Substitution of methyl group in AA by triflouromethyl, in 2TFAA, decreases and increases the C-C and C=C bond lengths, respectively, compared to the corresponding bond lengths in AA [15], indicative of electron withdrawing effect of CF_3 group in TFAA. Comparing the chelated ring bond lengths in 3PBD-1A, 3PBD-1G, and 4PBD-1 with those in AA, indicates that the C=O and C-C bond lengths are significantly longer and shorter, respectively, than those in AA. It is noteworthy that the O···O distances in the mentioned forms are less than that in AA. Therefore, it may be concluded that the resonance between the pyridyl and chelated rings significantly affect the structure of the chelated ring. It is also concluded that the IHB strengths of aforementioned forms are higher than that in AA. This is in agreement with the Wiberg bond orders (Table 6), and the natural charge results (Table 7). According to Table 7, the natural charges of 3PBD-1 (anti & gauche) and 4PBD-1 have similar behavior with the corresponding values in 2BA.

Comparison between the O···O and O···H distances in 2PBD-1 conformers (anti & gauche) with those in AA indicates different behavior of pyridyl group in these forms.

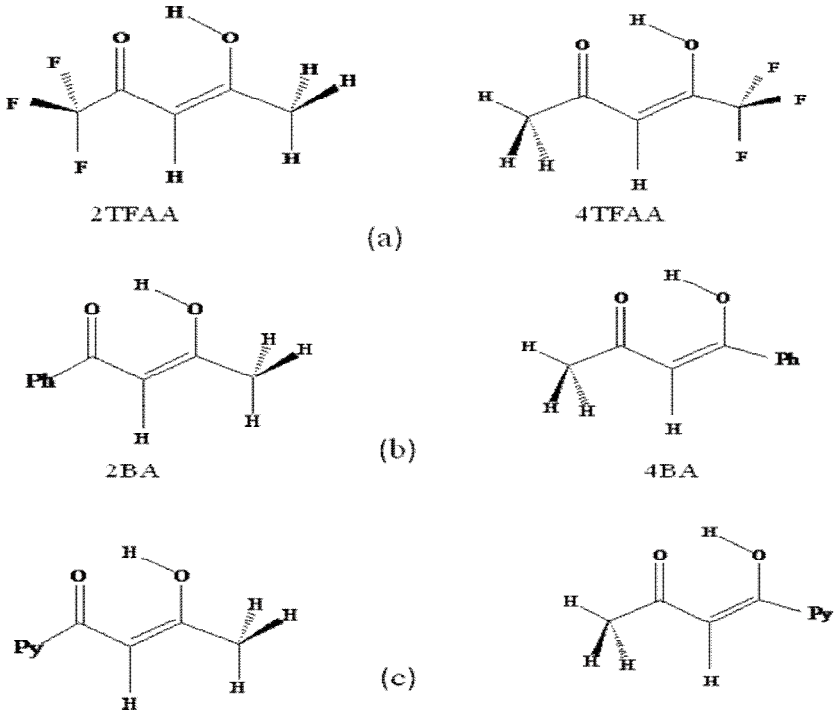


Fig. 7. The stable *cis*-enol forms of a) TFAA, b) BA, and c) nPBD.

In 2PBD-1G, the reduction of O···O and O···H distances in comparison with AA, demonstrate higher IHB strength (IHBs) in this molecule, while other structural parameters of chelated ring show no significant variation. Therefore, the increase in IHB of 2PBD-1G is due to the steric effect between pyridyl and chelated rings.

The trend in IHBs for 2BA, 2TFAA and nPBD-1 forms is:

2BA > 3PBD-1G ≅ 3PBD-1A ≅ 4PBD-1 ≅ 2PBD-1G > 2PBD-1A ≅ AA > 2TFAA

In the case of nPBD-3 tautomers, as in the case of 4BA, the resonance effect of phenyl ring causes an increase in the C=C bond length and a decrease in the C-C bond length compared to the corresponding values in AA, while these changes in 4TFAA are in opposite direction. By considering the nPBD-3 tautomers of nPBD isomers, it could be concluded that the O···O distance in 2PBD-3A, 3PBD-3G, 3PBD-3A and 4PBD-3 decreases in relative to AA and consequently their IHB strength increases. This is in agreement with the variation of C=C and C-C bond lengths, similar to the corresponding values in 4BA. Therefore, these results indicate the resonance effect of pyridine ring in 2PBD-3A, 3PBD-3G, 3PBD-3A and 4PBD-3. There is no significant difference between the chelated rings, structural parameters of 2PBD-3G and AA, indicating that IHB of 2PBD-3G is approximately similar to that in AA.

The trend in IHBs for four conformers is:

4BA > 3PBD-3A ≅ 3PBD-3G > 4PBD-3 > 2PBD-3A > AA ≅ 2PBD-3G

From theoretical results, it could be shown that the nPBD-3 isomers have stronger IHB in comparison with the nPBD-1 tautomers, except for 2PBD-3G, which its IHB is weaker than that in 2PBD-1G. According to the previous discussions, this is due to the steric effect in 2PBD-1G, which makes its IHB stronger than that in 2PBD-3G form. In the other nPBD-3 forms, which the pyridyl group is neighbor of hydroxyl group, the C=C and C=O bond lengths increase, while the C-C bond length decreases. These changes in the bond lengths indicate that the π-electron delocalization in the enol ring slightly increases by pyridine substitution for the methyl group in the hydroxyl side. When the pyridyl group is neighbor of the carbonyl group (in all nPBD-1) only the C=O bond length increases and changes in the other bond lengths are negligible. This result suggests that in nPBD-1 conformer, the pyridyl ring is conjugated only with the C=O group.

In all nPBD isomers, according to AIM and geometrical parameters results, as illustrated in Fig. 8, the intramolecular hydrogen bond strength show a discrepancy. According to Fig. 8, the IHB energies well correlate with the rO···O, rO···H and rO···H+rO-H(R′) distances. The linear correlation coefficients are 0.9552, 0.9683 and 0.9738, respectively. According to this data, correlation of IHB energy with the sum of O-H bond length and O···H distance, R′, is considerably better than the correlation between IHB energy and O···O distance. This result has been also reported for other bent intramolecular hydrogen bonded systems [34,35]. In Fig. 9, the correlation of IHB energies with the total electronic density, and its corresponding Laplacian in BCPs (Bond Critical Points) are illustrated. Excellent correlations between these topological parameters with IHB energies suggest that they could be used as good descriptors for investigation of IHB energy.

CONCLUSIONS

There are three isomers of 1-(n-pyridyl)butane 1,3-diones, “1-(2-pyridyl)butane 1,3-diones, 1-(3-pyridyl)butane 1,3-diones, and 1-(4-pyridyl)butane 1,3-diones” which each of them include 4, 4, and 2 stable *cis* enol forms, respectively. By applying DFT method, AIM and NBO analyses, IHBs of these forms are compared with each other, BA, TFAA and AA. By considering the mentioned calculated result, the following trend in the IHB strength is obtained for these isomers:

IHBs in 2PBD isomer: 2PBD-1G > 2PBD-3A > 2PBD-1A > 2PBD-3G

IHBs in 3PBD isomer: 3PBD-3A > 3PBD-3G > 3PBD-1G > 3PBD-1A

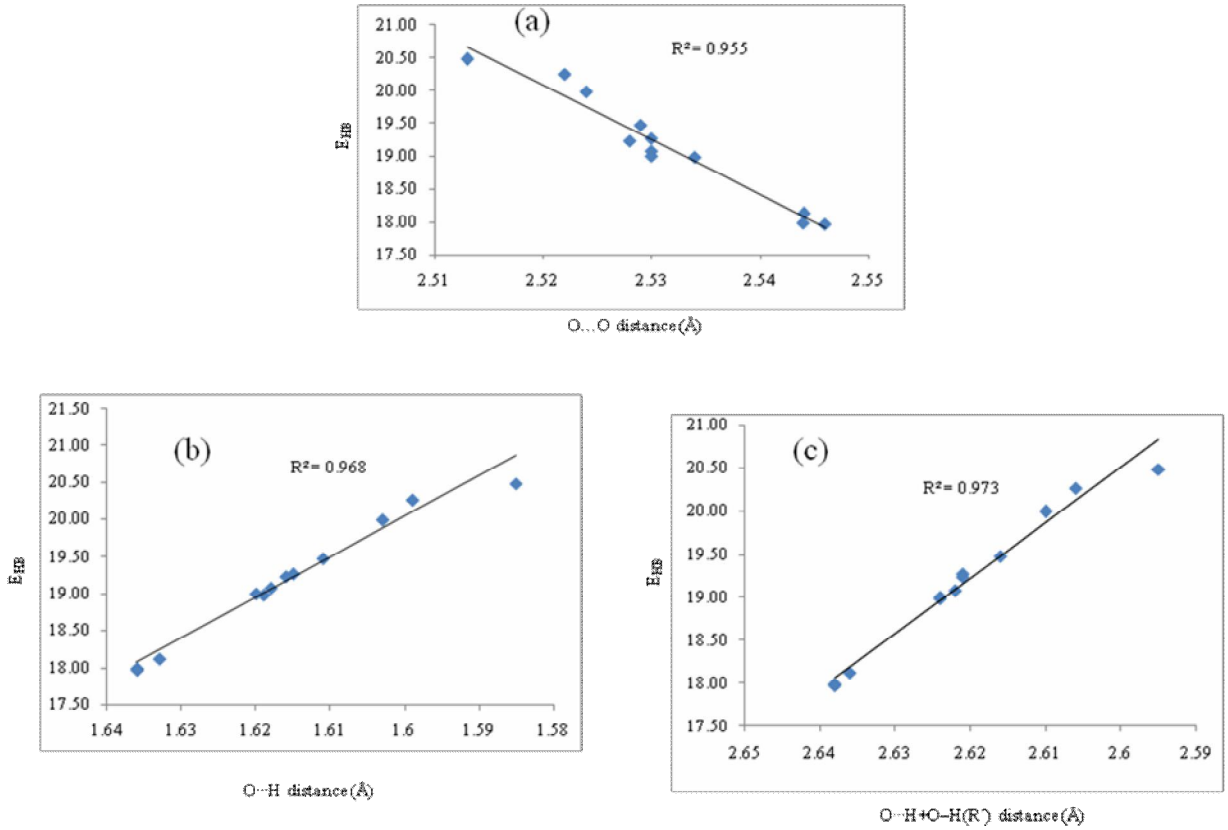


Fig. 8. The linear correlation between IHB energies (kcal mol^{-1}) and, (a) O…O distances (Å), (b) O···H distance (Å), and (c) O···H + H-O distances.

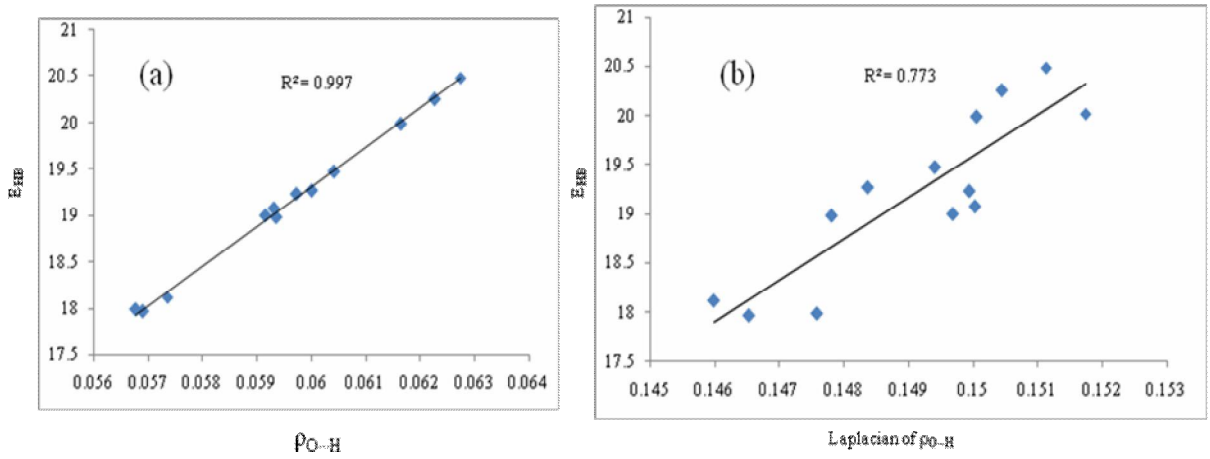


Fig. 9. The linear correlation between IHB energies (kcal mol^{-1}) and, (a) Total electronic density at O···H (BCP), (b) Laplacian of total electronic density at O···H (BCP).

The energy differences between all forms in three isomers, relative to their stable form, are 3.72-26.23, 3.51-6.28 and 2.38 kJ mol^{-1} in 2PBD, 3PBD and 4PBD, respectively. The above relative energies could be changed in the presence of solvent.

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