4-치환된 벤조산 2합체에서의 수소 결합 상호작용에 대한 이론적 연구

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Theoretical Studies of Hydrogen Bond Interactions in 4-Substituted Benzoic Acids Dimers

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요 약. 벤조산 유도체(NH_2, OH, H, F, Cl, CN, NO, NO_2) 의 두 형태를 6-311++G(d,p) 바탕 집합을 이용하여 MP2, DFT 및 HF 수준으로 연구하였으며, cis이성 질체가 더 안정하였다. 벤조산의 수소 결합 형성은 안정화 에너지를 이용하여 추산하였으며, 이합체에 대한 수소결합 에너지 계산치는 고리에서 협동 상호작용이 일어남을 보여주었다. 페닐 고리로 전자를 밀어내는 그룹(ERG)은 더 안정한 수소 결합이 형성하였다. 이합체에서 O-H 결합의 적색이동은 -565.3에서 -589.3 cm^{-1} 범위였으며, 상호 작용의 특성은 NBO 분석을 이용하여 연구하였다.

주제어: 수소 결합, 벤조산, 치환 효과, NBO 분석, DFT, MP2, HF

ABSTRACT. Two conformations of benzoic acid derivatives (NH_2, OH, H, F, Cl, CN, NO, NO_2) have been investigated at MP2, DFT and HF level using the 6-311++G(d,p) basis set. It was found that the *cis* isomers are more stable. Hydrogen bonding formation of benzoic acids has been estimated from stabilization energies. The calculated hydrogen-bonding energies of dimers showed a cooperative interaction in the cyclic ones. It was found that an electron-releasing group (ERG) into the phenyl rings resulted in the formation of more stable hydrogen bonding. Red shift of O–H bond was found from -565.3 to -589.3 for dimers. The natural bond orbital (NBO) analysis was applied to characterize nature of the interaction.

Keywords: Hydrogen bonding, Benzoic acid, Substituted effect, NBO analysis, DFT, MP2, HF

INTRODUCTION

Hydrogen bonds constitute a very interesting class of intermolecular interactions, which are of extreme importance in many fields of chemistry and molecular biology. The hydrogen bonding concept is a fundamental key to understand chemical structures, enzyme catalysis, material properties, self assembly phenomena, and functions of molecular and biological devices and machines.[1-3] It is well known that carboxylic acids form, in the gas phase and solution, cyclic dimer structure with two very strong O–H⋯O=C hydrogen bonds. Several experimental studies such as IR spectroscopy,[4,5] NMR spectroscopy,[6-8] X-ray crystallography,[9-11] microwave spectroscopy[12] vapor-density measurements[13] and thermal conductivity measurements[14] indicate that carboxylic acids form hydrogen-bonded cyclic dimers. In addition the characterization of

the hydrogen bonding interaction between carboxylic acids has been studied by a lot of theoretical calculations.[15-20]

The three types of H-bonding interactions which are most often discussed in the literature are weak, moderate, and strong.[21] In the X-H⋯Y that X is proton donor and Y is proton acceptor, the hydrogen bonding maybe evaluated geometrically by increase of X-H bond length and decrease of H⋯Y distance. In addition hydrogen bond angle for strong hydrogen bonds ranges from 170-180 degree. For the moderate and weak hydrogen bonds the angle is greater than 130 and 90 degree respectively.[22] Energetically the strength of the strong hydrogen bonding interactions varies from 4.0 to 40.0 kcal/mol. For the moderate and weak H-bonds, the strengths vary from 4-15 to 1-4 kcal/mol, respectively.[21-23]

The monomers of carboxylic acids may be found in two forms: *cis* and *trans* (*Fig.* 1). In the *cis* conformer the car-
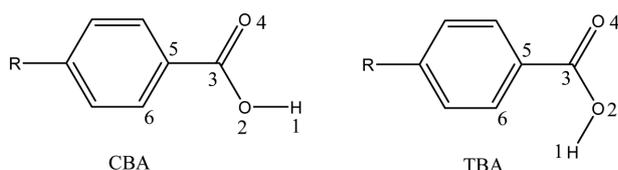
Fig. 1. *Cis* and *trans* forms of benzoic acid monomers: R=H, OH, NH2, F, Cl, CN, NO, NO2.

boxylic hydrogen atom pointing toward the carbonyl group, while in the *trans* conformer the two pointing away from each other.

The derivatives of benzoic acid are widely used in several applications, such as miticides, contrast media in urology, cholocystographic examinations and in the manufacture of pharmaceuticals. It also finds application in dyes, in curing tobacco, in preserving fruits juice, in many esters, as a mordant in cloth printing and as a reference standard in volumetric analysis. Benzoic acid derivatives also play a useful role in mosquito control by maintaining the vector population at a minimum level.[24] Benzoic acid is used as antifungal agents for superficial fungus infection of skin. Together with salicylic acids in ointments, it is also used for the treatment of ring worm in dogs and other species.[25] They form cyclic dimers, with two hydrogen bonds acting as a bridge between the monomers. The cyclic dimers thus formed can undergo double proton transfer and has been a subject of interest for many decades, partly because they can serve as prototypes for DNA base pairs.

To the best of our knowledge, systematic study of hydrogen bonding of 4-substituted benzoic acids have not been reported. Therefore, the present investigation was undertaken to study on the effect of substituents on strength of hydrogen bond of these molecules completely.

COMPUTATIONAL METHODS

In order to study the molecular properties of benzoic acids quantum mechanical calculations have been performed at different levels of theory, namely at Hartree-Fock (HF) level,[26-28] at second-order Møller-Plesset (MP2) perturbation theory level[29] and at the density-functional theory (DFT) level[30] using 6-311++G(d,p) basis set. DFT results were obtained using Becke's three parameter exchange functional along with the Lee, Yang and Parr correlation functional (B3LYP).[31,32] The calculations were performed on a Pentium IV workstation, at 3.0 GHz, running the Gaussian 98[33] package. For dimers of benzoic acid, it was assumed that two molecules are linked through two

equivalent hydrogen bonds and that the dimers are centrosymmetric; that is, there is an inversion center between the linked species. All the equilibrium isomers without imaginary frequency correspond to the minimum points on the potential surface. The uncorrected interaction energies were obtained by subtracting the energy of two fully optimized monomers from the energy of the dimer:

$$E_{int} = E_{A-B} - (E_A + E_B) \qquad (1)$$

Where E_A, E_B and E_{A-B} are the electronic energies of first benzoic acid molecule, second one and the dimer, respectively. The zero-point vibrational energy (ZPVE) corrections are applied in the present work based on following equations:

$$E_{int(ZPVE)} = E_{A-B(ZPVE)} - E_{A(ZPVE)} - E_{B(ZPVE)} \qquad (2)$$

Where $E_{A(ZPVE)}$, $E_{B(ZPVE)}$ and $E_{A-B(ZPVE)}$ are the sum of electronic and zero-point energies of first and second benzoic acid and aggregated system, respectively. To correct the basis set superposition error (BSSE), the counterpoise (CP) method is employed[34] as followed:

$$E_{int(BSSE)} = E_{A-B} - E_{A'}^{AB} - E_{B'}^{AB} \qquad (3)$$

Where $E_{A'}^{AB}$ and $E_{B'}^{AB}$ show calculated energies of acid A and B with their geometries in the AB complex using the basis function of the complex AB, respectively.

Finally the corrected interaction energies $E_{int(corr)}$, was calculated by addition of $E_{int(ZPVE)}$ and $E_{int(BSSE)}$ to interaction energy term (eq. 1):

$$E_{int(corr)} = E_{int} + E_{int(ZPVE)} + E_{int(BSSE)} \qquad (4)$$

The vibrational frequencies were computed for the optimized geometries of monomers and dimers of BAs. The harmonic frequency shift of the O-H stretching mode in the dimers, ν_{O-H}, was estimated by the following equation:

$$\Delta \nu_{O-H} = \nu_{O-H(Dimer)} - \nu_{O-H(Monomer)} \qquad (5)$$

The natural bond orbital (NBO) analysis was used to understand better the nature of the corresponding intermolecular interactions.[35]

RESULTS AND DISCUSSION

Monomers
Energy: The structure and numbering of two conformers of benzoic acid (BA) to presented in *Fig.* 1. For benzoic acid two conformations for the OH-group have been

Table **1.** Calculated total energies, relative stabilities and dipole moments of 4-substituetd benzoic acids at HF, DFT and MP2 levels using 6-311++G (d,p) basis set

R			NH$_2$	OH	H	F	Cl	CN	NO	NO$_2$
HF	*Cis*	μ	3.72	3.42	2.22	1.54	1.57	3.73	2.78	4.07
		E$_{tot}$	-473.487542	-493.320411	-418.434923	-517.316295	-877.35806	-510.186306	-547.108605	-621.958659
	Trans	μ	6.56	6.05	5.25	3.80	3.69	2.65	3.11	2.72
		Ec-Et	-8.35	-8.63	-8.08	-8.71	-8.60	-8.81	-8.49	-8.80
DFT	*Cis*	μ	4.15	3.35	2.13	1.37	1.37	3.50	3.07	3.77
		E$_{tot}$	-476.328602	-496.197699	-420.94825	-520.217166	-880.570800	-513.212287	-550.27327	-625.50838
	Trans	μ	6.95	5.97	5.05	3.64	3.65	2.43	2.74	2.47
		Ec-Et	-6.98	-7.24	-6.81	-7.35	-7.31	-7.54	-7.34	-7.54
MP2	*Cis*	μ	3.77	3.43	2.36	1.52	1.51	3.65	2.93	4.06
		E$_{tot}$	-475.015792	-494.864746	-419.781784	-518.859669	-878.841959	-511.818863	-548.814559	-623.887028
	Trans	μ	6.63	6.09	5.51	3.86	3.96	2.54	3.13	2.61
		Ec-Et	-6.23	-6.29	-5.98	-6.50	-6.44	-6.87	-6.64	-7.05

Total energies in Hartree, relative stabilities in kcal/mol, dipole moments in Debye

considered, the adopted nomenclatures are **CBA** and **TBA** for *cis* and *trans* of hydrogen with carbonyl group respectively (See *Fig.* 1).

The results of calculated total energies of CBAs, relative stabilities and dipole moments of benzoic acid and its derivatives presented in *Table* 1. Based on HF calculations it is clear that **TBA**s are more unstable than **CBA**s in the range of 8.08-8.81 kcal/mol. The results of *Table* 1 show that the DFT and MP2 calculation are not much different from HF results so DFT and MP2 methods predict that **CBA**s are more stable than **TBA**s in the range of 6.81 -7.54 kcal/mol and 5.98 -7.05 kcal/mol, respectively. The less stability of **TBA**s may be explained by van der Waals interaction between hydrogen of hydroxyl group and hydrogen of phenyl ring in the ortho position.

Dipole moment is the first derivative of the energy with respect to an applied electric field and is the measure of the asymmetry in the molecular charge distribution. The calculated total dipole moments for certain benzoic acids are given in *Table* 1 predicts that dipole moments of **TBA**s are more than **CBA**s. Therefore it is predicted that in the polar solvents the population of *trans* isomers is favor.

Geometry: The geometric parameters of isolated benzoic acid monomers calculated at the HF, B3LYP and MP2 levels using 6-311++G(d,p) basis set are presented in the *Table* 2.

The effect of replacing hydrogen of ring in the *para* with other groups on the geometrical parameters can be compared with benzoic acid. For example in the CBA the bond lengths of C=O (r_{34}) and C-C (r_{35}) is 1.2092 and 1.4865 Å at B3LYP level, respectively. It was found that electron donating groups (such as NH$_2$ and OH) cause an increase in C=O bond length and decrease in C3-C5 and

O-H bond lengths while electron withdrawing groups (such as NO$_2$) decrease C=O and increase C-C bond lengths. For instance C=O bond length calculated at DFT/6-311++G(d,p) level increased by 0.0027, and 0.0013 Å for NH$_2$, and OH groups and C-C bond length decreased by 0.0121 and 0.0075 Å for NH$_2$ and OH groups, respectively. This can be explained by direct resonance of electron releasing groups with carboxyl group. In addition C=O bond length in **TBA**s is shorter than **CBA**s and C-C bond length in **CBA**s are shorter than **TBA**s. This can be explained by the fact that **CBA**s phenyl ring and a carboxyl group are basically in the same plane thus in **CBA**s there is a direct resonance interaction between the 4-substituent group and carboxyl group, but in **TBA**s, carboxyl group placed out of the plane of the molecule and resonance in **TBA**s is poor.

It is notable that O2-C3-C5-C6 dihedral angle calculated by DFT method was found near zero for **CBA**s but for **TBA**s was found in the range of 17.68-25.7 degree. Interestingly dihedral angle for benzoic acid with electron donating groups such as NH$_2$ was found less than benzoic acid with electron withdrawing group. This difference can be explained again by direct resonance of electron releasing groups.

Dimers
Energy: Interaction energies were calculated for the 4-substituted benzoic acid dimers taking in to account the energy difference between the monomers and the complexes. The interaction energies were corrected for both ZPVE and BSSE (basis set superposition error) differences.

Based on HF and DFT calculations it is clear that

***Table* 2.** Some optimized geometric parameters of two *cis* and *trans* of 4-substituted benzoic acids at HF, DFT and MP2 levels using 6-311++G (d,p) basis set

Method		R	NH$_2$	OH	H	F	Cl	CN	NO	NO$_2$
HF	Cis	r_{12}[a]	0.9453	0.9455	0.9456	0.9457	0.9458	0.9461	0.9460	0.9462
		r_{34}	1.1879	1.1866	1.1854	1.1854	1.1848	1.1833	1.1835	1.1827
		r_{35}	1.4770	1.4804	1.4881	1.4854	1.4878	1.4929	1.4932	1.4949
		θ_{123}[b]	108.1	108.2	108.3	108.4	108.4	108.7	108.6	108.7
		θ_{234}	121.4	121.7	121.9	122.0	122.2	122.6	122.5	122.7
		θ_{356}	122.5	122.2	121.8	122.0	122.0	121.7	121.6	121.6
		Φ_{2356}[b]	0.07	0.00	0.01	-0.02	0.01	0.00	-0.04	0.01
	Trans	r_{12}	0.9404	0.9405	0.9409	0.9408	0.941	0.9413	0.9413	0.9414
		r_{34}	1.1803	1.1791	1.1782	1.1782	1.1777	1.1765	1.1766	1.1760
		r_{35}	1.4912	1.4932	1.5003	1.4984	1.5002	1.5042	1.5043	1.5055
		θ_{123}	112.2	112.3	112.2	112.4	112.4	112.6	112.5	112.7
		θ_{234}	119.8	120.0	120.3	120.3	120.4	120.8	120.7	120.9
		θ_{356}	123.7	123.4	122.6	123.0	122.9	122.4	122.3	122.3
		Φ_{2356}	20.01	21.83	24.94	23.48	24.33	27.00	27.60	28.23
DFT	Cis	r_{12}	0.9680	0.9681	0.9683	0.9684	0.9685	0.9687	0.9687	0.9688
		r_{34}	1.2119	1.2105	1.2092	1.209	1.2089	1.2074	1.2073	1.207
		r_{35}	1.4744	1.479	1.4865	1.4843	1.4855	1.4904	1.492	1.492
		θ_{123}	106.2	106.5	106.6	106.7	106.8	107.0	107.0	107.1
		θ_{234}	121.3	121.6	121.8	121.9	122.0	122.5	122.5	122.6
		θ_{356}	122.6	122.3	122.0	122.1	122.2	122.0	121.8	121.9
		Φ_{2356}	0.10	0.00	0.00	0.00	0.00	0.00	-0.01	0.00
	Trans	r_{12}	0.9638	0.9641	0.9645	0.9643	0.9644	0.9646	0.9648	0.9647
			1.2039	1.2026	1.2016	1.2015	1.2014	1.2003	1.2003	1.1999
			1.4895	1.4942	1.5002	1.4987	1.4995	1.5034	1.5043	1.5049
			110.5	110.6	110.6	110.8	110.9	111.1	111.0	111.1
		r_{34}	119.1	119.4	119.7	119.7	119.8	120.1	120.2	120.2
		r_{35}	123.9	123.5	122.9	123.2	123.2	122.9	122.5	122.7
		θ_{123}	17.68	20.18	22.69	21.95	21.89	24.44	26.45	25.70
MP2	Cis	r_{12}	0.9679	0.9680	0.9681	0.9682	0.9682	0.9684	0.9685	0.9686
		r_{34}	1.2141	1.2133	1.213	1.2128	1.2129	1.2123	1.2124	1.2124
		r_{35}	1.4828	1.4849	1.4897	1.4883	1.4885	1.4916	1.4921	1.4912
		θ_{123}	105.2	105.4	105.5	105.6	105.6	105.9	105.8	105.9
		θ_{234}	122.2	122.4	122.5	122.6	122.7	123.1	123.0	123.2
		θ_{356}	122.3	122.1	121.9	122.0	122.1	121.9	121.8	121.9
		Φ_{2356}	1.01	0.00	0.03	-0.01	0.00	-0.03	0.00	-8.32
	Trans	r_{12}	0.9641	0.9641	0.9643	0.9641	0.9642	0.9643	0.9643	0.9642
		r_{34}	1.2073	1.2068	1.2066	1.2064	1.2065	1.2061	1.2062	1.2063
		r_{35}	1.4939	1.4958	1.4992	1.4984	1.4985	1.501	1.5011	1.5009
		θ_{123}	108.1	108.2	108.3	108.5	108.5	108.8	108.7	108.9
		θ_{234}	120.2	120.4	120.5	120.6	120.6	120.9	120.8	120.8
		θ_{356}	122.7	122.6	122.2	122.4	122.5	122.3	122.1	122.3
		Φ_{2356}	29.09	28.99	30.77	30.29	29.13	31.09	32.09	31.07

[a]Bond lengths in Å, [b]bond angles and dihedral angles in degree

because of hydrogen bonding, aggregation of benzoic acid monomers is an exothermic process. It was found that the benzoic acid dimers with electron donating groups are slightly more stable than benzoic acid dimers with elec-tron withdrawing groups. The range of hydrogen bonding energies was found as 13.41-14.01 kcal/mol and 16.00-16.54 kcal/mol calculated by HF and DFT methods, respectively. With inclusions of ZPVE and BSSE correc-
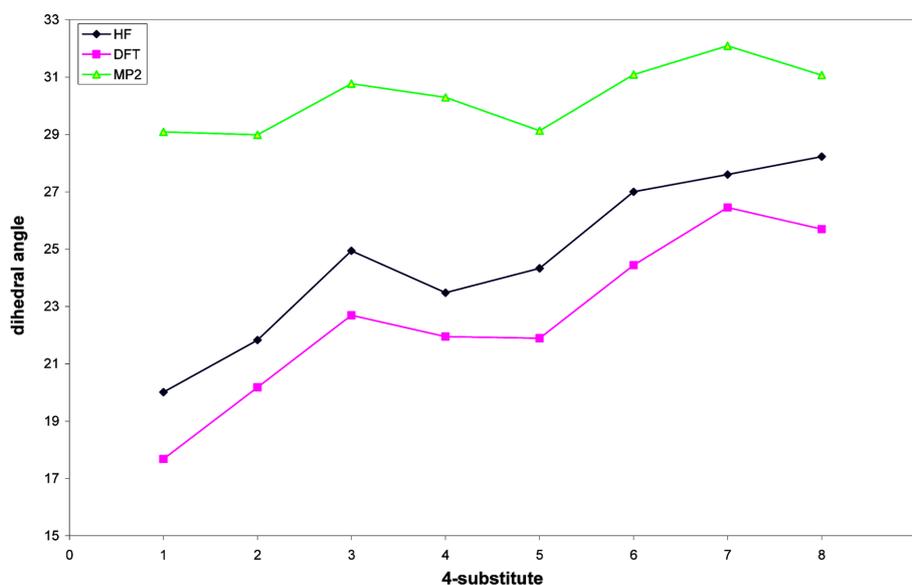
***Fig*. 2.** The dihedral angle changes (Φ_{2356}) of TBAs with change of 4-substituted. The groups from left to right are NH$_2$, OH, H, F, Cl, CN, NO, NO$_2$.

***Table* 3.** Calculated interaction energies, and corrected interaction energies of 4-substituetd benzoic acids dimers at HF and DFT levels using 6-311++G (d,p) basis set

	R	NH$_2$	OH	H	F	Cl	CN	NO	NO$_2$
HF	E_{int}	-13.88	-14.01	-13.79	-13.94	-13.77	-13.47	-13.59	-13.41
	E_{int} (ZPVE)	1.34	1.29	1.32	1.29	1.27	1.33	1.32	1.31
	E_{int} (BSSE)	0.79	0.85	0.81	0.86	0.78	0.74	0.80	0.78
	E_{int} (corr)	-11.75	-11.91	-11.65	-11.79	-11.73	-11.40	-11.47	-11.30
DFT	E_{int}	-16.33	-16.54	-16.35	-16.46	-16.34	-16.1	-16.08	-16.00
	E_{int} (ZPVE)	1.00	0.90	1.00	0.92	0.93	0.97	0.99	0.94
	E_{int} (BSSE)	0.77	0.79	0.79	0.84	0.76	0.75	0.78	0.78
	E_{int} (corr)	-14.56	-14.85	-14.55	-14.71	-14.65	-14.37	-14.30	-14.27

Hydrogen bonding energies in kcal/mol

tions the order of stabilities dose not changed and stabilities change to 11.30-11.91 and 14.27-14.85 kcal/mol calculated by HF and DFT methods, respectively. Now we consider effect of substituents on variation of hydrogen-bonding strength. Interestingly the results of our work which presented in *Table* 3 showed that the total hydrogen-bonding energy of benzoic acids enforced by introduction of ERG's. The order of strength of hydrogen bonding in the dimers with different substituents are OH>F>NH$_2$>Cl>H>NO>CN>NO$_2$ and OH>F>Cl>NH$_2$> H>CN>NO>NO$_2$ calculated by HF and DFT methods, respectively. As you can see a stronger ERG is slightly effective for enforcement of the hydrogen bond in the benzoic acid dimers. In this case the difference between hydrogen bonding of 4-OH substituted benzoic acid as the most stable benzoic acid dimer and 4-NO$_2$ substituted benzoic acid as the least stable one was found 0.60 and

0.54 kcal mol^{-1} for HF and DFT calculated methods, respectively. Because of Centro symmetric structure of dimers the calculated total dipole moments for certain benzoic acid dimers predict that all dipole moments of dimers are near zero (see *Table* 3).

Geometry: The energy difference method can be used only to evaluate the overall hydrogen-bonding energy of the two H-bonded systems. Identifying the strength of each individual H-bond using this procedure is impossible. The strength of a localized H-bond (X-H···Y) maybe found from the shortening of $d_{H···Y}$ (Y=O, N or F), the elongation of $d_{X–H}$ and the red shifts of υ_{XH}; all of these indirect parameters are easily calculated from the HF and DFT optimized results for dimers and related monomers.

In the *Fig*. 3 the optimized structure of 4- substiuted benzoic acid dimers are presented. In addition the results of selected optimized structural parameters of monomers
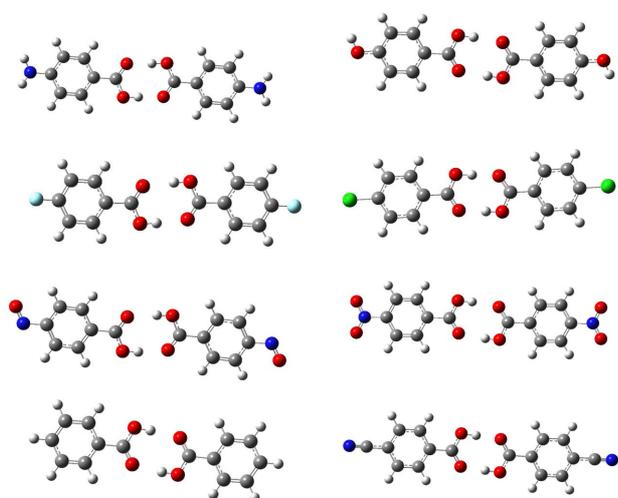
Fig. 3. The optimized structure of 4-substiuted benzoic acid dimmers.

and dimers of 4-substituted benzoic acid derivatives are collected in *Table* 4.

The comparisons of selected geometries in monomers show a correlation between them and nature of substituent on position 4. The comparison between the geometry parameters of the monomers and dimers shows that the association of two monomeric molecules into a dimer causes substantial changes in the bond lengths and angles. These perceptible differences are due to the effect of hydrogen bonding between the O and H atoms of the monomeric species. As expected, the O–H bond length increases with hydrogen bonding (See *Table* 4).

A close look at the *Table* 4 reveals that for O–H bond lengths, the largest increase in bond length relative to their monomers is 0.0151 Å for NH$_2$ diminishing to 0.0137 for NO$_2$ at HF/6-311++G(d, p) level (for comparison see *Table*

4). Note that the increases O–H bond lengths are proportional to electron donating power of substituents. In addition with going from electron releasing groups to electron withdrawing ones a regular increase in hydrogen-bonding length of O$_{4'}$···H$_1$ from 1.8143 Å and 1.6593 Å for NH$_2$ to 1.8271 Å and 1.6633 Å for NO$_2$ observed at HF and DFT methods, respectively.

From *Table* 4 it can be observed that the bond length C=O are increased in all 4-substituted benzoic acid dimers due to hydrogen bonding, as compared to those in free benzic acid monomers. The calculated hydrogen-bond lengths, C=O···H$_1$, decreased from 1.8271 Å and 1.6633 Å for 4-nitro benzoic acid to 1.8143 Å and 1.6593 Å for 4-amino benzoic acid calculated at HF and DFT levels, respectively. It should be noted that all dimers was found to be planar and dihedral angles are near zero.

Vibration analysis: Changes were observed in the calculated vibrational spectrum of benzoic acids going from monomers to dimers and they may confirm the results which obtained on the basis of the calculated hydrogen-bonding energies. For all of the dimers, the elongation of O–H bonds resulting in red shift of stretching vibrational frequencies.

The vibrational frequencies of selected bonds in the hydrogen bonding region of monomers and dimers of benzoic acids using B3LYP/6-311++G(d, p) are collected in *Table* 5. The B3LYP-calculated frequencies were scaled by a scaling factor of 0.958.[36] As you can see due to the participation of the O–H bond in hydrogen bonding υ (O–H) in dimers show a negative shift. If we have a close look at the *Table* 5, it is obvious with going from electron withdrawing groups to electron donating ones an irregular increasing of red shift was observed. The highest red shift

Table 4. Selected structural data[a] for the intermolecular hydrogen-bonded benzoic acid dimers

	R	NH$_2$	OH	H	F	Cl	CN	NO	NO$_2$
HF	$r_{14'}$[a]	1.8143	1.8161	1.8212	1.8201	1.8208	1.8262	1.8263	1.8271
	r_{12}	0.9604	0.9603	0.9600	0.9601	0.9601	0.9599	0.9599	0.9599
	r_{34}	1.2025	1.2013	1.1998	1.200	1.1994	1.1978	1.1979	1.1972
	r_{23}	1.3078	1.307	1.3054	1.3053	1.3046	1.303	1.3034	1.3024
	r_{35}	1.4764	1.4796	1.4875	1.4842	1.4868	1.4919	1.4923	1.4937
	$\Phi_{4'123}$[b]	0.0	0.0	0.1	0.1	0.0	0.0	0.0	0.0
DFT	$r_{14'}$[a]	1.6593	1.6602	1.664	1.6617	1.6628	1.6645	1.6659	1.6633
	r_{12}	1.0001	1.0002	0.9998	1.0001	0.9998	0.9998	0.9996	1.0001
	r_{34}	1.2331	1.2316	1.2301	1.2303	1.2298	1.2285	1.2282	1.2280
	r_{23}	1.3262	1.3243	1.3224	1.3223	1.322	1.32	1.3199	1.319
	r_{35}	1.4743	1.4788	1.4861	1.4836	1.4847	1.4894	1.491	1.4912
	$\Phi_{4'123}$[b]	0.0	-0.1	0.0	0.0	0.0	0.0	0.0	0.0

[a]All bond lengths are in Å.
[b]dihedral angles in degree.

Table **5.** Selected calculated stretching vibrational frequencies (cm^{-1}) and changes (cm^{-1}) in the IR frequencies from monomers to dimers using B3LYP/6-311++G(d, p)

R	NH$_2$	OH	H	F	Cl	CN	NO	NO$_2$
υO–H	3775.7	3774.6	3772.5	3772.5	3771.2	3769.3	3768.7	3768.7
υC=O	1773.2	1779.9	1785.0	1786.3	1786.2	1792.3	1791.3	1794.2
$\Delta\upsilon$OH	-589.3	-586.3	-574.7	-579.6	-575.8	-569.5	-565.3	-572.5
$\Delta\upsilon$C=O	54.7	55.3	54.6	56.0	54.6	55.8	54.3	55.2

Table **6.** Selected NBO charges for the most stable monomers and dimers at B3LYP/6-31++G(d,p) level of theory

R	NH$_2$	OH	H	F	Cl	CN	NO	NO$_2$
H1	0.483	0.485	0.485	0.487	0.487	0.490	0.490	0.490
O4	-0.616	-0.607	-0.600	-0.600	-0.597	-0.587	-0.585	-0.584
Δq H	0.030	0.029	0.029	0.027	0.027	0.025	0.025	0.025
Δq O	-0.069	-0.072	-0.073	-0.074	-0.074	-0.082	-0.077	-0.078

Table **7.** Selected second-order perturbation energies, E$^{(2)}$ calculated at 3LYP/6-311++G(d,p) for benzoic acid dimers in the gaseous phase

R	NH$_2$	OH	H	F	Cl	CN	NO	NO$_2$
LP (1) O4→σ*O2H1	8.76	8.76	8.71	8.79	8.77	8.78	8.77	8.84
LP (2) O4→σ*O2H1	21.76	21.61	21.21	21.35	21.20	20.77	20.74	20.86

The second-order perturbation energies E$^{(2)}$ from the NBO energetic analysis are given in kcal/mol

was found 589.3 cm^{-1}, which obtained for NH$_2$, substituted dimer. These are evidences for the substantial hydrogen bonds in cooperativity in structures with NH$_2$ substituents.

NOB analysis: Since the hydrogen bond properties is sometimes evaluated by charge distributions; for the better understanding of the problem, we considered the atomic charges for the included atoms. The natural population analysis was used to investigate substituent effect on charge changes which arise from the driving forces of hydrogen bond formation in dimers of benzoic acids. The calculated charge distributions for all dimers resulted from hydrogen bonding are presented in *Table* 6. It can be observed that, due to complexation, hydrogen atoms involving in hydrogen bonding gain more positive charges, the oxygen atoms which are acting as hydrogen acceptor, gain more negative charges and charges on the oxygen atoms that acting as hydrogen donor diminished as compared with monomers.

To estimate more precisely the nature of proper hydrogen bonds, we have performed detailed NBO analysis. The nature of the intermolecular hydrogen bonds was analyzed with the framework of the NBO procedure. *Table* 7 compiles some of the significant donor–acceptor interactions and their second-order perturbation energies, E$^{(2)}$ calculated at B3LYP/6-311++ G(d,p) level of theory. In the NBO analysis of hydrogen bond system, the charge transfer between the lone pairs of proton acceptor and anti bonding orbitals of the proton donor is the most important.

The analysis of NBO data show that all dimers possess two equivalent strong hydrogen bonds, and their second-order perturbation energies for interaction are in range of 20.74-21.76 kcal/mol. As a whole, the results of NBO analysis indicate that the intermolecular interactions in dimers with electron releasing groups are stronger than those dimers with electron withdrawing ones. Also benzoic acid dimer with NO substituent has the weakest hydrogen bonding and with NH$_2$ has the most strong hydrogen bonding.

CONCLUSIONS

On the basis of the calculated results, we have made the following conclusions:

a) The results of calculated total energies of benzoic acid monomers indicate that *cis* benzoic acids are more stable than *trans* benzoic acids.

b) The presence of substitutions at position 4 of benzoic acid dimers slightly influences the power of hydrogen bonding. With going from electron withdrawing substituents to electron releasing ones the strength of hydrogen bonding increases.

c) The hydrogen bond lengths, the distances between dimers and collinear angles also support the results which obtained upon binding energy values. Because of the charge density increase in the antibonding orbital of the O–H bond and the electron density delocalization, the O–H bond lengthening and therefore concomitant decrease in stretching vibrational frequency are observed.

d) In general, the results of NBO analysis indicate that the intermolecular interactions in the each dimer with going to more electron donating substituents, strength of hydrogen bonding in benzoic acid dimers slightly increase.

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