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QUANTUM CHEMICAL CALCULATIONS OF SOME BENZENE DERIVATIVES

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ABSTRACT

HOMO-LUMO energies, hardness, electronic and zero point energy, mulliken charges of benzene, fluorobenzene, chlorobenzene, bromobenzene, nitrobenzene, cyanobenzene, trifluoromethyl benzene, ethenylbenzene, di, tri, tetra and penta fluorobenzene molecules in gas phase and water phase for neutral and anionic form were calculted with B3lyp/6-31G(d,p) level by using G03 program and also hybridisation of these molecules were studied. Sum of electronic and zero-point energies found from the calculations performed in the gas phase is lower than made in the water phase.

Keywords: Benzene derivatives; HOMO; LUMO; DFT; Quantum Chemical Calculations.

ÖZET

HOMO-LUMO enerjileri, sertlik, elektronik ve sıfır noktası enerjisi, benzen, florobenzen, klorobenzen, bromobenzen, nitrobenzen, siyanobenzen, triflorometil benzen, etenilbenzen, di, tri, tetra ve penta florobenzen moleküllerinin nötr ve anyonik formları için gaz fazında ve su fazında mulliken yükleri G03 programı kullanılarak B3lyp / 6-31G (d, p) düzeyinde hesaplanmış ve bu moleküllerin hibridizasyonu çalışılmıştır. Gaz fazında yapılan hesaplamalarda bulunan elektronik ve sıfır nokta enerjilerinin toplamı su fazında yapılandan daha düşüktür.

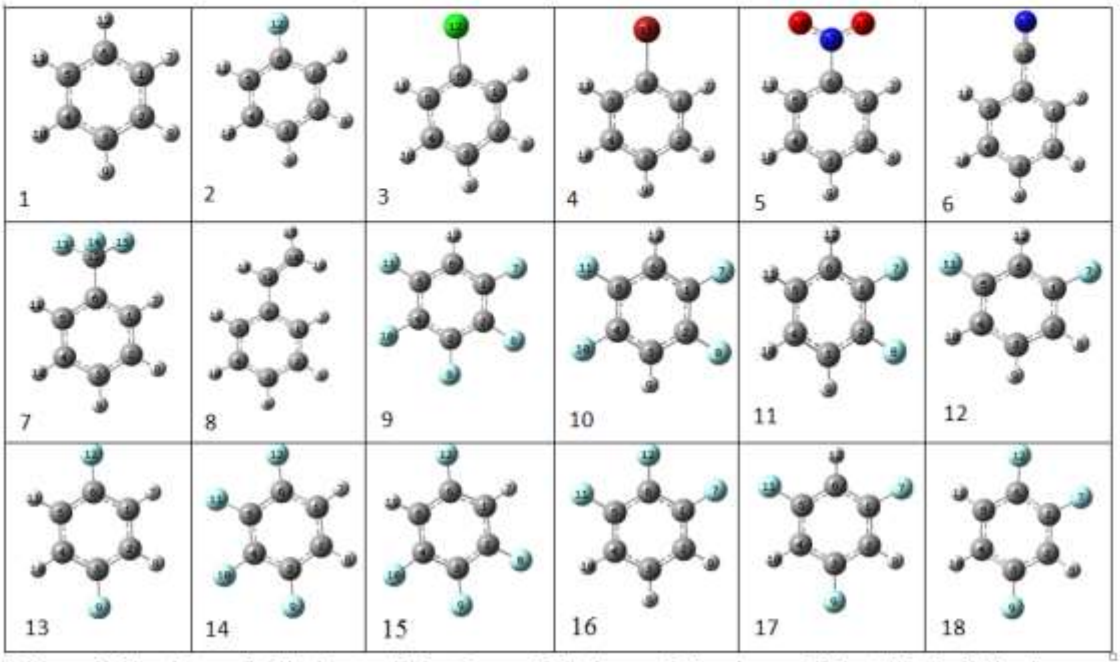
Anahtar Kelimeler: Benzen türevleri; HOMO; LUMO; DFT; Kuantum Kimyasal Hesaplamalar.

1. INTRODUCTION

Substituted benzenes like nitro-, chloro- and bromo-benzenes find many applications in the industry. Chlorobenzene is used as intermediary in the production of commodities such as herbicides, dye stuffs and rubber and as a high-boiling solvent in many industrial and laboratory applications. Chloro- and bromo-benzenes easily participate in substitution reactions and can be used to synthesize various derivatives. Most of the nitrobenzene is consumed in the production of aniline, which is a precursor to rubber chemicals, pesticides, azo dyes, explosives, and pharmaceuticals (Reid & Prausnitz, 1986; Sairam et al., 2020).

Fluorine-containing molecules have found applications in the pharmaceutical and agrochemical sector because of the thermodynamic and kinetic stability of C−F bonds, a property offering protection against enzymatic metabolism (Müller et al., 2007; Purser et al., 2008).

Today, pharmacophores often bear a trifluoromethyl or difluoromethyl motif in an aromatic system, thereby increasing the demand for methods to install or interchange these groups in a late-stage fashion (Lu et al., 2015; Sap, 2020). Both fluorine and trifluoromethyl are considered strong electron-withdrawing groups. However, their effects are slightly different when bonded to a benzene ring. Both tend to disable the ring, but less fluorine than CF3. Fluorine is ortho-para orientation and CF3 is meta-orientation. Various explanations have been proposed to explain these effects, including induction, resonance, and hyperconjugation (Holmes & Thomas, 1975). The aim of this research was to study effect of substitutions on sum of electronic and zero point energy, Fukui functions, HOMO and LUMO (Highest Occupied Molecular Orbital and Lowest Unoccupied Molecular Orbital) energies and hardness. Additionally, the effect of these substituents on hybridization has been studied. Studied benzen derivaties are given Fig. 1. The numbers under the molecules are used in the graphics and tables, and the names are not written.



1. Benzene, 2. Fluorobenzene, 3. Chlorobenzene, 4. Bromobenzene, 5. Nitrobenzene, 6. Cyanobenzene, 7. Benzotrifluoride, 8. Ethenylbenzene, 9. 1,2,3,4,5 pentafluorobenzene, 10. 1,2, 4,5 tetrafluorobenzene, 11.o-1,2 difluorobenzene, 12.m-1,3 difluorobenzene, 13.p-1,4 difluorobenzene, 14. 1,2,3,4 tetrafluorobenzene, 15.1,2,3 , 5 tetrafluorobenzene, 16.1,2,3 trifluorobenzene, 17.1,3,5 trifluorobenzene, 18.1,2,4 trifluorobenzene

Figure 1. Studied benzen derivaties.

2. MATERIAL AND METHODS

2.1. Computational Method

The molecular sketches of benzene derivaties (Payan-Gomez et al., 2010) were drawn using the GaussView 3.0. All the quantum calculations were performed with complete geometry optimization by using standard Gaussian03 software package (Frisch et al., 1998). The structural and electronic properties was carried out at the level of B3LYP with the 6-31G(d,p) basis sets (Young, 2001).

3. RESULTS AND DISCUSSION

3.1. Electronic and zero-point Energies

When the molecules 1, 2, 3 and 4 are compared, when F, Cl and Br groups are connected to the benzene molecule, respectively, it is seen that the energies of the molecules increase in the 7A Group from top to bottom. With this increase, we can say that the molar mass along the 7A group increases in that proportion with the attachment of larger elements. According to the group attached to benzene, we can sort sum of electronic and zero-point energies (au) as follows: F > Cl > Br. Likewise, in molecules, the higher the molar mass of the group bonded to benzene, the greater the energy as seen molecules 5-8.

Table 1. Sum of electronic and zero-point energies (au).

6-31G(d,p)	Gas	Water	Gas-anyon	Water-anyon
1	-232.158	-232.1613	-231.493705	-231.589
2	-331.398	-331.400559	-330.753445	-330.847
3	-691.762	-691.7669	-691.127937	-691.216
4	-2803.27	-2803.276	-2802.64035	-2802.73
5	-436.655	-436.6637	-436.147498	-436.117
6	-324.401	-324.4101	-323.769473	-323.859
7	-569.189	-569.1937	-568.543977	-568.635
8	-309.527	-309.5321	-308.874206	-308.963
9	-728.323	-728.3272	-727.727151	-727.807
10	-629.099	-629.1039	-628.4955	-628.58
11	-430.631	-430.6358	-429.997402	-430.088
12	-430.637	-430.6423	-429.999689	-430.09
13	-430.636	-430.6418	-430.0017	-430.09
14	-629.093	-629.0984	-628.476941	-628.559
15	-629.099	-629.1042	-628.492084	-628.576
16	-529.863	-529.8679	-529.236046	-529.323
17	-529.875	-529.8803	-529.257498	-529.345
18	-529.868	-529.8738	-529.254036	-529.342

When Fluorine groups are attached to the benzene ring, its energy increases as the number of connected groups increases and energy decreases as the number of groups connected decreases (molecules 11, 12, 13). If the fluorine groups are attached to the benzene ring in the ortho, meta and para position, sum of the electronic and zero point energy values found are -430.630728, -430.637030, -430.635961 au, respectively. The sum of the electronic and zero point energy values of 1,2,3,4-tetrachlorobenzene and 1,3,4,5-tetrachlorobenzene are found as -629.093419, -629.099406 au. There are 2 fluorine groups attached to fluoro benzene ortho positions in 16 molecules, 2 fluorine groups attached to fluoro benzene meta positions in 17 molecules and 2 fluorine groups attached to fluoro benzene meta and para positions in 18 molecules and the sum of the electronic and zero point energy values of them are respectively, -529.862847, -529.875244, -529.868215 au shows that the bonds in the ortho position to the benzene ring increase the energy.

The calculated sum of electronic and zero-point energies of 1, 3, 4 molecules in the gas phase are respectively, -232.157570, -691.761833, -2803.270994 au, and 232.161295, -691.766907, -2803.276018 in water phase indicates that the energy of the molecule calculated in the water phase is higher than the energy of the molecules calculated in the gas phase.

The energy required to remove 1 proton in the benzene ring in gas phase is 0.6639 au. The energy required to remove 1 proton from fluorobenzene, chlorobenzene, bromobenzene molecules in gas is 0.6443, 0.6339, 0.6306 au, respectively. The energy required to remove 1 proton in the benzene ring fluorobenzene, chlorobenzene, bromobenzene molecules in water phase is 0.5681, 0.5505, 0.5459, 0.5447, au, respectively. The energy required for the removal of 1 proton decreases in the gas and water phase as benzen > fluorobenzene > chlorobenzene > bromobenzene.

The energy required to remove 1 proton from 1,2 difluorobenzene, 1,3 difluorobenzene, 1,4 difluorobenzene molecules in gas phase is, respectively, 0.6333, 0.6373, and 0.6343 au and in water phase 0.5429, 0.5471, 0.5438 au indicates that the energy required for proton removal from meta-substituted benzene is the highest in gas and also in water phase. The energy required to remove 1 proton from nitrobenzene, cyanobenzene, benzotrifluoride and ethenylbenzene molecules in gas phase is respectively, 0.5076, 0.6313, 0.6449, 0.6532 and in water phase 0.5383, 0.5417, 0.5537, 0.5647, respectively indicates that the energy required for proton removal from ethenylbenzene, benzene is the highest in gas and also in water phase. Removal of a proton from the water phase is less than 14.42%, 14.56%, 13.87%, 13.63%, 6.05%, 14.19%, 14.15%, 13.55%, respectively, removal of a proton from the gas phase in molecules 1-8.

3.2. Fukui Functions

Fukui functions are common descriptors of site reactivity. They are defined as the derivative of the electron density with respect to the total number of electrons in the system at constant external potential u Fukui et al., 1954; Fukui, 1975). By evaluating the composition of the molecular orbitals, the condensed Fukui functions are calculated automatically. Table shows the compositions of the HOMO and the LUMO for molecule 1-18.

For the HOMO, the contributions of the C3 and C6 in benzene are 0.32% and for other carbons (C1, C2, C4, C5 are 24.17%, 25.35%, 24.18%, 25.36% respectively. When the fluorine substituent is attached to the 6th carbon atom in the benzene ring, the contribution of C3 and C6 atoms to HOMO increases from 0.32% to 24.33%, the contribution of the C3 atom to HOMO increases from 0.32% to 30.74%, the contribution of C1 and C5 atoms to HOMO decreases to 10.87%, and the contribution of C2,C4 atoms decreases by 6.53%.

In fluorobenzene, chlorobenzene, bromobenzene, nitrobenzene, cyanobenzene, benzotrifluoride, ethenylbenzene, the contribution of C6 atom to HOMO are 24.33%, 22.49%, 18.08%. 0.33%, 24.48%, 0.33%, 15.89% and the contribution of C3 atom to HOMO are 30.73%, 25.91%, 21.74%, 0,30%, 25.61%, 0.31%, 19.51% indicates that the most contribution of C3 and C6 atoms is seen in fluorobenzene.

In 1, 2, 3, 4, 5 pentafluorobenzene the contribution of C1-C6 atoms to HOMO in gas phase are 18.13%, 19.02%, 0.32%, 19.03%, 18.13%, 0.27% and in water are 18.21%, 19.42%, 0.33%, 19.41%, 18.22 %, 0.26% show that the contributions of C1-C6 atoms in the gas phase and water phase do not change significantly. In the anionic form of 1,2,3,4,5 pentafluorobenzene the contribution of C1-C6 atoms to HOMO in gas phase are 5.98%, 3.29%, 0.14%. 3.29%, 5.98%, 75.60% show that the contribution of C1-C6 atoms to HOMO varies considerably in anionic form.

Table 2. The compositions of the HOMO for molecules 1-18 calculated 6-31G(d,p) basis set in gas phase.

Molec.	Atoms/E_{HOMO}	1C	2C	3C	4C	5C	6C	7	8	9	10	11	12	13	14	15
1	-6.72	24.17	25.35	0.32	24.18	25.36	0.32	0.08	0.08	0.00	0.08	0.08	0.00			
2	-6.63	10.87	6.53	30.74	6.53	10.87	24.33	0.03	0.02	0.10	0.02	0.03	9.91			
3	-6.71	9.21	5.24	25.91	5.23	9.21	22.49	0.03	0.02	0.08	0.02	0.03	22.53			
4	-6.59	8.54	4.03	21.74	4.03	8.54	18.08	0.02	0.01	0.07	0.01	0.02	34.90			
5	-7.60	24.33	23.99	0.30	24.01	24.31	0.33	0.07	0.07	0.00	0.07	0.07	0.03	1.21	1.20	
6	-7.27	7.61	5.94	25.61	5.93	7.61	24.48	0.02	0.02	0.08	0.02	0.02	3.75	18.92		
7	-7.25	24.77	24.72	0.31	24.05	25.42	0.33	0.08	0.08	0.00	0.07	0.08	0.01	0.04	0.03	0.03
8	-6.05	9.50	2.36	19.51	3.66	8.67	15.89	0.03	0.01	0.07	0.01	0.03	11.24	0.04	28.82	0.09 0.08
9	-7.06	18.13	19.02	0.32	19.03	18.13	0.27	6.20	6.35	0	6.36	6.20	0			
10	-6.78	18.71	18.71	0.28	18.71	18.71	0.28	6.15	6.15	0	6.15	6.15	0			
11	-6.71	21.34	21.34	0.68	20.21	20.21	0.68	7.70	7.70	0	0.07	0.07	0			
12	-6.78	16.18	27.07	0.36	27.07	16.18	0.22	6.37	0.09	0	0.09	6.37	0			
13	-6.57	8.86	8.86	23.40	8.86	8.86	23.40	0.03	0.03	3.83	0.03	0.03	8.83			
14	-6.97	9.35	9.35	23.94	6.05	6.05	23.94	0.03	0.03	3.68	1.95	1.95	8.68			
15	-6.96	7.35	7.59	28.31	7.59	7.35	19.67	0.02	2.42	9.80	2.42	0.02	7.46			
16	-6.98	9.15	5.01	24.91	5.00	9.16	29.46	3.23	0.02	0.08	0.02	3.23	10.74			
17	-7.10	2.55	35.36	9.14	4.06	19.88	15.95	0.91	0.11	3.71	0.01	8.27	0.05			
18	-7.27	13.15	1.80	19.86	16.69	3.42	24.68	4.30	0	7.37	0.05	0.01	8.67			

Tablo 3. The compositions of the LUMO for molecules 1-18 calculated 6-31G(d,p) basis set in gas phase.

Molec.	Atoms/E_{LUMO}	1C	2C	3C	4C	5C	6C	7	8	9	10	11	12	13	14	15
1	0.07	28.16	1.33	20.20	28.15	1.33	20.21	0.18	0.00	0.13	0.18	0.00	0.13			
2	-0.26	23.86	25.13	0.65	25.13	23.86	0.73	0.15	0.16	0.00	0.16	0.15	0.01			
3	-0.36	23.95	25.05	0.66	25.02	23.97	0.71	0.15	0.16	0.00	0.16	0.15	0.02			
4	-0.37	23.90	25.04	0.66	24.96	23.99	0.71	0.15	0.16	0.00	0.16	0.15	0.11			
5	-2.44	8.42	0.89	11.62	0.89	8.42	5.25	0.04	0.00	0.06	0.00	0.04	24.17	20.09	20.09	
6	-1.42	11.72	4.24	25.54	4.24	11.72	20.57	0.06	0.02	0.15	0.02	0.06	7.20	14.45		
7	-0.74	10.51	6.74	30.29	6.53	10.74	27.41	0.06	0.04	0.19	0.04	0.06	4.78	0.59	1.47	0.57
8	-0.85	12.32	1.19	18.75	5.66	5.87	14.52	0.07	0	0.11	0.03	0.03	13.52	0.07	27.56	0.14 0.15
9	-0.82	9.48	7.17	29.52	7.17	9.47	30.61	0.91	0.70	3.16	0.70	0.91	0.21			
10	-0.84	8.66	8.66	30.79	8.66	8.66	30.79	0.84	0.84	0.21	0.84	0.84	0.21			
11	-0.38	9.03	9.04	31.60	8.23	8.24	31.60	0.87	0.87	0.21	0.05	0.05	0.21			
12	-0.41	8.03	9.21	35.67	9.21	8.03	27.77	0.77	0.06	0.23	0.06	0.77	0.19			
13	-0.59	24.47	24.47	0.73	24.47	24.47	0.73	0.16	0.16	0.01	0.16	0.16	0.01			
14	-0.71	25.74	25.74	0.89	20.95	20.95	0.89	0.17	0.17	0.02	2.23	2.23	0.02			
15	-0.67	21.59	24.91	0.87	24.91	21.59	0.69	0.15	2.56	0.01	2.56	0.15	0.01			
16	-0.42	6.50	10.21	35.68	10.19	6.52	26.45	0.64	0.06	0.23	0.06	0.64	2.81			
17	-0.38	29.88	1.59	20.21	24.58	1.65	16.71	2.98	0.01	2.00	0.17	0.11	0.11			
18	-1.42	16.94	26.92	2.15	17.14	31.11	3.10	1.74	0.18	0.16	0.11	0.20	0.25			

Tablo 4. The compositions of the HOMO for molecules 1-18 calculated 6-31G(d,p) basis set in water phase.

Molec.	Atoms/E_{HOMO}	1C	2C	3C	4C	5C	6C	7	8	9	10	11	12	13	14	15
1	-6.72	27.83	0.74	21.28	27.83	0.74	21.28	0.08	0	0.06	0.08	0	0.06			
2	-6.62	10.26	6.98	31.21	6.98	10.26	24.88	0.03	0.02	0.10	0.02	0.03	9.25			
3	-6.73	8.50	6.14	27.46	6.14	8.50	24.27	0.02	0.02	0.08	0.02	0.02	18.82			
4	-6.63	8.13	5.02	23.90	5.02	8.12	20.54	0.2	0.2	0.7	0.2	0.2	29.13			
5	-7.34	25.34	23.73	0.29	23.73	25.34	0.35	0.07	0.07	0	0.07	0.07	0.01	0.46	0.46	
6	-7.15	6.47	7.46	27.88	7.46	6.47	26.90	0.02	0.02	0.08	0.02	0.02	1.63	15.57		
7	-7.09	25.26	24.24	0.29	23.88	25.60	0.33	0.07	0.07	0	0.07	0.08	0.01	0.03	0.02	0.03
8	-6.05	9.28	2.43	19.44	3.62	8.58	15.82	0.03	0.01	0.06	0.01	0.02	11.50	0.04	28.98	0.09 0.08
9	-6.87	18.21	19.42	0.33	19.41	18.22	0.26	6.00	6.08	0	6.08	6.00	0			
10	-6.65	18.92	18.94	0.28	18.92	18.94	0.28	5.93	5.94	0	5.93	5.94	0			
11	-6.67	21.27	21.27	0.49	21.12	21.12	0.49	7.05	7.05	0	0.07	0.07	0			
12	-6.72	16.84	26.62	0.35	26.62	16.84	0.23	6.18	0.08	0	0.08	6.18	0			
13	-6.53	8.73	8.73	24.01	8.73	8.73	24.01	0.02	0.02	8.48	0.02	0.02	8.48			
14	-6.82	9.00	9.00	24.44	6.30	6.30	24.44	0.03	0.03	8.35	1.88	1.88	8.35			
15	-6.82	7.68	7.29	28.47	7.29	7.68	20.48	0.02	2.23	9.09	2.22	0.02	7.52			
16	-6.89	8.55	5.82	26.11	5.82	8.55	29.59	2.83	0.02	0.08	0.02	2.83	9.79			
17	-6.97	18.67	1.19	12.82	31.89	0.98	21.75	7.33	0	4.98	0.09	0.23	0.06			
18	-6.64	13.16	1.98	20.64	16.63	3.13	24.89	4.05	0.01	7.30	0.05	0.01	8.15			

In 1, 2, 3 molecules, the contribution of each of the C atoms attached to the F atom is 21.34% in the auto position, 27.07% in the meta position and 23.40% in the para position. This shows that the contribution of the C atom to which Fluorine is attached at the meta position is the highest.

Tablo 5. The compositions of the LUMO for molecules 1-18 calculated 6-31G(d,p) basis set in water phase.

Molec.	Atoms/E_{LUMO}	1C	2C	3C	4C	5C	6C	7	8	9	10	11	12	13	14	15
1	0.07	27.14	0.97	21.59	27.14	0.97	21.59	0.17	0	0.13	0.17	0	0.13			
2	-0.20	23.67	25.34	0.65	25.34	23.67	0.73	0.15	0.15	0	0.15	0.15	0.01			
3	-0.28	23.62	25.39	0.66	25.33	23.69	0.71	0.15	0.15	0	0.15	0.15	0.02			
4	-0.30	9.78	7.63	31.23	7.63	9.78	30.20	0.06	0.04	0.19	0.04	0.06	3.35			
5	-2.58	8.22	0.44	10.17	0.44	8.22	2.80	0.04	0	0.05	0	0.04	27.64	20.97	20.97	
6	-1.33	12.61	3.37	24.34	3.37	12.61	17.53	0.06	0.01	0.13	0.01	0.06	10.26	15.62		
7	-0.63	11.21	6.18	29.86	6.03	11.39	26.62	0.06	0.03	0.17	0.03	0.06	5.57	0.62	1.56	0.61
8	-0.86	12.53	1.14	18.81	5.71	5.91	14.57	0.07	0	0.10	0.03	0.03	13.30	0.06	27.45	0.14 0.14
9	-0.57	9.12	7.41	29.70	7.41	9.11	30.93	0.85	0.69	3.03	0.69	0.85	0.20			
10	-0.62	8.53	8.52	31.17	8.53	8.51	31.17	0.79	0.79	0.20	0.79	0.79	0.20			
11	-0.28	8.68	8.68	31.84	8.44	8.44	31.84	0.79	0.79	0.20	0.05	0.05	0.20			
12	-0.31	8.22	8.84	35.57	8.84	8.22	28.31	0.75	0.05	0.22	0.05	0.75	0.18			
13	-0.47	24.48	24.48	0.74	24.48	24.48	0.74	0.15	0.15	0.01	0.15	0.15	0.01			
14	-0.50	25.48	25.48	0.83	21.36	21.37	0.83	0.16	0.16	0.02	2.15	2.15	0.02			
15	-0.47	22.07	24.56	0.87	24.56	22.07	0.70	0.14	2.43	0.01	2.43	0.14	0.01			
16	-0.27	7.04	9.60	35.52	9.61	7.04	26.86	0.65	0.06	0.22	0.06	0.65	2.68			
17	-0.24	1.35	17.74	29.00	1.35	20.98	24.43	0.08	0.12	2.79	0	2.00	0.16			
18	-0.50	16.76	27.48	2.28	17.01	31.08	2.90	1.64	0.18	0.17	0.10	0.19	0.22			

Tablo 6. The compositions of the HOMO for anionic molecules 1-18 calculated 6-31G(d,p) basis set in gas phase.

Molec.	Atoms/E_{HOMO}	1C	2C	3C	4C	5C	6C	7	8	9	10	11	12	13	14	15	16
1	1.62	-1.14	2.79	4.58	80.02	4.58	2.79	0.16	1.33	1.28	1.28	1.33					
2	0.98	2.45	-0.03	2.97	3.89	78.25	6.95	1.41	0.07	1.13	1.75	1.66					
3	0.29	2.08	-0.02	2.85	3.64	73.33	6.94	1.41	0.05	1.12	1.83	6.78					
4	0.07	1.89	-0.01	2.76	3.33	68.93	6.72	1.36	0.04	1.08	1.79	12.09					
5	0.38	77.84	3.82	2.81	-0.02	2.60	7.16	1.58	1.10	0.07	1.16	0.60	0.77	0.51			
6	0.53	80.96	4.53	2.80	-0.12	2.73	4.39	1.35	1.21	0.14	1.19	0.57	0.26				
7	0.83	80.57	4.47	2.84	-0.12	2.77	4.14	1.44	1.21	0.13	1.25	1.03	0.07	0.10	0.10		
8	1.11	1.70	-0.11	2.78	4.28	79.82	4.33	1.66	0.10	1.23	1.31	0.57	1.50	0.09	0.02	0.01	
9	-0.53	5.98	3.29	0.14	3.29	5.98	75.60	1.78	1.06	0.02	1.06	1.78					
10	-0.30	3.21	5.91	76.31	5.91	3.21	-0.03	1.04	1.69	1.69	1.04	0.02					
11	0.67	6.98	3.48	-0.04	2.75	3.75	77.49	1.45	0.94	0.03	1.43	1.72					
12	0.75	6.96	78.68	3.82	3.01	-0.07	2.52	1.10	1.70	0.97	0.06	1.26					
13	0.69	0.02	2.29	6.79	78.44	3.76	3.37	0.04	1.60	1.11	1.94	0.64					
14	0.16	77.33	3.54	3.34	0.07	3.50	6.92	2.07	0.71	0.01	1.05	1.46					
15	0.21	2.47	0.04	3.19	6.07	76.79	5.99	1.40	0.01	0.94	1.71	1.48					

16	0.46	7.02	77.70	3.75	2.86	0.11	3.38	1.41	1.78	1.23	0.04	0.94
17	0.08	6.05	2.57	0.06	2.57	6.05	77.66	1.44	1.13	0.02	1.13	1.44
18	0.82	3.40	4.31	80.07	4.31	3.40	0.01	0.72	1.54	1.54	0.72	0.01

Tablo 7. The compositions of the LUMO for anionic molecules 1-18 calculated 6-31G(d,p) basis set in gas phase.

Molec.	Atoms/E_{LUMO}	1C	2C	3C	4C	5C	6C	7	8	9	10	11	12	13	14	15	16
1	5.69	0.58	21.04	28.11	0.49	28.11	21.05	0.00	0.15	0.16	0.16	0.15					
2	5.49	31.43	9.05	4.42	28.79	10.56	14.22	0.23	0.06	0.03	0.18	1.02					
3	4.79	30.77	4.60	10.32	31.16	4.41	17.63	0.22	0.03	0.07	0.19	0.60					
4	4.50	2.66	1.43	0.11	2.75	11.64	44.10	2.74	3.11	-0.01	1.24	30.22					
5	2.73	5.83	3.76	8.75	0.26	8.40	1.69	0.01	0.05	0	0.05	29.67	22.20	19.32			
6	3.94	5.36	15.54	21.78	0.59	16.73	15.33	0.07	0.14	0	0.10	10.18	14.18				
7	4.67	3.49	20.46	25.59	1.15	16.96	22.92	0.11	0.17	0	0.12	6.42	0.26	1.8	1.18		
8	4.09	14.14	0.42	14.02	11.03	3.56	7.87	0.09	0	0.09	0.05	21.82	0.11	26.51	0.15	0.16	
9	4.95	26.07	19.35	0.76	19.34	26.07	0.69	2.18	1.67	0.01	1.67	2.18					
10	5.02	13.70	2.91	31.43	2.91	13.70	32.60	0.98	0.26	0.26	0.98	0.27					
11	5.44	25.18	8.37	4.91	32.40	23.77	2.01	2.20	0.74	0.04	0.24	0.14					
12	5.17	22.43	3.23	32.74	13.01	2.02	24.17	1.79	0.20	0.10	0.12	0.18					
13	5.17	16.35	33.16	8.31	17.68	22.34	1.05	0.12	0.24	0.55	0.15	0.06					
14	4.98	8.81	29.72	8.14	5.69	28.96	13.82	0.20	0.66	0.43	2.49	1.08					
15	4.96	29.68	6.81	6.24	28.45	4.67	18.90	0.23	0.49	0.55	2.55	1.43					
16	5.11	23.83	0.95	30.92	21.86	0.75	17.71	2.05	0.18	0.17	0.02	1.57					
17	5.12	28.93	17.92	0.59	17.92	28.93	0.67	2.37	0.14	0.01	0.14	2.37					
18	5.19	21.59	25.83	0.48	25.83	21.59	0.80	1.77	0.16	0.16	1.77	0.01					

Tablo 8. The compositions of the HOMO for anionic molecules 1-18 calculated 6-31G(d,p) basis set in water phase.

Molec.	Atoms/E_{HOMO}	1C	2C	3C	4C	5C	6C	7	8	9	10	11	12	13	14	15
1	-3.48	-0.12	3.00	4.41	80.47	4.41	3.00	0.29	1.18	1.09	1.09	1.18				
2	-4.02	2.50	-0.02	3.24	3.91	78.72	6.51	1.34	0.17	1.00	1.60	1.04				
3	-4.34	2.13	-0.01	3.15	3.71	74.52	6.33	1.36	0.12	1.01	1.69	5.99				
4	-4.43	1.95	0.00	3.07	3.43	70.23	6.36	1.34	0.10	0.99	1.68	10.85				
5	-4.19	78.27	3.71	3.08	-0.01	2.62	6.67	1.43	0.97	0.15	1.18	0.55	0.86	0.51		
6	-4.11	81.36	4.38	3.06	-0.10	2.80	3.98	1.23	1.07	0.25	1.16	0.60	0.21			
7	-3.86	81.04	4.29	3.09	-0.10	2.82	3.79	1.27	1.09	0.23	1.21	1.00	0.06	0.11	0.11	
8	-3.62	2.77	-0.10	3.00	4.09	80.36	4.02	1.30	0.20	1.11	1.14	0.57	1.42	0.09	0.02	0.00
10	-5.01	3.12	5.64	77.08	5.63	3.12	-0.07	1.10	1.64	1.64	1.10	0.01				
11	-4.22	6.57	3.34	-0.07	3.01	3.77	78.12	1.34	1.00	0.08	1.28	1.56				
12	-4.16	6.49	79.44	3.79	3.22	-0.05	2.52	0.98	1.54	0.82	0.10	1.15				
13	-4.20	0.04	2.36	6.35	78.94	3.77	3.50	0.10	1.52	0.99	1.75	0.68				
14	-4.53	78.28	3.52	3.40	0.01	3.30	6.50	1.85	0.71	0.01	1.06	1.34				
15	-4.92	2.58	-0.07	3.10	5.78	77.60	5.67	1.31	0.01	0.98	1.64	1.40				

16	-4.34	6.57	78.56	3.74	3.10	0.14	3.21	1.29	1.60	1.07	0.06	0.95
17	-4.75	5.74	2.65	-0.06	2.65	5.74	78.44	1.37	1.05	0.03	1.05	1.37
18	-3.98	3.40	4.12	80.98	4.12	3.40	-0.05	0.72	1.30	1.30	0.72	0.02

Tablo 9. The compositions of the LUMO for anionic molecules 1-18 calculated 6-31G(d,p) basis set in water phase.

Molec.	Atoms/E_{LUMO}	1C	2C	3C	4C	5C	6C	7	8	9	10	11	12	13	14	15
1	1.16	0.59	22.31	26.84	0.49	26.82	22.35	0.00	0.15	0.15	0.15	0.15				
2	1.01	31.68	10.15	4.95	29.85	10.98	11.12	0.21	0.06	0.03	0.18	0.78				
3	0.60	31.76	5.22	11.35	31.19	3.84	15.63	0.21	0.03	0.07	0.18	0.51				
4	0.13	2.51	1.44	0.05	2.90	10.34	47.30	1.89	1.82	0.04	1.08	30.62				
5	-1.59	6.67	1.97	8.36	0.23	7.63	0.92	0.01	0.04	0.00	0.04	31.75	21.99	20.40		
6	-0.24	7.89	10.94	22.59	0.73	16.16	13.34	0.05	0.13	0.00	0.09	12.60	15.49			
7	0.51	4.93	16.84	27.36	1.62	16.68	22.99	0.09	0.17	0.01	0.11	6.53	0.28	1.20	1.21	
8	0.03	14.45	0.35	15.82	10.33	3.75	9.81	0.09	0.00	0.09	0.05	17.94	0.09	26.94	0.14	0.15
10	0.75	12.06	3.97	32.22	3.98	12.03	33.04	0.89	0.34	0.34	0.89	0.24				
11	1.05	15.77	26.86	3.06	13.60	31.99	4.94	1.23	2.26	0.02	0.09	0.19				
12	0.78	19.73	3.44	32.82	13.31	2.63	25.91	1.53	0.19	0.09	0.18	0.18				
13	0.78	17.03	32.48	5.95	18.22	24.02	1.36	0.11	0.21	0.38	0.15	0.09				
14	0.68	10.16	29.98	7.04	7.50	29.63	10.89	0.19	0.59	0.61	2.59	0.83				
15	0.69	29.80	5.57	8.33	28.88	4.26	17.91	0.21	0.42	0.75	2.50	1.36				
16	0.78	21.54	1.35	31.17	20.26	0.78	20.93	1.77	0.18	0.14	0.02	1.86				
17	0.77	27.57	19.41	0.62	19.41	27.57	0.67	2.23	0.14	0.01	0.14	2.23				
18	0.85	22.05	25.28	0.49	25.28	22.05	0.81	1.86	0.15	0.15	1.86	0.01				

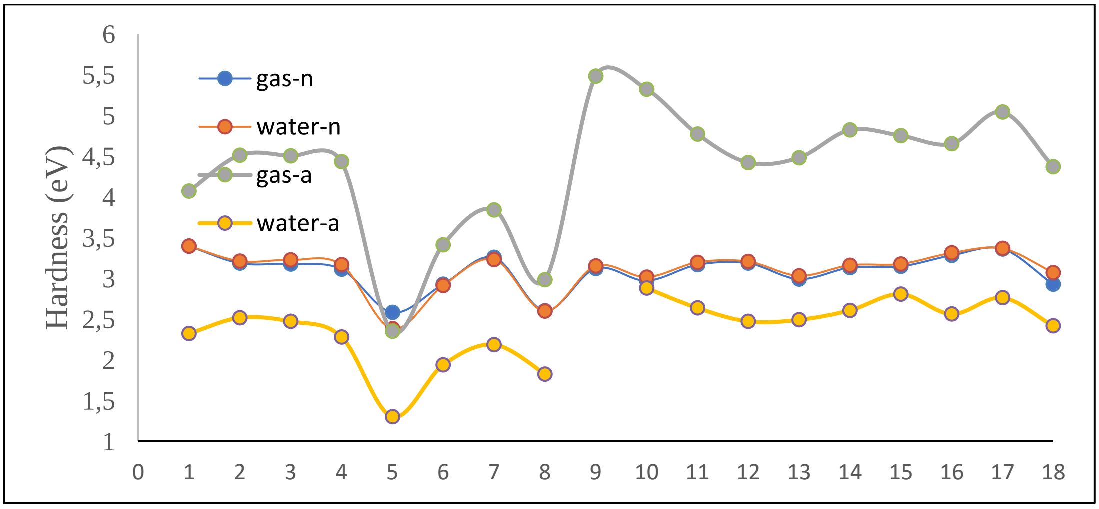


Figure 2. Relationship between theoretical hardness values in gas and water phase of benzene derivatives and anions examined by 6-31G (d, p) method.

One of the characteristics of aromatic compounds is a relatively large energy gap between HOMO and LUMO, which corresponds to the lower reactivity of aromatic compounds to electrophilic reagents (Minsky et al., 1985; De Proft & Geerlings, 2001). Chemical hardness (η) can be determined from the energy of these HOMO and LUMO as the following equation according to $\eta \cong \frac{1}{2}(\varepsilon_{HOMO} - \varepsilon_{LUMO})$. Calculated chemical hardness of the benzene derivatives under study in gas phase and in water phase for neutral and anionic form of them are given in Figure 2.

The gas phase hardness value of the benzene ring is 3.395 and it is seen that no matter what type of group is connected to the ring, it does not have an increasing effect on the hardness, on the contrary, it has a lowering effect. When the1, 2, 3 and 4 molecules are examined, the hardness-lowering effects of the 7A group increase as the period goes down. The order in hardness is 1 (3.395) > 2 (3.185) > 3 (3.175) > 4 (3.110)

The 5th molecule is the molecule with the lowest hardness among the molecules examined. The reason for this is due to the nitro groups, which are electron with drawing substituent (Ravi, 2011). The presence of groups with high electron attraction decreases LUMO and HOMO energies. Therefore, we can say that high electronegative atoms in the molecule have a hardness-reducing effect.

The hardnes value of molecules 11, 12, and 13 are found as 3.195, 3.205, 3.03, respectively means that means in the para position for fluoro substituents, the hardness is the least. The hardness value of molecules 16, 17, and 18 are found as 3.280, 3.360, 2.925, respectively means that the hardness 1,2,4-trifluorobenzene is the least. The hardness value of molecules 10, 14, and 15 are found as 2.970, 3.130, 3.145, respectively. Trifluorobenzene is the least. The number of fluoro substituents and positions of the sustituents effect the hardness value. The hardness values calculated in the water phase are higher than the hardness values calculated in the gas phase, except for 5-8 molecules. The hardness values calculated in the anionic form created by removing 1 proton from the molecule were recorded higher in the gas phase and lower in the water phase than the hardness values of the neutral form.

3.3. Mulliken Charges

Mulliken charges (Mulliken, 1955) are calculated by determining the electron population of each atom as defined in the basis functions. The mulliken charges of the carbon atoms belonging to the benzene ring calculated with 6-31g (d, p) base set at the B3LYP level of the studied benzene derivatives are given in the figure. Fluorine and nitro group induces a positive charge on the carbon to which it is attached (0.351 and 0.266) and a negative charge on the ortho carbon (-0.142 and -0.092). For CF3, the calculations indicate the carbon adjacent to the CF3 group to be negatively charged (-0.045).

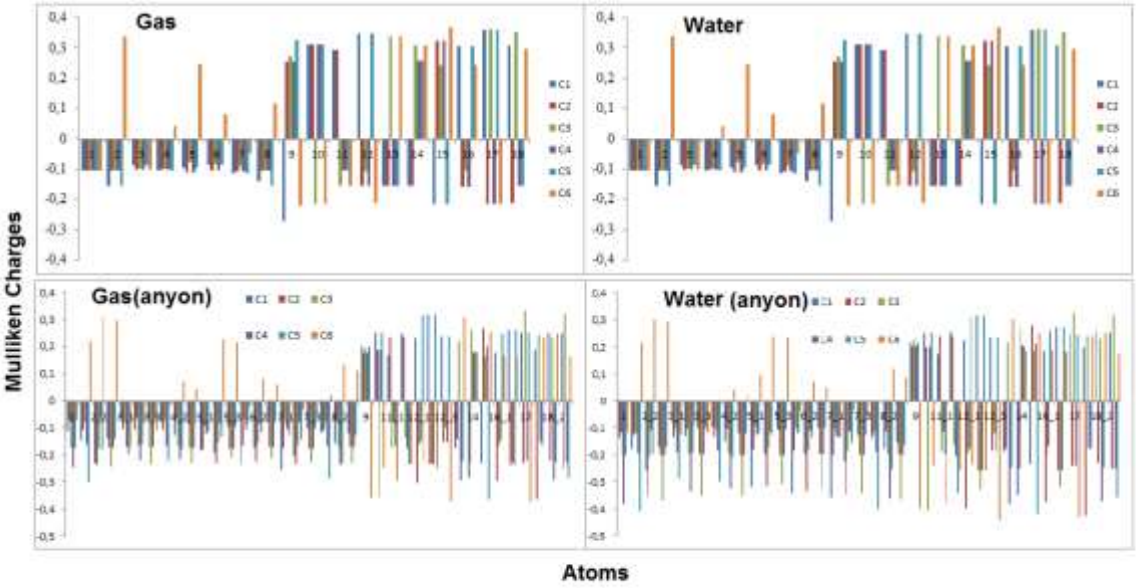


Figure 3. Theoretical mulliken values of benzene derivatives and anions investigated in gas and water phase.

When the mulliken charges (11, 12, 13 molecules) of the two groups bonded to benzene are compared according to each other (ortho, meta, para), the mulliken charge of the carbon atom to which the fluorine atoms in the meta position attached to the benzene ring is the highest electropositive.

In the 9 molecule, the Mulliken charges on the C1, C2, C3, C4, C5 atoms to which the F atoms are attached are 0.33 ē, 0.26 ē, 0.27 ē, 0.26 ē, 0.33 ē, respectively, and the Mulliken charge of the C6 atom to which the hydrogen is attached is -0.21 ē. The charge densities of the C3, C4, C5 atoms to which the F atoms are attached in 14 molecules are respectively 0.31 ē, 0.26 ē, 0.26 ē, 0.31 ē and the Mulliken charge of the C1, C3 atom to which the hydrogen is attached is -0.14 ē, -0.14 ē.

In the Mulliken calculations performed in the water phase, there was a slight decrease in the positive Mulliken charges compared to the gas phase and a slight increase in the negative charges.

3.4. NBO Analysis

We have executed NBO analysis for investigating charge transfer or conjugative interaction in molecular systems.

Table 10. Relationship between theoretical NBO values of benzene derivatives.

	C1-C2	**C2-C3**	**C3-C4**
1	0.7071C1(sp$^{1.74}$)+0.7071C2(sp$^{1.77}$)	0.7071C1(sp$^{1.77}$)+0.7071C2(sp$^{1.77}$)	0.7071C1(sp$^{1.77}$)+0.7071C2(sp$^{1.77}$)
2	0.7110C1(sp$^{1.77}$)+0.7032C2(sp$^{1.79}$)	0.7065C2(sp$^{1.75}$)+0.7065C3(sp$^{1.78}$)	0.7065C3(sp$^{1.77}$)+0.7077C4(sp$^{1.75}$)
3	0.7110C1(sp$^{1.77}$)+0.7032C2(sp$^{1.79}$)	0.7077C2(sp$^{1.75}$)+0.7065C3(sp$^{1.78}$)	0.7077C3(sp$^{1.75}$)+0.7065C4(sp$^{1.78}$)
4	0.7110C1(sp$^{1.78}$)+0.7032C2(sp$^{1.79}$)	0.7077C1(sp$^{1.75}$)+0.7065C2(sp$^{1.78}$)	0.7065C1(sp$^{1.78}$)+0.7077C2(sp$^{1.75}$)
5	0.7108C1(sp$^{1.76}$)+0.7034C2(sp$^{1.79}$)	0.7074C1(sp$^{1.77}$)+0.7068C2(sp$^{1.78}$)	0.7068C1(sp$^{1.78}$)+0.7074C2(sp$^{1.77}$)
6	0.7089C1(sp$^{1.75}$)+0.7053C2(sp$^{1.78}$)	0.7076C1(sp$^{1.78}$)+0.7066C2(sp$^{1.78}$)	0.7066C1(sp$^{1.78}$)+0.7076C2(sp$^{1.78}$)
7	0.7099C1(sp$^{1.76}$)+0.7043C2(sp$^{1.78}$)	0.7074C1(sp$^{1.77}$)+0.7068C2(sp$^{1.78}$)	0.7068C1(sp$^{1.78}$)+0.7074C2(sp$^{1.77}$)
8	0.7088C1(sp$^{1.75}$)+0.7054C2(sp$^{1.76}$)	0.7075C1(sp$^{1.78}$)+0.7067C2(sp$^{1.78}$)	0.7066C1(sp$^{1.77}$)+0.7076C2(sp$^{1.77}$)
9	0.7050C1(sp$^{1.71}$)+0.7092C2(sp$^{1.60}$)	0.7062C1(sp$^{1.67}$)+0.7080C2(sp$^{1.63}$)	0.7080C1(sp$^{1.63}$)+0.7062C2(sp$^{1.67}$)
10	0.7071C1(sp$^{1.67}$)+0.7071C2(sp$^{1.67}$)	0.7033C1(sp$^{1.55}$)+0.7109C2(sp$^{1.83}$)	0.7109C1(sp$^{1.83}$)+0.7033C2(sp$^{1.55}$)
11	0.7071C1(sp$^{1.69}$)+0.7071C2(sp$^{1.69}$)	0.7074C1(sp$^{1.50}$)+0.7068C2(sp$^{1.91}$)	0.7114C1(sp$^{1.71}$)+0.7028C2(sp$^{1.82}$)
12	0.7054C1(sp$^{1.55}$)+0.7088C2(sp$^{1.89}$)	0.7099C1(sp$^{1.74}$)+0.7043C2(sp$^{1.78}$)	0.7043C1(sp$^{1.78}$)+0.7099C2(sp$^{1.74}$)
13	0.7071C1(sp$^{1.76}$)+0.7071C2(sp$^{1.76}$)	0.7103C1(sp$^{1.85}$)+0.7039C2(sp$^{1.58}$)	0.7039C1(sp$^{1.58}$)+0.7103C2(sp$^{1.85}$)
14	0.7071C1(sp$^{1.75}$)+0.7071C2(sp$^{1.75}$)	0.7070C1(sp$^{1.89}$)+0.7072C2(sp$^{1.49}$)	0.7040C1(sp$^{1.74}$)+0.7102C2(sp$^{1.60}$)
15	0.7094C1(sp$^{1.88}$)+0.7048C2(sp$^{1.52}$)	0.7057C1(sp$^{1.70}$)+0.7085C2(sp$^{1.63}$)	0.7085C1(sp$^{1.63}$)+0.7057C2(sp$^{1.70}$)
16	0.7080C1(sp$^{1.48}$)+0.7062C2(sp$^{1.93}$)	0.7105C1(sp$^{1.71}$)+0.7037C2(sp$^{1.79}$)	0.7037C1(sp$^{1.79}$)+0.7105C2(sp$^{1.71}$)
17	0.7022C1(sp$^{1.58}$)+0.7119C2(sp$^{1.85}$)	0.7119C1(sp$^{1.85}$)+0.7022C2(sp$^{1.58}$)	0.7022C1(sp$^{1.58}$)+0.7119C2(sp$^{1.85}$)
18	0.7041C1(sp$^{1.53}$)+0.7101C2(sp$^{1.86}$)	0.7135C1(sp$^{1.81}$)+0.7006C2(sp$^{1.62}$)	0.7047C1(sp$^{1.55}$)+0.7095C2(sp$^{1.86}$)
	C4-C5	**C5-C6**	**C1-C6**
1	0.7071C1(sp$^{1.77}$)+0.7071C2(sp$^{1.77}$)	0.7071C1(sp$^{1.77}$)+0.7071C2(sp$^{1.77}$)	0.7071C1(sp$^{1.77}$)+0.7071C2(sp$^{1.77}$)
2	0.7032C4(sp$^{1.79}$)+0.7110C5(sp$^{1.77}$)	0.7050C5(sp$^{1.80}$)+0.7092C6(sp$^{1.56}$)	0.7050C1(sp$^{1.88}$)+0.7092C2(sp$^{1.57}$)
3	0.7065C4(sp$^{1.78}$)+0.7077C5(sp$^{1.75}$)	0.7032C5(sp$^{1.79}$)+0.7110C6(sp$^{1.77}$)	0.7010C1(sp$^{1.80}$)+0.7132C2(sp$^{1.56}$)
4	0.7032C1(sp$^{1.79}$)+0.7110C2(sp$^{1.178}$)	0.7068C1(sp$^{1.78}$)+0.7074C2(sp$^{1.53}$)	0.7068C1(sp$^{1.78}$)+0.7074C2(sp$^{1.53}$)
5	0.7034C1(sp$^{1.79}$)+0.7108C2(sp$^{1.76}$)	0.7001C1(sp$^{1.88}$)+0.7140C2(sp$^{1.63}$)	0.7001C1(sp$^{1.88}$)+0.7140C2(sp$^{1.63}$)
6	0.7053C1(sp$^{1.78}$)+0.7089C2(sp$^{1.75}$)	0.6938C1(sp$^{1.84}$)+0.7202C2(sp$^{1.83}$)	0.6938C1(sp$^{1.84}$)+0.7202C2(sp$^{1.83}$)
7	0.7043C1(sp$^{1.78}$)+0.7099C2(sp$^{1.76}$)	0.6991C1(sp$^{1.81}$)+0.7151C2(sp$^{1.78}$)	0.6991C1(sp$^{1.81}$)+0.7151C2(sp$^{1.78}$)
8	0.7058C1(sp$^{1.77}$)+0.7084C2(sp$^{1.76}$)	0.7008C1(sp$^{1.75}$)+0.7134C2(sp$^{1.97}$)	0.7014C1(sp$^{1.77}$)+0.7128C2(sp$^{1.93}$)
9	0.7092C1(sp$^{1.60}$)+0.7050C2(sp$^{1.71}$)	0.7092C1(sp$^{1.60}$)+0.7050C2(sp$^{1.71}$)	0.7041C1(sp$^{1.53}$)+0.7101C2(sp$^{1.85}$)
10	0.7071C1(sp$^{1.67}$)+0.7071C2(sp$^{1.67}$)	0.7033C1(sp$^{1.55}$)+0.7109C2(sp$^{1.83}$)	0.7033C1(sp$^{1.55}$)+0.7109C2(sp$^{1.83}$)
11	0.7071C1(sp$^{1.75}$)+0.7071C2(sp$^{1.75}$)	0.7028C1(sp$^{1.82}$)+0.7114C2(sp$^{1.71}$)	0.7074C1(sp$^{1.50}$)+0.7068C2(sp$^{1.91}$)
12	0.7088C1(sp$^{1.89}$)+0.7054C2(sp$^{1.55}$)	0.7013C1(sp$^{1.60}$)+0.7128C2(sp$^{1.84}$)	0.7013C1(sp$^{1.60}$)+0.7128C2(sp$^{1.84}$)
13	0.7071C1(sp$^{1.76}$)+0.7076C2(sp$^{1.76}$)	0.7103C1(sp$^{1.85}$)+0.7128C2(sp$^{1.58}$)	0.7103C1(sp$^{1.85}$)+0.7039C2(sp$^{1.58}$)
14	0.7071C1(sp$^{1.65}$)+0.7071C2(sp$^{1.65}$)	0.7102C1(sp$^{1.60}$)+0.7040C2(sp$^{1.74}$)	0.7070C1(sp$^{1.89}$)+0.7072C2(sp$^{1.49}$)
15	0.7048C1(sp$^{1.52}$)+0.7094C2(sp$^{1.88}$)	0.7126C1(sp$^{1.82}$)+0.7016C2(sp$^{1.59}$)	0.7126C1(sp$^{1.82}$)+0.7016C2(sp$^{1.59}$)
16	0.7062C1(sp$^{1.93}$)+0.7080C2(sp$^{1.48}$)	0.7047C1(sp$^{1.72}$)+0.7095C2(sp$^{1.62}$)	0.7047C1(sp$^{1.72}$)+0.7095C2(sp$^{1.62}$)
17	0.7119C1(sp$^{1.85}$)+0.7022C2(sp$^{1.58}$)	0.7022C1(sp$^{1.58}$)+0.7119C2(sp$^{1.85}$)	0.7022C1(sp$^{1.58}$)+0.7119C2(sp$^{1.85}$)
18	0.7063C1(sp$^{1.78}$)+0.7079C2(sp$^{1.73}$)	0.7077C1(sp$^{1.88}$)+0.7065C2(sp$^{1.51}$)	0.7079C1(sp$^{1.67}$)+0.7063C2(sp$^{1.70}$)

(C1-C2) NBO is formed from an $sp^{1.74}$ hybrid on C1 interacting with an $sp^{1.77}$ hybrid on C2, for benzene, formed from an $sp^{1.77}$ hybrid on C1 interacting with an $sp^{1.79}$ hybrid on C2 for fluorobenzene, formed from an $sp^{1.77}$ hybrid on C1 interacting with an $sp^{1.79}$ hybrid on C2 for chloro, benzene, formed from an $sp^{1.78}$ hybrid on C1 interacting with an $sp^{1.79}$ hybrid on C2 for bromoobenzene, formed from an $sp^{1.75}$ hybrid on C1 interacting with an $sp^{1.75}$ hybrid on C2 for fluorobenzene.

(C1-C6) NBO is formed from an $sp^{1.74}$ hybrid on C1 interacting with an $sp^{1.77}$ hybrid on C2, for benzene, formed from an $sp^{1.57}$ hybrid on C1 interacting with an $sp^{1.88}$ hybrid on C2 for fluorobenzene, formed from an $sp^{1.80}$ hybrid on C1 interacting with an $sp^{1.56}$ hybrid on C2 for chloro, benzene, formed from an $sp^{1.78}$ hybrid on C1 interacting with an $sp^{1.53}$ hybrid on C2 for bromoobenzene, formed from an sp^{188} hybrid on C1 interacting with an $sp^{1.63}$ hybrid on C2 for fluorobenzen shows that the groups attached to the C atom affect the type of hydration.

4. CONCLUSIONS

The results show that the energy required for the removal of 1 proton decreases in the gas and water phase as benzen > fluorobenzene > chlorobenzene > bromobenzene. The contribution of the C6 and C3 atoms to HOMO in gas and water phase is highest in fluoro benzene among the mono substituted benzene derivatives studied. The hardness of the nitrobenzene molecule was found to be the lowest among the molecules examined. The substituents attached to the C6 atom affect the contribution of the s and p orbitals in the hybridization of the C atoms in the bond formation.

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