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Comparison of the intramolecular hydrogen bond strength in F, Cl, Br, NO_2, and OMe substitutions of naphthazarin

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Abstract: The hydrogen bond strength, geometry optimization and ^1H NMR for naphthazarin (NZ) and its F, Cl, Br, NO_2 and OMe substitutions have been calculated at the B3LYP/6-31G** theoretical level.

The calculated chemical shifts of the chelated proton for all molecules, using GIAO method, are well correlate with the calculated geometrical parameters results. According to the calculated results, in general, substitutions of Cl and Br near the hydroxyl groups and near the carbonyl groups increases and decreases the strength of the hydrogen bond, respectively. The hydrogen bond strength of NZ decreased by substitution of F and NO_2 groups in the different positions of NZ and increased by substitution OMe groups.

By natural bond orbital (NBO) method, the effect of substitution on the hydrogen bond strength, the charge distributions, steric effects, and electron delocalization in the studied compounds were investigated. The natural bond orbital analysis very well explains the calculated results of substitutions on the hydrogen bond strength.

Keywords: Intramolecular hydrogen bond, DFT, Derivatives of naphthazarin, NBO.

Introduction

Naphthazarin (hereafter NZ) has been used historically as a rather expensive purple dye. It occurs naturally in the wood bark of Lomatiaoblique [1] and in walnut husks of Juglansm and schuricamaxim var. Sieboldianna Makino [2]. It can be prepared directly either by heating 1,5-dinitronaphthalene with sulfur and fuming sulfuric acid [3], or by double Friedel-Crafts acylation of either hydroquinone [4], or 1,4-dimethoxybenzene [5], with maleic anhydride in fused AlCl3-NaCl. Yields for both processes are generally low. An indirect, three-step procedure with dichloromaleic anhydride is usually employed today to produce larger quantities of NZ for laboratory use [6]. Cycloaddition reactions are generally the most useful and successful reactions of NZ. In particular, Diels-Alder reactions with NZ have found extensive use in the construction of anthracyclinone antibiotics [7].

Naphthazarin (5, 8-dihydroxy-1, 4-naphthoquinone) as a central core of quinone, has gained much attention in recent years owing to its properties (e.g. antitumor and antiviral activity, wound healing, antimicrobial, antithrombotic properties and their use in the development of cardioprotectivepreparations) [8–10]. This compound has been extensively studied theoretically [11–13] and experimentally by X-ray and neutron diffraction [14–17], mass spectrometry [18], ^{13}C [19–21], ^{17}O [22], and proton NMR, IR and Raman spectroscopy [11, 23–30].

A structure with C_{2V} symmetry has been suggested for NZ in solution with fast proton rearrangement from one pair of oxygen atoms to the other [31]. Vibrational spectroscopic studies by Schutte et al. [11] also support the C_{2V} structure for NZ, as do *ab initio* calculations of Mariam et al. [8, 13]. Ramondo and Bencivenni [30] interpreted the vibrational spectra of NZ based on

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HF/6-31G calculation. Fabriciova et al. [29], by considering the SERS spectroscopy, applied the results of HF/6-31G*calculation for the assignment of the Raman band frequencies of NZ. Some of quantum chemical calculations have done on the structure of NZ to obtain the effects of functional and basis sets on its calculated geometry [32]. According to the calculation at the B3LYP level, NZ exhibits a slightly weaker hydrogen bond compared with that in the normal β-diketones, such as acetylacetone [33].

The antitumor and antiviral activities of these compounds have attracted attentions to study the photochemical properties of NZ and its halogen substitutes [34]. Halogenation is an important reaction in the preparative chemistry of 1,4-naphthoquinones [35]. The resulting halogenated derivatives are convenient substrates for the synthesis of natural quinoid compounds and their analogs [36]. Bromination of a number of NZ derivatives having different substituents in the aromatic ring with molecular bromine in carbon tetrachloride was studied [37].

It has been shown that chloro-substituted aromatic compounds increases antibacterial activities [38–40], chemical reactivates [41, 42], and also affect on the intramolecular hydrogen bond strength [43–45]. Chlorinated naphtazarin derivatives have been also used as starting material for preparation of several anthracyclines (a group of natural antibiotics) [46] and some other compounds with biological activities [47–49].

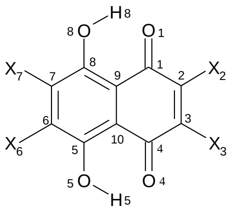
Methoxynaphthazarin and some of its derivtives produced by F. Solani. These are toxic to plants [50]. These pigments are present in the xylem of citrus trees in South Africa [51].Thawed xylem fluid samples were evaluated for NZ concentration using an enzyme-linked immunoabsorbent assay (ELISA) procedure [52].

The effect of Cl and methyl substitutions on the intramolecular hydrogen bond of NZ has been already reported [53, 54]. The aim of the present work is to demonstrate the effect of electron withdrawing, electron donating and steric effect of F, Cl, Br, NO_2 and OMe substitutions of NZ on the intramolecular hydrogen bond strength.

Results and discussion

Geometrical parameters:

The geometry of NZ and the numbering of the ring atoms and the geometrical parameters of F, Cl, Br, NO_2 and OMe substitutions of NZ are given in Figure **1** and in Table **1**, respectively. As illustrated in Table **1**, in general, analysis of bond lengths indicates that the O-H bond lengths and the O-H...O bond angles decreased and the O...O and O...H bond lengths increased by substitution of Cl or Br in the vicinity of carbonyl groups or F or NO_2 in the different positions of NZ, which suggests weaker hydrogen bond in these compounds than that in NZ.



NZ, X2,X3,X6,X7=H.
Mono Y NZ(a), X2,X3,X7=H, X6=Y
Mono Y NZ(b), X3, X6, X7= H, X2=Y
Di Y NZ(a), X6, X7= Y , X2, X3= H
Di Y NZ(b), X6,X7=H , X2, X3=Y
Di Y NZ(c) X2, X7= Y , X3, X6= H
Di Y NZ(d) X3, X7= Y , X2, X6= H
Tri Y NZ(a), X2, X7,X6= Y , X3= H
Tri Y NZ(b), X2, X3,X6= Y , X7= H
Tetra Y NZ, X2,X3,X6,X7=Y
Fluoro-substituted naphthazarin, Y=F
Chloro-substituted naphthazarin, Y=Cl
Bromo-substituted naphthazarin, Y=Br
Nitro-substituted naphthazarin, Y=NO_2
Methoxy-substituted naphthazarin, Y=OMe

Figure 1: Numbering system and the structure of NZ and its F, Cl, Br, NO2 and OME substitutions.

In nitro-substituted naphthazarin and fluoro-substituted naphthazarin, C=O bond lengths decreased. These declines in C=O bond lengths could be attributed to the decrease of π-electron delocalization by the electron withdrawing nature of NO_2 and F substituents. However substitution of Cl or Br in neighborhood of hydroxyl group and OMe in the vicinity of carbonyl or hydroxyl groups increases the O-H bond lengths and the O-H...O bond angles, and decreases the O...O and O...H distances, which suggests stronger hydrogen bond in these compounds than that in NZ. Proton chemical shift for O8-H8 and O5-H5 in NZ and its F, Cl, Br, NO_2 and OMe substitutions are compared in Table **2**. In general, the calculated proton chemical shift for the O-H in NZ by substitution of Cl or Br in neighborhood of hydroxyl group and OMe in the vicinity of carbonyl or hydroxyl groups is downfield compared to that in NZ. The calculated proton chemical shift for the O-H in NZ by substitution of Cl or Br in the vicinity of carbonyl group and F and NO_2

in the vicinity of carbonyl or hydroxyl groups is upfield compared to that inNZ. These conclusions are in good agreement with the calculated geometrical parameters results.

The calculated hydrogen bond strength, E_{HB}, of NZ and its derivatives are compared in Table **2**. These values are calculated per single hydrogen bond in NZ and its derivatives.

E_{HB} decreased in most of the compounds. In NZ with substitution of F,Cl, Br and NO_2in neighborhood of carbonyl group is expected decrease of E_{HB} because of electron withdrawing nature of these substitutions. It is expected that the E_{HB} to be increased by substitution of Cl, Br and OMe near the hydroxyl groups. However, as it is shown in Table **2**, E_{HB} in most of these compounds are also decreased. This decrease of E_{HB} can be justified by considering formation of an intramolecular hydrogen bond between the O...H group and Cl, Br and O atom of OMe.

Table 1: Comparison of calculated structural parameters for NZ and its F, Cl, Br, NO_2 and OMe substitutions optimized at the B3LYP/6-31G**level.

Bond lengths (l)	NZ	MonoF NZ(a)	MonoF NZ(b)	DiF NZ(a)	DiF NZ(b)	DiF NZ(c)	DiF NZ(d)	TriF NZ(a)	TriF NZ(b)	TetraF NZ	MonoCl NZ(a)	Mono Cl NZ(b)	Di Cl NZ(a)	Di Cl NZ(b)	Di Cl NZ(c)	Di Cl NZ(d)	Mono Br NZ(b)	Di Br NZ(a)	Di Br NZ(b)	Di Br NZ(c)	Di Br NZ(d)	Tri Br NZ(a)	Tri Br NZ(b)	Tetra Br NZ
C8-O8	1.336	1.333	1.335	1.331	1.334	1.332	1.331	1.331	1.332	1.33	1.334	1.334	1.328	1.334	1.328	1.333	1.334	1.329	1.333	1.328	1.329	1.327	1.332	1.327
C5-O5	1.336	1.332	1.335	1.331	1.334	1.3323	1.333	1.33	1.331	1.33	1.329	1.334	1.328	1.334	1.333	1.328	1.329	1.329	1.333	1.333	1.333	1.328	1.327	1.327
C1-O1	1.249	1.249	1.243	1.248	1.244	1.242	1.247	1.242	1.244	1.242	1.248	1.242	1.248	1.242	1.241	1.242	1.248	1.248	1.243	1.242	1.248	1.243	1.243	1.243
C4-O4	1.249	1.247	1.248	1.248	1.244	1.249	1.244	1.247	1.242	1.242	1.248	1.249	1.248	1.242	1.241	1.248	1.248	1.248	1.243	1.248	1.242	1.248	1.242	1.243
O8-H8	0.996	0.997	0.993	0.997	0.994	0.993	0.997	0.994	0.995	0.994	0.996	0.994	0.999	0.994	0.996	0.994	0.996	1	0.995	0.997	0.999	0.998	0.995	0.999
O5-H5	0.996	0.996	0.996	0.997	0.994	0.998	0.994	0.998	0.994	0.994	0.998	0.996	0.999	0.994	0.996	0.999	0.999	1	0.995	0.996	0.994	1.001	0.998	0.999
O1…H8	1.677	1.672	1.698	1.678	1.696	1.703	1.674	1.701	1.693	1.699	1.678	1.68	1.648	1.676	1.658	1.682	1.677	1.642	1.671	1.652	1.648	1.643	1.671	1.635
O4…H5	1.677	1.681	1.672	1.678	1.696	1.668	1.693	1.673	1.699	1.699	1.654	1.676	1.648	1.676	1.678	1.652	1.652	1.642	1.671	1.677	1.679	1.64	1.645	1.635
O1…O8	2.578	2.576	2.591	2.578	2.589	2.593	2.574	2.593	2.588	2.591	2.5786	2.574	2.557	2.57	2.558	2.575	2.577	2.555	2.566	2.554	2.556	2.549	2.566	2.542
O4…O5	2.578	2.579	2.573	2.578	2.589	2.571	2.589	2.574	2.59	2.591	2.561	2.576	2.557	2.57	2.577	2.558	2.56	2.555	2.566	2.577	2.574	2.552	1.645	2.542
Bond angles (°)																								
C1-C9-C8	119.6	119.7	119.1	120.0	119.1	147.0	118.9	118.5	119.2	118.5	119.7	119.1	119.1	119.1	118.5	119.1	119.1	119.7	119.2	119.2	118.6	119.0	119.0	119.2
C4-C10-C5	119.6	118.9	119.6	119.0	119.1	148.5	119.2	119.0	118.4	118.5	119.0	119.6	119.1	119.1	119.6	118.9	119.5	119.0	119.2	119.2	119.6	119.2	119.2	118.7
O8H8…O1	148.3	148.5	147.5	148.0	147.5	147.5	147.9	147.2	147.6	147.1	148.2	147.5	149.1	147.4	148.0	147.4	147.5	148.3	149.5	147.4	148.3	148.8	148.7	147.4
O5H5…O4	148.3	147.8	148.2	148.0	147.5	148.5	147.7	148.0	147.0	147.1	148.8	148.1	149.1	147.4	148.0	148.7	148.1	148.9	149.5	147.45	148.1	147.5	149.3	148.2

Bond lengths (l)	Mono NO2	Mono NO2 NZ(b)	Di NO_2 NZ(a)	Di NO_2 NZ(b)	Di NO_2 NZ(c)	Di NO_2 NZ(d)	Tri NO_2 NZ(a)	Tri NO_2 NZ(b)	Di NO_2 NZ(a)	Di NO_2 NZ(b)	Di NO_2 NZ(c)	Di NO_2 NZ(d)	Tri NO_2 NZ(a)	Tri NO_2 NZ(b)	Tetra NO_2 NZ	Mono OMe NZ(a)	Mono OMe NZ(b)	Di OMe NZ(a)	Di OMe NZ(b)	Di OMe NZ(c)	Di OMe NZ(d)	Tri OMe NZ(a)	Tri OMe NZ(b)	Tetra OMe NZ
C8-O8	1.333	1.333	1.33	1.331	1.329	1.323	1.325	1.329	1.33	1.331	1.329	1.323	1.325	1.329	1.326	1.339	1.336	1.335	1.336	1.339	1.338	1.335	1.335	1.336
C5-O5	1.331	1.333	1.33	1.331	1.331	1.331	1.325	1.327	1.33	1.331	1.331	1.331	1.325	1.327	1.326	1.335	1.336	1.335	1.336	1.335	1.335	1.336	1.338	1.336
C1-O1	1.246	1.243	1.244	1.242	1.24	1.245	1.237	1.24	1.244	1.242	1.24	1.245	1.237	1.24	1.237	1.252	1.249	1.251	1.254	1.252	1.257	1.252	1.253	1.254
C4-O4	1.246	1.247	1.244	1.242	1.244	1.238	1.242	1.239	1.244	1.242	1.244	1.238	1.242	1.239	1.237	1.252	1.253	1.251	1.254	1.255	1.253	1.255	1.255	1.254
O8-H8	0.995	0.993	0.996	0.992	0.993	0.998	0.994	0.992	0.996	0.992	0.993	0.998	0.994	0.992	0.992	0.998	0.993	1.001	0.996	1.001	1.012	0.996	0.996	1
O5-H5	0.996	0.995	0.996	0.992	0.994	0.992	0.996	0.992	0.996	0.992	0.994	0.992	0.996	0.992	0.992	1.005	1.00	1.001	0.996	1.001	0.995	1.007	1.006	1
O1…H8	1.686	1.702	1.687	1.708	1.709	1.649	1.683	1.715	1.687	1.708	1.709	1.649	1.683	1.715	1.72	1.67	1.671	1.643	1.648	1.595	1.567	1.647	1.661	1.632
O4…H5	1.679	1.681	1.687	1.708	1.691	1.697	1.678	1.713	1.687	1.708	1.691	1.697	1.678	1.713	1.72	1.598	1.65	1.643	1.648	1.646	1.662	1.605	1.588	1.632
O1…O8	2.582	2.592	2.579	2.593	2.591	2.554	2.57	2.596	2.579	2.593	2.591	2.554	2.57	2.596	2.595	2.577	2.565	2.558	2.551	2.515	2.506	2.552	2.564	2.545
O4…O5	2.575	2.579	2.579	2.593	2.583	2.581	2.571	2.592	2.579	2.593	2.583	2.581	2.571	2.592	2.595	2.524	2.56	2.558	2.551	2.561	2.564	2.533	2.516	2.545
Bond angles (°)																								
C1-C9-C8	119.6	119.1	119.0	119.0	118.4	118.6	118.3	119.0	119.0	119.0	118.4	118.6	118.3	119.0	118.4	120.0	119.2	119.4	119.5	118.5	118.9	119.1	119.8	119.4
C4-C10-C5	118.9	119.4	119.0	119.0	119.4	118.7	118.7	118.3	119.0	119.0	119.4	118.7	118.7	118.3	118.4	118.8	119.8	119.4	119.5	120.1	119.6	119.4	118.8	119.4
O8H8…O1	147.6	147.0	146.9	146.5	145.8	148.6	146.3	145.9	146.9	146.5	145.8	148.6	146.3	145.9	145.0	149.1	147.6	149.7	148.4	150.5	152.0	148.8	148.7	149.5
O5H5…O4	147.3	147.8	146.9	146.5	147.1	146.1	147.0	145.4	146.9	146.5	147.1	146.1	147.0	145.4	145.0	151.0	149.2	149.7	148.4	149.7	148.5	150.8	151.0	149.5

Table 2: Comparing several properties related to the hydrogen bond strength for NZ and its F, Cl, Br, NO_2 and OMe substitutions optimized at the B3LYP/6-31G** level.

	NZ	MonoF NZ(a)	MonoF NZ(b)	Di F NZ(a)	Di F NZ(b)	Di F NZ(c)	Di F NZ(d)	Tri F NZ(a)	Tri F NZ(b)	Tetra F NZ	MonoCl NZ(a)	MonoCl NZ(b)
δH8-O8[a]	13.46	13.56	13.12	13.39	13.14	12.99	13.40	13.01	13.21	13.06	13.34	13.36
δH5-O5[a]	13.46	13.34	13.46	13.39	13.14	13.58	13.22	13.45	13.03	13.06	13.98	13.42
E_{HB}(kJ/mol) [b]	60.25	59.58	54.84	47.02	57.16	39.84	45.04	41.50	56.19	43.96	58.07	56.36
E_{HB}(kJ/mol) [c]	60.25	43.76	59.68	47.02	57.16	60.37	55.73	46.45	40.88	43.96	46.91	58.53
	Di Cl NZ(a)	Di Cl NZ(b)	Di Cl NZ(c)	Di Cl NZ(d)	Tri Cl NZ(a)	Tri Cl NZ(b)	Tetra Cl NZ	MonoBr NZ(b)	DiBr NZ(a)	DiBr NZ(b)	Di Br NZ(c)	DiBr NZ(d)
δH8-O8[a]	14.09	13.38	13.86	13.96	13.98	13.27	14.01	13.37	14.17	13.44	13.96	14.01
δH5-O5[a]	14.09	13.38	13.31	13.23	14.06	13.91	14.01	13.42	14.17	13.44	13.29	13.26
E_{HB}(kJ/mol) [b]	49.16	53.66	44.43	55.79	44.48	56.16	47.05	56.74	45.66	49.98	41.60	43.79
E_{HB}(kJ/mol) [c]	49.16	53.66	57.93	47.03	47.07	45.0	47.05	58.51	45.66	49.98	57.60	55.84
	TriBr NZ(a)	Tri Br NZ(b)	Tetra Br NZ	Mono NO_2NZ(a)	Mono NO_2NZ(b)	Di NO_2 NZ(a)	DiNO_2 NZ(b)	Di NO_2 NZ(c)	Di NO_2 NZ(d)	Tri NO_2 NZ(a)	Tri NO_2 NZ(b)	Tetra NO_2NZ
δH8-O8[a]	14.12	13.32	14.18	13.30	13.1	13.29	13.13	12.96	14.24	13.44	13.00	12.89
δH5-O5[a]	14.15	14.01	14.18	13.38	13.50	13.29	13.13	13.33	13.14	13.57	12.99	12.89
E_{HB}(kJ/mol) [b]	40.99	54.94	44.19	56.86	53.98	59.37	53.37	-0.29	10.90	16.79	50.67	52.37
E_{HB}(kJ/mol) [c]	43.17	42.43	44.19	5.40	56.56	59.37	53.37	54.78	62.17	17.83	51.66	52.37
	Mono OMe NZ(a)	Mono OMe NZ(b)	Di OMe NZ(a)	Di OMe NZ(b)	Di OMe NZ(c)	Di OMe NZ(d)	Tri OMe NZ(a)	Tri OMe NZ(b)	Tetra OMe NZ			
δH8-O8[a]	13.52	13.84	14.01	13.52	14.31	15.33	13.58	13.36	13.92			
δH5-O5[a]	14.67	13.21	14.01	13.52	13.86	13.29	14.69	14.82	13.92			
E_{HB}(kJ/mol) [b]	58.53	53.76	34.93	54.66	21.57	38.64	22.96	56.47	32.18			
E_{HB}(kJ/mol) [c]	29.39	65.12	34.93	54.66	64.63	55.02	27.71	30.53	32.18			

[a] Hydrogen chemical shift (ppm)

[b] E_{HB}, hydrogen bond strength (energy difference between trans- and cis-enol forms) of O1...H8

[c] E_{HB}, hydrogen bond strength (energy difference between trans- and cis-enol forms) of O5...H5

Table 3: Selected natural charges (e) for NZ and its F, Cl, Br, NO_2 and OMe substitutions optimized at the B3LYP/6-31G** level.

	NZ	Mono F NZ(a)	Mono F NZ(b)	Di F NZ(a)	Di F NZ(b)	Di F NZ(c)	Di F NZ(d)	Tri F NZ(a)	Tri F NZ(b)	Tetra F NZ	Mono Cl NZ(a)	Mono Cl NZ(b)	Di Cl NZ(a)	Di Cl NZ(b)	Di Cl NZ(c)	Di Cl NZ(a)
O1	-0.585	-0.586	-0.568	-0.581	-0.570	-0.563	-0.582	-0.564	-0.571	-0.566	-0.582	-0.571	-0.579	-0.572	-0.566	-0.578
O4	-0.585	-0.580	-0.56	-0.581	-0.570	-0.587	-0.570	-0.582	-0.566	-0.566	-0.579	-0.583	-0.579	-0.572	-0.581	-0.569
H8	0.525	0.526	0.526	0.529	0.527	0.529	0.528	0.530	0.528	0.531	0.526	0.527	0.529	0.528	0.530	0.529
H5	0.525	0.528	0.526	0.529	0.527	0.527	0.527	0.530	0.530	0.531	0.528	0.526	0.529	0.528	0.527	0.528
O8	-0.679	-0.676	-0.674	-0.668	-0.670	-0.664	-0.668	-0.663	0.338	-0.663	-0.676	-0.674	-0.667	-0.672	-0.663	-0.666
O5	-0.679	-0.668	-0.678	-0.668	-0.670	-0.676	-0.672	-0.667	-0.663	-0.663	-0.668	-0.676	-0.667	-0.672	-0.674	-0.671
	Tri Cl NZ(d)	Tri Cl NZ(b)	Tetra Cl NZ	Mono Br NZ(a)	Mono Br NZ(b)	Di Br NZ(a)	Di Br NZ(b)	Di Br NZ(c)	Di Br NZ(d)	Tri Br NZ(a)	Tri Br NZ(b)	Tetra Br NZ	onoNO$_2$ NZ(a)	onoNO$_2$ Z(b)	i NO$_2$ Z(a)	DiNO$_2$ NZ(b)
O1	-0.566	-0.57	-0.567	-0.582	-0.572	-0.580	-0.574	-0.568	-0.579	-0.579	-0.572	-0.570	-0.574	-0.572	-0.563	-0.566
O4	-0.578	-0.568	-0.567	-0.580	-0.583	-0.580	-0.574	-0.580	-0.570	-0.568	-0.570	-0.570	-0.572	-0.577	-0.563	-0.566
H8	0.531	0.529	0.531	0.526	0.527	0.529	0.527	0.530	0.529	0.529	0.528	0.531	0.526	0.527	0.532	0.529
H5	0.530	0.531	0.531	0.528	0.526	0.529	0.527	0.527	0.528	0.530	0.530	0.531	0.530	0.526	0.532	0.529
O8	-0.663	-0.670	-0.662	-0.676	-0.674	-0.668	-0.673	-0.664	-0.667	-0.666	-0.671	-0.663	-0.670	-0.665	-0.664	-0.658
O5	-0.665	-0.662	-0.662	-0.669	-0.676	-0.668	-0.673	-0.674	-0.672	-0.664	-0.664	-0.663	-0.668	-0.668	-0.664	-0.658
	Di NO_2 NZ(c)	Di NO_2 NZ(d)	Tri NO_2 NZ(a)	Tri NO_2 NZ(b)	Tetra NO_2 NZ	Mono OMe NZ(a)	Mono OMeNZ(b)	DiOMe NZ(a)	Di OMe NZ(b)	DiOMe NZ(c)	DiOMe NZ(d)	TriOMeNZ(a)	TriOMe NZ(b)	Tetra OMNZ		
O1	-0.559	-0.561	-0.539	-0.555	-0.545	-0.597	-0.604	-0.593	-0.617	-0.609	-0.608	-0.613	-0.617	-0.617		
O4	-0.565	-0.547	-0.550	-0.555	-0.545	-0.591	-0.600	-0.593	-0.617	-0.607	-0.618	-0.607	-0.612	-0.617		
H8	0.534	0.531	0.534	0.531	0.537	0.525	0.525	0.528	0.525	0.528	0.528	0.527	0.525	0.528		
H5	0.528	0.529	0.532	0.535	0.537	0.529	0.525	0.528	0.525	0.525	0.525	0.529	0.529	0.528		
O8	-0.659	-0.647	-0.650	-0.654	-0.650	-0.679	-0.678	-0.685	-0.683	-0.696	-0.703	-0.681	-0.680	-0.687		
O5	-0.662	-0.659	-0.650	-0.654	-0.650	-0.698	-0.685	-0.685	-0.683	-0.684	-0.679	-0.693	-0.699	-0.687		

Table 4: Comparison of selected Wiberg bond indexes of NZ and its F, Cl, Br, NO$_2$ and OMe substitutions optimized at the B3LYP/6-31G**level.

	NZ	Mono F NZ(a)	Mono F NZ(b)	Di F NZ(a)	Di F NZ(b)	Di F NZ(c)	Di F NZ(d)	Tri F NZ(a)	Tri F NZ(b)	Tetra F NZ	Mono Cl NZ(a)	Mono Cl NZ(b)	DiCl NZ(a)	Di Cl NZ(b)	Di Cl NZ(c)	Di Cl NZ(a)	Tri Cl NZ(d)	Tri Cl NZ(b)	Tetra Cl NZ	Mono Br NZ(a)	Mono Br NZ(b)	Di Br NZ(a)
C1-O1	1.585	1.58	1.602	1.591	1.594	1.612	1.588	1.608	1.59	1.6	1.587	1.606	1.586	1.599	1.61	1.583	1.607	1.6	1.599	1.586	1.603	1.584
C8-O8	1.132	1.138	1.134	1.138	1.135	1.137	1.138	1.139	1.14	1.141	1.134	1.136	1.149	1.138	1.15	1.149	1.152	1.14	1.154	1.134	1.136	1.148
O8-H8	0.61	0.606	0.616	0.605	0.615	0.614	0.605	0.612	0.612	0.611	0.608	0.612	0.597	0.611	0.603	0.598	0.6	0.61	0.598	0.608	0.612	0.595
O1...H8	0.103	0.106	0.095	0.104	0.096	0.094	0.104	0.095	0.097	0.096	0.103	0.098	0.111	0.099	0.104	0.11	0.106	0.098	0.107	0.103	0.098	0.113
C4-O4	1.585	1.594	1.581	1.591	1.594	1.577	1.596	1.586	1.602	1.6	1.59	1.579	1.587	1.599	1.58	1.607	1.58	1.603	1.599	1.589	1.58	1.584
C5-O5	1.132	1.136	1.134	1.138	1.135	1.139	1.139	1.14	1.139	1.141	1.146	1.135	1.149	1.138	1.137	1.138	1.151	1.152	1.154	1.145	1.135	1.148
O5-H5	0.61	0.608	0.608	0.605	0.615	0.604	0.612	0.603	0.612	0.611	0.6	0.609	0.597	0.611	0.608	0.611	0.596	0.601	0.598	0.599	0.609	0.595
O4...H5	0.103	0.102	0.104	0.104	0.096	0.106	0.098	0.105	0.095	0.096	0.109	0.103	0.111	0.099	0.103	0.098	0.111	0.105	0.107	0.11	0.103	0.113
O1…O8	0.052	0.051	0.051	0.05	0.049	0.051	0.05	0.049	0.048	0.048	0.05	0.051	0.052	0.051	0.052	0.052	0.052	0.049	0.051	0.05	0.051	0.053
O4…O5	0.052	0.052	0.05	0.05	0.049	0.049	0.05	0.049	0.049	0.048	0.052	0.051	0.052	0.051	0.05	0.05	0.052	0.052	0.051	0.053	0.051	0.053

	Di Br NZ(b)	Di Br NZ(c)	Di Br NZ(d)	Tri Br NZ(a)	Tri Br NZ(b)	Tetra Br NZ	Mono NO$_2$ NZ(a)	Mono NO$_2$ NZ(b)	Di NO$_2$ NZ(a)	Di NO$_2$ NZ(b)	Di NO$_2$ NZ(c)	Di NO$_2$ NZ(d)	Tri NO$_2$ NZ(a)	Tri NO$_2$ NZ(b)	Tetra NO$_2$ NZ	Mono OME NZ(a)	Mono OME NZ(b)	Di OME NZ(a)	Mono Br NZ(b)	Di Br NZ(a)	Di Br NZ(b)	Di Br NZ(c)
C1-O1	1.596	1.606	1.582	1.601	1.596	1.593	1.602	1.599	1.616	1.601	1.62	1.598	1.64	1.615	1.631	1.56	1.566	1.567	1.603	1.584	1.596	1.606
C8-O8	1.139	1.149	1.148	1.152	1.14	1.154	1.136	1.141	1.142	1.148	1.146	1.171	1.158	1.151	1.154	1.135	1.13	1.129	1.136	1.148	1.139	1.149
O8-H8	0.61	0.602	0.598	0.598	0.609	0.595	0.61	0.616	0.604	0.616	0.611	0.595	0.606	0.617	0.612	0.606	0.615	0.595	0.612	0.595	0.61	0.602
O1...H8	0.1	0.105	0.11	0.108	0.1	0.11	0.1	0.092	0.1	0.09	0.09	0.107	0.094	0.087	0.086	0.107	0.098	0.115	0.098	0.113	0.1	0.105
C4-O4	1.596	1.58	1.603	1.577	1.598	1.593	1.604	1.588	1.616	1.601	1.604	1.631	1.618	1.62	1.631	1.567	1.553	1.567	1.58	1.584	1.596	1.58
C5-O5	1.139	1.137	1.138	1.15	1.151	1.154	1.139	1.141	1.142	1.148	1.144	1.142	1.159	1.153	1.154	1.118	1.131	1.129	1.135	1.148	1.139	1.137
O5-H5	0.61	0.608	0.611	0.594	0.599	0.595	0.604	0.616	0.604	0.616	0.611	0.616	0.603	0.612	0.612	0.581	0.6	0.595	0.609	0.595	0.61	0.608
O4…H5	0.1	0.103	0.099	0.113	0.107	0.11	0.102	0.1	0.1	0.09	0.097	0.091	0.099	0.088	0.086	0.128	0.113	0.115	0.103	0.113	0.1	0.103
O1…O8	0.051	0.052	0.052	0.052	0.05	0.052	0.049	0.051	0.047	0.051	0.048	0.053	0.048	0.049	0.047	0.05	0.051	0.053	0.051	0.053	0.051	0.052
O4…O5	0.051	0.05	0.05	0.052	0.052	0.052	0.049	0.053	0.047	0.051	0.05	0.05	0.05	0.049	0.047	0.058	0.049	0.053	0.051	0.053	0.051	0.05

	Di Br NZ(d)	Tri Br NZ(a)	Tri Br NZ(b)	Tetra Br NZ	Mono NO$_2$ NZ(a)	Mono NO$_2$ NZ(b)	Di NO$_2$ NZ(a)	Di NO$_2$ NZ(b)	Di NO$_2$ NZ(c)	Di NO$_2$ NZ(d)	Tri NO$_2$ NZ(a)	Tri NO$_2$ NZ(b)	Tetra NO$_2$ NZ	Mono OME NZ(a)	Mono OME NZ(b)	Di OME NZ(a)	Di OME NZ(b)	Di OME NZ(c)	Di OME NZ(d)	Tri OME NZ(a)	Tri OME NZ(b)	Tetra OME NZ
C1-O1	1.582	1.601	1.596	1.593	1.602	1.599	1.616	1.601	1.62	1.598	1.64	1.615	1.631	1.56	1.566	1.567	1.529	1.549	1.529	1.547	1.535	1.532
C8-O8	1.148	1.152	1.14	1.154	1.136	1.141	1.142	1.148	1.146	1.171	1.158	1.151	1.154	1.135	1.13	1.129	1.129	1.116	1.12	1.129	1.132	1.126
O8-H8	0.598	0.598	0.609	0.595	0.61	0.616	0.604	0.616	0.611	0.595	0.606	0.617	0.612	0.606	0.615	0.595	0.606	0.587	0.567	0.604	0.609	0.596
O1…H8	0.11	0.108	0.1	0.11	0.1	0.092	0.1	0.09	0.09	0.107	0.094	0.087	0.086	0.107	0.098	0.115	0.106	0.121	0.142	0.107	0.104	0.114
C4-O4	1.603	1.577	1.598	1.593	1.604	1.588	1.616	1.601	1.604	1.631	1.618	1.62	1.631	1.567	1.553	1.567	1.529	1.538	1.537	1.535	1.53	1.532
C5-O5	1.138	1.15	1.151	1.154	1.139	1.141	1.142	1.148	1.144	1.142	1.159	1.153	1.154	1.118	1.131	1.129	1.129	1.134	1.134	1.126	1.119	1.126
O5-H5	0.611	0.594	0.599	0.595	0.604	0.616	0.604	0.616	0.611	0.616	0.603	0.612	0.612	0.581	0.6	0.595	0.606	0.598	0.611	0.58	0.579	0.596
O4…H5	0.099	0.113	0.107	0.11	0.102	0.1	0.1	0.09	0.097	0.091	0.099	0.088	0.086	0.128	0.113	0.115	0.106	0.116	0.102	0.129	0.13	0.114
O1…O8	0.052	0.052	0.05	0.052	0.049	0.051	0.047	0.051	0.048	0.053	0.048	0.049	0.047	0.05	0.051	0.053	0.049	0.056	0.056	0.051	0.048	0.05
O4…O5	0.05	0.052	0.052	0.052	0.049	0.053	0.047	0.051	0.05	0.05	0.05	0.049	0.047	0.058	0.049	0.053	0.049	0.048	0.049	0.052	0.054	0.05

Table 5: Important pairwise exchange energies ΔE (i, j) (kcal/mol) interactions between NLMOs i, j for NZ and its F, Cl, Br, NO2 and OMe substitutions optimized at the B3LYP/6-31G** level.

NLMO(i)	Type	NLMO(j)	Type	NZ	Mono F NZ(a)	Mono F NZ(b)	Di F NZ(a)	Di F NZ(b)	Di F NZ(c)	Di F NZ(d)	Tri F NZ(a)	Tri F NZ(b)	Tetra F NZ	Mono Cl NZ(a)	Mono Cl NZ(b)	Di Cl NZ(a)	Di Cl NZ(b)	Di Cl NZ(c)	Di Cl NZ(d)
O8-H8	σ	O1	LP (2)	15.78	16.08	14.57	15.78	15.74	14.37	16.02	14.48	14.84	14.59	15.73	15.42	17.49	15.74	16.71	17.27

C1-O1	σ	Y	LP (2)	-	-	-	-	-	-	-	-	-	-	-	0.69	-	0.84	0.7	-
C1-O1	π	Y	LP (3)	-	-	0.65	-	0.55	0.64	-	0.65	0.58	0.56	-	0.82	-	0.92	0.82	-
O1	LP (1)	Y	LP (2)	-	-	-	-	-	-	-	-	-	-	-	0.79	-	0.95	0.82	-
O1	LP (2)	Y	LP (2)	-	-	-	-	-	-	-	-	-	-	-	0.52	-	0.65	0.52	-
C8- O8	σ	Y	LP (2)	-	-	-	-	-	-	-	-	-	-	-	-	1.2	-	1	0.98
O8	LP (1)	Y	LP (2)	-	-	-	-	-	-	-	-	-	-	-	-	1.76	-	1.51	1.45
O5-H5	σ	O4	LP (1)	1.14	1.17	1.17	1.16	1.26	1.15	1.21	1.19	1.29	1.28	1.15	1.16	1.14	1.38	1.17	1.4
O5-H5	σ	O4	LP (2)	15.78	15.67	16.07	15.78	15.74	16.34	14.83	16.1	14.59	14.59	17.1	15.88	17.49	15.74	15.8	15.38
O4	LP (1)	Y	LP (2)	-	-	-	-	-	-	-	-	-	-	-	-	-	0.95	-	0.78
C4-O4	π	Y	LP (3)	-	-	-	-	0.55	-	0.66	-	0.52	0.56	-	-	-	0.92	-	0.83
C5-O5	σ	Y	LP (2)	-	-	-	-	-	-	-	-	-	-	0.98	-	1.2	-	-	-
O5	LP (1)	Y	LP (2)	-	-	-	-	-	-	-	-	-	-	1.45	-	1.76	-	-	-
C1-O1	σ	O8-H8	σ	1.63	1.67	1.53	1.57	1.49	1.45	1.55	1.48	1.54	1.46	1.61	1.58	1.84	1.57	1.73	1.78
C4-O4	σ	O5-H5	σ	1.63	1.56	1.61	1.57	1.49	1.65	1.57	1.57	1.45	1.46	1.78	1.62	1.84	1.57	1.61	1.57
sum of pairwise steric exchange ΔE (i, j)				371.34	397.19	395.5	424.2	418.38	420.99	421.47	448.41	447.22	474.08	397.88	395.59	431.85	426.51	422.21	422.36

NLMO(i)	Type	NLMO(j)	Type	Tri Cl NZ(a)	Tri Cl NZ(b)	Tetra Cl NZ	Mono Br NZ(a)	Mono Br NZ(b)	Di Br NZ(a)	Di Br NZ(b)	Di Br NZ(c)	Di Br NZ(d)	Tri Br NZ(a)	Tri Br NZ(b)	Tetra Br NZ	Mono NO_2 NZ(a)	Mono NO_2 NZ(b)	Di NO_2 NZ(a)	Di NO_2 NZ(b)
O8-H8	σ	O1	LP (2)	17.13	15.66	17.45	15.82	15.47	17.76	15.97	17.01	17.44	17.57	15.99	18.07	15.25	14.3	15.24	14.02
C1-O1	σ	Y	LP (2)	0.7	0.84	0.85	-	0.67	-	0.84	0.67	-	0.67	0.84	0.85	-	-	-	-
C1-O1	π	Y	LP (3)	0.83	0.96	0.93	-	0.82	-	0.95	0.83	-	0.84	1	0.96	-	-	-	-
O1	LP (1)	Y	LP (2)	0.82	0.94	0.98	-	0.93	-	1.15	0.96	-	0.97	1.14	1.2	-	-	-	-
O1	LP (2)	Y	LP (2)	0.51	0.65	0.63	-	0.62	-	0.76	0.6	-	0.59	0.76	0.72	-	-	-	-
C8- O8	σ	Y	LP (2)	1.21	-	1.22	-	-	1.2	-	0.93	-	1.21	-	1.21	-	-	-	-
O8	LP (1)	Y	LP (2)	1.83	-	1.84	-	-	2.08	-	1.71	1.65	2.15	-	2.16	-	-	-	-
O5-H5	σ	O4	LP (1)	1.15	1.38	1.38	1.14	1.16	1.12	1.42	1.17	1.44	1.14	1.42	1.4	1.21	1.18	1.25	1.3
O5-H5	σ	O4	LP (2)	17.55	17.12	17.45	17.19	15.88	17.76	15.97	15.8	15.49	17.89	17.48	18.07	15.69	15.5	15.24	14.02
O4	LP (1)	Y	LP (2)	-	0.98	0.98	-	-	-	1.15	-	0.92	-	1.2	1.2	-	-	-	-
C4-O4	π	Y	LP (3)	-	0.85	0.85	-	-	-	0.95	-	0.84	-	0.92	0.96	-	-	-	-
C5-O5	σ	Y	LP (2)	1.21	1	1.22	0.91	-	1.2	-	-	-	1.2	0.96	0.85	-	-	-	-
O5	LP (1)	Y	LP (2)	1.77	1.52	1.84	-	-	2.08	-	-	-	-	1.73	2.16	-	-	-	-
C1-O1	σ	O8-H8	σ	1.8	1.56	1.79	1.62	1.59	1.9	1.6	1.78	1.81	1.87	1.59	1.88	1.53	1.52	1.47	1.48
C4-O4	σ	O5-H5	σ	1.84	1.73	1.79	1.8	1.62	1.9	1.6	1.61	1.58	1.9	1.78	1.88	1.54	1.6	1.47	1.48
sum of pairwise steric exchange ΔE(i, j) :				456.17	453.34	487.33	394.5	392.51	426.42	420.62	416.21	415.81	447.42	444.19	475.96	463.5	457.67	556.7	555.98

NLMO(i)	Type	NLMO(j)	Type	Di NO_2 NZ(c)	Di NO_2 NZ(d)	Tri NO_2 NZ(a)	Tri NO_2 NZ(b)	Tetra NO_2 NZ	Mono OMe NZ(a)	Mono OMe NZ(b)	Di OMe NZ(a)	Di OMe NZ(b)	Di OMe NZ(c)	Di OMe NZ(d)	Tri OMe NZ(a)	Tri OMe NZ(b)	TetraOMe NZ
O8-H8	σ	O1	LP (2)	13.98	17.35	15.3	13.62	13.43	16.19	15.94	17.79	17.37	20.69	22.95	17.43	16.55	18.35
C1-O1	σ	Y	LP (2)	-	-	-	-	-	-	-	-	-	-	-	-	-	-
C1-O1	π	Y	LP (3)	-	-	-	-	-	1.4	0.69	-	0.61	0.63	-	0.68	0.7	0.6
O1	LP (1)	Y	LP (2)	-	-	-	-	-	-	-	-	-	-	-	-	-	-
O1	LP (2)	Y	LP (2)	-	-	-	-	-	-	-	-	-	-	-	-	-	-
C8- O8	σ	Y	LP (2)	-	-	-	-	-	-	-		-	-	-	-	-	-
O8	LP (1)	Y	LP (2)	-	-	-	-	-	-	-		-	-	-	-	-	-
O5-H5	σ	O4	LP (1)	1.24	1.43	1.28	1.37	1.4	-	1.1	1.05	1.44	1.05	1.4	0.98	1.17	1.29
O5-H5	σ	O4	LP (2)	14.98	14.58	15.69	13.77	13.43	-	17.46	17.79	17.37	17.67	16.44	20.24	21.22	18.35
O4	LP (1)	Y	LP (2)	-	-	-	-	-	-	-	-	-	-	-	-	-	-
C4-O4	π	Y	LP (3)	-	-	-	-	-	-	-	-	0.61	-	0.71	-	-	0.6
C5-O5	σ	Y	LP (2)	-	-	-	-	-	-	-	-	-	-	-	-	-	-
O5	LP (1)	Y	LP (2)	-	-	-	-	-	-	-	-	-	-	-	-	-	-
C1-O1	σ	O8-H8	σ	1.41	1.39	1.5	1.41	1.34	1.72	1.56	1.89	1.61	2.16	2.3	1.74	1.65	1.82
C4-O4	σ	O5-H5	σ	1.51	1.42	1.58	1.39	1.34	-	1.7	1.89	1.61	1.78	1.66	2.06	2.17	1.82
C-H	σ	O1	LP (1)	-	-	-	-	-	-	1.65	-	1.79	1.82	1.72	2.2	-	1.89

C-H	σ	O4	LP (1)	-	-	-	-	-	-	-	-	1.79	-	-	1.99	1.86	1.89
C-H	σ	O5	LP (1)	-	-	-	-	-	2.37	-	2.16	-	-	3.22	3.41	1.46	2.35
C-H	σ	O8	LP (1)	-	-	-	-	-	-	-	2.16	-	2.41	-	-	2.92	2.35
sum of pairwise steric exchange ΔE(i, j)				554.29	561.12	655.3	648.03	739.73	446.37	442.21	511.49	516.84	516.42	518.06	582.66	584.1	650.93

Table 6: Selected second order perturbation energies [a] E^2 (donor-acceptor) for NZ and its with F, Cl, Br, NO_2 and OMe substitutions optimized at the B3LYP/6-31G** level.

Donor	Type	Acceptor	Type	Tri Cl NZ(a)	Tri Cl NZ(b)	Tetra Cl NZ	MonoBr NZ(a)	Mono Br NZ(b)	Di Br NZ(a)	Di Br NZ(	Di B NZ(c	Di Br NZ(d)	Tri Br NZ(a)	Tri Br NZ(b)	Tetra Br NZ	Mono NO_2NZ(a)	Mono NO_2NZ(b)	Di NO_2 NZ(a)
O1	LP (1)	O8-H8	σ*	5.89	5.54	5.95	5.08	5.57	5.47	5.67	5.95	5.48	6.05	5.68	6.14	5.04	4.96	5.15
O1	LP (2)	O8-H8	σ*	26.75	24.3	27.24	25.52	24.07	28.87	24.83	26.56	28.08	27.55	24.79	28.32	24.37	22.17	24.12
O4	LP (1)	O5-H5	σ*	5.48	5.88	5.95	5.05	5.38	5.11	5.47	5.67	5.12	5.59	6.03	6.14	5.16	5.08	5.15
O4	LP (2)	O5-H5	σ*	28.38	26.6	27.24	27.82	25.52	28.87	24.83	25.4	24.09	28.98	27.24	28.32	25.03	24.73	24.12
O1	LP (2)	C1-C9	σ*	10.86	10.95	10.64	10.73	11.17	10.37	10.87	10.93	10.48	10.77	10.92	10.51	11.14	11.18	11.5
O4	LP (2)	C4-C10	σ*	10.48	10.71	10.64	10.49	10.69	10.37	10.87	10.77	11.19	10.37	10.66	10.51	11.08	10.87	11.5
O8	LP (2)	C8-C9	π*	43.33	42.19	43.68	41.19	41.66	42.75	41.99	43.17	42.88	43.41	42.13	43.7	41.45	-	42.04
O5	LP (2)	C5-C10	π*	43.12	43.5	43.68	42.48	41.4	42.75	41.99	41.56	41.84	43.12	43.47	43.7	41.67	-	42.04
Donor	Type	Acceptor	Type	Di NO_2 NZ(b)	Di NO_2 NZ(c)	Di NO_2 NZ(d)	Tri NO_2 NZ(a)	Tri NO_2 NZ(b)	Tetra NO_2 NZ	Mono OMe NZ(a)	Mono OMe NZ(b)	Di OMe NZ(a)	Di OMe NZ(b)	Di OMe NZ(c)	Di OMe NZ(d)	Tri OMe NZ(a)	Tri OMe NZ(b)	Tetra OMe NZ
O1	LP (1)	O8- H8	σ*	4.95	5.02	5.52	5.53	4.94	5	5.03	5.67	5.33	5.97	6.54	6.2	5.88	5.68	5.99
O1	LP (2)	O8- H8	σ*	21.48	21.34	27.45	23.1	20.63	20.11	26.56	24.6	29.31	27.46	33.01	39.52	27.34	26.3	29.59
O4	LP (1)	O5- H5	σ*	4.95	5.06	5.29	5.3	5.01	5	-	5.37	5.33	5.97	5.31	5.68	5.77	5.68	5.99
O4	LP (2)	O5- H5	σ*	21.48	23.6	22.03	24.43	20.79	20.11	-	28.8	29.31	27.46	29.47	25.85	34.4	26.3	29.59
O1	LP (2)	C 1- C9	σ*	11.33	11.69	10.7	11.86	11.73	12.16	10.24	10.04	9.91	9.61	8.8	8.72	9.47	9.66	9.36
O4	LP (2)	C 4- C10	σ*	11.33	11.36	11.8	11.5	11.79	12.16	9.28	10.24	9.91	9.61	9.89	9.57	9.3	8.86	9.36
O8	LP (2)	C 8- C 9	π*	43.14	42.67	45.78	44.21	43.51	43.91	41.44	40.76	40.13	40.81	-	-	-	-	40.04
O5	LP (2)	C 5- C 10	π*	43.14	42.59	42.35	44.09	43.62	43.91	38.34	40.99	40.13	40.81	-	-	-	-	40.04

[a] Energy in kcal/mol.

NBO analysis:

Charge analysis:

The charge distribution calculated by the NBO method for the optimized geometries of for NZ and its F, Cl, Br, NO_2 and OMe substituted derivatives are tabulated in Table **3**. According to this table, the electron withdrawing effect of Cl or Br in neighborhood of hydroxyl group or carbonyl group reduces the natural charge on the O atoms. Decrease of the natural charge on O of C=O groups results in formation of weaker hydrogen bond.

The most obvious effect of substituting of the H atoms in NZ by the OMe groups in neighborhood of hydroxyl group or carbonyl group is increasing the charge on the O atoms. This is caused by the electron donating nature of the OMe group.

In nitro-substituted naphthazarin and fluoro-substituted naphthazarin the electron withdrawing effect of F and NO_2 in neighborhood of hydroxyl group or carbonyl group reduces the natural charge on the O atoms.

Bond orders:

The calculated Wiberg bond indexes [46] for NZ and its derivatives are collected in Table **4**. This table shows that the O...H bond order in NZ with substitution of Cl or Br in the vicinity of carbonyl groups is less than that in NZ, which suggests weaker hydrogen bond in these compounds than in NZ. However, the O...H bond order in NZ by substitution of Cl or Br near the hydroxyl groups is more than that in NZ, which suggests stronger hydrogen bond in these compounds than in NZ.

In most of the compounds of NZ with substitution of F and NO_2, the O...O and O...H bond orders is less than that in NZ, which suggests weaker hydrogen bond in these compounds than in NZ.

The O...O and O...H bond orders in NZ with substitution of OMe is more than that in NZ, which suggests stronger hydrogen bond in these compounds than in NZ.

It is noteworthy that the O-H bond order correlates very well with the calculated O...O distance. These results are in excellent agreement with the calculated geometrical parameters results and the calculated difference between chemical shifts of the hydroxyl group.

Steric effect:

Some of the most important pair wise steric exchanges are listed in Table **5**. Among these interactions, the interaction between σ orbital of O-H bond and LP (2) of O is the strongest one. There are several interactions between Cl and Br lone pairs and C-O and C=O bonds and O lone pairs. The interaction between σ orbital of O-H and LP (2) of O is increased by substitution of Cl or Br in the neighborhood of hydroxyl groups. The steric effect of Cl and Br in neighborhood of hydroxyl group is responsible for pushing the oxygen atoms toward each other, which results in shorter O…O distance and stronger hydrogen bond. In nitro-substituted naphthazarin and fluoro-substituted naphthazarin, there is no interaction between $NO_2$and F with O lone pairs. There are several interactions between σ orbital of C-H in OMe and O lone pairs that are responsible for pushing the oxygen atoms toward each other. For all molecules, the sum of steric effect of substitutions in neighborhood of hydroxyl group is more than that for substitutions in neighborhood of carbonyl groups. The sum of pairwise steric exchange ΔE (i, j) interactions for all compounds are increased by increase of substitutions.

Electron delocalization:

Delocalization of electron density between occupied Lewis type (bond or lone pair) NBO orbitals and formally unoccupied (antibond or Rydberg) non-Lewis NBO orbitals corresponds to a stabilizing donor–acceptor interaction. The energy of these interactions can be estimated by the second order perturbation theory [37].

Table **6** summarizes some of the second-order perturbative estimates of ‘‘donor–acceptor’’ interactions in the NBO basis of NZ and its derivatives. According to this table, there is significant difference between the interaction energies of NZ and its derivatives. The interaction energy between LP (2) of O atom and the σ* orbital of O-H in NZ with substitution of Cl or Br in the vicinity of carbonyl group is less than those in NZ which suggests weaker hydrogen bond in this compounds than that in NZ. This interaction increased by substitution of Cl or Br in neighborhood of hydroxyl groups, which causes increase of bond length of O-H and increase of strength of the hydrogen bond.

The interaction energy between LP (2) of O atom and the σ* orbital of O-H in nitro-substituted naphthazarin and fluoro-substituted naphthazarin is less than those in NZ which suggests weaker hydrogen bond in these compounds than that in NZ. This interaction energy increased by substitution of OMe in the different positions of NZ which causes increase of bond length of O-H and increase of strength of the hydrogen bond.

These results are in agreement with the calculated geometrical parameters results and the calculated difference between chemical shifts of the hydroxylic proton for all molecules.

Conclusion

The geometry of NZ and its F, Cl, Br, NO_2 and OMe substituents have been fully optimized at the B3LYP/6-31G** level. The hydrogen bond strength increased by substitution of Cl or Br in the vicinity of hydroxyl groups and decreased by substitution of Cl or Br in the neighborhood of carbonyl groups. The hydrogen bond strength of NZ decreased by substitution of F or NO_2 and increased by substitution OMe in the different positions of NZ. The geometrical parameters are in good agreement with the calculated geometrical parameters results and ^1H NMR calculations.

Natural bond orbital analysis indicate that the electron donating and steric effects are responsible for increasing the hydrogen bond strength in OMe substituents of NZ, but the electron-withdrawing effect of NO_2 and F decreases the hydrogen bond strength.

The steric effects of Cl and Br in neighborhood of hydroxyl group of ring increases the hydrogen bond strength, but the electron-withdrawing effect of Cl and Br in neighborhood of carbonyl decreases the hydrogen bond strength. The electronegativity of F is more than Cl, so when F is in the vicinity of carbonyl groups the hydrogen bond strength is decreased more than Cl. According to the above data (geometry, chemical shifts and NBO analysis) , in general, the following trend in the hydrogen bond strength is concluded:

OMe-NZ>Br(a) -NZ>Cl(a) -NZ> NZ>Br(b) -NZ >Cl(b) -NZ >F-NZ> NO_2-NZ

The (a) and (b) indicated that substitution is in neighborhood of hydroxyl group and neighborhood of carbonyl, respectively.

Experimental

All calculations were performed using Gaussian 03 [55] and NBO 5.0 [56] programs. The full geometry optimization of NZ and its Cl substitutions were performed with the hybrid density functional B3LYP [57–59], using 6-31G** basis set.

Wiberg bond index [60] were calculated using NBO 3.0 program implemented in Gaussian 03. The second order interaction energies [61], orbital population and natural steric analysis [62, 63], were performed at the B3LYP/6-31G** level using NBO 5.0 program, which applied the wave function information file generated by earlier version of NBO (3.0). The absolute shielding for NZ and its Cl substitutions, and tetramethylsilane (TMS) have been obtained using the gauge-includingatomic orbital (GIAO) method [64–66] at the B3LYP/6-31G** levelof theory. The predicted ^{1}H chemical are derived from equation $\delta = \sigma_0 - \sigma$, where δ is the chemical shift, σ is the absolute shielding, and σ_0 is the absolute shielding of TMS.

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