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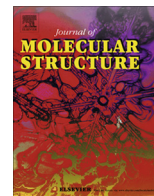


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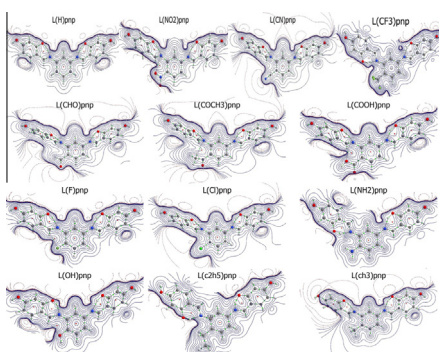
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HIGHLIGHTS

- We study the effects of various substituent groups on the hydrogen bond energy in the b(CH₃) pnp molecules.
- The hydrogen bond barriers with different substituent groups have been found.
- We study the impact of electron withdrawing and donating species on the intramolecular hydrogen bonds' covalent nature.
- We find a good relationship between topological properties.

GRAPHICAL ABSTRACT



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ABSTRACT

The effects of various substituent groups on the hydrogen bond energy in the 3,3'-dihydroxy-4,4'-[5-methyl-1,3-phenylenebis(nitrilomethylidyne)]-bis-phenol (L(CH₃)pnp) molecules is one of the factors controlling intramolecular proton transfer process in the molecule's functional group. In this work, we focused on the influence of different groups on this phenomenon, into the framework of the atom in molecules (AIM) theory. In addition, the calculations of transition state were performed to evaluate the proton transfer's energy barrier of the proton transfer in the Schiff base molecule Lpnp. Investigation the effect of the electron withdrawing groups including, CHO, CN, CF₃, NO₂, COOH, COCH₃, F, Cl and that of electron donating species consisting of NH₂, OH, C₂H₅, CH₃ on the covalent nature of the intramolecular hydrogen bond shows different results: decrease in the electron withdrawing ability reduces the covalent nature whereas, electron donating substituents increase it. The topological properties such as the bond critical point (BCP), ring critical point (RCP), the delocalization index DI, and the integrated properties of the interatomic surface $\delta(\text{O,H})$, $\delta(\text{N,H})$ and $H(\text{G} + \text{V})$ can all be considered as indicators to determine the strength of the intramolecular hydrogen bond.

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Introduction

Hydrogen bonding is the most important and ubiquitous interaction, which is found in liquids, solid and gas phase. These interesting interactions play a major role in the salvation process [1],

surface chemistry [2], proteins' secondary structure [3] and atmospheric chemistry [4]. Therefore, it is no surprise that this amazing chemical phenomenon has been studying widely in quantum chemistry.

One of the consequences of hydrogen bond formation is changing in the electron density distribution in both donor and acceptor molecules. In inorganic chemistry, the Schiff base's ligand and their metal complexes have a dominant role in several fields of catalyst,

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biochemistry, synthesis of enzymatic reactions [5–8]. The tetradenate ONNO donor Schiff bases form a main group of compounds, called Salen or Salophen, used in a wide variety of applications [9]. One of the main groups of Schiff base's ligand is Salen or Salophen, used in a wide variety of applications. The shift base molecule 3,3'-dihydroxy-4,4'-[5-methyl-1,3-phenylenebis(nitri-*l*omethylidyne)]-bis-phenol ($L(CH_3)pnp$) is a new shift base compound of the family of Salen that has been successfully synthesized by Beyram abadi et al. [10] and has particular importance in pharmaceutical industry.

The intramolecular hydrogen bond $N \cdots HO$ exists in two sites of $L(CH_3)pnp$ emphasizes this fact that proton transfer is possible on the either sides of this molecule. However, an in-depth study of molecule's topology properties by using AIM theory and investigation of transition state and also study of proton transfer barrier reveal that despite the possibility of proton transferring from both sites of molecules, only one of them stands chance of proton transfer [11–15]. If the protons transfer from both of sites, then energy barriers are considerably increased, and it becomes impossible for sites to transfer protons. Considering the energy barrier of hydrogen transfer in two sites of molecules and comparing them, it can be deduced that the site 1 of proton transferring, which is located in the para-position of CH_3 group get an opportunity to transfer the proton [10]. The hydrogen bond $N \cdots HO$ which is in the site 1 of $L(CH_3)pnp$, often plays an important role in biological and chemical processes [16]. The presence of various functional groups in the para-position of the molecule can have an enormous impact on the energy barrier of proton transfer and topological properties.

The aim of this work was to study the effects of electron donating and withdrawing substituents at the para-position on proton transfer in the Schiff base molecule $Lpnp$. Bader's atoms in molecules (AIM) theory [17] was applied to analyze the topological properties as the bond critical point (BCP) of the hydrogen bond and the ring critical point (RCP) which is included of $-CN \cdots HOCC-$. The delocalization index $DI(O,H)$ and integrated properties of interatomic surface $\delta(O,H)$, and intermediate structure analyses were also performed that obtain more helpful information about intramolecular proton transfer.

Computational details

Quantum-mechanical calculations carried out to optimize all geometries by the Gaussian03 Program [18] using the Becke3–Lee–Yang–Parr (B3LYP) functional [19,20] supplemented with the standard 6-311++G(d,p) basis set, and transition state structures were obtained by QST3 method [21]. To evaluate the intramolecular interaction energy the following equation, which is given by Espinosa and Molins [22], has been used. According to the properties of electron density distribution in the BCP we have [17]:

$$E = 0.5V$$

where V is the value of the local potential energy at the BCP for interaction. The theoretical calculation of delocalization index between H, N and H, O and transition state as well as topological analyses of electron density were performed with the aid of the AIM theory using the AIMAll program [23].

Results and discussion

Electrostatic potential analysis

The electrostatic potential, $V_S(r)$ [24], of $Lpnp$ is depicted in Fig. 1. In this figure, the negative potential region $V_S(r)$ is located

at the outermost part of H and shown in red¹ while the area of positive $V_S(r)$ which is shown in blue is located in the outermost part of O and N [25]. The interaction between the negative $V_S(r)$ region of N, O and the positive $V_S(r)$ region of H is a reliable evidence for formation of intramolecular hydrogen bond.

Geometrical parameters and energies

In Table 1, absolute energy values of three structures of the molecule are shown, which include E , G , ΔE^\ddagger and ΔG^\ddagger . In first glance, with decreasing order of electron-withdrawing and electron-donating abilities, the values of activation parameters increased and decreased, respectively [26].

All values of the bond lengths and intramolecular hydrogen bond's energies in $Lpnp$ substituted with different functional groups are presented in Table 2. The electron-withdrawing substituents, ranging from NO_2 to Cl and also the electron-donating substituents from NH_2 to CH_3 are listed [25]. In the decreasing order of electron-withdrawing and electron-donating ability, respectively. It seems that the hydrogen bond located in $(N \cdots OH)$ and $(NH \cdots O)$ show a slight increase from 9.36 to 14.51 kJ/mol in the bond energy. This is a small increase; however, based on the obtained values from TS, it can be concluded that the effects of the electron-withdrawing substituents were noticeably smaller than those of the electron-donating substituents.

There is a simple and good linear relationship between the bond lengths and the energies of the substitution groups; this illustrates that the decrease in the bond length, the increase in the hydrogen bond energy. Such a relationship is also seen in both products $(NH \cdots O)$ and reactants $(OH \cdots N)$ that in the transition state $(N \cdots H \cdots O)$ exists a same trend. The linear correlation coefficients for reactant, product, and transition state at BCP of $O \cdots H$ and $N \cdots H$, respectively, is 0.9988, 0.9594, 0.9502 and 0.9964. The obtained results are shown in the following diagrams in Fig. 2.

Also, inductive effects are inevitable result of the innate atoms electronegativity and dipolar property of the functional groups. These effects act either through the removal and placement of electron or space.

Halogen substituent for the reason of its electronegativity are deactivating because they withdraw electrons from aromatic ring by the carbon-halogen sigma bond but the substituents such as NO_2 , CN, CF_3 and carbonyls because of dipole properties of the functional groups withdraw electrons inductively.

In these cases the atom which directly bonded to the aromatic rings has a positive partial charge. Therefore, pull electrons from the ring having the resonance. It should be noted that the inductive effect is much effectual than intrinsic electronegative effect.

Resonant effects occur by the electron donating or withdrawing through the overlapping of p orbital with aromatic ring's π electrons or electron pairs. Substituents such as nitro, carboxyl and Ciano groups are linked to the aromatic ring by atoms having p orbital and thus aromatic ring's π electrons can be delocalized over these substituents. For examples, in the nitrobenzene and benzaldehyd resonant structure π electrons of aromatic ring are resonantly interchanged toward substituents. As a result, a positive charge is created on the ring and makes the ring inactive toward electrophilic attacks. By contrast, substituents as hydroxyl, methyl, ethyl and amino groups are electron donating by resonance effect so they donate their π electrons to the ring and make it active.

It may seem surprising that hydroxyl, methyl, ethyl and amino groups play activating role for aromatic ring while oxygen and nitrogen are both electronegative elements. In the other word, it

¹ For interpretation of color in Fig. 1, the reader is referred to the web version of this article.

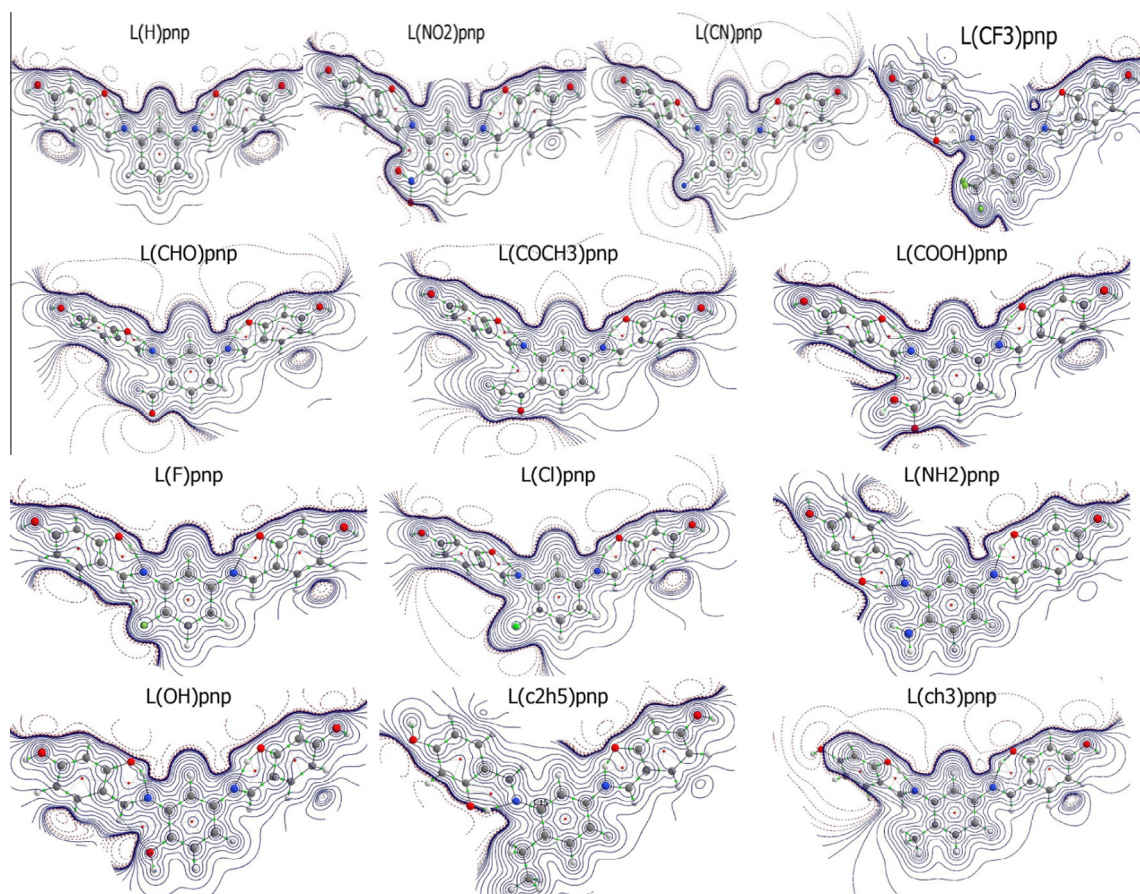


Fig. 1. Electrostatic potential map for 12 different functional groups including electron-withdraw and electron-donate.

Table 1

Absolute energy values of three structures of molecule with different functional groups.

	E (Hartree)			G (Hartree)			$\Delta E^\#$ (kJ/mol)	$\Delta G^\#$ (kJ/mol)
	OH	TS	NH	OH	TS	NH		
H	-1260.7707	-1260.7691	-1260.7729	-1260.8262	-1260.8251	-1260.8287	4.1663	2.8721
NO ₂	-1281.4677	-1281.4649	-1281.4655	-1281.5217	-1281.5186	-1281.5198	7.1711	8.1128
CN	-1274.4657	-1274.4624	-1274.4634	-1274.5213	-1274.5174	-1274.5192	8.6866	10.1534
CF ₃	-1518.9222	-1519.3362	-1519.3370	-1518.9796	-1519.3939	-1519.3949	7.344329	3.14757
CHO	-1295.5438	-1295.5394	-1295.5404	-1295.5995	-1295.5950	-1295.5969	11.5288	11.6826
COCH ₃	-1334.8452	-1334.8425	-1334.8435	-1334.9024	-1334.8996	-1334.9013	6.8801	7.3311
COOH	-1370.8142	-1370.8114	-1370.8123	-1370.8710	-1370.8681	-1370.8697	7.1449	7.7744
F	-1281.4677	-1281.4649	-1281.4655	-1281.5217	-1281.5186	-1281.5198	7.1711	8.1128
Cl	-1641.8221	-1641.8194	-1641.8201	-1641.8768	-1641.8745	-1641.8753	7.1630	6.0459
NH ₂	-1237.5589	-1237.5570	-1237.5575	-1237.6129	-1237.6109	-1237.6122	4.9267	5.2328
OH	-1257.4378	-1257.4354	-1257.4360	-1257.4928	-1257.4896	-1257.4911	6.2613	8.2518
CH ₂ CH ₃	-1260.7707	-1260.7685	-1260.7729	-1260.8262	-1260.8243	-1260.8287	5.7395	4.9705
CH ₃	-1221.4914	-1221.4893	-1221.4901	-1221.5467	-1221.5445	-1221.5457	5.4616	5.7180

is expected that these elements inductively make ring inactive but practically their electron donating resonance effects are preferred on that electron withdrawing inductive. So it seems that electron donating substituents with improve resonance effect on the ring have an important role to intramolecular proton transfer.

AIM analysis on the BCP

The Bader theory comes of ages as a very useful tool to analyze hydrogen bonds. The analysis of the BCPs' properties has generally been conducted to estimate the nature of hydrogen bonds [17,27–31]. The parameters such as the Laplacian of the electron density $\nabla^2\rho$, the electron energy density H_C that is the sum of the kinetic electron energy density (G_C) and the potential electron energy

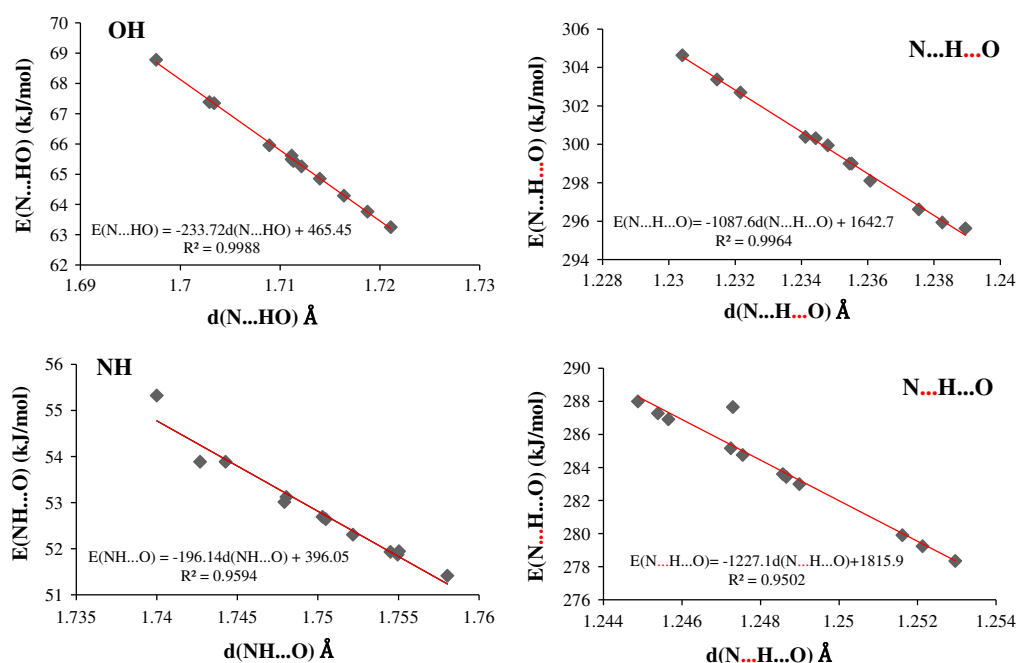
density (V_C), and as well as $-G_C/V_C$, derive from the Bader theory and imply the interaction type. For a negative value of a Laplacian, without a shadow of doubt the interaction is wholly covalent. If both $\nabla^2\rho$ and H_C be simultaneously positive mean that the interaction is non-covalent. If $\nabla^2\rho$ is positive while H_C is negative, and the $-G_C/V_C$ is smaller than 1, then the interaction nature is considered as partly covalent [32].

The topological parameters, like ρ_{BCP} , $\nabla^2\rho$, G_C , V_C , ($-G_C/V_C$) and H_C at the BCP of $N\cdots HO$, $O\cdots HN$, $N\cdots H\cdots O$ are represented in Table 3. The molecular graph of Lpnp is shown in Fig. 3. It appears from the molecular graph that there is a BCP between the H and N atoms, which are connected through two bond paths. The topological structure shows that the intramolecular hydrogen bond existed in the structure of schiff base molecule Lpnp.

Table 2

Bond lengths and intramolecular hydrogen bond's energies for all substituent groups.

	OH		NH		TS			
	$d(N\cdots HO)$ (nm)	$E(N\cdots HO)$ (kJ/mol)	$d(NH\cdots O)$ (nm)	$E(NH\cdots O)$ (kJ/mol)	$d(N\cdots H\cdots O)$ (nm)	$E(N\cdots H\cdots O)$ (kJ/mol)	$d(N\cdots H\cdots O)$ (nm)	$E(N\cdots H\cdots O)$ (kJ/mol)
H	1.708919	65.95698	1.758036	51.41588	1.247297	287.65296	1.236077	298.103
NO ₂	1.721081	63.25102	1.742687	53.88706	1.252963	278.34540	1.230407	304.6311
CN	1.718753	63.76388	1.74792	53.0148	1.248571	283.60123	1.234431	300.3158
CF ₃	1.732262	68.20127	1.781042	53.51524	1.277803	303.54374	1.231243	303.5437
CHO	1.716389	64.29117	1.752173	52.3065	1.247244	285.16211	1.235517	299.0002
COCH ₃	1.71214	65.26049	1.754949	51.87365	1.247547	284.75550	1.235453	298.9936
COOH	1.713972	64.85387	1.754505	51.93268	1.248991	282.99393	1.234122	300.3866
F	1.711158	65.49134	1.750287	52.69344	1.252129	279.2373	1.231454	303.3719
Cl	1.711334	65.43756	1.75049	52.64229	1.251616	279.90497	1.23216	302.6964
NH ₂	1.697578	68.77968	1.744267	53.88706	1.244878	287.99662	1.23895	295.6239
OH	1.703387	67.34734	1.748044	53.12367	1.248656	283.42940	1.234797	299.9432
CH ₂ CH ₃	1.711157	65.61463	1.739995	55.32333	1.245386	287.27520	1.238252	295.9322
CH ₃	1.702918	67.38407	1.755034	51.94711	1.245654	286.91318	1.237542	296.6142

**Fig. 2.** Diagrams and relationship between the $O\cdots H$ and $N\cdots H$ bond length and the bond energy for reactant, product, and transition state at BCP.

From the data shown in Table 3 the following results can be drawn: for the BCP of the hydrogen bond, the $\nabla^2\rho$ is positive, but H_C is negative, and the ratio of G_C to V_C , $-G_C/V_C$, ranges between 0.5 and 1; therefore, all values of topological parameters imply that the intramolecular hydrogen bond, is rather covalent in nature [25,33,34].

From Table 3, it seems that due to a decrease in the ability of electron withdrawing substituent groups which are located at the Para-position, ρ_{BCP} at the BCP reduce. In electron donor substitution groups as electron donor ability decreases, the value of ρ_{BCP} increases. It is worth mentioning that an increase in electron donor strength makes hydrogen bond stronger than withdrawing structures.

As the absolute values of G_C , V_C , and H_C increased, the $-G_C/V_C$ value decreased, but it still remained between 0.5 and 1, suggesting that there is an increase in the covalent portion. From the given data in Table 3, it can be found that with reduction of electron donor ability, the covalent portion increased while with a decrease in the ability of electron withdrawing the covalent portion also decreased. It is noteworthy that the order of ρ depends on the intramolecular hydrogen bond energies. Fig. 4 indicates

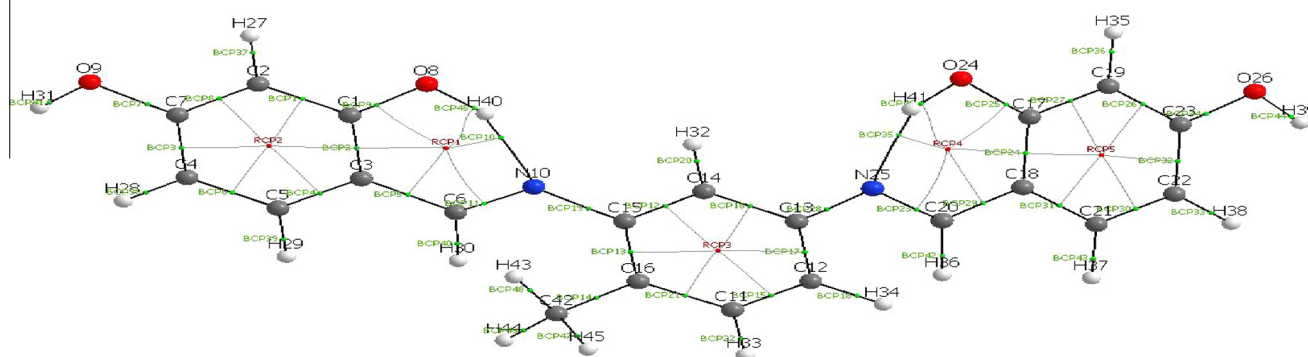
that there is a good linear relationship between ρ_{BCP} , H_C , $\nabla^2\rho$ with bond energy of the hydrogen bond; the larger value of ρ_{BCP} results in the stronger the hydrogen bond and the lower value of H_C at the BCP. Hence, in addition to the ρ_{BCP} , the H_C at the BCP can also be considered as strength criteria for intramolecular hydrogen bonds.

When we study the type of intramolecular hydrogen bond, it becomes clear that the hydrogen bond which exists between hydrogen and oxygen would have a larger covalent portion if H located at N. Therefore, it can be concluded that it is less likelihood to expose H on N and thus there is a greater tendency to form $N\cdots H$ hydrogen bond than that of $O\cdots H$. But, according to the obtained values of TS which shows a similar linear trend with correlation coefficients of ρ_{BCP} , H_C , $\nabla^2\rho$ equal 0.9988, 0.8521 and 0.8638, 0.8258 and 0.9996, 0.997, respectively, for $N\cdots H\cdots O$ and $N\cdots H\cdots O$. Furthermore, it can be observed that the values of ρ_{BCP} and H have a different trend and also the distance of $N\cdots H$ bond is less than that of $O\cdots H$ and also the values of ρ_{BCP} for $N\cdots H$ are greater than those of $O\cdots H$ bond. However, the energy barrier of N–H bond formation is high and thus the probability of N–H tautomeric is low.

Table 3

Topological properties at the BCP of the O···H and N···H bonds with several substitutes.

	OH							NH						
	BCP	ρ	$\nabla^2\rho$	G	V	H	$-G/V$	BCP	ρ	$\nabla^2\rho$	G	V	H	$-G/V$
H	37	0.0533	0.1111	0.0390	−0.0503	−0.0113	0.7761	39	0.0436	0.1358	0.0366	−0.0392	−0.0026	0.9329
NO ₂	35	0.0516	0.1117	0.0381	−0.0482	−0.0102	0.7895	42	0.0451	0.1382	0.0378	−0.0411	−0.0033	0.9206
CN	35	0.0519	0.1116	0.0383	−0.0486	−0.0104	0.7870	39	0.0445	0.1374	0.0374	−0.0404	−0.0030	0.9249
CF ₃	37	0.0546	0.1115	0.0399	−0.0520	−0.0121	0.7673	42	0.04483	0.1379	0.0376	−0.0408	−0.0032	0.9215
CHO	34	0.0523	0.1115	0.0384	−0.0490	−0.0106	0.7844	40	0.0441	0.1368	0.0370	−0.0399	−0.0028	0.9287
COCH ₃	34	0.0529	0.1114	0.0388	−0.0498	−0.0109	0.7799	37	0.0439	0.1362	0.0368	−0.0395	−0.0027	0.9305
COOH	35	0.0526	0.1115	0.0387	−0.0494	−0.0108	0.7819	39	0.0439	0.1363	0.0368	−0.0396	−0.0028	0.9303
F	36	0.0530	0.1112	0.0389	−0.0499	−0.0111	0.7785	38	0.0444	0.1369	0.0372	−0.0402	−0.0030	0.9260
Cl	35	0.0530	0.1113	0.0389	−0.0499	−0.0110	0.7789	37	0.0443	0.1369	0.0372	−0.0401	−0.0030	0.9265
NH ₂	35	0.0552	0.1106	0.0400	−0.0524	−0.0124	0.7636	42	0.0451	0.1382	0.0378	−0.0411	−0.0033	0.9206
OH	37	0.0542	0.1109	0.0395	−0.0513	−0.0118	0.7701	39	0.0446	0.1372	0.0374	−0.0405	−0.0031	0.9235
CH ₂ CH ₃	36	0.0532	0.1115	0.0389	−0.0500	−0.0112	0.7767	38	0.0459	0.1388	0.0384	−0.0422	−0.0037	0.9114
CH ₃	35	0.0542	0.1110	0.0396	−0.0514	−0.0118	0.7700	35	0.0439	0.1363	0.0368	−0.0396	−0.0028	0.9301
N···H···O														
H	3.2627	0.0544	0.1110	0.0396	−0.0515	−0.0119	0.7688	37.1364	0.0449	0.1375	0.0376	−0.0408	−0.0032	0.9213
NO ₂	3.2602	0.0546	0.1109	0.0397	−0.0517	−0.0120	0.7675	36.8881	0.0449	0.1376	0.0376	−0.0409	−0.0032	0.9206
CN	3.2578	0.0548	0.1109	0.0398	−0.0520	−0.0122	0.7662	36.6399	0.0450	0.1377	0.0377	−0.0410	−0.0033	0.9200
CF ₃	3.2524	0.1813	−0.3702	0.0694	−0.2314	−0.162	0.2999	41.9865	0.1562	0.1143	0.0921	−0.2128	−0.1207	0.4328
CHO	3.2553	0.0550	0.1109	0.0399	−0.0522	−0.0123	0.7648	36.3916	0.0451	0.1377	0.0377	−0.0411	−0.0033	0.9194
COCH ₃	3.2529	0.0552	0.1108	0.0400	−0.0524	−0.0124	0.7635	36.1434	0.0451	0.1378	0.0378	−0.0411	−0.0033	0.9188
COOH	3.2504	0.0554	0.1108	0.0401	−0.0527	−0.0125	0.7622	35.8951	0.0452	0.1379	0.0378	−0.0412	−0.0034	0.9182
F	3.2480	0.0556	0.1107	0.0402	−0.0529	−0.0126	0.7609	35.6469	0.0453	0.1380	0.0379	−0.0413	−0.0034	0.9176
Cl	3.2455	0.0558	0.1107	0.0403	−0.0531	−0.0128	0.7597	35.3986	0.0453	0.1380	0.0379	−0.0414	−0.0034	0.9169
NH ₂	3.2430	0.0560	0.1106	0.0405	−0.0533	−0.0129	0.7584	35.1503	0.0454	0.1381	0.0380	−0.0415	−0.0035	0.9163
OH	3.2406	0.0562	0.1106	0.0406	−0.0536	−0.0130	0.7571	34.9021	0.0455	0.1382	0.0380	−0.0415	−0.0035	0.9157
CH ₂ CH ₃	3.2381	0.0564	0.1106	0.0407	−0.0538	−0.0131	0.7559	34.6538	0.0455	0.1382	0.0381	−0.0416	−0.0035	0.9151
CH ₃	3.2357	0.0565	0.1105	0.0408	−0.0540	−0.0133	0.7546	34.4056	0.0456	0.1383	0.0381	−0.0417	−0.0036	0.9145

3,3'-dihydroxy-4,4'-[5-methyl-1,3-phenylenebis(nitrilomethyldiyne)]-bis-phenol : (L(CH₃)pnp)**Fig. 3.** The QTAIM molecular graph of (L(CH₃)pnp) (small red spheres, small green squares, and lines represent RCP, BCP, and bond paths, respectively). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

AIM analysis on the RCP

The RCP is a point of minimum electron density within the ring surface and a maximum on the ring line [35,36]. Table 3 gives the information about electron density ρ_{RCP} at the RCP and $\nabla^2\rho_{RCP}$ of the ring (H—O—C=C—N), produced by the hydrogen bond formation. The distance between the RCP and also the BCP of the hydrogen bond are included in Table 4.

From Table 4, it is known that decrease in the electron withdrawing order makes the bond strength weaker meaning that means ρ_{RCP} decrease. Along with this effect, the distance of the RCP–BCP decreased and increase in the electron donor order obviously raised the bond strength. These observations are compatible with Bader's AIM theory. The achieved results are shown in Fig. 5.

When the various electron donating and withdrawing groups replace with each other in the interesting position, in the most cases $d_{RCP \rightarrow BCP}$ for N···H and O···H, respectively, changes to 0.03 nm and 0.06 nm.

They are not noticeable values but the values with a difference in the energy and topology values at BCP remain constant.

Based on the data given in Fig. 6, good linear relationships exist between each parameter as ρ_{RCP} , $\nabla^2\rho$, $d_{RCP \rightarrow BCP}$ with hydrogen bond energy; the correlation coefficients of N···H and O···H, respectively, equal 0.9584, 0.9039, 0.8876, 0.9990, 0.9552 and 0.8927.

The largest amount of ρ_{RCP} , $\nabla^2\rho$ and $d_{RCP \rightarrow BCP}$ is indication of the highest hydrogen bond strength.

It means that the RCP properties as ρ_{RCP} , $\nabla^2\rho_{RCP}$ can be properly used to predict the behavior and strength of intramolecular hydrogen bond.

Delocalization index (DI(O,H), DI(N,H))

Based on the DI definition in the study of Fradera et al. [37], the DI is an amount of the electron pairs number shared by two basins. Although their definition cannot be an evidence for this idea that

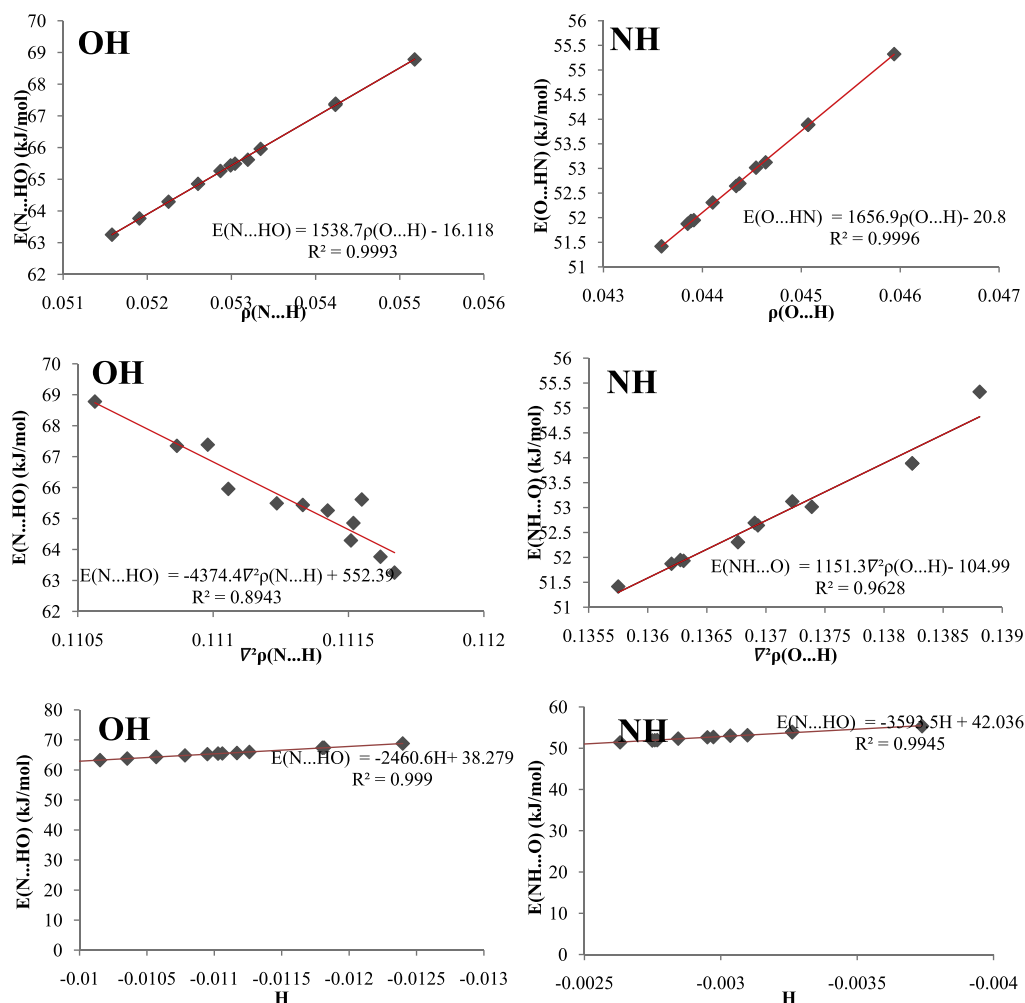


Fig. 4. Diagrams and relationship between the O...H and N...H topological properties at the BCP and the bond energy for reactant, product, and transition state.

Table 4

The topological properties at the RCP, the distance between RCP and BCP (ρ_{RCP} in atomic unit and $d_{RCP \rightarrow BCP}$ in nm).

	O—H					N—H			
	$d_{RCP \rightarrow BCP}$	ρ	$\nabla^2 \rho$	K		$d_{RCP \rightarrow BCP}$	ρ	$\nabla^2 \rho$	K
H	0.827702	0.018348	0.115748	−0.005127		0.821241	0.016911	0.108196	−0.004936
NO ₂	0.823894	0.018118	0.114212	−0.005094		0.825117	0.017061	0.109745	−0.005015
CN	0.82462	0.018164	0.114484	−0.005097		0.823715	0.017005	0.109181	−0.004988
CF ₃	0.830321	0.018451	0.116664	−0.005165		0.824303	0.017055	0.109569	−0.004999
CHO	0.825345	0.018205	0.114807	−0.005106		0.822726	0.016946	0.108696	−0.004968
COCH ₃	0.826565	0.018284	0.115347	−0.005118		0.821814	0.016925	0.108418	−0.004952
COOH	0.82462	0.018164	0.114484	−0.005097		0.823715	0.017005	0.109181	−0.004988
F	0.827095	0.018301	0.115428	−0.005119		0.823292	0.017014	0.109085	−0.004973
Cl	0.826918	0.018298	0.115409	−0.00512		0.823521	0.017006	0.109048	−0.004973
NH ₂	0.831126	0.01854	0.117092	−0.005151		0.824331	0.017113	0.109719	−0.004984
OH	0.829506	0.018435	0.11639	−0.005141		0.82372	0.017055	0.109351	−0.004977
CH ₂ CH ₃	0.827601	0.018325	0.115512	−0.005112		0.827739	0.017164	0.11147	−0.004983
CH ₃	0.829449	0.018449	0.11649	−0.005145		0.822312	0.016962	0.108593	−0.004948

delocalization index is a function for the bond order. Ánglyán et al. [12] has been found that it can explain about the covalent bond order.

The delocalization indexes between N...H and O...H, formed the intramolecular hydrogen bond are listed in Table 5.

With this information in hand, it can be seen that all the DI values were small implying that the covalent interactions between O—H and N—H were weak.

With considering donor and withdrawing groups, when the DI value increased, the covalent bonding made stronger.

In the one hand, along with the increase the electron withdrawing strength, there is a decrease in the DI value, meaning that covalent binding order reduced.

On the other hand, with reduction in electron donor strength and DI value reduced and also the covalent binding order decrease the obtained result are shown in Fig. 6.

There is also a good linear relationship between DI with the binding energies E , for which the linear correlation coefficients were 0.9872, 0.8859 and 0.9142, 0.8966, respectively, for O—H, N—H and N...H...O, N...H...O.

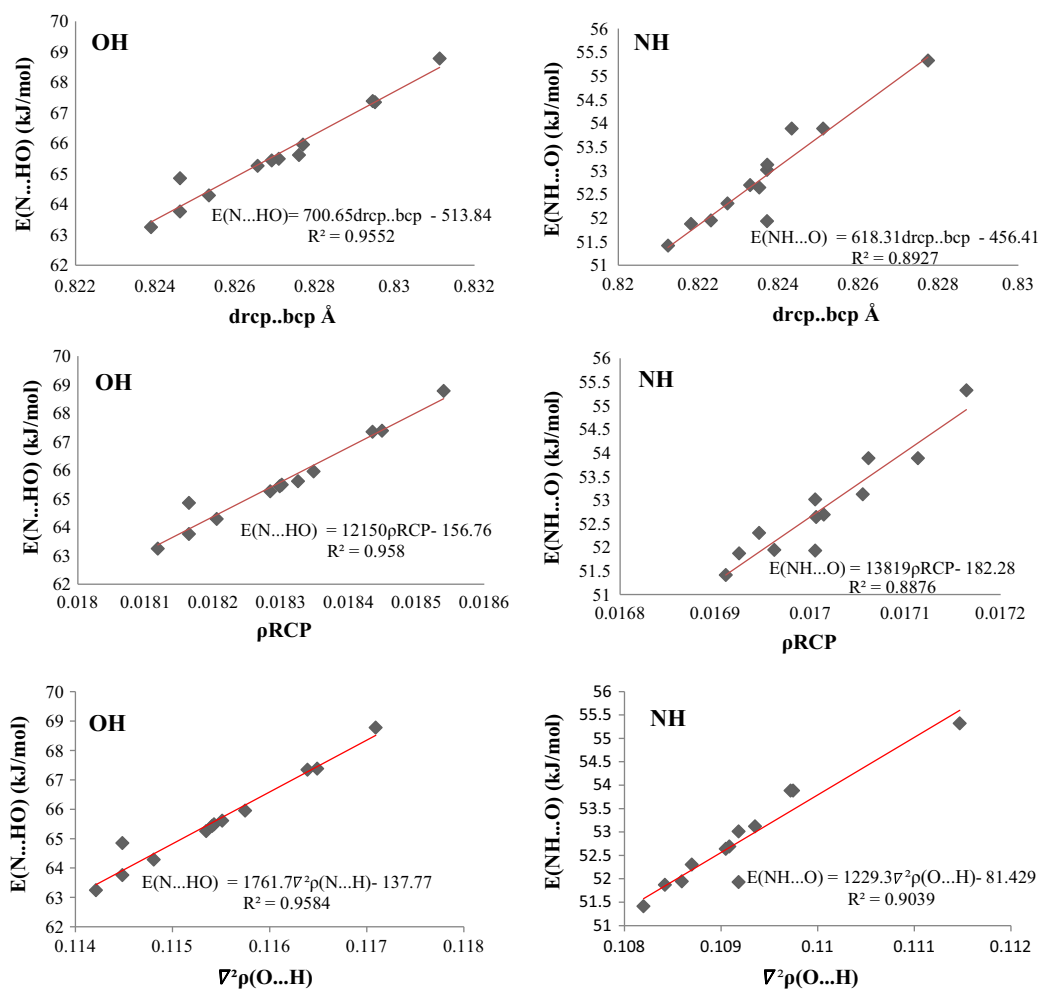


Fig. 5. Diagrams and relationship between the topological properties at the RCP and the bond energy.

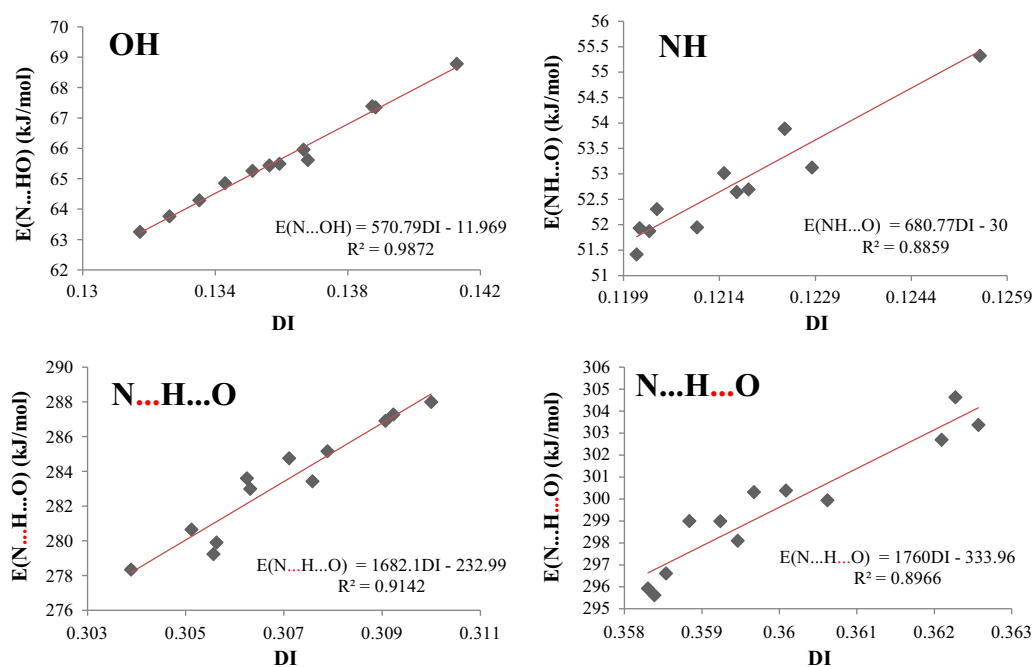


Fig. 6. Diagrams and relationship between the delocalization index and the bond energy for reactant, product.

Table 5
Charge transfer, delocalization index and integration of electron density over interatomic surface between O and H(DI(O,H)), N and H(DI(N,H)) of intramolecular hydrogen bond for reactant, product, and transition state.

	OH					NH			
	BCP	q(O,H)	DI(O,H)	$\delta(O,H)$		BCP	q(N,H)	DI(N,H)	$\delta(N,H)$
H	37	0.0854	0.1367	0.2685	39	0.1710	0.1201	0.2310	
NO ₂	35	0.0955	0.1317	0.2612	42	0.1595	0.1224	0.2352	
CN	35	0.0930	0.1326	0.2626	39	0.1622	0.1215	0.2336	
CF ₃	38	0.0943	0.1387	0.2724	41	0.1660	0.1223	0.2350	
CHO	34	0.0929	0.1335	0.2640	40	0.1606	0.1204	0.2320	
COCH ₃	34	0.0905	0.1351	0.2664	37	0.1647	0.1203	0.2313	
COOH	35	0.0915	0.1343	0.2654	39	0.1633	0.1202	0.2313	
F	36	0.0857	0.1359	0.2674	38	0.1729	0.1219	0.2339	
Cl	35	0.0871	0.1356	0.2670	37	0.1709	0.1217	0.2336	
NH ₂	35	0.0774	0.1413	0.2759	42	0.1595	0.1224	0.2371	
OH	37	0.0820	0.1388	0.2721	39	0.1791	0.1228	0.2352	
CH ₂ CH ₃	36	0.0822	0.1368	0.2684	38	0.2067	0.1255	0.2408	
CH ₃	35	0.0838	0.1387	0.2719	35	0.1754	0.1210	0.2325	
N...H...O									
H	35.5606	0.0802	0.1394	0.2728	37.1364	0.1845	0.1231	0.2365	
NO ₂	35.5956	0.0792	0.1400	0.2736	36.8881	0.1866	0.1233	0.2369	
CN	35.6305	0.0781	0.1405	0.2744	36.6399	0.1888	0.1236	0.2373	
CF ₃	35.2504	0.3583	0.3048	0.5108	41.9865	0.2105	0.3622	0.5764	
CHO	35.6655	0.0770	0.1410	0.2752	36.3916	0.1909	0.1238	0.2377	
COCH ₃	35.7005	0.0759	0.1416	0.2760	36.1434	0.1931	0.1240	0.2381	
COOH	35.7354	0.0749	0.1421	0.2769	35.8951	0.1952	0.1242	0.2385	
F	35.7704	0.0738	0.1427	0.2777	35.6469	0.1974	0.1244	0.2389	
Cl	35.8054	0.0727	0.1432	0.2785	35.3986	0.1995	0.1247	0.2393	
NH ₂	35.8403	0.0716	0.1437	0.2793	35.1503	0.2017	0.1249	0.2397	
OH	35.8753	0.0706	0.1443	0.2801	34.9021	0.2038	0.1251	0.2400	
CH ₂ CH ₃	35.9103	0.0695	0.1448	0.2809	34.6538	0.2060	0.1253	0.2404	
CH ₃	35.9452	0.0684	0.1454	0.2817	34.4056	0.2081	0.1256	0.2408	

Integrated properties of interatomic surface ($\delta(O,H)$, $\delta(N,H)$)

The integrated electron density over the interatomic surface gives valuable bonding information for the interacting atoms [38,39]. The electron density integrations over the inter-atomic surfaces of N, O with H in the schiff base molecule Lpnp was carried out and are reported in Table 5.

These values indicate that the increase in the electron withdrawing ability leads to the reduction of intramolecular hydrogen bond strength. Furthermore, the decrease of electron donor ability causes an increase in intramolecular hydrogen bond strength. These observations were almost the same as those of $\delta(O,H)$ in the electron withdrawing part, though for electron donor groups, reduction of the electron donor order makes the intramolecular hydrogen bond stronger.

A good linear relationship exists between $\delta(O,H)$, $\delta(N,H)$ with binding energy E , which are 0.943 and 0.9953, respectively. It has a same trend as ρ at BCP.

It means that the electron density integrations over the inter-atomic surface can be considered as a good criterion for determination of hydrogen bond strength.

Conclusion

The substituent effects on the intramolecular hydrogen bond in 3,3'-dihydroxy-4,4'-[5-methyl-1,3-phenylenebis(nitrilomethylidyne)]-bis-phenol were discussed. The analyses carried out in this work hint that the intramolecular hydrogen bond in the substituted-3,3'-dihydroxy-4,4'-[5-methyl-1,3-phenylenebis(nitrilomethylidyne)]-bis-phenol is partly covalent in nature; the para-position substituent electron-donating substituent increased the covalent nature of the intramolecular hydrogen bond, whereas the electron-withdrawing substituents dwindle it. Another result that can indicate is the topological properties, including

delocalization index and integrated properties of interatomic surface, which are useful tools for determination of hydrogen bond strength.

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