*J. Phys. Chem. A* **2008,** *112,* 3119−3126

# AIM Analysis of Intramolecular Hydrogen Bonding in *O*-Hydroxy Aryl Schiff Bases

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*Received: August 4, 2007; In Final Form: January 12, 2008*

AIM analysis was applied to study the changes in such topological parameters as the electron density at critical points of all the bonds of the molecule during the so-called nonadiabatic proton transfer in intramolecular hydrogen bonding in *o*-hydroxy aryl Schiff bases. Proton transfer is presented by a stepwise elongation and fixing of the hydroxyl bond with complete optimization of the rest of the parameters of the molecule by the B3LYP/6-311++G(d,p) method. A more detailed study of electron density changes at the critical points of the chelate and phenol rings in the stepwise proton-transfer process is presented. It was shown that the dependency of the electron density at the critical point of the chelate ring on tautomeric equilibrium is of a complicated character, whereas it is linear for the phenol ring. A complex study of the changes in the total electron density at the hydrogen bond, the quasi-aromatic ring, and in the whole molecule has been accomlished. The calculations of the intramolecular hydrogen bond by means of conformational and topological methods are discussed.

## 1. Introduction

This paper presents research on some important problems in the field of hydrogen bonding. The first problem covers the interrelations of the topological and structural parameters during proton transfer in the intramolecular hydrogen bridge. These dependencies have readily been analyzed in the literature,[1−8] which reveals the special interest in topological studies in the exploration of hydrogen bonding (see reviews in refs 9 and 10). The elaborations of the topological parameters of hydrogen bonding and the interpretation of strong hydrogen bonds as partly covalent in nature with the application of the AIM (atoms in molecules) theory[11] are important.[3] Using Bader's AIM theory, Koch and Popelier[12] developed some criteria to characterize weak interactions like hydrogen bonding. The criteria were tested on the basis of experimental data obtained for a proton sponge and its complexes in a paper by Mallison and Wozniak.[5] The second problem involves the interrelations of chelate and aromatic rings in tautomeric equilibrium.[13] The third matter to explore is research using quantum-mechanical calculations to estimate hydrogen bond energy. This problem is considered and studied in a series of papers published in *The Journal of Physical Chemistry*,[14] with the following calculational methods: cis/trans analysis; isodesmic/homodesmic reactions; local potential energy density; conformational analysis; ortho-para approach; molecular tailoring approach. This seems to be a real challenge and is therefore widely discussed nowadays.[15] To verify the local potential energy density method, we chose a conformational analysis and an empirical formula featured by Musin and Mariam.[15]

The proton-transfer process (a constituent of the second and third problems) as well as tautomeric equilibrium, both of which actively participate in biological processes, are the last tasks to fulfil.[17] It is noteworthy that tautomeric forms in physical chemistry are referred to as superposition of resonance structure.[18] The necessity to use some kind of tautomeric structure as a sum of canonical structures for *o*-hydroxy aryl Schiff bases is firmly approved in the literature[19] (Figure 1). According to experimental[20] and theoretical[21] studies, the CO and C2Cα bonds decrease while the C1C2 and CN bonds (numbering is presented in Figure 1) lengthen during proton transfer, the phenomenon being described by tautomeric terminology as alteration from the enol-imine (OH, or molecular) form into the keto-amine (HN, or proton transfer) form (Figure 2).

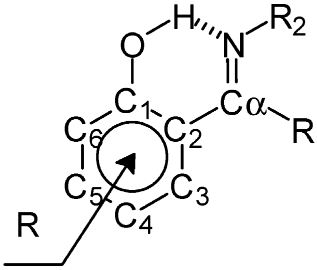

**Figure 1.** Diagram of *o*-hydroxy aryl Schiff base: 2-[(1*E*)-N-methylethanimidoyl)]phenol ($R_1 = R_2 = CH_3$), [(1*E*)-ethanimidoyl)]-phenol ($R_1 = CH_3$, $R_2 = H$), 2-[(*E*)-(methylimino)methyl]phenol ($R_1 = H$, $R_2 = CH_3$) and 2-[(*E*)-iminomethyl]phenol ($R_1 = R_2 = H$).

For our studies we chose *o*-hydroxy aryl Schiff bases (Figure 1), where the intramolecular proton-transfer process has been observed and carefully studied in both the ground state and the excited-state by a number of research groups.[22,23] *O*-Hydroxy aryl Schiff bases present an interesting object of study due to their wide potential application as liquid crystals,[24] nonlinear-optical materials,[25] anticorrosive materials,[26] and anticancer medicines.[27] *O*-Hydroxy aryl Schiff bases contain quasiaromatic hydrogen-bonding widely discussed in the literature.[3−5,10,13,21,23,28,29] The advantage of these compounds is their rather efficient change of acid−base equlibrium by substitution in the phenol moiety,[30] the nitrogen atom as well as the carbon atom of the imine fragment.[31] The options of substitutes, and particularly the steric effect of a bulky substitute, can bring about shortening of the hydrogen bridge up to extra-short ones.[32] Research on extra-short hydrogen bridges along with the low-energy barrier for proton transfer is of great importance in understanding biological processes.[33]

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10.1021/jp076253x CCC: $40.75

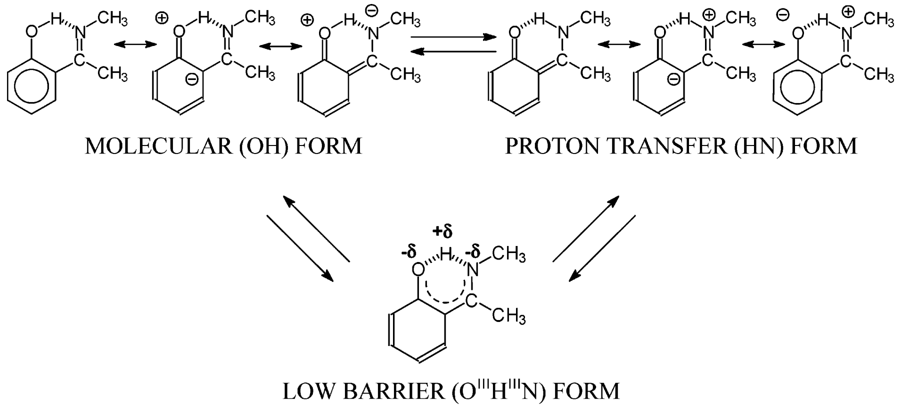

**Figure 2.** Scheme of tautomeric equilibrium in *o*-hydroxy aryl Schiff bases.

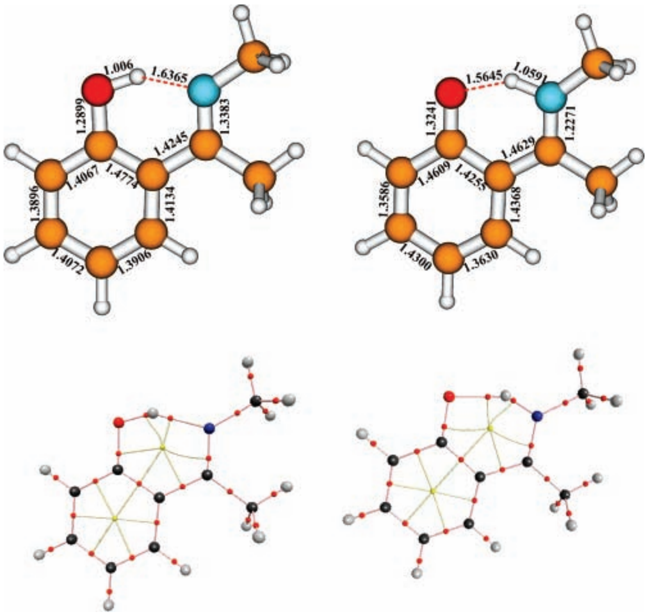

**Figure 3.** Molecular graphs of the 2-[(1*E*)-*N*-methylethanimidoyl)]-phenol, the corresponding molecular and proton transfer forms; large circles correspond to attractors attributed to nuclei and small circles correspond to the bond and ring critical points.

The above problems are acute objects of study in the field of hydrogen bonding and the aim of this paper is to present the interrelations between these phenomena.

## 2. Computational Details

The calculations were performed with Gaussian 03[34] sets of code using the 6-311++G(d,p) basis set[35] at the hybrid Hartree−Fock density functional (B3LYP).[36] The use of diffuse functions is the proper approach for studies of hydrogen bonding.[37] The one-dimensional approach was employed in performing the calculations at selected points along the proton-transfer reaction path. The approach is based on stepwise elongation of the hydroxyl bond length with full optimization of the remaining structural parameters (the so-called nonadiabatic approximation). This approach reflects the proton-transfer process in the intramolecular hydrogen bridge.

AIM analysis was performed using the AIM2000 program[38] with all the default options.

Figure 3 shows the bond paths, bond critical points, and ring critical points of *o*-hydroxy aryl Schiff base.

## 3. Results and Discussion

**3.1. Topological Analysis.** The aim of this paper is to describe more precisely the general picture of the impact of the proton-transfer process (the change in tautomeric equilibrium) in *o*-hydroxy aryl Schiff bases on the electron densities of the molecule's fragments as well as on their interrelations. To do this properly, we obtained the dependency of the electron density at the critical point on the bond length ($\rho_{BCP} = f(d(BL))$). A few examples of the functional relationships for the chosen bonds are given in Figure 4. The correlations reveal that shortening of the bond conditions the electron density increase at the critical point and vice versa. It is noteworthy that the correlations are linear for CC, CO, and CN bonds. Distinct exceptions are those for the hydroxyl (OH) and amine (HN) bonds, which are exponential (Figure 4). A pioneering example of an exponential type of correlation for bonds directly engaged in hydrogen bonding is presented in papers by Espinosa et al.[2] Generalization and elaboration of the dependencies on the basis of the experimental and calculated data were completed in refs 3 and 5. For a further and deeper study of hydrogen-bonding we obtained additional topological dependencies. The dependency between the electron density at the critical point of the phenol ring ($\rho_{RCP}$(ph)) and the length of the hydroxyl bond is approximately linear within the range from the OH form to the HN form (Figure 5a). It is linear in the range from the OH form (black square) to the HN form (black triangle) and undergoes no extremes in the proton-transfer process. It is obvious that this dependency describes the tautomeric equilibrium change only incompletely in view of the overlapping of the two fragments of this curve: OH form → TS transition state and TS transition state → HN form.

The dependency between the electron density at the critical point of the chelate ring ($\rho_{RCP}$(ch)) and the length of the hydroxyl bond ($\rho_{RCP}(ch) = f(d(OH))$) (Figure 5b) and the HN bond (Figure 5c) are more efficient and provide more essential information about the tautomeric equilibrium (the LBHB form in particular). A bell-shaped curve can be cut into three fragments. The first fragment, in the 0.9−1.25 Å range, refers to the prevailing molecular form; the second, in the 1.25−1.35 Å range, refers to the maximum values of electron density at the critical point of the chelate ring and describes a form with a low-energy barrier (the LBHB form), and the third fragment, in the 1.35−1.8 Å range, refers to the prevailing PT form. The identification of the ranges (the transition state in that number) based on calculation of the potential energy curve is reported in ref 39.

Another interesting phenomenon emerges: the reversed picture is observed for the dependencies of hydrogen bridge length on the electron density at the critical point of the phenol ring ($d(ON) = f(\rho_{RCP}(ph))$) and the chelate ring ($d(ON) = f(\rho_{RCP}(ch))$) (Figure 6a,b). The parabolic curve of the $d(ON) = f(\rho_{RCP}(ph))$ dependency (Figure 6a) can be subdivided into the three

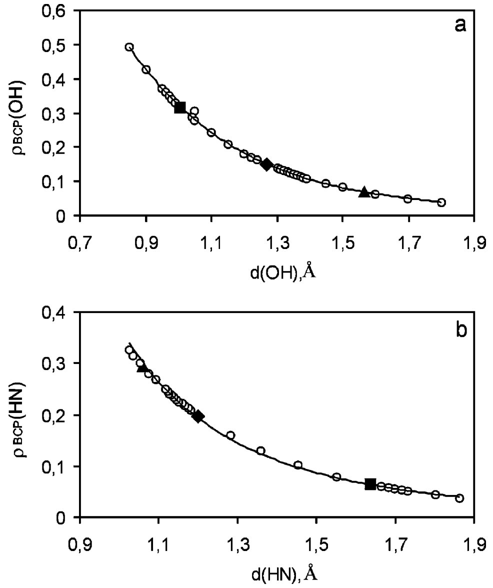

**Figure 4.** Correlations between the electron density at (a) the OH bond critical point ($\rho_{BCP}$(O−H), a.u.) and OH bond length ($d$(OH), Å), (($\rho_{BCP}$(OH) = $0.2018d^4$(OH) − $1.6104d^3$(OH) + $4.8361d^2$(OH) − $6.5648d$(OH) + 3.4607, $R^2 = 0.9988$), (b) the HN bond critical point ($\rho_{BCP}$(HN), a.u.) and HN bond length ($d$(HN), Å), ($\rho_{BCP}$(HN) = $0.3714d^{-3.582}$(HN), $R^2 = 0.9987$). Black points mean: ■ − OH form, ♦ − TS and ▲ − HN form. The graphs of the linear correlations between the electron density at the CC, CN, and CO bond critical point ($\rho_{BCP}$(CC), a.u.) and CC, CN and CO bond length ($d$(CC), Å) are not presented: $\rho_{BCP}$(CN) = $-0.8424d$(CN) + 1.4564, $R^2 = 0.9999$; $\rho_{BCP}$(CO) = $-0.801d$(CO) + 1.3784, $R^2 = 0.998$); $\rho_{BCP}$(C2Cα) = $-0.4647d$(C2Cα) + 0.9548, $R^2 = 0.9976$; $\rho_{BCP}$(C1C2) = $-0.4837d$(C1C2) + 0.9841, $R^2 = 0.9970$; $\rho_{BCP}$(C1C6) = $-0.4655d$(C1C6) + 0.9605, $R^2 = 0.9595$; $\rho_{BCP}$(C2C3) = $-0.5361d$(C2C3) + 1.0543, $R^2 = 0.9455$; $\rho_{BCP}$(C3C4) = $-0.5214d$(C3C4) + 1.0356, $R^2 = 0.9344$; $\rho_{BCP}$(C4C5) = $-0.5264d$(C4C5) + 1.0422, $R^2 = 0.9689$; $\rho_{BCP}$(C5C6) = $-0.5896d$(C5C6) + 1.1293, $R^2 = 0.9575$.

ranges mentioned above, this facilitates the description of the tautomeric equilibrium. However, $d$(ON) = $f$($\rho_{RCP}$(ch)) appears to be approximately linear and does not differentiate between molecular and proton transfer forms. It is interesting that the maximum value of the electron density at the critical points of the chelate ring is obtained for the shortest hydrogen bridge (the transition state, TS, marked with a black rhombus in the figures).

Of importance is the fact that the correlations between the hydrogen bridge length and the electron density at the critical point of every bond are of parabolic shape (figures are not shown). The exception is the $d$(ON) = $f$($\rho_{BCP}$(OH)) correlation, which is an example of Morse function (Figure 6c).

The linear dependencies between the electron density at the critical point of the chelate ring and both the electron density at the OH bond critical point ($\rho_{RCP}$(ch) = $f$($\rho_{BCP}$(OH))) and OH bond length ($\rho_{RCP}$(ch) = $f$($d$(OH))) for $o$-hydroxybenzaldehyde and its fluoro derivatives are presented in ref 3f as well as in the scatterplot of $\rho_{BCP}$(ON) = $f$($\rho_{RCP}$(ph)) for the enaminone derivatives.[3c] However, the dependencies between the electron density at the critical point of the chelate ring and the OH and HN bond lengths obtained and described in this paper take an a bell-shaped form (Figure 5b,c). Moreover, a linear dependency is not observed for the $\rho_{RCP}$(ch) = $f$($\rho_{BCP}$(OH)) and $\rho_{RCP}$(ch) = $f$($\rho_{BCP}$(HN)) correlations (Figure 7), which in turn are a reversed Morse function and a parabola, respectively. It is noticeable that Grabowski and Malecka[3i] recently succeeded in obtaining a more complete $\rho_{RCP}$(ch) = $f$($\rho_{BCP}$(H···Y)) scatterplot for 3(aminomethylene)pyran-2,4-dione derivatives which is in full agreement with our results. One should point out that the unequal influences of the oxygen and nitrogen atoms on proton movement in the quasi-aromatic formation result in different shapes of $\rho_{RCP}$(ch) = $f$($\rho_{BCP}$(OH)) (Morse curve) and $\rho_{RCP}$(ch) = $f$($\rho_{BCP}$(HN)) (parabolic curve; Figure 7), and, consequently, the difference in these dependencies demonstrates the heterogeneity of the hydrogen bonding. Note that $\rho_{RCP}$(ph) = $f$($\rho_{BCP}$(OH)) and $\rho_{RCP}$(ph) = $f$($\rho_{BCP}$(HN)) are described by $\rho_{RCP}$(ph) = $0.0216(\rho_{BCP}(\mathrm{OH}))^{0.0291}$ and $\rho_{RCP}$(ph) = $-0.0042\rho_{BCP}$(HN) + 0.0212 (figures are not shown) and they do not have extremes in the transition state range.

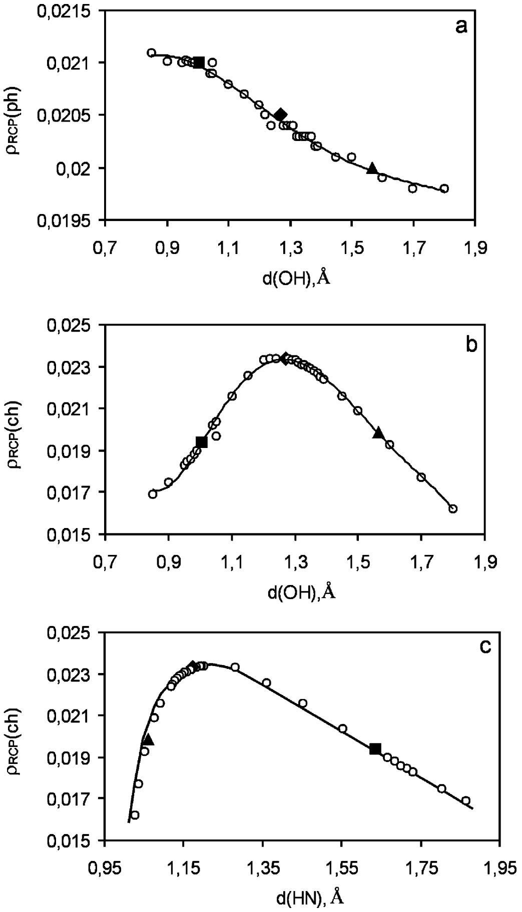

**Figure 5.** Correlations between electron density at the phenol and chelate rings critical points ($\rho_{RCP}$(ph) and $\rho_{RCP}$(ch), a.u.) and OH bond length ($d$(OH), Å): (a) $\rho_{RCP}$(ph) = $-0.0047d^4$(OH) + $0.0274d^3$(OH) − $0.0582d^2$(OH) + $0.0515d$(OH) + 0.005; $R^2 = 0.9897$, (b) $\rho_{RCP}$(ch) = $-0.2261d^5$(OH) + $1.5964d^4$(OH) − $4.4147d^3$(OH) + $5.941d^2$(OH) − $3.8685d$(OH) + 0.9912; $R^2 = 0.9947$, and (c) $\rho_{RCP}$(ch) = $-0.1984d^4$(HN) + $1.228d^3$(HN) − $2.8287d^2$(HN) + $2.862d$(HN) − 1.0479; $R^2 = 0.9832$. Black points mean: ■ − OH form, ♦ − TS and ▲ − HN form.

The linear dependency $d$(ON) = $f$($\rho_{RCP}$(ch)) shows that strengthening of the hydrogen bond (hydrogen bridge length reduction[40]) evokes an increase in the electron density at the critical point of the chelate ring; therefore, this parameter can be applied as a descriptor of the hydrogen-bonding strength. A similar conclusion was drawn in ref 3f on the grounds of the linear dependence of the hydrogen-bonding energy, calculated as the difference of two conformers, from the electron density at the critical point of the chelate ring.

Making use of the HOMA and HOSE aromaticity indices,[41] ref 13c reports the interrelations between the phenol and chelate rings during the proton-transfer process in the intramolecular

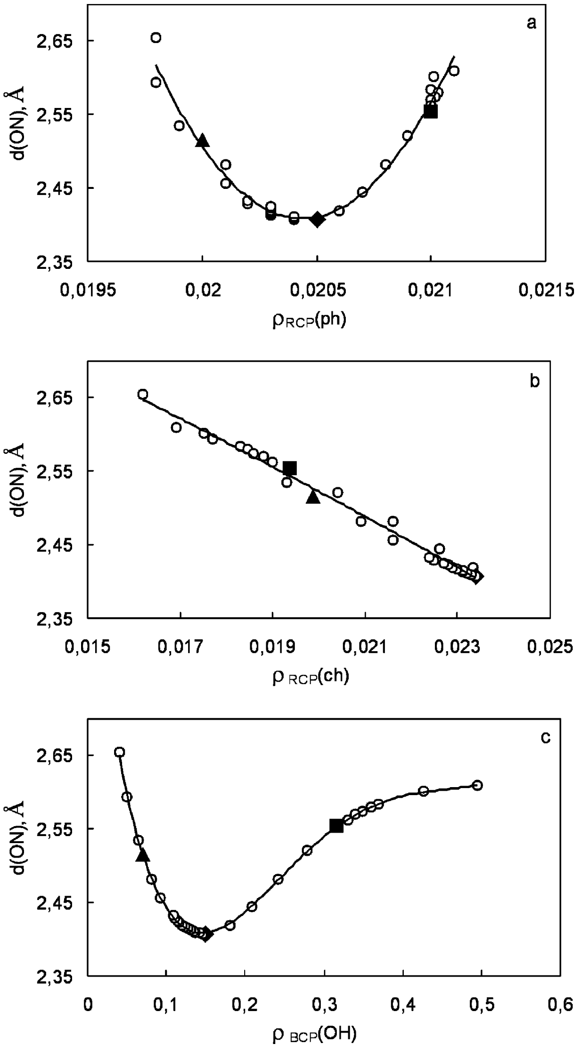

**Figure 6.** Correlations between hydrogen bond length (d(ON), Å) and electron density at the phenol and chelate rings ($\rho_{RCP}$(ph) and $\rho_{RCP}$(ch), a.u.), and the OH bond critical points ($\rho_{BCP}$(OH), a.u.): (a) $d$(ON) = $509546\rho_{RCP}{}^2$(ph) − $20830\rho_{RCP}$(ph) + 215.29; $R^2 = 0.975$, (b) $d$(ON) = $-34.029\rho_{RCP}$(ch) + 3.2029; $R^2 = 0.9892$, and (c) $d$(ON) = $-64.944\rho_{BCP}{}^5$(OH) + $164.88\rho_{BCP}{}^4$(OH) − $148.31\rho_{BCP}{}^3$(OH) + $58.979\rho_{BCP}{}^2$(OH) − $9.636\rho_{BCP}$(OH) + 2.494; $R^2 = 0.9995$. Black points mean: ■ − OH form, ♦ − TS and ▲ − HN form.

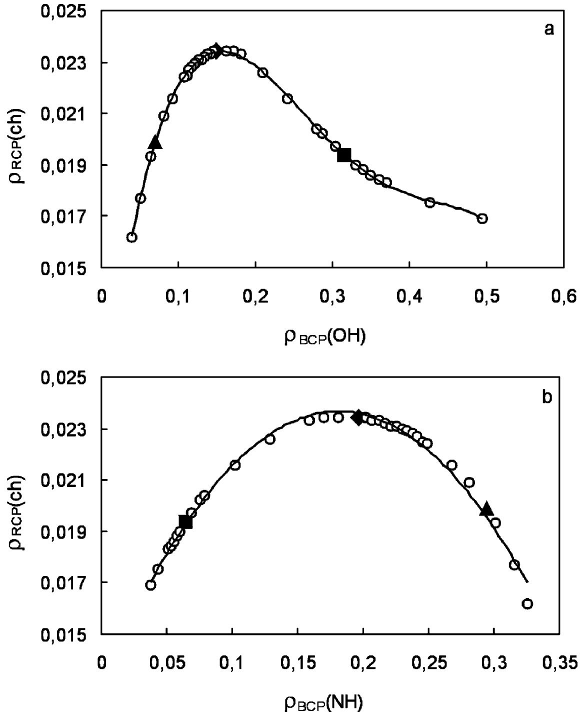

**Figure 7.** Correlation between the electron density at the chelate ring critical point ($\rho_{RCP}$(ch), a.u.) and the electron density at (a) the OH bond critical point ($\rho_{BCP}$(OH), a.u.) and b) the HN bond critical point ($\rho_{BCP}$(HN), a.u.): (a) $\rho_{RCP}$(ch) = $-0.822\rho_{BCP}{}^5$(OH) − $0.8012\rho_{BCP}{}^4$(OH) + $2.1393\rho_{BCP}{}^3$(OH) − $1.199\rho_{BCP}{}^2$(OH) + $0.2323\rho_{BCP}$(OH) + 0.0088; $R^2 = 0.9996$ and (b) $\rho_{RCP}$(ch) = $-0.3213\rho_{BCP}{}^2$(HN) + $0.1165\rho_{BCP}$(HN) + 0.0131; $R^2 = 0.9908$. Black points mean: ■ − OH form, ♦ − TS and ▲ − HN form.

hydrogen bridge. The development of AIM theory in the description of the critical points of the ring[42] makes it possible to work out the interrelations between the aromatic and chelate moieties by means of topological analysis. To this end, two dependencies $\rho_{RCP}(\mathrm{ch}) = f(\rho_{RCP}(\mathrm{ph}))$ and $\Sigma\rho(\mathrm{ch}) = f(\Sigma\rho(\mathrm{ph}))$, are presented in Figure 8a,b. The first shows the electron density at the critical point of the chelate ring as a function of the electron density at the critical point of the phenol ring.[38] This dependency is a parabolic curve showing an increase up to the transition state point with a subsequent decrease in the electron density at the critical point of the chelate ring with a steady increase in the electron density of the phenol ring during the proton-transfer process (Figure 8a); the dependency is very much like those described above (cf. Figures 6a and 7b). The second is the correlation between the sum of all the electron densities at the critical points of the chelate ring bonds plus the electron density at the critical point of the chelate ring ($\rho(\Sigma\mathrm{ch}) = \rho_{BCP}(\mathrm{OH}) + \rho_{BCP}(\mathrm{CO}) + \rho_{BCP}(\mathrm{C1C2}) + \rho_{BCP}(\mathrm{C2C\alpha}) + \rho_{BCP}(\mathrm{CN}) + \rho_{BCP}(\mathrm{HN}) + \rho_{RCP}(\mathrm{ch})$) and the sum of all electron densities at the critical point of the phenol ring ($\rho(\Sigma\mathrm{ph}) = \rho_{BCP}(\mathrm{C1C2}) + \rho_{BCP}(\mathrm{C2C3}) + \rho_{BCP}(\mathrm{C3C4}) + \rho_{BCP}(\mathrm{C5C6}) + \rho_{BCP}(\mathrm{C6C1}) + \rho_{RCP}(\mathrm{ch})$) for every point along the reaction path. This dependence is a Morse function of complicated character (Figure 8b). The complexity is that the first stage of the proton-transfer process brings about a decrease in the sum of the electron densities at the chelate and phenol moieties, reaching its extreme at structural parameters of the hydrogen bridge $d(\mathrm{OH}) \approx 1.12$ Å and $d(\mathrm{ON}) \approx 2.46$ Å, which are not the transition state parameters. This represent a significant difference from the above relationships for which the transition state is a turning point. The next stage of the proton-transfer process leads to an increase in the sum of electron densities at the critical points of the chelate ring with a subsequent decrease in the sum of the electron densities at the critical points of the phenol ring. It is remarkable that these trends are generally connected with the nonlinearity of the changes at the electron density of the critical points of the OH and HN bonds. One should also note that no extreme is observed at the transition state.

The dependency of the hydrogen bridge length on the sum of the electron densities in the chelate ring ($d(\mathrm{ON}) = \mathrm{f}(\Sigma\rho(\mathrm{ch}))$) presents a gamma-shaped curve (Figure 9). The dependency to report is of a new type in the study of hydrogen bonding. The right part of the curve (decreasing) corresponds to the process of tautomeric equilibrium change from the molecular form to the LBHB form and the left part (ascending, in accordance with the arrow) from the LBHB form to the PT form. A dependency $d(\mathrm{ON}) = f(\Sigma\rho)$, where $\Sigma\rho$ is the sum of all the electron densities at the critical points of the CC, CN, CO, OH, and HN bonds, looks in the similar way. It is noted that (1) the analyzed type of dependency reveal the complicated nature of the change in the sum of electron densities at the

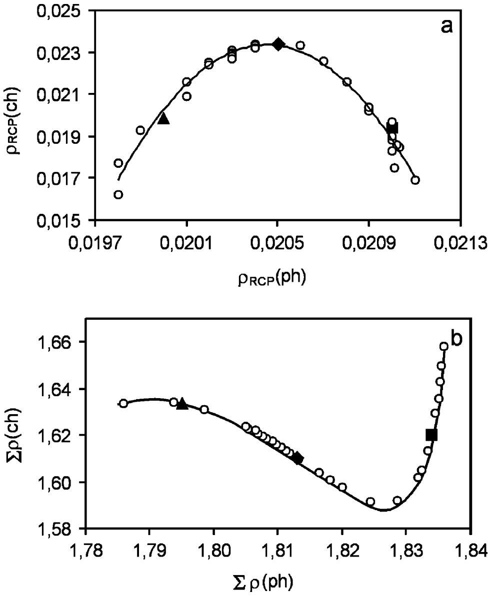

**Figure 8.** Correlations between (a) the electron density at the chelate ring critical point ($\rho_{\mathrm{RCP}}$(ch), a.u.) and the electron density at the phenol ring critical point ($\rho_{\mathrm{RCP}}$(ch), a.u.) and (b) the sum of the electron densities at the chelate ring critical point ($\rho_{\mathrm{RCP}}(\mathrm{ch}) + \rho_{\mathrm{BCP}}(\mathrm{OH}) + \rho_{\mathrm{BCP}}(\mathrm{HN}) + \rho_{\mathrm{BCP}}(\mathrm{CO}) + \rho_{\mathrm{BCP}}(\mathrm{CN}) + \rho_{\mathrm{BCP}}(\mathrm{C1C2}) + \rho_{\mathrm{BCP}}(\mathrm{C2C\alpha})$) and the sum of the electron densities at the phenol ring critical point ($\rho_{\mathrm{RCP}}(\mathrm{ph}) + \rho_{\mathrm{BCP}}(\mathrm{C1C2}) + \rho_{\mathrm{BCP}}(\mathrm{C2C3}) + \rho_{\mathrm{BCP}}(\mathrm{C3C4}) + \rho_{\mathrm{BCP}}(\mathrm{C4C5}) + \rho_{\mathrm{BCP}}(\mathrm{C5C6}) + \rho_{\mathrm{BCP}}(\mathrm{C6C1})$). (a) $\rho_{\mathrm{RCP}}(\mathrm{ch}) = -15092\rho_{\mathrm{RCP}}{}^{2}(\mathrm{ph}) + 617.34\rho_{\mathrm{RCP}}(\mathrm{ph}) - 6.2899$; $R^2 = 0.9719$ and (b) $\Sigma\rho(\mathrm{ch}) = 87165\Sigma\rho^4(\mathrm{ph}) - 62780000\Sigma\rho^3(\mathrm{ph}) + 0.006\Sigma\rho^2(\mathrm{ph}) + 0.6\Sigma\rho(\mathrm{ph}) + 916023$; $R^2 = 0.9415$. Black points mean: ■ − OH form, ♦ − TS and ▲ − HN form.

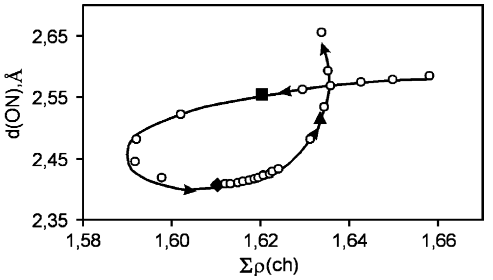

**Figure 9.** Correlations between the hydrogen bond length ($d$(NO), Å) and the sum of electron densities at the chelate ring critical point and the bond critical points in the chelate chain ($\rho_{\mathrm{RCP}}(\mathrm{ch}) + \Sigma\rho$(bond−bond in the chelate ring)). Black points mean: ■ − OH form, ♦ − TS and ▲ − HN form.

critical points of the molecules during the tautomeric equilibrium change, (2) the sum of the electron densities at the critical points of the molecule in the molecular state is slightly larger (3.4945 a.u.) than that in the proton transfer (3.4668 a.u.) and transition states (3.4684 a.u.), and (3) the most neutral state in terms of the topological conception turns out to be the transition state. These results picture a scheme for the changes in the topological situation of the $o$-hydroxy aryl Schiff bases during the proton-transfer process.

**3.2. Comparison of Intramolecular Hydrogen-Bonding Energies Obtained by Conformational and Topological Methods.** One of the main tasks in intramolecular hydrogen bond research has been estimation of its energy.[14,15,43] The basic method of calculation to estimate hydrogen bond energy is conformational analysis,[14,15,43,44] which rests upon estimating the non-hydrogen-bonded conformer with the least energy ($E_{\min}$(conformer without HB)). The energy difference between the two conformers is taken as the measure of intramolecular hydrogen bond ($E_{\mathrm{HB}} = E(\text{conformer with HB}) - E_{\min}(\text{conformer without HB})$).

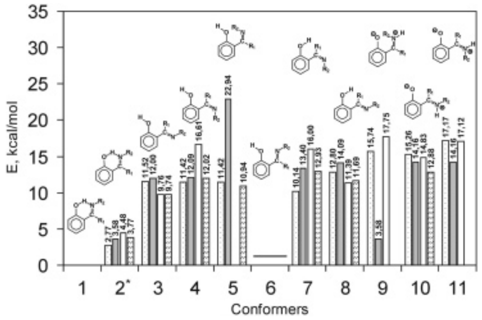

**Figure 10.** Scheme of the conformer energy obtained with B3LYP/6-311++G(d,p) for 2-[(1$E$)-$N$-methylethanimidoyl)]phenol (first columns: $R_1 = R_2 = CH_3$), [(1$E$)-ethanimidoyl)]phenol (second columns: $R_1 = CH_3$, $R_2 = H$), 2-[($E$)-(methylimino)methyl]phenol (third columns $R_1 = H$, $R_2 = CH_3$) and 2-[($E$)-iminomethyl]phenol (fourth columns; $R_1 = R_2 = H$). Structure 2 presents a tautomer.

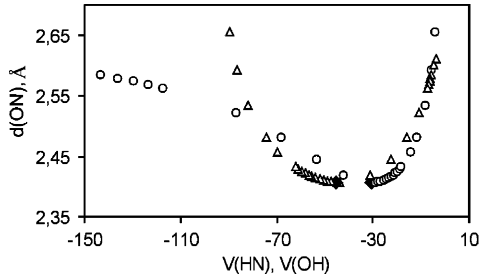

**Figure 11.** Correlations between the hydrogen bond length ($d$(ON), Å) and potential energy density $V(r_{\mathrm{CP}})$ for the OH bond ($d(\mathrm{ON}) = f(V(\mathrm{OH}))$ - triangle) and the HN bond ($d(\mathrm{ON}) = f(V(\mathrm{HN}))$ - circle). Black points mean the transition state.

However, estimating the hydrogen bond energy is a laborious task because of the need to detect all possible conformers and consider all local interrelations (steric and additional hydrogen bonds in that number). To this end, we calculated all possible conformers by the B3LYP/6-311++G(d,p) method and analyzed the relationships for selected $o$-hydroxy aryl Schiff bases (2-[(1$E$)-$N$-methylethanimidoyl)]phenol (I), [(1$E$)-ethanimidoyl)]phenol (II), (2-[($E$)-(methylimino)methyl]phenol (III), and 2-[($E$)-iminomethyl]phenol (IV)) (Figure 10). Conformers 4, 5, and 7 cannot be taken for estimating the hydrogen-bonding energy in view of the lack of steric repulsion of the methyl groups, this kind of repulsion being evident in conformer 1. As to IV, the energy of its conformer 5 is visibly reduced because of the formation of an H−O···H−N intramolecular hydrogen bond, and therefore, this conformer also cannot be used in estimating the energy of O−H···N hydrogen bonding. One should note that for obtaining the local energy minima, the B3LYP/6-311++G(d,p) method turned out to be irrelevant in the case of some conformers. For example, conformer 6 (obtained by the B3LYP/6-31G(d,p) method[39]), which is a basic conformer for obtaining the hydrogen-bonding energy in a series of molecules,[14,15,43−45] was not detected by the B3LYP/6-311++G(d,p) method. According to the aforementioned observations it is conformer 3 which is the most appropriate in estimating the hydrogen bond energy for the compounds. The data obtained by conformational analysis report that the energy of the hydrogen bonding decreases according to the sequence $E_2 > E_1 \gg E_3 \approx E_4$ (Table 1 and Figure 10).

**TABLE 1: Calculated Structural Parameters ($d$, Å), Electron Densities at BCP and RCP ($\rho$, a.u.), Energetic Topological Parameters ($H(r_{CP})$), Total Electron Energy Density at BCP, $G(r_{CP})$, Electron Kinetic Energy Density at BCP, $V(r_{CP})$, Electron Potential Energy Density at BCP, ($r_{CP}$ is OH or HN), Energy of Proton Transfer ($E_{PT} = E_2 - E_1$, kcal/mol), and Energy of Hydrogen Bond ($E_{HB}$, kcal/mol)**

| | $d$(OH) | $d$(HN) | $d$(ON) | $\rho$(OH) | $\rho$(HN) | $\rho$(ch) | $\rho$(ph) | $H$(OH) | $H$(HN) | $G$(OH) | $G$(HN) | $V$(OH) | $V$(HN) | $E_{HB}$[a] | $E_{HB}$[b] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Molecular (OH) Form | | | | | | | | | | | | | | | |
| I | 1.0060 | 1.6365 | 2.5540 | 0.3157 | 0.0645 | 0.01937 | 0.02100 | −93.45 | −2.81 | 15.03 | 5.26 | −108.48 | −8.08 | 11.52 | 14.95 |
| II | 1.0013 | 1.6565 | 2.5578 | 0.3202 | 0.0599 | 0.01880 | 0.02096 | −96.15 | −2.32 | 15.29 | 4.98 | −111.44 | −7.03 | 12.00 | 14.72 |
| III | 0.9944 | 1.7378 | 2.6316 | 0.3281 | 0.0498 | 0.01800 | 0.02070 | −99.30 | −1.46 | 15.43 | 4.15 | −114.73 | −5.62 | 9.76 | 10.86 |
| IV | 0.9941 | 1.7287 | 2.6174 | 0.3280 | 0.0499 | 0.01780 | 0.02103 | −99.78 | −1.45 | 15.52 | 4.22 | −115.30 | −5.67 | 9.74 | 11.52 |
| Proton Transfer (HN) Form | | | | | | | | | | | | | | | |
| I | 1.5645 | 1.0591 | 2.5153 | 0.0695 | 0.2943 | 0.01987 | 0.01988 | −2.79 | −67.52 | 6.57 | 11.85 | −9.36 | −79.38 | | 17.54 |
| II | 1.6405 | 1.0452 | 2.5300 | 0.0574 | 0.3032 | 0.01852 | 0.02000 | −1.57 | −71.37 | 5.49 | 11.65 | −7.06 | −83.02 | | 16.51 |
| III | 1.6966 | 1.0432 | 2.5782 | 0.0505 | 0.3084 | 0.01800 | 0.01995 | −1.08 | −72.05 | 4.79 | 11.87 | −5.87 | −83.92 | | 13.53 |
| IV | 1.7534 | 1.0336 | 2.5884 | 0.0439 | 0.3142 | 0.01710 | 0.01980 | −0.58 | −74.59 | 4.22 | 11.80 | −4.80 | −86.40 | | 12.98 |

[a] Calculated by the conformational method. [b] Calculated by the formula from ref 16.

The energy of intermolecular hydrogen bonding is estimated as the difference between the energies of the complex and its components, while the energy of intramolecular hydrogen bonding is defined as the difference between the energies of two conformers.[15] One of the most reliable approaches to estimating the energy of intramolecular hydrogen bonding by means of the conformational method is presented in ref 44. Unfortunately, such a scheme cannot be applied in our calculations because of the lack of conformer 6.

We also studied the dependencies of electron potential energy density ($V(r_{CP})$), electron kinetic energy density ($G(r_{CP})$) and total electron energy density ($H(r_{CP})$) on OH and HN bond lengths (Figure not shown) for the intramolecular hydrogen bridge in *o*-hydroxy aryl Schiff bases, which are quite similar to the intermolecular F•••H•••F hydrogen bonds presented in ref 2g. The values for the local electron density of energy V(H•••N), which is linearly related ($E = {}^{1}/_{2}V(\mathrm{BCP})$[2b]) to the energy of hydrogen bonding, show a $E_1 > E_2 > E_4 > E_3$ sequence. It is important that this series is confirmed by the sequence of $\rho_{BCP}$(HN) values for the compounds under study (Table 1). One knows that the electron density at the critical point of the H•••Y bond is linked to the hydrogen-bonding energy.[2]

A convincing confirmation of the topological results is the structural data, namely the hydrogen bridge length (cf. Table 1), which is an indisputable characteristic of the strength of hydrogen bonding.[40] Using these structural data one can obtain the values of the hydrogen-bonding energy by means of a formula ($-E_{HB} = (-5.554 \times 10^5)\exp(-4.12d(\mathrm{ON}))$, where $d$(ON) is the hydrogen bridge distance) presented by Musin and Mariam.[16] This sequence reveals a marked difference between *o*-hydroxy aryl ketimines (I and II) and *o*-hydroxy aryl aldimines (III and IV). The reason is the significant steric effect of the methyl group of the imine fragment, which reduces the hydrogen bridge to a considerable extent. This phenomenon was thoroughly described in a review paper.[23a] This effect is strongest for I owing to the presence of two methyl groups. As a consequence, I has the shortest hydrogen bridge, whereas III and IV hardly possess steric repulsion in their imine fragments, which greatly attenuate hydrogen bonding. The hydrogen bonding in IV is somewhat stronger due to the greater basicity of the nitrogen atom evoked by the essential polarization of the N−H bond. These considerations demonstrate the reliability of the topological method applied to obtaining data on hydrogen-bonding strength. However, the values of the hydrogen-bonding energy obtained by means of the equation $E = {}^{1}/_{2}V(\mathrm{BCP})$ are somewhat different from the real ones, this fact being stated earlier in a paper by Coppens.[46]

To define the energy of intermolecular hydrogen-bonding Espinosa et al.[2b] developed the equation $E = {}^{1}/_{2}V(\mathrm{BCP})$, which indicates that a V(BCP) increase leads to hydrogen bond strengthening. However, the obtained parabolic dependency $d(\mathrm{ON}) = f(V(\mathrm{HN}))$ features a consequent hydrogen bridge increase (a $d$(ON) decrease) up to the transition state and then its weakening ($d$(ON) lengthening) with $V$(HN) growth. The first part of the picture is consistent with the notion of Espinosa et al., while the second is not. This phenomenon shows the intramolecular hydrogen bond to be more complicated than the intermolecular one. This is corroborated by the dissociation which is the basis of the equation $E = {}^{1}/_{2}V(\mathrm{BCP})$ for the intermolecular hydrogen bond: X−H bond lengthening brings about a hydrogen bond break and the formation of an ion pair, while in the case of the intramolecular hydrogen bond it provokes the formation of the proton transfer form. Thus, for an estimation of the hydrogen-bonding energy it is reasonable to consider two dependencies: $d(\mathrm{ON}) = f(V(\mathrm{HN}))$, stretching to the transition state (the curve with one arrow, Figure 11) and describing the molecular form, and $d(\mathrm{ON}) = f(V(\mathrm{OH}))$, describing the proton transfer form (the curve with two arrows) after the transition state. This approach is in accordance with Espinosa's approach and the theory of hydrogen bonding.

## 4. Conclusions

The most complete scheme of the topological changes was studied. The changes in electron density have been examined at the critical points of all the bonds and rings in *o*-hydroxy aryl Schiff bases depending on tautomeric equilibrium. The linear character of the electron density changes at the critical points of the CC, CO, and CN bonds and the phenol ring was defined by stepwise non-adiabatic proton transfer in the hydrogen bridge, whereas the bonds indirectly involved in the hydrogen bonding are of an exponential character. The changes in the topological parameters at the critical point of the chelate ring are parabolic and more informative in tautomeric equilibrium. The dependencies between hydrogen bridge length and total electron density in the molecule critical points and electron density in the chelate ring critical points were elaborated. The dependencies $\rho_{RCP}(\mathrm{ch}) = f(d(\mathrm{OH}))$; $\rho_{RCP}(\mathrm{ch}) = f(\rho_{RCP}(\mathrm{OH}))$ and $\rho_{RCP}(\mathrm{ch}) = f(d(\mathrm{HN}))$; $\rho_{RCP}(\mathrm{ch}) = f(\rho_{RCP}(\mathrm{HN}))$ revealed the inequality of the relationships between the proton with a proton-donor and with a proton-acceptor.

Topological and conformational analyses were employed in calculating the hydrogen-bonding energy in the *o*-hydroxy aryl Schiff bases under study. The trends obtained by the topological method are in accordance with the structural results. It was demonstrated that the topological method turns out to be much more reliable in estimating hydrogen-bonding strength than conformational analysis.

**Acknowledgment.** The authors acknowledge the financial support of a KBN grant and the Wrocław Center for Networking and Supercomputing for generous computer time.

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