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Density Functional Theory Study of Intramolecular Hydrogen Bonding and Proton Transfer in *o*-Hydroxyaryl Ketimines

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The potential energy surface and the reaction pathway for the intramolecular hydrogen transfer in *o*-hydroxyaryl ketimines are characterized using DFT methods. Structural changes in the proton-transfer process in quasi-aromatic hydrogen bonding are described. A transition state and a state with a low proton-transfer barrier were studied in sterically compressed *o*-hydroxyaryl ketimines (2(*N*-methyl-α-iminoethyl)phenols) possessing two potential minimums. The potentials for proton vibration in the OH and HN tautomers of *o*-hydroxyaryl ketimines were investigated and anharmonic frequencies were determined. Solvent and substituent effects were analyzed. The energies of the various conformers of the OH and HN tautomers were compared with the related forms of *o*-hydroxyaryl aldimine.

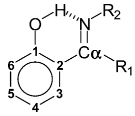
Introduction

Proton transfer plays a key role in numerous biological and physicochemical processes.[1] Recently, a controversial suggestion of the involvement of LBHB (low-barrier hydrogen bonds, LBHB, also known as Speakman−Hadži hydrogen bonds)[2] in enzyme catalysis[3] was brought forward. Short-strong hydrogen bonds, which are characterized either by a low-energy barrier for proton transfer or by its complete lack, clearly need more investigation. The existence of LBHBs has been verified by X-ray[4] and neutron diffraction methods[5] in the solid state and by NMR[6] and IR[7] spectroscopy in solution, and criteria defining the existence of LBHBs are presented in the literature.[3,8,9]

Sterically modified *o*-hydroxyaryl ketimines were selected for the study of the nature of the intramolecular hydrogen bond (see Scheme 1). These compounds are noted for creating a so-called quasi-aromatic chelate ring[10] and for a strong steric effect,[11] which leads to shortening of the ON intramolecular hydrogen bridge to a distance of approximately 2.459 Å.[11g] A key feature in forming strong hydrogen bonds is pK_a matching of the two functions involved in the hydrogen bond (in this case the OH and the $C{=}NH$ groups). However, pK_a is not a sufficient condition for the formation of a strong hydrogen bond.[12]

A major goal of this paper is to study hydrogen bonding in *o*-hydroxyaryl Schiff bases and to theoretically describe the proton-transfer process and particular tautomeric forms. To analyze the relations between structural parameters and the proton position in the intramolecular hydrogen bond, quantum-mechanical calculations are used. Successful use of this method was presented in refs 13 and 14. The DFT and MP2 methods applied in the study of both intra- and intermolecular short-strong hydrogen bonds as well as LBHBs are also described.[15−17] The consequent stage of the paper is the study of the influence of environment and substituent in the phenol ring of *o*-hydroxyaryl ketimines on spectroscopic characteristics. In conclusion we present a conformational analysis that enables the comparison of the hydrogen-bonding strength for two types of *o*-hydroxyaryl Schiff bases.

SCHEME 1 : Nomenclature Used in This Paper[a]



[a] *o*-Hydroxyaryl aldimines refers to compounds where R_1 is hydrogen; *o*-hydroxyaryl ketimines refers to compounds where R_1 is alkyl or aryl (Scheme 1). Both *o*-hydroxyaryl aldimines and *o*-hydroxyaryl ketimines refer to *o*-hydroxyaryl Schiff bases.

Methodology

The DFT calculations were carried out using the Gaussian 98 program suite.[18] The B3LYP/6-311++G(d,p) approximation was used in the present study. One-dimensional energy profiles were obtained by performing the DFT[19] calculations at selected points along the proton-transfer reaction path. The interaction with the dielectric continuum in the system is modeled by the self-consistent reaction field (SCRF) method,[20] for which the electric permittivity (ϵ) is used to characterize the surroundings. A complete optimization of the structure was performed for each electric permittivity.

Three approaches were applied in the intramolecular proton-transfer studies. The first is based on the stepwise elongation of the hydroxyl bond length with full optimization of the remaining geometric parameters (nonadiabatic approximation). The second rests on the stepwise elongation of the OH/NH bond length while optimizing the COH/CNH and the CCOH/CCNH dihydral angle for the fixed geometry of the optimized structures (adiabatic approximation). The third rests on stepwise elongation of the hydroxyl bond length for the fixed geometry of the optimized structure (single-point approximation). The first approach pictures the proton-transfer process in the intramolecular hydrogen bridge, which is “slow” process being in equilibrium with solvent organization. The second and third

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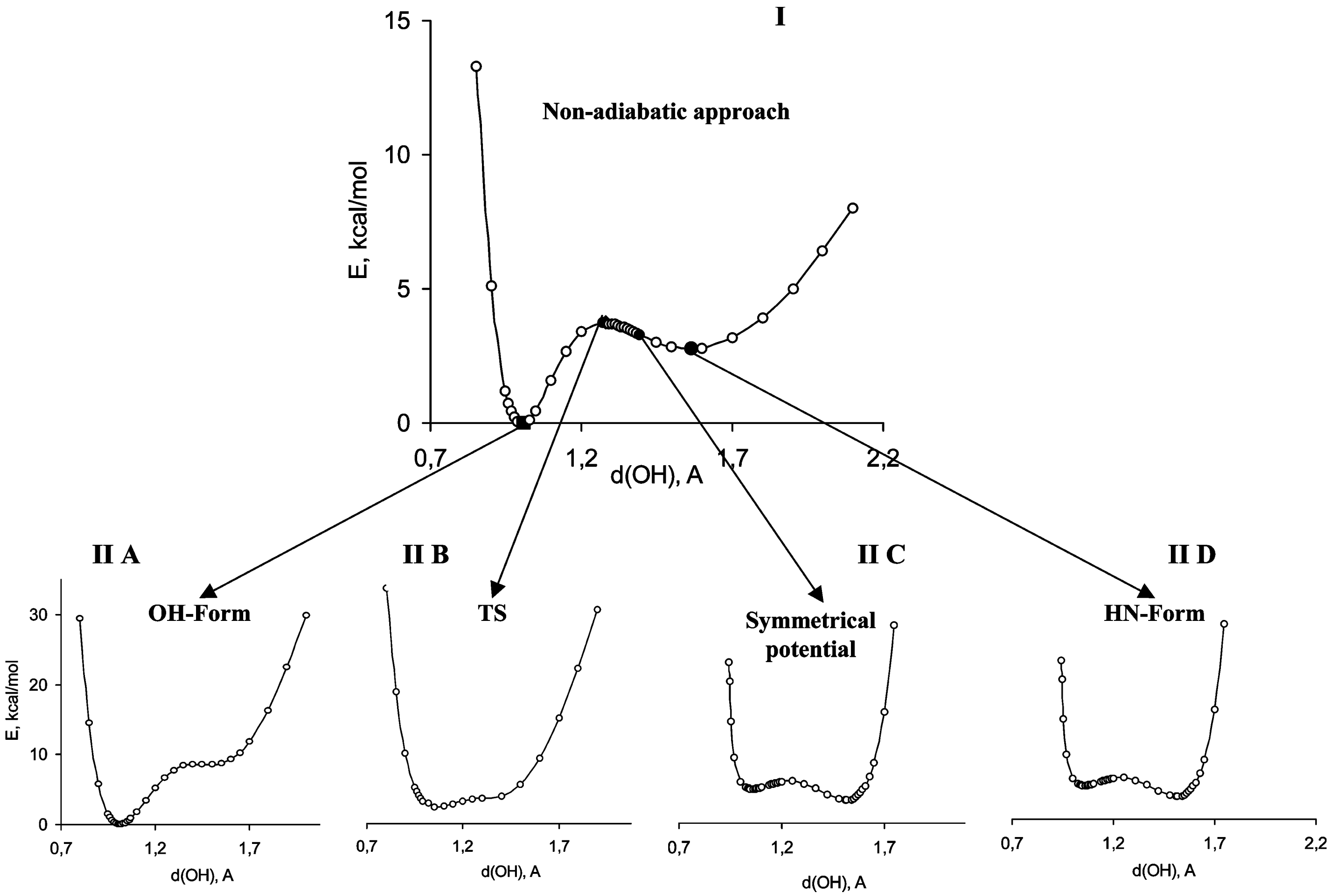
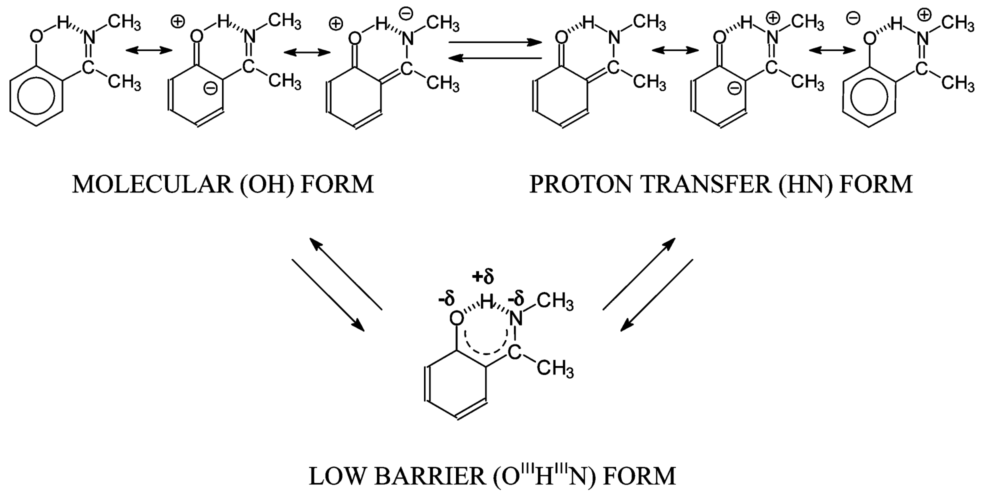


Figure 1. Nonadiabatic (top) and adiabatic potential (bottom) functions for the proton displacement (B3LYP/6-311++G(d,p) calculation) for 2-(*N*-methyl-α-iminoethyl)phenol.

SCHEME 2 : Tautomeric Equilibrium in *o*-Hydroxyaryl Schiff Bases



approaches display the nature of the spectroscopic potential in which the vibration of a light proton ("fast" process) in a hydrogen bond is virtually separated from the movements of the heavy atoms. However, it should be borne in mind that the movement of the hydrogen atom is coupled to the electron framework of the molecule even if the molecular geometry stays fixed. The consequence is modification of the electron charge distribution according to the change in the hydrogen atom's position. The studied systems contain relatively strong hydrogen bonds and the theoretically obtained spectral characteristics within the harmonic approximation (Gaussian 98) are not valid for describing the properties of real states.[21] The SHOOT program of Mavri et al.[22] was used to determine the energy levels of the calculated adiabatic potentials. The program also allows us to characterize the proton's position at a particular vibrational level.

Results and Discussion

The potential energy curves were obtained as described in the "Methodology" section: curve **I** for the first approach and curves **IIA−IID** for the second (Figure 1). Curve **I** presents

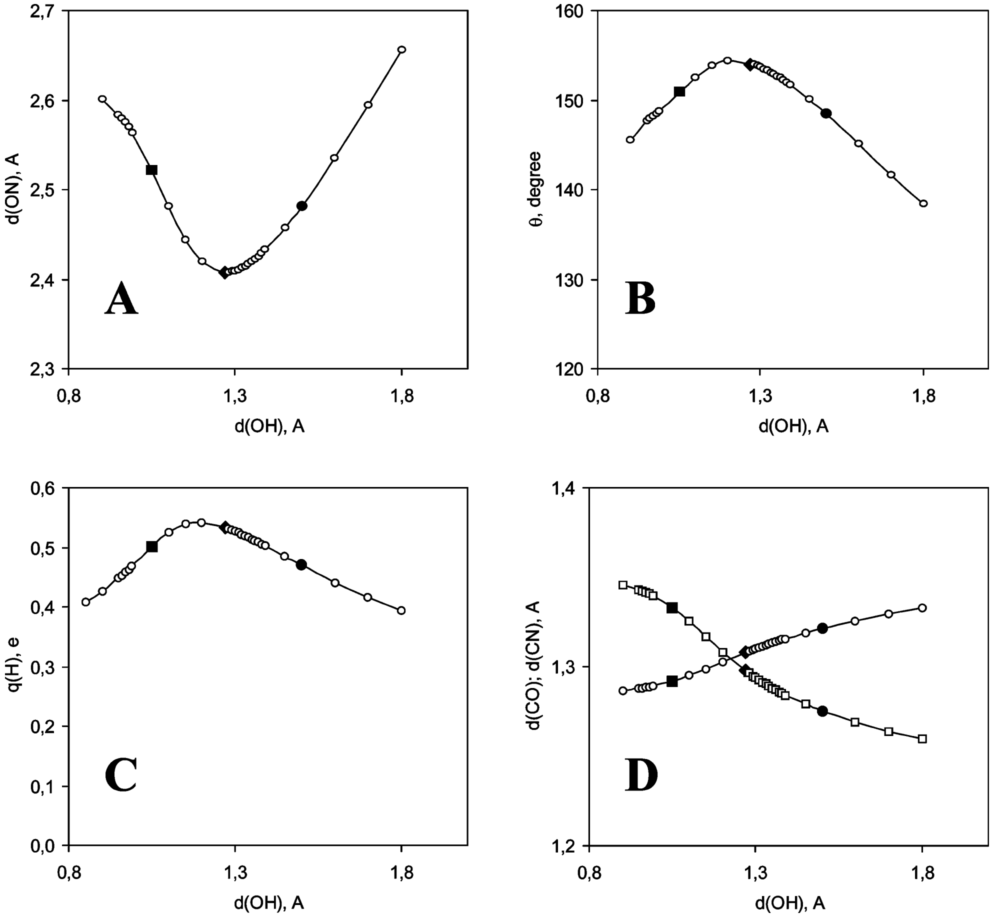


Figure 2. Calculated structural trends in 2-(*N*-methyl-α-iminoethyl)phenol: (A) d(O···N) = f(d(OH)); (B) θ(OHN) = f(d(OH)); (C) (■) d(CO) = f(d(OH)), (○ ,●) d(CN) = f(d(OH)). Mulliken charge density change at the hydrogen atom (D) vs proton transfer within the intramolecular hydrogen bond (B3LYP/6-311++G(d,p). Black points mean: (■) OH form; (◆) TS; (●) HN form.

the calculated potential energy change of the molecule in the process of the stepwise proton transfer at full optimization of the molecule geometry. The curve is marked by two clearly expressed potential minima, corresponding to two configurations of the molecule. The deeper minimum (global) is observed for the OH form where the proton is located closer to the proton-donor atom, whereas the less deep minimum (local) refers to the HN form in which the proton is found in the vicinity of the proton-acceptor atom. The barrier for the proton transfer and potential energy gap between two potential minima are 2.8 kcal/mol and 3.73 kcal/mol, respectively. It is noteworthy that a height of the energy barrier for the proton transfer in malonaldehyde of 6 kcal/mol was obtained on the basis of infrared spectra,[23] which is also in agreement with microwave data.[24] In the theoretical study by McAllister,[15] 2 kcal/mol was suggested as the upper limit for the height of the energy barrier for proton transfer for LBHBs.

Under experimental conditions, the variations in molecule geometry and, consequently, the proton's position in the hydrogen bridge can be modified by changing: (1) the acid−base abilities of the proton acceptor and the proton donor, (2) the strength of the π-electronic coupling in the O−C=C−C=N chelate chain, which acts as an acid−base regulator between the proton donor and the proton acceptor, and (3) steric effects of either the alkyl or aryl group attached to the azomethine bond. The influence of the environment should also not be neglected,[25] because it can play a negative role on the stabilization of the transition state in solutions,[26] taking into account that the solution is characterized by the disorder of the solvent environment, which induces an asymmetry of the hydrogen bond. All the described effects are capable of undergoing a process of either mutual strengthening or weakening, which makes it rather difficult for them to obtain a the potential with a symmetric minimum.

In the course of the calculations, a geometry of the molecule was found that leads to a symmetrical adiabatic potential; this geometry is marked as black points on potential curve **I**. The symmetrical potential point is not observed at the maximum of the nonadiabatic potential curve (the transition state; see Figure 1, TS potential) as is assumed in the case of a homo-nuclear hydrogen bridge. In the transition state, the heavy atoms distance is the shortest and is equal to 2.4071 Å (d(OH) = 1.2768 Å). However, a symmetrical potential is observed for the optimized structure when d(ON) = 2.4195 Å (d(OH) = 1.35 Å). This phenomenon is predicted in view of the more distinct electronegativity of the phenolic oxygen compared with the imine nitrogen.

A difference between the adiabatic potential curves of the OH and HN form is observed. For the OH tautomer, the adiabatic potential is a visibly asymmetric curve of double-well shape (OH-Form curve, Figure 1) and the local energy minimum (hydroxyl bond length between 1.4 and 1.6 Å) is observed approximately 10 kcal/mol higher than the global one. The adiabatic potential curve for the HN tautomer has two almost equivalent minima (HN form, Figure 1).

To describe the tautomeric equilibrium (Scheme 2) and the related proton-transfer process, we introduce plots vs the OH distances. The dependencies d(ON) = f(d(OH)) (Figure 2A) and

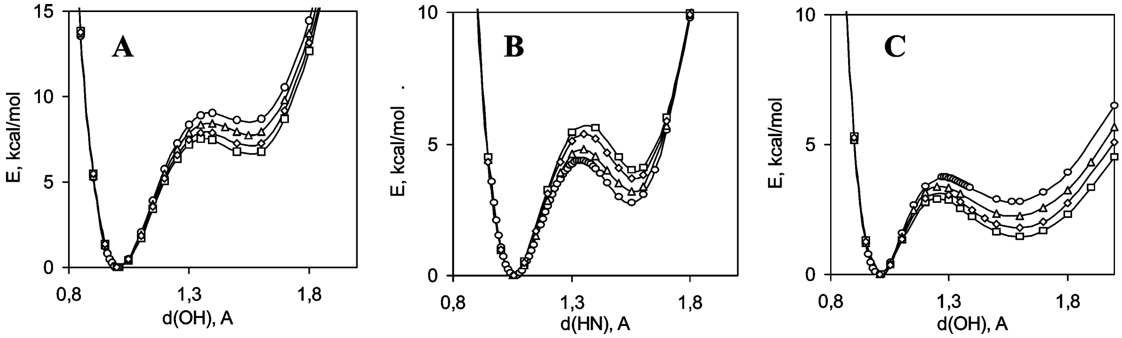


Figure 3. Adiabatic (A and B) and nonadiabatic (C) potential curves as a function of electric permittivity obtained by B3LYP/6-311++G(d,p) calculations for 2-(*N*-methyl-α-iminoethyl)phenol: (A) OH form geometry; (B) HN form geometry; (C) full optimization potential. Key: (○) gas phase; (△) $\epsilon = 2.3$; (◇) $\epsilon = 35$; (□) $\epsilon = 47$. Energies for both the global minimum and that of the HN are all set to zero to facilitate a comparison of potential shapes.

TABLE 1: Calculated (B3LYP/6-311++G(d,p)) Structural Parameters, Dipole Moments, and Energy for 2-(*N*-methyl-α-iminoethyl)phenol[a]

ϵ	tautomer	$E_{HN} - E_{OH}$[a]	$E_{OH(0)} - E_{OH(i)}$[b]	$E_{HN(0)} - E_{HN(i)}$[a]	d(OH)[a]	d(HN)[a]	d(ON)[a]	μ[a]	θ(OHN)[a]	d(CO)[a]	d(C=N)[a]
1	OH		0.00		1.006	1.636	2.554	3.47	149.3	1.338	1.290
	HN	2.80		0.00	1.566	1.059	2.516	5.21	146.3	1.271	1.324
2.3	OH		0.42		1.007	1.632	2.552	3.83	149.5	1.339	1.290
	HN	2.23		0.98	1.573	1.058	2.522	5.88	146.3	1.272	1.323
35	OH		0.97		1.010	1.623	2.547	4.30	149.8	1.340	1.290
	HN	1.45		2.32	1.596	1.056	2.536	6.83	145.7	1.272	1.321
47	OH		0.98		1.010	1.622	2.547	4.31	149.8	1.340	1.290
	HN	1.43		2.35	1.595	1.053	2.546	6.85	145.7	1.272	1.321
78	OH		0.99		1.010	1.622	2.547	4.32	149.8	1.340	1.290
	HN	1.41		2.39	1.596	1.053	2.546	6.89	145.7	1.272	1.321

[a] Distances (d) in Å, angles (θ) in degrees, dipole moments (μ) in debye, energy (E) in kcal/mol. [b] i refers to the electric permittivity.

θ(OHN) = f(d(OH) (Figure 2B) indicate that during the proton-transfer process the length of the hydrogen bond is reduced and made more linear. This phenomenon progresses up to the transition state, where we observe the shortest and the most linear hydrogen bond. At this point the positively charged hydrogen atom (Figure 2C) holds the acceptor and donor atoms extremely close despite the electrostatic repulsion between them. The further proton-transfer process causes hydrogen bond weakening, as seen by the elongation of d(NO) and the decrease in the OHN angle. These facts are consistent with experiment.[27]

A reduction of the C−O bond length and elongation of the imine bond length at the proton transfer (Figure 2D) are observed, which can be explained by the increasing π-electronic coupling in the quasi-aromatic O−C=C−C=N chain between the acid and base centers. Specific structural parameters describing the hydrogen bond moiety are presented in Table 1 together with the modification in solvent permittivity.

Influence of Environment on Proton Transfer in *o*-Hydroxyaryl Ketimine. The environmental impact on the compounds with short hydrogen bonds is a subject of discussion in the literature.[28] Calculations including variation of the electric permittivity have been carried out for the two tautomeric states. The obtained adiabatic potential curves for the molecular tautomer reveal growing anharmonicity with increasing electric permittivity (Figure 3A). The opposite dependency is observed for the HN tautomer, where an increase in the electric permittivity leads to an energy increase of the local minimum (the one closer to the oxygen atom) relative to that of the global minimum (Figure 3B).

Complete optimization of the structures in the nonadiabatic approach leads to a description of stationary states; the potential curves are shown in Figure 3C and presented in detail in Table 1. The electric permittivity increase causes shortening of the hydrogen bond length for the molecular form and an increase in the OHN angle, whereas for the HN form one can observe a shortening of the HN bond and an elongation of the hydrogen bridge (Table 1) as well as an OHN angle decrease. What is more, the permittivity increase results in a diminishing of the barrier for proton transfer (Figure 3C). The permittivity increase leads to the enhancement of the dipole moments of both the OH and HN tautomers, while the energy gap between these states decreases (Figure 3C, Table 1).

Influence of Substitution in the Phenol Ring on the Spectral Characteristics of the Tautomers. A previous paragraph demonstrated the influence of the bulk permittivity of the solvent on the shape of the potential for proton movement in *o*-hydroxyaryl ketimines. The properties of tautomers also depend on the acid−base properties of the interacting groups. Three molecules with increasing acidity were selected (**1K**, 2(*N*-methyl-α-iminoethyl)phenol, **2K**, 5-fluoro-2(*N*-methyl-α-iminoethyl)phenol, and **3K**, 4,6-dichloro-2(*N*-methyl-α-iminoethyl)-phenol) to study the influence of acid−base properties on the potential for proton movement. Adiabatic potentials for proton vibrations are presented in Figure 4. Parts A and B of Figure 4 show the potentials for the OH and HN tautomers. The trends of the potentials are very similar to those obtained in relation to increasing permittivity. For the OH tautomer the increase in acidity of the phenol moiety leads to modifications in the potential similar to those seen on permittivity increase. The potential becomes more anharmonic, and the relative energy of the second minimum decreases. For the HN tautomer there is an opposite direction of changes; the energy of the local minimum increases with the pK_a of phenol and the potential in the global minimum becomes narrower and more harmonic.

A detailed description of the spectroscopic properties of the particular tautomers for 2(*N*-methyl-α-iminoethyl)phenols ob-

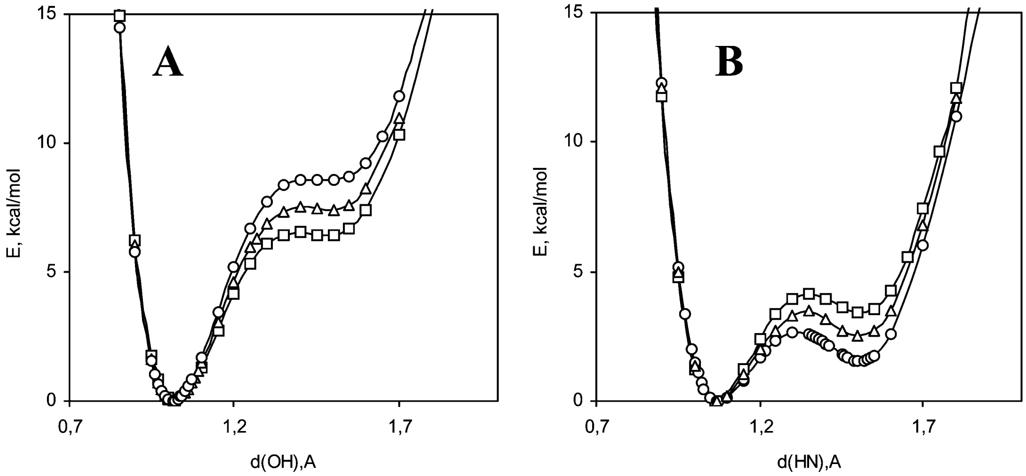


Figure 4. Influence of the acidity of the phenol part of the *o*-hydroxyaryl ketimines on the adiabatic potential shape in *o*-hydroxyaryl Schiff bases: (A) OH tautomers; (B) HN tautomers; (○) compound **1K**; (△) compound **2K**; (□) compound **3K**. Energies for both the global minimum and that of the HN form are all set to zero to facilitate a comparison of potential shapes.

tained with the SHOOT program[22] are presented in Figure 5. Numerical characteristics of the particular tautomers are given in Table 2. Among the *o*-hydroxyaryl ketimines, the weakest hydrogen bond in the OH tautomer is in the nonsubstituted compound (**1K**) and the two lowest vibrational levels are located within the potential minimum. Nevertheless, the second level ($v = 1$) has a proton probability function extending to the second minimum as well. The calculated average O−H distance for level of the $v = 1$ level is sufficiently increased as compared with the $v = 0$ state (1.2584 and 1.0550 Å, respectively). This effect is less for the deutero-substituted (OD) compound **1K**; the average OD distances are 1.1182 and 1.0302 Å for the $v = 1$ and $v = 0$ levels. Very interesting are the small values of the calculated ν(OH) vibration frequencies: 1830.8 and 1550.9 cm^{-1} for the OH and OD species, respectively. Not only the small values of the ν(OH) frequencies but also the calculated isotopic spectroscopic ratio (ISR = 1.18) show that the intramolecular hydrogen bonds are rather strong in this compound.

The calculations also allow a description of the vibrational characteristics of ν(NH). The vibrational levels of ν(NH) are presented in Figure 5A and the numerical data can be found in Table 2. The ν(NH) vibrations calculated by second approach appear to be very strongly perturbed by hydrogen bonding. The calculated anharmonic ν(NH) frequencies are at 643.4 and 646.6 cm^{-1} for the OH and OD species of compound **1K**, respectively. The isotopic spectroscopic ratio appears to be close to 1 (0.995), which is characteristic of very strong hydrogen bonds.[29] The calculated average parameter r_0 is 1.1458 Å at the $v = 0$ level and the proton located nearer to the center of the hydrogen bridge at the $v = 1$ level ($r_1 = 1.4621$ Å). The $v = 1$ level approaches the $v = 0$ level, indicating that even at room temperature some population of this state is possible, and therefore, it results in a very strong delocalization of the proton position, which is also rather large at the $v = 1$ level. A large amplitude of the proton movement in the ground state was observed. This demonstrates how difficult it is to determine the average position of a proton in diffraction experiments.

Similar trends for ν(OH) and ν(HN) were also obtained for the compounds **2K** and **3K** (Table 2). Generalization of the data obtained shows that the band shift of the stretching vibration ν(OH) in the area of low frequencies (for the second and third approaches: 1831 → 1631 → 1434 and 2317 → 2170 → 2094, respectively) is observed during the growth of the hydrogen-bonding strength in the sequence **1K** < **2K** < **3K**. However, a reverse tendency is characteristic of the HN form, where the weakening of the hydrogen-bonding evokes a shift of the ν(HN) band toward higher frequencies (for the second and third approaches: 643 → 700 → 843 and 2076 → 2203 → 2278, respectively). It is interesting that both approaches have similar trends, the only difference being that the bands obtained for the second approach are located at frequencies higther (1400−1800 cm^{-1} for the molecular and 600−800 cm^{-1} for the proton-transfer forms) than these obtained by the third approach (2100−2300 cm^{-1} for molecular and proton-transfer form). The two sequences resulting from the second and third approaches define positions of the ν(XH) stretching vibration bands of *o*-hydroxyaryl Schiff bases in a polar environment (e.g., in the solid state)[11e] and in a nonpolar solvent,[11a] respectively.

Conformers of *o*-Hydroxyaryl Schiff Bases in the Ground State. Obtaining the energy due to an intramolecular hydrogen bond is an experimentally difficult task. Therefore, ab initio and semiempirical calculations were used to throw light on this problem.[30−35] The basic method of calculation of hydrogen bond energy is a conformational analysis (so-called Schuster method),[30] which bases 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 ($E_{\mathrm{HB}} = E$(conformer with HB) − $E_{\min}$(conformer without HB)). Estimating of hydrogen bond energy is a laborious task because of the necessity to detect all possible conformers. Conformer analysis is carried out here for the *o*-hydroxyaryl ketimines. The results for the *o*-hydroxyaryl ketimines and the *o*-hydroxyaryl aldimines (Scheme 3) are discussed in parallel. Conformer **1** presents the state with an intramolecular hydrogen bond of the OH form, and conformer **2** is the state after proton transfer. The numbers in the diagram represent the increments of energy in comparison with conformer **1**. In the case of conformer **2**, this accounts for energy increase upon intramolecular proton transfer. It is interesting that, due to introducing the methyl group as R_1, steric repulsion reduces the difference between the OH and HN tautomers; thus it more strongly stabilizes the HN tautomer. The other conformers do not contain an intramolecular hydrogen bond. They can be used as reference states for estimating the energy of an intramolecular hydrogen bond,[33d] i.e., **3**−**8** for the OH tautomer and **9**−**11** for the HN tautomer. Conformers **3** and **4** describe the states when both the OH and C=N−R_2 groups are rotated away from the planar conformation with the intramolecular hydrogen bond. The difference between them is

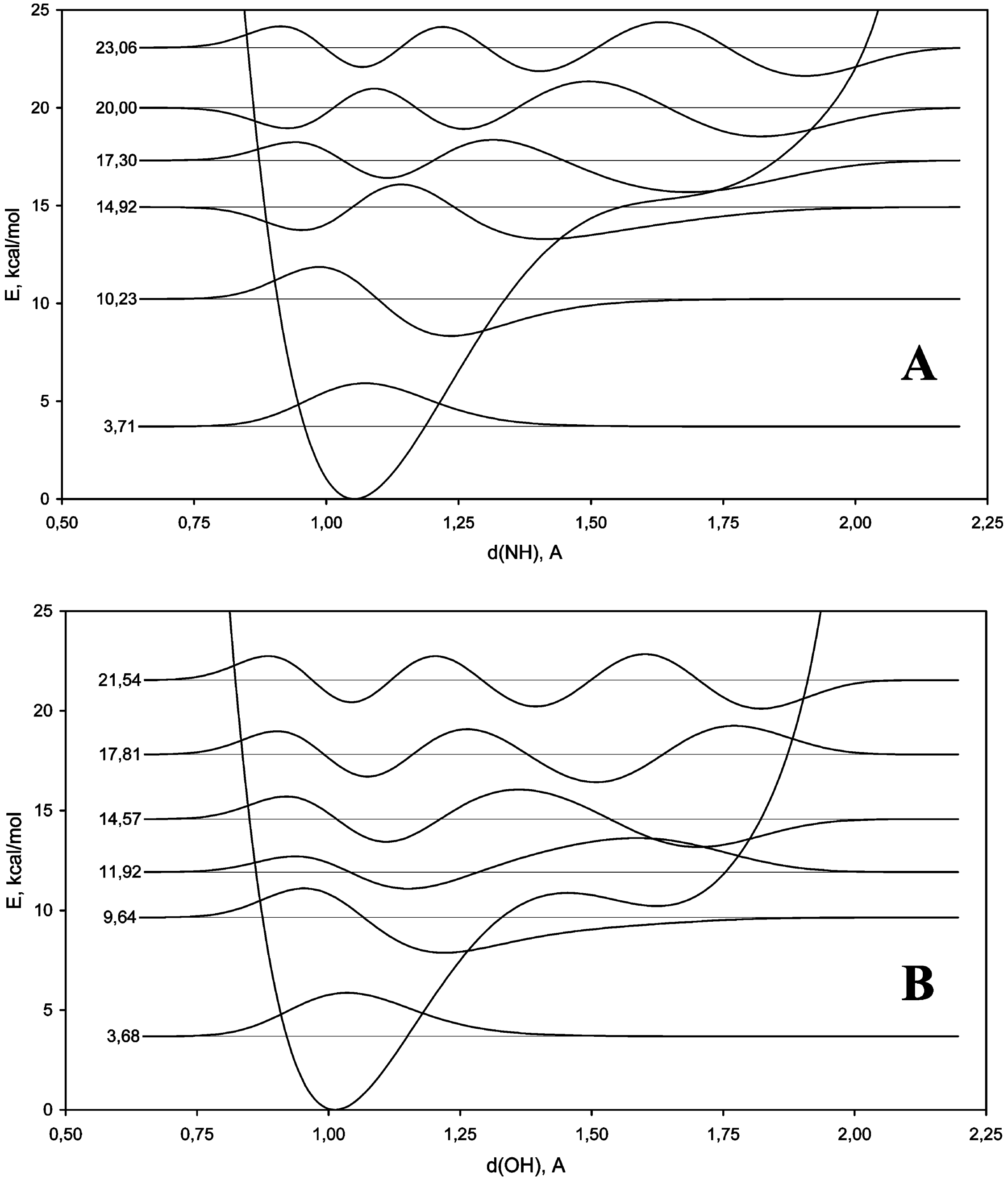


Figure 5. Potential energy curve for compound **3K** (A, HN form; B, OH form) calculated by single-point approach and the vibrational levels obtained by the SHOOT program.

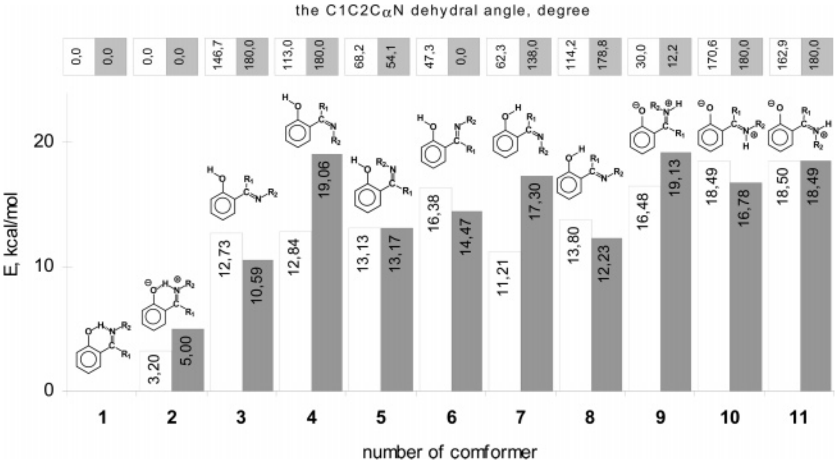
TABLE 2: Spectral Characteristics of the Adiabatic Potentials of Compounds 1K−3K Obtained from the SHOOT Program

compound	form	*d*(ON)	level	*d*(AH)[a]	*d*(AD)[a]	eigenvalues[a]	*ν*(AH)[a]	*ν*(AD)[a]	ISR
1K	OH	2.5537	0	1.0556	1.0302	3.60			
			1	1.2584	1.1182	8.82	1831	1551	1.181
	HN	2.5160	0	1.1458	1.1014	2.94			
			1	1.4621	1.485	4.78	643	647	0.995
2K	OH	2.5447	0	1.0628	1.0462	3.44			
			1	1.2977	1.1544	8.11	1631	1443	1.130
	HN	2.5241	0	1.1759	1.1246	2.64			
			1	1.4029	1.4172	4.64	700	597	1.174
3K	OH	2.5354	0	1.0717	1.0524	3.32			
			1	1.3317	1.1928	7.42	1434	1322	1.084
	HN	2.5225	0	1.1446	1.1075	2.88			
			1	1.4155	1.4024	5.29	843	802	1.05

[a] A means O or N, distances (*d*) in Å, energy (eigenvalues) in kcal/mol, *ν*(AH) in cm^{-1}.

the R_2 group is placed nearer to the phenyl ring in **4**, which results in a serious energy increase in conformer **4** for 2(*N*-methyliminomethyl)phenol and the conformation is planar. In the 2(*N*-methyl-α-iminoethyl)phenol, the methyl group makes

SCHEME 3: Energy Scheme (B3LYP/6-31G(d,p)) for Rotamers and Tautomers of 2(*N*-methyl-α-iminoethyl)phenol (White; $R_1 = CH_3$, $R_2 = CH_3$) and 2(*N*-methyliminomethyl)phenol (Gray; $R_1 = H$, $R_2 = CH_3$)



the most important impact on steric repulsion, the conformation becomes nonplanar, and the energy difference between conformers **3** and **4** appears negligible.

Breaking the intramolecular bond by rotation around the C−O and C−C(α) bonds provokes a larger energy decrease in 2(*N*-methyl-α-iminoethyl)phenol than in the 2(*N*-methyliminomethyl)phenol, which would suggest that the intramolecular hydrogen bond is stronger in *o*-hydroxyaryl ketimine, which is true if we use criteria such as O···N distances. However, the energy in the intramolecular hydrogen bond could be overestimated for *o*-hydroxyaryl ketimines due to the steric crowding in conformer **3**. It is obvious from Scheme 3 that the imine group is twisted out of the ring plane. However, mutual compensation of resonance and steric effects in the nonplanar structures could take place. On the basis of the above discussion of Scheme 3, one can estimate the energy of the formation of the intramolecular hydrogen bond as 10.59 kcal/mol in 2(*N*-methyliminomethyl)phenol and 12.73 kcal/mol in 2(*N*-methyl-α-iminoethyl)phenol (conformers **5**, **7** for the OH form and conformers **9**, **11** for the HN form excluded due to the missing steric repulsion between the methyl groups like in conformers **1** and **2**). In the proton-transfer state one can estimate the energy of intramolecular hydrogen bonding as the difference between conformer **10** (16.78) and conformer **2** (5.00), which is equal to 11.8 kcal/mol.

Conclusions

The process of intramolecular proton transfer in *o*-hydroxyaryl ketimine was investigated in detail using DFT (B3LYP/6-311++G(d,p)) calculations. The nonadiabatic potential shape for the proton-transfer process was calculated including full optimization of all the parameters of a molecule, while gradually changing the hydroxyl bond length in the range 0.8−2 Å. Shortening and linearization of the hydrogen bridge increased until the transition state. From this point on, the trend was reversed. In the transition state we observed the shortest hydrogen bridge (d(ON) = 2.4071 Å); however, there is no symmetrical potential for the proton vibration. A symmetric potential was found at d(ON) equal to 2.4195 Å, where the proton was located at the center of the hydrogen bridge. A very large amplitude of the proton movement in the LBHB state was predicted. The adiabatic potential for proton vibrations was also calculated along the reaction pathway. The stationary O−H···N and O^-···H−N^+ states were described. In both tautomers, two minimum potentials for proton vibrations were found.

The influence of solvent on the potential shape was studied within the SCRF model. For the OH tautomer the increase in electric permittivity led to larger anharmonicity of the proton vibrations and to a lowering of the energy for the local minimum. The opposite effect was found for the HN tautomer.

The calculations performed for 2(*N*-methyl-α-iminoethyl)phenol, 5-fluoro-2(*N*-methyl-α-iminoethyl)phenol and 4,6-dichloro-2(*N*-methyl-α-iminoethyl)phenol showed that increased acidity of the phenolic part leads to potential changes in the same direction as the polarity of the environment. The vibrational levels of the anharmonic potentials for the three *o*-hydroxyaryl ketimines were determined with the aid of adiabatic approaches employing the SHOOT program. The anharmonic frequencies calculated by the adiabatic approaches were found to be in the range of 1830−1430 cm^{-1}, indicating a strong hydrogen bond in *o*-hydroxyaryl ketimines.

The hydrogen bond energies were determined by comparison of the intramolecularly hydrogen-bonded case with a reference state. Among the states with a broken intramolecular hydrogen bond, the conformer with both hydroxyl and imine groups rotated away from the hydrogen-bonding configuration had the lowest energy. The energy of the intramolecular hydrogen bond was estimated to be 10.56 kcal/mol in the 2(*N*-methyliminomethyl)phenol and 12.73 kcal/mol for the 2(*N*-methyl-α-iminoethyl)phenol. In the latter case the reference states with open hydrogen bonds are nonplanar due to steric effects and estimation of the energy of the intramolecular hydrogen bond becomes less certain.

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References and Notes

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