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Steric and aromatic impact on intramolecular hydrogen bonds in *o*-hydroxyaryl ketones and ketimines

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ABSTRACT: X-ray measurements at 100 K and quantum-mechanical calculations showed a domination of the enol (OH) form in *o*-hydroxyaryl ketones [6-methoxy-2-hydroxyacetophenone (**6OMeK**), 4-methoxy-2-hydroxyacetophenone (**4OMeK**), 5-chloro-4-methyl-2-hydroxybenzophenone (**5Cl4MeK**) and 2-hydroxyacetonaphthone (***o*-HAN**)], whereas a prevailing proton-transfer (NH) form was found in *o*-hydroxyacetonaphthylimine [2-(*N*-methyl-α-iminoethyl)naphthol (***o*-HIN**)]. The effective mechanism of the reduction in hydrogen bridge length due to steric repulsion in the *o*-hydroxyaryl ketones is presented. The following phenomena were found: a decrease in phenol ring aromaticity caused by the proton-transfer process, dependence of the HOMA index of aromaticity on the HOSE index defining the destabilization of the chelate ring and a dependence of the HOMA index on the lengths of the carbonyl bonds. Moreover, a correlation between phenol ring aromaticity [HOMA(phenol)] and the pseudo-aromatic ring [HOSE(chelate)] is shown. Correlations between structural parameters of the chelate ring [d(C—O), $d(\mathrm{C_{aryl}}—\mathrm{C_{alkyl}})$] and aromatic rings [HOMA(phenol)] of the *o*-hydroxyaryl ketimines and ketones are presented. Copyright © 2005 John Wiley & Sons, Ltd.

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KEYWORDS: intramolecular hydrogen bonding; proton transfer; *o*-hydroxyaryl ketone; *o*-hydroxyaryl ketimine; aromaticity; HOMA and HOSE indices

INTRODUCTION

o-Hydroxy Schiff's bases have been a subject of great interest in biology, chemical physics and technology.[1–3] The particularly interesting photo- and thermochromic properties of these compounds, investigated for the first time by Senior and Shepheard[1] in 1909, have been actively studied throughout the last century in a number of scientific centres.[2–10] Moreover, the crystallographic method employed[11] suggested the appearance of the salicylamine photoproduct in the solid state. A series of papers[6–10] presented the proton-transfer process in Schiff's bases in both the ground and excited states. The simultaneous existence of two tautomeric forms also in the solid ground state was demonstrated by crystallographic analysis.[7c] The structural aspects of tautomeric equilibrium can be better understood when the OH and NH forms are presented as a superposition of canonical structures (Scheme 1). The necessity of applying at least two resonance structures in the description of the NH form in molecules with intramolecular π-electron coupling between substituents has been reported.[6–9]

Despite the structural analogy, *o*-hydroxy aromatic ketones seem to contrast with Schiff's bases, as the existence of the proton transfer form in the solid ground state of the former compounds is still in question. All the structures of the *o*-hydroxyacetophenones listed so far in the Cambridge Structural Database (CSD)[12] are presented in the OH form. The question of the character of the proton transfer forms occurring in the excited state has been the subject of careful scrutinity of *o*-hydroxyacetonaphthalene using emission spectroscopy and quantum-mechanical calculation.[13,14]

To study the nature of the intramolecular hydrogen bond, *o*-hydroxy ketimines and ketones were selected for comparison (Scheme 2). These were four different *o*-hydroxyphenyl ketones with methyl and phenyl substituents (R) in the —C(R) = O group, which, in our experience, lead to a shortening and consequent strengthening of the hydrogen bonds. As shown previously, in the case of *o*-hydroxy ketimines, such a substitution makes the proton transfer reaction easier. In previous studies it was also shown that the phenyl ring has effects similar to those of methyl or ethyl groups because of the perpendicular arrangement of this substituted ring. It was interesting to study such an effect in a 2-hydroxybenzophenone derivative. Comparison of **6OMeK** and **4OMeK** should allow one to understand the effect of the modified position of the

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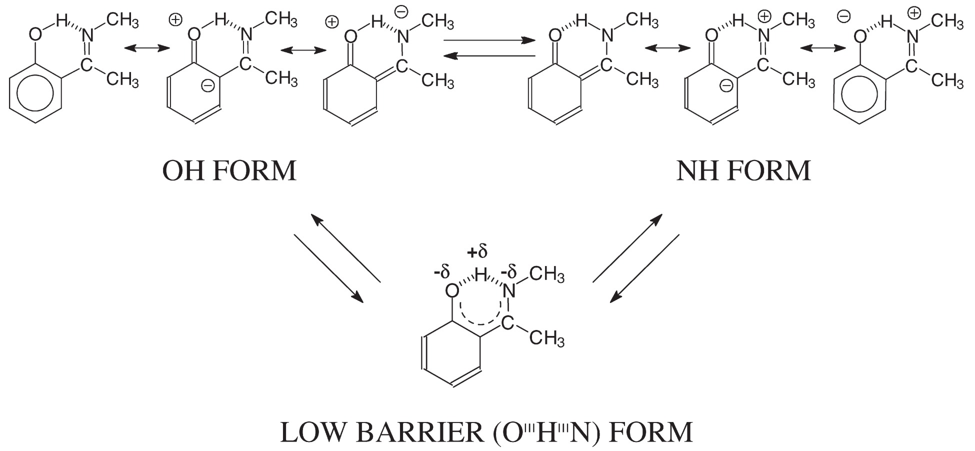
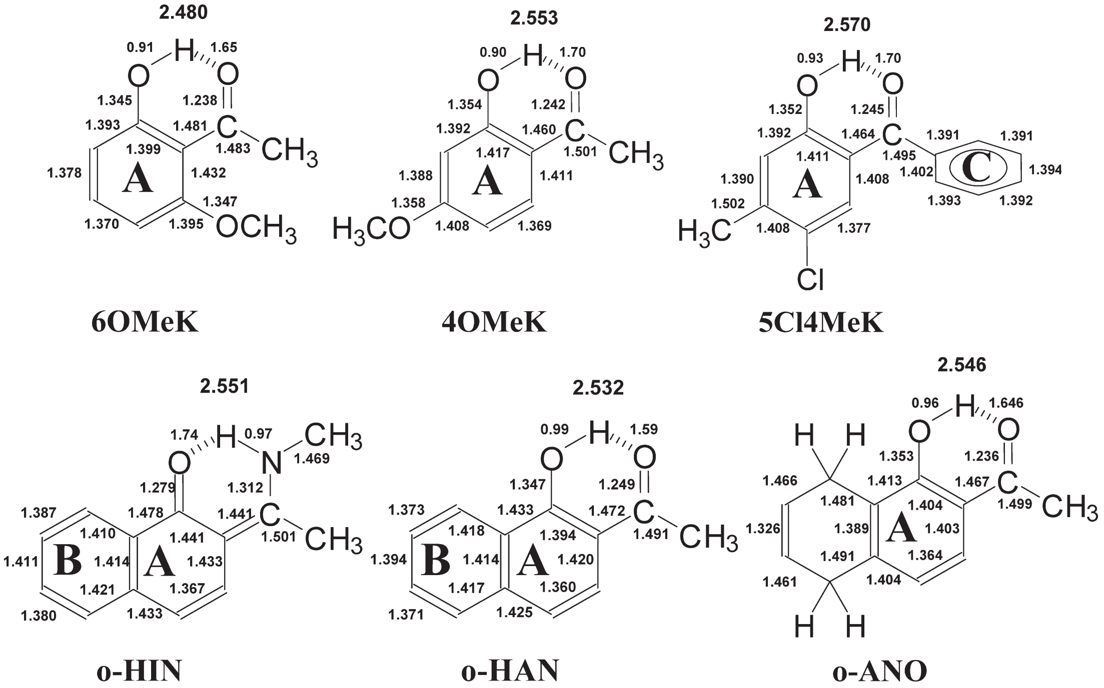


Scheme 1



Scheme 2. The crystal data for **6OMe**, **4OMeK**, **5Cl4MeK**, ***o*-HIN** and ***o*-HAN** from this work and crystal data for ***o*-ANO** are taken from Ref. 25

same substituent. Naphthyl ketone is a specific case because of a possible additional stabilization of the NH state. This compound was directly compared with the analogous ketimine, representative of a group of compounds already widely studied.

According to literature data,[15a,b] these compounds contain the so-called pseudo-aromatic ring [chelate ring, quasi-aromatic, mesohydric or prototropic tautomerism, resonance-assisted hydrogen bond (RAHB)], which is defined by strong π-electronic coupling modifying the acid and base centres. A qualitative explanation based on π-electronic system coupling through the p-orbital of hydrogen was put forward by Shygorin.[15] Wider experimental and theoretical studies, and a semi-empirical interpretation based on the feedback mechanism through the donor—C=C—C=acceptor (chelate) chain and introduction of the RAHB term were presented by Gilli and co-workers.[16] Multipolar and topological analysis of x-ray and neutron data provided a deeper study of the electronic density distribution of the pseudo-aromatic ring.[17] High formal charges were found on both the acceptor and donor atoms and also on the hydrogen in the short hydrogen bond, and the existence of a partly covalent and partly electrostatic character of the O—H—O interactions was suggested. Therefore, the relations between the structural parameters of the pseudo-aromatic and aromatic rings are obviously important for modelling the physicochemical properties of Schiff's base molecules. For this purpose, the HOMA (harmonic oscillator model of aromaticity) [Eqn (1)] and HOSE (harmonic oscillator stabilization energy) [Eqn (2)] indices[18] are applied to determine the degree of phenol ring aromaticity and destabilization of the chelate chain.

$$\mathrm{HOMA} = 1 - \frac{\alpha}{n}\sum_{r=1}^{n_1}\left(R_{\mathrm{opt}} - R_i\right)^2 \tag{1}$$

where n is the number of bonds, α is an empirical constant and R_{opt} and R_{i} are optimal and individual bond lengths.[18]

$$\mathrm{HOSE} = 301.15\left[\sum_{r=1}^{n_1}\left(R'_r - R_0^{\mathrm{s}}\right)^2 k'_r + \sum_{r=1}^{n_2}\left(R''_r - R_0^{\mathrm{d}}\right)^2 k''_r\right] \tag{2}$$

where $R_r{}'$ and $R_r{}''$ are the lengths of the π bonds in the real molecule and n_1 and n_2 are the numbers of single and double bonds, respectively. The single and double bond reference lengths R_0^{s} and R_0^{d} were taken from Ref. 18. The force constants were calculated by $k_r = a + bR_r$, where the parameters a and b were taken from Ref. 18.

EXPERIMENTAL AND COMPUTATIONAL

The synthesis of 2-(N-methyl-α-iminoethyl)naphthol (***o*-HIN**) from stoichiometric mixtures of 2-hydroxyacetonaphthone and methylamine in methanol was performed according to Ref. 19. The *o*-hydroxy ketones were purchased from Aldrich and recrystallized from methanol.

The intensity data were collected at 100 K using a Kuma KM4CCD diffractometer and graphite-monochromated Mo Kα (0.71073 Å) radiation generated from an x-ray tube operating at 50 kV and 35 mA. The images were indexed, integrated and scaled using the KUMA data reduction package.[20] The experimental details together with crystallographic data for all the compounds are given in Table 1S (Supplementary material). The structure was solved by direct methods using SHELXS97[21] and refined by the full-matrix least-squares method on all F^2 data (SHELXL97).[22] Non-hydrogen atoms were refined with anisotropic thermal parameters; hydrogen atoms were included from $\Delta\rho$ maps and refined isotropically. CCDC-227363 for ***o*-HIN**, 229995 for **6OMeK**, 229996 for **4OMeK**, 229997 for **5Cl4MeK** and 227364 for ***o*-HAN** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax +44 1223336033; e-mail deposit@ccdc.cam.ac.uk).

Ab initio molecular orbital calculations using DFT theory (B3LYP)[23] with the 6–311++G(d,p) basis set were performed for the full geometry optimizations with the Gaussian 98 program.[24] All parameters were fully optimized for each OH distance, changing gradually within the range 0.8–2 Å.

RESULTS AND DISCUSSION

The molecular structures and atom labelling are presented in Fig. 1. Details on the crystallographic data and structure refinement of the compounds studied are given in Table 1S (Supplementary material).

The crystallographic data obtained show the prevalence of the OH form (the hydrogen located close to the hydroxyl oxygen) in the aryl ketones studied (Fig. 1). This experimental result is also supported by DFT calculations. In the calculated potential energy curves [Fig. 2(A)] of the *o*-hydroxyaryl ketones, the only global minimum was found in the vicinity of the hydroxyl oxygen (Table 1). It should be pointed out that the calculation is fully consistent with the quantum-mechanical calculations [B3LYP/6–31G(d,p)] carried out for ***o*-HAN**.[14b] Nevertheless, in contrast to the *o*-hydroxyaryl ketones, the predominance of the NH form (the hydrogen is located close to the nitrogen) in *o*-hydroxyacetonaphthylimine is confirmed by both the x-ray study (Fig. 1) and DFT calculations.

The additional aromatic ring (**B**) in ***o*-HAN** influences the potential curve, inducing a considerable lowering of the potential curve in the proton-transfer range [d(OH) = 1.4–1.5 Å) [Fig. 2(A)]. Nevertheless, a stable NH form for ***o*-HAN** is not observed. A more distinct effect of the influence of naphthyl bonding occurs in *o*-hydroxyaryl ketimine (***o*-HIN**) where, for the first time, the DFT methods employed have shown that the minimum close to the nitrogen is lower than that near the oxygen [Fig. 2(B)] in the *o*-hydroxyaryl ketimines. The difference between the local and global minima is estimated as 1.47 kcal mol^{-1} (1 kcal = 4.184 kJ) [B3LYP/6–311++G(d,p)].

In the phenyl ring of the **6OMeK** and **4OMeK** ketones, the influence of the methoxy group on hydrogen bonding has a double character. First, the methoxy group in the *meta*-position to the hydroxyl group provides an insignificant increase in the acidity of the phenol moiety,[26] which is equal for both methoxy compounds and unlikely to lead to differences in the hydrogen bridges in **6OMeK** and **4OMeK**. Second, the electronic effect of the methoxy group in the 4- and 6-positions stipulates a greater basicity of the carbonyl group of **4OMeK** and **6OMeK** than in acetophenone. The spectroscopic studies revealed equal strengths of the intermolecular hydrogen bonds in both 2- and 4-methoxyacetophenone with 4-fluorophenol complexes,[27] so the basicities of the 2- and 4-methoxyacetophenones are nearly the same,

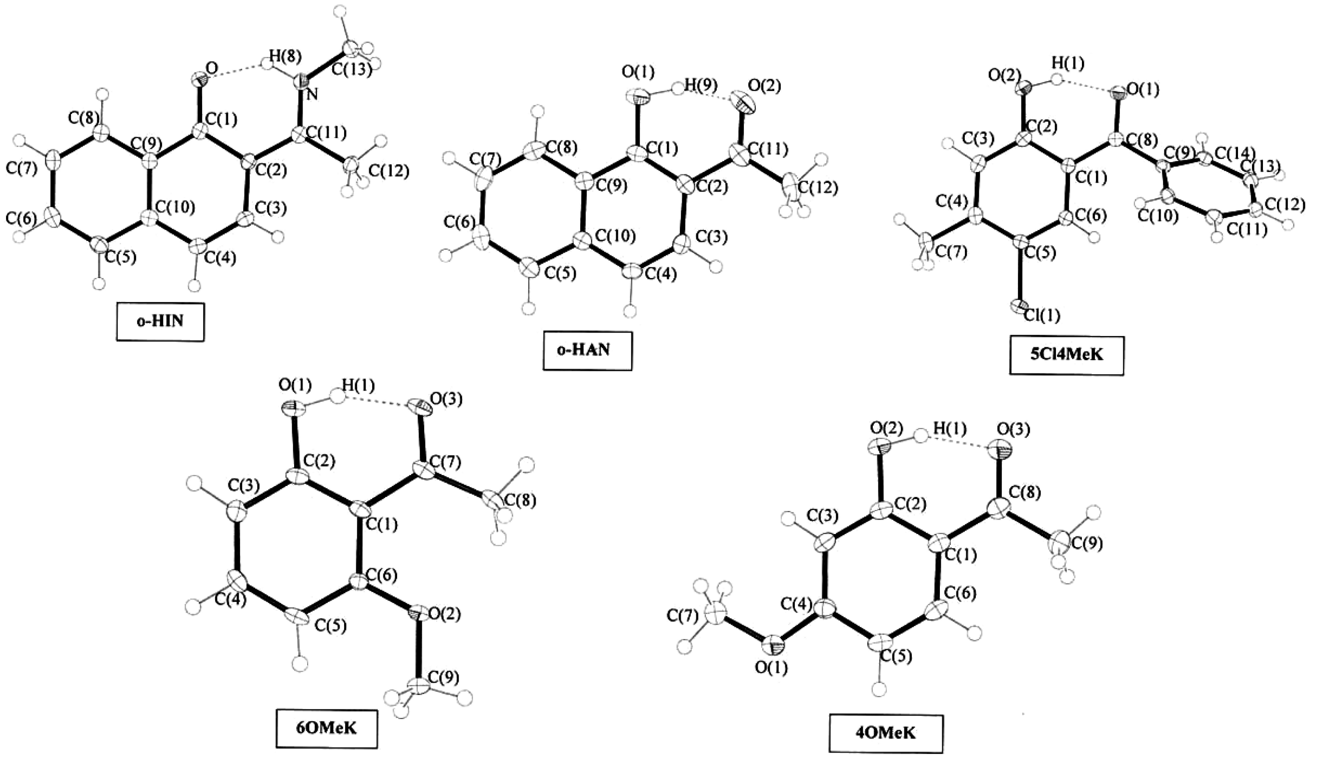


Figure 1. ORTEPIII diagram showing the molecular structure and atom labelling scheme of ***o*-HIN**, **6OMeK**, **4OMeK**, **5Cl4MeK** and ***o*-HAN**. The displacement ellipsoids of the non-H atoms are shown at the 50% probability level. The intramolecular hydrogen bond is shown as a broken line

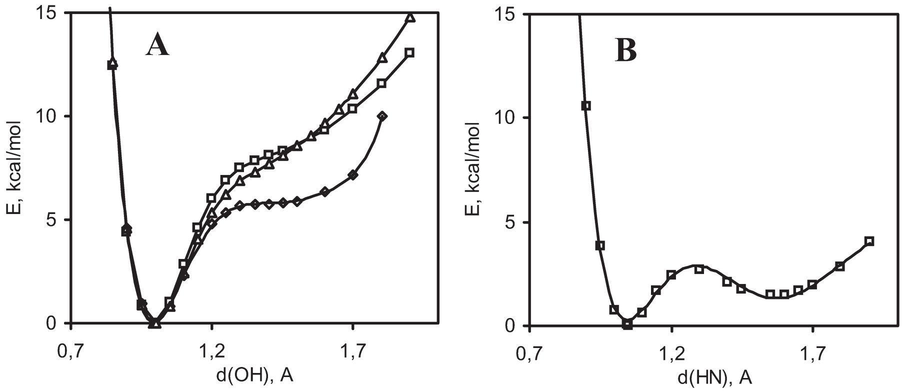


Figure 2. Calculated proton transfer energy potential [B3LYP/6–311 + + G(d,p)] for the *o*-hydroxyaryl ketones [(A) ***o*-HAN** (◇), **4OMeK** (□) and **6OMeK** (Δ)] and for *o*-hydroxyacetonaphthoneimine [(B) ***o*-HIN**]. To perform the calculation of the potential curve for **4OMeK**, the *cis*-position of the methoxy group was chosen as more advantageous than the *trans*-position ($\Delta E_{cis-trans} = 1.06\,\mathrm{kcal\,mol^{-1}}$), this advantage also being supported by the x-ray results (Fig. 1)

with pK_{HB} values of 1.11 and 1.10, respectively. The aforesaid observations suggest that the strengths and lengths of the hydrogen bridges in **4OMeK** and **6OMeK** should be equal. However, the experimental picture looks different: the hydrogen bond is shorter in **6OMeK** than in **4OmeK**, both experimentally and in the theoretical prediction. This phenomenon can be clearly explained by the rather strong steric repulsion between the 6-methoxy group and the acetyl moiety and, consequently, a shortening of the hydrogen bridge (Table 1).

The calculated potential curves of the compounds are a source of additional information on the hydrogen bridge. The buttressing effect of the 6-methoxy group leads to some symmetrization of the potential curve [cf. the potential curves **6OMeK** and **4OMeK** in Figure 2(A)]. Stronger symmetrization of the potential curve was found in the Schiff's bases, resulting from steric repulsion of the methyl group on the ketimine fragment.[9b]

The above observations are a classical example of the so-called buttressing effect. Consequences of the impact

Table 1. Selected bond lengths (Å) and angles (°) of hydrogen bonds at 100 K (esds in parentheses) and DFT [B3LYP/6–311 + + G(d,p)] calculations[a]

Compound	Method	Type HB	d(OH)	d(HX)[b]	d(OX)	α(OHX)	d(C—O)	d(C═X)
***o*-HIN**	X-ray	O···H—N	1.74(2)	0.97(2)	2.551(2)	138	1.279(2)	1.312(2)
	DFT	—	1.641	1.041	2.550	143	1.261	1.332
	—	O—H···N	1.018	1.586	2.521	150	1.332	1.293
6OMeK	X-ray	O—H···O	0.90(3)	1.65(4)	2.480(2)	153	1.345(3)	1.238(3)
	DFT	—	0.996	1.596	2.499	149	1.335	1.241
4OMeK	X-ray	O—H···O	0.91(2)	1.70(2)	2.553(2)	155	1.354(2)	1.242(2)
	DFT	—	0.992	1.668	2.562	148	1.338	1.240
5Cl4MeK	X-ray	O—H···O	0.93(2)	1.70(2)	2.570(2)	153	1.352(2)	1.245(2)
	DFT	—	0.987	1.689	2.571	146	1.340	1.239
***o*-HAN**	X-ray	O—H···O	0.99(2)	1.59(2)	2.532(2)	157	1.347(3)	1.249(2)
	DFT	—	0.996	1.632	2.534	148	1.333	1.240

[a] Concerning the calculated length of the hydrogen bridge, it is slightly larger for **6OMeK** and **4OMeK**, whereas it practically coincides with the experimental values for ***o*-HAN**, **5Cl4MeK** and ***o*-HIN**.
[b] Where X = O for ketones and N for ketimine.

of steric squeezing on hydrogen bonding have been discussed in the literature.[9,28–31] Experimental (x-ray and IR) data and theoretical (DFT) calculations of an additional bulky substituent in the 6-position of *o*-hydroxy Mannich bases provide evidence of hydrogen bridge shortening due to steric repulsion.[28] Employing NMR results, Hansen *et al.*[29] reported a splitting of the bridge proton band by a change in the methyl group's steric hindrance due to deutero substitution in this group. The steric effect is also responsible for the alteration in basicity of the proton sponge[30] and urocanic acid.[31] A more detailed analysis of the steric interaction energy, crystallographic data and quantum-mechanical calculations for the *o*-hydroxyaryl ketimines was presented in previous papers.[9,10] Analysing the data on the *o*-hydroxy aromatic ketones available in the CSD, one could affirm that only a bulky substituent in the 6-position leads to a visible reduction in hydrogen bridge length. The absence of this type of substitution indicates a weak energy of steric repulsion in the *o*-hydroxy ketones, and this phenomenon is not observed. One should point out that the steric repulsion energy in the *o*-hydroxy ketones (1–2 kcal mol^{-1}) is significantly less than in the *o*-hydroxy ketimines (6–7 kcal mol^{-1}). Steric repulsion energy was calculated using the non-bonded interaction parameters taken from the MM3 force field. The interaction between two methyl groups (or methyl and hydrogen for molecules with low steric repulsion) and also neighbouring carbon and hydrogen atoms in the phenol ring were accounted for.[9b,d,32]

A comparison of the crystallographic structures of **5Cl4MeK** and 5-chloro-2-hydroxybenzophenone[33] provides evidence of the hydrogen bridge length remaining indifferent to the influence of methyl group substitution in the 4-position. This can be explained by a compensating repercussion of the above-mentioned substitution on the acidic (some weakening[26]) and basic (some increasing[34]) centres. Regarding the impact of the phenyl ring **C** in **5Cl4MeK** on hydrogen bridge length (Scheme 2), its steric and electronic effects are rather attenuated on account of its perpendicular position with respect to the phenol ring (cf. also 4-methoxy-2-hydroxybenzophenone[35] with **4OMeK**), although it is possible to observe an insignificant elongation of the hydrogen bridge on passing from 5-chloro-2-hydroxybenzophenone[33] to 5-chloro-2-hydroxyacetophenone.[32]

A comparison of two *o*-hydroxyacetyl analogues [***o*-HAN** and 2-acetyl-5,8-dihydronaphthalen-1-ol[25] (***o*-ANO**)] makes it possible to trace the double impact of an additional aromatic ring on the chelate chain. From one side, the additional aromatic moiety stipulates a reduction in the phenolic C—O bond and an elongation of the carbonyl bond (Scheme 2), a phenomenon supposed to enlarge the content of the quinoid form. Simultaneously, hydrogen bridge shortening (from 2.546 to 2.532 Å) and hydroxyl bond elongation (from 0.963 to 0.990 Å) are observed. From the other direction, the additional aromatic ring acts as an imbalance of the quinoid form on account of C1—C2 bond shortening (from 1.404 to 1.394 Å) and C2—C11 bond lengthening (from 1.467 to 1.472 Å).

An analysis of the mutual impact of the aromatic and chelate rings is possible provided that the *A* parameter[9a] and HOMA and HOSE indices[18] are applied. These indices describe the average squared deviation of bond lengths from an average value (*A*), aromaticity (HOMA) and the energy required for a decline from standard aromaticity (HOSE). The parameters taken to function as standards were the single bonds C—O and C—C and the double bonds C═C and C═N presented in Ref. 18. The use of these parameters for each of the rings demonstrates the existence of a structural–aromatic balance between the **A** and **B** rings. For both ***o*-HAN** and ***o*-HIN** a decrease in **A** ring aromaticity is observed, this ring being the most sensitive in view of the vicinity of chelate formation. A transition from the enol structure

Table 2. Values of A,[9a] HOSE and HOMA indices[18] for ***o*-HIN**, **6OMeK**, **4OMeK**, **5Cl4MeK**, ***o*-HAN**, ***o*-ANO**, **BEIN** and **S1**

	$A \times 10^{-6}$(Å)			HOSE (kJ mol^{-1})			HOMA		
Compound	**A**	**B**	**C**	**A**	**B**	**C**	**A**	**B**	**C**
***o*-HIN**	1106	223	—	88.0	44.8	—	0.310	0.878	—
6OMeK	383	—	—	34.0	—	—	0.890	—	—
4OMeK	268	—	—	36.9	—	—	0.908	—	—
5Cl4MeK	151	—	14	35.9	—	29.6	0.937	—	0.988
***o*-HAN**	599	398	—	54.1	38.6	—	0.746	0.873	—
***o*-ANO**[a]	257	—	—	35.2	—	—	0.917	—	—
BEIN[a]	1245	412	—	70.0	29.7	—	0.505	0.893	—
S1[a]	360	—	—	36.0	—	—	0.897	—	—
—	428	—	—	36.0	—	—	0.879	—	—

[a] Crystal data for ***o*-ANO** (2-acetyl-5,8-dihydronaphthalen-1-ol), **BEIN** [2-(*N*-benzyl-α-iminoethyl)naphthol], **S1** [2-(*N*-methyl-α-iminoethyl)phenol] taken from Refs 25, 9c and 9d, respectively.

o*-HAN** to the proton-transfer structure ***o*-HIN** leads to a stronger loss of **A** ring aromaticity, which is supported by an increase in the parameter A (from 599 to 1106) and a decrease in the HOMA index (from 0.746 to 0.310) (Table 2). It should be pointed out that the energy required for **B** ring stabilization is larger in ***o*-HIN** (HOSE = 44.8 kJ mol^{-1}) than in ***o*-HAN** (HOSE = 38.6 kJ mol^{-1}); similar changes were also traced for the **A** ring. The pseudo-aromatic ring formation is observed to enforce a decreased aromaticity in the **A** ring in both the OH and NH forms. However, in contrast to this decrease, the aromaticity of the **B** ring tends to increase with respect to the naphthalene rings (HOMA = 0.810[18]). It should be emphasized that the aromaticity of the **B** ring reaches a certain saturation {HOMA(o*-HAN**) = 0.873, HOMA(***o*-HIN**) = 0.878, HOMA(**BEIN**-2-[*N*-benzylidene-α-iminoethyl]naphthol) = 0.893[9c]}, and is therefore practically equal in both forms. These particular observations are consistent with the fact that the proton-transfer process is balanced by changes in the chelate chain and aromatic rings.

A more common description of the influence of proton transfer on the chelate chain and the phenol ring can be calculated using relations between the hydroxyl bond length, the HOSE(chelate) index corresponding to the energy of destabilization of the chelate chain and the HOMA(phenol) index defining the degree of aromaticity. The aromatic HOMA index describes the distortion of the π-electronic component and the resonance stabilization of an aromatic moiety.[18c,36] The HOMA(phenol) = f[d(OH)] and HOMA(phenol) = f[HOSE(chelate)] correlations obtained [Fig. 3(A) and (B)] show the existence of a double interrelation of the chelate ring with the hydrogen bridge and π-electronic component of aromatic rings also. This system may either enhance or attenuate the hydrogen bond, depending on circumstances. The HOMA(phenol) = f[d(OH)] correlation illustrates that the proton-transfer process (hydroxyl bond elongation) causes dearomatization of the phenol ring (the HOMA index decrease). The HOMA(phenol) = f[HOSE(chelate)] correlation exhibits a linear correlation of phenol ring dearomatization with the energy required for stabilization of the chelate ring. This correlation is justified for both the *o*-hydroxyaryl ketimines and the ketones, but in the case of the ketones the aromaticity changes are considerably smaller in view of the predominant OH form. An

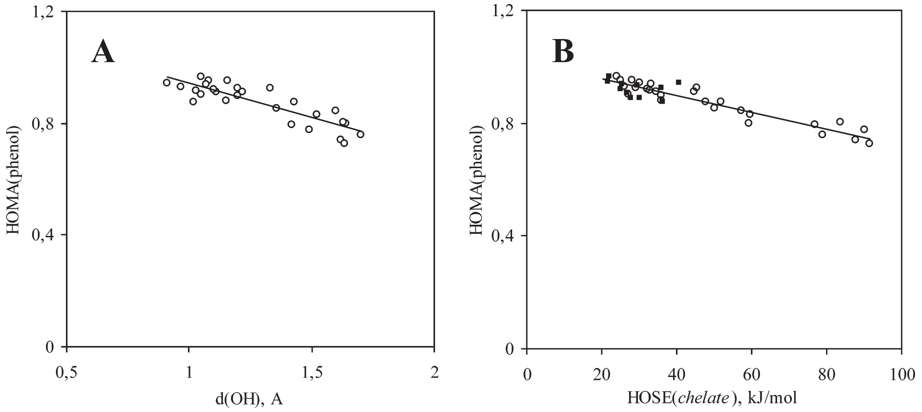


Figure 3. Scatterplot of the HOMA(phenol) aromaticity index versus d(OH) bond length [HOMA(phenol) = $-0.246\,d(\mathrm{OH}) + 1.188$; $R = 0.867$] (A) and the HOSE(chelate) destabilization index [HOMA(phenol) = -0.003HOSE (chelate) + 1.018; $R = 0.951$] (B). Open circles and closed squares correspond to the *o*-hydroxyaryl ketimines[9] and the *o*-hydroxyaryl ketones,[12] respectively

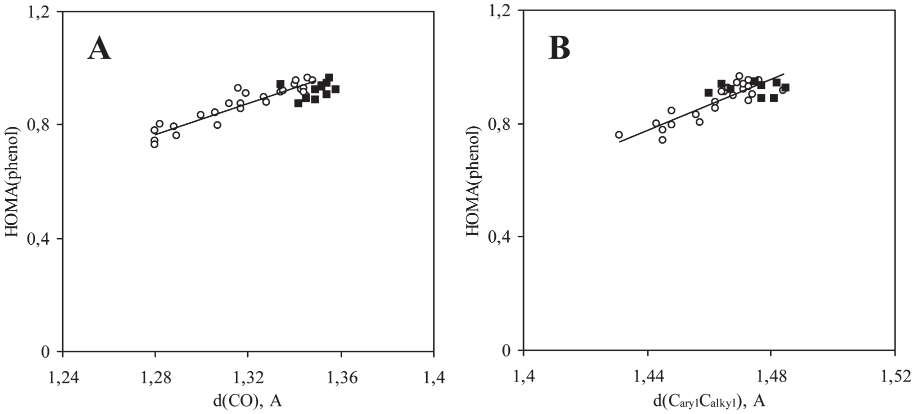


Figure 4. Scatterplot of the HOMA(phenol) aromaticity index *versus* *d*(CO) bond length [HOMA(phenol) = 2.768 *d*(CO) − 2.778; $R = 0.930$] (A) and *d*(C_{aryl}—C_{alkyl}) bond length [HOMA(phenol) = 4.567 *d*(C_{aryl}—C_{alkyl}) − 5.800; $R = 0.875$] (B). Open circles and closed squares correspond to the *o*-hydroxyaryl ketimines[9] and the *o*-hydroxyaryl ketones,[12] respectively

exception from linearity is the aromaticity of the **A** ring of naphthalene derivatives (**BEIN** and ***o*-HIN**), this phenomenon occurring for the reason mentioned above. These facts led us conclude the following: the proton-transfer process induces simultaneous dearomatization of the phenol ring and destabilization of the pseudo-aromatic moiety.

An additional inference can be made on the basis of such correlations as the HOMA(phenol) index versus the CO phenolic bond length and the HOMA(phenol) index versus the C_{aryl}—C_{alkyl} bond length [Fig. 4 (A) and (B)]. The shortenings of the C—O and C_{aryl}—C_{alkyl} bonds is preceded by a build-up of π-electronic density along these bonds that results in distortion of the π-electronic component of the phenol ring and loss of aromaticity. What is important to emphasize is that an extremely strong distortion of the π-electronic component of the aromatic **A** ring belonging to the α-hydroxynaphthyl analogues leads to a reduction in the C—O and C_{aryl}—C_{alkyl} bond lengths and, consequently, to stabilization of the NH form.

CONCLUSIONS

Five structurally similar compounds were been studied by x-ray diffraction and DFT calculations. On the basis of these methods, the prevailing NH form in 2-(*N*-methyl-α-iminoethyl)naphthol and the OH form in the *o*-hydroxy ketones has been demonstrated.

A significant reduction in hydrogen bond length caused by the buttressing effect in 6-methoxy-2-hydroxyacetophenone has been shown.

A peculiarity of the hydrogen bonding under study rests on the relations between the proton-transfer process and the aromaticity of the system. The proton-transfer process stipulates destabilization of the chelate chain and distortion of π-electronic coupling in the phenol ring. Concerning the naphthyl analogues, their reaction to proton transfer is more specific. In *o*-hydroxyacetonaphthoneimine one observes a significant decrease in the aromaticity of the ring adjacent to the chelate bonding, whereas the remote ring's aromaticity increases. The presence of π-electronic balance between adjacent aromatic rings facilitates obtaining the NH form.

Supplementary material

Table 1S: Crystal data and structure refinement for **o-HIN**, **6OMeK**, **4OMeK**, **5Cl4MeK** and **o-HAN**, availale in Wiley Interscience.

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