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Structural and aromatic aspects of tautomeric equilibrium in hydroxy aryl Schiff bases[†]

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The synthesis and X-ray measurements of four Schiff bases were carried out at 100 K. The HOMA and HOSE aromaticity indices were estimated on the basis of the experimental data. The aromaticity of the phenyl ring and the chelate chain was analysed. A comparison of the aromaticity of naphthalene and phenyl derivatives of hydroxy aryl Schiff bases is presented. The balance between the aromaticity of adjacent rings of the naphthalene fragment and its effect on proton transfer is defined. Research on the interrelations between aromaticity and the intramolecular proton transfer in hydroxy aryl Schiff bases is shown. Copyright © 2008 John Wiley & Sons, Ltd.

Keywords: intramolecular hydrogen bonding; crown ether; proton transfer; Schiff base; aromaticity; HOMA and HOSE indices

INTRODUCTION

Intramolecular quasiaromatic hydrogen bonding[1] and the aromaticity notion are studied in this paper.[2–12] Lately these phenomena have aroused great interest and difference of opinion.[13–27] Gilli *et al*.[13] introduced a contemporary definition of a resonance-assisted hydrogen bond (RAHB) and conducted an investigation of quasiaromatic bonding on the basis of both VB theory and crystallographic studies.[13,14] According to Reference [15], RAHB is found in the intramolecular as well as in the intermolecular hydrogen bond. This confirmation corroborates the opinion suggested in Reference [16]. This phenomenon rests upon conjugation through the hydrogen bridge and the chelate chain,[17] which leads to smoothing of the acid-basic equilibrium. The existence of π-electronic coupling in the chelate chain influencing the X—H bond was presented by Grabowski[18] by means of quantum mechanical calculations. It should be underlined that coupling through the hydrogen bridge was not predicted in that paper. However, some divergences were found in References [20,21], where a significant negative charge on the protono-donor and the protono-acceptor was determined. Recently, the existence of RAHB was questioned by Elguero and Del Bene,[22,23] who showed that a quasiaromatic formation fails to change the coupling constant $^1J(XY)$, which is an indicator of hydrogen bond strength.[24] It is noteworthy that the discussion of the existence of π-electronic coupling via a hydrogen bond is not new. Shygorin,[16] who was a pioneer in discovering significant strengthening of hydrogen bonding under quasiaromatic assistance (saturation of a chain closed by a hydrogen bridge with p-electrons), explained this phenomenon by π-electronic conjugation in the chain as well as via a hydrogen bridge. With respect to π-electronic coupling through the hydrogen bridge, its existence was questioned by Luckiy,[25,26] who supported the opinion about hydrogen bonding assistance by π-electronic conjugation in a chelate chain, but rejected π-electronic assistance via a hydrogen bridge (using semi-empirical calculations and measurement of ionization potential). One should note that the visible decrease in the ν(XH) band's integral intensity in IR spectra of *o*-hydroxy aryl Schiff bases (with quasiaromatic formation) compared with *o*-hydroxy aryl Mannich bases (without quasiaromatic formation) and complexes of phenols with amines[27] definitely corroborates the existence of quasiaromatic formation and its uniqueness. The specificity of *o*-hydroxy aryl Schiff bases is also exposed through the phenyl ring's aromaticity, which decreases upon proton transfer,[7,28] similar to the complexes of phenols with amines.[29]

This paper reports on studies of the interrelation between the hydrogen bridge, the chelate ring (O—C=C—C=N) and aromatic formations. In a previous paper[7] we investigated the change in aromaticity in *o*-hydroxy phenyl Schiff bases depending on tautomeric equilibrium (Scheme 1). In this paper we widened the range of our research, completing it with naphthalene derivatives and comparing them with phenyl derivatives.

EXPERIMENTAL AND COMPUTATIONAL

The synthesis of the hydroxy aryl Schiff bases from stoichiometric mixtures of ketones and anilines in methanol was performed according to Reference [30].

The intensity data were collected at 100 K using a Kuma KM4CCD diffractometer and graphite-monochromated MoKα (0.71073 Å) radiation generated by an X-ray tube operating at 50 kV and 35 mA. The images were indexed, integrated and

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[†] *This paper is dedicated to Professor T.M. Krygowski on the occasion of his 70th birthday.*

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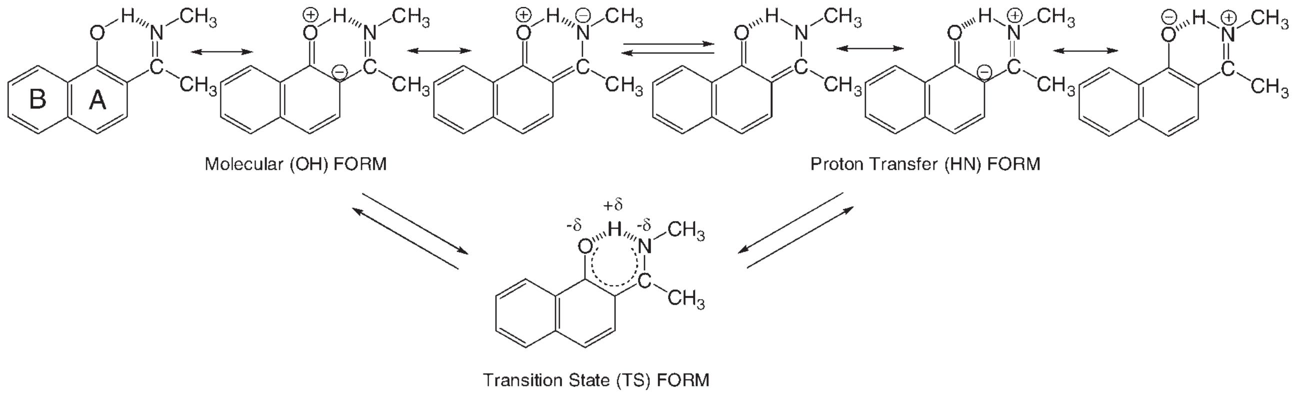


Scheme 1. A scheme of tautomeric equilibrium in *o*-hydroxy aryl Schiff bases

scaled using the KUMA data reduction package.[31] The data were corrected for Lorentzian and polarization effects. Absorption correction was omitted. The structure was solved by direct methods using SHELXS97[32] and refined by the full-matrix least-squares method on all F^2 data (SHELXL97).[33] Non-hydrogen atoms were refined with anisotropic thermal parameters; hydrogen atoms were included from $\Delta\rho$ maps and refined isotropically. CCDC-679628 for α-phenyl-4-(5′-chloro-2′-hydroxybenzalamino) benzene (**I**), CCDC-679627 for *N*-(4′-benzo-15-crown-5)-3,5-dichloro-2-hydroxyphenylaldimine (**II**), CCDC-679626 for 2-(1-phenylamino-ethyl)-naphthalene-1-ol (**III**) and 679625 for 1-[(4′-cyanophenylimino)methyl]-2-naphthol (**IV**) 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) 1123-336-033; e-mail: deposit@ccdc.cam.ac.uk.

The HOMA and HOSE aromaticity indices were calculated by the following formulae:[34,35]

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

where n is the number of bonds, α an empirical constant and R_{opt} and R_{i} the optimal and individual bond lengths taken from Reference [36].

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

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 the single and double bonds, respectively. The reference single and double bond lengths R_0^{s} and R_0^{d} were taken from Reference [36]. The force constants were calculated as $k_r = \mathrm{a} + \mathrm{b}R_r$. The constants a and b were taken from Reference [36]. The higher the HOMA aromaticity index with respect to the more aromatic formation, the more delocalized the π-electrons of the formation. The HOSE index means the energy required to stabilize an aromatic formation up to the standard state, in our case the energy required to feedback a chelate formation to an enol-imine state (O—C=C—C=N).

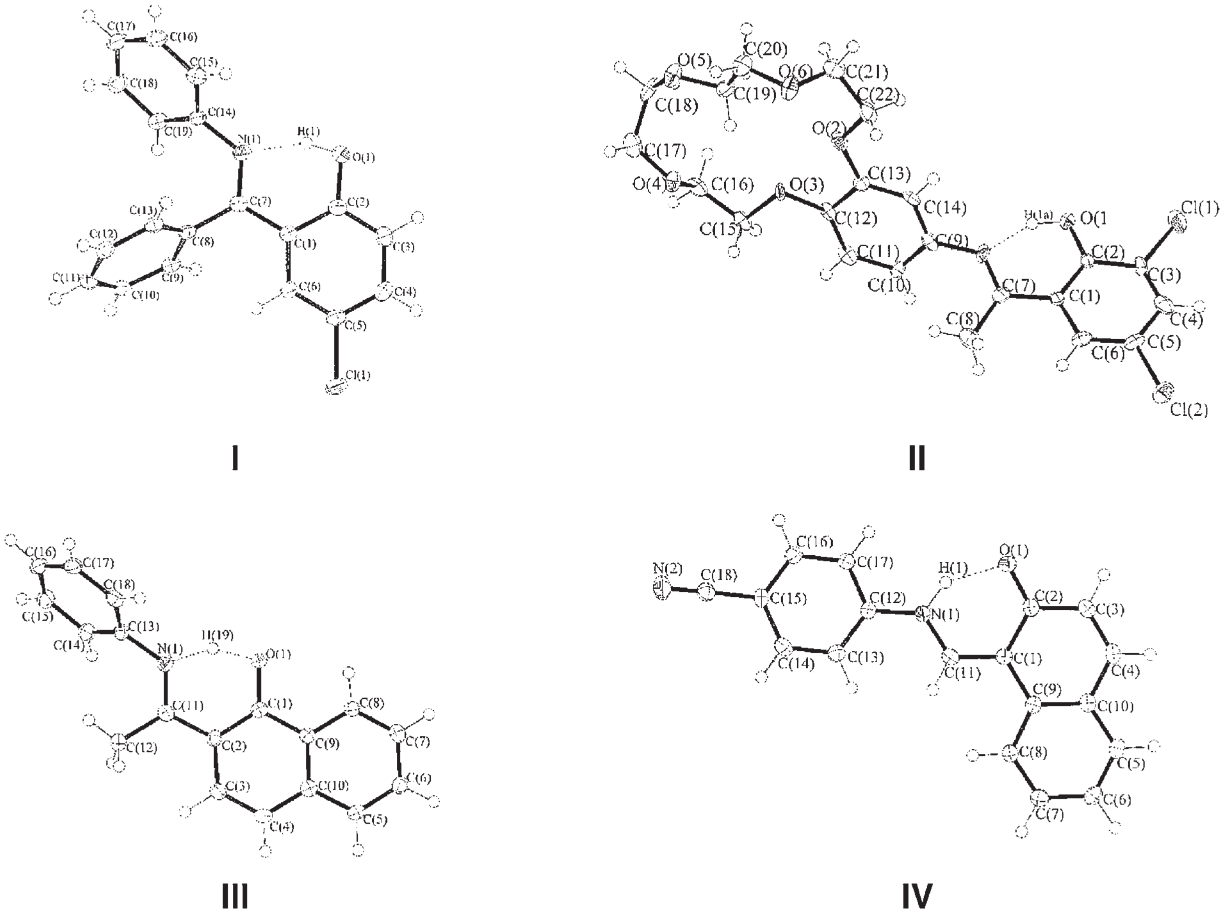
It is necessary to note that in the calculations of the HOMA and HOSE aromaticity indices, the OH and H…N bonds were not taken into account due to the absence of π-electronic coupling via a hydrogen bridge (as stated in References [22,23,25,26]).

RESULTS AND DISCUSSION

The molecular structures with atom labelling are presented in Fig. 1.

Structural aspect of tautomeric equilibrium

The structure of the hydroxy aryl Schiff bases in the OH form dominates over the HN form in the Cambridge Crystallographic Database.[37] The described phenyl and naphthalene derivatives of the hydroxy aryl Schiff bases embrace three tautomeric forms: the OH, the HN and the LBHB (low-barrier hydrogen bonds) forms. The structures of compounds **I** and **II** show prevalence of the OH form. This phenomenon is supported by both the location of the hydrogen atom close to the nitrogen atom in the hydrogen bridge and the lengths of the C—O and C=N bonds (the extended C—O bond and the reduced C=N bond) which correspond to the lengths of the bonds of the OH form.[38] The prevalence of the OH form is conditioned by the weakened basicity of the nitrogen atom resulting from the electron-withdrawing activity of the phenyl ring. This phenomenon takes place despite the strong acidity of the hydroxyl group due to the chlorine substituents in the phenol moiety. We observed the HN form for these substituents in the *N*-alkyl derivatives of the *o*-hydroxy aryl Schiff bases.[39] The structure of compound **III** reveals the prevalence of the LBHB form, and equalization of the bonds in the chelate chain also supports this fact. One should underline that there are very few structures of such type of *o*-hydroxy aryl Schiff bases in the Cambridge Crystallographic Database[37] and they were obtained only for the *o*-hydroxy aryl ketimines.[39–42] The next compound (1-[(4′cyanophenylimino)methyl]-2-naphthol) presents the HN form in the solid state, which is unexpected: a compound without cyanic substitution (1-[(phenylimino)methyl]-2-naphthol) takes the OH form,[43–45] whereas a cyanic substituent must weaken the nitrogen atom basicity on account of the –M mesomeric and –I inductive effects. The paradoxical observation of the proton transfer is explained by the coupling of two resonances (rather reinforced due to the molecule flattening) in the chelate chain



I

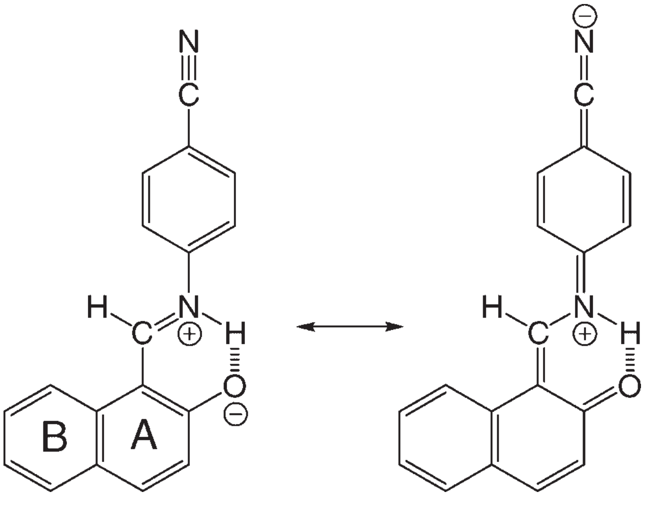
II

III

IV

Figure 1. An ORTEPIII diagram showing the molecular structure and the atom labelling scheme of α-phenyl-4-(5′-chloro-2′-hydroxybenzalamino)-benzene (**I**), *N*-(4′-benzo-15-crown-5)-3,5-dichloro-2-hydroxyphenyl-aldimine (**II**), 2-(1-phenylamino-ethyl)-naphthalene-1-ol (**III**) and 1-[(4′-cyanophenylimino)methyl]-2-naphthol (**IV**). 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

and the cyanic group (Scheme 2), as well as the influence of crystal packing and short contacts ($d(H_5O_1) = 2.57(2)$ Å, $d(H_{13}N_2) = 2.55(2)$ Å, $d(H_{17}O_1) = 2.50(2)$ Å), leading to the domination of the HN form in compound **IV**.



Scheme 2. A scheme of resonance coupling between cyanic group and chelate chain in 1-[(4́-cyanophenylimino)methyl]-2-naphthol

Evaluating the state of tautomeric equilibrium in the compounds, a transition from the OH form to the HN form is observed according to the sequence **I** → **II** → **III** → **IV**. This sequence is obtained from the changes in the lengths of the C—O and ON bonds. The reduction in the C—O bond according to the sequence ($d(C{-}O) = 1.353(2)$ Å (**I**) $>$ 1.333(8) Å (**II**) $>$ 1.312(2) Å (**III**) $>$ 1.274(2) Å (**IV**), Table 1) indicates the increase in the quinonoid form. This sequence is also consistent with the changes in hydrogen bridge length: the strengthening of the hydrogen bond from the OH form to the transition state form ($d(ON) = 2.516(2)$ Å (**I**) $>$ 2.493(6) Å (**II**) $\cong$ 2.496(2) Å (**III**), Table 1) and the proton transfer of the HN form ($d(ON) = 2.555(2)$ Å (**IV**), Table 1). However, this trend is not in full agreement with the sequence for the C=N bond ($d(C{=}N) = 1.281(6)$ Å (**II**) $<$ 1.301(2) Å (**I**) $<$ 1.318(2) Å (**III**) $<$ 1.330(2) Å (**IV**), Table 1) owing to the elongated C=N bond for compound **I**. Such a 'discrepancy' is grounded on a mesomeric effect of the phenyl ring attached to the C7 atom of compound **I** (Fig. 1), which brings about elongation of the C=N bond. The aforesaid observations state that the most reliable characteristic in the evaluation of tautomeric equilibrium in the hydroxy aryl Schiff bases appears to be the C—O bond. This fact is consistent with the inference for the hydrogen bonding complexes of phenols with pyridines.[46] Another common feature of the studied hydroxy aryl ketimines (**I**, **II**, **III**) and the hydroxy naphthalene aldimine (**IV**) is the *N*-phenyl

Table 1. Selected bond lengths (Å) and angles (°) hydrogen bonds at 100 K (*esds* in parentheses) and the HOMA, HOSE aromaticity indices

Compound	Form	d(OH)	d(HN)	d(ON)	α(OHX)	d(CO)	d(CN)	d(C_1C_2)	d($C_{aryl}C_{im}$)	HOMA(**A**)	HOMA(**B**)	HOSE(**A**)	HOSE(**B**)	HOMA(ch)	HOSE(ch)
I	O–H...N	0.93(3)	1.65(3)	2.516(2)	154(3)	1.353(2)	1.301(2)	1.418(2)	1.469(2)	0.934	—	32.1	—	0.189	26.2
II	O–H...N	0.97(6)	1.58(6)	2.493(6)	155(6)	1.333(8)	1.281(8)	1.419(8)	1.473(9)	0.917	—	30.4	—	0.239	34.8
III	O...H...N	1.28(3)	1.32(3)	2.496(2)	148(2)	1.312(2)	1.318(2)	1.412(3)	1.448(9)	0.559	0.881	69.9	38.4	0.604	52.5
IV	O...H–N	1.68(2)	1.01(2)	2.555(2)	143(2)	1.274(2)	1.330(2)	1.455(2)	1.396(2)	0.198	0.911	93.7	40.0	0.703	117.5

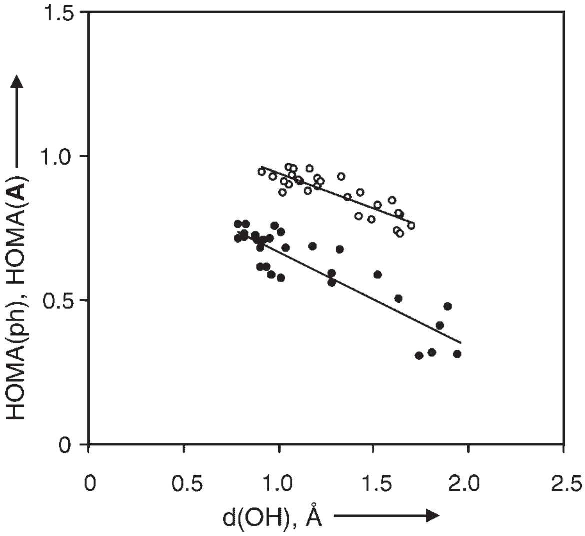


Figure 2. Scatter plot of the HOMA(ph) and HOMA(**A**) aromaticity indices *versus* d(OH) bond length. Open and filled circles correspond to the phenyl (data taken from Reference [7]) and naphthalene derivatives of hydroxy Schiff bases, respectively.

fragment. However, this fragment behaves differently for different compounds. In hydroxy naphthalene aldimine, this ring lies in the plane of the naphthalene fragment in view of the strong π-conjugation which, in turn, is disrupted in the hydroxy aryl ketimines because of the steric effect of the methyl group (**II**, **III**) or the phenyl ring (**I**).

Aromatic aspect of tautomeric equilibrium

This section presents the dependences of aromaticity on tautomeric equilibrium. Figure 2 features two correlations: the phenyl ring's aromaticity *versus* the hydroxyl bond length (HOMA(ph) = f(d(OH)) and the **A** naphthalene ring's (ring adjacent to the chelate chain, Scheme 1) aromaticity *versus* the hydroxyl bond length (HOMA(**A**) = f(d(OH)). It is important that the length of the hydroxyl bond can be used as an indicator of the degree of proton transfer in a hydrogen bridge and an estimation of the tautomeric equilibrium. The observed correlations are linear in approximation both for the phenyl ring and the **A** ring's aromaticity. However, a significant difference is seen between the behaviour of the **A** ring's aromaticity of the naphthalene derivatives and the aromaticity of the phenyl ring. Under the prevalence of the OH form of the phenyl ring, the aromaticity is larger than that of the **A** ring of the naphthalene derivatives (ΔHOMA $\approx$ 0.25). This phenomenon is well grounded considering the smaller aromaticity of the naphthalene rings (HOMA $\cong$ 0.8)[36] with respect to the aromaticity of the benzene ring (HOMA $\cong$ 1).[36] However, a much larger difference is seen for the HN form (ΔHOMA $\approx$ 0.45), where the HOMA index is ~0.3 for the naphthalene derivatives and ~0.75 for the phenyl ones. This reveals a larger loss of the **A** ring's aromaticity compared with the phenyl ring's aromaticity under the proton transfer process. Assuming aromaticity as a criterion of the degree of proton transfer (HOMA(ph) = f(d(OH)), we can confirm that the HN form is easier to reach in the naphthalene derivatives than in the phenyl ones. This can be explained by the HOMA(**A**) = f(HOSE(ph)) and HOMA(**B**) = f(HOSE(ch)) dependences (Fig. 3),

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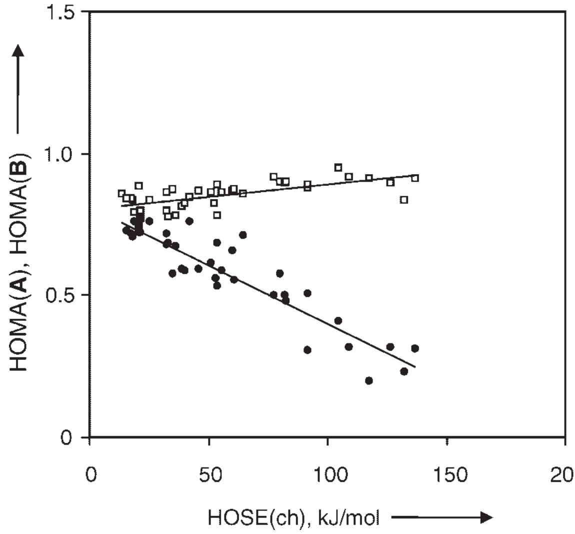

Figure 3. Scatter plot of the HOMA(**A**) and HOMA(**B**) aromaticity indices *versus* the HOSE(ch) index. Black circles and open squares correspond to the **A** and **B** naphthalene rings, respectively

which establish that the proton transfer process (the increasing HOSE(ch) value[7]) brings about a weakening of the **A** ring's aromaticity on the one hand and an increase in the **B** ring's aromaticity on the other. The above comparison of the phenyl and naphthalene derivatives shows that the aromaticity balance between the **A** and **B** rings enhances the destabilization (according to the HOSE index) of the chelate chain, namely the OH form, and facilitates the proton transfer process. These considerations speak in favour of a larger efficiency of the resonance assistance between the chelate chain and the aromatic formation adjacent to the chelate chain. As for the hydroxy aryl Schiff bases it is reasonable to divide the π-electronic resonances into two: the first being in the chelate chain and the second between π-conjugation in the chelate chain and an aromatic formation (phenyl, naphthalene formation and so on).

The difference is also characteristic of the HOMA(ph) = *f*(HOSE(ch)) and the HOMA(**A**) = f(HOSE(ch)) correlations (Fig. 4). This figure features two correlations for the phenyl and naphthalene derivatives. Values of the HOMA and HOSE indices for particular tautomeric forms are different for the phenyl and naphthalene derivatives, respectively. For phenyl derivatives the HOSE(ph) index is within the range of $\approx$30–40 kJ/mol for the OH form and $\approx$70–100 kJ/mol for the HN form; the HOMA(ph) index is found within the range of $\approx$1–0.9 for the OH form and $\approx$0.8–0.7 for the HN form. For the naphthalene derivatives, these values are different: the HOSE(**A**) index is within the range of $\approx$20–60 kJ/mol for the OH form and $\approx$80–140 kJ/mol for the HN form; the HOMA(**A**) index is found to be within the range of $\approx$0.8–0.5 for the OH form and $\approx$0.5–0.2 for the HN form. Based on these data we confirm that the HOMA and HOSE aromaticity indices can be applied in estimating the prevalence of a particular tautomeric form for a particular aromatic formation (phenyl or naphthalene etc).

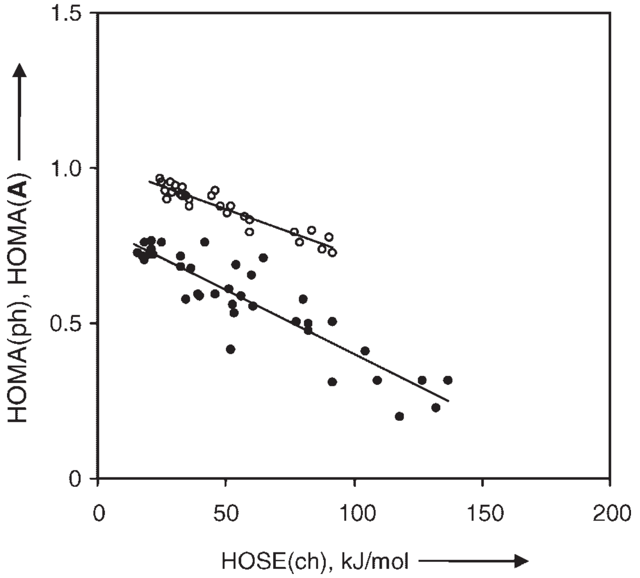

Figure 4. Scatter plot of the HOMA(ph) and HOMA(**A**) aromaticity indices *versus* the HOSE(ch) index. Open and black circles correspond to the phenyl (data taken from Reference [7]) and naphthalene derivatives of hydroxy Schiff bases, respectively

The most interesting is the nonlinear HOMA(ph), HOMA(**A**) = f(HOMA(ch)) dependence, which demonstrates that a transition from the OH tautomeric form to the HN tautomeric form calls forth a decrease in the phenyl ring's aromaticity and an increase in the chelate chain's aromaticity. Noticeably, the chelate chain's aromaticity of the HN form is approximately stable, whereas the phenyl ring's aromaticity tends to decrease. The explanation for this phenomenon lies in the re-distribution of the rate of the canonical structures for the HN tautomeric form. The growing prevalence of the keto-amine canonical structure causes a weakening of the **A** naphthalene ring's aromaticity (this confirmation is well substantiated for the phenolic complexes in papers by Krygowski[2,29]), while the re-distribution between the zwitter-ionic canonical structures and the keto-amine canonical structures hardly changes the chelate chain's aromaticity. This reasoning gives proof of the rational use of canonical structures in the description of the proton transfer tautomeric form in the hydroxy aryl Schiff bases (Fig. 5).

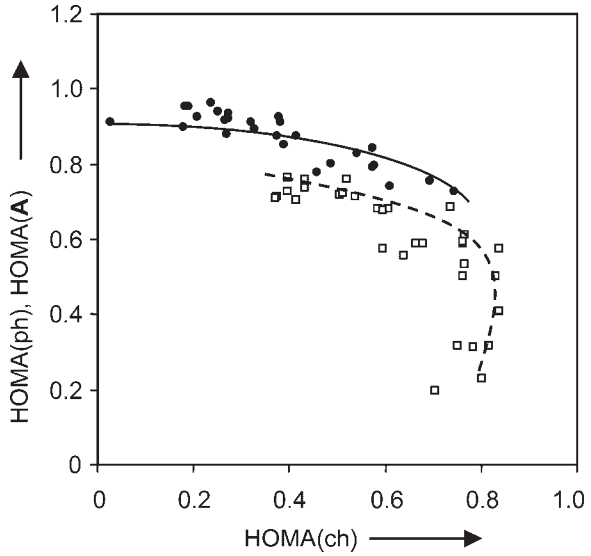

Figure 5. Scatter plot of the HOMA(ph) and HOMA(**A**) aromaticity indices *versus* the HOMA(ch) index. Black circles and open squares correspond to the phenyl and naphthalene hydroxy Schiff bases, respectively

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CONCLUSIONS

This paper scrutinized crystallographic structural data of four hydroxy aryl Schiff bases in three different tautomeric forms. The crystallographic structure of the *o*-hydroxy aryl Schiff base in combination with crown ether was solved for the first time. Compounds of this type can serve as light-optical switches,[47] elements of electronic memory[48] and biologically active compounds.[49] The analysis of the structural parameters of the hydroxy aryl Schiff bases was completed for tautomeric forms. It was found that the CO bond is the most reliable characteristic for defining tautomeric equilibrium.

We accomplished an analysis of aromaticity with the assistance of the HOMA and HOSE aromaticity indices of the phenyl and naphthalene derivatives of the hydroxy aryl Schiff bases. It was shown that the intramolecular proton transfer process in the hydroxy naphthalene Schiff bases brings a simultaneous decrease in the **A** ring's (adjacent to the chelate chain) aromaticity and an increase in the aromaticity of the **B** ring (distant from the chelate chain). Moreover, it was found that the aromatic system, strongly coupled with the chelate formation, plays an important role in describing tautomeric equilibrium.

The logical reasons for the rational use of canonical structures in describing tautomeric equilibrium in Schiff bases were elucidated. The aromaticity balance was studied: the increase in π-electron delocalization in the chelate chain during the decrease in π-electron delocalization in the adjacent aromatic ring and the increase in π-electron delocalization in the distant aromatic ring under the shift of tautomeric equilibrium into the direction of the proton transfer form.

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