Theoretical study on the intramolecular hydrogen bond in chloro-substituted \(N,N\)-dimethylaminomethylphenols.

I. Structural effects

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Received 12 November 2003; revised 2 December 2003; accepted 2 December 2003

Abstract

Ab initio and density functional calculations are applied to study the influence of an increasing number of chlorine substituents on the properties of the intramolecular hydrogen bond in substituted Mannich bases. It is shown, that not only the acidity of the proton donor, which depends on the number of chlorine atoms at the aromatic ring, but also steric interactions modify the geometry of the hydrogen bond. Specific interactions of O–Cl· · ·H–O hydrogen-bonding in some derivatives are estimated by calculations on related chlorophenols.

Keywords: Ab initio calculations; DFT methods; Mannich bases; Intramolecular hydrogen bonding; Substituent effects

1. Introduction

Studies on intramolecular hydrogen bonding have become increasingly popular in the past [1–24]. These systems are attractive because they have a quite high thermodynamic stability and a uniform structure [20–25]. The stability of intramolecularly hydrogen-bonded complexes allows to perform experimental studies in a wide range of temperatures and solvents. This feature facilitates the interpretation of proton transfer reaction studies [22,23].

Many investigations on the structure and on the spectroscopy of intramolecular hydrogen bonds are devoted to molecules with \(\pi\)-electronic coupling between the acid and base centres, attached to the same aromatic ring [1–19]. In such systems, e.g. Schiff bases, the intramolecular proton transfer reaction proceeds comparatively easily. One can observe double fluorescence [26] as well as thermochromic and photochromic properties [27] related to it. These molecules are potent materials for molecular memory and optical switch devices [28] or fluorescent probes of biological systems [29]. In these molecules, intramolecular electron coupling leads to a strengthening of the hydrogen bonds in so-called resonance assisted hydrogen bonds [30].

In the past, we have studied the properties of intramolecular hydrogen bonding in model systems of a more general character—in ortho-hydroxy-\(N\)-alkylaminomethylphenols, so called Mannich bases [20–24]. Due to the presence of a methylene bridge between proton donor and proton acceptor parts of the molecule, the \(\pi\)-electronic coupling between acid and base centres in these compounds is reduced to a high extent.

In the previous works of this series [31,32], the properties of the intramolecular hydrogen bond of the simplest possible Mannich bases, ortho-aminomethylphenol (AP), and \(N\)-dimethyl-ortho-aminomethylphenol (DMAP) were studied, applying ab initio and density functional methods for the analysis of the IR spectra and the structure modifications upon the formation of the intramolecular hydrogen bonding. These results have been compared to the properties of the monosubstituted benzene subunits, phenol (PH), benzylamine (BA) and dimethylbenzylamine (DMBA). We have found, however, that the comparison of quantum mechanical calculations of the structure and
force constants of the hydrogen bonded and related open conformers is a more promising way to study the spectroscopic and structural consequences of intramolecular hydrogen bonding. It was demonstrated that the intramolecular hydrogen bond in Mannich bases reveals changes characteristic for the participation of ortho-quinonoid resonance structures despite the strong reduction of π-electronic coupling within those molecules. The pattern of both the structure and force constants changes was highly consistent.

The aim of the present work is to extend the study of the previously established effects of intramolecular hydrogen bond formation to molecules with stronger intramolecular interactions, as a function of increasing acidity of the phenolic part of the molecules. We have selected the four N-dimethylaminomethylphenols substituted with one to four chlorine atoms at the phenol ring: 2-N-dimethylamino-4-chlorophenol (1), 2-N-dimethylaminomethyl-4,6-dichlorophenol (2), 2-N-dimethylaminomethyl-3,4,6-trichlorophenol (3) and 2-N-dimethylaminomethyl-3,4,5,6-tetrachlorophenol (4). The unsubstituted compound (DMAP (0)) was also considered for comparative reasons (Scheme 1).

The acidity of the phenolic part of the Mannich bases increases gradually with the number of chlorine atoms [33]. In accordance to that, the values of \( \Delta pK_a = [pK_a(BH^+) - pK_a(AH)] \), commonly used [34–36] in the analysis of the properties of hydrogen bonds, increases too. As the basic part of the molecule (the N-dimethylaminomethyl group) does not change, the influence of the acidic part on the hydrogen bond can be followed directly. We have correlated the calculated structural parameters of the intramolecular hydrogen bond with the experimentally established trends when varying the extent of the chlorine substitution, expressed by \( \Delta pK_a \).

In the case of chloro-substituted Mannich bases, no experimental information on the gas phase structures is available. A direct comparison with structures derived from the ab initio calculations is, therefore, impossible. Some crystal structures of these compounds are known. The X-ray data were recently reviewed and correlated with the \( \Delta pK_a \) scale [22]. The detailed comparison of experimental and calculated structures by ab initio and DFT methods will be presented elsewhere [37].

Generally, it was found that the calculated values reproduce the experimental trends quite well and in most cases also the numerical values of the parameters, especially if one considers some increase of the strength of hydrogen bonding in condensed phases due to polarization effects as well as the long range interactions, which are mainly of attractive character.

2. Computations

The quantum chemical calculations were performed with the GAUSSIAN 98 program package [38]. Full geometry optimisation was performed at MP2 and B3LYP levels with the 6-31G(d,p) basis set and by B3LYP/D95(d,p).

3. Results and discussion

3.1. Comparison of the structural parameters in the hydrogen bonded and open conformers

In previous detailed analyses it was shown [31,32], that convenient measures of the structural changes upon formation of intramolecular hydrogen bonds are the differences between closed and open conformers, where the effect of mutual, electronic interactions between substituents is eliminated to high extent. For these reasons, we have optimised the structures of hydrogen bonded and open forms of the selected Mannich bases with various chlorine substituents. The open forms were obtained by rotation of the O–H bond around the C–O axis by 180° as well as by rotation of the methylamino group by 180° around the C2–C7 bond (Scheme 2).

3.1.1. Bond lengths

Previous studies [31,32] have indicated, that the most sensitive structural parameters upon intramolecular hydrogen bond formation are the O–H, C–O, C1–C2 and C2–C7 bond lengths. Changes in O–H and C–O bonds are direct consequences of the formation of hydrogen bonds, whereas C1–C2 and C2–C7 distance changes can be more related to intramolecular rearrangement and to steric and electronic interactions. If only the acid–base interaction determines the structures, one can expect some smooth correlation of these parameters on \( \Delta pK_a \). Steric interactions and specific influence of particular substituents may cause some irregularities for such a correlation.

The dependence of the O–H bond length on \( \Delta pK_a \) for the open and hydrogen bonded conformers, calculated at three different levels of theory, are presented in Fig. 1a. The \( pK_a \)
values used for particular compounds are: 9.92 for phenol, 9.30 for \textit{p}-chlorophenol, 8.45 for \textit{o}-chlorophenol, 7.80 for 2,4-dichlorophenol, 7.05 for 2,4,5-trichlorophenol and 6.24 for 2,3,4,5-tetrachlorophenol \cite{33}. The \( pK_a \) of \( N \)-dimethylbenzylamine was taken as equal to 8.9 \cite{39,40}.

Evidently, there are separate groups of points for the open and hydrogen bonded conformers. The influence of the number of substituents on the length of the O–H bond in the open forms seems to be rather limited. A small increase of this distance observed for the molecules able to form an alternative hydrogen bond to an \textit{ortho}-positioned chlorine atom in the open forms of \( 2,3 \) and \( 4 \) is probably resulting from these weak interactions. The average effect of the O–H· · ·N hydrogen bond formation on the O–H bond length is about 0.026 Å in DMAP and reaches 0.036 Å in \( 4 \). The tendency to elongation of this bond upon increase of the phenol acidity in hydrogen bonded conformers is evident from the presented correlations. However, to obtain the ‘pure’ effects of the O–H· · ·N hydrogen bonding, the influence of the O–H· · ·Cl hydrogen bonds have to be independently estimated in the open forms of compounds \( 2–4 \).

The dependence of C–O bond lengths on \( \Delta pK_a \) is somewhat smaller but of similar magnitude as for the H–O

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig1}
\caption{(a) Dependence of calculated O–H bond lengths (in Å) on \( \Delta pK_a \) of Mannich bases 0–4. (0 = DMAP, 1 = 4-chloro-DMAP; 2 = 4,6-dichloro-DMAP; 3 = 3,4,6-trichloro-DMAP; 4 = 3,4,5,6-tetrachloro-DMAP. (b) Dependence of calculated C–O bond lengths (in Å) on \( \Delta pK_a \) of Mannich bases 0–4. Open symbols represent the structural data of the open form of Mannich bases, filled symbols stand for hydrogen-bonded Mannich bases (squares—B3LYP/6-31G(d,p); circles—B3LYP/D95(d,p); triangles—MP2/6-31G(d,p)).}
\end{figure}
bond length (0.016 Å per $pK_a$ units, Fig. 1b), but the bond lengths decrease with increasing $\Delta pK_a$. Our calculations show that this is not specific for hydrogen bonding, as in the case of the open species similar tendencies as a function of $\Delta pK_a$ are observed. Nevertheless, some additional decrease of the order of 0.015 Å, resulting from the O–H · · · N hydrogen bond formation is observed.

One may especially stress a different behaviour the O–H and C–O bond lengths on the substitution. The length of the O–H bond is not sensitive to the number of chlorine substituents unless the group is not hydrogen bonded, while the C–O bond is equally sensitive in both conformers. The position of the points on the graphs (Fig. 1) for the open forms of compounds 2–4 also depends on the O–H · · · Cl hydrogen bond formation. In order to follow these effects, one should compare to calculations for the open and hydrogen-bonded forms of chloro-substituted, related phenols.

The C1–C2 distance, as it was shown previously [32], is affected by two factors. First, there is an increase of the ortho-quinonoid resonance structure in the ground electronic state after formation of intramolecular hydrogen bond. Secondly, an increase of the surroundings rigidity occurs due to formation of the chelate ring. Both effects should lead to an increase of the length of this bond, evidently mirrored a corresponding decrease of the related force constant (cf. [31,32]).

In the series of compounds 0–4, an increase of 0.007 ± 0.002 Å of this bond length is observed (Table 1).

All applied methods, in average, do not predict any increase of these differences with $\Delta pK_a$ in molecules 0–2. However, a larger increase is observed for compounds 3 and 4. Some irregular changes in bond lengths observed in the last compounds are resulting probably from steric interaction of chloro-substituents located at position 3. It can influence also the other dependences on $\Delta pK_a$ (see further).

Generally, the C2–C7 distances should be shortened upon intramolecular hydrogen bond formation as a consequence of the participation of this bond in ortho-quinonoid resonance structure in closed conformers [31]. This was indeed observed for compounds 0–2. (Table 2).

In the contrary, for compounds 3 and 4 an increase of this bond length was obtained. Steric interaction of the chlorine atom substituted at position 3 is probably responsible for that. Although, the changes of the bond length on chlorine substitution are small, no correlation with $\Delta pK_a$ can be seen.

O· · ·N and H· · ·N distances are directly related to the strength of the hydrogen bonding, and are commonly used as indicators of hydrogen bond formation. Fig. 2 shows the dependence of O· · ·N and H· · ·N distances on $\Delta pK_a$ in the closed forms of Mannich bases. Evidently, there is an increase of the hydrogen bond strength with $\Delta pK_a$.

Interestingly, a stronger decrease of both O· · ·N and H· · ·N distances is observed for compounds 3 and 4, where a chlorine substituent is located next to N-dimethylaminomethyl group. Some external squeezing of the chelate ring by this substituent leads to an additional increase of the hydrogen bond strength. This effect can be related to the shortening of the hydrogen bonds in sterically modified ortho-hydroxy Schiff bases [11].

It is not possible to correlate the O· · ·N and H· · ·N distances with $\Delta pK_a$ for the open conformers, because they mainly depend on steric interactions, similar to the NCCC torsional angle.

### 3.2. The effects of the intramolecular hydrogen bonding to ortho-chloro-substituents

The results of the structure calculations of all parent (to studied Mannich Bases) phenols and ortho-chlorophenol (applied to increase the data set for correlations) are presented in Fig. 3a and b.

Fig. 3a presents the correlation of the O–H distances with the $pK_a$ values of the phenols. This parameter is linearly related to $\Delta pK_a$ of Mannich bases because of the constant value of $pK_a$ (BH$^+$), benzylamine in our case.

The O–H distances in phenol and chlorine substituted phenols show a negligible dependence on their $pK_a$ values. There exists a difference between the distances of the open and the hydrogen-bonded forms, but much less than in Mannich bases, indicating a much weaker hydrogen bond between the acidic proton and the chlorine atom in ortho position. A dependence of the C–O distances on the $pK_a$ values of phenols can be observed, similar to Mannich bases but significantly smaller. The values for the open phenols (non-hydrogen-bonded forms) are slightly reduced in comparison to the open forms of Mannich bases, those for

### Table 1

<table>
<thead>
<tr>
<th>Compound</th>
<th>B3LYP/6-31G(d,p)</th>
<th>MP2/6-31G(d,p)</th>
<th>B3LYP/D95(d,p)</th>
</tr>
</thead>
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<td></td>
<td>HB Open Diff.</td>
<td>HB Open Diff.</td>
<td>HB Open Diff.</td>
</tr>
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<td>0</td>
<td>1.413 1.406 0.007</td>
<td>1.410 1.403 0.007</td>
<td>1.417 1.409 0.008</td>
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<tr>
<td>1</td>
<td>1.413 1.406 0.007</td>
<td>1.410 1.403 0.007</td>
<td>1.417 1.409 0.008</td>
</tr>
<tr>
<td>2</td>
<td>1.414 1.407 0.007</td>
<td>1.410 1.403 0.007</td>
<td>1.417 1.410 0.007</td>
</tr>
<tr>
<td>3</td>
<td>1.417 1.408 0.009</td>
<td>1.412 1.404 0.008</td>
<td>1.420 1.411 0.009</td>
</tr>
<tr>
<td>4</td>
<td>1.414 1.405 0.009</td>
<td>1.409 1.401 0.008</td>
<td>1.418 1.409 0.009</td>
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</table>
Table 2
C2–C7 distances in the open and hydrogen-bonded (HB) conformers of chloro-substituted Mannich bases, distances in Å

<table>
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<tr>
<th>Compound</th>
<th>B3LYP/6-31G(d,p)</th>
<th>MP2/6-31G(d,p)</th>
<th>B3LYP/D95(d,p)</th>
</tr>
</thead>
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<td>Diff.</td>
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<td>1.519</td>
<td>-0.005</td>
</tr>
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<td>1.519</td>
<td>-0.004</td>
</tr>
<tr>
<td>2</td>
<td>1.516</td>
<td>1.520</td>
<td>-0.004</td>
</tr>
<tr>
<td>3</td>
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<td>0.002</td>
</tr>
<tr>
<td>4</td>
<td>1.520</td>
<td>1.518</td>
<td>0.002</td>
</tr>
</tbody>
</table>

Fig. 2. (a) Dependence of calculated N···O distances (in Å) on ΔpKₐ of Mannich bases 0–4. (b). Dependence of calculated N···H distances (in Å) on ΔpKₐ of Mannich bases 0–4. For the description of symbols see Fig. 1.

Fig. 3. (a) Dependence of O–H bond lengths (in Å) in open and hydrogen-bonded phenols on pKₐ (P₀ = phenol, P₁ = 4-chlorophenol, P₁₀ = 2-chlorophenol, P₂ = 2,4-dichlorophenol, P₃ = 2,4,5-trichlorophenol, P₄ = 2,3,4,5-tetrachlorophenol. (b) Dependence of C–O bond lengths (in Å) in open and hydrogen-bonded phenols. Open symbols for free phenols. Black symbols for phenols forming O–H···Cl hydrogen bond. For the description of symbols see Fig. 1.
the hydrogen-bonded forms show almost identical behaviour. Taking into account the effects of the O–H· · ·Cl interactions, we were able to calculate the pure effects of the increase of the strength of the O–H· · ·N hydrogen bonding.

Fig. 4 presents the corrected, increments in O–H and C–O distances resulting from the formation of O–H· · ·N intramolecular hydrogen bonding as a function of increasing $DpK_a$ values. The dependence of O–H bond lengths on $DpK_a$ has an average slope equal to 0.0024 Å per pK_a unit. Some effects of an additional strengthening of the intramolecular hydrogen bonds by chlorine substitution at position 3 can be seen for compounds 3 and 4. This interaction increases, additionally to above mentioned correlation, the O–H bond length on 0.005 Å.

There exists a pronounced influence of steric enhancement of intramolecular hydrogen bonding due to interaction of the chlorine atoms at position 3. On the other hand, the effects of the increased acid–base interactions on O–H bond length are stronger than on C–O distance. The slope in Fig. 1b is the result of both—direct influence of substituents on the structure (which is also active in phenols) and the influence of electronic interactions between acid–base centres (related to the $DpK_a$).

### 3.3. Phenol ring distortions

In the discussion on the structural effects of the intramolecular hydrogen bond formation in AP (ortho-hydroxyaminomethylphenol) and DMAP we have used some characteristics, which describe changes in the structure of phenol ring. It was found, that the formation of intramolecular hydrogen bond leads to bond length changes in the phenol rings, to a pattern characteristic for ortho-quinonoid resonance structure, suggesting some kind of electron coupling between substituents despite the preventing function of the methylene bridge [31,32].

The effect of bond length modifications can be expressed by means the value of average square of deviations the bond lengths from the mean bond length $d$ in the phenyl ring used later as $A$ parameter.

$$A = \frac{\sum (d_i - d)^2}{6} \times 10^6$$

The values of the parameter $A$ and the average bond lengths are collected in Table 3 for the aromatic rings of all compounds involved in this study.

The average values of bond lengths in the ring, calculated in the procedure of the $A$ evaluation, can be used (Fig. 5) to describe how the substituents influence on the effects of the formation of intramolecular hydrogen bonding.

Two different trends are observed. The first concerns the differences between closed (hydrogen bonded) and open forms. The curves for the closed forms of the Mannich bases are located higher than those of the open forms. The difference reflects the effects of charge migration in the direction of the chelate ring formed. Such an effect was demonstrated directly by dipole moment measurements [41, 42]. Generally, the same dependences can be observed for the series of phenols, although the difference between open and closed forms is much smaller there.

The second observation concerns the general behaviour of the average C–C ring distance with increasing chlorine.
substitution. Relative to benzene, a slight decrease is observed for the first two compounds followed by a stronger increase for the higher substituted compounds. This pattern is observed for the series of Mannich bases as well as for the series of phenols. Comparison with the analogous series of chlorine-substituted benzenes revealed the very same pattern. Mono- and $p$-dichloro-substitutions lead to slight (0.001 and 0.002 Å, respectively) reductions of

<table>
<thead>
<tr>
<th>Compound</th>
<th>B3LYP/6-31G(d,p)</th>
<th>MP2/6-31G(d,p)</th>
<th>B3LYP/D95(d,p)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Closed</td>
<td>Open</td>
<td>Closed</td>
</tr>
<tr>
<td>Benzene</td>
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<td>1.3962</td>
<td></td>
</tr>
<tr>
<td>N-dimethyl benzylamine</td>
<td>1.3972</td>
<td>1.3971</td>
<td></td>
</tr>
<tr>
<td>Phenol</td>
<td>1.3965</td>
<td>1.3959</td>
<td>1.4027</td>
</tr>
<tr>
<td>4-Chloro phenol</td>
<td>1.3954</td>
<td>1.3950</td>
<td>1.4013</td>
</tr>
<tr>
<td>2,4-Dichloro phenol</td>
<td>1.3956</td>
<td>1.3959</td>
<td>1.3953</td>
</tr>
<tr>
<td>2,4,5-Trichloro phenol</td>
<td>1.3966</td>
<td>1.3969</td>
<td>1.3962</td>
</tr>
<tr>
<td>2,3,4,5-Tetra chlorophenol</td>
<td>1.4000</td>
<td>1.4005</td>
<td>1.3994</td>
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<tr>
<td>Pentachloro phenol</td>
<td>1.3964</td>
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<td></td>
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<td>DMAP</td>
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</tr>
<tr>
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<td>1.3994</td>
<td>1.4006</td>
</tr>
<tr>
<td>3,4,5,6-Terpa-DMAP</td>
<td>1.4049</td>
<td>1.4029</td>
<td>1.4039</td>
</tr>
</tbody>
</table>

Fig. 5. (a) Dependence of average ring bond lengths in Mannich bases 0–4 on $\Delta pK_a$. (b) Dependence of average ring C–C bond lengths in chloro-substituted phenols; numbering of phenols is the same as in Fig. 3. For the description of symbols see Fig. 1.
the average C–C distance, whereas the more crowded tri- and tetrachloro-substitutions lead to increases relative to benzene. The effect is strongest in hexachlorobenzene where the calculated average C–C distance is about 0.008 Å larger than in benzene.

The variations of the \( A \) values for Mannich bases and phenols are given in Fig. 6. From Fig. 6a (cf. also Table 3) it follows, that the distortion of the phenol rings (described by the \( A \) parameter) increases with the number of substituted chlorine atoms. Also for the Mannich bases, a substantial increase is seen between the open forms and the closed ones. The last compound in the series, the tetrachloro-substituted Mannich base behaves differently—the \( A \) value decreases drastically. This results from the already mentioned increase of the average C–C distance in the higher substituted rings. Phenols (Fig. 6b) have generally lower values for the parameters \( A \); the values of this parameter also increase with the number of substituted chlorine atoms into ring. There are no anomalies in the correlations at tetrachlorophenol. We have additionally determined the structure of pentachlorophenol by B3LYP/6-31G(d,p) method and found that the parameter \( A \) is equal to 18 and is more than two times less than for tetrachlorophenol (Table 3), which indicates that a full substitution of the aromatic systems results in a more symmetric ring geometry.

Generally, the differences of bond lengths in the rings increase in the series with the number of chlorine substituents, the effect for compounds with intramolecular hydrogen bonding is at least twice as high as than for the related chlorophenols.

4. Summary

In the discussion of the structural consequences of the formation of an intramolecular hydrogen bond in chloro-derivatives of \( N \)-dimethylaminomethylphenol, we intended to analyse the effects of increasing the acidity of the phenolic parts of the molecules, but it appeared that one has to consider carefully a direct effect of the substituents on the structure of the studied compounds in order to explain the structural trends. Because of that, also the modifications of the structural parameters of chlorophenols with \( \Delta pK_a \) were discussed.

The combined analysis of the structure of chloro-substituted Mannich bases and related phenols leads to the following conclusions concerning the influence of increasing the strength of the intramolecular hydrogen bonds as well as of increasing the number of Cl-substituents on the structural parameters.

The O–H distance does not depend on the number of the chlorine substituents in the phenols and Mannich bases, if this group is not engaged in hydrogen bonding, e.g. in the open conformers. When the O–H⋯N hydrogen bonds are formed in the case of the Mannich bases, the O–H distance becomes strongly dependent on the number of introduced substituents, in a way parallel to the increased acidity of the phenol. The observed effect of O–H bond extension in Mannich bases is of the order of 0.015 Å when \( \Delta pK_a \) increases by four units (cf. Fig. 4a). A dependence on the number of substituents was not observed for the O–H⋯Cl hydrogen bonds. There, the effect is one order of magnitude smaller in
phenols forming intramolecular O–H⋯Cl hydrogen bonds (cf. Fig. 3a).

Contrary to this, very distinct effects resulting from both, the formation of the hydrogen bond and the number of chlorine substituents are observed for the C–O distance in the open as well as in the closed forms of Mannich bases. The average distance between correlation lines for the open and closed forms amounts to 0.0015 Å, which can be taken as average effect of the formation of intramolecular O–H⋯N hydrogen bond.

The O⋯N and H⋯N distances show a typical correlation on \( \Delta pK_a \), demonstrating a direct dependence of the strength of hydrogen bonds on the number of chlorine atoms (through changes of \( pK_a \) values). Nevertheless, a discontinuity of the correlation lines is observed (Fig. 2), suggesting an additional increase of the strength of intramolecular hydrogen bonds. Similar effects are seen when considering the dependence of O–H and C–O distances on \( \Delta pK_a \) (Fig. 4). Some irregularities are also observed in dependence of C1–C2 and C2–C7 bond lengths on \( \Delta pK_a \), which can be attributed to steric effect of chlorine atom substitution at position 3 of the phenol ring of compounds 3 and 4. The calculations demonstrate, that this steric interaction of the substituent located next to the methylene group squeezes externally the chelate ring, leading to a pronounced increase of the strength of the intramolecular hydrogen bond.

Parameters \( d \), the average bond lengths in the rings, and \( A \), bond length distributions, were applied to describe the perturbations of the ring geometry. The average geometry shows an unusual parabolic dependence on \( \Delta pK_a \), both for the open and hydrogen-bonded conformers, as well as for the phenols. Changes of \( d \), after correction for the direct substituent effect, suggest the charge flow in the direction of the new-formed chelate ring. This effect does not depend pronouncedly on \( \Delta pK_a \). The bond length distribution becomes less uniform upon increasing the number of chlorine atoms, but is twice so strong in the systems with O–H⋯N hydrogen bonding than for the open conformers.

Acknowledgements

The authors wish to thank the ÖAD for financial support within the Polish–Austrian exchange program (18/2002), the ZID of the University Vienna and the University of Wroclaw for computational facilities.

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