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Structural modifications resulting from proton transfer in complexes of phenols with pyridine[†]

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ABSTRACT: The structural consequences of proton transfer in complexes of phenol (**1**), 2,6-dichlorophenol (**2**), 4-nitrophenol (**3**) and 2,6-dichloro-4-nitrophenol (**4**) with pyridine were analyzed on the basis of results of B3LYP/6–31G** calculations. Three methods of describing the progress of proton transfer are proposed: the O—H [*d*(OH)] and C—O [*d*(CO)] bond lengths and the fraction X_{PT} of the proton transfer form, calculated from the values of the dipole moments. The *d*(OH) parameter reveals behaviour near to X_{PT} and can be used as a universal measure of the degree of proton transfer. The *d*(CO) parameter gives nearly linear dependences for various structural parameters, but independent estimation of the specific effects of the substituents is necessary, as separate correlations for each complex are found. A role of resonance interaction in systems containing a *p*-NO_2 substituent is demonstrated. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: phenols; pyridine; structure; density functional theory; proton transfer; hydrogen bond complexes

INTRODUCTION

Molecular geometry appears to be a rich source of chemical information;[1] intra- and intermolecular interactions lead to changes in geometry which, in turn, provide information about the strength and nature of these interactions. The effective use of this information requires the establishment of reliable relationships between the geometry and the properties of molecular systems. This problem is especially interesting in systems with hydrogen bonding, where interactions[2,3] can vary over a broad range, from very weak to very strong. Studies on this topic have become increasingly popular in recent years.[1,4–12] Hydrogen bonding provides catalytic mechanisms for many reactions, including enzyme catalysis and the transmission of ions through biological membranes.[13] The extent of proton transfer (X_{PT}) has been shown to be one of the most important characteristics of the hydrogen bond. Systematic studies on the geometric implications of proton transfer have been very scarce in the literature so far.

In previous work,[14] such studies were undertaken in our laboratory, based on experimental results. Density functional theory (DFT) B3LYP/6–31G(d,p) calculations were performed[15] on the structure of the complex of 2,6-dichlorophenol with pyridine as a function of the degree of proton transfer modulated by increasing the O$\cdots$H distances within the range found in the experiment. The purpose of that study was to give a theoretical description of the observed tendencies in 15 crystal structures of 2,6-dichlorophenols and various pyridine derivatives,[14] partly because of the wide spread of experimental points, resulting mainly from differences in the crystal packing forces. The calculations reproduced the tendencies in agreement with the experiment. It was also found that including corrections to the reaction field in the calculations, with reasonable values of Onsager sphere radius and electric permittivity, led to a better description of the experiment.

Generally, one can expect that the dependences obtained can allow a description of the character of a complex on the basis of various structural parameters; the position of the proton of the OH group is not the most precisely determined parameter by x-ray crystallography. It appeared, however, in calculations on six different phenols with trimethylamine[16] that the structural parameters obtained were not only functions of X_{PT} and that more extensive studies were necessary on its inductive, resonance and steric relationships. In this study, we aimed to establish theoretical dependences between various structural parameters and the degree of proton transfer in complexes of phenol (**1**), 2,4-dichlorophenol (**2**), 4-nitrophenol (**3**) and 2,6-dichloro-4-nitrophenol (**4**) (Scheme 1) with pyridine.

In such a way, the modification of the strength of acids and the specific interaction of particular substituents can be analysed. It was also of interest to establish the extent to which the substitution in the phenol ring influences the geometric characteristics of pyridine, which is specific

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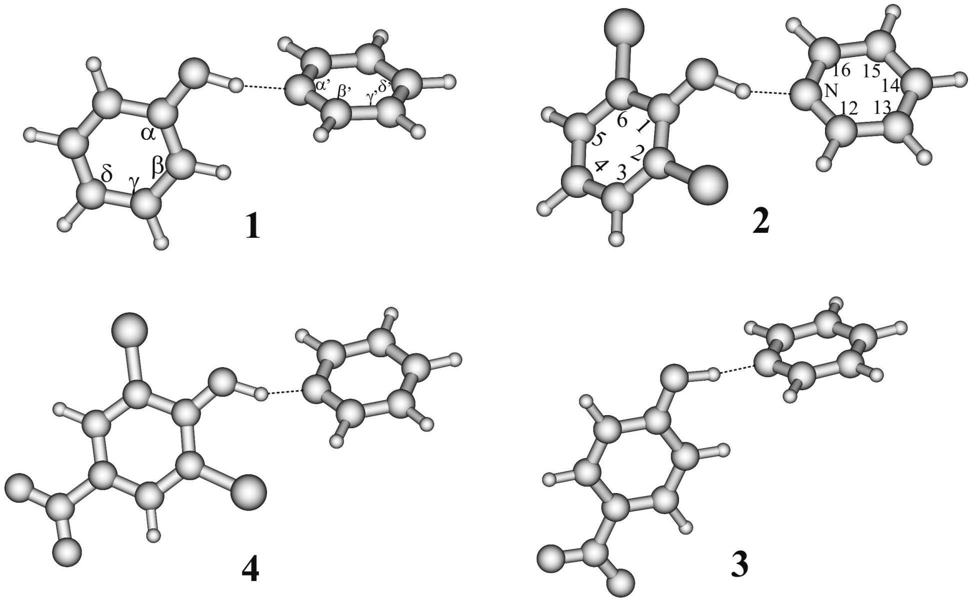
[†] Selected paper presented for a special issue dedicated to Professor Otto Exner on the occasion of his 80th birthday.



Scheme 1

for the complexes studied here and related to the very interesting problem of the transmission of π-electron coupling through the hydrogen bridge.[17,18]

METHODS OF CALCULATION

The calculations were performed with the DFT B3LYP/6–31G(d,p) method, which is known to be sufficient for the description of the structure of complexes with hydrogen bonds[19] (see also Refs 7 and 20). To understand the influence of the surroundings, parallel calculations were performed taking into account the reaction field effect, with an Onsager sphere radius of 4.75 Å and a permittivity of 4.5, which is an average of experimental values obtained for a few complexes with a low and high degree of proton transfer (R. Jakubas and I. Majerz, unpublished results).

The OH distances were varied in steps of 0.1 Å within the range 0.8–2.1 Å. For each fixed $O\cdots H$ distance all the other parameters were fully optimised. Such an approach is valid in performing comparisons with experimental structures.

The degree of proton transfer can be characterized by the O—H distance [*d*(OH)] or the C—O distance [*d*(CO)]. It was shown previously that the structure parameters give more linear correlations with *d*(CO) than with *d*(OH).[15,16]

The formal degree of the proton transfer (X_{PT}) was estimated on the basis of the dependence of the calculated dipole moment on *d*(OH). This dependence was of sigmoid shape, which allows the limiting values of the dipole moments for pure molecular (μ_{HB}) and pure proton transfer complexes (μ_{PT}) to be established. For a given μ_i, X_{PT} can be calculated according to the equation resulting from the additivity of the molar polarizability:

$$\mu_i{}^2 = X_{PT}\mu_{PT}{}^2 + (1 - X_{PT})\mu_{HB}{}^2 \qquad (1)$$

Such an approach was first used by us in previous work.[15] In this analysis of the structural consequences of proton transfer, we applied the results of calculations, not experimental structures. According to Kovacs *et al.*,[4] with such an approach one avoids some random errors resulting from crystal packing forces. Deviations from experiment can be considered as systematic ones and should not strongly influence the conclusions concerning the relative structural changes in a series of compounds or structures. The presented figures and correlation equations were obtained with 14 calculated points in each case. The curves were prepared by graphically connecting particular points.

RESULTS AND DISCUSSION

Potential for proton transfer

Results of theoretical calculations allow the dependence of the energies of the complexes on the degree of proton transfer to be presented (Fig. 1).

The potentials were calculated for fixed O—H distances where all the other parameters are optimized. One observes a strong increase in energy on O—H shortening, starting from the optimal geometry, and a considerably weaker energy increase when the O—H distance is extended. pK_a values are 9.99, 6.90, 7.15, and 3.68 for phenols **1**–**4**, respectively.[21]

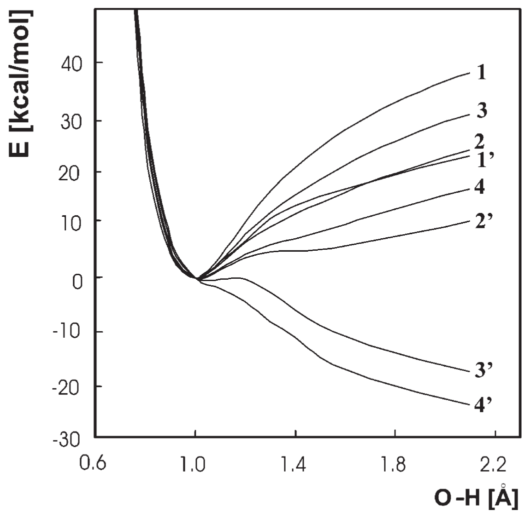


Figure 1. Dependence of the potential energy on O···H distance. Other parameters were optimized. Curves 1–4 concern the complexes with phenol (**1**), 2,6-dichlorophenol (**2**),[1] 4-nitrophenol (**3**) and 2,6-dichloro-4-nitrophenol (**4**) and curves. 1′–4′ the complexes, in the same order, calculated taking into account the reaction field correction

The stronger the proton donor, the lower is the energy for complexes with proton transfer. This shape of the potential results from the fact that when a proton nearly reaches the optimal distance from a proton-acceptor atom, further extension of the O···H distance moves the whole pyridinium molecule away and the increase in energy results mainly from the work of charge separation. The increase in permittivity in the calculations with the Onsager reaction field correction (curves **1′**–**4′**) consequently decreases this work and energy. There is no source of radical energy increase as in calculations with fixed X(H)···Y distance (cf. Fig. 2). The presented picture suggests that the proton-transferred complexes are comparatively labile in the sense that this distance can easily be modified by interaction with the surroundings which is not very strong. Including the electrostatic interaction with the surroundings in the calculations leads to the formation of a second minimum in **3′** and **4′**. Such a situation can be observed in the crystal, where the polar surrounding strongly interacts with polar molecules. The reason for such specific behaviour of compounds containing the 4-NO_2 substituent is a resonance stabilization of the 4-nitrophenolates.

The different character of the potential for the proton movement within a hydrogen bridge of fixed geometry (one can call it an adiabatic potential) is illustrated in Fig. 2.

The optimized geometry of some characteristic structures [cf. Figs 1 and 3(A)] at d(OH) = 1.0, 1.3, 1.7 and 2.1 Å (in parentheses in Fig. 2) was selected: the first for the enol (OH) type of complex, the second for the shortest bridges [cf. Fig. 3(A)], the third for the proton transfer form [d(OH) = 1.7 Å] and the fourth when the zwitterionic hydrogen bridge is extended [d(OH) = 2.1 Å]. Then

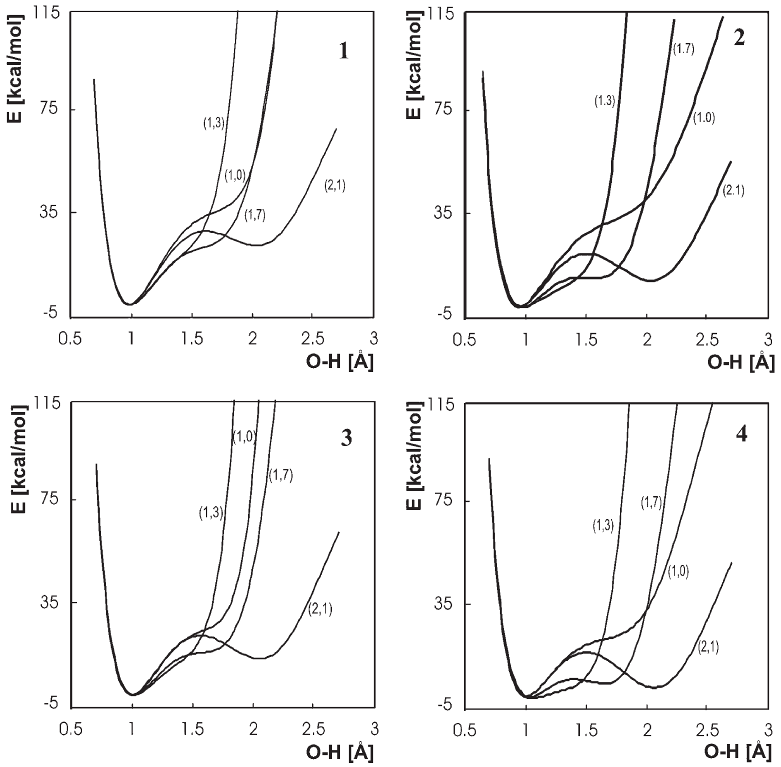


Figure 2. ‘Adiabatic’ potentials for the proton movement within the hydrogen bridge (in **1**–**4**) calculated for a fixed geometry of other atoms. The potentials for **2** are according to Ref. 15. The numbers in parentheses are the O···H distance fixed in the procedure of energy minimization in calculations described in constructing the potentials in Fig. 1

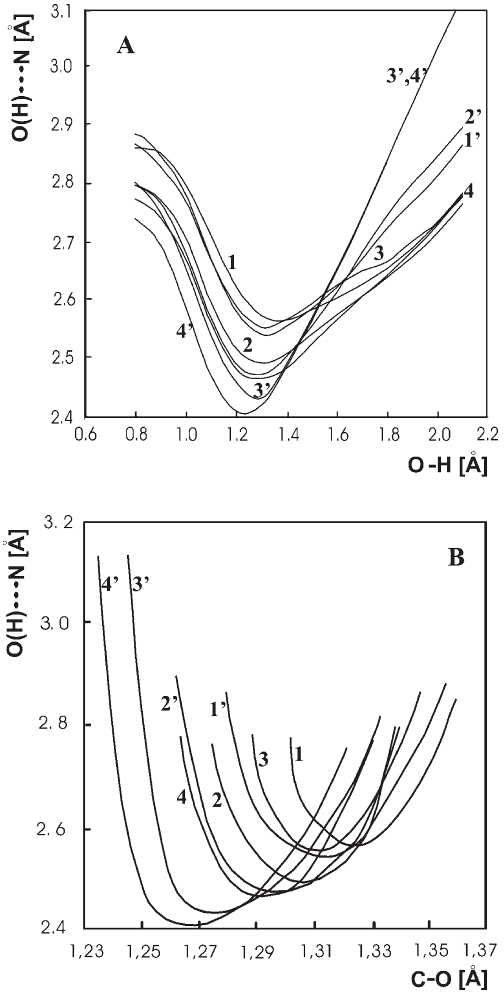


Figure 3. Dependence of the length of the O(H)···N hydrogen bridge on proton transfer: (A) as a function of *d*(OH) and (B) as a function of *d*(CO). The numbering of the complexes is as in Fig. 1. These were obtained in the procedure of the optimization of the structures at fixed O···H distances

the potential energy was calculated by varying the proton position within the $d(\mathrm{OH}) = 0.8$–2.1 Å range for fixed geometries of the other atoms. Such potentials describe the proton movement for a fixed geometry of a complex and can also be used for describing the vibrational levels of OH stretching in an anharmonic representation. It becomes a very important approach in the interpretation of the ν_s(X–H) band shape in systems with a hydrogen bond (see, for example, Refs 22–24). Such a potential determines the probability of proton location. For the shortest hydrogen bridges [$d(\mathrm{OH}) \approx 1.3$Å], one minimum potential is formed, whereas for longer bridges the second minimum develops. One observes that with increasing acidity of the phenols, the second minimum becomes more pronounced. For the strongest of the studied complexes (**4**) it is as deep as for the O—H···N molecular form.

Geometry of the complexes

Figure 3 shows how the O(H)···N bridge length changes with the degree of proton transfer, characterized by *d*(OH) (A) and *d*(CO) (B). The dependences are of a parabolic-like shape with the minimum at about 50% of the proton transfer [$d(\mathrm{OH}) \approx 1.3$ Å for all curves]. The acidity increase of the proton donor leads to a downshift of the curves; for the phenol–pyridine complex the minimum O(H)···N distance is at ~2.55 Å, whereas for the complex of the strongest of the studied phenols (**4**) it decreases to 2.45 Å. In each case, introducing the reaction field correction decreases the left part of the curve [Fig. 3(A)], whereas for proton transfer complexes (the right part) the O(H)···N distances increase: the higher the permittivity, the lower is the attraction between the charged components of a complex.

One obtains a different picture when using the C—O bond length as a parameter [Fig. 3(B)]. Regular, parabolic-like curves are obtained. With increasing strength of the hydrogen bond, the curves move towards the shorter bridges [as in Fig. 3(A)]. *d*(CO) and the minima are shifted to lower values. For the phenol complex (**1**) the minimum is at $d(\mathrm{CO}) = 1.325$ Å, whereas for the 2,6-dichloro-4-nitro derivative (**4**) it appears at 1.29 Å. Including the reaction field correction leads to a further decrease in both O(H)···N and C—O distances.

The different features of the O(H)···N dependence on *d*(OH) and *d*(CO) suggest that the last two general measures of proton transfer progress are not linearly interrelated, which is clearly seen in Fig. 4.

The dependences for various complexes are of sigma type, but with increasing hydrogen bond strength they move to lower *d*(CO), in a nearly parallel way. Accounting for the reaction field leads to a decrease in *d*(CO) values, stronger for the ionic complexes. The greatest

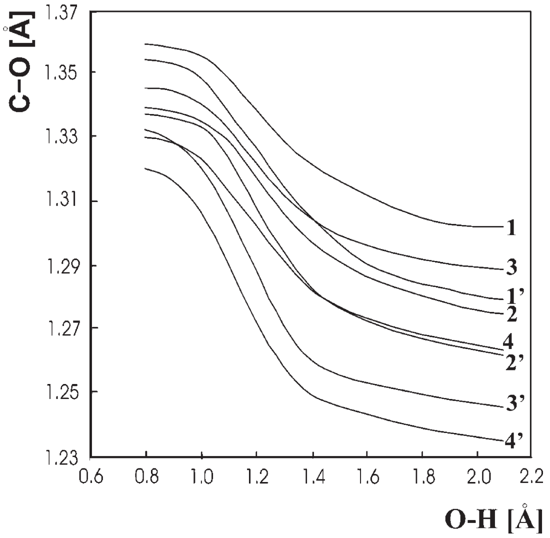


Figure 4. Correlations between *d*(CO) and *d*(OH) obtained in the process of proton transfer for particular complexes. Line numbering as in Fig. 1

effect was observed in the 4-nitrophenol–pyridine complex. It is clear that a single value of d(CO) cannot be used as an indication of the degree of proton transfer for various complexes.

At this point one can ask about the possibility of direct correlation of the parameters with X_{PT}. For this purpose, the X_{PT} values derived from the calculated functions of the dipole moment on d(OH) (see Methods of calculation section) can be used.

One can state that there is a nearly uniform dependence of X_{PT} on d(OH) in all complexes [Fig. 5(A)], especially in comparison with Fig. 5(B). Consequently, the d(OH) values can be taken as nearly universal measures of X_{PT}, weakly dependent on the type of hydrogen bond. These dependences are not linear, in contrast to the curves shown in Fig. 5(B), demonstrating correlations between the parameters d(CO) and X_{PT}. They are linearly related (the calculated correlation factors are within the range 0.984–0.998 Å), but they form separate lines for different complexes, with similar slope. For a given d(CO), very different X_{PT} can be estimated depending on the complex. Therefore, when one compares different complexes, one should apply the d(OH) parameter, which roughly describes the state of a complex (the progress in proton transfer). To predict changes in parameters for a particular complex, one should use d(CO), which more linearly correlates with the given structure parameter. Better linearity of the dependence on d(CO) than on d(OH) has already been reported for the complex of 2,6-dichlorophenol with pyridine, and seemed better in describing the experimental data.[15]

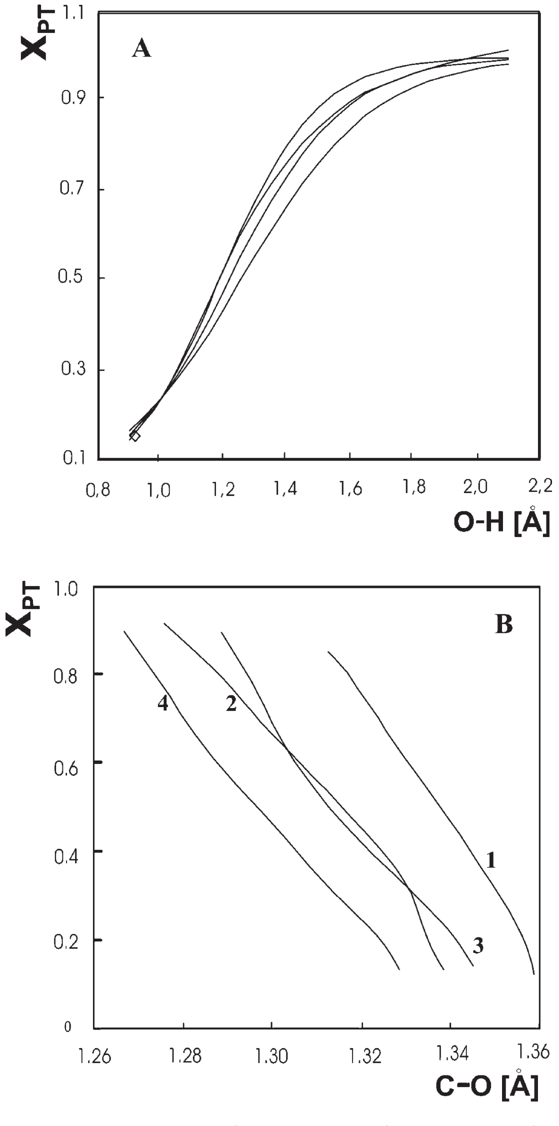


Figure 5. Dependence of the degree of proton transfer X_{PT} on (A) d(OH) and (B) d(CO)

Geometry of phenol rings

According to the statistical description of the experimental data concerning the influence of substituents on the geometry of aromatic rings,[25,26] the largest effects are observed for the α-*ipso* angle, and bonds with participation of the C-*ipso* atom. We expect a similar feature when discussing the structural consequences of proton transfer in phenol rings. It is interesting, however, which role resonance interactions play, as they also modify the parameters which are remote from the C-*ipso* atom.

In accordance with the above reasoning, it is better to present the dependences of these particular parameters in the correlation with d(CO) as more regular than with d(OH).

Figure 6(A) presents the correlation of the C_1-*ipso* angle (α) of the phenols on d(CO). These dependences have high linear correlation factors, but are specific for each complex. This is also observed in correlations of α as a function of X_{PT} [Fig. 6(B)]. It is known that each substituent in the ring makes changes in the ring angles, not only *ipso* (α), but also β, γ and δ.[25,26] In particular complexes there are different substituents, differently located with respect to the OH group. Hence there is a combination of several factors whose total effect is not simple to estimate,[27] particularly as non-additivity of the interactions is possible. It is seen that 2,6-dichloro-substituted molecules form a separate group from those which do not contain *ortho* substituents. On the other hand, the values of particular parameters in the complexes can be compared with related ones in the free phenols with the same pattern of substituents. Such a comparison is presented in Table 1, as it concerns the molecular forms of the complexes. All these structures were obtained as a result of full structural optimization. As shown in Fig. 1, only the tautomer with the O—H$\cdots$N hydrogen bond forms a stationary state in ‘free’ complexes.

The parameters for molecular (OH$\cdots$N) complexes and related ones for free phenols appear not to be identical. The differences characterize the effects of the formation of hydrogen bonds. Calculated values for phenols cannot be used directly to predict the particular

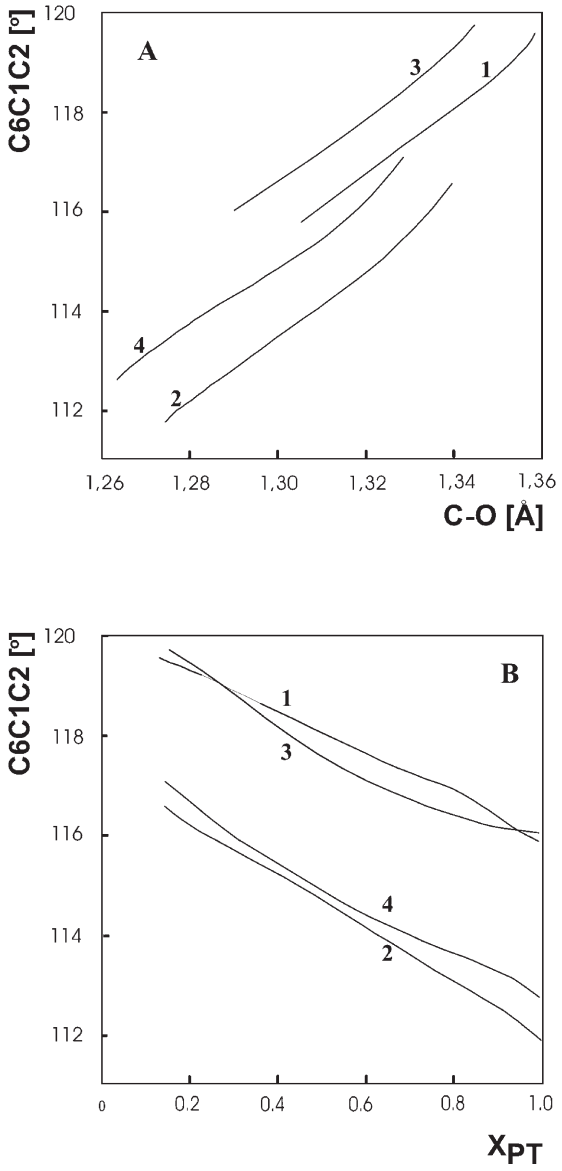


Figure 6. Correlation of the α angle in the phenol ring and (A) d(CO) and (B) X_{PT}

parameters in the complexes, because this requires corrections to the hydrogen bonding effects. A more detailed inspection of the data in Table 1 indicates that the formation of hydrogen bonding of molecular form changes the ring parameters in the direction of an increasing role of the *p*-quinoid resonance structure. On the other hand, the linear relationship between d(CO) or X_{PT}, revealing similar slopes for various complexes, can be used for predicting the relative effects on the increasing degree of proton transfer for a particular complex. The amplitude of changes in the α angle is of the order of 4–6° and the slope is negative with respect to X_{PT}. A simultaneous increase in the OC1C6 angle can be mentioned, which compensates the α angle decrease, probably because of the reduction of the 'AGIBA' effect on

Table 1. Comparison of the structural parameters in O(H)···N complexes of phenols with pyridine and related phenols

	Compound							
Parameter	Phenol	Phenol in complex	2,6-Dichlophenol	2,6-Dichlorophenol in complex	4-Nitrophenol	4-Nitrophenol in complex	2,6-Dichloro-4-nitrophenol	2,6-Dichloro-4-nitrophenol in complex
Bond length (Å)								
C1—C2	1.3987	1.4036	1.4047	1.4088	1.4029	1.4098	1.4093	1.4149
C1—C6	1.3993	1.4031	1.4055	1.4122	1.4034	1.4093	1.4098	1.4191
C2—C3	1.3957	1.3953	1.3909	1.3928	1.3890	1.3875	1.3856	1.3865
C3—C4	1.3947	1.3953	1.3932	1.3919	1.3940	1.3958	1.3918	1.3912
C4—C5	1.3978	1.3979	1.3948	1.3949	1.3971	1.3986	1.3932	1.3943
C5—C6	1.3925	1.3921	1.3919	1.3899	1.3863	1.3845	1.3871	1.3839
C—O	1.3683	1.3563	1.3493	1.3351	1.3571	1.3407	1.3409	1.3229
O—H	0.9664	0.9862	0.9701	0.9949	0.9668	0.9956	0.9711	1.0068
Bond angle (°)								
C2C1C6	120.05	119.30	117.24	116.11	120.27	119.36	117.79	116.46
C1C2C3	119.76	119.96	122.22	122.35	119.96	120.23	122.12	122.30
C2C3C4	120.53	120.82	119.20	119.77	119.13	119.46	117.94	118.63
C3C4C5	119.30	119.03	120.03	119.66	121.50	121.16	122.21	121.72
C4C5C6	120.75	120.76	120.12	119.93	119.30	119.35	118.84	118.67
C5C6C1	119.60	120.12	121.19	122.18	119.84	120.43	121.10	122.21

the proton detachment.[28] For the OC1C2 angle these effects work in opposite directions, and in consequence one observes a dependence with a maximum; after the proton transfer, the OC1C2 angle begins to decrease. The calculated dependences of the α angle on d(CO), after corrections to the reaction field, do not change slope, but shift parallel to the lines.

The β angles also change regularly with d(CO), but with the opposite trend and with a gradient half as large. The ordering of particular complexes in β dependences is opposite to those for the α parameter; when α takes the highest values, the β values are one of the lowest among the complexes. Both β angles are not perfectly equivalent.

The γ angles decrease as β with d(CO), but with about a fourfold lower slope. The δ angles increase with d(CO), showing good linear correlations; R^2 is within the limits 0.92–0.99. The amplitude of changes in δ is not greater than 1°. The changes in the β and γ angles compensate the effects on α and δ to keep the sum of ring angles constant. Parallel changes in α and δ suggest some increase in resonance interactions upon proton transfer.

Concerning the distances, one can mention a very good, and practically unique for all the studied compounds, dependence of the C1—C2 and C1—C6 distances on d(CO) (Fig. 7). This can be explained as the result of direct electronic coupling between the C—O, C1—C2 and C1—C6 bonds through the change in the hybridization on the C1 atom. One can calculate the common linear dependence of the C1—C2 bond length on d(CO):

$$d(\mathrm{C1}{-}\mathrm{C2}) = -0.446d(\mathrm{CO}) + 2.008; \quad R^2 = 0.99 \quad (2)$$

and for the C1—C6 bond:

$$d(\mathrm{C1}{-}\mathrm{C6}) = -0.424d(\mathrm{CO}) + 1.977; \quad R^2 = 0.96 \quad (3)$$

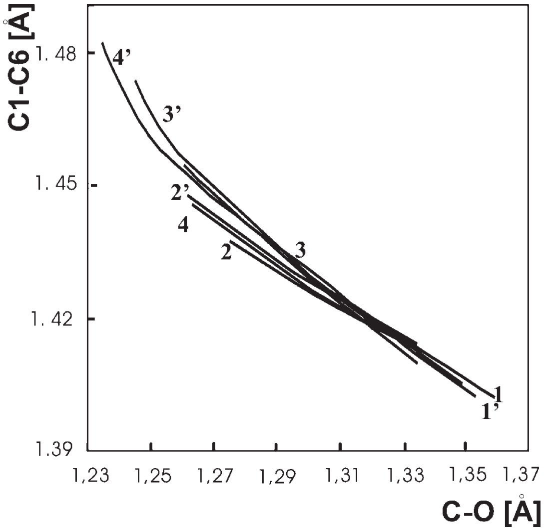


Figure 7. Dependence of C1—C6 distance on d(CO). Line numbering as in Fig. 1

or even a common linear correlation for both distances:

$$d(\mathrm{C1}{-}\mathrm{C}) = -0.437d(\mathrm{CO}) + 1.995; \quad R^2 = 0.96 \quad (4)$$

On average, decreasing the CO distance by 0.01 Å leads to a simultaneous increase in the C1—C2 and C1—C6 bond lengths by 0.005 Å. Figure 7 also demonstrates that accounting for the reaction field in complexes with a 4-NO_2 substituent strongly increases the C1—C distances. Simultaneously, d(CO) becomes smaller than for any case without the reaction field effect.

The C2—C3 and C6—C5 distances decrease with proton transfer progression on average by about 10% of the changes in d(CO). The dependences are arranged in two groups: the distances for compounds not containing a p-NO_2 group are within the range 1.39 ± 0.003 Å, whereas for compounds with a p-NO_2 group, the π-electron coupling through the molecule promotes the p-quinoid structure, which shortens these bonds, giving values in the range 1.383–1.377 Å. The decrease in these bond lengths with the progression of proton transfer indicates an increase in the resonance interaction, when the O atom of phenol becomes more negatively charged.

The C3—C4 and C4—C5 bond lengths are within the range 1.39–1.40 Å and their dependence on proton transfer is negligible. One exception is found for the 4-NO_2 group-containing compounds in calculations accounting for the reaction field corrections. In the proton transfer form, the lengths of the bonds containing the C4 atom increase to 1.425–1.435 Å, which is also related to enhanced resonance interactions.

As a collective measure of ring bond differentiation, one can use the value of the variance of these bonds ($\bar{d}$ is the calculated average bond length in the ring):

$$A = \frac{1}{n}\sum_{i}^{n}(d_i - \bar{d}_i)^2 \quad (5)$$

The A values increase strongly with proton transfer. The dependences of A reveal a sigmoid character of the function of d(OH) [Fig. 8(A)]. Such a representation allows an estimation of the levels of A for the molecular and ionic forms of the complexes.

As one can expect, the lowest amplitude of the increase is for the complex of unsubstituted phenol. Intermediate values are for chloro and nitro derivatives. In this case, the steric chloro and mesomeric NO_2 group interactions give nearly the same effects. The simultaneous influence of both types of groups increases the observed effects (in the complex of **4**). Calculations which account for the reaction field corrections give about twice the increase in A, especially large for compounds with a p-NO_2 group, where $A \times 10^6$ reaches a level of 1800 and 2200 for compounds 3′ and 4′, respectively. This demonstrates a strong increase in the content of the p-quinoid resonance form by the polar surroundings.

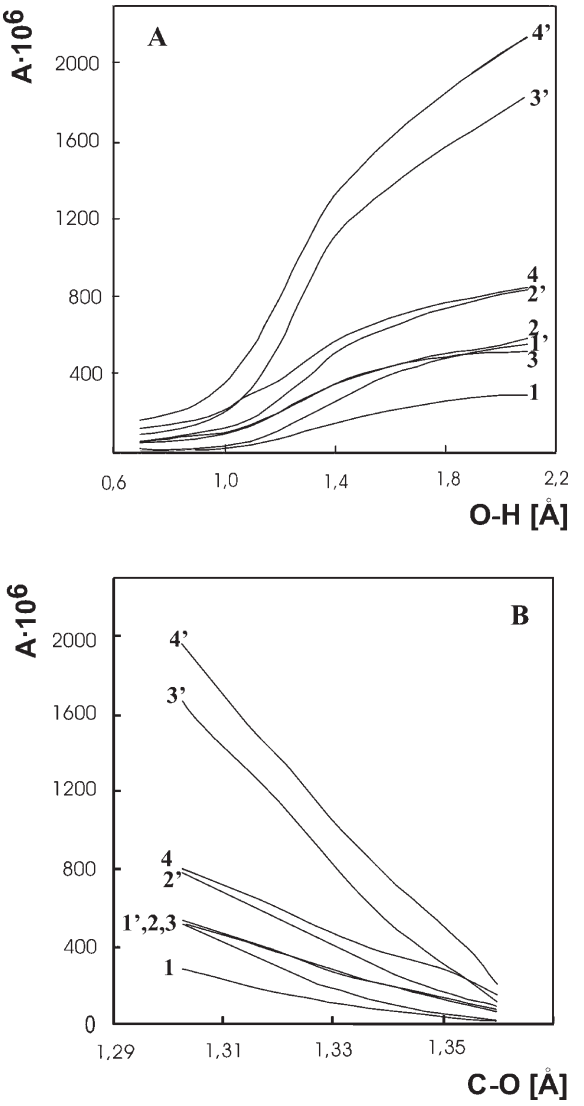


Figure 8. Dependence of the parameter *A* (see text) on (A) *d*(OH) and (B) *d*(CO)

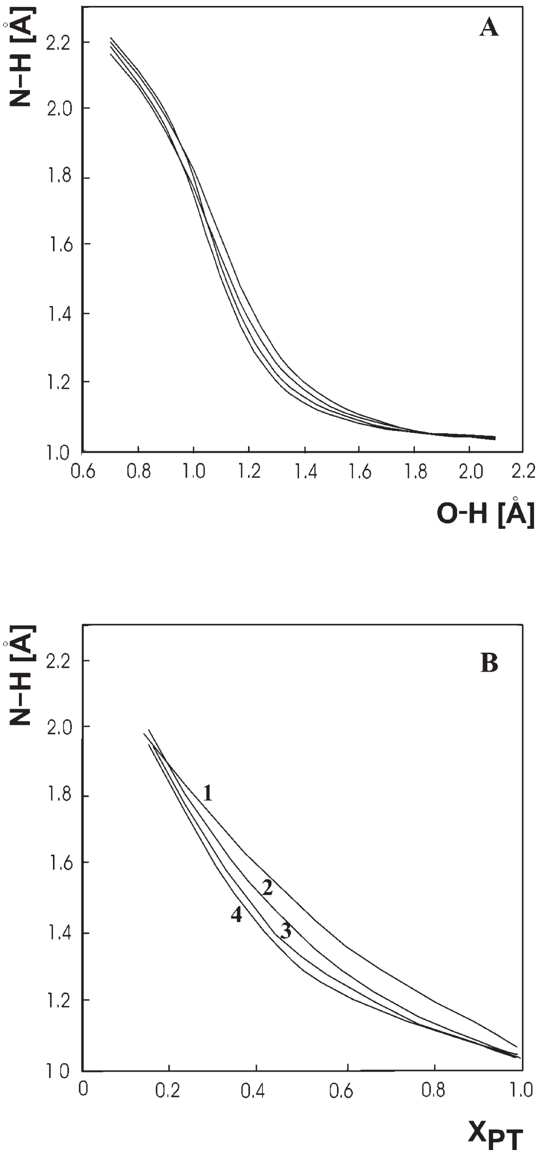


Figure 9. (A) Interrelationship between N—H and O—H distances and (B) correlation of N···H distance with X_{PT}

The dependences on C—O distance are more linear. This shows that the redistribution of the ring bond lengths and the modification of the C—O bond lengths have a common source, namely enhancement of resonance interactions upon progress in proton transfer.

Finally, one must mention the very interesting and very unique dependence of N—H on O—H distances. Previously,[15] it was established that the introduction of an external electrostatic interaction does not alter the correlation. This was explained as a result of fulfilling the rule of valence conservation for the proton in a hydrogen bond.[29] The independence of hydrogen bond strength and the specific effects of substituents [Fig. 9(A)] implies that the N—H/O—H correlation really reveals a universal feature and can be used for predicting the second parameter despite the fact that the hydrogen bonds can have a different character.

Figure 9(B) shows that, individually, the N···H distance depends on X_{PT} in different ways in particular complexes. With a stronger hydrogen bond the N···H distance appears to be shorter for a given degree of proton transfer (X_{PT}). The NO_2 group seems to enhance this effect.

Modification of the pyridine ring structure

Internal ionization of the complexes by proton transfer also leads to modification of the structure of the pyridine ring. Especially interesting is to the extent to which these effects depend on the degree of proton transfer and on substitution in a remote fragment of the molecule, i.e. the pyridine ring.

As the proton approaches the pyridine ring, it induces very substantial geometric changes there. In general, one can state that there is an increase in the symmetry of the

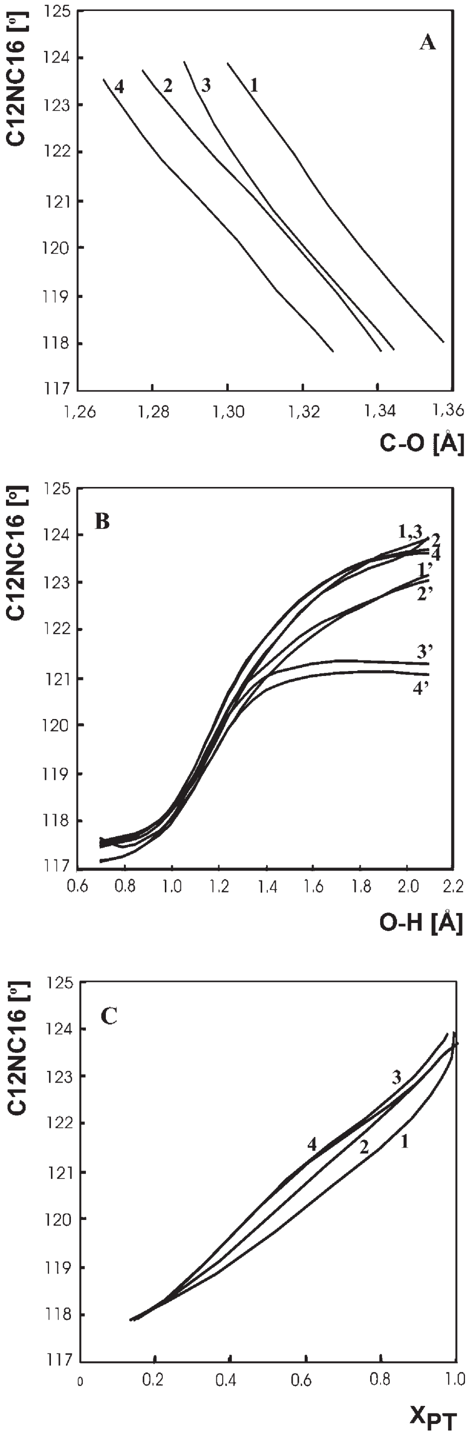


Figure 10. Dependence of CNC angle in pyridine ring on (A) d(CO), (B) d(OH) and (C) X_{PT}. Line numbering as in Fig. 1

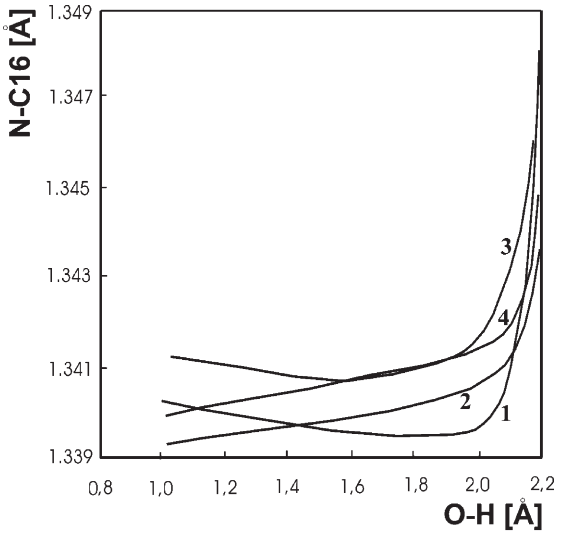


Figure 11. Dependence of N—C bond length in pyridine on the degree of proton transfer [d(OH)]

ring, formation of the N^+—H bond also makes this part of the pyridine ring similar to the more symmetric phenyl ring, and the parameter A decrease with X_{PT}. Many of the parameters change, as in the phenyl ring, almost linearly with d(CO). In such a way it changes the CNC angle [Fig. 10(A)]. The correlation functions with similar slopes are very good (the squares of the correlation coefficients are greater than 0.99). Particular lines are separated for each complex, also with respect to the geometry of the pyridine rings: d(CO) is not a direct measure of the degree of proton transfer. The dependences can be used for predicting changes in the CNC angle on proton transfer from the correlations for particular complexes. The most striking is the fact that the dependence has an opposite slope from that of the C_1 (α) angle in the phenol ring (cf. Fig. 6).

A very uniform dependence of the CNC angle on d(OH) can be pointed out [Fig. 11(B)]. A decrease in this angle in the proton transfer (PT) state, when the reaction field is accounted for, can be mentioned. It is especially pronounced ($\sim 3°$) for the complexes containing the 4-NO_2 group. It also shows that the properties of the pyridine ring depend on the structural modification of phenol, but it is observed only in a polar surrounding.

One should expect the most direct answer to the question about such an influence from the dependences on X_{PT} [Fig. 10(C)]. Figure 10(C) shows that there is some specificity for each complex: the CNC angles are slightly different for a given X_{PT} in particular complexes. The NO_2 group-containing complexes (**3** and **4**) again show a stronger deviation from the dependence for **1**.

The β' angles show symmetry (angle NC16C15 $\approx$ NC12C13). They decrease with proton transfer in order to compensate the CNC angle increase; one can expect that $\Delta\beta$ should be nearly equal to $0.5\Delta\alpha$. On the basis of experimental[30] and theoretical[20] correlations between $\Delta\beta$ and $\Delta\alpha$ resulting from various substitutions in the benzene ring, it was found that the proportionality factor is 0.591. The dependence of the β angle on d(CO) in phenol engaged in various complexes with water molecules was demonstrated to be linear.[31] In our studies on the structural consequences of proton transfer, very similar dependences were found, with the square of the correlation factor larger than 0.99. The parameters of the dependence $\beta' = 67.83d(\mathrm{CO}) + 32.15$ found predict very similar effects, as found by Ramondo *et al.*[31]

The γ' angles increase very slightly with decreasing d(OH). After the proton transfer an enhancement of the order of 1° is observed.

The δ' angles change similarly to the α' angles, suggesting resonance interaction, but these angles typically change 4–5-fold less than the CNC angle. This can be characterized by the linear correlation

$$\delta' = 1.6229X_{\mathrm{PT}} + 118.43 \tag{6}$$

Separate correlation lines have to be made when δ' is related to d(CO).

Correlation of N—C bond length and proton transfer are very characteristic and similar for different complexes (Fig. 11). A more pronounced increase in the N—C bond lengths only appears for the complete proton transfer ($X_{\mathrm{PT}} > 90\%$). The pyridine ring bond lengths seem to be insensitive to proton movement until the pyridinium cation is formed. The C12—C13 and C16—C15 bond lengths decrease with the proton's approach to the pyridine ring in accordance with the *p*-quinoid valence bond pattern. The slopes of the lines for different complexes are similar, and the average correlation equation for both C12—C13 and C16—C15 is

$$d(\mathrm{CC}) = 0.089d(\mathrm{CO}) + 1.27 \tag{7}$$

The C13—C14 and C14—C15 bond lengths increase with the progression of proton transfer, but the extent of changes in the whole range is less than 0.005 Å.

CONCLUSIONS

B3LYP/6–31G(d,p) calculations were performed on the structure dependence on the degree of proton transfer in complexes of phenol, 2,6-dichlorophenol, 4-nitrophenol and 2,6-dichloro-4-nitrophenol with pyridine to explain the role of particular substituents in the observed correlations.

Regular changes in bond lengths and valence angles with the degree of proton transfer were found. Correlation equations were presented which can be used for predicting particular parameters. The correlations are presented as parametric functions of d(OH) and d(CO). The dependences where the degree of proton transfer is characterized by d(OH) are S-shaped, whereas as functions of d(CO) they are nearly linear. The dependences on d(OH) are uniform for all complexes, whereas those on d(CO) are specific for particular complexes. The most uniform character is revealed by the dependence of d(NH) on d(OH), resulting from the valence conservation rule for the proton involved in the hydrogen bond.

The calculated values of the dipole moment allowed the estimation of the degree of proton transfer (X_{PT}). d(OH) shows a non-linear but uniform dependence on X_{PT} for different complexes, whereas d(CO) as a function of X_{PT} forms linear dependences which are different for complexes of particular phenols. The specific interaction of substituents on C—O bond lengths is a source of this effect. The structural modifications concern both the phenol and pyridine rings. Transmission of electronic effects of substituents in the phenol ring through the hydrogen bridge to pyridine was seen. Proton transfer induces an increase in the amount of the *p*-quinoid resonance form in both rings, especially in systems with a *p*-NO_2 substituent.

The different characters of the adiabatic and non-adiabatic potentials for proton movement within the hydrogen bridge were demonstrated.

The structural and spectroscopic implications resulting from the character of these potentials were pointed out.

The calculations performed clearly demonstrate that increasing the polarity of the surroundings within the framework of the Onsager model strengthens the enol type of complexes ($\mathrm{PhO{-}H \cdots NC_5H_5}$), whereas zwitterionic ones ($\mathrm{PhO^- \cdots H{-}N^+C_5H_5}$) become weaker and longer.

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