

Structural manifestations of proton transfer in  
complexes of 2,6-dichlorophenols with pyridines

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DFT B3LYP/6-31G(d,p) calculations were performed to describe the proton transfer reaction pathway in the 2,6-dichlorophenolate of pyridine. The aim of these calculations was to establish the character of the dependence of the structure parameters on the proton transfer and comparing the results with known structures, *e.g.* the 2,6-dichloro-4-nitro- and pentachlorophenolates of pyridines. To make this comparison more reliable, the calculations were repeated with the use of a reaction-field correction with the Onsager radius and electric permittivity taken from the solid-state measurements. The calculations show that the second approach gives a better description of the structural modifications during the proton transfer.

## 1. Introduction

In the course of previously reported spectroscopic and crystallographic studies on the nature of the hydrogen bond in complexes of pentachloro- and 2,6-dichloro-4-nitrophenols with pyridines, a series of crystal structures of complexes within different positions of the proton was obtained, characteristic of a uniform structure in the central part of the complexes (Malarski *et al.*, 1987*a,b*; Majerz *et al.*, 1989, 1990, 1991, 1992, 1993, 1994; Majerz, Sawaka-Dobrowolska & Sobczyk, 1995, 1996; Majerz, Malarski & Sawaka-Dobrowolska, 1995; FOMWIN, GADGUN, GADGUNO2, LAWLIE, LOLSUA, NUKBIE, PABBAV, PARNAX, PEZXIB, POCVUY, REPMUU, SAZGIJ, YIDKEB, ZOKSUN, ZUWMAF). These studies report on 2,6-dichlorophenol derivatives with non-*ortho* substituted pyridines. By comparing the structural characteristics in such series in order of increasing O—H distance some kind of ‘structural titration’ with respect to various molecular parameters can be obtained. In solution, these systems cover the full range of hydrogen bond strength, from the weakest to the strongest (Malarski *et al.*, 1982). In the literature such dependencies are available, but generally for a limited number of parameters, particularly for atoms directly involved in the formation of a hydrogen bridge. Well known correlations between  $A-H$  and  $H \cdots B$  distances for homo- and heteronuclear bridges (Steiner, 1998) are based in the majority of cases on neutron diffraction measurements, because of the known difficulties in obtaining the precise location of the proton using the X-ray method. The dependence of  $A-H$  lengths on  $A \cdots B$  distances has often been presented (Steiner & Saenger, 1994). The dependence of the  $A-H \cdots B$  angle on the  $H \cdots B$  distance was presented, but

the points were scattered because non-uniform structure units were compared (Olovson & Jonsson, 1976). Steric interactions within the complex can strongly differentiate when moving from one complex to another.

The aim of the present paper is to compare the experimental correlations for various parameters of the complexes and relate them to the results of DFT, B3LYP/6-31G(d,p) calculations. In the literature information exists that such a method is sufficient to describe the structure of hydrogen-bonded complexes (Lampert *et al.*, 1997). To consider the polarization effect in the crystal the corrections on reaction field as implemented into the *Gaussian98* programs set (Frisch *et al.*, 1998) were performed. Using the reaction-field corrections we applied the volume of a single molecule in a crystal unit cell to establish the Onsager cavity radius, which is 4.5 Å for the complex of pentachlorophenol with 4-methylpyridine, which seems to be in the middle of a range of studied hydrogen bond strengths. The electric permittivity was taken as 4.75 which also was determined for this crystal. The presented structures of complexes of chlorophenols with pyridines provided extensive data in order to correlate between various structural parameters and the strength of the hydrogen bond (Malarski *et al.*, 1987*a,b*; Majerz *et al.*, 1989, 1990, 1991, 1992, 1993, 1994; Majerz, Sawaka-Dobrowolska & Sobczyk, 1995, 1996; Majerz, Malarski & Sawaka-Dobrowolska, 1995; *cf.* Table 1 of Majerz *et al.*, 1997).

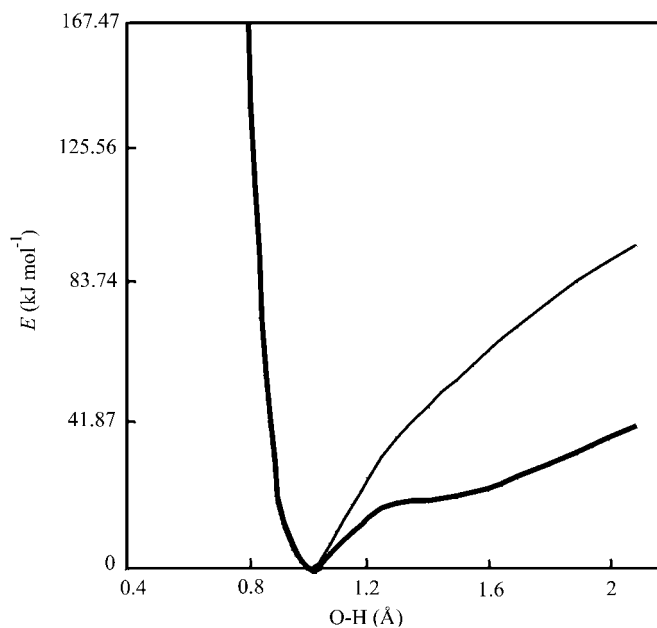
The strength of hydrogen bonding, however, is not quantitatively defined and different approaches are used in the literature. In solutions, as a virtual measure of the hydrogen bond strength, the values of  $\Delta pK_a [= pK_a(BH^+) - pK_a(AH)]$ , for  $A-H \cdots B$  systems] are used. It was shown (Huyskens & Zeegers-Huyskens, 1964) that it correlates, particularly in polar solutions, with a degree of proton transfer. The linear correlation with  $\log K_{PT}$ , where  $K_{PT}$  is the equilibrium constant of the proton transfer reaction, was stated. In the approach based on crystallographic data, we shall use the position of the proton as a measure of the degree of proton transfer. In the case of solutions it was found that there are generally two types of correlation with the physicochemical characteristics of hydrogen bonds on  $\Delta pK_a$  (Sobczyk & Rospenk, 1980). Some changes resemble titration curves, which are also called S-shaped dependencies. These are changes of dipole moments (Ratajczak & Sobczyk, 1969), vibration frequencies in basic parts of the complexes (Rospenk *et al.*, 1977) or quadrupole moments (Grech *et al.*, 1979; Nogaj *et al.*, 1990). Such a dependency describes the radical change of a given property upon protonation. The second type of dependency describes the strength of mutual interactions between partners. Such a dependency shows the maxima or minima and sometimes is called a  $\Lambda$ -type correlation. The  $^1H$  NMR shift of the  $A-H$  group or  $\nu(A-H)$  frequency shift on  $\Delta pK_a$  is described by such a correlation.

The experimental correlation between some selected structural parameters, taken from the 16 determined crystal structures, has already been performed (Majerz *et al.*, 1997). It was shown, for example, that the C—O bond lengths in phenols depend on  $\Delta pK_a$  according to an s-type curve, while

the N $\cdots$ O bond lengths depend on  $d(OH)$  according to a  $\Lambda$ -shaped curve. The dependency of  $d(N\cdots O)$  on  $d(C-O)$  is not clear-cut. The point scattering may be due to the crystal packing forces. From Fig. 2 of Majerz *et al.* (1997) it can be seen that the authors were not able to decide on the shape at the minimum. Some kind of double minimum dependency was proposed. Now it is clear from our calculations that it should be a parabolic curve.

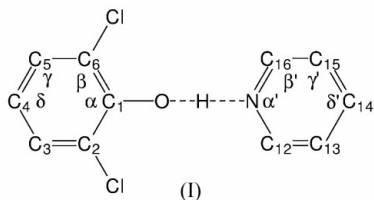
It is interesting to study the character of the various correlations by quantum chemical calculations and to compare them with the experimental data.

Two complexes of pentachlorophenol with substituted pyridines have been studied by semiempirical, quantum chemical methods (Koll & Majerz, 1994). Almost free rotation around the H $\cdots$ N axis was found in the calculations of the isolated complex. In comparison to the experimental data it appeared that the crystal packing forces determined the planarity of complexes. On the other side the linearity of the hydrogen bond in O—H $\cdots$ N-type complexes was impossible to achieve either in the gas phase or in the solid state, because of the steric repulsion within the complex. Correlation functions were calculated, reproducing the experimental dependence of some selected structural and electronic parameters on the strength of the hydrogen bond. To account for the polarization effects of the environment the calculations were performed by applying the reaction-field corrections at electric permittivities of 1, 2, 5 and 7. The precision of the semiempirical calculations is, however, not very high. Contemporary *ab initio* and DFT methods are able to reproduce the structure of the molecules almost as accurately as in crystallographic determinations. Additionally they allow for the description of the proton position, which cannot be



**Figure 1**  
Dependence of the energy (B3LYP/6-31G(d,p)) of the 2,6-dichlorophenol pyridine complex on the O $\cdots$ H distance; calculations for isolated complexes (thin line) with corrections on reaction (thick line). The energy is related to the minimum level for each potential.

precisely determined in X-ray experiments. To achieve this one constructs the potential for the proton movement within the hydrogen bridge. In this work the DFT B3LYP/6-31G(d,p) method was used to calculate such a potential for the complex of 2,6-dichlorophenol with pyridine [see (I)].



Such a system presents all the principal structural features of the complexes studied experimentally.

## 2. Results and discussion

### 2.1. Potential shape for the proton movement

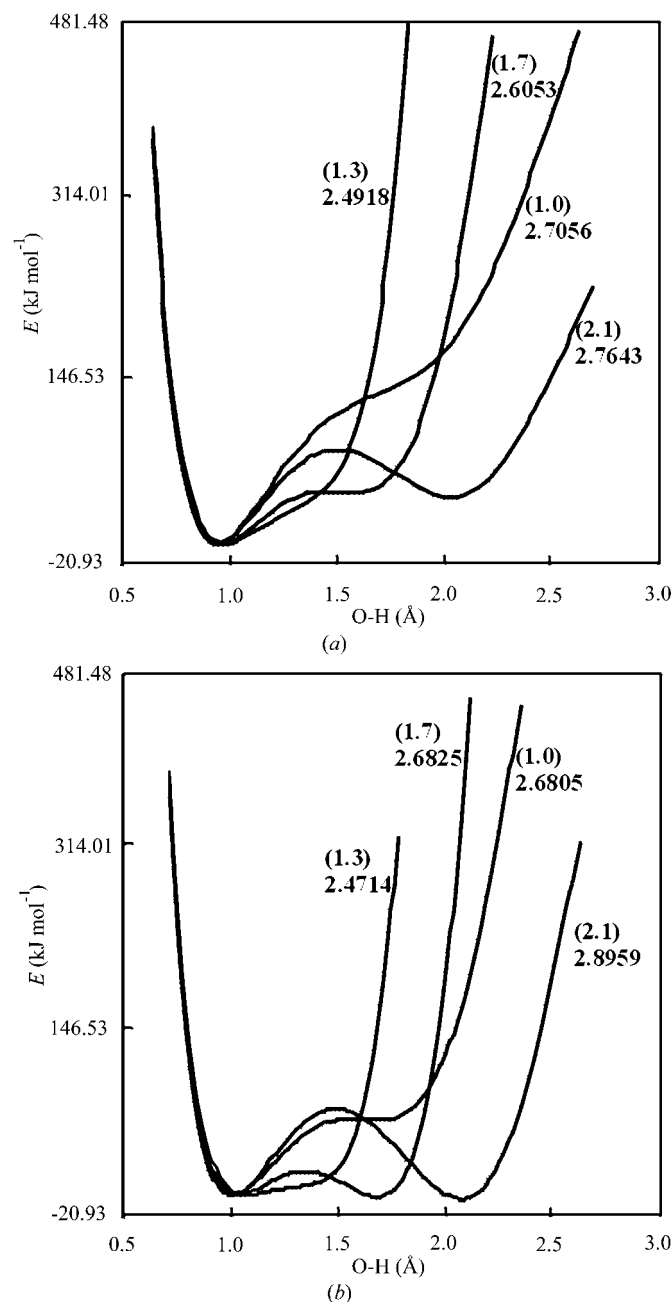
In order to follow the effects of the change in proton localization achieved in the crystal structures by modulating the acid–base properties of interacting molecules, one can perform calculations for complexes with fixed O–H distances selected from the range of experimentally known O–H distances. All the other parameters of the complexes were optimized. The lengths of the O–H···N hydrogen bridges were adapted in this procedure to the particular O–H distance. Such a potential could be termed non-adiabatic owing to the fact that all atom positions have been optimized for a particular proton position. The potential calculated with the reaction-field correction included gives significantly lower energies at the larger O–H distance than the potential without this correction (Fig. 1).

The local energy minimum for the  $O^- \cdots H-N^+$  equilibrium state should also be mentioned; the reaction field stabilizes the proton transfer tautomer. The left part describes the low polar complexes and its shape practically does not change, as with the energy at the O–H···N minimum. Such a potential describes the ‘quasistatic’ energy change on proton transfer and can be directly related to the experimental structures of hydrogen bonds with a different localization of the proton. The potentials presented in Fig. 1 have an unusual shape if we compare with Fig. 2, which describes the proton vibrations. Such potentials are in use for example in the discussion of proton location for hydrogen bonds with a given O(H)···N length, as well as for zero-point energy corrections. These potentials are adiabatic in the sense of weak coupling between proton vibrations and movement of heavy atoms.

Fig. 2 presents such potentials for hydrogen bonds of selected lengths, taken for a few points of the curves shown in Fig. 1. Fig. 2(a) shows the potentials obtained for the gas phase calculations, while Fig. 2(b) shows the potentials obtained accounting for the reaction field.

Some potentials do not seem to depend strongly on the interaction with the solvent (*cf.* Figs. 2a and b). Closer

inspection of these figures shows, however, that the interaction with the solvent leads to a larger decrease in the energy of the right part, making the second minimum more developed. The ‘adiabatic’ potentials were calculated for the structures with fixed O(H)···N distances, established as the result of structural optimization for selected O–H distances. The O(H)···N distances become shorter in polar surroundings for the ‘molecular’ hydrogen bonds (the O–H tautomer). The opposite feature is observed for ionic forms;  $d(OH) = 1.7$  or



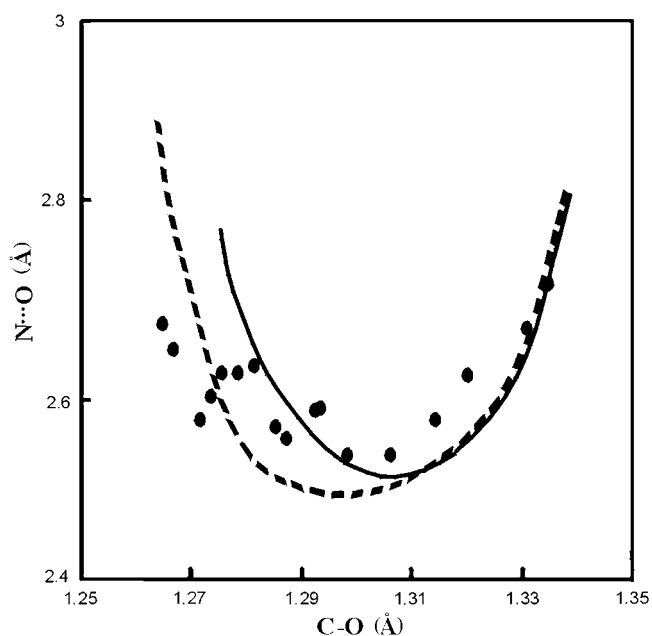
**Figure 2** Adiabatic potentials for the proton movement within the hydrogen bond, calculated for the structures optimized at selected O–H distances (in parentheses, Å). The numbers without parentheses are optimized O···N distances (in Å): (a) the ‘gas phase’ calculations; (b) calculated with the reaction-field corrections taken into account. The potential energy values related to the level of enol form a minimum for each calculation.

2.1 Å. In such a case it appears that the most important are electrostatic interactions, which decrease in polar surroundings. These potentials were obtained for the frozen geometries of all the atoms, except hydrogen in the  $O\cdots H\cdots N$  bridge, and describe the dynamics of proton movement within the bridge. The amplitude of such a motion appears to be quite large. Especially interesting is the situation in short hydrogen bonds, where the proton is dynamically located in the center of

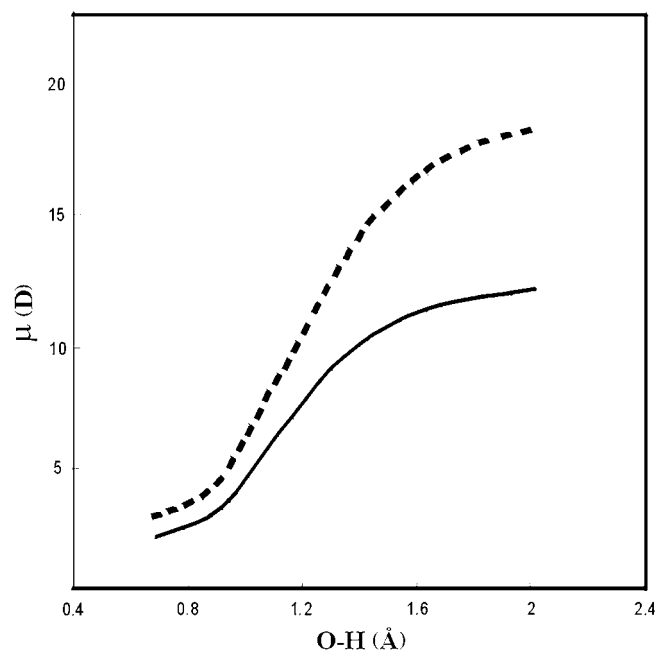
the bridge. Even for states with the pronounced character of the  $O^-\cdots H-N^+$  bonds, the localization of the proton near the  $O^-$  atom also seems to be probable. It demonstrates how difficult it is to estimate the proton position from X-ray experiments.

## 2.2. Structural modification upon proton transfer

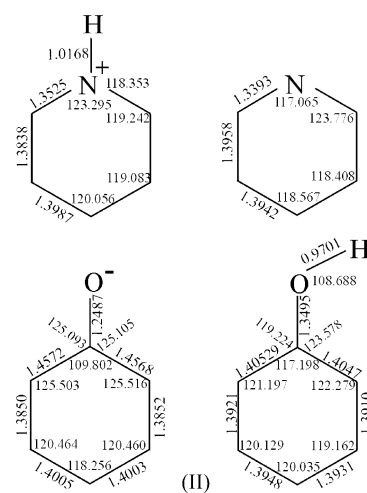
Here we will discuss the modifications of the calculated structural parameters on the proton transfer reaction and compare with the experimental values obtained for a series of complexes of 2,6-dichloro derivatives of phenol with derivatives of pyridine. Independently calculated structures of isolated parts of the complexes, namely 2,6-dichlorophenol, pyridine and the related phenolate anion and pyridinium cation can be taken as some kind of reference state for purely molecular and zwitterionic complexes.



**Figure 3**  
Correlation between the hydrogen bond length ( $N\cdots O$  distance) and the phenol  $C-O$  bond length: — 'gas phase'; --- with reaction-field correlations, ● experimental points.



**Figure 4**  
Dependency of the calculated values of the dipole moment of the complex on the  $OH$  distance. — 'gas phase'; --- with the reaction field.



The most informative, compared with experiment, seems to be the dependency of the  $O\cdots N$  distance on the length of the  $C-O$  bond. Both parameters correlate strongly with the strength of the hydrogen bond (Majerz *et al.*, 1997) and the positions of the heavy atoms are better defined than hydrogen. Fig. 3 contains such a correlation which is presented as two different lines: one for the calculations in the gas phase and the second accounting for the reaction field. The experimental points are scattered around the theoretical lines. The character of the dependency appears to be greater when describing this experiment than that previously obtained (Majerz *et al.*, 1997). The calculations predict that such a dependency is of parabolic shape (Fig. 3).

The right side of the curves appears to be almost identical to that calculated by accounting the reaction field. On the left side the difference between the two lines is more pronounced, resulting probably from the larger dipole moments of zwitterionic forms than molecular ones.

Fig. 4 demonstrates the calculated dipole moment increase with the degree of proton transfer. The interaction with the surroundings leads to an additional increase in the dipole moment, especially for the states after the proton transfer; the

reaction-field effect results from the mutual polarization of the molecule and its surroundings.

The S-shaped character of the curves in Fig. 4 resembles the dependency of  $\Delta\mu$  (an increase in the polarity of hydrogen bonds) on  $\Delta pK_a$  (Ratajczak & Sobczyk, 1969).

Fitting these curves with the logarithmic function  $\log \mu = \xi d(\text{OH}) + C$ , similar to that used for the  $\Delta\mu/\Delta pK_a$  dependence, one obtains the limit values of the dipole moment of the molecular form  $\mu_{(\text{HB})}$ , which is equal to 1.46 and 1.84 D for the 'gas phase' calculations and with reaction-field corrections, respectively. Related values of  $\mu_{(\text{PT})}$ , the dipole moment of the proton transfer form, are 12.90 and 20.12 D, respectively.

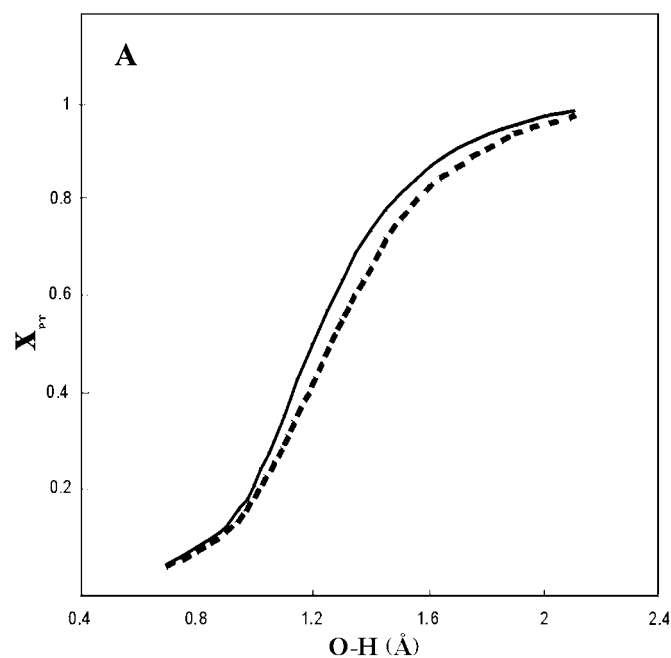
Having at your disposal  $\mu_{(\text{HB})}$  and  $\mu_{(\text{PT})}$  allows  $x_{\text{PT}}$  to be determined; the molar fraction of the proton transfer form for each calculated value of  $\mu$  is as follows

$$\mu^2 = (1 - x_{\text{PT}})\mu^2(\text{HB}) + x_{\text{PT}}\mu^2(\text{PT}).$$

Such a procedure describes, in principle, the equilibria in solution (Huyskens & Zeegers-Huyskens, 1964; Ratajczak & Sobczyk, 1969), but was successfully applied in the literature to also discuss the properties of hydrogen bonds in the solid state. For example, the analysis of the values of nuclear quadrupole resonance absorption in complexes with chlorine substituents (Nogaj, 1987).

Further, it was interesting to correlate such  $x_{\text{PT}}$  values obtained with the  $d(\text{OH})$  parameter we applied as an experimental indicator of the proton transfer progress in specific complexes in the solid state.

Such correlations are presented in Fig. 5. The similarity between both curves should be mentioned. There is a common dependence between  $x_{\text{PT}}$  and  $d(\text{OH})$ , which demonstrates that

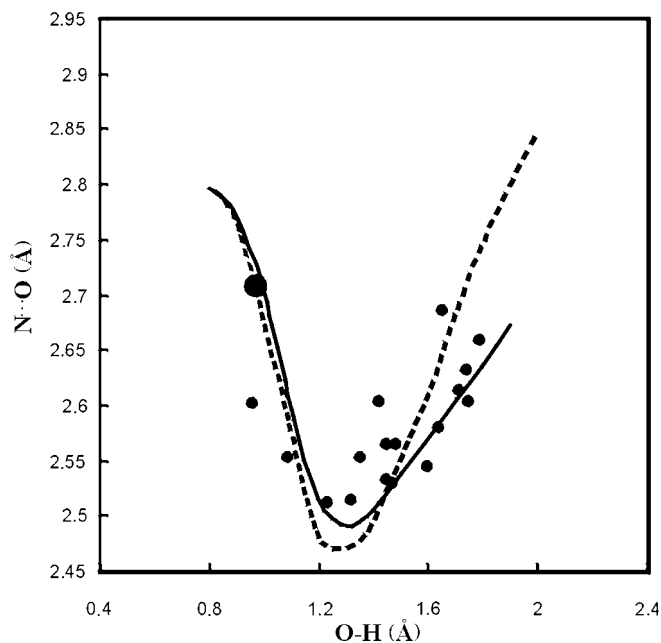


**Figure 5**  
Correlation between  $x_{\text{PT}}$  – the formal degree of proton transfer calculated:  $x_{\text{PT}}$  and  $d(\text{OH})$ , in Å; — for the gas phase calculations; --- for the calculations with the reaction-field correction.

the last parameter [ $d(\text{OH})$ ] can really be used as an experimental characteristic of the progress in the proton transfer reaction.

Fig. 6 presents the dependency of the  $\text{O}(\text{H})\cdots\text{N}$  hydrogen bond lengths on the  $\text{O}\cdots\text{H}$  distance. The left sides of the dependencies concern the molecular (OH) hydrogen bonds, which are characterized by the small polarity of the complexes. The reaction field does not influence this part of the dependency much. The right sides show the different lines for the calculations with and without the reaction field. Most characteristic is the elongation of hydrogen bridges of zwitterionic character, while placed in polar surroundings. The experimental points deviate from theoretical ones forming the wider parabola. This, however, seems to be an artifact resulting from the uncertainty of the proton position. It is known that even for free phenols the  $\text{O}-\text{H}$  distance should be longer than 0.97 Å (Lampert *et al.*, 1997). In such a case one should shift all the experimental OH distances to the right in the left sides, and to the left in the right side; in the last case the  $\text{N}-\text{H}$  distances are too short. A point which reproduces the result from the neutron diffraction experiment (larger size in Fig. 6; Majerz, 2004) exactly fits the theoretical curve, which suggests that the calculated curves properly reproduce the dependency of the  $\text{N}\cdots\text{O}$  distance on  $d(\text{OH})$ .

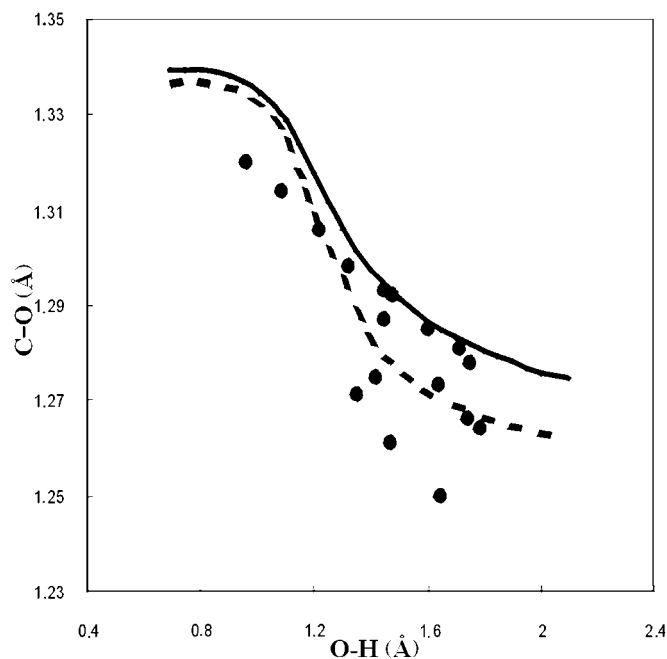
Fig. 7 describes the calculated dependency of the  $\text{C}-\text{O}$  bond lengths on the position of the proton. In the literature, the analogous dependency of the  $\text{C}-\text{O}$  bond length on the  $\Delta pK_a$  values of complexes was presented (*cf.* Majerz *et al.*, 1997). The length of this bond significantly changes (1.37–1.35 Å for molecular complexes and drops to 1.28–1.25 Å after the proton transfer). The correlation is described by a



**Figure 6**  
Dependency of the hydrogen bond length ( $\text{N}\cdots\text{O}$  distance) on the  $d(\text{OH})$  parameter. — 'gas phase' calculations; --- calculated with reaction-field corrections; ● experimental X-ray results (taken from the neutron diffraction experiment).

sigmoidal curve. The polarization of the surroundings leads to a clear shortening of the CO bond in zwitterionic forms, indicating that hydrogen bonds become weaker. The experimental points show even shorter C—O distances than those calculated. Generally the scattered experimental points are better described by the curve obtained with reaction-field corrections. In discussion of the character of the hydrogen bond in the solid state the C—O bond length is often used as a characteristic parameter which is less affected by experimental uncertainty than the proton position.

The dependency of  $H\cdots N$  on  $O\cdots H$  distances is important and very often used in the discussion of the nature of the hydrogen bond. Such dependency, presented in Fig. 8, demonstrates a very unusual property which has not been previously mentioned in the literature – the correlation lines do not depend on the reaction-field corrections. It can be explained as a result of fulfilling the rule of additivity of the valence of the H atom in the hydrogen bridge. Such an interpretation was given by Steiner on the basis of neutron diffraction results (Steiner, 1998). One can certainly expect that O—H or  $HN^+$  experimental distances are too short for enol or zwitterionic complexes of 2,6-dichlorophenols with pyridines. Correction of these effects seems to lead to a good reproduction of the experimental points by theoretical lines. In the range of the strongest interactions, where the proton is localized in the vicinity of the center, the distinction of the experimental points from the theoretical curve looks less pronounced. The charge of the valence electrons here is more uniformly distributed along the hydrogen bridge. It is interesting if such an observation can be repeated for other groups of complexes with different hydrogen bonds.



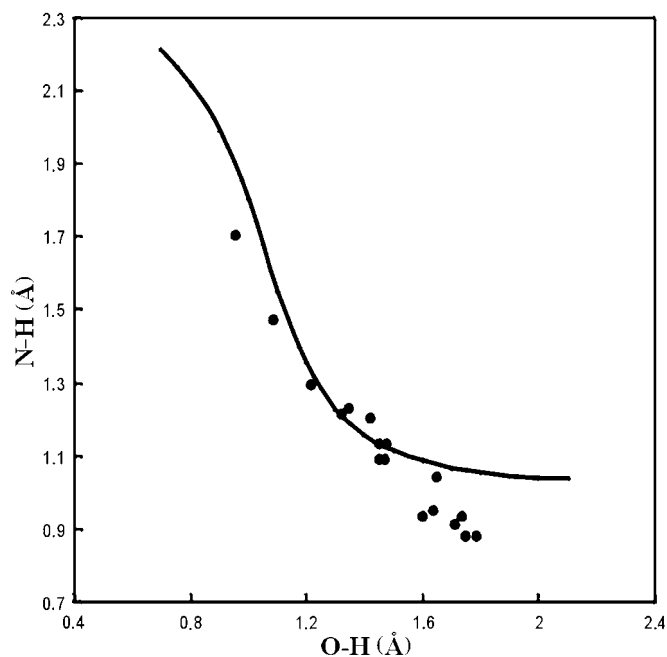
**Figure 7**  
Dependency of the C—O distance in phenol on the O—H distance. — ‘gas phase’; --- with reaction-field corrections; ● experimental points.

A change of the proton position within the hydrogen bridge should be accompanied by some geometry modifications both in the phenol and pyridine rings. Such systematic observations have not been discussed in the literature so far. Comparing the experimental structures of phenol and the phenolate ion as well as pyridine with the pyridinium cation [(II)] one can expect to see changes in the geometry of phenol in the direction of the paraquinoid structures upon ionization (visible shortening of C5—C6 and C3—C2 bond lengths, extension in others, decrease in the  $\alpha$  and  $\delta$  angles). The character of the geometric changes in the pyridine ring upon protonation appears to be similar to that discussed above for the phenol ring (II), except for the  $\alpha$  and  $\alpha'$  angles. The C2C1C6 angle of phenol ( $117.2^\circ$ ) decreases to  $109.8^\circ$  in the phenolate anion, while the  $\alpha'$  (C12NC16) angle in pyridine ( $117.1^\circ$ ) increases to  $123.3^\circ$  for the pyridinium cation. The largest changes are in the vicinity of  $C_{ipso}$  in phenol, also suggesting some influence from the inductive interactions.

The contribution of the quinoid resonance forms, as was demonstrated in intramolecular hydrogen bonds (Melikova *et al.*, 2000), leads to the differentiation of ring bond lengths. Some generalized characteristics of this effect were proposed: the **A** parameter, which is an average, squared bond-length difference in relation to the average bond length ( $\bar{d}$ ) of the ring, in a given estimation

$$A = 1/n \sum_{i=1}^n (d_i - \bar{d})^2 \times 10^6.$$

Fig. 9 presents the dependencies of such a parameter on  $d(OH)$  in the phenol ring. The regular dependencies are S-



**Figure 8**  
Dependency of the N—H distance on the O—H distance. The calculations with and without the reaction field give exactly the same line; ● experimental points.

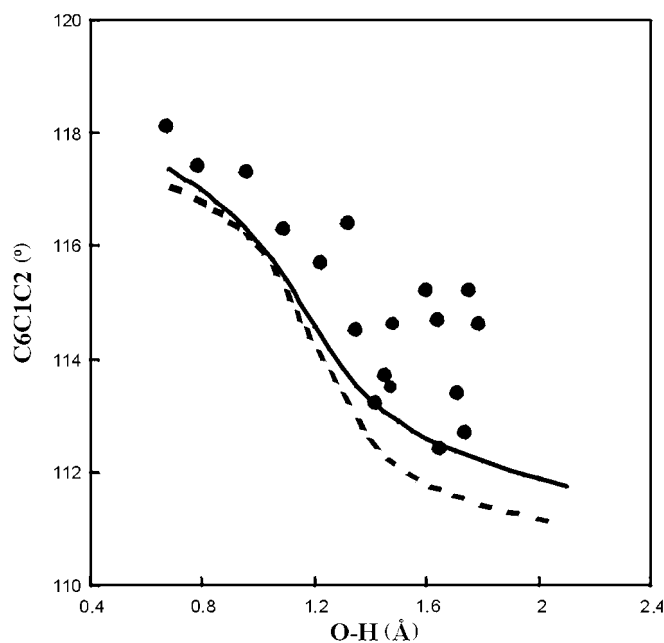
shaped. It can be clearly seen that the surroundings induce a considerable increase in the structural effects.

The calculations also allow discussion on the correlations of particular structural characteristics of the rings on the parameters describing the progress in the proton transfer.

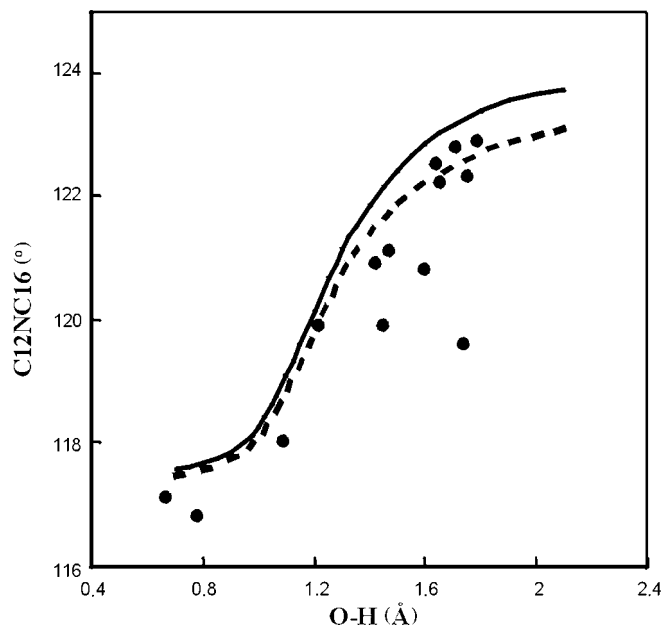
Fig. 10 (a) presents, for example, the dependency of the  $\alpha$ -*ipso* angle in the phenol ring on  $d(\text{OH})$ . The theoretical curves are S-shaped with greater changes in the calculations with the reaction field. The experimental points are all above the theoretical lines. Far from the calculated value of  $110^\circ$  [cf. (II)] are the experimental  $\alpha$  angles for zwitterionic forms. Despite the complete proton transfer the parameters of isolated ions cannot be determined; the hydrogen bond acts in the direction of the mild structural modifications. The opposite direction of changes is observed for the C—N—C angle in pyridine (Fig. 10b). This dependency is also characterized by a sigmoidal curve, with similar changes of *ca*  $6^\circ$ . The experimental points are located below the theoretical lines; the line calculated with the reaction-field correction seems more accurate in describing the experimental points.

Detailed analysis of the results obtained in the calculations demonstrates that using the C—O distance in place of O—H as a parameter to describe the character of a particular hydrogen bond allows much simpler, nearly linear correlations to be obtained. It allows a much clearer description of the structural consequences of the proton transfer reaction. The common dependency of the phenol  $\alpha$  angle on the C—O distance calculated for points without and with the reaction-field correction gives  $\alpha = 70.744 (\pm 0.009)d(\text{CO}) + 21.686 (\pm 0.001)$ , with a rather large correlation coefficient ( $R^2 = 0.9895$ ). The differences between  $\alpha$  angles obtained in both types of

calculations are very small. The experimental points are described by the equation with a roughly similar slope  $\alpha = 61.064(\pm 0.009)d(\text{CO}) + 36.278(\pm 0.001)$ , but are, on average,  $2^\circ$  higher than the calculated points. The much lower correlation factor ( $R^2 = 0.8105$ ) results from a comparatively high scatter of experimental points. Both experimental values and calculations show that the C2C1C6 ( $\alpha$ ) angle decreases strongly upon proton transfer (decreasing the C—O distance), suggesting the predominance of resonance effects. Inductive



(a)



(b)

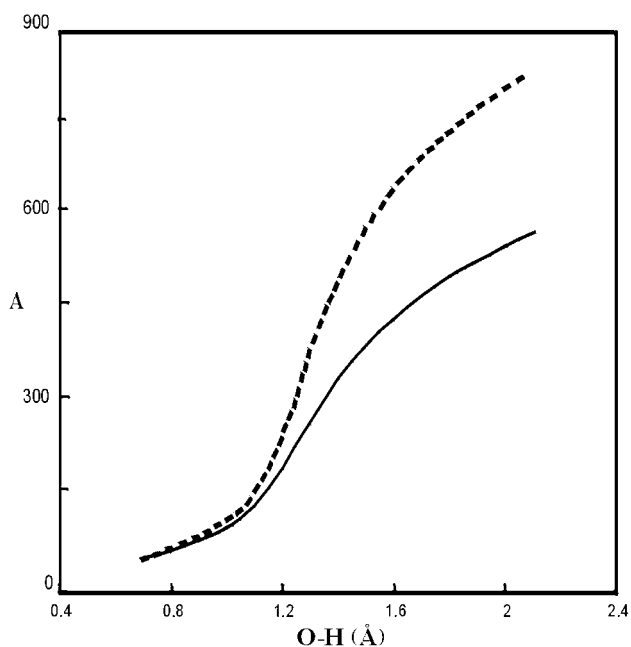


Figure 9

Dependency of the generalized parameter **A** (see text) of the differentiation of bond lengths on  $d(\text{OH})$  in the phenol ring; — 'gas phase' calculations; --- calculations with accounting reaction-field corrections.

Figure 10

Dependency of the  $\alpha$ -*ipso* angle (a) in phenol and (b) in pyridine on  $d(\text{OH})$ . — 'gas phase'; --- for the calculations with force-field corrections; ● experimental points.

and electrostatic interactions would increase this angle owing to the enhanced *sp* hybridization of the C1 atom.

The linear dependency of the C16NC12 angle ( $\alpha'$  in pyridine), in the wide range of  $d(\text{CO})$ , was also found but with the opposite slope in relation to the  $\alpha$  angle in phenol. In this representation the two independent lines for calculations with and without the reaction field were found. Nevertheless, the correlation coefficients for each are very high at  $R^2 = 0.9944$  and  $0.9923$ , respectively. The experimental points are nearer the curve with corrections on the environmental interaction.

Better linear behavior with respect to the  $d(\text{CO})$  distance than  $d(\text{OH})$  in the correlations discussed above appears to be more clear if the fact that  $d(\text{CO})$  almost linearly correlates with  $x_{\text{PT}}$  is mentioned (see Fig. 11):

(i)  $x_{\text{PT}} = -13.883(\pm 0.452)d(\text{CO}) + 18.748(\pm 0.589)$ ,  $R^2 = 0.9822$  for the free complex calculations and

(ii)  $x_{\text{PT}} = -11.369(\pm 0.289)d(\text{CO}) + 15.321(\pm 0.375)$ ,  $R^2 = 0.9916$  for the calculations with the reaction-field corrections.

For a given  $x_{\text{PT}}$ , the distance  $d(\text{CO})$  appears to be shorter when the reaction field is included in the calculations.

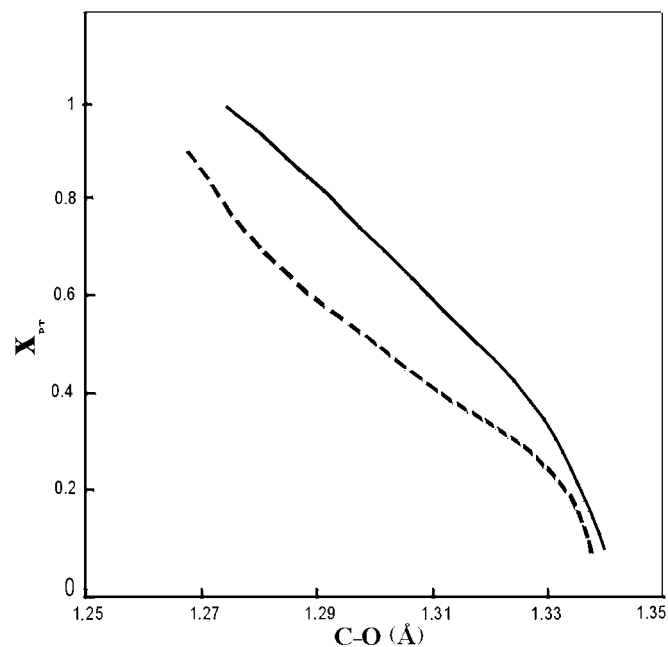
The differences decrease when points approach the molecular complexes with much lower dipole moments. Similar linearization of the correlation was found in the case of  $A/d(\text{CO})$  dependency in comparison to  $A/d(\text{OH})$  (cf. Fig. 9). The linear correlations obtained are:  $A = -11636(\pm 213)d(\text{CO}) + 15631(\pm 277)$  ( $R^2 = 0.9917$ ) and  $A = -7587.7(\pm 295)d(\text{CO}) + 10217(\pm 385)$  ( $R^2 = 0.9899$ ) for the calculations without and with the reaction-field corrections. The linear dependency of the ring bond length differentiation ( $A$ ) on  $d(\text{CO})$  means that shortening of the C—O bond length upon proton transfer has a resonance character.

The linear correlations with respect to  $d(\text{CO})$  were found for many other structural parameters. The calculated changes

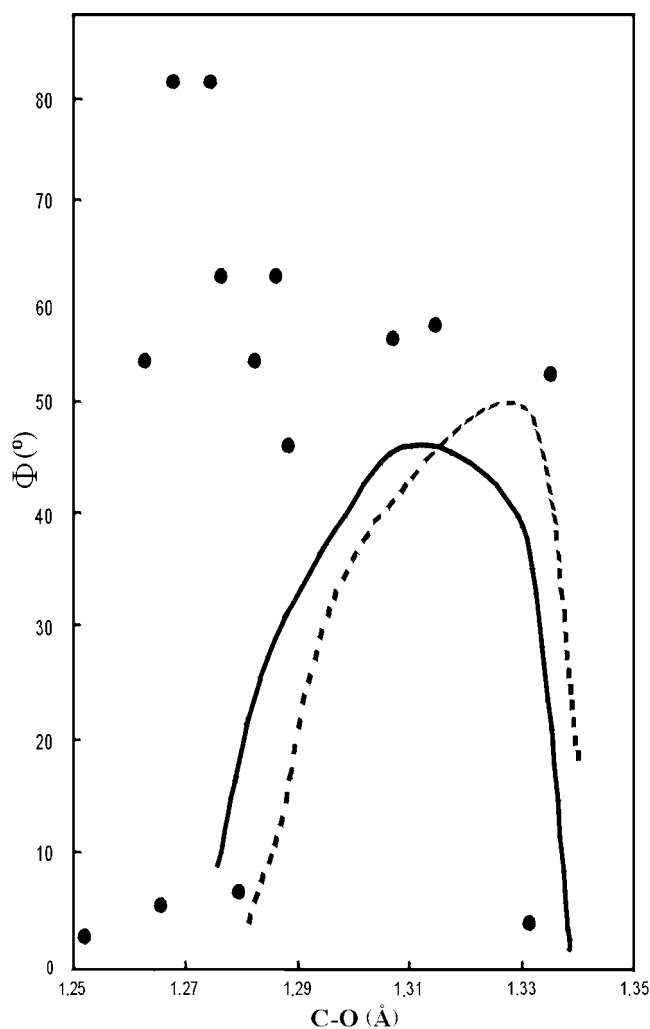
of the C3C4C5 ( $\delta$ ) angle can be described by the correlation  $\langle \text{C3C4C5} = 12.49(\pm 0.333)d(\text{CO}) + 103.080(\pm 0.548)$  ( $R^2 = 0.9777$ ). Calculations with the reaction-field corrections give an even better linear correlation;  $\langle \text{C3C4C5} = 17.65(\pm 0.395)d(\text{CO}) + 96.17(\pm 0.512)$ ;  $R^2 = 0.9935$ . The experimental points are very well reproduced by the last correlation line, but for definitely ionic structures this angle becomes nearly unperturbed ( $121 \pm 1^\circ$ ), which calculations do not predict. An increase in the  $\beta$  angles [ $\text{C3C2C1} (\beta_2)$  and  $\text{C5C6C1} (\beta_6)$ ] compensate for the decrease in  $\alpha$  and  $\delta$  angles of the phenyl ring.

The average correlation equation is  $\langle \beta = -37.74(\pm 0.543)d(\text{CO}) + 172.51(\pm 0.875)$ ;  $R^2 = 0.9738$  when counting the reaction field. The experimental points follow these theoretical tendencies, but particular parameters are on average  $2^\circ$  less than theoretical ones.

Calculations predict the shortening of the C2—C3 and C5—C6 bond lengths as a result of proton transfer [ $d(\text{C—C}) = 0.0702(\pm 0.001)d(\text{CO}) + 1.2979(\pm 0.0002)$ ,  $R^2 = 0.8524$ ]. The scatter of the experimental values ( $\pm 0.02 \text{ \AA}$ ) is higher than



**Figure 11**  
Dependency of the proton transfer degree ( $x_{\text{PT}}$ ) on  $d(\text{CO})$ . — ‘gas phase’; --- calculated taking into account the reaction field.



**Figure 12**  
Dependency of the angle between normal vectors to the rings of phenol and pyridine on  $d(\text{CO})$ . — ‘gas phase’; --- calculations taking into account the reaction field; ● experimental points.



the amplitude (0.007 Å) of these bond length changes in the range of calculated structures. The amplitudes of the C1–C6 and C1–C2 bond length changes are much larger and approach the level of 0.04 Å. These distances increase with the degree of proton transfer. The common correlation for both bonds calculated with and without the reaction-field corrections is:  $d(\text{C1–C2}, \text{C1–C6}) = -0.4361(\pm 0.001)d(\text{CO}) + 1.992(\pm 0.002)$ ;  $R^2 = 0.9744$ . The experimental values fulfil the dependency with a similar slope, but with a much larger spread of points ( $R^2 = 0.508$ ). On average, the experimental points are 0.015 Å lower than those calculated.

All the angles in pyridine change in the opposite direction to those in the phenol ring. Nevertheless, ionization, as in the phenol ring, leads to an increase in the length of the N–C12 and N–C16 bonds, but with the slope lower than for the related bonds in the phenol ring;  $d(\text{N–C}) = -0.0862(\pm 0.020)d(\text{CO}) + 1.455(\pm 0.013)$ ;  $R^2 = 0.7439$ . The low correlation coefficient substantially increases (to ca 0.94) when one calculates separately N–C12 and N–C16 with and without the reaction-field correction. An increase in the C–N distances makes them more similar to the C–C bond lengths, which leads to a decrease in the pyridine ring bond lengths.

The C12–C13 and C16–C15 bond lengths decrease with proton transfer;  $d(\text{C–C}) = 0.1145(\pm 0.007)d(\text{CO}) + 1.2409(\pm 0.009)$ ;  $R^2 = 0.9722$ . A similar direction of changes to those in the phenol rings can be noted, but with the amplitude of changes twice the size (see Fig. 12).

The experimental value of the angle between the planes of the phenol and pyridine rings changes irregularly with  $d(\text{OH})$  or  $d(\text{CO})$ . The reason is that the packing forces act very specifically in each molecule. Calculations show that complexes should be planar for weak molecular and proton transfer complexes. For the strongest complexes, *i.e.* the middle values of  $d(\text{CO})$ , the attraction between the two parts of the complex is so strong that the rings turn the hydrogen bond axis to decrease the O(H)···N distances (Fig. 12). This effect can be partially responsible for some of the differences between the experimental and calculated values of the parameters.

### 3. Conclusions

In this work we attempted to describe the structural modification on progression of the proton transfer in the 2,6-dichlorophenol complex with pyridine by DFT B3LYP/6-31G(d,p) calculations. The calculations were undertaken to explain the experimental data for the series of complexes containing the moiety 2,6-dichlorophenol/pyridine. Owing to experimental errors and the influences of the environment, such correlations for the experimental data are characterized by a rather large spread of results.

The calculations were performed by changing the O–H distance gradually from 0.8 to 2.1 Å, while all the other parameters were adapted at each O–H distance. Only such a ‘quasistatic’ approach allows the comparison with experimental structures at equilibrium. The differences between the potential energy function on  $d(\text{OH})$  and adiabatic ones,

obtained to describe the proton dynamics and its localization within the bridge, are explained.

Two types of dependency of the structural parameters on  $d(\text{OH})$  were found. In most cases they were logarithmic S-shaped, but some, for example, the O···N distance on the C–O bond length, were of the  $\Lambda$  (with minimum) type.

The reaction-field corrections were also taken into account, which led to an improvement in the correlation between calculated and experimental results. It was found, however, that some of the correlations do not depend on the reaction-field interaction. For example,  $d(\text{N···H})/d(\text{O···H})$  forms one universal dependency which can be classed as evidence of the validity of the valence conservation rule for the H atom in the hydrogen bond.

The calculated dependency of the dipole moment of the complex on  $d(\text{OH})$  allowed the border values of the dipole moments for the molecular and proton transfer states to be established. Thereafter, the  $x_{\text{PT}}$  values (degree of proton transfer) were obtained. It was shown that this dependency reveals an univocal S-shaped function on  $d(\text{OH})$ . It demonstrates that the experimental  $d(\text{OH})$  parameter can be a measure of proton transfer. More detailed studies have shown, however, that  $d(\text{CO})$  is the more useful parameter, because it correlates almost linearly with  $x_{\text{PT}}$ . The linear correlations of various parameters on  $d(\text{CO})$  were established and can be used for the prediction of particular parameters. The average bond length differentiation ( $\Delta$ ) values and their dependency on proton transfer were used. In the discussion it was also shown that this parameter better correlates with  $d(\text{CO})$  than  $d(\text{OH})$ . The differentiation of bond lengths in the pyridine ring decreases, while for the phenyl ring it increases owing to the progress in proton transfer. It was found that the bond length values in pyridine change in the opposite direction to those in the phenyl ring. Many other correlations presented here have not yet been discussed in the literature.

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