FULL PAPER

Proton Transfer Influence on Geometry and Electron Density in Benzoic Acid–Pyridine Complexes

by **Irena Majerz**

Faculty of Pharmacy, Wroclaw Medical University, Borowska 211a, PL-50-556 Wroclaw (phone: +48-71-7840305;
fax: +48-71-7840307; e-mail: majerz@yahoo.com, irena.majerz@umed.wroc.pl)

The influence of the proton transfer on the geometry of donor and acceptor molecule in benzoic acid–pyridine complexes is investigated by theoretical calculations at the B3LYP/6-311++G** level of theory. Systematic shifts of the H-atom in the H-bond are reflected in the geometry of the COOH group and the lengths of aromatic ring bond lengths of the proton acceptor. Changes in electron densities have been studied by atoms in molecules analysis. A systematic natural bond orbital analysis has been performed to study the proton transfer mechanism. Two donor orbitals are engaged in the proton transfer process which is accompanied by a change in orbital delocalization of H-atom that can switch between two donor orbitals so the path of proton transfer in intermolecular H-bond is not determined by the orbital shape. Theoretical results have been confirmed by experimental results published previously.

Keywords: Hydrogen bonds, Proton transfer, Benzoic acid–pyridine complexes, Atoms in molecules analysis, Natural bond orbital analysis

Introduction

Hydrogen bonding is the interaction that determines mutual location of the proton donor and the proton acceptor, and organizes molecules in liquid and molecular packing in crystal. As H-bonds are responsible for structural properties, their investigation is important in material sciences including production of optical devices [1 – 3] and molecular machines [4]. It is also known that H-bonds play very important role in biological systems, catalysis in enzymatic reaction [5], and conversion of light into energy [6][7].

The most important phenomenon determining the character of H-bond is location of the H-atom between the proton donor and proton acceptor atoms. For OH···O, OH···N (NH···O), and NH···N, the H-bond strength can change in a very broad range from relatively strong interaction of partially covalent character with the H-atom located close to the bridge centre to the very weak ones with H-atom shifted to the acceptor or donor. In other types of H-bonds, the dominant H-atom location is at the H-atom donor. By changing the H-atom location between the proton donor and the proton acceptor, it is possible to change the strength and properties of H-bond. The main parameters which determine the H-atom location in H-bond are the proton donor and proton acceptor properties. In the strongest H-bonds, the location of the H-atom can also be modified by temperature and electric properties of the complex environment.

Because the shift of the H-atom in the H-bond influences the molecular and material properties, proton transfer can be investigated with many experimental methods, such as dipole moment measurement [8][9], vibrational [9][10], NMR [11], NQR [12], and UV [13] spectroscopy or determination of crystal structure [1][14]. All these experimental methods have been used to investigate the H-bonds in the most typical group of compounds in which transfer of the H-atom is possible.

The most typical complexes with intermolecular H-bond investigated for a long time are the complexes of phenols [9][15] and carboxylic acids [8][16] with tertiary amines. *Mannich* and *Schiff* bases are typical compounds with intramolecular H-bond [17]. For these groups of compounds, the physical and spectroscopic parameters are correlated with molecular parameters of the complex components or with parameters describing the properties of the complex environment.

The best method for investigation of H-bond in the solid state is determination of the structure and correlation of the structural parameters with distances in the H-bond. A precise determination of the H-atom position is possible by neutron diffraction, and for this reason, the structures of complexes with strong H-bond measured by neutron diffraction are especially important [14]. The experimental methods can be supported by the theoretical calculations. It was found that the DFT calculations can correctly reproduce the molecular structure with the H···F interaction [18]. Recently, it has been shown that

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DOI: 10.1002/hlca.201500183

optimization of the structure of AcOH–Me_3N complex not only gives a correct O···N distance of 2.729 Å, but it can also lead to correct reproduction of the IR spectrum of the OHN complex with a strong H-bond [19].

Theoretical investigation of the structure with the H-atom moving from donor to acceptor is very important to determine the systematic structural changes taking place when the influence of the proton transfer on geometry of the donor or acceptor molecule is very limited, comparable with the accuracy of experiment or when it is masked by packing effects or surrounding ion effects.

Theoretical calculations could bring complementary data if amount of similar H-bonded complexes with different proton transfer degree is limited. Comparison of experimental and theoretical results for this same group of the H-bonded complexes can be used in investigation of the systematic effects caused by change in the H-bond strength [20].

The proton transfer in a strong H-bond can influence the geometry of proton donor and proton acceptor, and significantly modify chemical and physical properties of the H-bonded materials. For OH···O, OH···N (NH···O), and NH···N H-bonds, every location of the H-atom in the H-bond is possible. The H-atom can be located at the donor or acceptor atom, and in the strongest H-bonds, it can be placed close to the centre of the H-bond. Shifting of the H-atom is reflected not only in the geometry of the H-bond but also in the geometry of proton donor and proton acceptor. For complexes of phenols with tertiary amines, it was found that the degree of proton transfer can be estimated not only by the OH and NH distance but also by the C–O bond length [15][20].

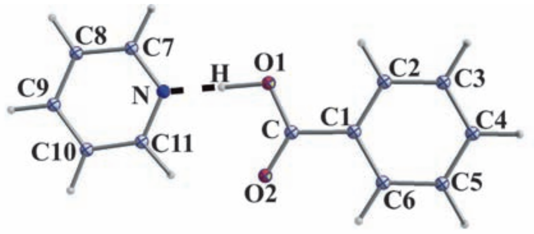
All the experimental effects resulting from transfer of the H-atom from the donor to the acceptor are connected with rearrangement of the electron cloud in the H-bond. The investigation of the electrons engaged in the H-bond could explain the experimental correlations and bring to light on the mechanism of the proton transfer. Theoretical chemistry delivers two methods for the description of electrons in the chemical bond. The first of them, confirmed by experimental measurements, is the quantum theory of atoms in molecules (AIM, QTAIM). The second, traditional chemical approach is connected with the valence bond and molecular orbitals. Although the natural bond orbital model (NBO) is commonly used in chemistry, both theoretical descriptions play complementary roles [21]. The NBO can deliver descriptors analogous to the QTAIM method and can be transformed into ‘natural atoms in molecules’ (NAIM) [22].

Complexes of carboxylic acids with tertiary amines belong to the traditional systems used to investigate the intermolecular H-bonds. One of the first spectroscopic correlations linking location of the stretching C=O/COOH band with proton donor properties was performed for pyridine–carboxylic acid system in $CHCl_3$ and in the solid state [16]. Proton transfer degree in carboxylic acid–pyridine complexes was investigated by dipole moment measurement [23]. NQR frequencies of many carboxylic acids with tertiary amines were correlated with ΔpK_a value [12]. NMR investigation of carboxylic acids gave information on the mechanism of the proton transfer and general properties of the H-bond [24].

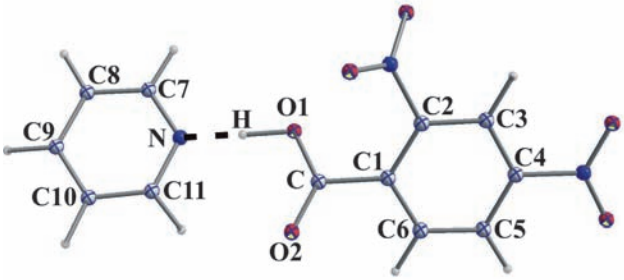
Among many complexes of carboxylic acids with tertiary amines, there are those with very strong and short H-bond. In these complexes, the H-atom in H-bond can be moved by changes in temperature. The structures of 2,4-dichlorobenzoic acid with pyridine [25] and 3,5-dinitrobenzoic acid with 3,5-dimethylpyridine [26] were measured by neutron diffraction at different temperatures. Besides, experimental data cover a relatively narrow range of proton transfer degree and are insufficient to analyze the structural properties in full range of the proton transfer starting from the geometry with the H-atom located at the donor to the geometry with the H-atom shifted to the acceptor. The intermediate range of the strongest H-bond with the H-atom located close to the middle of the H-bond should be more precisely investigated than it has been possible for the experimentally determined structures. Both complexes, 2,4-dichlorobenzoic acid with pyridine [25] and 3,5-dinitrobenzoic acid with 3,5-dimethylpyridine [26], are characterized by strong OHN H-bond but in both complexes the H-atom is located far from the H-bond center. To analyze continuous proton transfer, the experimental structures must be complemented with results of theoretical calculations.

The aims of this work are as follows:

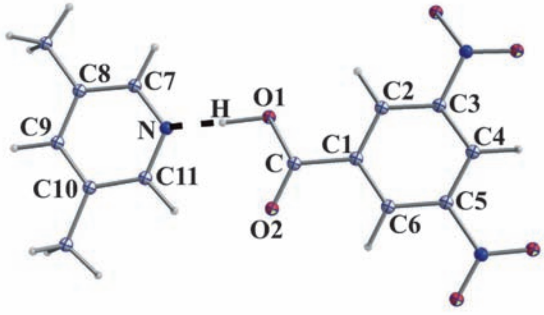
1. To check if the geometrical changes in the H-bond in benzoic acid–pyridine complexes are similar to those in other OHN complexes with intermolecular H-bond.
2. To answer the question if the CO and CC bond lengths of the COOH/C=O group could be used as a measure of the H-bond strength. Experimental data collected in the crystal database spread in broad range of CO and CC bond lengths but a general tendency of changes under shifting of the H-atom is observed. In complexes of 2,4-dinitrobenzoic acid with pyridine and 3,5-dinitrobenzoic acid with 3,5-dimethylpyridine published previously [25][26], the H-atom shifts in a limited range so it is not possible to investigate the full range of the distance changed when the H-atom shifts from donor to acceptor.
3. To check if other bonds in proton donor or in proton acceptor molecule are sensitive to the proton transfer. The structures of complexes of 2,4-dinitrobenzoic acid with pyridine and 3,5-dinitrobenzoic acid with 3,5-dimethylpyridine measured with neutron diffraction were insufficient to obtain full set of structures with systematic shifting of the H-atom from the donor to the acceptor. Except optimization of the structures of these complexes with the H-atom systematically shifted, also the structure of benzoic acid with pyridine has been investigated as a reference compound. All the investigated complexes are shown in *Fig. 1*.



Benzoic acid–pyridine complex



2,4-Dinitrobenzoic acid–pyridine complex



3,5-Dinitrobenzoic acid–3,5-dimethylpyridine complex

Fig. 1. Structures of the investigated complexes.

4. The most important aim of this work is investigation of the mechanism of the proton transfer expressed by the changes in the electronic structure under the proton migration.

Results and Discussion

Potential Energy Curves

The transfer of the H-atom from donor to acceptor is determined by the shape of the potential energy curve for the H-atom moving in the H-bond. The shape of potential energy curve is connected with experimental data: dipole moment, neutron diffraction, NMR, and IR spectra. For carboxylic acids, the shape of the potential energy curve was previously discussed in [24].

The shape of the potential energy curve of the investigated complexes is shown in *Fig. 2*. All the complexes are molecular with only one energy minimum characteristic for the H-atom located at the donor atom. Low-energy barrier for the complex of 2,4-dinitrobenzoic acid with pyridine and for the complex of 3,5-dinitrobenzoic acid with 3,5-dimethylpyridine suggest the possibility of the proton transfer to the acceptor. Very well shaped minimum at 1.0 Å for the complex of benzoic acid with pyridine confirms molecular character of this complex.

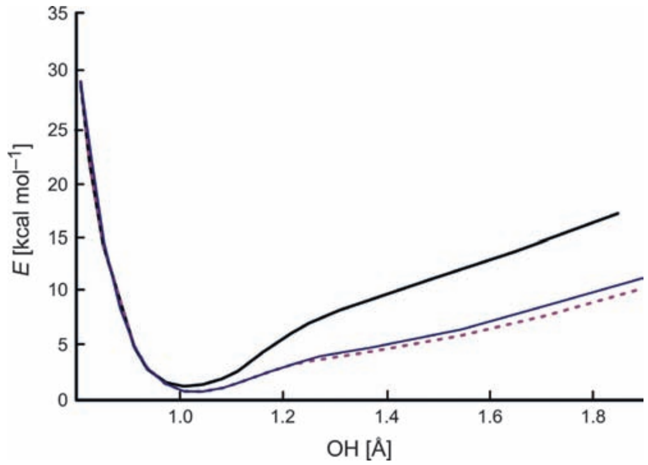


Fig. 2. Potential energy curves for H-atom motion in the investigated complexes. Black line, complex of benzoic acid with pyridine; blue line, complex of 2,4-dinitrobenzoic acid with pyridine; purple line, complex of 3,5-dinitrobenzoic acid with 3,5-dimethylpyridine.

Geometrical Parameters of the H-Bond and COOH Group

Systematic elongation of the H–O bond kept constant with 0.05 Å step and optimization of the rest of the H-bonded complex results in change in the NH and O(1)···N distances.

In *Fig. 2*, the theoretical correlations calculated for the complex of pyridine with benzoic acid and 2,4-dinitrobenzoic as well as for 3,5-dimethylpyridine with 3,5-dinitrobenzoic acid are compared with the experimental data measured for the complexes of 2,4-dinitrobenzoic acid with pyridine and 3,5-dinitrobenzoic acid with 3,5-dimethylpyridine. The structures of 2,4-dinitrobenzoic acid [25] and 3,5-dinitrobenzoic acid complexes [26] were determined with neutron diffraction at different temperatures, changed from 30 to 330 K. Both complexes are characterized by strong O(1)HN H-bond in which the location of the H-atom is sensitive to temperature and the O(1)H and NH distances precisely reflect the H-atom shift in the H-bond. Because the structures were measured with neutron diffraction, the standard deviation for H–O(1) and NH bonds were 0.004 Å for 30 K and 0.01 Å for 300 K, and the precisely determined distances can be compared with the theoretical calculations. Correlations of both distances with H–O(1) bond length shown in *Fig. 2* are identical to the respective correlations for other O(1)HN complexes [15][20]. Analogous correlations for

OHN and NHN H-bond [27] were compared with the experimental data taken from CSD database and confirmed general character of this correlation which is determined by constant valency of the H-atom moving from donor to acceptor. Also the correlation of the N···O(1) distance (*Fig. 3a*) is similar to the correlations for phenol–tertiary amine complexes [15][20]. The points illustrating the experimental structures determined with neutron diffraction at different temperatures and different proton transfer degree included in the correlation are located at the theoretical curves and confirm their general character.

It can be expected that the geometry of the COOH group is sensitive to the proton transfer. Changes in C–O(1) and C–C(1) bond linking the COOH group to the benzoic acid aromatic ring shown as a function of the H–O(1) bond length (*Fig. 4*) confirm this expectation. Shifting of the H-atom to the acceptor causes equalization of both CO bonds and elongation of the C–C(1) bond.

Sensitivity of the O(1)–C=O(2) angle of the COOH group to the proton transfer is insignificant and the angle changes in the range of *ca.* 2°. Although only three proton donors have been investigated, theoretical correlations show the sensitivity of the proton transfer process to the substituents in the benzoic acid ring. In another theoretical measure of the proton transfer, other than the parameters of the H-bond, the difference in both CO bonds can be suggested (*Fig. 4*). The correlation of difference between the CO bond lengths in the COOH group with the H–O(1) bond length presented in *Fig. 5* confirm that this parameter can be used as a measure of the proton transfer degree for carboxylic acid intermolecular complexes. The correlation has sigmoidal shape with the inflection point at the OH values characteristic for central location of the H-atom in the H-bond.

The change in the C–C(1) bond length is systematic but limited only to 0.04 Å so it cannot be useful for determination of the proton transfer degree in the X-ray structures. Differences between the theoretical curves and the experimental data show that the influence of the proton transfer on the geometry of the COOH group is hidden by effects of packing of the complex in the crystal lattice. Additional effects that influence the spreading are thermal motions and anharmonicity of vibrations of the COOH group as well as isotropic refinements of the structures determined by diffraction (*i.e.*, time averaged over the motions) [28] so the shorter CO distances are observed at higher temperatures. Excellent agreement is observed for the experimental and theoretical NH and O(1)···N bond lengths but not for C=O(2) and C–C(1) bonds. This result is confirmed by the experimental correlation for solid carboxylic acid complexes [29] in which general tendency to equalization of C–O(1) and C=O(2) under shifting of the H-atom to the acceptor is seen, but the experimental values are also influenced by packing in the crystal lattice. The correlation of C–C(1) bond lengths with the proton transfer degree is not observed for the experimental data available in the CSD base. It is characteristic that the experimental data in *Fig. 4* are not located at the theoretical curves. It is not strange taking into account the spreading of the C–O(1) and C=O(2) experimental bond lengths for the H-bond complexes of benzoic acids collected in the CSD base published previously (*Fig. 5*) [26]. Also the correlations of CO and C–C(1) bond lengths for 2,4-dichlorobenzoic acid [25] confirm the sensitivity to the proton transfer, but do not allow determination of general correlation of these bond lengths with the proton transfer degree. The dependence of CO and C–C(1) bond lengths on the proton transfer degree can be established by theoretical calculations but the experimental

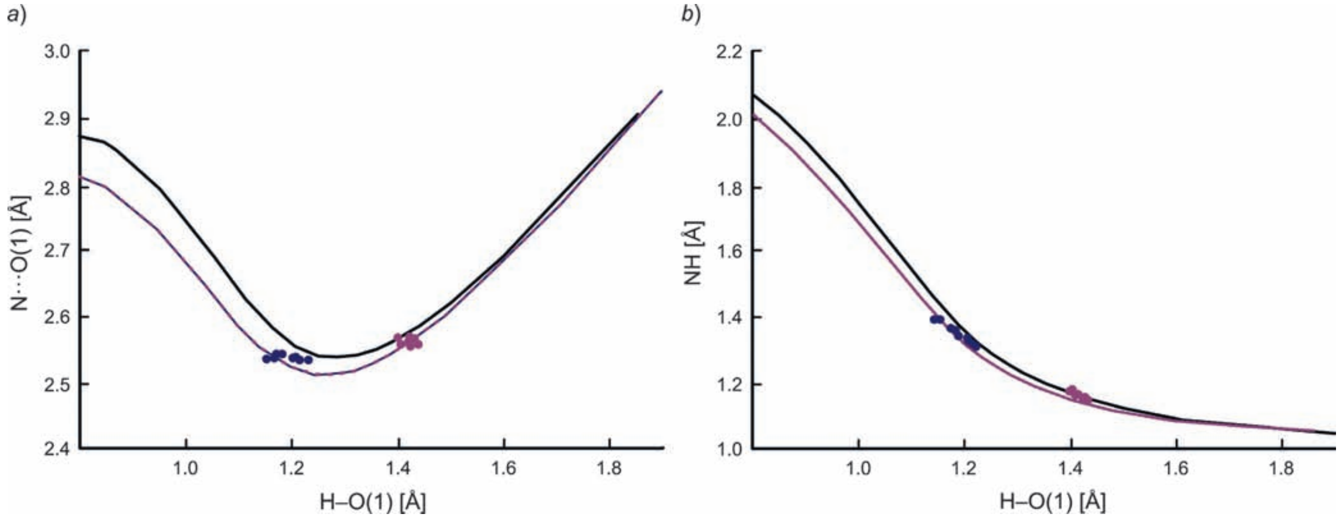


Fig. 3. Correlations of geometrical parameters of the H-bond. *a*) N···O(1) bridge length as a function of the H–O(1) bond length. *b*) Relation between NH and H–O(1) bond lengths. Black line, complex of benzoic acid with pyridine; blue line, complex of 2,4-dinitrobenzoic acid with pyridine; purple line, complex of 3,5-dinitrobenzoic acid with 3,5-dimethylpyridine. The blue line coincides with the black line. The dots represent experimental values measured previously [25][26].

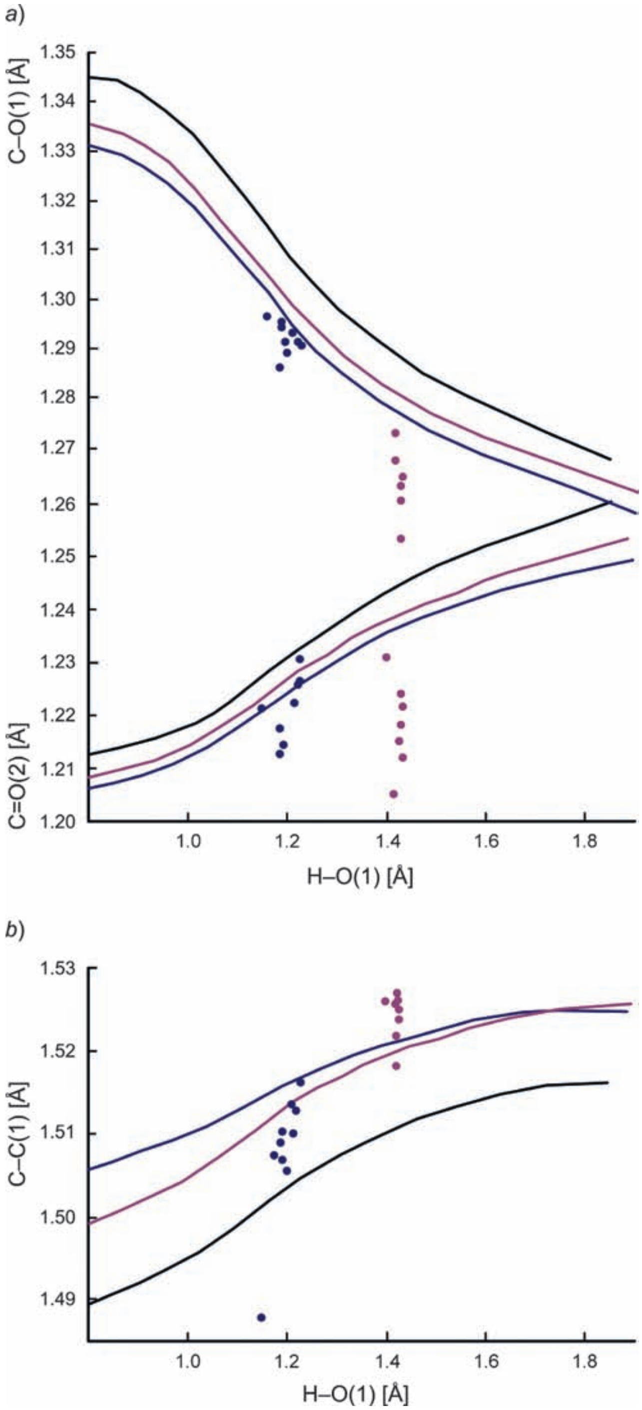


Fig. 4. Correlations of the bond lengths in the COOH group with the H–O(1) bond length. *a*) CO (C–O(1), C=O(2)). *b*) C–C(1) Bond linking the COOH group with the aromatic ring. Black line, complex of benzoic acid with pyridine; blue line, complex of 2,4-dinitrobenzoic acid with pyridine; purple line, complex of 3,5-dinitrobenzoic acid with 3,5-dimethylpyridine. The dots represent experimental structures [25][26].

bond lengths can be influenced by packing and substituent effects, and could be different from the theoretical prediction.

The influence of solid state is reflected in the angle between aromatic rings of the benzoic acid and pyridine. For experimental structures, this angle was changed systematically in the range of 8 – 11 and 78 – 83° for the complex of 3,5-dinitrobenzoic acid with 3,5-dimethylpyridine and pyridinium 2,4-dinitrobenzoate, respectively. For the optimized molecules, these angles are close to 0° for the complex of 3,5-dinitrobenzoic acid with 3,5-dimethylpyridine and 37 – 60° for 2,4-dinitrobenzoic acid with pyridine. For the latter compound, the theoretical dependence of the angle formed between aromatic rings of benzoic acid and pyridine with the H–O(1) bond length shows that the location of the H-atom in the middle of the H-bond results in flattering of the complex. This observation has been not confirmed by the experimental results. Because of flexibility of the H-bond, the general conformation of the complex can be easily modified and electric and packing properties of the surrounding of the molecule determine the angle between aromatic planes and the effect of the H-bond strength can be masked by these effects.

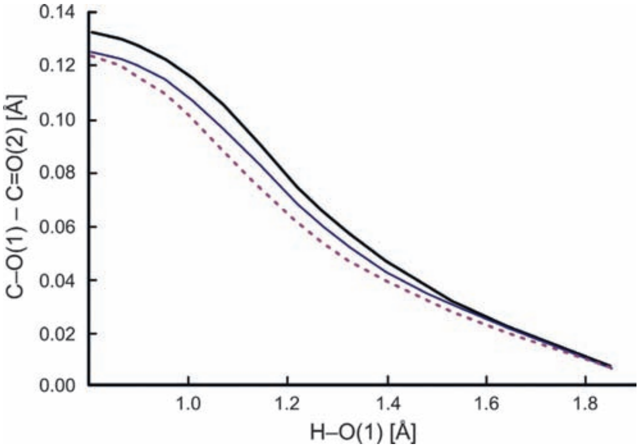


Fig. 5. Correlations of difference between the CO bond lengths in the COOH group with the H–O(1) bond length. Black line, complex of benzoic acid with pyridine; blue line, complex of 2,4-dinitrobenzoic acid with pyridine; purple line, complex of 3,5-dinitrobenzoic acid with 3,5-dimethylpyridine.

Geometrical Parameters of Proton Donor and Proton Acceptor

As shown previously [15][20][30], for the complexes of phenols with tertiary amines, the CO bond length can be used as a measure of the proton transfer degree. Also, the CCO angle in the phenol linked to the OH group were sensitive to the transfer of the H-atom. On the contrary, the geometry of the aromatic ring of benzoic acids is not sensitive to shifting of the H-atom in intermolecular H-bond. In complexes of carboxylic acid with pyridines, the influence of the proton transfer is evident in the geometry of the pyridine ring on the contrary to the complexes of phenols. *Fig. 5* shows theoretically obtained changes in the NC and CC bond lengths in pyridine ring under the proton transfer. It is characteristic that the CC bonds are more elongated than the NC bonds in the

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proton acceptor. Also, the angles in pyridine ring change systematically with the proton transfer and their correlations with the OH bond length have sigmoidal shape analogously to the correlations of the bond lengths.

Because the changes in the bond lengths presented in *Fig. 6* are very limited, the comparison of the experimental values measured with accuracy typical of the diffraction methods with the bond length determined theoretically to the precision of 0.0001 Å is not reasonable, and for this reason in *Fig. 6*, the experimental values have not been included. However, the correlations in *Fig. 6* present the theoretical dependencies, which can illustrate the influence of the proton transfer on the proton acceptor geometry.

NBO Analysis of the Investigated Complexes

Shifting of the H-atom from the proton donor to the proton acceptor causes reorganization of the electrons around the atoms involved in the H-bond. These changes can be expressed by changes in the electron densities at Bond Critical Point (BCP) but detailed investigation of the proton transfer mechanism must include more precise analysis. The NBO model based on *Löwdin*'s concept of 'natural' localized orbitals provides the most accurate possible natural *Lewis* structure [31][32] in which the electron density is localized on the bonding orbitals and the lone pairs with empty antibonding orbitals. The highest possible percentage of the electron density is treated as the chemical bonds, localized electrons or nonbonding lone pairs [33][34]. Occupancy of the valence antibonding orbitals reflects departure from an idealized localized *Lewis* structure. Natural localized molecular orbital (NLMO) is a linear combination of the parent NBO with contribution of the antibonding orbital and the percentage of the NBO in NLMO gives an intrinsic measure of the accuracy of the natural *Lewis* structure. If orbitals are strictly localized, the percentage of the NBO in NLMO is higher than 99% which happens often in typical organic compounds.

Investigation of the molecular orbitals at every step of H-atom moving from the donor to the acceptor along the H-bond explains the mechanism of the proton transfer. Previously [26], the NBO analysis was performed for the experimental structures of complex of 3,5-dinitrobenzoic acid with 3,5-dimethylpyridine and pyridinium 2,4-dinitrobenzoate with precise determination of the proton location upon temperature change. These experimental structures referred to real proton transfer process but even a combination of the molecular complex (complex of 3,5-dinitrobenzoic acid with 3,5-dimethylpyridine) with similar complexes of ionic character (pyridinium 2,4-dinitrobenzoate) was insufficient to cover full range of the proton transfer starting from the structure with the H-atom located at the donor up to the structure with the H-atom located close to the acceptor. The NBO

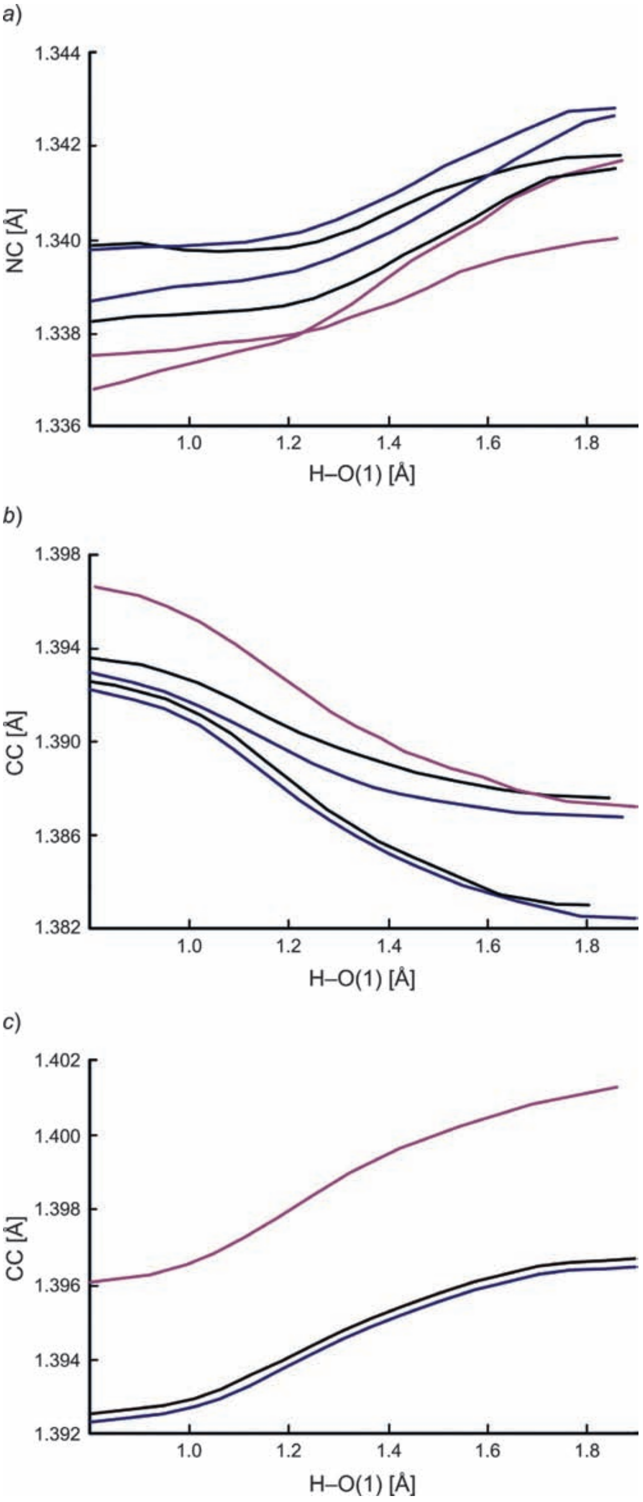

Fig. 6. Correlations of the bond lengths in the pyridine acceptor molecule with the H–O(1) bond length. *a*) NC(7), NC(11). *b*) CC Close to the CN bond (C(7)C(8) and C(10)C(11)). *c*) CC Including the C-atom in *para* position to the N-atom (C(8)C(9) and C(9)C(10)). Black line, complex of benzoic acid with pyridine; blue line, complex of 2,4-dinitrobenzoic acid with pyridine; purple line, complex of 3,5-dinitrobenzoic acid with 3,5-dimethylpyridine.

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analysis of the theoretical structures optimized at different H–O(1) bond lengths can reproduce the full range of the proton transfer degree.

To better understand the nature of H-bond and the changes in the proton donor and the proton acceptor taking place upon the proton transfer, the orbitals engaged in the H-bond are analyzed. *Fig. 7* presents the molecular orbitals which can be engaged in the proton transfer process: the H–O and H–N bonds, and lone pairs at the O- and N-atoms. The H–O bond exists in a limited range of the proton transfer. At H–O bond length = 1.05 Å, participation of the H-atom in the H–O NBO orbital is lower than 20% and the molecular orbital connected with the H–O bonding orbital disappears. For the same H–O bond length, the O3 orbital arises (*Fig. 5*). Similarly, when the participation of the H-atom in the NBO orbital gets higher than 20%, the lone pair at the N-atom is replaced by a H–N bond. Among the orbitals in *Fig. 6*, only the O1 orbital is not very sensitive to the proton transfer. The participation of the H-atom in the O1 lone pair of the O-atom can be neglected, so this orbital does not participate in the proton transfer process although small changes in this orbital have also been detected.

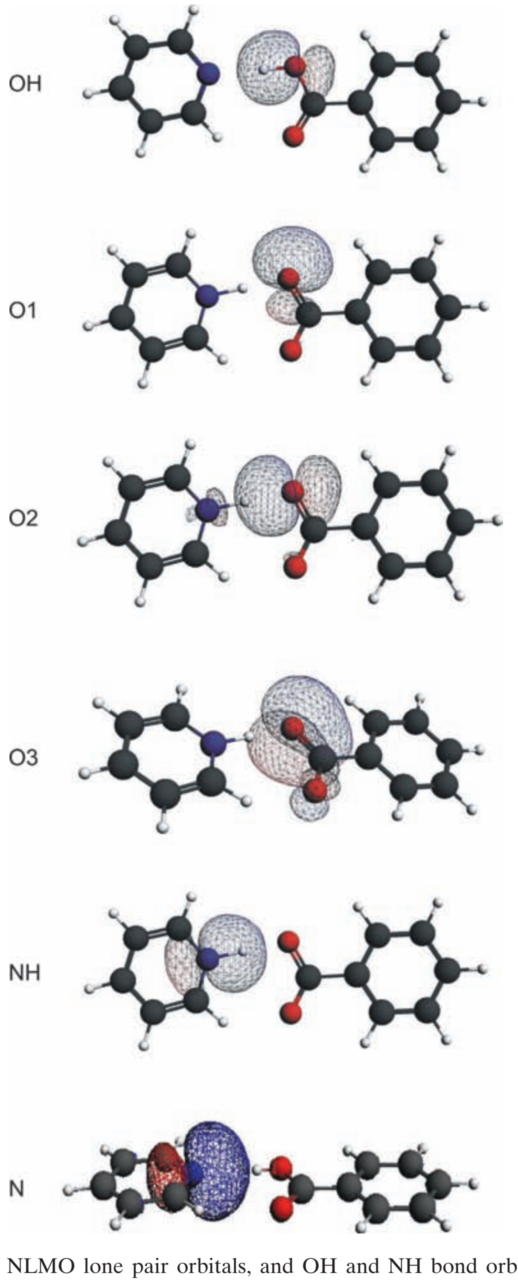

Fig. 7. NLMO lone pair orbitals, and OH and NH bond orbitals in the proton donor and the proton acceptor in benzoic acid–pyridine complex.

As shown previously [26], the proton transfer process is connected with changes in delocalization of the orbitals on the proton donor and the proton acceptor. A measure of delocalization is the percentage of the NBO in the NLMO. From among the lone pairs in *Fig. 7*, the most delocalized are O2 and O3 orbitals at the O-atom. Also, delocalization of the lone pair on the pyridine N-atom is significant. The OH and NH bonding orbitals and the O1 lone pair are not delocalized and their contribution in NLMO is higher than 99%. Delocalization of the NLMO orbitals sensitive to the proton transfer is very significant and the percentage of parent NBO is decreased up to 80%. *Fig. 8* presents the correlations of participation of the NBO orbitals in their respective NLMOs. The correlation of percentage of the NBO in NLMO with H–O bond length characterizing the O3 and O2 orbitals has a lambda shape. Sigmoidal shape is characteristic of the plot illustrating the percentage contribution of the pyridine N-atom lone pair in the NLMO. The plot showing the correlations of the percentage contribution of the NBO in NLMO with H–O bond length for the O2 and O3 orbitals can be described by a lambda shape with extremes at the OH distance characteristic of central location of the H-atom. If the H-bond is the strongest, delocalization of O2 orbital is the greatest but O3 orbital becomes more localized than for the weaker H-bonds. It is characteristic that for the strongest H-bond delocalization of O2 and O3 orbitals is the same.

The Points Representing the Experimental Structures Confirm the Theoretical Correlations in Fig. 8

Delocalization of the lone pairs is related to the contribution of the H-atom in NLMO and if the molecular orbital is more delocalized, the contribution of the H-atom is more significant. *Fig. 9* presents the correlations of the H-atom percentage contribution in NLMO with H–O(1) bond length and these plots reflect the pathway of the H-atom from the donor atom to the acceptor. By checking in which orbital the contribution of the H-atom is the highest, it is possible to conclude about the mechanism of the proton transfer process. For the orbitals in *Fig. 7*, the highest participation of the H-atom is seen in the O-atom lone pair parallel to the H-bond (O2) and in the lone pair of the pyridine N-atom.

For the weak molecular H-bonds, the H-atom is engaged in the H–O(1) bond (broken line in *Fig. 9a – c*).

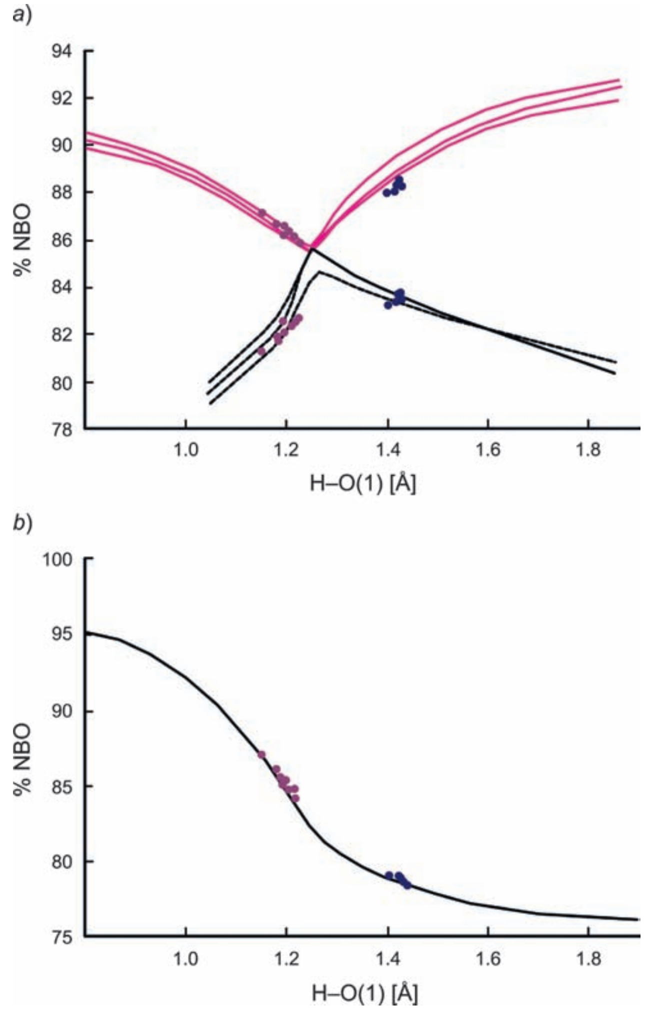

Fig. 8. Percentage of the parent NBO orbitals in delocalized NLMO. *a*) O2 (upper curves) and O3 (lower curves) lone pair orbitals of the donor O-atom. *b*) Lone pair of the N-atom acceptor. The dots represent values calculated for the experimental structures measured previously [25][26].

Strengthening of the H-bond and elongation of the H–O(1) bond is connected with a decrease in the H-atom participation in the H–O bond. At the contribution of 20%, this bond disappears and the O3 lone pair at the O-atom donor appears (black line in *Fig. 8a – c*). At longer H–O distances, the H-bonded H-atom can participate in the O3 orbital as in benzoic acid–pyridine (*Fig. 9a*) and 3,5-dinitrobenzoic acid–3,5-dimethylpyridine complexes (*Fig. 9c*), but it can also be shared between the O3 and O2 orbitals as for the complex of 2,4-dinitrobenzoic acid with pyridine (*Fig. 9b*). Shifting of the H-atom to the center of O···N distance can be realized by participation of the H-atom in both O2 and O3 orbital. Movement of the H-atom to the acceptor is reflected by an increase in the H-atom percentage contribution in the pyridine N-atom lone pair and at percentage of 20% of the H-atom in the N-atom lone pair, the NH bond is formed (*Fig. 9d*).

Theoretical curves in *Figs. 8* and *9* are confirmed by the orbitals determined for the experimental structures measured by neutron diffraction. Because the H-atom in the experimental structures is moved upon temperature change in a very limited range, it was not possible to reproduce the evolution of the orbitals correctly [26]. Theoretical calculations reproduce the correlations which would be difficult to be obtained including only the experimental structures with limited values of the H–O(1) distance. Theoretical investigation of the proton transfer process combined with the calculation performed for the experimental structures brings information on the proton transfer mechanism and results obtained for the experimental structures confirm the theoretically obtained correlations.

Conclusions

1. Theoretical curves presenting the correlations of the distances in the H-bond (H–O(1), H–N, O(1)···N) under the proton transfer are identical with those for other OHN intermolecular complexes investigated previously [25][26]. Experimental results obtained by neutron diffraction method for 2,4-dinitrobenzoic acid with pyridine and 3,5-dinitrobenzoic acid with 3,5-dimethylpyridine follow the theoretically predicted correlations.
2. The CO and C–C(1) bond lengths of the COOH group are sensitive to the proton transfer but the experimental results do not coincide with the theoretical dependence. Besides showing sensitivity to the proton transfer degree, the bond lengths in the COOH group are sensitive to the substituents in the benzoic acid ring.
3. The proton transfer does not influence the geometry of the benzoic acid ring. The bond lengths in the proton acceptor pyridine ring change systematically with elongation of the H–O(1) bond length. Because of the influence of substituent, the bond lengths in pyridine ring cannot be used as a universal measure of the proton transfer degree.
4. The electron density at the critical points in the H-bond and in the COOH group is related to the bond length and changes upon the proton transfer. For the CN (NC(7), NC(11)) bonds in the proton acceptor ring, this change is different for particular compounds.
5. The NBO analysis brings information on the mechanism of the proton transfer in which two donor O-atom lone pairs and a lone electron pair of acceptor are engaged. The most characteristic are changes in delocalization of the COOH group O-atom lone pairs with equalization of the delocalization at 50% of the proton transfer. The participation of the H-atom electrons in two donor's lone pairs is similar. The participation of the H-atom in two donor's lone pairs confirms the possibility of shifting of the H-atom in intermolecular H-bond along many directions.

I thank the *Wroclaw Centre for Networking and Supercomputing* for generously granting the required computer time.

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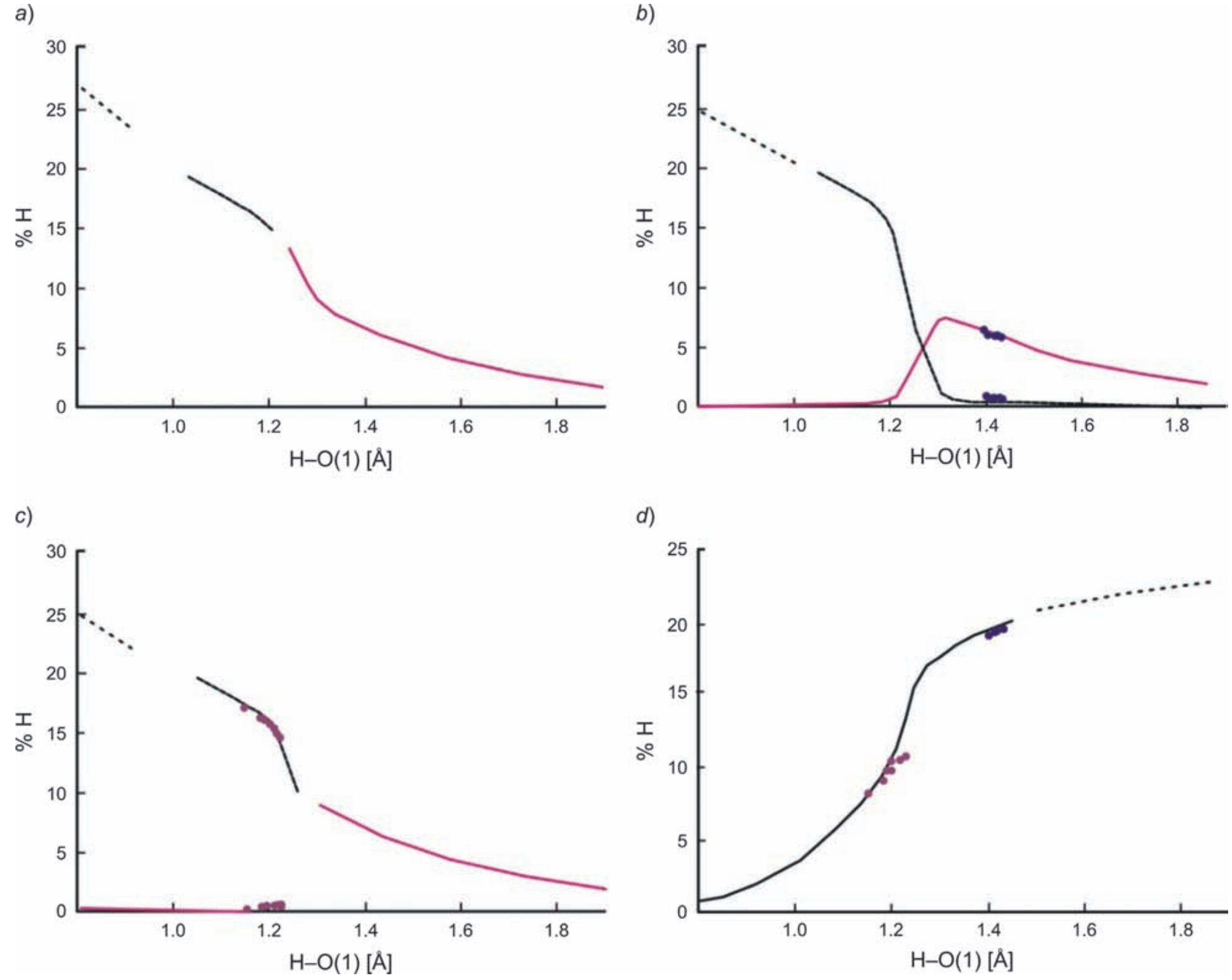

Fig. 9. Percentage contribution of the proton NBO orbital in delocalized NLMO of donor (*a* – *c*) and acceptor (*d*). *a*) Benzoic acid–pyridine complex. *b*) Pyridinium 2,4-dinitrobenzoate complex. *c*) 3,5-Dinitrobenzoic acid–3,5-dimethylpyridine complex. Broken line, OH (NH) bond; black line, O3 (N) orbital; purple line, O2 lone pair orbital. The dots represent experimental values measured previously [25][26].

Calculations

The experimental geometry of the investigated compounds was fully optimized at the B3LYP/6-311++G** level of theory using the GAUSSIAN09 [35] system and to check that the result geometry reached the energy minimum vibrational frequencies were calculated. In the next step of the calculation, the OH distance was kept constant and all other geometrical parameters were optimized. This method reproduces nonadiabatic movement of the H-atom in very broad range, from very close location to the donor up to shifting it to the acceptor. For each of the investigated compounds, the OH bond length was changed from 0.7 to 2.1 Å in steps of 0.05 Å with other geometrical parameters optimized. In the correlations, the OH distances are limited to the physical values 0.8 – 1.9 Å. The atom coordinates of the optimized structures were used to perform the NBO analysis with the NBO5.0 [36] at hybrid B3LYP level implemented in ADF [37] without any optimization with *Slater* basis sets used in ADF program.

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Received July 13, 2015
Accepted January 25, 2016

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