Strong OHO Hydrogen Bond. How much covalency?

Irena Majerz

► To cite this version:

Irena Majerz. Strong OHO Hydrogen Bond. How much covalency?. Molecular Physics, 2008, 105 (17-18), pp.2305-2314. 10.1080/00268970701556244 . hal-00513127

HAL Id: hal-00513127

<https://hal.science/hal-00513127>

Submitted on 1 Sep 2010

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Strong OHO Hydrogen Bond. How much covalency?

Journal:	<i>Molecular Physics</i>
Manuscript ID:	TMPH-2007-0208
Manuscript Type:	Full Paper
Date Submitted by the Author:	04-Jul-2007
Complete List of Authors:	Majerz, Irena; University of Wroclaw, Faculty of Chemistry
Keywords:	Hydrogen bonding, AIM analysis, phosphoric acid – urea complex

Strong OHO Hydrogen Bond. How much covalency?

Irena Majerz*

Faculty of Chemistry, University of Wrocław, Joliot-Curie 14, 50-383 Wrocław, Poland

Keywords: Hydrogen bonding, AIM analysis, phosphoric acid – urea complex

Abstract

In the strong OHO hydrogen bond of the phosphoric acid-urea 1:1 complex, the proton shifts gradually with temperature from the donor towards the acceptor atom, passing through the center of the hydrogen bond at around 315 K. The AIM parameters were evaluated for the published neutron structures at different temperatures. The values of the electron density, its Laplacian, and the energy densities at both the critical points between the proton and the oxygen atoms in the OHO hydrogen bond were correlated with the OH and HO distances. Changes in the AIM parameters of the strong hydrogen bond were compared with those of the weak NHO bond in this complex.

**Corresponding author:* I. Majerz, Faculty of Chemistry, University of Wrocław, Joliot-Curie 14, 50-383 Wrocław, Poland
E-mail: maj@wchuwr.chem.uni.wroc.pl Tel: (+48)(71)375-7353 Fax: (+48)(71)3-282-348

Introduction

The hydrogen bond has been intensively investigated for many years, but many fundamental problems concerning proton transfer are still open. Especially interesting and important are short, strong hydrogen bonds with a central location of the proton between the donor and acceptor atoms. In recent years much attention has been devoted to strong hydrogen bonds because of their important role in biological reactions and as a transition state in enzymatic catalysis [1]. Direct investigation of the hydrogen bond in biological systems is not easy and for this reason simple complexes with inter- and intramolecular hydrogen bonds are widely used as model compounds reflecting the general features of the strong hydrogen bond. Among the most important questions concerning the hydrogen bond is the mutual dependency of the position of the proton migrating through the hydrogen bond center and changes in the electron density, which is responsible for the electrostatic and covalent character of the hydrogen bond.

The parameter which determines all hydrogen bond properties is the position of the proton in the hydrogen bridge. However, very accurate determinations of the proton's position in such short hydrogen bonds by neutron diffraction are relatively few. A very well-investigated compounds with short OHO hydrogen bonds is the phosphoric acid-urea 1:1 complex. Many neutron studies of this compound have been made at different temperatures in the 100-350 K range [2 - 5]. As the temperature increases, the bond length changes from 2.400(5) to 2.430(9) Å [2, 3] and the proton moves from the acceptor (urea) to the donor (phosphoric acid), passing through the hydrogen bond center at around 315 K. The hydrogen bond in the phosphoric acid-urea complex changes from molecular to ionic through the very strong bond with a symmetrical proton location, and this complex is currently being intensively investigated with many

experimental [2 - 6] and theoretical methods [7 - 9] as a model compound illustrating general features of the strong hydrogen bond. The geometrical parameters of the OHO bond at different temperatures are summarized in [2]. The neutron structures of the phosphoric acid-urea 1:1 complex measured at different temperatures appear to be good objects for investigating the influence of proton transfer on the electron cloud at the hydrogen atom as well as at the proton donor and acceptor atoms.

Whereas neutron diffraction delivers the precise position of the proton, X-ray diffraction gives information about the distribution of the electron cloud around the hydrogen bond. These two methods, combined with analysis of the Fourier maps, may deliver a complete description of the strong OHO hydrogen bond in the phosphoric acid-urea 1:1 complex [6].

While experimental electron density is able to show what the electron cloud looks like, the AIM theory [10] gives quantitative parameters describing the electron density at the critical points. Interatomic interactions can be examined through atom in molecule (AIM) topological analysis of the electron density distribution $\rho(r)$ developed by Bader [10]. AIM theory is based on the properties of $\rho(r)$, the gradient vector $\nabla\rho(r)$ and the Laplacian $\nabla^2\rho(r)$. The theory of AIM provides a partition of the molecular space into atomic basins associated with basins of local zero flux in the gradient vector field of the electron density and the basins correspond to topologically defined atoms. At the extremes of $\rho(r)$ the $\nabla\rho(r)$ vanishes and these points are named the critical points (CP) and classified according to the three eigenvalues ($\lambda_1, \lambda_2, \lambda_3$) of diagonalized Hessian matrix of $\rho(r)$. Stable critical points belong to one of four categories: maxima in $\rho(r)$ correspond to attractors attributed to nuclei, minima correspond to cage critical points (CCPs), and the saddle points in $\rho(r)$ correspond to bond critical point (BCPs) or ring critical points (RCPs). Each critical point is labeled by the pair of numbers where the first is the number of nonzero λ eigenvalues of Hessian of $\rho(r)$ and the second is the difference between the nonzero and the negative λ eigenvalues. The nuclear critical point is labeled (3, -3), the cage critical point is labeled (3, +3) and the bond and ring

critical point (3, -1) and (3, 1) respectively. The zero flux surface where $\nabla\rho(r) = 0$ splits the molecule in fragments linked by bond paths described as (3, -1). Two atoms are determined to be bonded if they exist at either ends of a common bond path, this being defined as the set of two gradient paths extending from the BCP. AIM theory is a quantitative description of charge density that allows examining the number and the nature of critical points in and around molecule. The set of BCPs defines the network of bond paths and characterizes the interaction between atoms. A critical point (CP) is characterized not only by its density, location, curvatures and associated signs but also by the potential and kinetic energy of electrons at critical points which can be evaluated from topological parameters of electron density. Analysis of topological parameters of critical points and bond paths which link critical points is an entire, quantitative description of the molecule and the interactions in molecular system.

AIM parameters not only describe the electron density, but also allow an evaluation of the potential and kinetic energy of the electrons at BCPs which describe the properties of the chemical bond. This is especially important considering the untypical properties of the hydrogen bond compared with other chemical bonds.

Theoretical calculations of very strong hydrogen bonds indicate its partially covalent character, which increases with hydrogen bond strength [11]. This process is connected with rearrangement of the electron cloud when the proton passes through the center of the hydrogen bond [12].

In this paper, another approach is suggested which can be useful in the analysis of the electron density in strong hydrogen bonds: the neutron structure with a precise location of hydrogen is used to perform an AIM analysis of the electron density. The systematic investigation of AIM parameters results in a quantitative description of the changes in electron density in the proton transfer process based on the experimental neutron structure.

The relationships of the electron density at the BCPs and the theoretical distance between the proton and proton donor in the lowest energy structure were studied earlier. The aim of this study, not realized until now, is to correlate the electron density at the BCPs of very strong hydrogen bonds with geometrical parameters of the hydrogen bridge, accurately determined by neutron diffraction. The temperature evolution of the OHO hydrogen bond in the phosphoric acid-urea complex offers a unique possibility to investigate the change in the electron density from a molecular complex through a very strong, symmetric hydrogen bond to an ionic complex with the proton transferred closer to the acceptor. The presence of strong OHO and weak NHO hydrogen bonds in this complex makes possible a comparison of the relationships of a strong hydrogen bond and those of a weak bond, in which the proton does not pass through the hydrogen bridge center.

Experimental

All the neutron structures of the phosphoric acid-urea 1:1 complex are available in the CCD base (ref.-codes: CRABAMPO1-2, CRABAMPO5-8, CRABAMPO10-25). These structures were used to evaluate the wave function at the B3LYP/6-311++G** level using the Gaussian 03 program [13]. AIM analysis was performed with the AIM2000 program [14] with all the default options. The integration of atomic properties over atomic basins was performed in natural coordinates, with a tolerance of 0.001 per integration step. The analysis was concentrated on localizing of the bond critical points (BCP) in strong OHO hydrogen bond for which the electron densities ($\rho(r)$) and Laplacians ($\nabla^2\rho(r)$) were calculated. The eigenvalues of Hessian of electron density at BCP were used to calculate the electronic kinetic energy density ($G(r)$), potential energy density ($V(r)$) and total energy density ($H(r)$). Also the distances of the BCPs to proton

in OHO hydrogen bond ($\text{H1-BCP}_{\text{H1}\dots\text{O1}}$ and $\text{H1-BCP}_{\text{H1}\dots\text{O2}}$) as well as the distances of BCPs to the bond centre were analyzed.

The most important step in AIM analysis is finding the bond critical points (BCPs) located on the gradient path, which reflects the interaction between the atoms. For the lowest energy structure, these gradient paths correspond to the chemical bonds. For this reason, AIM analysis is usually preceded by optimization of the molecular structure. Sometimes the crystal structure is used as the starting point in the optimization process, and the AIM parameters evaluated for the optimized structure are used to discuss the interaction in the solid state [15]. Another approach is the single-point calculation performed for the solid-state structure in which the molecule is not optimized [16]. For typical covalent bonds, both methods can give similar results. For hydrogen-bonded complexes, an additional question is which calculation method can correctly reproduce the geometry of the hydrogen bond. This question is especially important for very strong hydrogen bonds. Compared with the weak NHO bond in the phosphoric acid-urea 1:1 complex, the very strong OHO bond is not correctly reproduced. In the experimental solid-state structure, the proton in the OHO bond is located close to the hydrogen bridge center, but in the optimized structure, regardless of the calculation method, it is located at the donor atom. The calculated $\text{O}\cdots\text{O}$ distance is also elongated and closer to values typical for weak, molecular hydrogen bonds. Compared with the OHO hydrogen bond, the weak NHO hydrogen bond is reproduced quite well in the optimization process. It is known that the OHO hydrogen bond in the phosphoric acid-urea complex is better reproduced applying periodic boundary conditions [7]. The calculated $\text{O}\cdots\text{O}$ distance of 2.42 Å is close to the neutron structure at 15 K (2.416 Å), but the OH bond lengths, which in the neutron structure are equal to 1.158 and 1.267 Å,

are 1.105 and 1.329 Å, respectively, after optimization. The plane-wave DFT calculation locates the proton closer to the hydrogen-bridge center than the single molecule optimization, although both OH distances are still very far from the experimental values in the solid state. In this study the plane-wave calculations were performed with the CASTEP program [17] using the CRAMP01 [5] neutron structure as the starting point. The DFT method implemented in CASTEP reproduces the cell parameters very well ($a = 17.578$, $b = 7.5258$, $c = 9.0705$; for the neutron structure $a = 17.43(2)$, $b = 7.43(2)$, $c = 8.97(2)$ Å), but the geometry of the strong OHO hydrogen bond is still far from the experimental values. The O...O distance is 2.5619, O-H is 1.0954, and O...H is 1.2669 Å. Despite the shortening of the O...O distance and elongation of O-H, the central location of the proton in the strong hydrogen bridge is not achieved.

The difficulties in reproducing of the experimental geometry of the short hydrogen bridge by theoretical methods are closely related to the character of the strong hydrogen bond. Symmetric position of the hydrogen in crystallographic studies results from average character of structure over many unit cells and thermal movements of atoms so the neutron diffraction experiment reflects a vibrational average, which shifts with temperature as vibrational populations change.

Neutron diffraction localizes the proton in strong hydrogen bond in the middle of the hydrogen bridge but the most probable position of the proton is described by the potential for the proton movement in the hydrogen bridge. For the strong hydrogen bond the PES can be a double minimum curve with a low barrier between the minima or a single minimum curve. In both cases neutron experiment finds proton in the middle of the O...O distance when it can be localized in one of the minima or on the top of the energy barrier as an unstable geometry. In case of the potential energy curve with one broad minimum the proton can be delocalized around the centre of the hydrogen bridge. The potential energy curve for OHO hydrogen bond in phosphoric acid-urea 1:1 complex calculated in this work is in agreement with the result published previously [9].

It is characterized by one unsymmetrical minimum and the second minimum is seen as a shoulder. If treat the shoulder as a second minimum, it is located close to the top of the energy barrier. Such a nonsymmetrical shape of the potential energy curve shows that proton motion in strong hydrogen bond is very sensitive to nonequivalence of both oxygen atoms engaged in the hydrogen bond as they are parts of different molecules. The change of temperature from 150 to 335 K slightly modifies the shape of the curve so the energy of the first excited vibrational level changes from 2.74 to 3.00 kcal/mol. The shape of the potential energy curve illustrates the dynamic of the proton in strong hydrogen bond which can easily without any barrier move between both oxygen atoms. Thus, determination of exact position of minimum on the potential energy surface becomes difficult and the neutron measurement gives an averaged geometry of the proton bridge.

The problem as to which calculation method correctly reproduces the strong hydrogen bond in the solid state is still open. As the aim of this study was just to investigate the electron density in the strong solid-state OHO hydrogen bond as the proton moves with temperature, reproduction of the solid-state structures was done by single-point calculations at the B3LYP/6-311++G** level for each neutron structure measured at different temperatures. The lowest energy structure of the complex obtained as a result of optimization at this level consists of molecular OHO and NHO hydrogen bonds with the proton located at the proton donors, i.e. phosphoric acid and urea, respectively. In the optimized structure the OHO bond is 2.571 Å long, with OH distances of 1.016 and 1.555 Å. The NHO bond is equal to 2.862 Å, with NH and OH distances of 1.024 and 1.847 Å, respectively.

The optimized OHO hydrogen-bond parameters differ considerably from the neutron structures and cannot be included in the correlations, whereas the results for the very weak NHO bond can be used as the reference structure of the weak hydrogen bond in vacuum.

Results and discussion

The notation of the atoms in the two hydrogen bonds and the critical points are shown below.

As shown in the scheme, the BCPs were found between the proton and both oxygen atoms in the OHO bond as well as between the proton and oxygen and nitrogen in the NHO hydrogen bond. The value of the electron density at the BCP between H2 and O3 is typical for a weak hydrogen bond, while that between H2 and N1 illustrates a covalent bond. Of the BCPs connected with the two hydrogen bonds, only the value of $\rho(r)$ connected with O3-H2 fulfills the criteria for a hydrogen bond given in [18, 19], but only this critical point is connected with the weak hydrogen bond.

1. Electron densities at BCPs

As shown in [18], $\rho(r)$ at the BCP increases with hydrogen bond strength and describes the degree of charge concentration in the bond path, so it can be used as a characterization of the bond order. In Fig 1a are shown the relationships of $\rho(r)$ between the two critical points of the OHO bridge in the phosphoric acid-urea 1:1 complex and OH distances, and it appears that both relationships can be described by a common straight line: $y = -0.4835x + 0.7487$, $R^2 = 0.9791$. Fig. 1 shows that the two OH distances in the strong OHO bridge can be used as a measure of hydrogen-bond

strength. For strong OHO hydrogen bonds, the two BCPs are equivalent, which is reflected in similar values of $\rho(r)$. For this reason it is possible to plot the relationship between the electron density and the O...H distance common to both BCPs of the OHO hydrogen bond in the phosphoric acid-urea complex. There are only two molecular complexes with the proton located closer to the phosphoric acid oxygen, but investigation of the relationship common to both BCPs in the OHO hydrogen bond also makes it possible to find the relationship for molecular complexes: $y = 0.4823x - 0.4175$, $R^2 = 0.9896$. The two straight lines for the molecular and ionic complexes have similar slopes but opposite sign, which is obvious for homonuclear OHO hydrogen bonds. The crossing point of these two lines shows the parameters of the shortest of the known OHO hydrogen bridges. The O...H bond length is 1.2074 Å and the value of the electron density at the BCP is 0.1648, so the O...H bond length in intermolecular OHO cannot be shorter than 1.2074 Å and at this bond length the highest bond order, equal to 0.1648, is reached.

The electron density at the BCP of the weak O...H hydrogen bond changes in the 0.02 - 0.032 range exceeds the value 0.002 au used as criterion of hydrogen bond existence [19]. The electron density of the covalent NH bond changes in the 0.32 - 0.38 eÅ³ range. A similar common relationship of $\rho(r)$ to the distances in the weak NHO hydrogen bond is impossible due to the significant differences in the $\rho(r)$ values at both BCPs. Equalization of the $\rho(r)$ values of the OHO bridge can be used as a criterion for the existence of a strong hydrogen bond and appears to be more precise than the geometrical parameters of the hydrogen bridge.

The changes in electron density at both BCPs of the strong OHO hydrogen bond are dependent on each other. Increasing the electron density at the BCP of one O...H causes

a decrease at the second according to the linear relationship: $y = -0.8059x + 0.295$, $R^2 = 0.9502$. The optimized geometry, which reflects the structure in vacuum, can be included in this relationship, which reflects its general character. For the weak NHO hydrogen bond, the temperature changes in electron density at both BCPs are about ten times lower than for the strong OHO hydrogen bond and the relationship linking the two BCPs can be described by a second-order polynomial.

To illustrate the significant change in the electron density in the OHO hydrogen bond compared with the weak NHO bond it is also possible to analyze its percentage participation at a particular BCP, taking the sum of both electron densities in the OHO hydrogen bridge as 100% (Fig. 1b). General rearrangement of the electron cloud in the strong hydrogen bond is connected with a change of 40-70% of the electron density. It is possible to relate the percentage of electron density at the BCP to OH distance and the relationship is analogous to that of the electron density shown in Fig. 1a and can also be used to find the parameters of the strongest OHO hydrogen bridge with the proton located at the center. For the weak NHO hydrogen bond, the temperature shift changes only 6-9% of the electron cloud.

The sequence of the bond paths in the phosphoric acid-urea complex closes into a ring, and the ring critical point (RCP), characterized as (3,+1), appears. In this complex, the RCP is not located close to any BCPs where both critical points annihilate, so the ring structure is stable. RCP values do not correlate with any geometrical parameters, but the relationship of the RCP electron density to the electron density at the bond's critical points shows which BCP has the most influence at the ring critical point. The changes in BCP electron density for all the OH and NH bonds are similar, but the R^2 of their linear relationships with RCP electron density differ significantly. The worst correlation

is for the BCP in the N1-H2 bond, whereas the best is for the BCP of O3...H2, the weakest interaction among the analyzed bonds. Modification of the electron clouds in the center of the ring is realized through a change in the electron density of the weakest interaction.

2. Laplacian of the electron density

AIM parameters such as the Laplacian of the electron density ($\nabla^2\rho(r)$), the kinetic energy density ($G(r)$), the potential energy density ($V(r)$), and the energy density ($H(r)$) are very useful in characterizing a chemical interaction and the Laplacian is a basis for a general classification of the interatomic interaction. According to the value of the Laplacian, the interactions can be divided in two general classes. The first class describes the cases where the electric charge is concentrated between two nuclei and is called a "shared-shell" interaction ($\nabla^2\rho(r) < 0$), while the second class, the "closed-shell" interaction, is characterized by depletion of the charge in the interatomic space and concentration toward each of the interacting nuclei ($\nabla^2\rho(r) > 0$). Hydrogen bonds and Van der Waals' complexes belong to the closed-shell type. Covalent and polar bonds represent the shared-shell interaction.

The $\nabla^2\rho(r)$ values for N1-H2 and O3...H2 bond are typical of covalent and weak hydrogen bonds and for the analyzed compound at 150 K equal -1.917 and 0.087 respectively. The values of $\nabla^2\rho(r)$ at both BCPs in the OHO hydrogen bond are positive, which is typical for a hydrogen bond, but very close to zero and change within the 0.0149 – 0.091 range. According to [20], the value of $\nabla^2\rho(r)$ in the 0-1 range confirms the special character of the interaction, which is intermediate between closed-shell and sheared-shell. The interaction belongs to the closed shall type, but allows the local concentration of charge, and for this reason it has a contribution of the shared-shell

interaction. The positive but very close to zero value of $\nabla^2\rho(r)$ at the BCP in $O1\cdots H1$ and $H1\cdots O2$ indicates a partially covalent character of the strong OHO hydrogen bond. The relationship common to both OHO BCPs, including complexes with the proton located closer to the acceptor, is $\nabla^2\rho(r) = -1.1868(O\cdots H) + 1.5056$, $R^2 = 0.9667$, and for the OHO complexes with the proton closer to the donor atom $\nabla^2\rho(r) = 1.1967(O\cdots H) - 1.3729$, $R^2 = 0.9975$. The possibility to relate values of $\nabla^2\rho(r)$ to the $O\cdots H$ distances of both BCPs with the same line, as in the $\rho(r)$ relationship, once again confirms the equivalence of the two BCPs in the strong hydrogen bond. In such a bond, both oxygen atoms can be treated as proton donors or proton acceptors.

3. Energy of electrons at a BCP

Because $(\hbar/4m)\nabla^2\rho(r) = 2G(r) + V(r)$ [11], where $G(r)$ is the electronic kinetic energy density and $V(r)$ the potential energy density at a BCP, investigation of the components of the Laplacian can bring new light to the properties of the strong OHO hydrogen bond in the phosphoric acid-urea 1:1 complex. The potential energy of electrons ($G(r)$) expresses the pressure exerted on electrons at the BCP by other electrons. The kinetic energy ($V(r)$) reflects the pressure exerted by electrons at the BCP on other electrons. The total energy ($H(r)$), equal to $V(r) + G(r)$, shows the balance between these two energies. The kinetic energy density is always positive and the potential energy is always negative, so for a closed-shell interaction the kinetic energy contribution is greater than that of the potential energy. In the case of a shared-shell interaction, the potential energy dominates. If $G(r) < |V(r)| < 2G(r)$, the interaction has partially covalent and partially electrostatic character and $H(r)$, the balance of potential and

electrostatic energy, describes the interaction more precisely than the Laplacian of the electron density.

To deduce the potential and kinetic energy densities of the electron at a BCP, the eigenvalues of the Hessian matrix of the electron density may be used. It was shown [21, 22] that the curvature of the electron density (λ_3) at the BCP in a hydrogen bond is related to the kinetic energy density at the BCP along the direction of the path and that both values are connected by the linear function $G(r) = a\lambda_3$ ($a = 15.3(1) \text{ \AA}^5 \text{ kJ}^{-1} \text{ mol}^{-1} \text{ atomic unit volume}^{-1}$). Another linear relationship was found between the sum $\lambda_1 + \lambda_2$ and the local contribution to the potential energy density: $V(r) = 35.1(7) (\lambda_1 + \lambda_2)$. The relation between $\lambda_1 + \lambda_2$ and λ_3 reflects the dependence of kinetic and potential energy at the BCP [23]. This correlation for molecular hydrogen bonds of different length shown in [23] was fitted using the exponential equation $\lambda_1 + \lambda_2 = 2.5(1 - \exp(0.11\lambda_3))$. In a situation where the general correlation between $\lambda_1 + \lambda_2$ and λ_3 is known, the values for the phosphoric acid-urea complex should be compared with the relationship found previously. These relationships for the investigated compound are similar in shape to those presented in [23], but the second-order polynomial fit appeared to be better than the exponential one. The equations for the O1...H1 and H1...O2 BCPs are $y = -66.836x^2 + 101.16x - 39.139$, $R^2 = 0.9887$ and $y = -80.105x^2 + 127.56x - 51.837$, $R^2 = 0.7731$, respectively. Inserting the values for the OHO and NHO BCPs of the phosphoric acid-urea complex into the relationship presented in [23] is only partially successful. The values for the H2...O3 critical point agree with the exponential fitting performed for other hydrogen bonds, although the relationship between $\lambda_1 + \lambda_2$ and λ_3 for the H2...O3 BCP is linear because of the limited range of λ_3 values. The values of $\lambda_1 + \lambda_2$ for the BCP in N-H2 differ significantly from those discussed above because the

N-H bond is covalent and cannot be treated as a hydrogen bond. The main difference between the relationship of $\lambda_1 + \lambda_2$ versus λ_3 presented earlier [23] and the analogous relationship for the phosphoric acid-urea complex is seen for both OH bonds in the OHO hydrogen bridge. According to [23], if λ_3 changes within the 0.7 to 0.9 range, as it does for both OH BCPs of the phosphoric acid-urea complex, $\lambda_1 + \lambda_2$ should be about zero. For both OH bonds, $\lambda_1 + \lambda_2$ changes from -0.8 to -1.4. Comparing the values of $\lambda_1 + \lambda_2$ for the two OH bonds in the strong OHO hydrogen bond with those for the weak $O3 \cdots H2$ bond and the covalent $N1-H2$ bond, the specificity of the strong hydrogen bond once again becomes evident.

Potential and kinetic energy densities have been calculated for the OHO and NHO critical points of the phosphoric acid-urea complex according to the equations presented in [21], i.e. $G(r) = 15.3\lambda_3$, $V(r) = 35.1(\lambda_1 + \lambda_2)$, and $H(r) = G(r) + V(r)$, and the energy relationships for the OHO hydrogen bond are shown in Fig. 2. It is possible to draw, analogously to $\rho(r)$ and $\nabla^2\rho(r)$, a common relationship between the energies and the OH distances for the two BCPs in the OHO hydrogen bond. The potential energy densities at the BCP of the $H2 \cdots O3$, N-H, and OHO bonds change within a similar range.

Significant differences are seen in the kinetic energy density expressing the mobility of the electrons at a BCP. It is lowest for the N-H bond (-112 to -87), higher for the molecular $H2 \cdots O3$ hydrogen bond (-50 to -37), and highest for the strong OHO hydrogen bond (-37 to -30). Comparison of the energy shows the feature of the electron density at BCP responsible for the differentiation of the interaction. It is the mobility of the electrons at a BCP which determines whether a bond is a covalent bond, a weak molecular hydrogen bond, or a strong hydrogen bond.

When $|V(r)|/G(r) > 1$, the charge at a BCP is concentrated, which causes a strengthening of the interaction. According to [20], the distance of $|V(r)|/G(r)$ is > 1 is defined as the covalent distance at which the molecular orbital becomes stable. $H(r) = G(r) + V(r) < 0$ is the sufficient condition for building the molecular orbital even when the electron density at the BCP is depleted and its Laplacian is > 0 . In Fig. 3a, a comparison of $|V(r)|/G(r)$ for the covalent N-H bond, the weak hydrogen $H_2 \cdots O_3$ bond, and the strong $O_1 \cdots H_1$ and $H_1 \cdots O_2$ bonds is shown. The value of $|V(r)|/G(r)$ for the weak hydrogen bond is close to 1, which means that in the weak $H_2 \cdots O_3$ bond a concentration of local charge takes place and the molecular orbital is formed. The highest $|V(r)|/G(r)$ values, of over 7, characterize the covalent N-H bond. The values for strong OHO bridges are located in the intermediate range between these two values. The picture once again expresses the intermediate character of the strong hydrogen bond. Fig 3b focuses on the relationship for OHO hydrogen bonds, which can be described by a linear equation common to both OHO bonds. This relationship allows determining an OH distance of 1.3458 Å at which the existence of the molecular orbital is possible. At all distances less than 1.3458 Å, the OHO hydrogen bond has some contribution of covalent character which increases with shortening of the OH distance.

In a situation where $H(r)$ is < 0 and the atom–atom interaction has a contribution of covalency, the covalence degree (CD) can be defined as $CD = H(r)/\rho(r)$, describing the total pressure per electron density unit at the BCP [20]. With strengthening of the bond, CD increases. $H(r)/\rho(r)$ for the BCPs at the N-H, $H_2 \cdots O_3$ and the $O_1 \cdots H_1$, $H_1 \cdots O_2$ bonds are compared in Fig. 4. The CD for the strong hydrogen bond is closer to that of a typical covalent N-H bond than to the weak $H_2 \cdots O_3$ bond. For the weak OH bond, the CD value is very sensitive to the bond length and drastically decreases with elongation

of the weak hydrogen bond. Fig. 4b shows the changes in CD for the BCP between the proton and proton donor and the proton (dark points) and proton acceptor (empty points). The covalent degree for the proton donor decreases with shortening of the distance to the proton and exceeds the lowest value when the proton passes through the hydrogen bridge center. The CD for the BCP between the proton and proton acceptor increases from the value for a central location of the proton. Both OHO bonds in the strong OHO bridge are less covalent when the proton reaches the central location between the donor and the acceptor.

4. Localization of the BCPs

While the distance of the atom to the BCP is a measure of the atomic radius of the atom, the shift of the BCP from the bond midpoint indicates the polarization of the bond. As can be expected from the atomic radii values, both critical points in the OHO and NHO hydrogen bonds are located very close to the proton when the distances to the proton donor and the proton acceptor are long. The linear relationships of the distances of the two BCPs to the proton in the OHO bond are shown in the Fig. 5a. The common relationship of the distance of the BCP to the proton engaged in the OHO hydrogen bond, $y = 0.5981x - 0.4307$, $R^2 = 9840$, seems to be worse than the previous relationships, although the R^2 value for the common equation is not significantly different from the previous ones. Both linear relationships show a decrease in the proton atomic radius with strengthening of the hydrogen bond. In a strong hydrogen bond the electron cloud of the proton disappears, which is connected with the decrease in its atomic radius. The shortest possible atomic radius of the proton in the very short OHO hydrogen bridge can be found as equal to 0.29 Å.

When the proton passes through the hydrogen bond center, its distance to the BCP connected with the OH of the proton donor (phosphoric acid) is longest. The analogous

distance of the proton and the BCP of the OH bond of the proton acceptor (urea) is the closest. A central location of the proton is connected with a significant rearrangement of its electron density around the proton and the lowest value of its atomic radius. Because the atomic radius is connected the atomic volume, it can be expected that with a central location of the proton in a short OHO hydrogen bond the atomic volume is the lowest. The atomic volume is found by integration over the atomic basin of the proton. Unexpectedly, the relationships to both OH distances are rather poor when the relationship to the O...O bridge length shown in Fig. 5b is correct. The atomic volume of the proton for the shortest O...O, equal to 2.400 Å, is 9.19 [a.u.] and this value is the lowest which can be reached for the strongest OHO hydrogen bond. Analogous dependencies for the NHO hydrogen bond are linear, but a discussion of a common relationship for the distances of both BCPs to the proton is rather not sensible. Compared with the previous relationship of the values at BCP, which are described by the line common to both critical points, the distance of the BCP to the bond center, which reflects the polarization of the bond, is separate for the BCP describing the proton donor and proton acceptor part of the phosphoric acid-urea complex (Fig 6). Regardless of the bond length, the OH bond to the proton acceptor (urea) is more polarized than the OH bond to the proton donor (phosphoric acid). This difference probably reflects the unsymmetrical surroundings of both oxygen atoms in the OHO hydrogen bond. Each is a part of a different molecule.

Conclusions

Systematic analysis of the AIM parameters of BCPs located in the OHO hydrogen bridge of the phosphoric acid-urea complex in which the proton moves near the center

of the strong OHO hydrogen bond shows that the electron density in the hydrogen bridge is very sensitive to the proton transfer process. The electron density in the strong OHO hydrogen bond is a few times higher than that of the weak molecular NHO hydrogen bond, and shifting of the proton causes it to change significantly, which is reflected in the AIM parameters describing the BCPs in the hydrogen bond.

For the shortest OHO bridge, both oxygen atoms become equivalent and the difference between proton donor and acceptor disappears. Some relationships give common lines for both OH bonds. This fact can be used as a better criterion of the symmetry of the hydrogen bridge than its distances.

AIM analysis finds that the order of the OH bonds in the strongest OHO bridges can reach a value of 0.16.

Comparison of a strong hydrogen bond with a weak hydrogen bond and a covalent bond illustrates the intermediate character of the strong hydrogen bond between the other two. The strong hydrogen bond is rather more similar to a covalent bond than to a weak hydrogen bond. This similarity is expressed in the covalence degree parameter, which is similar for the strong hydrogen bond and covalent bond, while for the weak hydrogen bond it is significantly lower.

AIM analysis finds the potential and kinetic energy densities of electrons at a BCP. Comparison of the particular energies for different kinds of bonds shows that the potential energy is similar in all of them. The difference in the bond character is realized

1
2
3
4 by a change in the value of the kinetic energy density, which is connected with the
5
6 mobility of the electrons at BCPs. Increasing kinetic energy is also connected with a
7
8 strengthening of the hydrogen bond. In the strongest hydrogen bonds, the electrons at
9
10 BCPs achieve higher mobility and the bonds become simultaneously more polarized.
11
12

13 14 15 16 **Acknowledgment** 17

18 The Wroclaw Centre for Networking and Supercomputing is acknowledged for
19
20 generous computer time. It is also my great pleasure to thank the referee for helpful
21
22 comments.
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

References

1. G.A. Jeffrey, W. Saenger. *Hydrogen bonding in biological structures*, Berlin: Springer, 1991.
- [2] C.C. Wilson. *Acta Cryst.*, **B57**, 435 (2001).
- [3] C.C. Wilson, K. Shankland, N. Shankland. *Z. Kristallogr.*, **216**, 303 (2001).
- [4] E.C. Kostanek, W.R. Busing. *Acta Cryst.*, **B28**, 2454 (1972).
- [5] B.L. Rodrigues, R. Tellgren, N.G. Fernandes. *Acta Cryst.*, **B57**, 353 (2001).
- [6] A. Parkin, S.M. Harte, A.E. Goeta, C.C. Wilson. *New J. Chem.*, **28**, 718 (2004).
- [7] C.C. Wilson, C.A. Morrison. *Chem. Phys. Lett.*, **362**, 85 (2002).
- [8] C.A. Morrison, M.M. Siddick, P.J. Camp, C.C. Wilson. *J. Am. Chem. Soc.*, **127**, 4042 (2005).
- [9] F. Fontaine-Vive, M.R. Johnson, G.J. Kearley, J.A.K. Howard, S.F. Parker. *J. Am. Chem. Soc.*, **128**, 2963 (2006).
- [10] R.F.W. Bader, *Atoms in Molecules: A quantum Theory*, Oxford University Press, New York, 1990.
- [11] A.H. Pakiari, K. Eskandari. *J. Mol. Struct. Teochem*, **759**, 51 (2006).
- [12] L.F. Pacios, O. Galvez, P.C. Gomez. *J. Chem. Phys.*, **122**, 214307 (2005).
- [13] Gaussian 03, Revision A.9, Gaussian, Inc., Pittsburgh PA, 2004.
- [14] F. Biegler-König, J. Schönbohm, D. Bayles. *J. Comput., Chem.*, **22**, 545 (2001).
- [15] C. Foces Foces, I. Alkorta, J. Elguero. *Acta Cryst.*, **B56**, (10182000).
- [16] P. Luger, M. Weber, G. Szeimies, M.J. Pätze., *Chem. Soc. Perkin Trans. 2*, 1956 (2001).; T. M. Klapoetke, P. Mayer, A. Schulz, J.J. Weigand. *J. Am. Chem. Soc.*, **127**, 2032 (2005).

- [17] M.D. Segal, P.L.D. Lindan, M.J. Probert, C.J. Pickard, P.J. Hasnip, S.J. Clark, M.C. Paye. *J. Phys. Cond. Matt.*, **14**, 2717 (2002).
- [18] U. Koch, P.L.A. Popelier. *J. Phys. Chem. A*, **99**, 9747 (1995).
- [19] P.L.A. Popelier. *J. Phys. Chem. A*, **102**, 1873 (1998).
- [20] E. Espinosa, I.A. Alkorta, J. Elguero, E.J. Molins. *J. Chem. Phys.*, **117**, 5529 (2002).
- [21] E. Espinosa, M. Souhassou, H. Lachekar, C. Lecomte. *Acta Cryst.*, **B55**, 563 (1999).
- [22] S. Wojtulewski, S.J. Grafovski. *J. Mol. Struct.*, **645**, 287 (2003).
- [23] E. Espinosa, C. Lecomte, E. Molins. *Chem. Phys. Lett.*, **300**, 745 (1999).

Figure Captions

1.a) $\rho(r)$ at $O1\cdots H1$ and $H1\cdots O2$ BCP as a function of $O1\cdots H1$ and $H1\cdots O2$, respectively.

b) percentage participation of electron density at the BCP correlated with $O1\cdots H1$ and $H1\cdots O2$. The sum of $\rho(r)_{O1\cdots H1}$ and $r(\rho)(r)_{H1\cdots O2}$ is 100%.

Unfilled points: $O1\cdots H1$ bond, filled points: $H1\cdots O2$ bond, triangles show complexes with the proton located closer to the donor atom.

2. Potential energy of electrons (G) a), Kinetic energy (V) b), Total energy (H) c), at BCP as function of the bond distances. Unfilled points: $O1\cdots H1$ bond, filled points: $H1\cdots O2$ bond, triangles show complexes with the proton located closer to the donor atom.

3. Relationship of $|V|/G$ at BCP and bond distance. a) comparison of covalent, the strong OHO hydrogen bond, and the weak $H2\cdots O3$ bond, b) $|V|/G$ as a function of the OH distances of the OHO hydrogen bond. Unfilled points: $O1\cdots H1$ bond, filled points: $H1\cdots O2$ bond, triangles show complexes with the proton located closer to the donor atom (molecular complexes).

4. a) Comparison of the covalent degrees of the covalent bond and strong and weak hydrogen bonds. b) Change in covalent degree of the $O1\cdots H1$ and $H1\cdots O2$ bonds as a function of bond distances.

5. a) The distance of the proton in the OHO hydrogen bond in the phosphoric acid-urea 1:1 complex to the BCPs of the $O1\cdots H1$ and $H1\cdots O2$ bonds as a function of bond distance.

b) Relationship of the atomic volume of H1 (integrated within the 0.001 isodensity) to $O1\cdots O2$ distance.

6. Relationship of the distances of the $O1\cdots H1$ and $H1\cdots O2$ BCPs to the OH bond center to OH distance.