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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.

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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 (λ_1, λ_2, λ_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 eigenvalus 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 (H1-BCP$_{H1\ldots O1}$ and H1-BCP$_{H1\ldots O2}$) 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 O···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 O···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 1.847Å, 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.
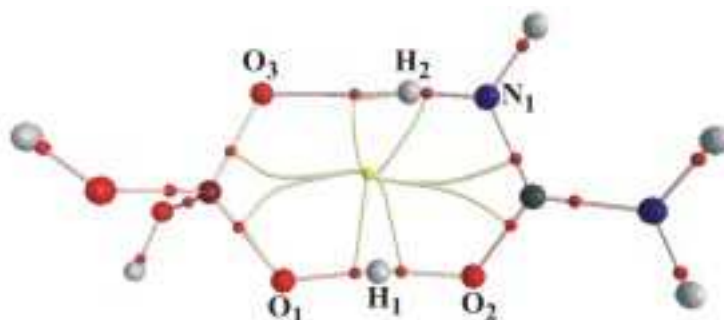
As shown in the scheme, the BCPs were found between the proton and both oxygen

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 intermolecuclar 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 e$Å^3$ 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···H1

and H1···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 $\nabla^2\rho(r) = -1.1868(O···H) + 1.5056$, $R^2 = 0.9667$, and for

the OHO complexes with the proton closer to the donor atom $\nabla^2\rho(r) = 1.1967(O···H) -$

1.3729, $R^2 = 0.9975$. The possibility to relate values of $\nabla^2\rho(r)$ to the O···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-shall 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) = aλ_3 (a = 15.3(1) Å^5 kJ^{-1}mol^{-1}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(0.11λ_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···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···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···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 $|V(r)|\backslash G(r) > 1$, the charge at a BCP is concentrated, which causes a strengthening

of the interaction. According to [20], the distance of $|V(r)|\backslash G(r)$ 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

$|V(r)|\backslash G(r)$ for the covalent N-H bond, the weak hydrogen H2···O3 bond, and the strong

O1···H1 and H1···O2 bonds is shown. The value of $|V(r)|\backslash G(r)$ for the weak hydrogen

bond is close to 1, which means that in the weak H2···O3 bond a concentration of local

charge takes place and the molecular orbital is formed. The highest $|V(r)|\backslash G(r)$ values, of

over 7, characterize the covalent N2-H2 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, H2···O3 and the O1···H1, H1···O2

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 H2···O3 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

by a change in the value of the kinetic energy density, which is connected with the mobility of the electrons at BCPs. Increasing kinetic energy is also connected with a strengthening of the hydrogen bond. In the strongest hydrogen bonds, the electrons at BCPs achieve higher mobility and the bonds become simultaneously more polarized.

Acknowledgment

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 Grafowski.. *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 $\rho(r)_{O1\ldots H1}$ and $r(\rho)(r)_{H1\ldots O2}$ is 100%.

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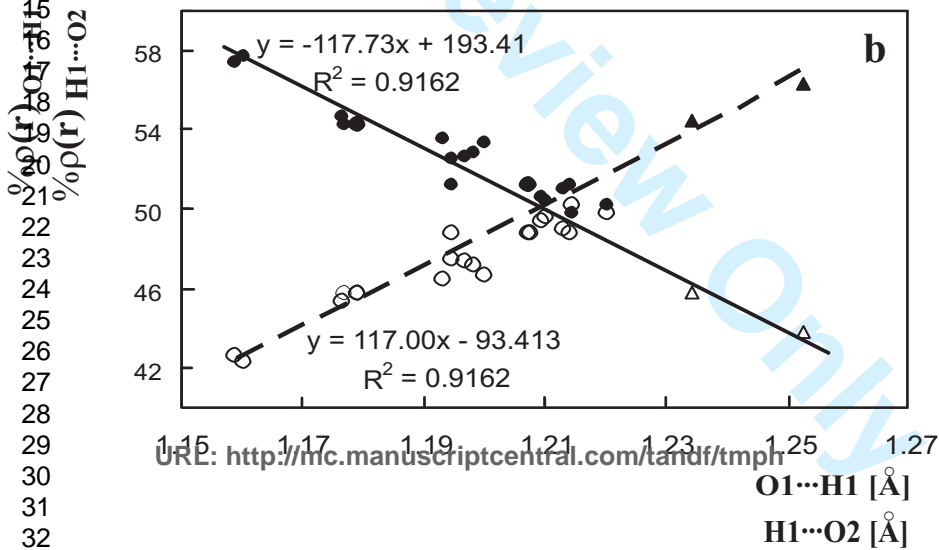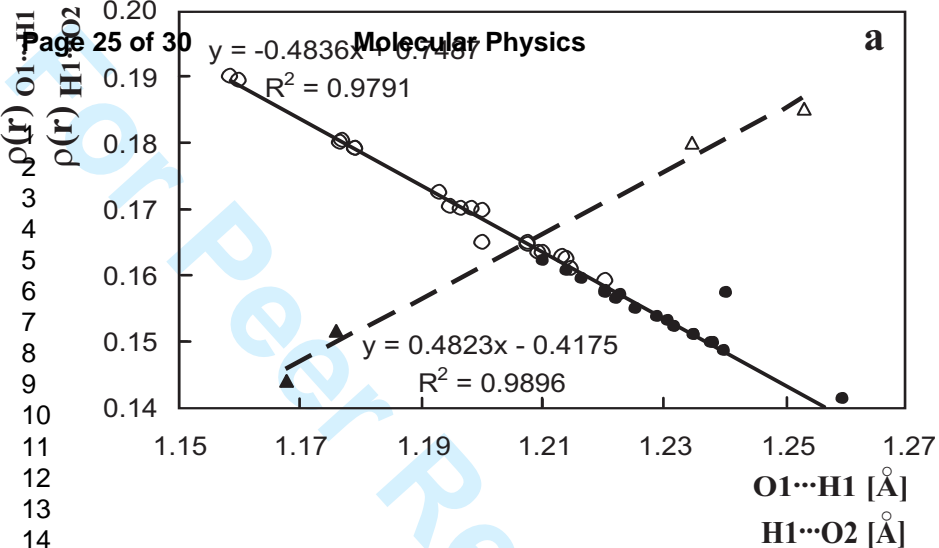
with the proton located closer to the donor atom.

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
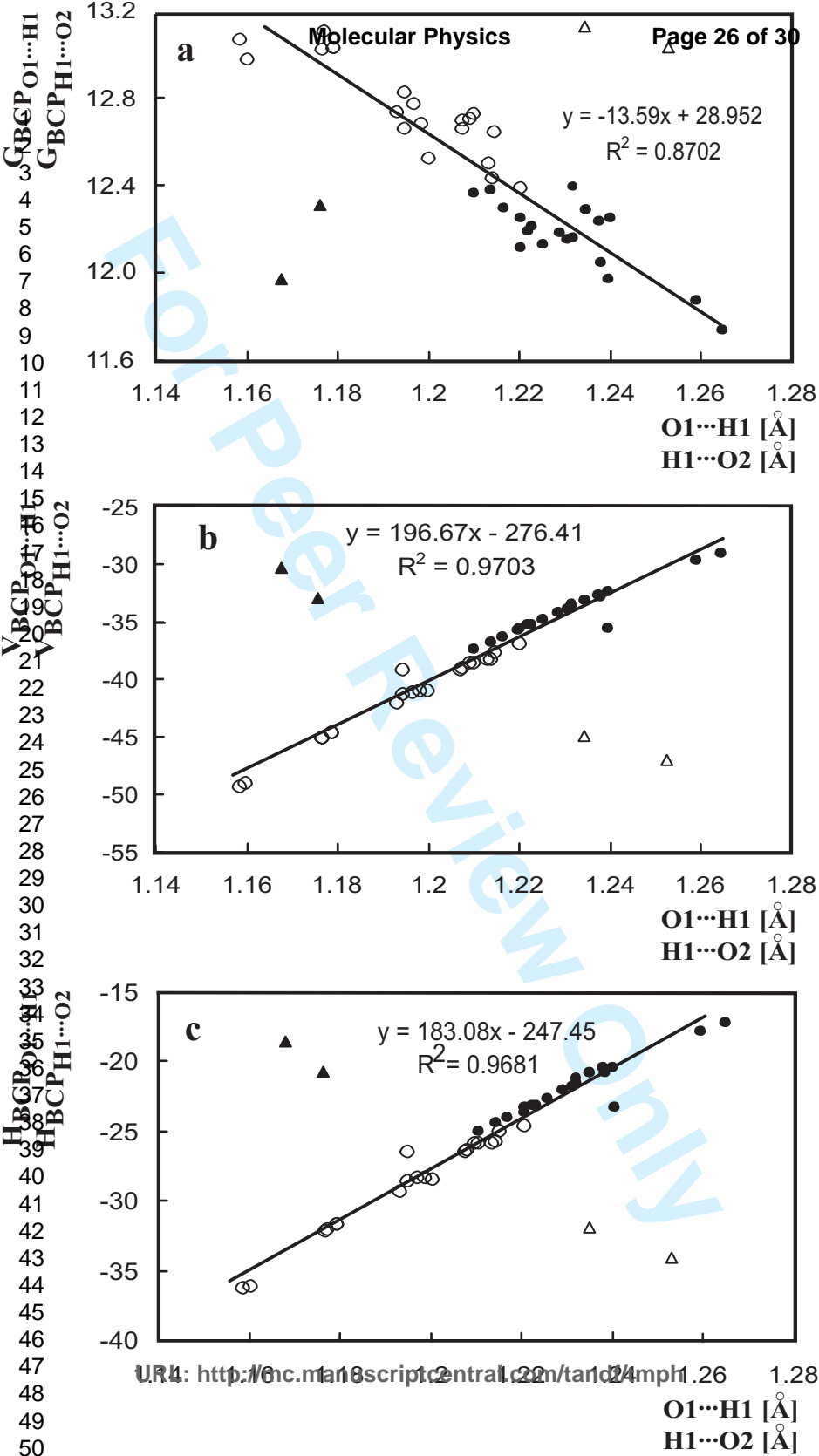
atom (molecular complexes).

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
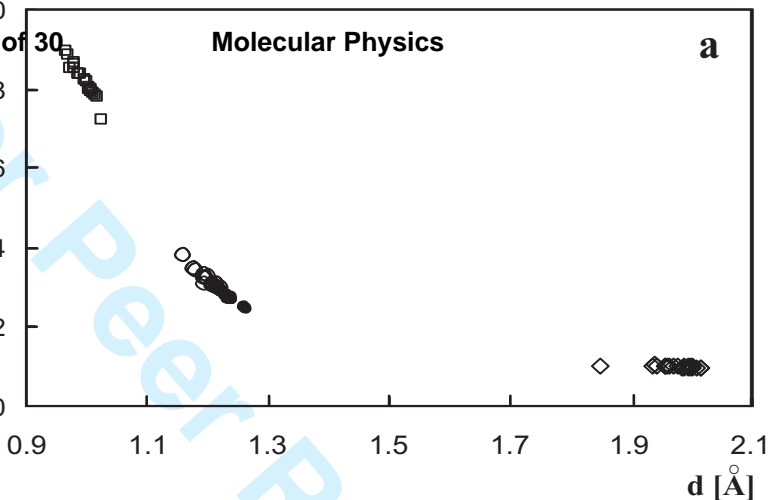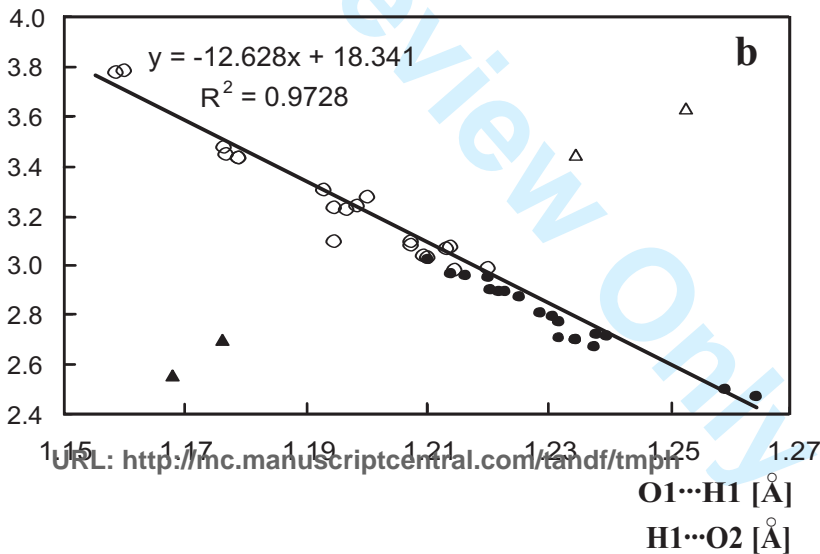
function of bond distances.

5. a) The distance of the proton in the OHO hydrogen bond in the phosphoric acid-urea

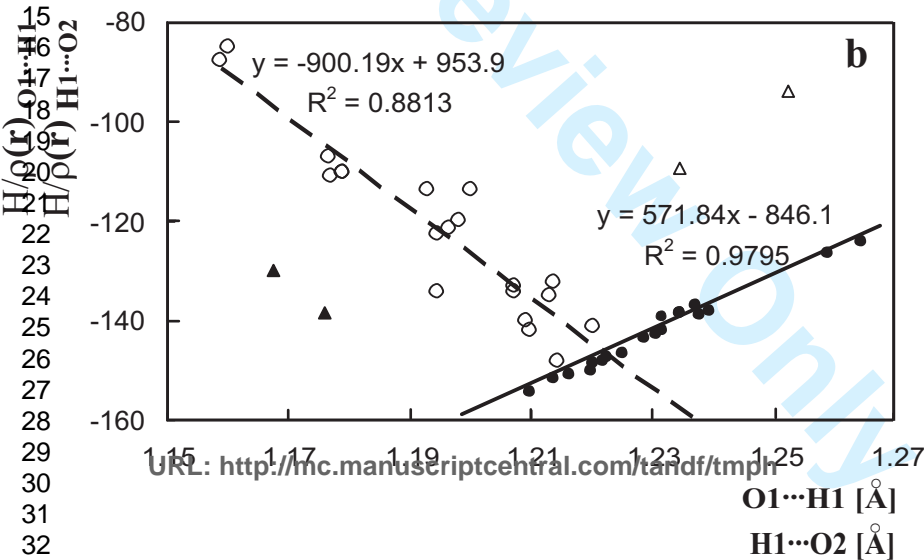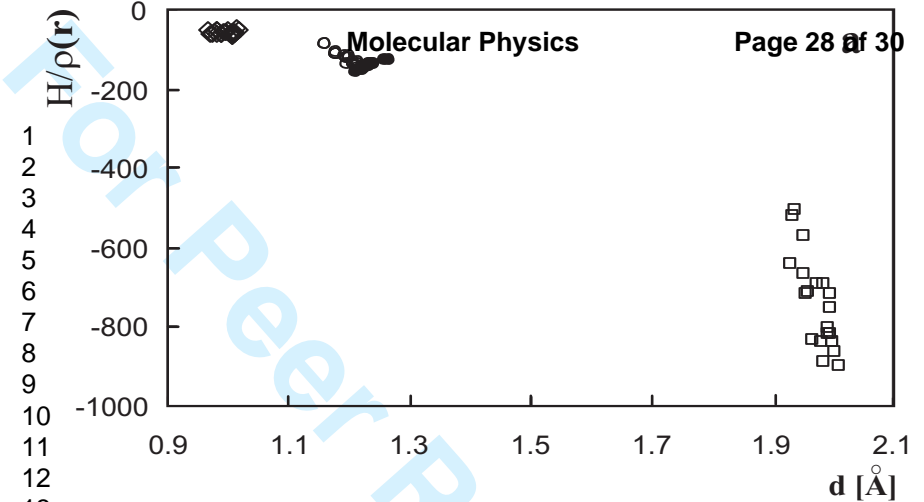1:1 complex to the BCPs of the O1···H1 and H1···O2 bonds as a function of bond

distance.

b) Relationship of the atomic volume of H1 (integrated within the 0.001 isodensity) to

O1···O2 distance.

6. Relationship of the distances of the O1···H1 and H1···O2 BCPs to the OH bond center

to OH distance.

Molecular Physics

Molecular Physics

a Molecular Physics

y = 0.6392x - 0.3853

$R^2 = 0.9924$

y = 0.5198x - 0.3379

$R^2 = 0.9734$

O1···H1 [Å]

H1···O2 [Å]

b

y = 17.254x - 32.2

$R^2 = 0.933$

O1···O2 [Å]