Influence of Proton Transfer Degree on the Potential Energy Surface for Two Very Short Hydrogen Bonds

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Dedicated to Professor Dušan Hadži on the occasion of his 90th birthday

Abstract

The influence of temperature on the proton location in hydrogen bonds has been systematically studied by neutron diffraction in only a few crystal structures. Two of these are the 1:1 complex of urea – phosphoric acid with an OHO hydrogen bond and 4-methylpyridine –pentachlorophenol with an OHN hydrogen bond. Based on these earlier determined crystal structures the potential energy surface (PES) at different temperatures has now been determined by DFT calculations at the B3LYP/6-31++G** level of theory using the Gaussian03 system. In general PES is practically unchanged as the proton moves from the donor to the acceptor. This is not surprising as the crystal structure does not undergo significant changes as the proton successively moves along the hydrogen bond. For both complexes PES is characterized by only one minimum, which is not located at the centre where the distances of the proton to the bridge atoms are the same. The experimental proton positions are located close to the calculated energy minima; the slight deviations are probably an effect of the crystalline environment which has not been taken into account in the calculations.

Keywords: Short hydrogen bonds, potential energy surface, proton transfer

1. Introduction

The hydrogen bond has been intensively investigated for a long time which is connected with its importance in many fields of physics, chemistry, crystal engineering[1] and life sciences.[2] Although there are many general reviews on hydrogen bonding[3] many properties still need to be studied. As an example, proton transfer, which is an important step in the formation and breaking of hydrogen bonds and is significant in most biological processes, is still not properly known. A commonly adopted proton transfer mechanism is the concept of constant bond order as the proton moves along the hydrogen bond.[4] Pauling's functional representation of the principle of conservation of bond order is derived from the relation

$$d(\rho) - d(1) = \Delta d = -a \ln \rho \qquad (1)$$

where $d(\rho)$ is the interatomic distance for a fractional bond with bond order ρ and $d(1)$ is the corresponding single bond length. In a transfer reaction X–H + Y = X··H··Y = X + H–Y it is postulated that the sum (n) of the bond orders ρ_1 and ρ_2 for X··H and H··Y, respectively, will remain constant and equal to 1 along the proton transfer path.[5] This path is here called the Bond Order Reaction Coordinate (BORC). This concept of constant bond order is very useful in interpretation of systematic trends in the bond lengths in related compounds. Another concept for the proton transfer mechanism is that proton moves along the lowest energy path – the Quantum-Mechanically derived Reaction Coordinates (QMRC).

It has been found that both concepts are not mutually excluded. For typical *intermolecular* hydrogen bonds the BORC and QMRC curves are identical and the proton transfer takes place along the lowest energy path while keeping a constant valency equal to one.[6] In the case of *intramolecular* hydrogen bonds the BORC and QMRC curves are different and proton transfer is preferably realized along the QMRC curve without keeping the proton valency constant.[6]

Proton transfer is only possible in strong hydrogen bonds and the process may be triggered by changes in the environment or temperature. The influence of successive changes of the temperature on the proton location has been studied by neutron diffraction in only a few cases. One of these is the 1:1 complex of urea – phosphoric acid with an OHO hydrogen bond,[7] another is the complex of 4-methylpyridine – pentachlorophenol with an OHN hydrogen bond.[8] The refcodes of these compounds in CSD[9] are used in the following, the first CRBAMP[7] the second GADGUN, RAKQOJ.[8]

Theoretical investigation of the above complexes may answer the following questions concerning the proton transfer process:

- Is the shape of potential energy surface (PES) dependent on the temperature?
- Where is the proton located relative to the minimum energy?
- What is the proton transfer path when the temperature is changed?

2. Calculations

The crystal structures have been determined by neutron diffraction and the experimental data are taken from the CSD data base.[9] DFT calculations have been carried out at the B3LYP/6-31++G** level of theory using the Gaussian03 system.[10] The crystallographically determined coordinates for all atoms, except for the H atom involved in the hydrogen bond, were kept fixed and the potential-energy surface was generated for O–H (or N–H) distances successively changed in 0.04 Å steps. The proton was then moved along the O_1–H and O_2–H (or N–H) directions, where these directions were defined by the oxygen and hydrogen positions corresponding to the OHO (OHN) angles in the crystal structures. The PES has been evaluated for each neutron structure at the different temperatures.

3. Results

The potential energy surface for the 4-methylpyridine – pentachlorophenol complex at 200 K is shown in Fig. 1 and for the urea – phosphoric acid complex at 283 K in Fig. 2. The complexes are characterized by strong intermolecular OHN and OHO hydrogen bonds. For the 4-methylpyridine – pentachlorophenol complex every PES is typical for a linear intermolecular hydrogen bond, and the QMRC curve is identical with the BORC curve (Fig. 1). For the strong intermolecular OHO hydrogen bond in the urea – phosphoric acid complex it would be expected that the QMRC curve should be identical with BORC as this has been previously found to be a general feature of intermolecular hydrogen bonds.[6] However, in this case the

QMRC curve (yellow dotted) is not identical with BORC (blue). The reason is that the complex participates in a closed ring containing both a strong OHO and weak NHO hydrogen bond. This ring does not deviate significantly
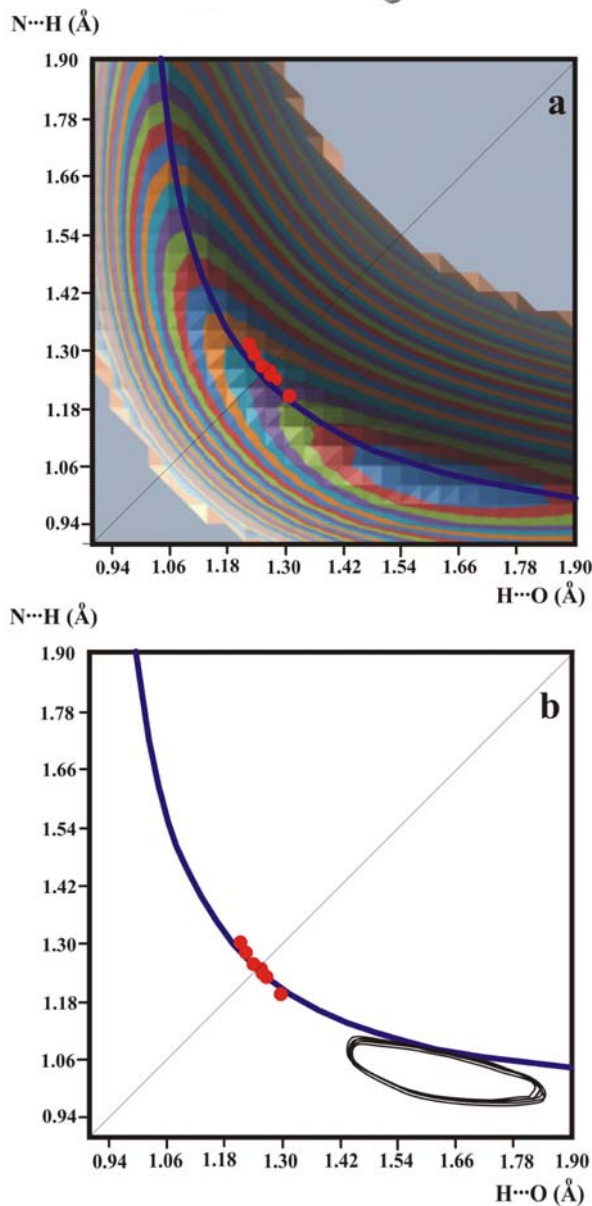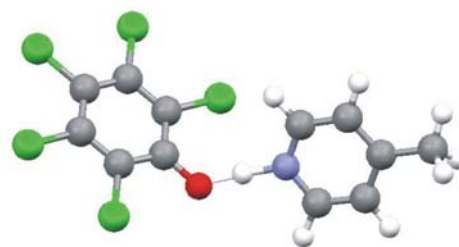

Fig. 1. 4-methylpyridine – pentachlorophenol complex: (a) PES at 200 K; the blue curve is the QMRC curve, which in this case is identical with the BORC curve. (b) the location of the potential energy minima at the different temperatures. Experimental proton positions from the neutron studies at different temperatures are marked as red points; for temperatures cf. Table 1.

from planarity; the urea and phosphoric oxygen atoms deviate from the plane by less than 0.25 Å. The distance of these atoms from the plane and the geometry of the weak NHO hydrogen bond (N···O around 2.95 Å) are not sensi-
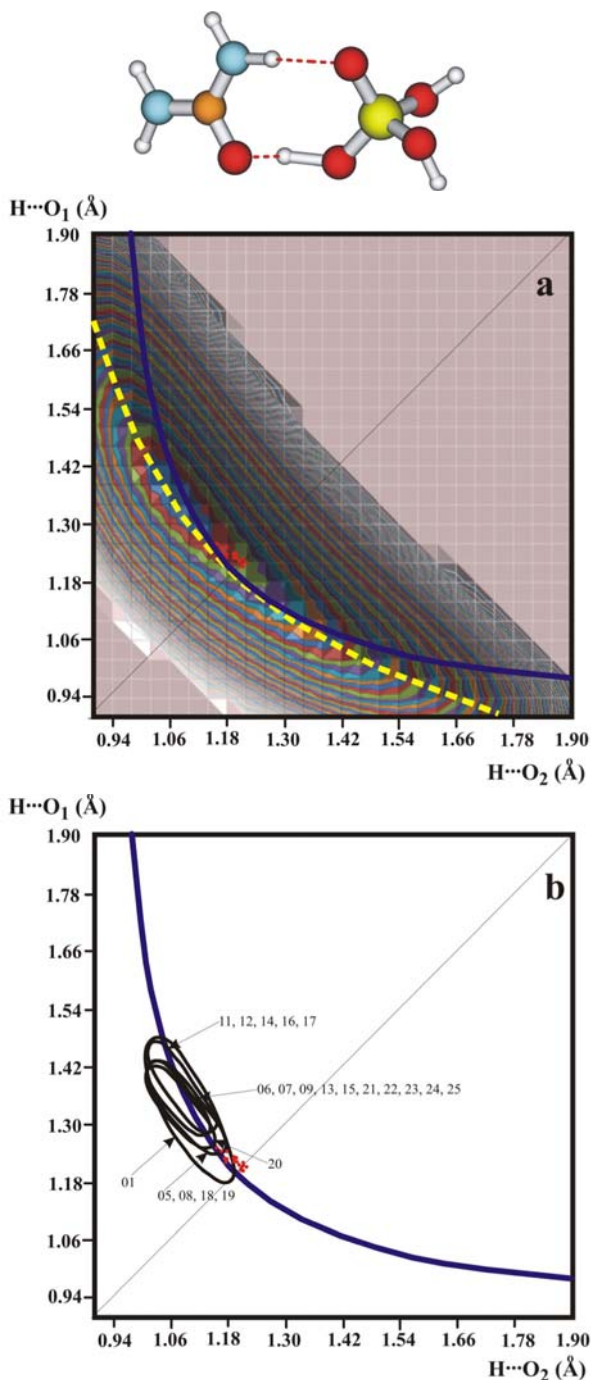

Fig. 2. Urea – phosphoric acid complex: (a) PES at 283 K; the blue curve is the QMRC curve, the dotted yellow the BORC curve, which in this case is not identical with the QMRC curve. (b) the location of the potential energy minima at the different temperatures; the numbers refer to the numbers in the CSD data base, as shown in Table 2. Experimental proton positions from the neutron studies at different temperatures are marked as red points, for temperatures cf. Table 2.

tive to temperature. Participation of the OHO hydrogen bond in this closed ring is connected with the slight non-linearity of this bond, which is not typical for strong inter-molecular hydrogen bonds (Table 2). Accordingly this complex has some features corresponding to an *intramolecular* hydrogen bond. The QMRC curve therefore slightly deviates from the BORC curve, as shown in Fig. 2.

It is characteristic that for both compounds the lowest energy level is not located at the centre of the diagram close to the diagonal line. The location of the energy minimum far from the centre, which should be characteristic for the strongest hydrogen bonds, is especially seen for the complex of pentachlorophenol with 4-methylpyridine. For both complexes the main conclusion is that in general PES is practically unchanged as the proton moves from the donor to the acceptor. This is not surprising as the crystal structure does not undergo significant changes as the proton successively moves along the hydrogen bond. However, certain small changes in PES can be seen for the urea – phosphoric acid complex: PES for CRBMAP01 at 100 K is slightly different from PES at other temperatures. In this case the OHO bond is non-linear and the difference between O···H and H···O is largest among the structures and PES is calculated by moving the proton along OH with the OHO angle kept constant. Both factors, nonlinearity of the hydrogen bond and difference between OH values, result in a PES which is different from the other structures of this complex.

Taking into account the change of the shape of the potential energy curve which generally occurs as the proton moves along the hydrogen bridge[11] it would be expected that the shape of the lowest energy minimum would also be changed at the same time. The minimum could be elongated along the BORC curve or a second minimum could be formed, corresponding to a location of the proton at a second equilibrium position. For both complexes PES is characterized by only one minimum, which is not located at the centre where the distances of the proton to the bridge atoms are the same. Even for identical bridge atoms, as in the 1:1 complex of urea – phosphoric acid, the donor and acceptor parts of the complex are different and the energy minimum of PES is not located at the bridge centre. For the complex of pentachlorophenol with 4-methylpyridine the difference between proton donor and acceptor is larger and the energy minimum is located further away from the centre. Taking PES into account the proton should accordingly be located at the donor oxygen atom. Experimental proton positions are marked as filled (red) circles in the diagrams. In both compounds the experimental points are far from the energy minima.

In the pentachlorophenol – 4-methypyridine complex the proton is closer to nitrogen at 200 K but it is successively shifted to the center of the O···N bond around 100 K. Below 100 K the proton has been transferred to oxygen (Table 1). The energy barrier for this transfer process is around 5 kcal/mol.

Table 1. Geometrical parameters of the hydrogen bonds in the 4-methylpyridine –pentachlorophenol complex. OH–HN is the difference between the O···H and H···N distances, which illustrates the deviation of the proton from the center of the hydrogen bridge.

CSD refcode	Temp [K]	O···N [Å]	O···H [Å]	H···N [Å]	OH–HN [Å]	OHN [°]
GADGUN05	200	2.525	1.228	1.306	–0.078	170.5
GADGUN04	150	2.519	1.229	1.300	–0.071	169.6
GADGUN03	125	2.519	1.241	1.288	–0.047	169.6
RAKQOJ01	100	2.513	1.258	1.265	–0.007	170.1
RAKQOJ	80	2.513	1.266	1.255	0.011	170.9
RAKQAV02	60	2.515	1.275	1.249	0.026	170.9
RAKQAV01	45	2.513	1.279	1.242	0.037	170.8
RAKQAV	20	2.506	1.309	1.206	0.103	170.4

In the urea – phosphoric acid complex the proton is close to the center of the O1···O2 hydrogen bond from 350 to 283 K but it is successively shifted closer to O1 as the temperature is lowered down to 100 K (Table 2). In this case there is evidently no transfer of the proton from the donor O1 to the acceptor O2. It must be remarked that there is a large spread in the experimentally determined distances listed in Table 2, even in those determined at the same temperature. The reason is that these neutron data were collected in very short time and the precision is therefore limited. However, taking the average distances the general tendency is quite clear.

temperature but also to the surroundings of the proton in the crystal or in the liquid which can be expressed for example by the electric permittivity. For this reason it is difficult to estimate the characteristics of strong hydrogen bonds which are drastically different for the molecules in vacuum and in a crystal structure. To investigate the influence of the packing effect and the crystalline environment on the location of the energy minimum it would be interesting to perform a similar calculation of PES for the complex in the crystal. Optimization of the crystal structure of the urea – phosphoric acid complex[12] gives parameters of the hydrogen bridge which deviate slightly from

Table 2. Geometrical parameters of the hydrogen bonds in urea – phosphoric acid complex. O1H–HO2 is the difference between the O1···H and H···O2 distances.

CSD refcode	Temp [K]	O1···O2 [Å]	O1···H1 [Å]	H1···O2 [Å]	O1H–HO2 [Å]	OHO [°]
CRAMP25	350	2.419	1.216	1.209	0.007	171.6
CRAMP18	335	2.430	1.226	1.214	0.012	169.7
CRAMP17	330	2.419	1.221	1.208	0.013	169.6
CRAMP24	325	2.419	1.210	1.215	–0.005	172.4
CRAMP16	320	2.425	1.222	1.214	0.008	169.5
CRAMP15	315	2.433	1.219	1.221	–0.002	180.0
CRAMP14	310	2.431	1.239	1.201	0.039	170.0
CRAMP13	305	2.422	1.231	1.199	0.032	171.0
CRAMP23	283	2.417	1.214	1.210	0.004	171.2
CRAMP08	283	2.403	1.235	1.179	0.056	169.0
CRAMP09	283	2.420	1.252	1.180	0.072	168.9
CRAMP11	283	2.421	1.223	1.207	0.016	169.9
CRAMP12	283	2.422	1.238	1.193	0.045	170.3
CRAMP07	280	2.417	1.240	1.195	0.045	166.1
CRAMP22	275	2.418	1.229	1.195	0.034	172.4
CRAMP06	250	2.405	1.237	1.176	0.061	170.0
CRAMP21	250	2.420	1.231	1.197	0.034	171.2
CRAMP20	200	2.402	1.235	1.176	0.059	170.6
CRAMP19	150	2.411	1.253	1.168	0.085	169.9
CRAMP05	150	2.400	1.231	1.178	0.053	170.1
CRAMP01	100	2.409	1.259	1.159	0.1	170.2

A central location of the proton in the experimental structure is determined by suitable pK_a values of the proton donor and acceptor entities but also by influence of the surroundings in the crystal structure. The location of the proton in the short hydrogen bond is very sensitive to the

the experimental values and with a proton position which deviates not only from the energy minimum but also from the BORC curve. The optimized O···O, O–H and H···O distances are 2.562, 1.096 and 1.267 Å, respectively. However, according to other results obtained previously[6]

the experimental proton position in the strong hydrogen bond is located on the BORC curve close to its center when the structures for optimized geometry of single molecules are close to the energy minimum.

4. Conclusions

In both complexes the energy minima are located at the BORC curve. The shape of the PES is not changed when the proton is shifted in the hydrogen bridge and the only effect may be a displacement of the energy minimum along the BORC curve. The pentachlorophenol – 4-methypyridine complex contains a typical intermolecular hydrogen bond, and the QMRC curve is identical with the BORC curve. In the urea – phosphoric acid complex there is a closed ring containing both a strong OHO and weak NHO hydrogen bond. Accordingly this complex has some features corresponding to an *intramolecular* hydrogen bond. The QMRC curve therefore slightly deviates from the BORC curve.

The experimental proton positions are located close to the energy minima of PES but not necessarily within the lowest energy minima. The proton is transferred along the BORC curve when the temperature is changed, corresponding to delivery of energy to the system. This means that the rule of constant valency of the proton is fulfilled even if the motion of the proton is connected with additional energy.

5. Acknowledgements

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Povzetek

Na nekaterih kristalnih strukturah smo sistematično preučevali vpliv temperature na položaj protona v vodikovi vezi. Dve izmed teh struktur sta kompleks uree in fosforne kisline v razmerju 1:1 z OHO vodikovo vezjo ter 4-metilpiridin – pentaklorofenol z OHN vodikovo vezjo. Na osnovi predhodno določenih kristalnih struktur smo določili ploskve potencialne energije (PES) pri različnih temperaturah z DFT izračuni na nivoju B3LYP/6-31++G** z uporabo programa Gaussian03. V splošnem se PES pri premiku protona iz donorja na akceptor ne spremeni, kar pa ni presenetljivo, saj v kristalni strukturi ne pride do opaznih sprememb, ko se proton premika vzdolž vodikove vezi. Pri obeh kompleksih se na PES pojavi le en minimum, ki pa ni lociran na sredini, kjer bi bila razdalja protona do mostovnih atomov enaka. Eksperimentalno določena lega protona je podobna izračunanemu minimumu; rahla odstopanja so najbrž posledica kristalne okolice, ki je pri računu nismo upoštevali.