Temperature-Dependent Single-Crystal Neutron Diffraction Study of the Strong OHN Hydrogen Bond in Pyridinium 2,4-Dinitrobenzoate

Irena Majerz*,† **and Matthias J. Gutmann**‡

Faculty of Chemistry, University of Wroclaw, Joliot-Curie 14, PL 50-383 Wroclaw, Poland, Rutherford Appleton Laboratory, ISIS Facility, Chilton Didcot, Oxfordshire OX11 0QX, United Kingdom

Received: January 26, 2008; Revised Manuscript Received: July 17, 2008

The structure of pyridinium 2,4-dinitrobenzoate was studied by neutron diffraction at 300, 270, 240, 210, 180, 150, 120, 90, 60, and 30 K. With temperature change, the O•••H bond length changes from 1.403(10) Å at 300 K to 1.424(4) Å at 30 K. The proton shifts in the hydrogen bridge toward the acceptor nitrogen atom. Temperature-dependent changes in the strong OHN hydrogen bond were analyzed by using both the neutron structure and the atom-in-molecule approach. The results are compared with those for other strong OHN hydrogen bonds.

Introduction

The importance of the hydrogen bond is well-known, because it is very abundant in biological systems responsible for the molecular and macroscopic properties of materials, molecular recognition, and supramolecular structure. Among hydrogen bonds, the strongest ones are particularly important because they are proposed to occur in intermediates of chemical[1] and enzymatic[2] reactions.

All properties of a hydrogen bond are determined by the degree of proton transfer in the hydrogen bridge. The primary parameters determining the degree of proton transfer are the acid−base properties of the proton donor and proton acceptor. The commonly used parameter is ΔpK_a, that is, the difference between the values of pK_b of the proton acceptor and pK_a of the proton donor ($\Delta pK_a = pK_b - pK_a$). In hydrogen-bonded complexes with low ΔpK_a, the proton is located closer to the donor. In those of ionic-pair type with high ΔpK_a, the proton is shifted to the acceptor. For a narrow, intermediary range of ΔpK_a, the hydrogen bond may become very strong, the distance between the proton donor and acceptor is shortened, and the proton can be located close to the center of the hydrogen bridge. These very strong hydrogen bonds are, in addition to the properties of the proton donor and acceptor, also sensitive to temperature and the surroundings of the hydrogen bridge.

Long ago, ΔpK_a was related to the free enthalpy of the reaction of proton transfer from the donor to acceptor[3] and the degree of proton transfer was correlated with the tautomeric equilibrium of the molecular and proton transfer forms of the hydrogen bond.[4] Since then, the model of tautomeric equilibrium is commonly used in interpreting all kinds of experimental data describing the hydrogen bond not only in solutions but also in the solid state. According to this model, in the ΔpK_a range in which the hydrogen bond is intermediate between molecular and ionic, both these forms should exist in proportion to the degree of proton transfer, and in the strongest hydrogen bonds with 50% proton transfer, both forms should be of equal amount. Tautomeric equilibrium between the molecular and ionic forms of the hydrogen bond can easily be realized in solutions, but in the solid state, it can only take place when the proton is disordered between two crystallographic positions. Investigation of the neutron structures which can precisely determine the position of the proton in the strongest hydrogen bonds is not only important for practical reasons but can also verify the model of proton transfer used for many years in investigations of the hydrogen bond.

Very strong hydrogen bonds are rather rare, and only a few such complexes have been investigated by neutron diffraction, which allows for a precise localization of the proton in the hydrogen bridge.[5−12] Among them, heteronuclear hydrogen bridges are especially difficult to access. Temperature investigations of the neutron structures of strongly hydrogen-bonded systems are very important because they directly reveal the proton transfer process, but they are limited to only three examples.[5−7,12] The continuous proton migration from donor to acceptor in a strong hydrogen bond has been systematically investigated only in the 4-methylpyridinium-pentachlorophenol complex[12] by using neutron diffraction. Disordering of the proton was not found in any of the investigated neutron structures of the strong hydrogen bond.

Pyridinium 2,4-dinitrobenzoate ($\Delta pK_a = 3.78$) is a complex with a strong hydrogen bond.[13] The X-ray structure of this compound determined at 299 and 100 K shows very short hydrogen bridges, measuring 2.561(3) and 2.547(3) Å, respectively. Such a short and temperature-sensitive O•••N distance is the best evidence that the hydrogen bond in pyridinium 2,4-dinitrobenzoate is one of the strongest OHN bridges. At both temperatures, the proton is located at the acceptor nitrogen atom. With temperature decreasing, the O•••N hydrogen bridge is shortened, and the O•••H distance is sensitive to temperature. The stronger the hydrogen bond is, the more sensitive to temperature; therefore, it can be expected that at a lower temperature, below 100 K, the proton could pass through the hydrogen bond's center. The main difference between the hydrogen bond in pyridinium 2,4-dinitrobenzoate and the hydrogen bond in 4-methylpyridine-pentachlorophenol is the proton disorder between two positions: one is adjacent to the N atom, and the other is adjacent to the O atom. Temperature change in the hydrogen bridge in pyridinium 2,4-dinitrobenzoate causes a change in the distribution of the proton between the two positions,[13] whereas in the hydrogen bond in 4-methylpy-

---

* Corresponding author. E-mail: maj@wchuwr.chem.uni.wroc.pl.

† University of Wroclaw.

‡ ISIS Facility.

10.1021/jp800781p CCC: $40.75

TABLE 1: Summary of Data Collection and Refinement Parameters[a]

diffractometer	SXD neutron time-of-flight Laue diffractometer									
wavelength range (Å)	0.37 − 8.77									
compound	pyridinium 2,4 dinitrobenzoate, C12H9N3O6									
molecular weight (g/mol)	291.2									
crystal size	~10 × 2 × 5 mm^3 (two crystals used simultaneously for data collection)									
symmetry	triclinic, space group $P1$, $Z = 2$									
T (K)	30	60	90	120	150	180	210	240	270	300
a (Å)	7.420	7.430	7.442	7.454	7.469	7.483	7.497	7.513	7.528	7.545
b (Å)	7.944	7.947	7.958	7.966	7.976	7.985	7.995	8.009	8.022	8.038
c (Å)	11.303	11.312	11.324	11.336	11.346	11.359	11.372	11.390	11.408	11.428
α (deg)	92.47	92.51	92.62	92.69	92.76	92.87	92.95	93.07	93.18	93.29
β (deg)	103.73	103.70	103.57	103.44	103.27	103.07	102.85	102.55	102.23	101.88
γ (deg)	110.53	110.53	110.57	110.61	110.656	110.71	110.76	110.83	110.90	110.95
V (Å^3)	600.24	601.78	604.26	606.60	609.30	612.15	615.05	618.73	622.57	626.86
ρ_{calc} (g cm^{-3})	1.61	1.61	1.60	1.59	1.59	1.58	1.57	1.56	1.55	1.54
refinement	SHELX, refined on F^2, $1/[\sigma(F_o)]^2$ weights, isotropic extinction, all atoms treated anisotropic									
number of refls	18120	16471	14731	13525	11304	10670	9706	8355	7372	5822
unique refls $I > 2\sigma$	6154	5427	4627	4099	3463	3089	2672	2350	2057	1750
N parameters	289	289	289	289	289	289	291	289	289	289
$R(F)$	0.085	0.087	0.090	0.091	0.090	0.090	0.088	0.089	0.086	0.090
$wR(F^2)$	0.184	0.180	0.180	0.178	0.167	0.167	0.168	0.166	0.166	0.164
extinction	0.0088	0.0088	0.0089	0.0092	0.0093	0.0100	0.0103	0.0111	0.0108	0.0116
absorption coeff.	$2.770 + 0.0155\lambda$									

[a] E.s.d.'s on all lattice parameters are 0.002 Å, and on lattice angles, 0.013−0.015°.

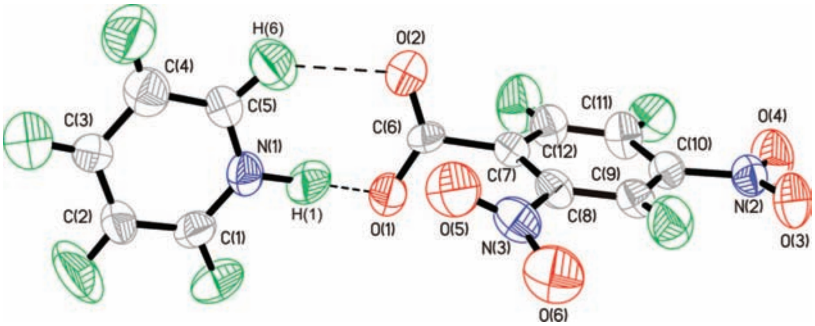

Figure 1. Neutron diffraction crystal structure of pyridinium 2,4-dinitrobenzoate at 300 K. Displacement ellipsoids are drawn at the 50% probability level.

ridine-pentachlorophenol, the proton continuously migrated with temperature change.

Investigation of the neutron structure of pyridinium 2,4-dinitrobenzoate could tell us about the mechanisms of the migration of the proton through the hydrogen bond's center. If the neutron structure confirms the change in occupancy of the two proton positions with temperature, it would confirm the proton-transfer equilibrium model of proton transfer in strongly hydrogen-bonded systems. This model involves some rigid and perhaps asymmetric double-well potential where thermal energy merely changes the population of the two wells.

Experimental Section

Crystals of pyridinium 2,4-dinitrobenzoate were grown from acetonitrile solutions. Neutron diffraction data in the temperature range 30−300 K were collected by using the SXD instrument at the ISIS facility at Rutherford Appleton Laboratory (U.K.).[14] To facilitate efficient data collection, two crystals were co-mounted and exposed simultaneously, similarly as was was done in ref 15. Data were treated by using the locally available SXD2001 software,[16] and refinements were carried out by using SHELX[17] with a $1/\sigma^2(I)$ weighting scheme for all data sets. A separate scale factor was included per crystal and orientation, to allow compensating for the crystal sizes and effect of the crystals exposed to slightly different parts of the incident neutron beam when changing orientation. To investigate properties of the electron density of the experimental structures with precisely determined proton position, for each neutron structure, the wave functions were evaluated at B3LYP/6-311++G** level of theory with the Gaussian program.[18] The wave functions were used as the input to the AIM200 program,[19] with all the default options. Details of the data collection and refinement parameters are summarized in Table 1.

Results and discussion

1. Parameters of the OHN Hydrogen Bond in Pyridinium 2,4-Dinitrobenzoate. In order to localize the proton as a function of temperature, the structure of pyridinium 2,4-dinitrobenzoate was studied by neutron diffraction. The structure of the investigated compound is shown in Figure 1. According to Table 1, temperature slightly influences the cell parameters of pyridinium 2,4-dinitrobenzoate. The most sensitive to temperature are the b length and β angle of the crystal cell, changing according to the equations $b = 0.0003T + 7.9266$, $R^2 = 0.9831$ and $\beta = -0.0069T + 104.16$, $R^2 = 0.9517$. The temperature dependence of the cell volume is in accordance to second-order polynomial $V = 0.0002T^2 + 0.0459T + 598.7$, $R^2 = 0.9997$. Other parameters of the crystal cell are almost insensitive to the temperature change. Because the intermolecular O···H−N hydrogen bond is parallel to the b axis, it can be stated that the hydrogen bond has a contribution into thermal expansion of the crystal.

The parameters of the OHN hydrogen bridge as function of temperature are collected in Table 2.

The X-ray structure measured previously[13] suggested that the OHN hydrogen bond in pyridinium 2,4-dinitrobenzoate, characterized by a very short O[13]···N distance, was among the shortest hydrogen bonds in which the proton can move through

TABLE 2: Parameters of the Hydrogen Bridge in Pyridinium 2,4-Dinitrobenzoate

	O1···N1 [Å]	O1···H1 [Å]	H1−N1 [Å]	OHN [°]	O1−C6 [Å]	C6=O2 [Å]	C6−C7 [Å]	H6···O2 [Å]
X-ray[13] 299 K	2.561(3)	1.51(3)	1.05(3)	177(3)	1.263(3)	1.222(3)	1.513(3)	2.53(3)
X-ray[13] 100 K	2.547(3)	1.49(3)	1.06(3)	178(3)	1.266(2)	1.226(2)	1.517(2)	2.56(2)
300	2.568(6)	1.403(10)	1.171(9)	172.1(7)	1.232(5)	1.206(6)	1.527(5)	2.427(9)
270	2.568(5)	1.418(8)	1.157(8)	171.7(6)	1.255(4)	1.214(5)	1.519(4)	2.4221(8)
240	2.565(4)	1.423(7)	1.148(7)	172.5(6)	1.254(4)	1.216(4)	1.522(4)	2.425(7)
210	2.567(4)	1.427(6)	1.145(6)	172.5(5)	1.262(3)	1.214(4)	1.524(3)	2.423(6)
180	2.563(3)	1.425(6)	1.144(5)	172.5(5)	1.264(3)	1.217(4)	1.525(3)	2.420(6)
150	2.566(3)	1.423(5)	1.148(5)	172.8(4)	1.269(3)	1.219(3)	1.524(3)	2.420(5)
120	2.564(3)	1.425(5)	1.144(5)	172.3(4)	1.275(3)	1.218(3)	1.526(3)	2.421(5)
90	2.562(3)	1.422(5)	1.146(5)	172.3(4)	1.275(2)	1.220(3)	1.525(2)	2.415(5)
60	2.562(2)	1.422(4)	1.146(4)	172.3(3)	1.276(2)	1.222(3)	1.527(2)	2.414(4)
30	2.565(2)	1.424(4)	1.147(4)	172.0(3)	1.275(2)	1.224(3)	1.526(2)	2.414(4)

the hydrogen bond's center by temperature change. The neutron measurement shows an O···N distance significantly longer than those of the shortest OHN hydrogen bridges. The larger value of the O···N distance is in accordance with the location of the proton, which, in all the neutron structures measured in the range of 30−300 K, is located closer to the acceptor nitrogen atom and does not pass through the center of the hydrogen bridge. Decreasing temperature causes a slight shortening of the O···N hydrogen bridge, realized by shortening of NH bonds and lengthening of the OH. The temperature changes of the OH and NH bonds are more significant in the 210 −300 K temperature range. At 210 K, the NH distance reaches the value 1.145(6) Å, very close to covalent NH bond lengths which cannot be shortened with temperature lowering. For this reason, below 210 K, the changes of O···H bond length as well as C6=O2 and C6−C7 are less significant than those at higher temperatures. The continuous shortening of the O···N bridge with temperature lowering is connected with continuous elongation of C6−O1 bond and shortening of the H6···O2 weak hydrogen bond which changes from 2.427(7) Å at 300 K to 2.414(5) Å at 30 K ($O\cdots H = -7(E-08)T^2 + 7(E-05)T + 2.4113$, $R^2 = 0.8312$). These changes show sensitivity of both covalent and weak interactions located in the vicinity of the hydrogen bond to the location of the proton in the hydrogen bridge. In Figure 2 and Table 1 are shown the changes in the hydrogen bridge parameters. The O···N, O···H, and NH distances of the hydrogen bond in pyridinium 2,4-dinitrobenzoate and their relative sensitivity to temperature confirm the moderately strong character of the hydrogen bond, which does not undergo a temperature change as significant as that of the strongest OHN hydrogen bond in the complex of pentachlorophenol with 4-methylpyridine[12] but is still different from the weak $N^+-H\cdots O^-$ hydrogen bonds which are not temperature sensitive.

In complexes of carboxylic acid with pyridines, changes in the degree of proton transfer are also reflected in the geometry of the COOH group of the proton donor. For molecular complexes, the CO bond lengths are characteristic for single and double bonds. When the proton is shifted to the acceptor, both lengths become equal; therefore, their difference can be used as a measure of the proton-transfer degree.[20] Another parameter sensitive to proton transfer is the C−C bond length linking the COOH group with the aromatic ring. All theses parameters are gathered in Table 1, and in Figure 2, the temperature changes of all the parameters with temperature are shown. Unexpectedly, the bond lengths in the carboxylic group are more sensitive to temperature than the parameters of the hydrogen bridge. The C6−O1 bond length systematically decreases with increasing temperature. The changes in C=O are more limited; therefore, the difference between the two bond lengths in the range of 30−300 K does not reach the zero value characteristic for the carboxylate group. With increasing temperature, the bond length C6−C7 becomes shorter, which reflects its partially double character connected with the delocalization of the electron cloud in the carboxylate group.

2. Comparison of the Hydrogen Bridge in Pyridinium 2,4-Dinitrobenzoate with Other Strong OHN Hydrogen Bonds. To compare the strength of the hydrogen bond in pyridinium 2,4-dinitrobenzoate with the strengths of other OHN hydrogen bonds for which the protons' location in the hydrogen bridge is precisely determined, it is worthwhile to analyze the geometrical parameters of all the known neutron structures of short OHN hydrogen-bonded complexes. Whereas short homonuclear hydrogen bridges are quite common, there are very few neutron structures with strong heteronuclear hydrogen bonds. The shortest O···N distance of 2.506(2) Å is in the 4-methylpyridine−pentachlorophenol complex at 20 K.[12] In the 1:2 adduct of benzene-1,2,4,5-tetracarboxylic acid and 4,4′-bipyridyl,[6] the O···N distance is 2.520(4) Å at 200 K, and in pyridine-3,5-dicarboxylic acid,[5] the O···N distance at 15 K equals 2.523(2) Å. The temperature sensitivity of the O···N, OH, and NH distances is a particular feature of the strong hydrogen bond not observed in weak hydrogen bonds. In all these complexes, the geometry of the hydrogen bridge is sensitive to temperature, and with temperature increase, the short O···N distance lengthens, and the proton shifts through the hydrogen bond's center. The NH distances of all the compounds mentioned above as a function of temperature are compared in ref 5. In comparison with these NH distances, this distance is shorter in pyridinium 2,4-dinitrobenzoate, and temperature does not cause significant changes in it. As in the strongest hydrogen bond, the proton passes through the center of the hydrogen bridge, and the OH and NH bond lengths are comparable, the best criterion of hydrogen bond strength being the difference between the OH and NH distances. The relationship of this value with temperature for the complexes with strong OHN hydrogen bonds is shown in Figure 3. Equalization of the OH and NH bonds takes place in the strongest OHN bridge. Figure 3a allows us to estimate the temperature at which the short hydrogen bridge is the strongest, and each change in temperature causes a weakening of the hydrogen bond. For the 4-methylpyridine−pentachlorophenol complex, this is 81 K; for the 1:2 adduct of benzene-1,2,4,5-tetracarboxylic acid and 4,4′-bipyridyl 234 K and for pyridine-3,5-dicarboxylic acid, this is 154 K. The temperature of equalization of the distances in the strong hydrogen bond is significantly different in the analyzed compounds. The specificity of the compounds is not seen in the relationship of the NH and OH bonds shown in Figure 3 b. The common relationship for phenol and benzoic acid seems to have the character of a general dependency of OHN hydrogen

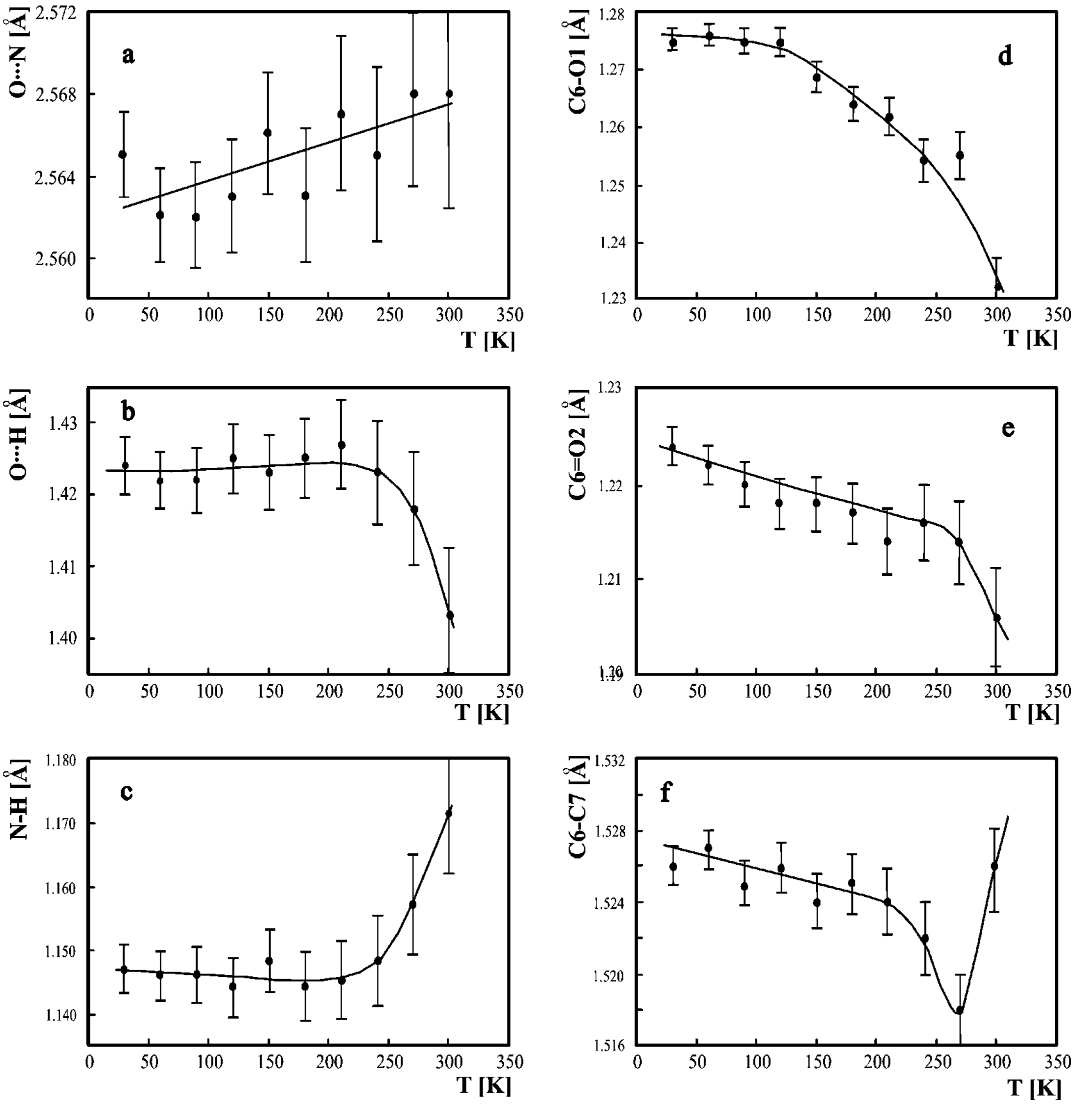

Figure 2. Temperature changes in the distances in the hydrogen bridge and carboxylate group of pyridinium 2,4-dinitrobenzoate. (a) O···N, (b) O···H, (c) NH, (d) C6−O1, (e) C6═O2, (f) C6−C7.

bond regardless of the chemical character of the proton donor and proton acceptor. The dependency in Figure 3c relates the O···N hydrogen bridge length with the difference between the OH and NH bond lengths, which is used as the measure of hydrogen bond strength. An analogous relationship was analyzed previously[21] and described by using Pauling's[22] theory of valence bond orders. Repeating this relationship is aimed at analyzing more precisely the region of the strongest hydrogen bonds, which is crucial for the shape of the relationship. The theoretical curve was calculated by using the equations and parameters for OHN hydrogen bonds as used in ref 23. The number of experimental points in Figure 3c is not sufficient to perform a new correlation, but general features of the differences between the theoretical curve and the experimental neutron structural data are seen. The correlation curve is symmetrical according to the valence bond theory, but the curve fitted to the experimental points should consist of two branches of different slope for positive and negative OH−NH values. The scattering of the experimental points is caused by the inaccuracy of the measurements, but their significant magnitudes can also be caused by the specific properties of the proton-donor and proton-acceptor molecules, as was shown in a theoretical analysis of phenol-trimethylamine complexes.[24] The main difference between the theoretical curve and the experimental points is seen in the region of lowest O···N values. The experimental O···N distances are higher than the values on the theoretical curve. The neutron structures reproduce the curve calculated by using the empirical anharmonic corrections.[21] Anharmonic ground-state vibrations cause elongation of the O···N bridge length, and this effect is especially important for the shortest bonds for which anomalous structural and spectroscopic effects are observed. All these differences suggest that more measurements of the neutron structure of the OHN hydrogen bond complexes are needed to complete the experimental curve and then to evaluate the general equations and parameters used in the valence bond theory.

3. Atom-in-Molecule Analysis of Strong OHN Hydrogen Bonds. The atom-in-molecule (AIM) theory has been widely used to characterize intermolecular interactions and, among them, also hydrogen bonds.[25−27] Analysis of the electron density in the AIM method is based on a partition of the molecular space into atomic basins associated with local zero flux in the gradient vector field of the electron density, $\rho(r)$. The basins correspond to topologically defined atoms. At the extremes of $\rho(r)$, $\nabla\rho(r)$ vanishes, and these points are called the critical points (CPs). The presence of a common bond path between two atoms is equivalent to the existence of a bond linking these two atoms. The minimum of the electron density on the bond

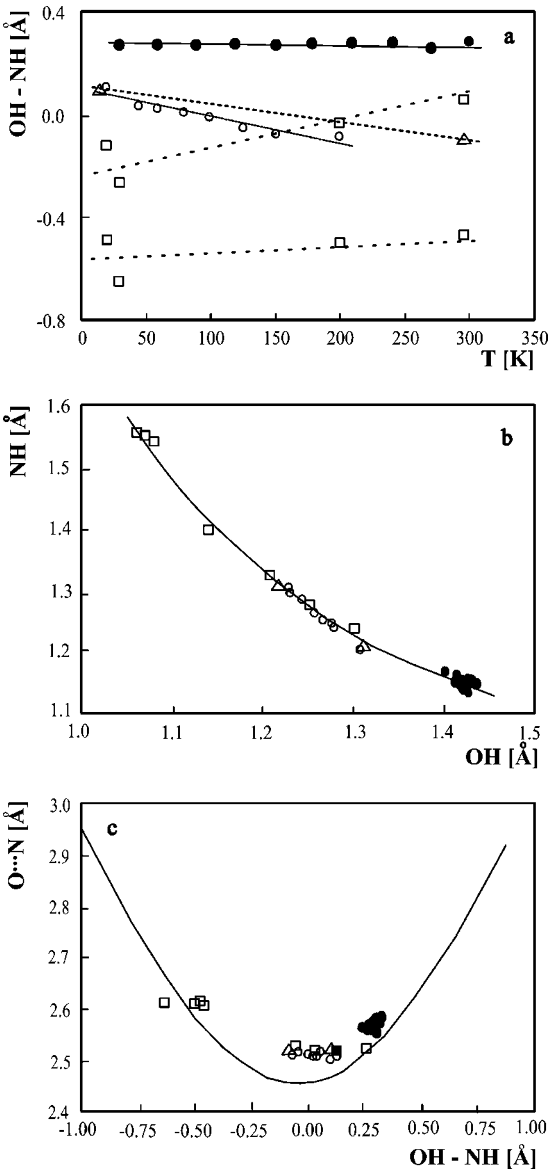

Figure 3. Comparison of the geometric parameter of the strong hydrogen bonds. (a) Relation between the difference in OH and NH distances and temperature. (b) Relation between NH and OH bond lengths. (c) Dependency of N···O bridge length and the difference between OH and NH. The experimental neutron bridge parameters are compared with the theoretical curve calculated according to ref 22: $p_1 = \exp(-(r_1 - r_1°)/b_1)$, $p_2 = \exp(-(r_2 - r_2°)/b_2)$, $p_1 + p_2 = 0$, $r_1 = r_{OH}$, $r_2 = r_{NH}$, where p_1 and p_2 are the corresponding valence-bond orders of the diatomic units, $b_1 = 0.371$, $r_1° = 0.942$, $b_2 = 0.385$, $r_2° = 0.992$ Å. ●, pyridinium 2,4-dinitrobenzoate; ○, 4-methylpyridine–pentachlorophenol complex;[12] □, 1:2 adduct of benzene-1,2,4,5-tetracarboxylic acid and 4,4′-bipyridyl;[6] Δ, pyridine-3,5-dicarboxylic acid.[5]

TABLE 3: Electron Density at BCPs of the OHN Hydrogen Bridge (au)

T [K]	$\rho(r)_{O\cdots H}$	$\rho(r)_{NH}$
Pyridinium 2,4-Dinitrobenzoate		
300	0.0946	0.2233
270	0.0933	0.2221
240	0.0979	0.2274
210	0.0969	0.2295
180	0.0974	0.2299
150	0.0980	0.2273
120	0.0974	0.2294
90	0.0982	0.2286
60	0.0982	0.2282
30	0.0975	0.2280
4-Methylpyridine Pentachlorphenol Complex		
200	0.1638	0.1511
150	0.1640	0.1528
125	0.1586	0.1579
100	0.1513	0.1679
80	0.1478	0.1722
60	0.1444	0.1751
45	0.1421	0.1782
20	0.1308	0.1963
1:2 Adduct of Benzene-1,2,4,5-tetracarboxylic Acid and 4,4′-Bipyridyl		
296	0.1621	0.1508
200	0.1356	0.1805
30	0.1069	0.2309
20	0.1279	0.1947

path is called the bond CP (BCP), and the values of the electron density and of other topological parameters of the CP were proposed as criteria of the character of the interaction between the two atoms located at the ends of the bond path. In the case of a hydrogen bond, the value of the electron density at the BCP is a measure of the strength of the hydrogen bond. In this study, the AIM analysis was performed for the neutron structures in which the location of the proton in the hydrogen bridge is precisely determined. In addition to the relationships of the bond lengths in the hydrogen bridge, analysis of the electron densities at the BCPs located between the proton and proton donor and the proton and proton acceptor characterizes the hydrogen bond in the analyzed complexes with a strong OHN hydrogen bond.

In Table 3 are collected the values of electron densities at bond CPs in the OHN hydrogen bridge calculated for neutron structures with strong OHN hydrogen bonds.

In Figure 4a, the electron densities at the BCPs between the OH and NH atoms are correlated with the difference between the OH and NH distances. An increase in the electron density at one of these BCPs is accompanied by a decrease at the other. It could be expected that at a difference between the OH and NH bond lengths equal to 0, which means a central location of the proton in the hydrogen bond, the two relationships will cross. This crossing point appears, however, not at 0 but at a value of −0.0468. This means that the electron density is spread equally at both CPs of the hydrogen bridge when the NH bond is 0.0468 Å longer than the OH bond. The common value of electron density is 0.1579 au. Except for the identical values of both distances in the hydrogen bridge, which is used as the criterion for the strongest hydrogen bond, a better criterion of hydrogen bond strength is equalization of the electron density at both CPs located in the hydrogen bridge. The difference in the OH and NH distances found for equal values of the electron densities is in accordance with the minimum of the curve fitted for OHN hydrogen bonds according to the Pauling valence-bond order theory (Figure 3c). The difference between the OH and NH bond distances in the OHN hydrogen bridge is expressed in Figure 4b by the relationships between the percentage of the contribution of the electron density at the particular BCPs of the hydrogen bridge and the OH and NH bond lengths. The sum of the two electron densities at the BCPs in the OH and NH bonds is equal to 100%. This figure shows the general tendency of decreasing electron density with increasing bond length and the significant difference between the OH and NH bonds. For the latter, the electron density is always higher, regardless of the degree of proton transfer.

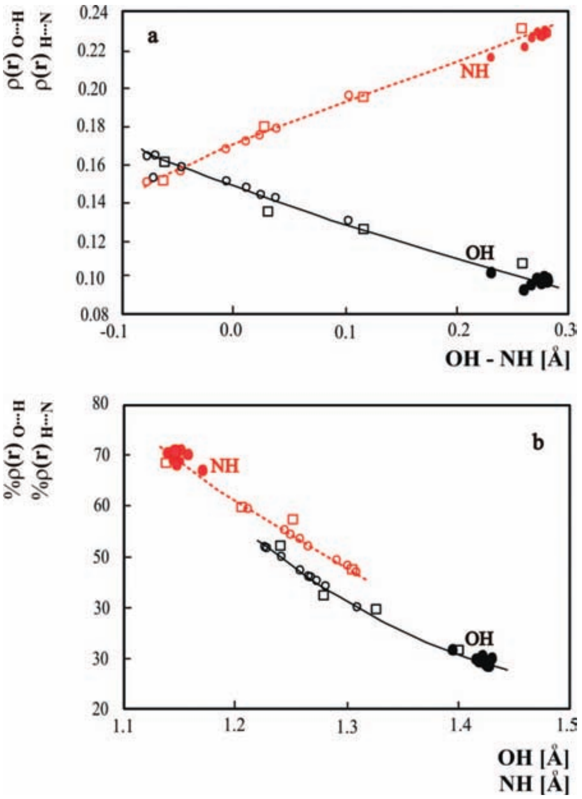

Figure 4. (a) Relationship of the $\rho(r)$ at the OH and NH BCPs with OH−NH difference. (b) Rrelationship of the percentage of $\rho(r)$ at the OH and NH BCPs with the OH and NH distances. $\rho(r)_{OH} + \rho(r)_{NH} = 100\%$. ●, pyridinium 2,4-dinitrobenzoate; ○, 4-methylpyridine−pentachlorophenol complex;[12] □, 1:2 adduct of benzene-1,2,4,5-tetracarboxylic acid and 4,4′-bipyridyl.[6]

Conclusions

The hydrogen bond in pyridinium 2,4-dinitrobenzoate is an example of strong hydrogen bond with proton located at the nitrogen acceptor atom, and no proton migration through the hydrogen bond center has been found. The bond lengths of O···H and NH change systematically in the range 210−300 K. Below 210 K, these changes are not significant because the NH bond length becomes close to covalent bonds. The dependency of NH versus OH bond length has general character and is common for the hydrogen bonded complexes of phenols and benzoic acids. The shifting of the proton in the hydrogen bridge reflects in the change of other bond lengths participating in the ring formed by OHN and CHO hydrogen bonds. A review of neutron structures of strong OHN in which the proton transfer process is realized under the temperature changes does not confirm proton-transfer equilibrium in the proton transfer process as coexistence of two tautomeric forms.[4] X-ray diffraction results published previously for pyridinium 2,4-dinitrobenzoate provide information about the distribution of the electron cloud around the hydrogen bond. This result was confirmed by AIM analysis of the electron density, which with temperature change moves from the OH to NH bond CP. Results described in this paper suggest that the proton-transfer equilibrium model commonly used from many years in hydrogen-bond literature to describe the proton transfer in liquids and solid states should be replaced by equilibrium of the electron density which can be shifted between bond CPs in the hydrogen bridge when proton is transferred in the hydrogen bond.

Acknowledgment. The Wroclaw Center for Networking and Supercomputing is acknowledged for generous computer time.

References and Notes

(1) Hibbert, F.; Emsley, J. *Adv. Phys. Org. Chem.* **1990**, *26*, 255.
(2) Cleland, W. W.; Kreevoy, M. M. *Science* **1994**, *264*, 1887.
(3) Barrow, M. G. *J. Am. Chem. Soc.* **1956**, *78*, 5802.
(4) Huyskens, P.; Zeegers-Huyskens, Th. *J. Chim. Phys.* **1964**, *61*, 84.
(5) Cowan, J. A.; Howard, J. A. K.; McIntre, G. J.; Lo, S. M.-F.; Williams, J. D. *Acta Crystallogr.* **2005**, *B61*, 724.
(6) Cowan, J. A.; Howard, J. A. K.; McIntre, G. J.; Lo, S. M.-F.; Williams, J. D. *Acta Crystallogr.* **2003**, *B59*, 794.
(7) Wilson, C. C. *Acta Crystallogr.* **2001**, *B57*, 435.
(8) Wilson, C. C.; Shankland, K.; Shankland, N. *Z. Kristallogr.* **2001**, *216*, 303.
(9) Kostanek, E. C.; Busing, W. R. *Acta Crystallogr.* **1972**, *B28*, 2454.
(10) Rodrigues, B. L.; Tellgreen, R.; Fernandes, N. G. *Acta Crystallogr.* **2001**, *B57*, 353.
(11) Olovsson, I.; Ptasiewicz-Bk, H.; Gustafsson, T.; Majerz, I. *Acta Crystallogr.* **2001**, *B57*, 311.
(12) Steiner, T.; Majerz, I.; Wilson, C. C. *Angew. Chem., Int. Ed.* **2001**, *40*, 2651.
(13) Sobczyk, L.; Lis, T.; Olejnik, Z.; Majerz, I. *J. Mol. Struct.* **2000**, *552*, 233.
(14) Keen, D. A.; Gutmann, M. J.; Wilson, C. C. *J. Appl. Crystallogr.* **2006**, *39*, 714.
(15) Gutmann, M. J. *SXD2001*; ISIS Facility, Rutherford Appleton Laboratory: Oxfordshire, England, 2005.
(16) Wilson, C. C. *J. Appl. Crystallogr.* **1997**, *30*, 184.
(17) Sheldrick, G. M. *SHELXL97*; University of Göttingen: Germany, 1997.
(18) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision A.9; Gaussian, Inc.: Wallingford, CT, 2004.
(19) Biegler-König, F.; Schönbohm, J.; Bayles, D. *J. Comput. Chem.* **2001**, *22*, 545.
(20) Borthwick, P. W. *Acta Crystallogr.* **1980**, *B36*, 628.
(21) Limbach, H.-H.; Pietrzak, M.; Sharif, S.; Tolstoy, P. M.; Shenderovich, I. G.; Smirnov, S. N.; Golubev, N. S.; Denisov, G. S. *Chem. Eur. J.* **2004**, *10*, 5195.
(22) Pauling, L. *J. Am. Chem. Soc.* **1947**, *69*, 542.
(23) Steiner, Th. *J. Phys. Chem. A* **1998**, *102*, 7041.
(24) Kwiatkowska, E.; Majerz, I.; Koll, A. *Chem. Phys. Lett.* **2004**, *398*, 130.
(25) Bader, R. F. W. *Atoms in Molecules: A Quantum Theory*; Oxford University Press: New York, 1990.
(26) Koch, U.; Popelier, P. L. A. *J. Phys. Chem.* **1995**, *99*, 9747.
(27) Popelier, P. L. A. *J. Phys. Chem.* **1998**, *102*, 1873.

JP800781P