Bidentated Hydrogen Bond from [O−H···N−N···H−O] to [O−···+H−N−N−H+···−O] Structures in Solids

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Heteronuclear bidentated N−H−O hydrogen bonds in the (4,4′-bipyridine)(polynitrophenols)₂ system were revealed in terms of X-ray structural analyses, ab-initio calculations, and vibrational spectra. 4,4′-Bipyridine (AA) and polynitrophenols (D) acted as Brønsted base and acid in solids, respectively. The bidentated hydrogen-bonding interaction in solids was modified between [D⁻···⁺H−AA−H⁺···⁻D] and [D−H···AA···H−D] through regulating Brønsted acid−base conditions.

Introduction

Hydrogen-bonding interaction plays an important role to realize the structures and dynamic behaviors in a wide range of materials from dielectrics to supramolecules to biological systems.[1] In general, the proton in the hydrogen bond is static. On the other hand, dynamic processes in the hydrogen bonds are the critical phenomena for the proton conductivity in ice[2] and for the proton transfer (PT) in the photosynthetic reaction[3] and the enzymatic reaction.[4] The PT processes in the enzymatic reaction are promoted by the formation of a very strong hydrogen bond in the intermediate state, which is important for the realization of the effective enzymatic reaction.[4,5] Very strong heteronuclear N−H−O hydrogen bonds in the enzymatic reaction sites such as triose-P isomerase, citrate synthase, and aconitase are observed between the oxygen site of glyceraldehydes-3-P or acetyl-CoA and the nitrogen site of histidine.[4,6] The multiple strong heteronuclear N−H−O hydrogen bonds and PT processes in them are important for the formation of transition structures in enzymatic reactions. Although these should be a critical intermediate state in the enzymatic reactions, the nature of these intermediate complexes has not been examined thoroughly due to the small number of the strong multiple N−H−O hydrogen bonds. Here we examined very strong bidentated N−H−O hydrogen-bonded molecular complexes of [(H−D)···(A−A)···(H−D)] in the solid. A−A and H−D are 4,4′-bipyridine (BPY) and polynitrophenol (NP), respectively, which have one proton-donating oxygen and two proton-accepting nitrogen sites. In these complexes, the inter-crossing of the PT state from the [D−H···A−A···H−D] to the [D⁻···⁺H−A−A−H⁺···⁻D] type was observed.

Experimental Section

Infrared (IR, 400−7600 cm⁻¹) spectra measurements were carried out on KBr pellets using a Perkin-Elmer Spectrum 2000

spectrophotometer with a resolution of 1 cm⁻¹. The IR spectra were measured at 300 K in a cryogenic refrigerating system (Daikin UV202A).

Complexes (BPY)(TNP)₂(H₂O) (**1**), (BPY)(2,4-DNP)₂ (**2**), and (BPY)(2,5-DNP)₂ (**3**) were grown by slow evaporation of 1:2 molar mixtures of BPY and NP from H₂O−C₂H₅OH (8:2) solution and then dried in a vacuum. Elem anal. C₂₂H₁₆N₈O₁₅ (**1**) found: C, 41.66; H, 2.74; N, 17.02. Calc: C, 41.78; H, 2.55; N, 17.72. C₂₂H₁₆N₆O₁₀ (**2**) for found: C, 50.51; H, 2.95; N, 15.86. Calc: C, 50.40; H, 3.05; N, 16.03. C₂₂H₁₆N₆O₁₀ (**3**) found: C, 50.32; H, 3.21; N, 15.93. Calc: C, 50.40; H, 3.05; N, 16.03.

Crystallographic data were collected with a Rigaku Raxis-Rapid diffractometer using Mo Kα (λ = 0.710 73 Å) radiation from a graphite monochromator. The structures were solved and refined using the program Crystal Structure (Single-crystal structure analysis software, Ver. 3.0; Rigaku Corporation and Molecular Structure Corporation: 2002). The structure refinements were performed by a full matrix least-squares method on F^2. Parameters were refined using the anisotropic temperature factors in all crystals, and the positions of hydrogens were determined by differential Fourier analysis. The same proton positions were obtained under the structural analysis without the inversion center on the BPY molecule. Crystal data of **1**: C₂₂H₁₆O₁₅N₈, FW 632.41, yellow-orange plate, 296 K, space group *C*2/*c* (#15), *a* = 29.749(2) Å, *b* = 5.2799(2) Å, *c* = 20.736(1) Å, β = 130.0318(8)°, *V* = 2493.9(2) Å³, *Z* = 4, ρ_{calcd} = 1.684 g cm⁻³, 18235 measured, 2836 unique, 1601 observed (*I* > 2.20σ(*I*)), *R* = 0.038, R_w = 0.065, GOF = 1.15. Crystal data of **2**: C₂₂H₁₆O₁₀N₆, FW 524.40, yellow plate, 296 K, space group *Pbcn* (#60), *a* = 15.0526(9) Å, *b* = 7.0861(3) Å, *c* = 22.008(1) Å, *V* = 2347.4(2) Å³, *Z* = 4, ρ_{calcd} = 1.484 g cm⁻³, 29144 measured, 2901 unique, 1673 observed (*I* > 2.20σ(*I*)), *R* = 0.047, R_w = 0.058. GOF = 1.08. Crystal data of **3**: C₂₂H₁₆O₁₀N₆, FW 524.40, yellow plate, 296 K, space group *P*2₁/*n* (#14), *a* = 4.9300(4) Å, *b* = 19.793(1) Å, *c* = 11.6871-(7) Å, β = 92.022(3)°, *V* = 1139.7(1) Å³, *Z* = 2, ρ_{calcd} = 1.528 g cm⁻³, 15341 measured, 2546 unique, 1458 observed (*I* > 2.20σ(*I*)), *R* = 0.059, R_w = 0.064, GOF = 1.16.

The relative potential energies of the (BPY)(NP)₂ unit were calculated from the atomic coordinates of X-ray crystal structural

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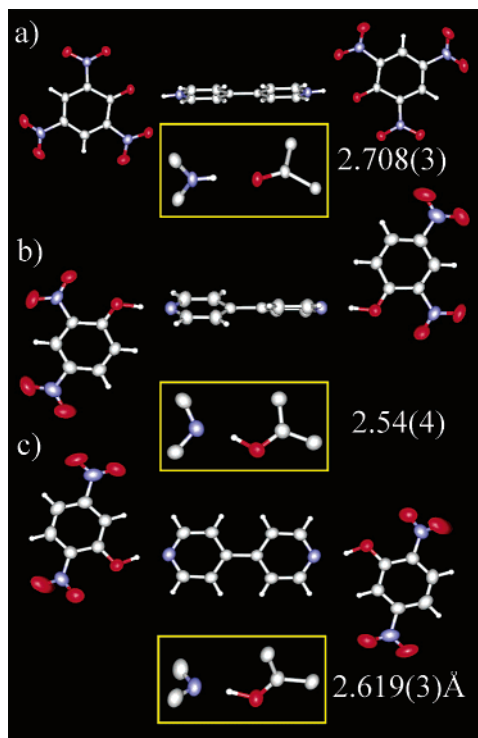§ National Institute of Advanced Industrial Science and Technology.

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Figure 1. Fundamental N−H−O hydrogen-bonded [NP···BPY···NP] units. (a) Proton-transferred [TNP⁻···H2BPY²⁺···TNP⁻] unit in complex **1**. (b) [2,4-DNP···BPY···2,4-DNP] unit in complex **2**. (c) [2,5-DNP···BPY···2,5-DNP] unit in complex **3**. Inset figures show the expansion at the N−H−O hydrogen-bonded sites and N−O distances.

TABLE 1: Physical and Structural Parameters of Complexes 1−3

	1	**2**	**3**
ΔpK_{a1}[a]	−2.33	1.27	2.46
ΔpK_{a2}[a]	−4.41	−0.81	0.38
d_{N-O}, Å	2.708(3)	2.54(4)	2.619(3)
d_{N-H}, Å	0.84(3)	1.43(4)	1.58(6)
d_{O-H}, Å	1.92(3)	1.12(4)	1.07(6)
$\angle_{N-H-O}$, deg	156.8(3)	173.8(3)	162.2(4)
d_{N-H}(calc), Å	1.05, 1.80	1.52	1.62
ν_{N-H-O}, cm⁻¹	2750	>1000	2380
T_{mp}, K	522.5	425.0	401.9

[a] ΔpK_{a1} and ΔpK_{a2} are pK_a(NP) − pK_{a1}(BPY) and pK_a(NP) − pK_{a2}(BPY), respectively.
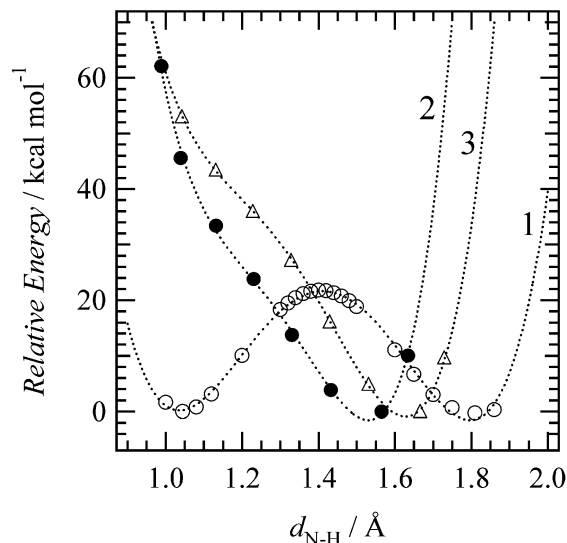

Figure 2. Calculated potential curves for N−H−O proton coordinates in the [NP···BPY···NP] units of complexes **1**−**3**. Relative energies (kcal mol⁻¹) for each proton coordinate are plotted versus the N−H distance (d_{N-H}, Å). The dashed lines are guides for the eye. The proton positions and relative energies are optimized by the HF/6-31G(d,p) and MP2/6-31G(d,p) methods, respectively.

analysis. The atomic coordinate, except for two hydrogen-bonding protons, was fixed as the coordinates obtained by X-ray structural analysis. The proton positions in two N−H−O hydrogen bonds were symmetrically moved as a parameter of N−H distance (d_{N-H}, Å). Since the hydrogen-bonding proton coordinate depends on N−H distance, N−H−O angle, and dihedral angle, the hydrogen-bonding proton coordinate was optimized by the HF/6-31G(d,p) method for a fixed N−H distance. The relative energies for the fixed coordinate were obtained by MP2/6-31G(d,p) calculation.

Results and Discussion

Complexes (BPY)(TNP)₂(H₂O) (**1**), (BPY)(2,4-DNP)₂ (**2**), and (BPY)(2,5-DNP)₂ (**3**) were examined to modify the hydrogen bonds of [(H−D)···(A−A)···(H−D)] in the solid; here TNP, 2,4-DNP, and 2,5-DNP are 2,4,6-trinitrophenol, 2,4-dinitrophenol, and 2,5-dinitrophenol, respectively. Figure 1 shows the crystals structures of complexes **1**−**3**. The BPY molecules were located on the center of inversion in all cases. Identical proton positions were obtained under the structural analysis without the inversion center on the BPY molecule. In the fundamental structural unit of [NP···BPY···NP], BPY is connected by two N−H−O hydrogen bonds with two NP molecules (Figure 1). The angles between normal to the pyridine and the phenol ring planes in the complexes **1**−**3** are 75.5, 86.6, and 15.6°, respectively. Complex **1** contained a H₂O molecule in the crystal, in which the O−H···O hydrogen-bonding interaction (O(2)−O(8) = 2.801(2) Å) was observed between the water molecule and the oxygen atom of the nitro group of TNP. The effective intermolecular interaction except for the hydrogen bonds was not observed within the range of van der Waals contacts. Table 1 tabulated the physical and structural parameters of complexes **1**−**3**.

The phenolic protons of TNP were transferred to the BPY in complex **1** (Figure 1a). The resulting 4,4′-bipyridinium dication (H2BPY²⁺) and two phenolate anions formed a [D⁻···⁺H−AA−H⁺···⁻D] type ionic hydrogen-bonding interaction. The hydrogen-bonded N−O distance of 2.708(3) Å is ∼0.2 Å shorter than the standard N−O hydrogen-bonded distance (∼2.9 Å).[7] The N−H (0.84 Å) and O−H (1.92 Å) distances indicate the localization of protons at the nitrogen site. In the case of complex **3**, the phenolic protons of 2,5-DNP remained at the oxygen sites (Figure 1c), which provided a [D−H···AA···H−D] type neutral hydrogen bond without the PT process. The N−O distance 2.619(3) Å in complex **3** is shorter than that of complex **1**. The N−H and O−H distances 1.58(5) and 1.07(5) Å indicate the localization of protons at the oxygen site. The protons of 2,4-DNP in complex **2** were also observed at the phenolic oxygen sites (Figure 1b). However, the N−O distance 2.54(4) Å is extremely short and the protons are located between the nitrogen and oxygen sites with the N−H and O−H distances 1.43(3) and 1.12(4) Å, respectively. In the strong hydrogen bonds in complex **2**, both the [D−H···AA···H−A] and [D⁻···⁺H−AA−H⁺···⁻D] configurations contribute to the hydrogen-bonding interaction.

Figure 2 shows the potential curves for proton coordinates of complexes **1**−**3**. In complex **1**, the double-minimum potential curve corresponding to the mixture of [D−H···AA···H−A] and [D⁻···⁺H−AA−H⁺···⁻D] configurations was observed with the

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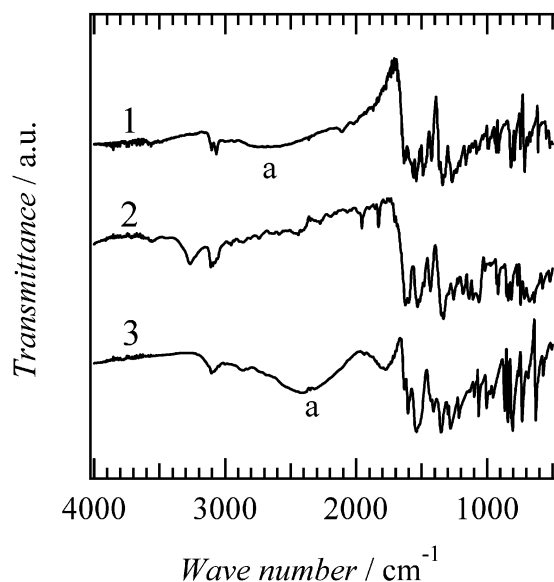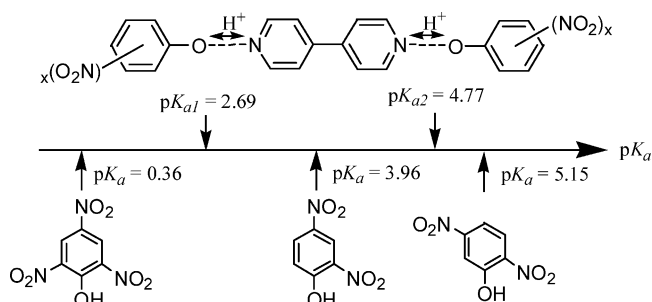
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Figure 3. Vibrational spectra of complexes **1**–**3** at 300 K (500–4000 cm^{-1}). The a-bands are the intermolecular N–H–O asymmetric stretching mode.

SCHEME 1: pK_a of (BPY)(TNP)$_2$ (**1**), (BPY)(2,4-DNP)$_2$ (**2**), and (BPY)(2,5-DNP)$_2$ (**3**) Complexes

D] structures of complexes **1**–**3** in terms of Brønsted acid–base interactions.

BPY has two proton-accepting sites with p$K_{a1} = 2.69$ and p$K_{a2} = 4.77$, respectively, while the pK_a values of TNP, 2,4-DNP, and 2,5-DNP are 0.36, 3.96, and 5.15, respectively (Scheme 1).[13] In the (BPY)(NP)$_2$ system, two parameters, ΔpK_{a1} (pK_a(NP) $-$ pK_{a1}(BPY)) and ΔpK_{a2} (pK_a(NP) $-$ pK_{a2}(BPY)), which vary from complex **1** (-2.33 and -4.41) to complex **2** (1.27 and -0.81) to complex **3** (2.46 and 0.38), respectively (Scheme 1), are important to determine the type of hydrogen bond. Among them, the ΔpK_{a1} and ΔpK_{a2} values of complex **2** are close to zero with different sign from each other. Higher acidity of TNP than those of BPY completely moves the phenolic protons to nitrogen sites for both negative ΔpK_a values, which results in the [D$^-$$\cdots$$^+$H–AA–H$^+$$\cdots$$^-$D] hydrogen-bonded structure. The positive ΔpK_a values of complex **3** mean the protons remain at the oxygen site. In the case of complex **2**, the ΔpK_a condition becomes an intermediate between those for complexes **1** and **3**, which results in a very strong N–H–O heteronuclear bidentated hydrogen-bonded [D–H$\cdots$AA$\cdots$H–D] structure.

Conclusion

The nature of heteronuclear bidentated N–H–O hydrogen bonds in the (BPY)(NP)$_2$ system was revealed in terms of X-ray structural analyses, ab-initio calculations, and vibrational spectra. The bidentated hydrogen-bonding interaction in solids was controlled between [D$^-$$\cdots$$^+$H–AA–H$^+$$\cdots$$^-$D] and [D–H$\cdots$AA$\cdots$H–D] through regulating the Brønsted acid–base condition. Very strong bidentated N$\cdots$H–O hydrogen bonds were obtained in the pK_a condition of pK_{a1}(BPY) < pK_a(NP) < pK_{a2}(BPY). Further investigation of these bidentated hydrogen-bonding [D$\cdots$H$\cdots$AA$\cdots$H$\cdots$D] structures from the viewpoints of dynamic properties of protons in solids is now in progress.

Supporting Information Available: The atomic coordinates, anisotropic thermal parameters, and bond lengths for crystals **1**–**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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$d_{N–H}$ equilibrium distances of 1.05 and 1.80 Å and a barrier height of 20 kcal mol^{-1}. However, the protons in complex **1** are localized at the N–H sites from the structural analysis, which should be related to the stabilization of the ionic form by the gain of Madelung energy. On the other hand, complexes **2** and **3** show the single-minimum potential curves, in which the protons are localized at the O–H sites in the [D–H$\cdots$AA$\cdots$H–D] hydrogen-bonded configuration. The optimized N–H distances for complexes **2** and **3** were 1.52 and 1.62 Å, respectively, which were slightly longer than those obtained by structural analysis. The equilibrium proton positions in the crystal are slightly shifted to the N–H side due to the contribution from the [D$^-$$\cdots$$^+$H–AA–H$^+$$\cdots$$^-$D] configuration, which is favorable to gaining the Medelang energy.

Vibrational spectra of complexes **1**–**3** are shown in Figure 3. The intermolecular antisymmetric N–H–O stretching modes (ν^a) in the IR energy region are broader and are shifted to lower energy through the formation of a strong hydrogen bond.[1a,8,9] Complexes **1** and **3** showed the ν^a mode with a broad a-band around 2750 and 2380 cm^{-1} (300 K), respectively, while that of complex **2** was not clearly observed in the energy region above 1000 cm^{-1}. The obscurity of the ν^a mode in complex **2** should be due to a large red-shift at around several hundred wavenumbers and a broad line width due to the formation of extremely strong hydrogen bonds.[1e,9] Complex **1** is composed of TNP anions, which was also confirmed by the higher melting point (522.5 K) than those of complexes **2** (425.0 K) and **3** (401.9 K). The ionic [D$^-$$\cdots$$^+$H–AA–H$^+$$\cdots$$^-$D] crystal lattice has higher thermal stability than that of [D–H$\cdots$AA$\cdots$H–D]. The contribution from the ionic hydrogen-bonded configuration in complex **2** increases the thermal stability ∼20 K more than that of **3** despite the same molecular weights for these two complexes.

The formation of a single N–H–O hydrogen bond in (pyridine)(phenol) complexes has been discussed in terms of Brønsted acid–base interaction between the proton donor (HD) and acceptor (A) molecules.[9–12] The complexes with ΔpK_a (pK_a(HD) $-$ pK_a(A)) at around zero have an intermediate hydrogen-binding interaction between [D–H$\cdots$A] and [D$^-$$\cdots$H–A$^+$].[9] We consider the bidentated hydrogen-bonded [D$\cdots$H$\cdots$AA$\cdots$H$\cdots$

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