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Unusual Hydrogen-bonding Networks Consisting of π -Extended 4,4'-Bipyridines and Chloranilic Acid

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Hydrogen-bonding networks of π -extended 4,4'-bipyridines, 2,5-di(4-pyridyl)thiophene (1), 2,5-di(4-pyridyl)furan (2) and 1,4-di(4-pyridyl)benzene (3) with 2,5-dichloro-3,6-dihydroxy-1,4-benzoquinone (chloranilic acid, CA) have been investigated. The dipyridyl compounds afforded complexes 4 [(dication of 1)·(monoanion of CA)₂], 5 [(dication of 2)·(dianion of CA)·(MeOH)] and 6 [(3)·(dication of 3)·(dianion of CA)·(H₂O)₆] with CA. X-ray structure analyses revealed the formation of unusual molecular tape and sheet structures involving N–H···O, O–H···O, C–H···O and N–H···N hydrogen bonds, where the aromatic spacer groups play an important role in constructing the unique crystal structures.

Keywords: Crystal engineering; Hydrogen-bonding network; π -Extended bipyridines; Chloranilic acid

INTRODUCTION

Hydrogen bonds are flexible compared to coordination bonds and covalent bonds [1,2], and have been very important in supramolecular chemistry [3,4], as well as in crystal engineering studies [5–11]. They have been much used for preparing novel materials with electronic, magnetic, optical, or catalytic properties [3–13]. However, there are only a few examples of hydrogen-bonding systems involving intermolecular electron-transfer interactions [14,15]. Benzoquinones containing dihydroxy and halide/cyanide groups can afford such systems because they have excellent proton-donating and electron-accepting properties and undergo multi-stage protonation and deprotonation

processes [16–18]. They can be associated with various proton-acceptors and electron donors to afford new supramolecular architecture [16,17]. We have recently reported that the simple combination of chloranilic acid (CA) with dipyridyl compounds leads to the formation of a variety of networks such as linear chains, zigzag tapes and square grid structures [19], where charge-transfer interactions take place between molecules. We have also shown that the formation of neutral, monoanion, and dianion states of CA can be controlled by proton transfer [20]. The structures and properties of the hydrogen-bonding complexes can be tuned by the substituents on the anilic acids [21]. We have now used dipyridyl compounds containing π -conjugated groups as proton acceptor and investigated their complexation with chloranilic acid as proton donor. Introduction of a π -conjugated spacer to dipyridyl compounds has been considered to increase intermolecular π – π interactions and decrease Coulombic repulsion in the dication states.

EXPERIMENTAL

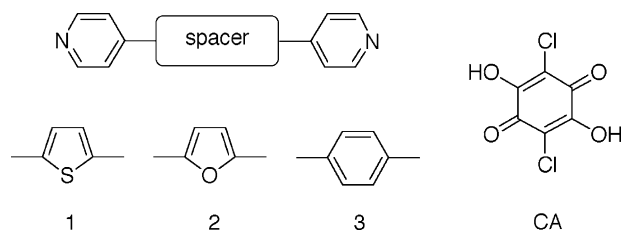
Preparation

4,4'-Dipyridyl compounds 1–3 containing thiophene, furan, and benzene as spacers were prepared on the basis of palladium-catalyzed cross-coupling reactions [22]. Complexes 4–6 were obtained as single crystals by placing equal molar amounts of 1–3 and CA in an H-shaped tube filled with

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TABLE I Crystal data and summary of data collection parameters

	4	5	6
Molecular formula	C ₂₆ H ₁₄ Cl ₄ N ₂ O ₈ S	C ₂₁ H ₁₆ Cl ₂ N ₂ O ₆	C ₃₈ H ₃₈ Cl ₂ N ₄ O ₁₀
Molecular weight	656.25	463.26	781.62
Crystal dimensions/mm	0.25 × 0.05 × 0.02	0.30 × 0.15 × 0.10	0.30 × 0.10 × 0.05
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	C2/c	P $\bar{1}$	P $\bar{1}$
T/K	296	296	296
Unit cell			
<i>a</i> /Å	12.906(12)	9.3965(5)	9.1353(4)
<i>b</i> /Å	14.055(12)	10.0796(7)	9.3240(3)
<i>c</i> /Å	13.750(12)	10.7956(7)	11.3740(5)
α /°	90	94.695(5)	91.267(4)
β /°	97.93(2)	102.408(4)	99.142(4)
γ /°	90	91.962(5)	107.228(4)
<i>V</i> /Å ³	2470(4)	993.8(1)	911.13(6)
Z	4	2	1
Density calc./g cm ⁻³	1.765	1.548	1.425
Absorption coeff./mm ⁻¹	0.624	3.330	2.157
Radiation	Mo-K α	Cu-K α	Cu-K α
<i>R</i> _{int}	0.1450	0.0174	0.0229
Measured reflections	2913	4285	3967
Independent reflections	2799	4059	3729
Reflections with <i>I</i> > 2 σ (<i>I</i>)	1244	3142	2609
<i>R</i> ₁	0.1587	0.0399	0.0437
<i>wR</i> ₂	0.3511	0.1021	0.1109
GOF	1.235	1.013	1.000



acetonitrile, methanol and a mixture of acetonitrile–acetone, respectively.

X-ray Crystallographic Analysis

Reflection data for **4** were collected on a Rigaku/MSM Mercury CCD diffractometer using Mo-K α radiation ($\lambda = 0.71070$ Å) at 296 K. Reflection data for **5** and **6** were collected on an Enraf-Nonius CAD4 diffractometer using Cu-K α radiation ($\lambda = 1.54178$ Å) at 296 K. No absorption correction was applied except for in the case of **5**. Absorption correction for **5** was applied using empirical procedures based on azimuthal Ψ scans of seven reflections having an Eulerian angle, χ , near 90°. All structures were solved by direct methods and refined by full-matrix least-squares on F^2 with SHELX-97 [23]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms of **4** and **5** were refined by using a riding model, and those of **6** were localized in the Fourier map and refined isotropically. Crystal data and a summary of data collection

parameters are shown in Table I. Crystallographic data (excluding structure factors) for **4**, **5** and **6** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 193043–193045, respectively.

RESULTS AND DISCUSSION

Complex **4** has the composition (dication of **1**)-(monoanion of CA)₂ and crystallizes in a monoclinic space group C2/c. It involves N⁺–H···O hydrogen bonds on both sides of **1** with a thiophene ring and O–H···O hydrogen bonds between the CA molecules. No infinite molecular tape structure is observed. In addition, a molecular sheet structure formed via C–H···O hydrogen bonds between **1** and CA. Between the molecular sheets, two types of overlap exist for the monoanion of CA. The distances between the ring planes for CA–CA and CA–pyridine are 3.15(1) and 3.32(2) Å, respectively. The structural views and their intermolecular hydrogen-bonding distances are shown in Fig. 1.[†] It should be noted that one proton of CA is transferred to the nitrogen atoms of **1** to produce the monoanion of CA and the dication of **1**. The bond lengths of CA support the monoanionic structures [24–27].

Complex **5** has the composition (dication of **2**)-(dianion of CA)·(MeOH)[‡] with triclinic P $\bar{1}$ space group. Both the pyridyl rings of **2** are protonated to

[†]The hydrogen bond labeled c in Fig. 1 seems to be a head-on approach of two hydrogen atoms, and the position of the hydrogen atom may be uncertain. Because of the low quality of the crystal, we could not refine the hydrogen atom isotropically.

[‡]The solvated methanol is disordered over two sites with occupancies of 0.592(6) and 0.408(6), respectively. The carbon and oxygen atoms of the disordered methanol were localized in the Fourier map and refined isotropically.

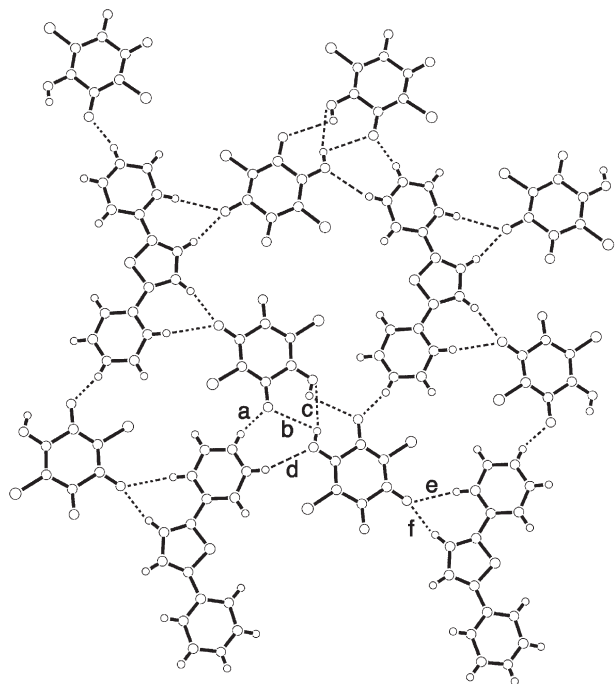


FIGURE 1 Intermolecular contacts in the molecular sheet of **4**, where (a) (N–H···O): H···O 1.93, N···O 2.74(1); (b) (O–H···O): H···O 2.68, O···O 2.99(1); (c) (O–H···O): H···O 2.62, O···O 3.41(2); (d) (C–H···O): H···O 2.62, C···O 3.51(1); (e) (C–H···O): H···O 2.60, C···O 3.50(2); (f) (C–H···O): H···O 2.18, C···O 3.09(1) Å.

form a molecular tape structure via bifurcated interionic $N^+–H···O$ and $N^+–H···O^-$ hydrogen bonds with CA molecules (Fig. 2). These hydrogen bond motifs are robust and similar to the supramolecular synthon that we previously reported to

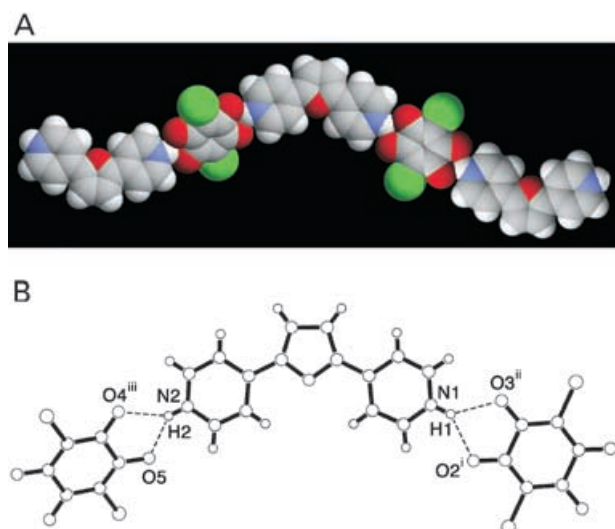


FIGURE 2 (a) Molecular tape structure of **5**. (b) Hydrogen-bonding pattern of **5**, where N1–H1···O2ⁱ, H1···O2ⁱ 2.06, N1···O2ⁱ 2.783(2) Å, N1–H1···O2ⁱ 141.2°; N1–H1···O3ⁱⁱ, H1···O3ⁱⁱ 2.07, N1···O3ⁱⁱ 2.779(2) Å, N1–H1···O3ⁱⁱ 139.5°; N2–H2···O4ⁱⁱⁱ, H2···O4ⁱⁱⁱ 2.08, N2···O4ⁱⁱⁱ 2.802(2) Å, N2–H2···O4ⁱⁱⁱ 141.5°; N2–H2···O5, H2···O5 2.04, N2···O5 2.741(2) Å, N2–H2···O5 138.2°; symmetry code *i*: $-x + 1, -y + 1, -z + 3$; *ii*: $x - 1, y + 1, z + 1$; *iii*: $-x + 1, -y + 1, -z + 1$.

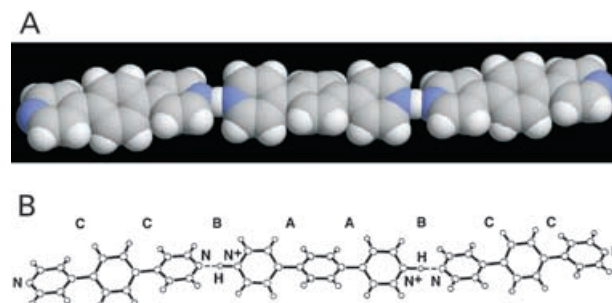


FIGURE 3 (a) Molecular tape structure of **6**. (b) Hydrogen-bonding pattern and the dihedral angles between the ring planes of **6**, where $N^+–H$ 1.20(5), $H···N$ 1.48(5), $N^+···N$ 2.680(3) Å, $N^+–H···H$ 178(4)°; dihedral angle A: 29.8(2), B2: 25.4(1), C: 32.1(2)°.

afford tape-like networks [16,17]. The dipyriddy molecule **2** is nearly planar as shown by the small dihedral angles [3.5(1)° and 7.6(1)°] between the pyridine and furan rings. Although one CA molecule is almost coplanar with **2** with a small dihedral angle of 5.9(2)°, another molecule is twisted with a dihedral angle of 47.5(2)°. The tape structures stack along the *b* axis, where the intertape distance is 3.27(1) Å.

Complex **6** has the composition (3)·(dication of 3)·(dianion of CA)·(H₂O)₆. X-ray structure analysis reveals the existence of a tape-like structure consisting of only **3** and a sheet-like structure consisting of CA and water molecules. The tape structure is formed by $N^+–H···N$ hydrogen bonding between neutral **3** and diprotonated **3** as shown in Fig. 3, where the $H···N$ and $N^+···N$ distances are 1.48(5) and 2.680(3) Å, respectively. The neutral and dication structures of **3** are nonplanar and the dihedral angles between the benzene ring and dipyriddy groups [29.8(2) and 32.1(2)°] are larger compared to the corresponding angles of **1** and **2** in complexes **4** and **5**. This is attributable to the larger steric interaction of the benzene ring. The hydrogen bond between the two pyridyl groups is almost linear with an angle of 178(4)°. Such a hydrogen-bonding tape-like network formed by neutral and dication molecules is the first example to the best of our knowledge. This type of hydrogen bonding is of interest from the viewpoint of proton transfer since a mixed protonated state seems to be easily achieved due to the small activation energy of proton transfer [28].

The planar sheet-like network formed by hydrogen bonds between the dianion of CA and water molecules is also observed (Fig. 4). The intermolecular O···O distances in the molecular sheet lie between the range of 2.714(3) to 2.981(3) Å. This type of unusual two-dimensional hydrogen-bonding network is also the first example in CA complexes. The molecular tape of **3** is stacked as neutral–dication–neutral to form a two-dimensional columnar structure as shown in Fig. 5a. The molecular sheet consisting of CA and water molecules is obliquely

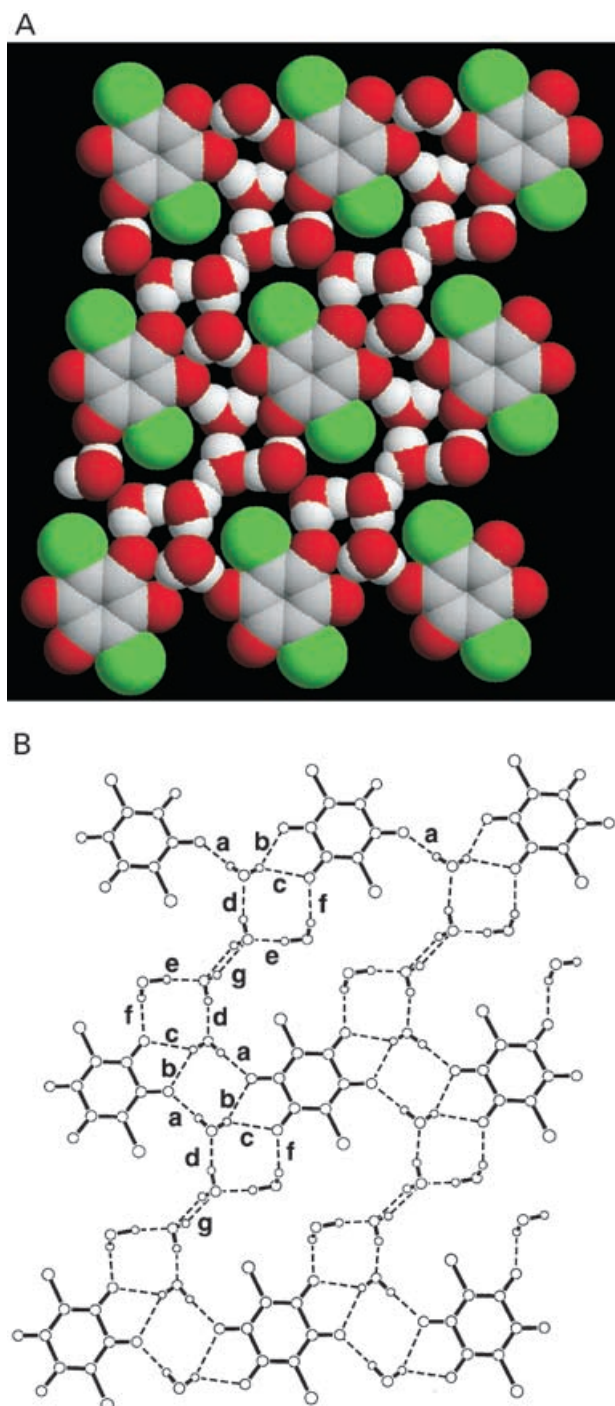


FIGURE 4 (a) Two-dimensional hydrogen-bonding sheet of CA and water molecules of **6**. (b) Intermolecular O \cdots O distances in the hydrogen-bonding sheet of **6**, where *a*: 2.831(3), *b*: 2.981(3), *c*: 2.894(3), *d*: 2.784(4), *e*: 2.734(4), *f*: 2.714(3), *g*: 2.748(6) Å.

located between the columns of **3** (Fig. 5b). The dihedral angles between the CA ring and the benzene ring are 82.5(2) $^\circ$ for dication **3** and 61.5(2) $^\circ$ for neutral **3**. The C–H \cdots π intermolecular interactions are also observed between the tapes of **3** and the sheets of CA. The C–H \cdots π distances between the least-squares planes of the CA dianions and the hydrogen and carbon atoms in the benzene

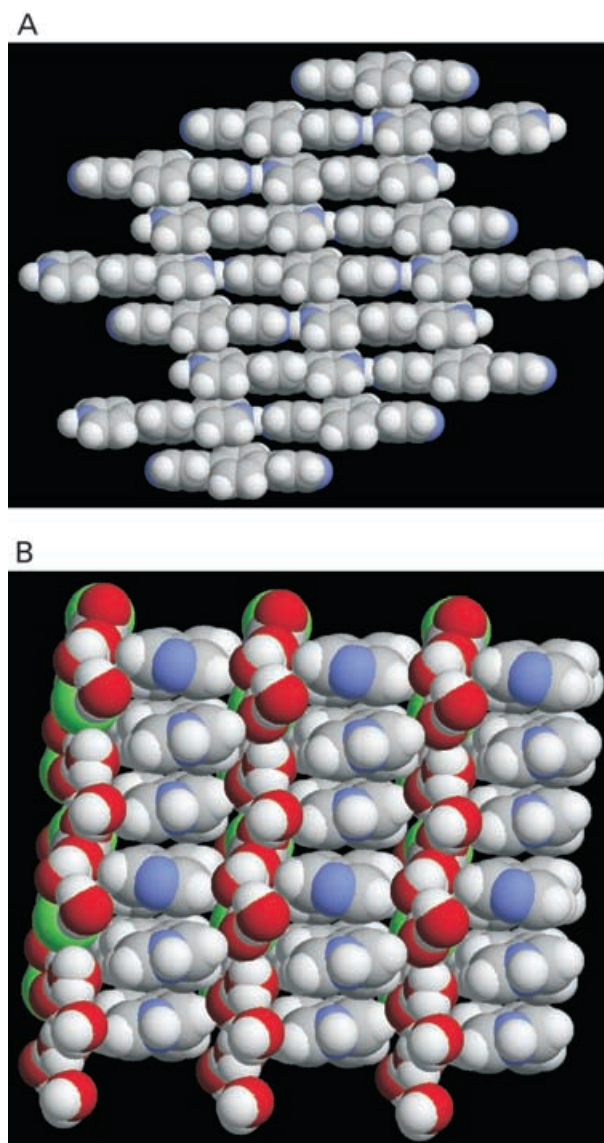


FIGURE 5 (a) Stacking of the molecular tape structure of **6**. (b) Crystal structure of **6**. The angles between the CA ring and the benzene ring of dication and neutral **3** are 82.5(2) $^\circ$ and 61.5(2) $^\circ$, respectively.

ring of neutral **3** are 2.73(2) (H \cdots π) and 3.44(1) (C \cdots π) Å.

CONCLUSION

We have found that unusual crystal structures can be constructed using π -extended dipyrindyl compounds with CA molecules. The crystal structures are strongly dependent on the spacer group. Although the details of the relationship between the crystal structures and the spacer group are still ambiguous, it should be noted that the structure of the complex of the twisted molecule **3** is completely different from those of the planar molecules **1** and **2**. We believe that more elaborate crystal engineering

would be possible by changing the spacer group and/or substituents on the anilic acid. Such work would be also important for exploring novel properties induced by proton and/or electron transfer.

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