Novel supramolecular synthon in crystal engineering: ionic complexes of 4,4′-bipyridine and 1,2-bis(2-pyridyl)ethylene with 2,5-dichloro-3,6-dihydroxy-1,4-benzoquinone

Md. Badruz Zaman,*[ab] Masaaki Tomura[b] and Yoshiro Yamashita*[b]

[a] *Department of Applied Chemistry and Chemical Technology, University of Dhaka, Dhaka 1000, Bangladesh. E-mail: zaman@ims.ac.jp*
[b] *Institute for Molecular Science, Okazaki 444-8585, Japan. E-mail: yoshiro@ims.ac.jp*

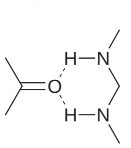
Received (in Cambridge, UK) 23rd March 1999, Accepted 26th April 1999

4,4′-Bipyridine (BPY) and 1,2-bis(2-pyridyl)ethylene (2-PDE) form bifurcated hydrogen bonds with 2,5-dichloro-3,6-dihydroxy-1,4-benzoquinone (chloranilic acid, 2H-CLA) to afford $[\text{BPY-2H}]^{2+}[\text{CLA}]^{2-}$ 1 and $[\text{2-PDE-2H}]^{2+}[\text{CLA}]^{2-}$ 2; their crystal structures exhibit a new type supramolecular synthon and links as molecular chains and zigzag tapes, respectively.

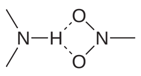
Supramoleculer synthons establish the conceptual relationship between crystal engineering and organic synthesis. Most recently, a variety of supramolecular synthons have been drawn by Desiraju[1,2] to identify the design elements for intermolecular interactions in solid. These supramolecular synthons have allowed structural chemists, organic/inorganic chemists and crystallographers to utilize the new concepts of supramolecular strategy, target identification, and synthetic methodology as parts of successful crystal engineering.

Since benzoquinone-type molecules with dihydroxy groups undergo multi-stage deprotonation and protonation processes, it is interesting to use such molecules to form characteristic intermolecular hydrogen-bonded networks.[3] On the other hand, bidentate bridging ligands are widely used with inorganic compounds to construct stable supramolecular complexes with well-designed geometries and strictly controlled self-assembly.[4] Therefore, we reasoned that by combining bipyridinium-type molecules with organic counterparts, supramolecular assemblies would be formed which exhibited intermolecular interactions. With this in mind we have used bipyridines and centrosymmetric dihalodihydroxybenzoquinones to form hydrogen-bonded networks. Thus a new type of supramolecular synthon **IV** has been exploited to understand noncovalent donor–acceptor (DA) interactions in the design of new supramolecular architectures.

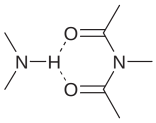
Although synthons affording three-center hydrogen bonds (**I** and **II**) have been well-documented as supramolecular patterns,[5,6] synthons involving two carbonyl groups are very rare. To the best of our knowledge, the only example of synthon **III** is a recent report with an amide structure,[2] and synthon **IV** is unknown. We now report the successful realization of our aim, with the synthesis and X-ray crystal structures of the complexes from diprotonated 4,4′-bipyridine ($[\text{BPY-2H}]^{2+}$) and 1,2-bis(2-pyridyl)ethylene ($[\text{2-PDE-2H}]^{2+}$) with a dianion of 2,5-dichloro-3,6-dihydroxy-1,4-benzoquinone (chloranilate, $[\text{CLA}]^{2-}$), both of which feature novel supramolecular synthon **IV**.



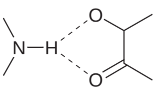
I



II



III



IV

The complexes† were prepared by reacting BPY and 2-PDE with an equal amount of chloranilic acid (2H-CLA) in acetone and/or a mixture of acetone–MeOH. The single crystals grew by the diffusion method over a period of two days. The crystal structures‡ reveal that molecular complexes $[\text{BPY-2H}]^{2+}[\text{CLA}]^{2-}$ **1** and $[\text{2-PDE-2H}]^{2+}[\text{CLA}]^{2-}$ **2** are formed where proton transfer takes place. The component molecules are combined *via* three-centre hydrogen bonded interactions to build a linear molecular chain or a zigzag molecular tape. The structural views of the molecular chain for **1** and the molecular tape for **2** are shown in Fig. 1 and 2, respectively.

In both **1** and **2**, bifurcated interionic $[\text{N}^+\text{–H}\cdots\text{O}^-$ and $\text{N}^+\text{–H}\cdots\text{O}]$ hydrogen bonds between the nitrogen atoms of the cations and the two oxygen atoms from the anion are observed. The different N···O (2.62–3.00 Å) distances§ are associated with strong and weak hydrogen bonding interactions.[5] The N···O distances are shorter than the mean distances observed for the hydrogen bonds between anilic acids and organic donors,[3,7] indicating the strength of the charged hydrogen bond interactions. The bond lengths in the anions, such as the double

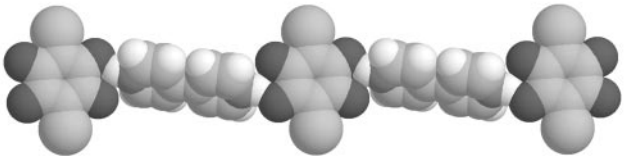


Fig. 1 View of the molecular chains of **1**.

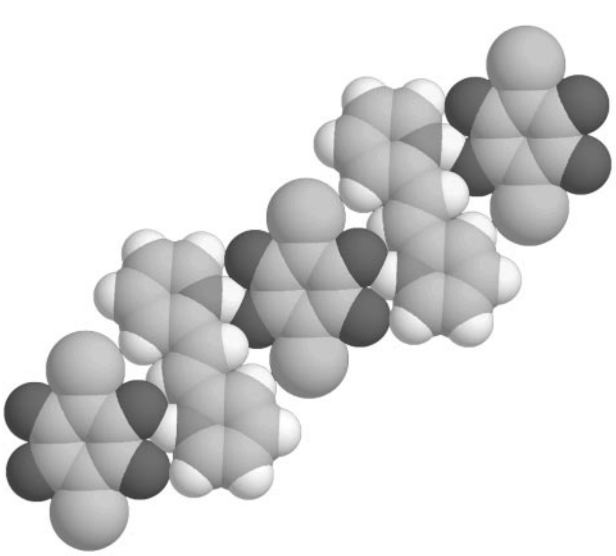


Fig. 2 View of the molecular tapes of **2**.

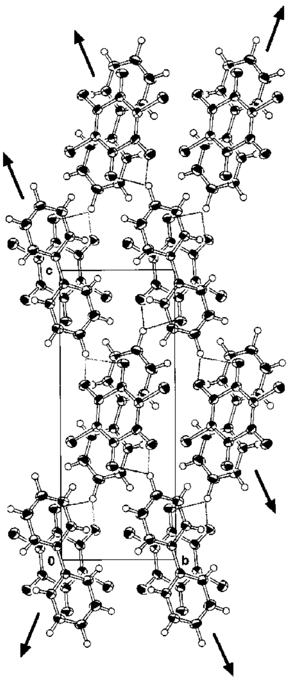


Fig. 3 Crystal packing of **1** viewed along the crystallographic *a* axis. This figure shows the cross-linked chains forming layers.

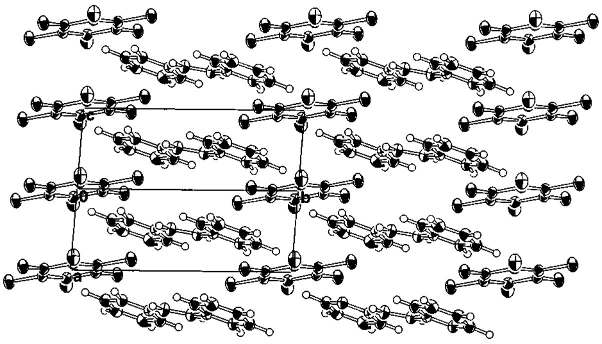


Fig. 4 Crystal packing of **2** viewed along the diagonal line of the *ac* plane. This shows the segregated stacking of the complex.

bonds (C=O, 1.235 Å for **1** and 1.238 Å for **2**) and the single bonds (C–O, 1.256 Å for **1** and 1.252 Å for **2**), are consistent with the molecular geometry of the chloranilate dianion.[7] The dihedral angles between the planes of the cations and anions are 65.8 and 23.6° for **1** and **2**, respectively.

In complex **1** one-dimensional molecular chains are observed toward the two cross diagonal lines within the *bc* plane. A view of such a two-directions cross-linked chain structure of complex **1** is shown in Fig. 3. Moreover, this structure reveals alternating DA-type pairs between the cation and anion molecules (the average distance and angle between the least-squares planes of the cation and anion are 3.42 Å and 3.8°) along the crystallographic *a* axis. Interestingly, complex **2** shows a segregated stacking assembly as DD- and AA-type pairs (Fig. 4), that is, no crossover association is observed in the tapes. The change of position of the nitrogen atoms in the ligands modifies the stacking arrangement though the supramolecular synthon pattern **IV** is unchanged. The *trans*-configuration of the linked ethylene group of the precursor 2-PDE seems to produce zigzag tape structure **2**.

This result not only describes a new supramolecular synthon motif but also highlights the molecules which will allow the design of further supramolecular architectures based on simple components. The present structures are the first examples; further studies in the field of crystal engineering will produce further enhancements, with the eventual creation of new supramolecular synthons and supramolecular architectures *via* investigation of geometrically and stoichiometrically matched donor and acceptor molecules.[8]

Notes and references

† *Selected data* for **1**: 98%, mp 228–230 °C (decomp.) (Calc. C, 47.90; H, 3.52; N, 6.98. Found: C, 47.30; H, 3.31; N, 6.86%). For **2**: 95%, mp 215–218 °C (decomp.) (Calc. C, 55.26; H, 3.09; N, 7.16. Found: C, 55.14; H, 2.84; N, 7.19%). Solid-state electronic spectra [22.9, 27.9, 36.4 × 10^3 cm^{-1} (for **1**) and 18.7, 30.3, 40.9 × 10^3 cm^{-1} (for **2**) are consistent with chloranilate dianions (ref. 9). The FT-IR spectra of **1** and **2** show similar broad bands around 2100 and 2600 cm^{-1} and an intense band around 3100 cm^{-1} (N$^+$H stretching vibration). This proves the intermolecular N$^+$–H···O$^-$ and N$^+$–H···O hydrogen bonded system.

‡ *Crystal data* for **1**: $C_{16}H_{10}Cl_2N_2O_4$, M = 365.16, monoclinic, space group $P2_1/n$, a = 8.2377(7), b = 5.965(6), c = 15.089 (1) Å, β = 94.986(8)°, V = 738.7(1) Å^3, Z = 2, T = 293 K, μ(Cu-Kα) = 52.11 cm^{-1}, R_1 = 0.0366 and wR_2 = 0.0932 for 1265 data with $I > 2\sigma(I)$. For **2**: $C_{18}H_{12}Cl_2N_2O_4$, M = 391.21, triclinic, space group $P\bar{1}$, a = 9.855(1), b = 11.245(1), c = 3.9057(6) Å, α = 91.34(1)°, β = 99.69(1)°, γ = 111.702(8)°, V = 394.7(1) Å^3, Z = 1, T = 293 K, μ(Mo-Kα) = 4.40 cm^{-1}, R_1 = 0.033 and wR_2 = 0.034 for 1258 data with $I > 3\sigma(I)$. Non-hydrogen atoms were refined anisotopically and all hydrogen atoms were clearly localized in the Fourier maps and refined isotropically. CCDC 182/1235. See http://www.rsc.org/suppdata/cc/1999/999/ for crystallographic files in .cif format.

§ Intermolecular hydrogen bonds: for **1**: N$^+$···O$^-$, 2.63 Å; N$^+$H···O$^-$, 1.74 Å; N$^+$···O, 3.00 Å; N$^+$H···O, 2.26 Å; for**2**: N$^+$···O$^-$, 2.62 Å; N$^+$H···O$^-$, 1.73 Å; N$^+$···O, 3.00 Å; N$^+$H···O, 2.33 Å.

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Communication 9/02305D