

One-dimensional supramolecular tapes in the co-crystals of 2,5-dibromo-3,6-dihydroxy-1,4-benzoquinone (bromanilic acid) with heterocyclic compounds containing a pyrazine ring unit

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Supramolecular synthons formed with 2,5-dibromo-3,6-dihydroxy-1,4-benzoquinone (bromanilic acid) and heterocyclic aromatic compounds, phenazine, quinoxaline and pyrazine were successfully used in the design of robust one-dimensional supramolecular tapes.

The design of new molecular architectures for crystal engineering has generated great interest in recent years.^{1–4} In particular, supramolecular patterns based on the tapes, ribbons and sheets, which are formed with hydrogen bonding, are very important for crystal engineering and materials science.⁵ For the purpose of designing crystal structures and controlling molecular aggregations, Desiraju has proposed the term *supramolecular synthons*, which act as "building blocks" in crystal engineering.⁶ A large number of the synthons identified so far involve directional intermolecular interactions such as hydrogen bonding, C–H...O,⁷ C–H...π,⁸ N...Cl⁹ and S...N¹⁰ interactions. We have recently reported the novel supramolecular synthon formed with 2,5-dichloro-3,6-dihydroxy-1,4-benzoquinone (chloranilic acid) and 4,4'-bipyridine¹¹ or dipyritylacetylenes,¹² and have shown the utility of this robust and reproducible synthon for constructing one-dimensional supramolecular tapes. Moreover, benzoquinone derivatives with two hydroxy groups show both electron accepting and proton donating properties and undergo multi-stage protonation and deprotonation processes.¹³ Our ultimate goal is to control electron transfer between donor and acceptor molecules¹⁴ in a crystal through thermodynamic transformation¹⁵ of hydrogen bonds. With this in mind we have now carried out co-crystallization of 2,5-dibromo-3,6-dihydroxy-1,4-benzoquinone **1** (bromanilic acid) with heterocyclic aromatic compounds phenazine **2**,¹⁶ quinoxaline **3** and pyrazine **4**. We report here the crystal structures involving the one-dimensional tape patterns of the three co-crystals.

The 1 : 1 co-crystals **5**, **6** and **7** were isolated from an acetonitrile solution of **1** with **2**, **3** and **4**, respectively. Single crystals suitable for X-ray analysis were grown at room temperature by a diffusion method using an H-tube. The X-ray crystallographic analyses for **5**, **6** and **7** were carried out, and the crystal data and details of measurements are summarized in Table 1. Co-crystals **5**, **6** and **7** basically have the same structural pattern, that is, the one-dimensional supramolecular tapes are generated *via* the self-assembly of two molecules

through hydrogen bonding, and the segregated stacks of each molecule are formed. Fig. 1, 2 and 3 show the structures of the one-dimensional tapes in **5**, **6** and **7** with geometrical parameters for the tapes, respectively.

Table 1 Crystal data and details of measurements^a for co-crystals **5**, **6** and **7**^b

Property	5	6	7
Formula	C ₁₈ H ₁₀ Br ₂ N ₂ O ₄	C ₁₄ H ₈ Br ₂ N ₂ O ₄	C ₁₀ H ₆ Br ₂ N ₂ O ₄
<i>M</i>	478.1	428.04	377.99
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>m</i>	<i>C</i> 2/ <i>m</i>
<i>a</i> /Å	12.419(7)	7.951(2)	8.502(1)
<i>b</i> /Å	3.9288(4)	22.853(4)	6.890(2)
<i>c</i> /Å	17.469(5)	3.913(1)	10.858(2)
β /°	107.87(4)	90.69(2)	100.80(1)
<i>V</i> /Å ³	811.2(5)	711.0(3)	624.8(2)
<i>Z</i>	2	2	2
<i>T</i> /K	296(2)	296(2)	296(2)
μ (Mo-K α)/mm ^{–1}	5.025	5.721	6.494
Measured reflections	1481	1782	1729
Unique reflections	1389	1674	623
<i>R</i> ₁ [<i>F</i> , <i>I</i> > 0.0308]	0.0308	0.0556	0.0743
<i>wR</i> ₂ [<i>F</i> ² , <i>I</i> > 0.0742]	0.0742	0.1384	0.1828

^a The data for **5** and **7** were measured on a Rigaku R-Axis IV imaging plate area detector using Mo-K α radiation (λ = 0.71070 Å). An absorption correction was not applied. The data for **6** were collected on a Rigaku AFC-7R diffractometer using Mo-K α radiation (λ = 0.71070 Å). Absorption correction was applied using empirical procedures based on azimuthal ψ scans of three reflections having an Eulerian angle, χ , near 90°. ^b All structures were solved by direct methods and refined by full-matrix least-squares on *F*² with SHELX97.¹⁹ All non-hydrogen atoms were refined anisotropically. Hydrogen atoms of **5** and **6** were localized in the Fourier maps and refined isotropically. Hydrogen atoms of **7** were placed geometrically and refined by using a riding model. Click [here](#) for full crystallographic data (CCDC no. 1350/23).

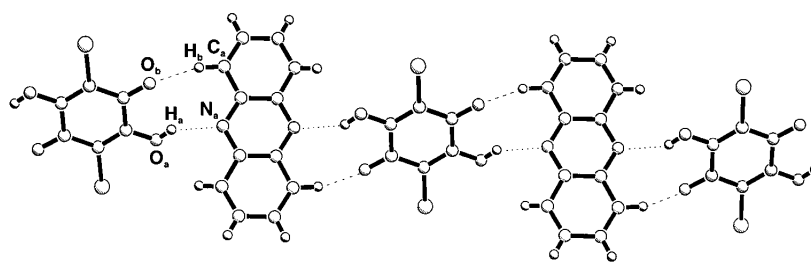


Fig. 1 One-dimensional tape in co-crystal **5**. Hydrogen bonding parameters are (in Å): N_a-H_a 2.04, N_a-O_a 2.75, N_a-O_b 3.43, O_b-H_b 2.51, O_b-C_a 3.33. The dihedral angle between the least-squares planes for **1** and **2** is 43.9° .

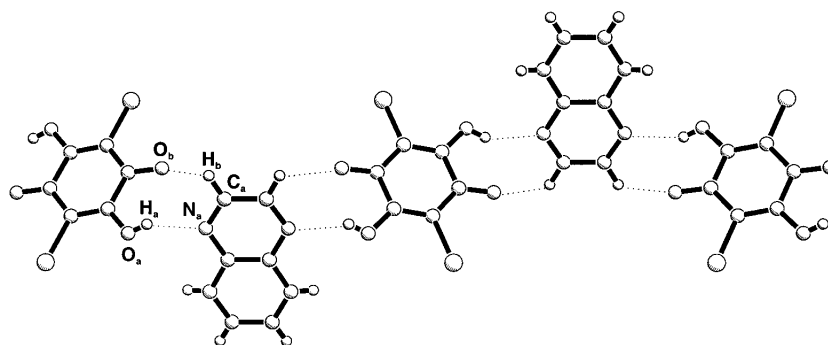


Fig. 2 One-dimensional tape in co-crystal **6**. Hydrogen bonding parameters are (in Å): N_a-H_a 2.05, N_a-O_a 2.70, N_a-O_b 2.98, O_b-H_b 2.80, O_b-C_a 3.14. The dihedral angle between the least-squares planes for **1** and **3** is 49.7° .

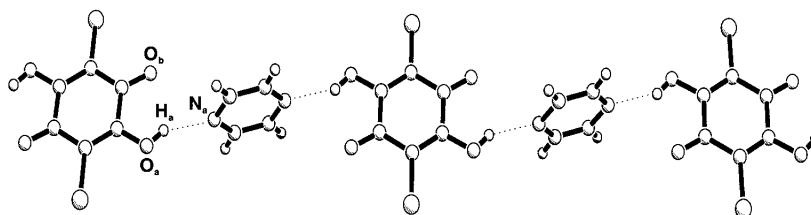


Fig. 3 One-dimensional tape in co-crystal **7**. Hydrogen bonding parameters are (in Å): N_a-H_a 1.96, N_a-O_a 2.69, N_a-O_b 3.09. The dihedral angle between the least-squares planes for **1** and **4** is 90° .

A significant difference in the distances of the $O-H\cdots N$ hydrogen bonds of the one-dimensional tapes is not observed, while the dihedral angle between the least-squares planes for **1** and **4** in co-crystal **7** differs considerably from those for others. The planes for **1** and **4** lie on the mirror plane and are perpendicular to each other. In the case of the tapes in **5** and **6**, the $C-H\cdots O$ interactions^{7,16} are found between the carbonyl groups of **1** and the aromatic hydrogens in the benzo parts of **2** and **3**. The $C-H\cdots O$ interactions may reduce the dihedral angle within the tape structure. The symmetry of the heterocyclic compounds also affects the structure of the tapes. Only **3** is not symmetrical about the $N-N$ axis in the molecule. Thus, the tape formed from **1** and **3** in co-crystal **6** does not have a straight structure but a zigzag one. For the co-crystals **5**, **6** and **7**, no proton transfer from **1** to the nitrogen atoms of heterocyclic compounds is observed.[‡]

The crystal structures of **5**, **6** and **7** are shown in Fig. 4, 5 and 6, respectively. The segregated unistacks of each molecule are observed in the co-crystals **5** and **6**. This packing motif is essentially the same as those previously obtained from the co-crystals of chloranilic acid with 1,2-bis(2-pyridyl)ethylene¹¹ or 2,2'-

dipyridylacetylene.¹² This fact suggests that there is a "structure-preserving" ability of the supramolecular synthon formed from anilic acids. Moreover, this type of segregated columnar structure is very important for organic conducting materials such as the tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ) charge transfer complex.¹⁷ The interstack distances are 3.45 Å for **1** and **2** in **5**, and 3.42 and 3.64 Å for **1** and **3** in **6**, respectively. In the co-crystals **5** and **6**, the intertape $Br\cdots Br$ contacts¹⁸ are also observed (3.59 Å for **5**, 3.73 Å for **6**) to be shorter than the sum of the van der Waals radii (3.90 Å). The co-crystal **7** crystallizes in the monoclinic space group $C2/m$. Each molecule **1** and **4** is stacked in a two-dimensional fashion and forms layers which are perpendicular to each other (Fig. 6). Within the layers, the minimum distances between the least-squares planes for the molecules are 3.45 and 4.08 Å for **1** and **4**, respectively.

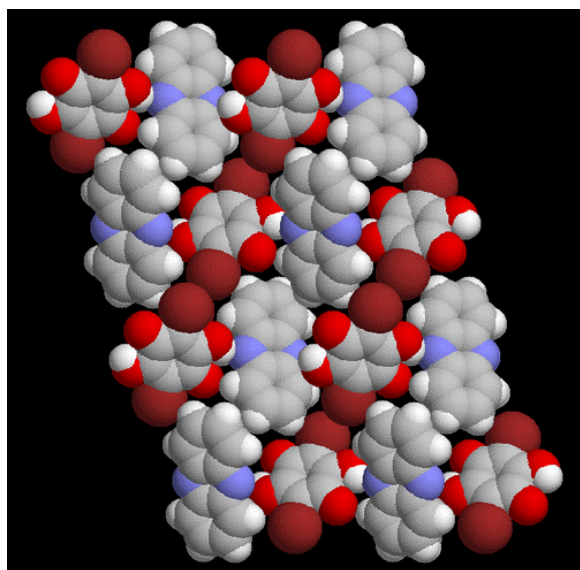


Fig. 4 Crystal structure of **5** viewed along the *b* axis.

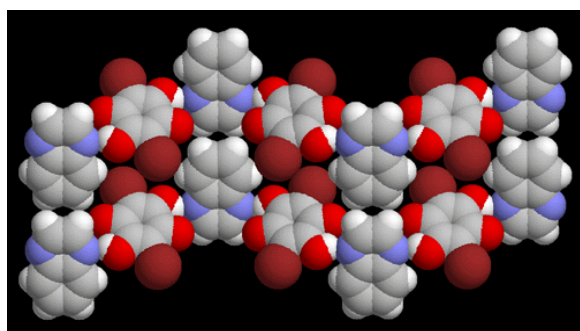


Fig. 5 Crystal structure of **6** viewed along the *c* axis.

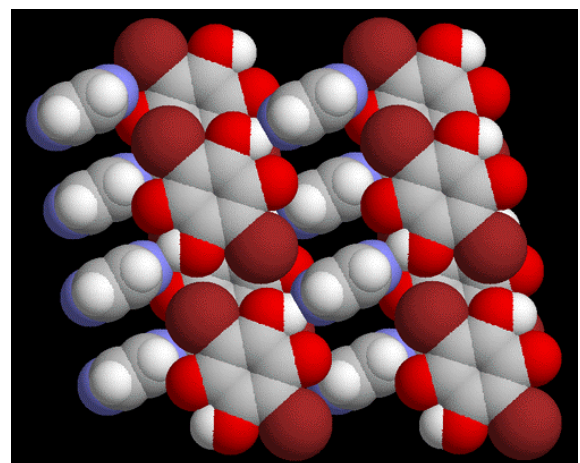


Fig. 6 Crystal structure of **7** viewed along the *b* axis.

The above results suggest that the supramolecular synthon formed with anilic acids and heterocyclic compounds can yield the robust one-dimensional supramolecular tapes and realize preserved interesting crystal structures. Studies on the characterization of physical properties of the co-crystals **5**, **6** and **7** and the construction of new molecular architectures using the supramolecular synthon described here are now in progress.

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Footnotes

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‡ The calculations of the Löwdin atomic charge (6-31G**/3-21G) for each nitrogen atom using the GAMESS program²⁰ (**2**–0.1535, **3**–0.1489, **4**–0.1508, 4,4'-bipyridine –0.1893, 2,2'-dipyridylacetylene –0.1768, 3,3'-dipyridylacetylene –0.1879, 4,4'-dipyridylacetylene –0.1871) support the experimental results on proton transfer.

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