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Zurina Shaameri [a] & William Jones [a]

[a] University of Cambridge, Department of Chemistry, Lensfield Road, Cambridge, CB2 1EW, U.K.

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Molecular Complexes between 2,2'-Biphenyl Dicarboxylic Acid and Phenazine: Anhydrous and Hydrated Forms

ZURINA SHAAMERI and WILLIAM JONES

University of Cambridge, Department of Chemistry, Lensfield Road, Cambridge, CB2 1EW, U.K.

The formation of co-crystals of 2,2'-biphenyl dicarboxylic acid and phenazine is reported. By utilizing different solvents during the crystal preparation, two types of co-crystals, i.e. anhydrous and hydrated, were observed to form. The conformation of the component molecules and the packing arrangement within each co-crystal are described and discussed. In both co-crystals, the generation of a cyclic motif involving one weak (C-H...O) and one strong (O-H...N) hydrogen bonds are observed. Hydrogen bond geometries of the two types of interactions in the cyclic motif for both complexes are reported and discussed.

Keywords: Hydrogen bonding; Coupling; Synthon; Co-crystals; Crystal engineering

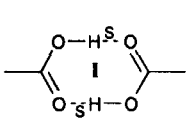
INTRODUCTION

Intermolecular forces, especially hydrogen bonds, are known to play an important role in controlling intermolecular orientation and packing within organic crystals.[1-5] Adjacent molecules in crystal structures are frequently held together by well-defined spatial

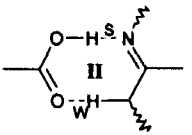
arrangements of intermolecular interactions defined as a synthon,[4] or coupling.[5,6]. A common form of spatial arrangement is the cyclic motif (synthon I). In particular a cyclic coupling unit involving both weak (C-H•••O) and strong (O-H•••N) hydrogen bonds, which will be referred to as synthon II, has been recognised as a crystal engineering tool.[6]

Co-crystal formation of phenazine with various carboxylic acids has been discussed earlier.[6,7] Various packing arrangements were developed including linear and crinkled tapes. In all cases the supramolecular structure of the co-crystal was dependent on the geometry (e.g. *cis* or *trans*) of the dicarboxylic acid. The structure of the individual molecules is also significant.

In this paper, we report on the formation of co-crystals of phenazine with 2,2'-biphenyl dicarboxylic acid. This biphenyl acid was chosen to introduce some possible flexibility via rotation around the phenyl-phenyl bond of the acid molecules in crystal packing. This is in contrast to the work of Batchelor *et al*[7] where cis-trans olefinic dicarboxylic acids were used. Two types of co-crystals are observed : an anhydrous form and a hydrated form.



Synthon I



Synthon II

EXPERIMENTAL

Preparation of co-crystals

Co-crystals of the anhydrous complex **1** were prepared by dissolving equimolar amounts of 2,2'-biphenyl dicarboxylic acid and phenazine in ethyl acetate. Similarly, co-crystals of the hydrated complex **2** were prepared by dissolving equimolar amounts of the acid and the base in diethyl ether. The solutions were then left undisturbed in small vials at room temperature to evaporate slowly. The vials containing these solutions were covered by paraffin films with pin holes to control the rate of evaporation and exclude dust particles.

Crystal structure determinations

Single crystals of **1** and **2** were obtained as light yellow needles and deep yellow cubes, respectively. The crystal used for the diffraction studies was 0.35 x 0.30 x 0.15 mm for **1** and 0.40 x 0.35 x 0.25 mm for **2**.

Preliminary examinations and data collections were performed with an Enraf-Nonius CAD-4[8] four-cricle diffractometer with graphite monochromated Mo K_α radiation (λ = 0.71069 Å). All data was collected at room temperature and an $\omega/2\theta$ scan type was used with variable scan speed. 25 high-angle intense reflections were selected from the full data set collected between a θ range of 1.5 to 25 degrees. The final high-angle cell parameters were obtained by least squares refinement. The software TEXSAN[9] was used to process the data from the CAD-4 and all data were corrected for Lorentz and polarisation

Table 1 Crystallographic data of complexes **1** and **2**.

	1	**2**
Chemical formula	$C_{21.5}H_{16}NO_6$	$C_{20}H_{16}NO_5$
Formula weight	384.35	350.34
Crystal system	Triclinic	Monoclinic
Space group	P-1	$P2_1/c$
a / Å	5.7365(9)	10.3140(10)
b / Å	9.7650(10)	13.1870(9)
c / Å	19.054(3)	13.056(2)
α (°)	83.150(10)	90
β (°)	82.210(10)	93.560(10)
γ (°)	75.420(10)	90
V / Å^3	1019.4(2)	1772.3(3)
Z	2	4
D_c / gcm^{-3}	1.252	1.313
μ(Mo-K_α) / mm^{-1}	0.093	0.095
F(000)	400	732
θ range (°)	2.16 to 24.94	1.98 to 24.95
h	-6 to 6	0 to 12
k	-11 to 11	0 to 15
l	0 to 22	-15 to 15
Reflections collected	3922	3282
Independent reflections	3569	3101
R_{int}	0.0177	0.0245
R_1	0.0426	0.0513
wR_2	0.0985	0.1171
Goodness of fit on F^2	1.016	1.018

effects. The centrosymmetric space groups of **1** (P-1) and **2** ($P2_1/c$) were determined from systematic absences in the intensity data. The crystal structures were solved using direct methods from SHELXS86[10] and were then refined using SHELXL93.[11]

Non-hydrogen atoms were located from electron density maps and refined with anisotropic thermal parameters. Hydrogen atoms on the acid groups were located from difference Fourier maps and refined isotropically. Hydrogen atoms on the phenyl groups were fixed geometrically and refined using the riding model. Crystallographic data for both complexes in this study are given in Table 1.

RESULTS AND DISCUSSION

Complex 1

Complex **1** crystallises in the triclinic crystal system. An extended molecular tape of 2,2'-biphenyl dicarboxylic acid and phenazine in a 1:1 stoichimetry is generated via the synthon I (Figure 1(a)). As expected the tape is crinkled as a result of the phenyl rings of the acid not being co-planar (torsion angle -99.1° compared to -106.3° and -119.3°.angles (two molecules in the asymmetric unit) reported by Fronczek *et al.* for the pure acid.[12]

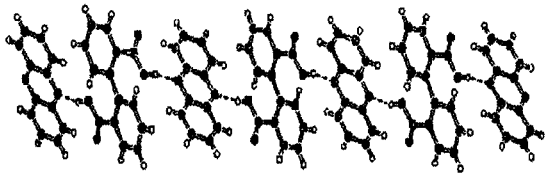


Figure 1(a) Anhydrous complex **1** of 2,2'-biphenyl dicarboxylic acid and phenazine: View from above the tape.

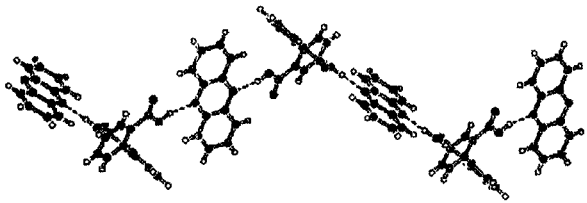


Figure 1(b) Anhydrous complex **1**: View from the side of the tape.

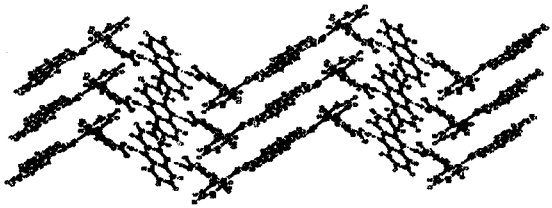
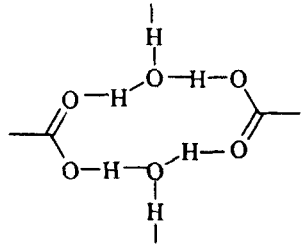


Figure 1(c) Stacking of tapes in complex **1**.

It is also observed that the tapes are stacked via π-π interactions of the phenazine molecules. Hydrogen bond geometries for the O-H...N interactions in the tape are shown in Table 2 and for C-H...O in Table 3.

Complex **2**

In **2** water molecules form O-H...O hydrogen bonds with the dicarboxylic acid molecule (Figure 2(a)) to produce one-dimensional tapes via synthon III. Phenazine molecules then hold the chains together by coupling with the acids from adjacent chains via synthon II (Figure 2(b)). This combination leads to the formation of a two-dimensional network as shown in Figure 2(c)). The acid in **2** has a similar torsion angle, i.e. -100.2° to that in complex **1**



Synthon III

Hydrogen bond geometries for the O-H...N and C-H...O type interactions between the acid and the phenazine in **2** are shown in Table 2 and Table 3, respectively.

Table 2 Distances and angles for the O-H•••N interaction.

Complex	O-H / Å	H•••N / Å	O•••N / Å	O-H•••N
1	1.125	1.661	2.761	164.4°
2	0.959	1.786	2.727	166.0°

Table 3 Distances and angles for the C-H•••O interaction.

Complex	C-H / Å	H•••O / Å	C•••O / Å	C-H•••O
1	0.930	2.644	3.508	154.7°
2	0.930	2.521	3.405	159.0°

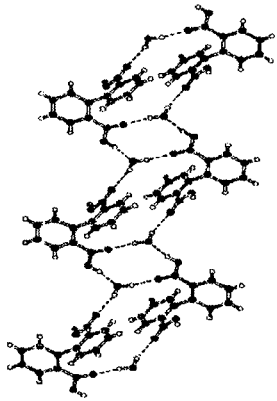


Figure 2(a) Hydrated complex of 2,2'-biphenyl dicarboxylic acid and phenazine (**2**): Acid-water chain showing synthon III.

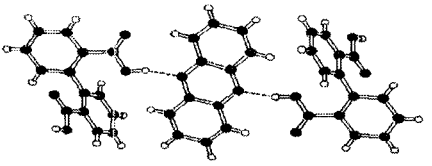


Figure 2(b) Complex **2**: Acid-base trimer via synthon II.

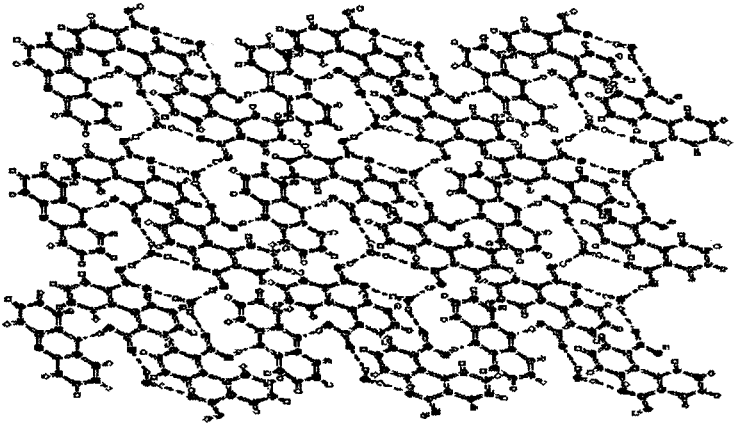


Figure 2(c) Complex **2**: View from above the corrugated sheet structure.

Synthon II in complexes 1 and 2

The H•••N and O•••N bond lengths for the O-H•••N interaction in synthon II for **1** and **2** are in agreement with expected values (i.e. between 1.5 to 2.2 Å for H...N and close to 2.8 Å for O...N. The H•••O

and C•••O distances for the C-H•••O interaction in **1** and **2** also lie within the range expected for a weak hydrogen bond. The H•••O distance of 2.644 Å in **1** and 2.521 Å in **2** fall within the proposed ranges of 2.2 to 3.2 Å. The C•••O distances of 3.508 Å and 3.405 Å in **1** and **2**, respectively, also fall within the ranges of 3.2 to 4.0 Å expected for a weak hydrogen bond. Bond angles involved in synthon II in both complexes lie within the range of 160° ± 20° expected for a normal/weak hydrogen bond.

CONCLUSIONS

2,2'-biphenyl dicarboxylic acid and phenazine can successfully generate molecular complexes through molecular recognition involving a weak (C-H•••O) and strong (O-H•••N) cyclic hydrogen bond motif.

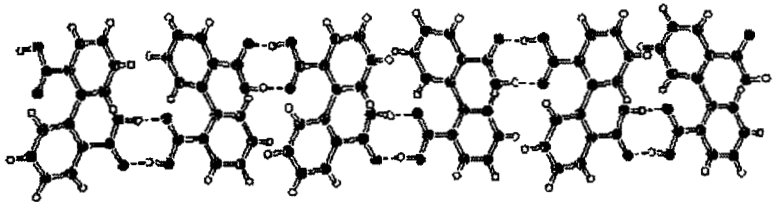


Figure 4(a) Packing of 2,2'-biphenyl dicarboxylic acid: view from above the tape.

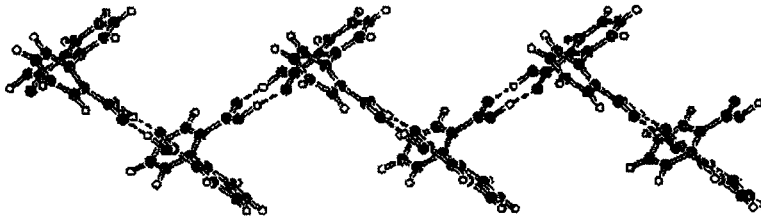


Figure 4(b) Acid crystals of 2,2'-biphenyl dicarboxylic acid : View from the side of the tape.

Two forms of complexes were produced. Diethyl ether as solvent resulted in the crystallization of a hydrated complex (co-crystallisation under argon/nitrogen gas from dry ether produced the anhydrous complex.) The inclusion of water in an organic crystal structures is not an uncommon occurrence, being closely linked to the optimisation of hydrogen bonding patterns.[1,2]

It is interesting to compare the one-dimensional tape in **1** with that of the pure acid that has a similar tape structure[12] – see Figure 4(a) and (b). The stacking arrangement of the tape in **1** is also similar to that in the pure acid, particularly in the herringbone arrangement of the acid molecules. The similar torsion angles of the biphenyl group that are observed in **1** and **2** are different to that found in the pure acid. This confirms that it is possible for the acid to twist around the phenyl-phenyl bond to optimise crystal packing.

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