

# A unique co-crystallisation motif for bis(4-pyridyl)acetylene involving S<sup>⋯</sup>spC interactions with a fused 1,3-dithiole ring.

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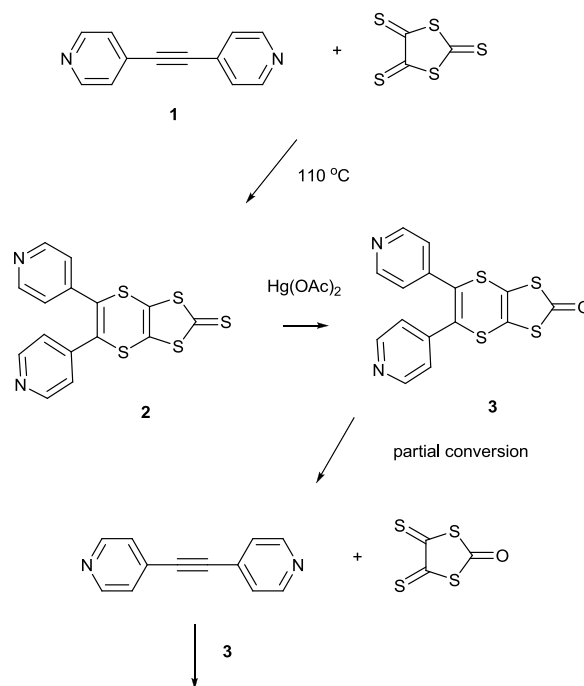
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The crystal structure of a novel 1:2 co-crystal formed from bis(4-pyridyl)acetylene and the oxo compound 5,6-bis(pyrid-4'-yl)-1,3-dithiol[4,5-b]1,4-dithiin-2-one is described. The alkyne and pairs of the oxo compound alternate along stacks in the crystal with remarkably short contacts (< 3.3 Å) to the alkyne from S and C atoms of the oxo compound. The structure is further stabilised by  $\pi$ - $\pi$  stacking of pyridine rings and weak hydrogen bonding.

The study of co-crystals, crystals that consist of two or more molecular components, is an important aspect of crystal engineering with applications in the generation of novel NLO materials,<sup>1</sup> solvent-free organic synthesis,<sup>2</sup> photographic films<sup>3</sup> and formulation of active pharmaceutical ingredients.<sup>4</sup> The key factor for the formation of co-crystals are specific intermolecular interactions that stabilize the two component solid versus the separate crystalline pure compounds. In the large majority of cases this heteromolecular interaction is achieved by the formation of hydrogen bonds between complementary molecular units. In this paper we report an interesting and unusual case of the formation of a co-crystal promoted in particular by the interaction between a conjugated bis(4-pyridyl)  $\pi$ -system and the sulfur atoms of a  $\pi$ -conjugated organosulfur system.

Bis(4-pyridyl)acetylene (bpa) **1** is a compound suitable for the construction of supramolecular structures through formation of hydrogen bonds or by coordination to metal ions, since it has pyridine nitrogen atoms at the ends of a linear and rigid molecule with extended  $\pi$ -conjugation. The crystal structure of pure bpa has not been reported, since its crystals, despite a good appearance, are poorly diffracting. However, the Cambridge Structural Database (CSD) contains 29 structures containing bpa, of which twenty are metal complexes and nine are 1:1 co-crystals with hydrogen bonding between components.<sup>5</sup> As in other bis(pyridyl) systems, bpa usually forms 1D or 2D grid networks associated by H-bonds of the type O-H $\cdots$ N or N-H $\cdots$ N e.g with phthalic acid,<sup>6</sup> 3-aminophenol<sup>7</sup> or in the inclusion compound with 1,3,5-tris(diisopropylhydroxysilyl)benzene.<sup>8</sup> During the synthesis of pyridine functionalised (vinylenedithio)-TTF type donors from bpa we found that bpa forms a 1:2 co-crystal, **4**, with the intermediate oxo compound product **3** (Scheme 1).<sup>9</sup> Thus, bpa is converted to the bicyclic thione **2** by a hetero Diels-Alder reaction with 1,3-dithiole-2,4,5-trithione, and **2** is then converted to oxo compound **3** using mercuric acetate and the product purified by chromatography. However, co-crystals **4** were formed by slow



**4**: 1:2 corcrystal of **1** and **3**.

Scheme 1: Structure diagrams for 1-4.

evaporation of an ethyl acetate solution of a fraction of the oxo compound **3** over a period of several days. Some of the oxo compound has presumably undergone a retro-Diels-Alder reaction to produce the bpa and 2-oxo-1,3-dithiole-4,5-dithione, or alternatively a small quantity of **1** has remained unseparated from the start of the synthesis. Pure oxo compound **3** could only be characterised as a fine powder, so no single crystal diffraction measurement was possible. The crystal structure of **4**, the 1:2 co-crystal of **1** and **3**, was measured by X-ray diffraction at 150(2) K.

The crystal structure of **4** is dominated by several intermolecular interactions and short contacts (Tables 1-2). Among them the most prominent are the ones between the alkyne group of bpa and sulfur atoms from **3**. The complex crystallizes in the monoclinic space group C2/c, and the asymmetric unit consists of one molecule of oxo compound **3** and half a molecule of bpa **1**, with the bpa molecule lying across a centre of symmetry. The ORTEP plot with the atom numbering is shown in Figure 1. The bpa molecule is planar

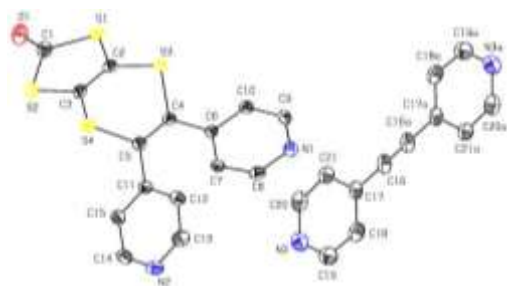


Figure 1: ORTEP diagram of the components of the molecular complex **4** with atomic displacement parameters drawn at the 40% probability level and the atomic numbering scheme. H atoms are omitted for clarity.

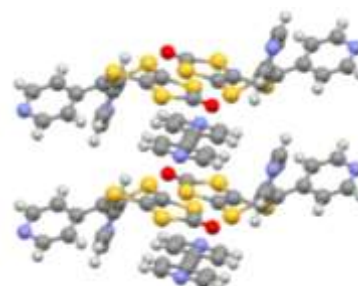


Figure 3: Side view of the stacking of pairs of **3** and bpa along the *b* axis.

(r.m.s. deviation of fitted atoms: 0.015 Å), the lengths of the exocyclic C≡C and C–C bonds (1.198(4) and 1.434(3) Å) are typical for a biarylalkyne<sup>10</sup> and the bond angle at nitrogen (116.0(2)°) is typical of an unprotonated pyridine. In the oxo compound **3**, the five-membered dithiole ring and its two attached sulfur atoms, comprising atoms O(1), C(1), S(2), S(3), C(2), C(3), S(4) and S(5), are essentially planar (r.m.s deviation of fitted atoms: 0.043 Å). However the dithiin ring shows a flexing about the S–S vector of 129.5(1)°. The planes of the two pyridyl substituents lie at 66.4(1)° to each other, and at 84.8(1)° and 35.9(1)° to the plane of the dithiole ring, so that the former lies roughly perpendicular to the dithiole ring and the latter extends out. The bond lengths and angles in the oxo compound are similar to those reported for the corresponding thione **2**,<sup>9</sup> except that the two C–S bonds to the carbonyl carbon are significantly longer than the corresponding bonds to the thione carbon (1.775(2) & 1.789(2) Å, *cf.* 1.737(232) & 1.737(2) Å). Selected bond distances and bond angles are given in Tables S1 and S2 respectively.

The crystal structure of **4** is formed of mixed stacks along the *b* axis composed of centrosymmetrically related molecules of **3** lying side by side and alternating with a molecule of bpa (Figures 2-3). The centres of symmetry between the molecules of **3** and the centre of the molecule of bpa lie on the same axis parallel to *b*. The distance between consecutive molecules of bpa or dimers of **3** along the stack corresponds to a unit cell translation. Between the pair of

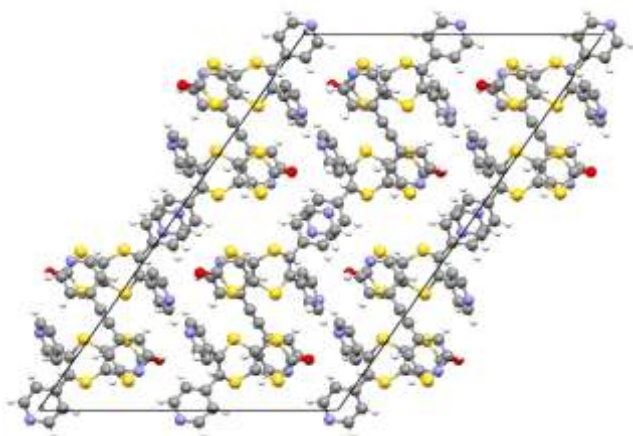


Figure 2: Crystal packing of **4** viewed along the *b* axis.

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molecules of **3** there are two S(dithiole)⋯C(pyridine) contacts of 3.524(3) Å and the closest S⋯S contact is 3.8333(9) Å between dithiole and dithiin S atoms. Molecules of bpa lie across the pair of molecules of **3** so that each half of the molecule lies over a dithiole ring (Figure 4a). Thus, each bpa is sandwiched between two pairs of dithiole rings. One member of each pair lies closer to the bpa than the other, and these two particular dithioles are related by the centre of symmetry at the centre of the bpa molecule. The centroid of the bpa's pyridine ring lie 3.622 and 3.842 Å from the centroids of the dithiole rings of **3** directly above and below. The average planes of the bpa and dithiole rings lie at 9.37(7)°. There are remarkably short C⋯S and C⋯C interactions, in the range 3.269(2)–3.49(2) Å and 3.283(3)–3.395(3) Å respectively, between bpa and atoms lying along one edge of two molecules of **3** (Figure 4b). Thus, the dithiin S atom, S(3), makes contacts of 3.269(2) and 3.452(2) Å with the two alkyne C atoms (C(16) & C(16')) and the dithiole S atom, S(1), makes a contact of 3.495(2) Å with an alkyne C atom, so that the *sp*<sup>2</sup> C atom C(2) connecting these two S atoms lies just 3.283(3) Å from this alkyne C atom. This dithiole C atom and its bonded neighbour, C atom C(3), are also involved in short contacts with the *ipso* and an *ortho* C atoms, C(17) and C(18), of the pyridine ring of bpa (3.395(3) and 3.383(3) Å respectively).

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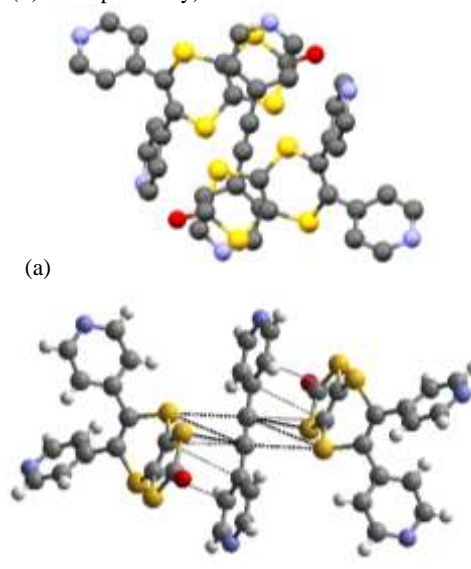


Figure 4: Interactions between bpa and the two closer molecules of **3**, showing (a) the overlap of pyridine rings of bpa with the dithiole rings of **3** and (b) shortest contacts (S⋯C, black; C⋯C, grey).

Nyburg and Faerman have demonstrated that the bonded sulfide S atom has an asymmetric shape with a van der Waals radius of *ca* 1.6 Å in the plane of the sulfide group, but *ca* 2.0 Å perpendicular to this plane.<sup>11</sup> It can be noted that for the shortest S---C contact to the alkyne (3.269 Å), that from dithiin sulfur atom S3, the vector between the two interacting atoms lies at 71.3° to the normal to the plane of the sulfide group (defined by C2, S3 and C4) so lies not far out of the sulfide plane. In contrast the only S---C(alkyne) contact from dithiole sulfur atom S1 (3.495 Å), the vector between the interacting atoms, lies at 25.7° to the normal to the corresponding sulfide plane (C1,S1 C2) so much closer to being perpendicular to that plane... Nevertheless, both contact distances are within the corresponding sums of the van der Waals radii of the atoms involved, as is the C...C interaction with the alkyne.

Thus, within a stack the alkyne group of bpa interacts with just two of the four neighbouring molecules of **3**, one above and one below. The other two molecules of **3** however are involved in a rather long  $\pi(\text{C})\cdots\text{H}$  contact with bpa, involving the C(7) carbon atom of a pyridine ring of **3** with the H(18) hydrogen atom of bpa. The C...H separation is 2.733(2) Å and the H---C vector is near to perpendicular with the  $\pi$  surface (Figure 5) making an edge to face contact between aromatic rings.

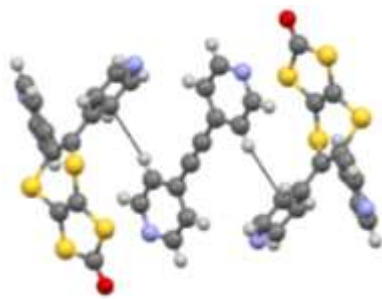


Figure 5: C-H... $\pi$  interaction between bpa and the more distantly placed molecules of **3**.

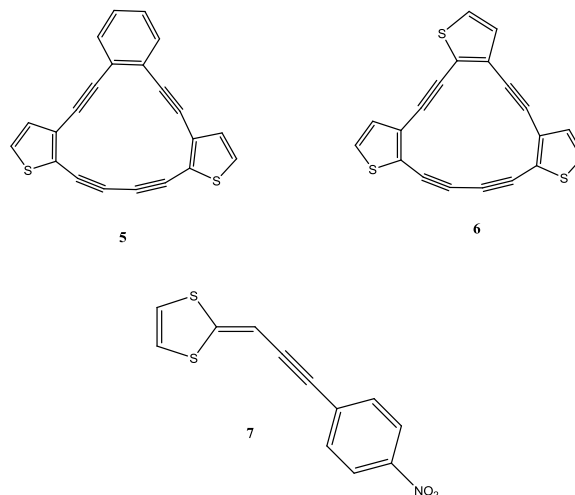
In the *a* direction the stacks of **1** and **3**, related by the *C* centring, interact by  $\pi$ - $\pi$  stacking of the pyridine rings which extend out from molecules of **3** (Figure 6a). The separations between pyridine planes are 3.333 and 3.666 Å. The nitrogen atoms of these intercalating pyridine rings make a N...H-C contact of 2.603(2) Å with the H(7) hydrogen atom of the second pyridine substituent of a molecule of **3** in the next stack. The only close contacts between stacks in the *c* direction, which are related by the *c* glide, are of type O(1)...H(12)-C(12) (2.523(2) Å) between the carbonyl group of **3** and the H(12) hydrogen atom of the pyridine ring of the next molecule of **3** (Figure 6b), with the result that molecules of **3** are linked into chains which cut through the stacks.

Table 1: Hydrogen bond distances [Å] and angles [°] in co-crystal **4**.

D-H...A	D(H...A)	d(D...A)	<(DHA)
C(7)-H(7)...N(2)	2.603(2)	3.263(3)	126.9(2)
C(12)-H(12)...O(1)	2.523(2)	3.332(3)	143.2(2)
C(18)-H(18)... $\pi$	2.733(2)	3.668(3)	168.3(2)

Table 2: Summary of the short contacts [Å], with their e.s.d.s, involving the alkyne group of bpa operating in co-crystal **4**.

S(1)-C(16)	3.495(2)	C(2)-C(16)	3.283(3)
S(3)-C(16)	3.452(2)	C(2)-C(17)	3.395(3)
S(3)-C(16)#	3.269(2)	C(3)-C(18)	3.383(3)



Scheme 2: Structural diagrams of **5-7**.

The two S...C and C...C close contacts between the alkyne group of bpa and organosulfur ring of **3** which are < 3.3 Å are remarkably short. Although intermolecular close contacts between organic sulfides and alkynes have been observed before, there are very few less than 3.4 Å, e.g. in the sterically unencumbered molecules **5**, **6** and **7** (3.231(4), 3.378(4) & 3.388(2) Å), the first two involving thiophene S...*sp*C<sup>12</sup> and the latter a vinylidenedithiole S...*sp*C.<sup>13</sup>

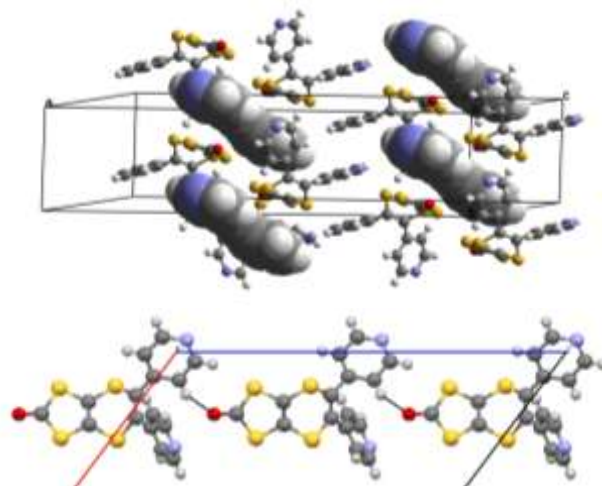


Figure 6: a) Stacking of pyridine rings belonging to adjacent stacks along the *a* axis, bpa molecules shown in space-filling style.; b) Chains of oxo molecules in **4** showing the H-bonds C(12)-H(12)...O(1) = 2.523(2) Å.

In conclusion, the co-crystal **4** shows a rich network of

interactions, with the most remarkable being those of S---spC type. This may lead to ideas for using a sulfur network to orient other chemical species. In this case there was little scope for strong hydrogen bonding interactions, commonly observed with pyridine systems.

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## Notes and references

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‡ **Synthesis of 4:** Oxo compound **3** was prepared from thione **2** by treatment with mercuric acetate in chloroform and purified by flash chromatography as has been described.<sup>9</sup> On one occasion single crystals of **4** were obtained from the slow evaporation of ethyl acetate solution of a chromatography fraction. CHNS (C<sub>21</sub>H<sub>12</sub>N<sub>3</sub>OS<sub>4</sub>): calc. C 56.0, H 2.7, N 9.3, S 28.4; found C 57.0, H 2.7, N 10.0, S 26.0. **Crystallographic data of 1:** C<sub>21</sub>H<sub>12</sub>N<sub>3</sub>O<sub>2</sub>S<sub>8</sub>, M<sub>r</sub> = 901.15 gmol<sup>-1</sup>, monoclinic, space group C2/c, a = 31.9495(6) Å, b = 7.3661(2) Å, c = 20.7736(6) Å, β = 125.1160(10)°, U = 3999.09 Å<sup>3</sup>, Z = 4, D = 1.497 gcm<sup>-3</sup>, μ (Mo Kα) = 0.494 mm<sup>-1</sup>, T = 150 K 15741 reflections measured, 3762 unique, final R(F<sup>2</sup>) = 0.0356 using 3037 reflections with I > 4.0 σ(I), wR (all data) = 0.0889, S = 1.027. The data were collected on a Bruker AXP APEX CCD area detector diffractometer equipped with an Oxford Cryosystems low temperature device at 150(2) K in the ω and φ scans mode. A semi-empirical absorption correction was carried out using the program SADABS.<sup>14</sup> Data collection, cell refinement and data reduction were done with the SMART and SAINT programs.<sup>15</sup> The structure was solved by direct methods using SIR97<sup>16</sup> and refined by full-matrix least-squares methods with SHELXL97<sup>17</sup> program using the WinGX software package.<sup>18</sup>

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