

## Hydrogen-bonded zigzag chains in 2,2'-dithiodibenzoic acid–1,3-di-4-pyridylpropane (1/1)

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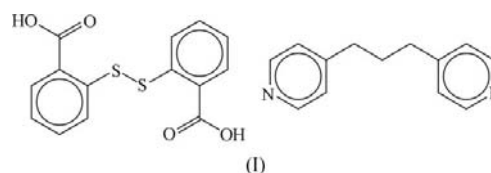
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The title 1:1 cocrystal,  $C_{14}H_{10}O_4S_2 \cdot C_{13}H_{14}N_2$  or  $H_2L \cdot bpp$ , has the two components connected by  $O-H \cdots N$  hydrogen bonds to generate a one-dimensional zigzag chain running along the crystallographic  $a$  direction. These chains are further stacked into a three-dimensional supramolecular network by weak  $C-H \cdots O$  and  $C-H \cdots \pi$  contacts. Comparison of the structural differences with previous findings suggests that deprotonated forms, hydrogen-bonding sites and flexible ligand conformations become significant factors that influence the topological arrangement and binding stoichiometry of the resulting cocrystals.

### Comment

Recently, the design and preparation of cocrystals with desired structures have attracted considerable interest in supramolecular chemistry and crystal engineering fields due to their potential application in materials science (Zaworotko, 2001; Beatty *et al.*, 2002), molecular recognition (Ghosh *et al.*, 2006) and pharmaceutical chemistry (Remenar *et al.*, 2003). To date, the most extensively observed cocrystals are those prepared from carboxylic acid and pyridine-type molecules. In this regard, since it possesses multiple hydrogen-bonding sites, a relatively flexible conformation and a variable degree of deprotonation, 2,2'-dithiodibenzoic acid ( $H_2L$ ) is a promising candidate for binary or tertiary cocrystals. Several  $H_2L$ -based cocrystals with 4,4'-bipyridine-type bases (Bi *et al.*, 2002; Hu *et al.*, 2004; Broker & Tiekink, 2007), isonicotinohydrazide (Meng *et al.*, 2008), isomeric  $n$ -pyridinealdazines ( $n = 2, 3$  or 4) (Broker *et al.*, 2008), 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (Basiuk *et al.*, 1999) or hexamethylenetetramine (Li *et al.*, 2001), and/or common solvent molecules (Murugavel *et al.*, 2001; Kang *et al.*, 2002; Kresinski & Fackler, 1994; Cai *et al.*, 2006), have been well documented, with the acid and base components forming chain-based polymer topologies *via* classical  $O-H \cdots N$  hydrogen bonds.

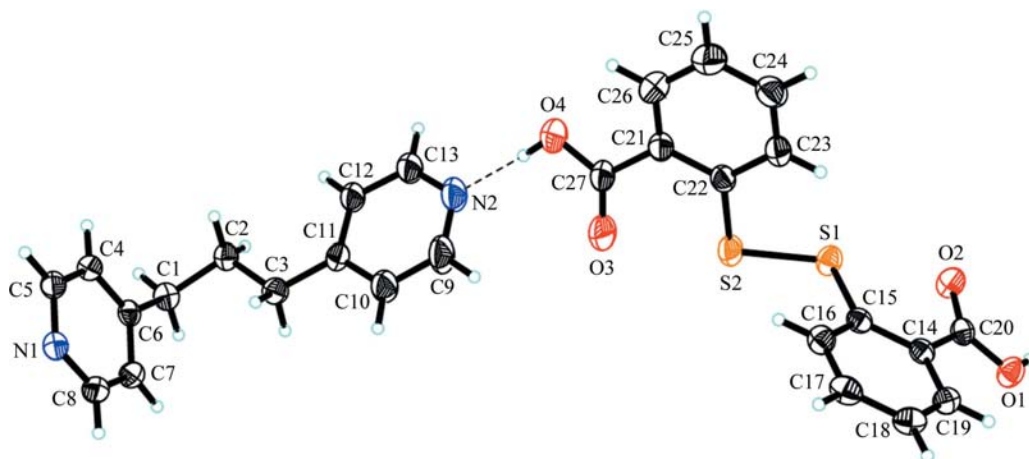
To investigate further the influence of framework flexibility on the resulting topology of  $H_2L$ -based cocrystals, 1,3-di-4-pyridylpropane (bpp) was selected to cocrystallize with  $H_2L$  in a mixed solvent, giving the title 1:1 cocrystal, (I). In addition to offering two hydrogen-bonding acceptor sites, bpp can also exhibit *anti-anti*, *anti-gauche* and *gauche-gauche* conformations (Niu *et al.*, 2006), resulting from free rotation about the C–C single bonds, which may potentially induce novel supramolecular aggregation patterns.



The asymmetric unit of (I) is shown in Fig. 1. When viewed along the central S–S bond, the  $H_2L$  molecule adopts a characteristic L-shaped conformation [torsion angle  $C15-S1-S2-C22 = 95.43(10)^\circ$ ]. A search of the Cambridge Structural Database (CSD, Version 5.30; Allen, 2002) yielded a mean value over 40 hits for  $H_2L$ -type structures of  $\pm 86^\circ$  for this C–S–S–C torsion angle. The carboxylic acid residues are almost coplanar with their respective benzene rings, and the carbonyl O atoms are adjacent to the S atoms, with  $S \cdots O$  separations of 2.628 (2) and 2.665 (2) Å. In the neutral bpp molecule, the  $C1-C2-C3-C11$  [ $179.41(18)^\circ$ ] and  $C6-C1-C2-C3$  [ $62.0(2)^\circ$ ] torsion angles are consistent with an *anti-gauche* conformation.

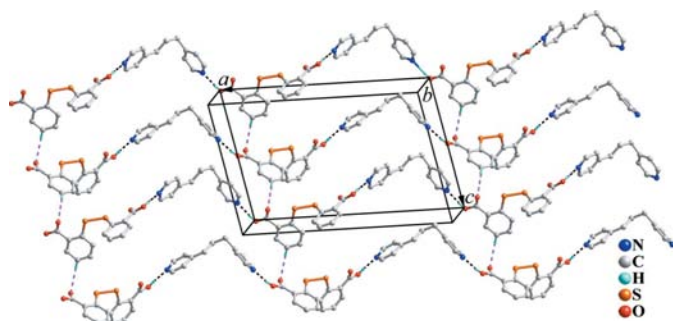
In the crystal structure of (I), the neutral  $H_2L$  and bpp molecules are linked alternately by  $O1-H1 \cdots N1(x+1, y, z)$  and  $O4-H4' \cdots N2$  hydrogen bonds (Table 1) to generate a twisted zigzag chain extending along the crystallographic  $a$  axis. These chains are further linked into a two-dimensional layer parallel to the (010) plane by weak  $C-H \cdots O$  interactions (Table 2 and Fig. 2). Weak  $C-H \cdots \pi$  contacts involving the  $C10-H10$  group of bpp and an adjacent  $C21-C26$  ring of  $H_2L$  are observed across centres of inversion between the layers, leading to a three-dimensional network [ $H10 \cdots Cg1 = 2.75$  Å,  $C10 \cdots Cg1 = 3.556(3)$  Å and  $C10-H10 \cdots Cg1 = 145^\circ$ , where  $Cg1$  is the centroid of the  $C21-C26$  ring at  $(1-x, 1-y, 1-z)$ ].

To explore the structural features of  $H_2L$  in cocrystals, various kinds of multifunctional N-heterocycles have already been used as cocrystallization agents 'B' with  $H_2L$  (see Fig. 3). The stoichiometric ratios of the components in the known cocrystals are 1:2, 1:1, 2:1, 2:3 and 3:1 (see Fig. 3). What can be obtained depends in part on the molar ratio of the materials used, as well as on the steric congestion of the secondary cocrystal agents. Various 1:1 and 2:1 cocrystals can be isolated by controlling the molar ratio of the raw materials for the  $H_2L$  and B components, but only a 2:3  $H_2L$ -2-pyridinealdazine (CSD refcode SODKIG; Broker *et al.*, 2008) cocrystal can be reproducibly obtained despite the use of different molar ratios of the reactants. The  $O-H_{acid} \cdots N$  synthon is always present in these systems. In addition, as a binary organic acid,  $H_2L$  can



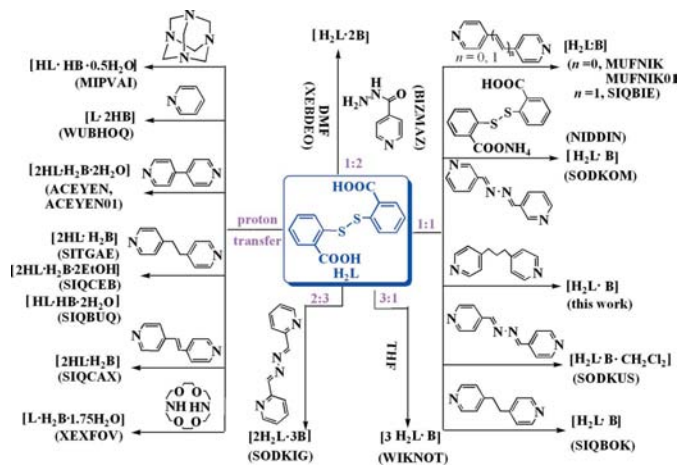
**Figure 1**

The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. The dashed line indicates the intermolecular O—H...N hydrogen bond.



**Figure 2**

The two-dimensional supramolecular network in (I) formed by O—H...N and C—H...O contacts (dashed lines).



**Figure 3**

Cocrystals of 2,2'-dithiodibenzoic acid. The references for the CSD refcodes are: ACEYEN (Hu *et al.*, 2004); ACEYEN01 (Broker & Tiekink, 2007); BIZMAZ (Meng *et al.*, 2008); MIPVAI (Li *et al.*, 2001); MUFNIK (Bi *et al.*, 2002); MUFNIK01 (Broker & Tiekink, 2007); NIDDIN (Murugavel *et al.*, 2001); SIQBOK, SIQBIE, SIQBUQ, SIQCA, SIQCEB and SITGAE (Broker & Tiekink, 2007); SODKIG, SODKOM and SODKUS (Broker *et al.*, 2008); WIKNOT (Kresinski & Fackler, 1994); WUBHOQ (Kang *et al.*, 2002); XEBDEO (Cai *et al.*, 2006); XEXFOV (Basiuk *et al.*, 1999).

potentially act as a neutral molecule or as a singly or doubly deprotonated anion in cocrystals. Only eight examples are currently known (see Fig. 3) involving deprotonated  $HL^-$  and/or  $L^{2-}$  anions, and here the O—H<sub>acid</sub>...N hydrogen-bond synthon is replaced by charge-assisted O—H...O<sup>-</sup> and N—H...N<sup>+</sup> hydrogen bonds. The crystal structures all have a chain-based polymer topology, despite the variable binding stoichiometry. These hydrogen-bonded chains exhibit twisted-linear, zigzag and/or helical topologies. In addition, C—H...O and C—H... $\pi$  contacts also contribute to the supramolecular aggregate patterns.

The  $H_2L$  and  $B$  components can sometimes cocrystallize with solvent molecules such as  $H_2O$ ,  $CH_2Cl_2$ , dimethylformamide, tetrahydrofuran or EtOH, leading to ternary hydrogen-bonded compounds (see Fig. 3). Here, solvent interference in the cocrystallization process can significantly direct the crystallization towards a particular crystal structure. In the case of  $2HL$ -*trans*-1,2-di-4-pyridylethane ethanol disolvate (CSD refcode SIQCEB; Broker & Tiekink, 2007), the solvent ethanol molecules are found in the rectangular columns formed by the  $HL^-$  anions and bipyridinium dication. In contrast, the water molecules in  $H_2L$ -hexamethylenetetramine hemihydrate (CSD refcode MIPVAI; Li *et al.*, 2001) act as bridges in the formation of a ladder-like double-chain.

Thus, the degree of deprotonation, the available hydrogen-bonding sites and the flexible conformation of the components, together with any solvent molecule intervention, are all important factors in governing the supramolecular structures of cocrystals.

## Experimental

To an acetone–water solution (1:1, 2.0 ml) of  $H_2L$  (15.3 mg, 0.05 mmol) was added dropwise an ethanol–water solution (1:1, 3.0 ml) of bpp (30.8 mg, 0.1 mmol) with constant stirring. The mixture was stirred for a further 1 h at room temperature and then filtered. The resulting yellow filtrate was allowed to evaporate at room temperature. Pale-yellow block-shaped crystals of (I) suitable for

**Table 1**

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1—H1...N1 <sup>i</sup>	0.82	1.81	2.622 (2)	172
O4—H4'...N2	0.82	1.78	2.597 (3)	175
C18—H18...O2 <sup>ii</sup>	0.93	2.59	3.433 (3)	150

Symmetry codes: (i)  $x + 1, y, z$ ; (ii)  $x, -y + \frac{1}{2}, z + \frac{1}{2}$ .

X-ray diffraction were obtained within one week in 62% yield. Elemental analysis calculated for C<sub>27</sub>H<sub>24</sub>N<sub>2</sub>O<sub>4</sub>S<sub>2</sub>: C 64.27, H 4.79, N 5.55%; found: C 64.27, H 4.55, N 5.63%.

*Crystal data*

C <sub>14</sub> H <sub>10</sub> O <sub>4</sub> S <sub>2</sub> ·C <sub>13</sub> H <sub>14</sub> N <sub>2</sub>	<i>V</i> = 2565.8 (3) Å <sup>3</sup>
<i>M<sub>r</sub></i> = 504.60	<i>Z</i> = 4
Monoclinic, <i>P</i> 2 <sub>1</sub> / <i>c</i>	Mo <i>K</i> α radiation
<i>a</i> = 20.9613 (13) Å	$\mu$ = 0.24 mm <sup>-1</sup>
<i>b</i> = 9.3021 (5) Å	<i>T</i> = 296 K
<i>c</i> = 13.3790 (8) Å	0.24 × 0.23 × 0.14 mm
$\beta$ = 100.3990 (10)°	

*Data collection*

Bruker SMART CCD area-detector diffractometer	12563 measured reflections
Absorption correction: multi-scan ( <i>SADABS</i> ; Sheldrick, 2002)	4508 independent reflections
<i>T<sub>min</sub></i> = 0.944, <i>T<sub>max</sub></i> = 0.967	3399 reflections with <i>I</i> > 2σ( <i>I</i> )
	<i>R<sub>int</sub></i> = 0.022

*Refinement*

<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )] = 0.035	318 parameters
<i>wR</i> ( <i>F</i> <sup>2</sup> ) = 0.117	H-atom parameters constrained
<i>S</i> = 1.08	$\Delta\rho_{\max}$ = 0.23 e Å <sup>-3</sup>
4508 reflections	$\Delta\rho_{\min}$ = -0.21 e Å <sup>-3</sup>

H atoms were located in difference maps, but were subsequently placed in calculated positions and treated as riding, with C—H = 0.93 Å and O—H = 0.82 Å, and with *U<sub>iso</sub>*(H) = 1.2*U<sub>eq</sub>*(C,O).

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics:

*SHELXTL* (Sheldrick, 2008) and *DIAMOND* (Brandenburg & Berndt, 1999); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG3122). Services for accessing these data are described at the back of the journal.

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