

## Hydrogen-bonded layers in the 1:2 cocrystal of 2,2'-dithiodibenzoic acid with isonicotinohydrazide

Xiang-Gao Meng,<sup>a\*</sup> Yi-Long Xiao,<sup>b</sup> Hang Zhang<sup>a</sup> and Chun-Shan Zhou<sup>a</sup>

<sup>a</sup>Key Laboratory of Pesticides and Chemical Biology, Ministry of Education, College of Chemistry, Central China Normal University, Wuhan 430079, People's Republic of China, and <sup>b</sup>College of Physical Science and Technology, Central China Normal University, Wuhan 430079, People's Republic of China

Correspondence e-mail: mengxianggao@mail.ccn.edu.cn

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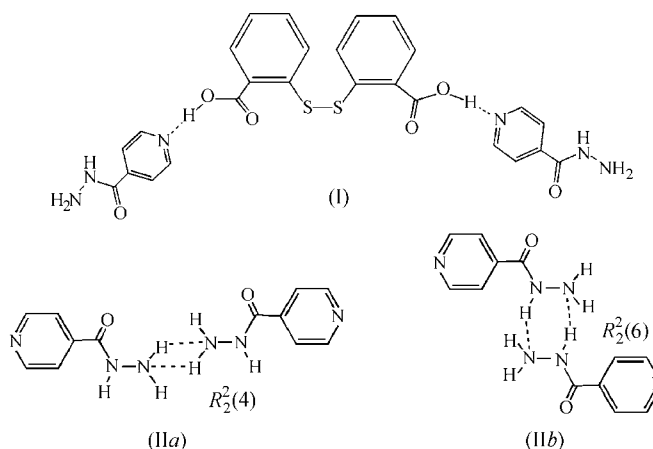
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Cocrystallization of 2,2'-dithiodibenzoic acid with isonicotinohydrazide from methanol solution yields the 1:2 cocrystal 2,2'-dithiodibenzoic acid–isonicotinohydrazide (1/2),  $C_{14}H_{10}O_4S_2 \cdot 2C_6H_7N_3O$ . The component molecules are linked by intermolecular O—H...N, N—H...O, N—H...N and C—H...O hydrogen bonds into layers running parallel to the (010) plane, and these layers are further linked into a three-dimensional framework structure by means of weak aromatic  $\pi$ – $\pi$  stacking interactions. As a potential cocrystallization agent, isonicotinohydrazide may be used for effective and versatile synthetic supramolecular strategies utilizing hydrogen bonding of specific molecular building blocks.

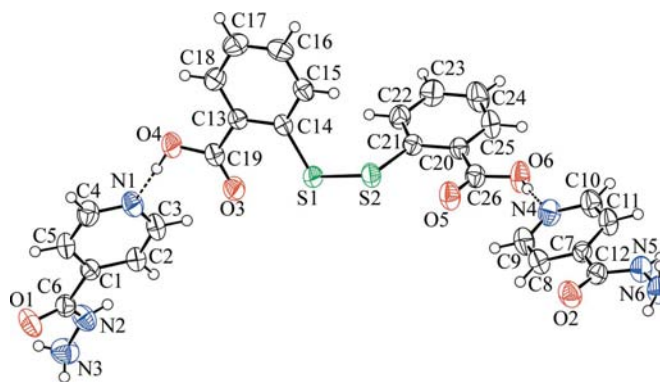
### Comment

Molecular recognition, a central concept in supramolecular chemistry resulting from a delicate balance of shape, size and functional complementarity, may allow for the assembly of individual entities into complex multicomponent aggregates with desirable connectivities and metrics (Steed & Atwood, 2000; Lehn *et al.*, 1996; Lehn, 1995). Although there are a variety of supramolecular interactions from which to choose, the hydrogen-bonded synthon involving the carboxylic acid group remains the most widely used for designing purely organic-based architectures owing to its strength, directionality, specificity and potential for electronic/geometric fine-tuning (Aakeröy *et al.*, 2002, 2005, 2006; Aakeröy & Salmon, 2005; Braga & Grepioni, 2005; Varughese & Pedireddi, 2006). 2,2'-Dithiodibenzoic acid (DSDA), possessing two carboxylic acid groups, has often been employed as a bridging ligand in metal coordination chemistry (Murugavel *et al.*, 2001); however, because of its insolubility in water, only a few molecular adducts based on DSDA have been reported to date (Li *et al.*, 2001; Cai *et al.*, 2006; Kang *et al.*, 2002; Hu *et al.*, 2004). With the aim of investigating the structural diversity arising

from two hydrogen-bonded RCOOH groups and an N-containing heterocycle in the solid state, we used isonicotinohydrazide (INAH) as a potential cocrystallization agent. We report here the crystal structure of the title compound, (I).



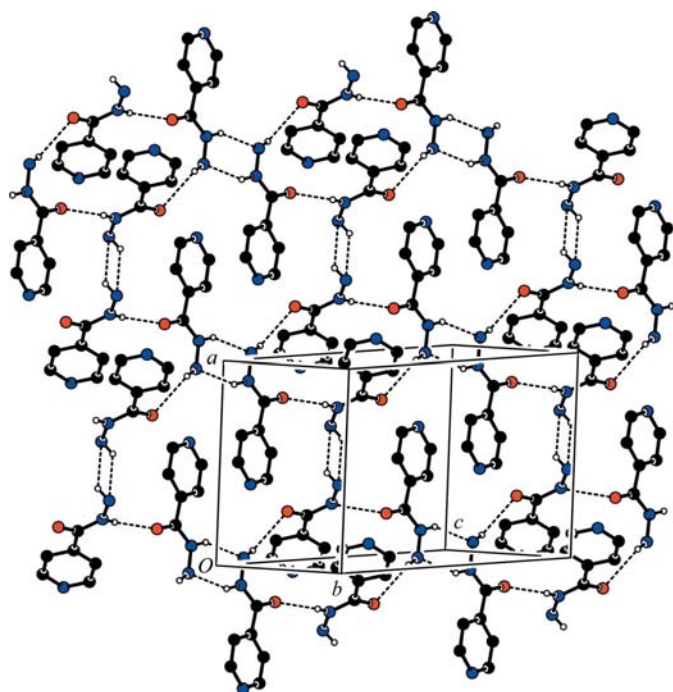
The asymmetric unit of (I) comprises one DSDA and two INAH molecules, which are linked by the expected carboxylic acid–N(heterocycle) hydrogen bonds (Fig. 1). The dihedral angle between the two benzene rings [ $76.0(1)^\circ$ ], the length of the disulfide bridge [ $2.052(1) \text{ \AA}$ ] and the average S—C bond distance [ $1.782(3) \text{ \AA}$ ] in DSDA are all comparable to those observed in some reported analogues [Cambridge Structural Database (Allen, 2002) refcodes ACEYEN (Hu *et al.*, 2004), MIPVAI (Li *et al.*, 2001), MUFNIK (Bi *et al.*, 2001), WUBHOQ (Kang *et al.*, 2002), XEBDEO (Cai *et al.*, 2006) and XEXFOV (Basiuk *et al.*, 2006)]. According to the definitions of a cocrystal proposed by Aakeröy & Salmon (2005), (I) can be regarded as the first binary acyl hydrazine-containing cocrystal. In DSDA, the C—O bond lengths in both carboxyl groups [C19—O3 =  $1.211(3) \text{ \AA}$ , C19—O4 =  $1.309(3) \text{ \AA}$ , C26—O5 =  $1.209(3) \text{ \AA}$  and C26—O6 =  $1.316(3) \text{ \AA}$ ] agree well with those tabulated in the *International Tables for Crystallography* (1992, Vol. C, Table 9.5.1.1, pp. 685–706) for a carboxyl group attached to a benzene ring [ $1.305(20)$  and



**Figure 1**  
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Dashed lines indicate hydrogen bonds.

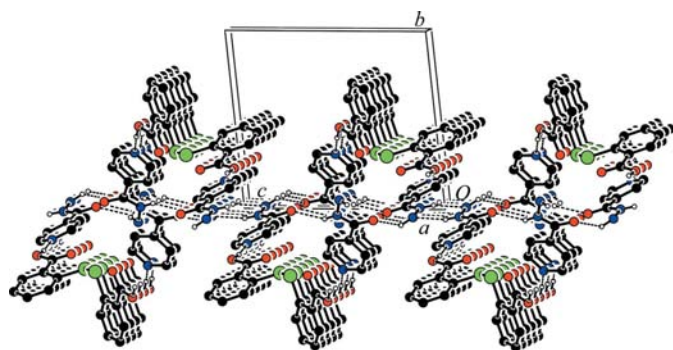
1.226 (20) Å]. In the INAH molecules, the C3—N1—C4 and C9—N4—C10 angles [117.5 (3) and 116.6 (3)°, respectively] are also consistent with the conformation of the C—N—C angle [116.3 (16)°] in unprotonated pyridine molecules (Allen, 2002), although the magnitude of the s.u. values prevents any firm conclusions being drawn from this comparison. Owing to the difference between the basicity of the N atoms in pyridine and in the hydrazine group, INAH may be used as a linker agent in constructing binary or ternary cocrystals.

In the supramolecular structure of (I) (Fig. 2), the INAH molecules form two types of hydrogen-bonded dimers [(IIa)



**Figure 2**

Part of the crystal structure of (I), showing the two-dimensional layer formed only by INAH molecules running parallel to the (010) plane. Hydrogen bonds are shown as dashed lines. For clarity, the DSDA molecules and H atoms not involved in the motif have been omitted.



**Figure 3**

Part of the crystal structure of (I), showing the formation of the (010) two-dimensional layer composed of hydrogen-bonded DSDA and INAH molecules. Hydrogen bonds are shown as dashed lines. For clarity, H atoms not involved in the motif have been omitted.

and (IIb) in the scheme above]. The molecular components are further linked by N—H···O and C—H···O hydrogen bonds into two-dimensional layers, and adjacent layers are then linked by weak  $\pi$ – $\pi$  stacking interactions into a three-dimensional framework that can be analyzed in terms of several substructures.

Firstly, INAH molecules are linked by intermolecular N2···O2<sup>i</sup>, N3···N3<sup>iii</sup>, N5···N6<sup>iv</sup> and N6···O1<sup>vii</sup> hydrogen bonds (symmetry codes as in Table 1) into two-dimensional layers (layers A) running parallel to the (010) plane. These layers comprise four types of centrosymmetric hydrogen-bond motifs, namely  $R_2^2(4)$ ,  $R_2^2(6)$ ,  $R_4^4(18)$  and  $R_8^8(18)$  (Fig. 2); the reference layer is in the domain  $-0.380 < y < 0.380$ . Although the  $R_2^2(4)$  motif exists frequently in nature, it has only been discussed in detail in a few reports (Glidewell *et al.*, 1996; Eppel & Bernstein, 2008); the other three motifs are all commonly observed in hydrogen-bonded supramolecular complexes (Bernstein *et al.*, 1995). The two-dimensional layers are further augmented by weak C9—H9···O1<sup>vi</sup> hydrogen bonds [C···O = 3.292 (4) Å and C—H···O = 140°] and strong  $\pi$ – $\pi$  stacking interactions between inversion-related N4-containing pyridine fragments. The face-to-face pyridine rings are strictly parallel, with an interplanar spacing of 3.612 (1) Å and a centroid–centroid separation of 3.707 (1) Å, corresponding to a ring offset of 0.832 (1) Å.

Secondly, DSDA molecules are linked to INAH molecules by the remaining two strong (O4···N1 and O6···N4) and also by two weak (N3···O3<sup>ii</sup> and N6···O5<sup>v</sup>) hydrogen bonds, expanding the above-mentioned two-dimensional layers into the domain  $-0.811 < y < 0.811$  (denoted layer B); this layer is about two times thicker than layer A (Fig. 3). Finally, neighbouring B layers are linked by rather weak  $\pi$ – $\pi$  stacking interactions between parallel symmetry-related C20–C25 benzene rings, with a centroid–centroid distance of 4.298 (2) Å, an interplanar spacing of 3.584 (2) Å and a larger ring offset of 2.372 (1) Å. The two strongly bent C—H···S hydrogen bonds (Table 1) may exist only because of steric effects and not because of the creation of hydrogen bonds (Domagala *et al.*, 2003).

In summary, this study provides a foundation for effective and versatile synthetic supramolecular strategies by using INAH molecules as a molecular building block. It should be possible to construct a wide variety of heteromolecular architectures with predetermined connectivities and dimensions.

## Experimental

All reagents and solvents were used as obtained without further purification. Equivalent molar amounts of 2,2'-dithiodibenzoic acid (0.1 mmol, 0.0306 g) and isonicotinohydrazide (0.2 mmol, 0.0274 g) were dissolved in 95% methanol (10 ml). The mixture was stirred for 10 min at ambient temperature and then filtered. The resulting light-brown solution was kept in air for two weeks. Plate-like pale-yellow crystals of (I) suitable for single-crystal X-ray diffraction analysis grew at the bottom of the vessel by slow evaporation of the solution (yield 6.8.2 mg, 10%, based on a 1:2 cocrystal).

## Crystal data

$C_{14}H_{10}O_4S_2 \cdot 2C_6H_7N_3O$	$\gamma = 84.345 (1)^\circ$
$M_r = 580.63$	$V = 1319.14 (19) \text{ \AA}^3$
Triclinic, $P\bar{1}$	$Z = 2$
$a = 9.8821 (8) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 11.0170 (9) \text{ \AA}$	$\mu = 0.26 \text{ mm}^{-1}$
$c = 12.2592 (10) \text{ \AA}$	$T = 298 (2) \text{ K}$
$\alpha = 83.444 (1)^\circ$	$0.10 \times 0.06 \times 0.04 \text{ mm}$
$\beta = 88.054 (1)^\circ$	

## Data collection

Bruker SMART APEX CCD area-detector diffractometer	12845 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1997)	5145 independent reflections
$T_{\min} = 0.886$ , $T_{\max} = 0.990$	3619 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.040$

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.057$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.137$	$\Delta\rho_{\text{max}} = 0.30 \text{ e \AA}^{-3}$
$S = 1.05$	$\Delta\rho_{\text{min}} = -0.22 \text{ e \AA}^{-3}$
5145 reflections	
385 parameters	

Table 1

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$N2-H2A \cdots O2^i$	0.82 (3)	2.14 (3)	2.884 (3)	150 (3)
$N3-H3A \cdots O3^{ii}$	0.843 (18)	2.44 (3)	3.148 (4)	142 (3)
$N3-H3B \cdots N3^{iii}$	0.80 (3)	2.545 (15)	3.068 (7)	124.5 (18)
$N5-H5A \cdots N6^{iv}$	0.87 (3)	2.18 (3)	2.947 (4)	148 (3)
$N6-H6B \cdots O5^v$	0.86 (2)	2.356 (12)	3.177 (4)	160 (3)
$C9-H9 \cdots O1^{vi}$	0.93	2.53	3.292 (4)	140
$N6-H6A \cdots O1^{vii}$	0.90 (2)	2.520 (16)	3.187 (3)	131.3 (16)
$O4-H4A \cdots N1$	0.98 (4)	1.66 (4)	2.642 (3)	174 (3)
$O6-H6 \cdots N4$	0.93 (4)	1.71 (4)	2.629 (3)	171 (4)
$C15-H15 \cdots S2$	0.93	2.64	3.176 (3)	117
$C22-H22 \cdots S1$	0.93	2.68	3.197 (3)	116

Symmetry codes: (i)  $x-2, y, z$ ; (ii)  $-x, -y, -z+1$ ; (iii)  $-x-1, -y, -z+1$ ; (iv)  $-x+4, -y, -z$ ; (v)  $x+1, y, z$ ; (vi)  $-x+1, -y, -z+1$ ; (vii)  $-x+2, -y, -z+1$ .

H atoms bonded to C atoms were positioned geometrically ( $C-H = 0.93 \text{ \AA}$ ) and treated as riding [ $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ ]. H atoms bonded to N and O atoms were found in difference maps and the N-H and O-H distances were refined freely [the refined distances are given in Table 1;  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$  and  $1.5U_{\text{eq}}(\text{O})$ ].

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

PLATON (Spek, 2003); software used to prepare material for publication: PLATON.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3220). Services for accessing these data are described at the back of the journal.

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