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Journal of Sulfur Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gsrp20

Synthesis, crystal structures and non-bonded S···S contacts with O—H···O/O—H···S hydrogen bonds in isomeric hydroxyphenyl-1,3-dithianes

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Published online: 13 Feb 2013.

To cite this article: Mrityunjoy Datta , Allen D. Hunter & Matthias Zeller (2013) Synthesis, crystal structures and non-bonded S···S contacts with O—H···O/O—H···S hydrogen bonds in isomeric hydroxyphenyl-1,3-dithianes, Journal of Sulfur Chemistry, 34:5, 502-511, DOI: 10.1080/17415993.2012.762919

To link to this article: http://dx.doi.org/10.1080/17415993.2012.762919

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Journal of Sulfur Chemistry, 2013
Vol. 34, No. 5, 502–511, http://dx.doi.org/10.1080/17415993.2012.762919

Synthesis, crystal structures and non-bonded $S\cdots S$ contacts with $O{-}H\cdots O/O{-}H\cdots S$ hydrogen bonds in isomeric hydroxyphenyl-1,3-dithianes

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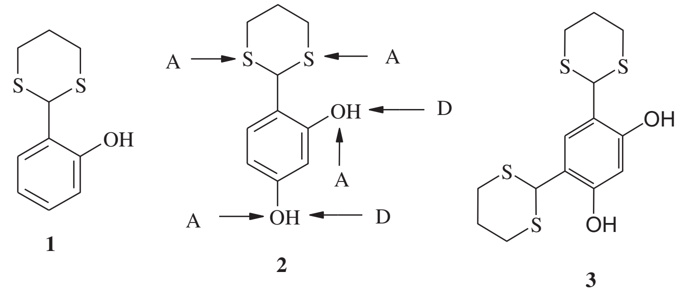
(*Received 7 November 2012; final version received 27 December 2012*)

The synthesis of isomeric hydroxyphenyl-1,3-dithianes and the role of sulfur in them to generate different engineered solids based on non-bonded $O\cdots S$ contacts and $O{-}H\cdots S$ hydrogen bonds are presented. With an increasing number of OH groups and dithiane rings (*e.g.* **2**, **3**), the role of $O{-}H\cdots S$ interactions becomes less prominent and the strong $O{-}H\cdots O$ hydrogen bonds along with $C{-}H\cdots\pi$ and π–π stacking interactions dominate the packing arrangement of the hydroxyphenyl-1,3-dithianes.



hydrogen-bond sites (A= acceptor, D = donor)

Keywords: hydroxyphenyl-1,3-dithianes; crystal structures; hydrogen bond; non-bonded contacts; synthesis

1. Introduction

Understanding and harnessing non-covalent interactions are of contemporary interest in biology, chemistry and material science (*1–6*), and the use of hydrogen bond motifs for designing and

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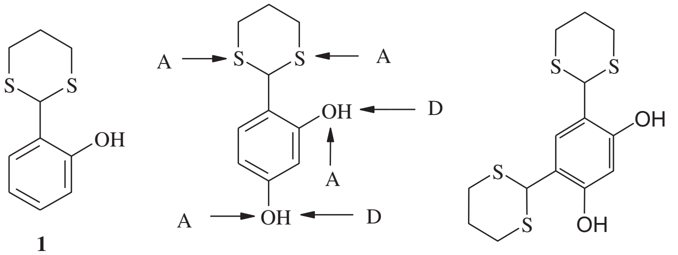
exploiting crystal structures has been widely used in crystal engineering (*7*, *8*). Both classical (N—H· · ·X and O—H· · ·X; X = O, N) and weak hydrogen bonds (C—H· · ·X; X = O, N) play a significant role in the formation of supramolecular assemblies of a wide range of molecular architechtures (*9–12*). In this aspect, the use of sulfur atoms for controlling the packing of organic crystal structures seems to be in contrast to nitrogen, oxygen, etc. much less commonplace (*13*, *14*). This may be due, perhaps, to its infrequent occurrence in organic crystals, but also due to its relatively low electronegativity, and thus the much weaker hydrogen bonds is able to form, which makes sulfur atoms a less obvious choice as a means for controlling the molecular architecture of crystalline compounds.

We reported the use of sulfur of dithiane rings in isomeric hydroxyphenyl-1,3-dithianes to generate different engineered solids based on non-bonded O· · ·S contacts and O—H· · ·S hydrogen bonds (*15*). In continuation of this work, we describe in this paper how the systematic variation of the number of phenolic hydroxyl groups and dithiane rings influences the hydrogen bonding interactions and packing of the molecules in the solid state. In this context, we report the synthesis and hydrogen bonding schemes of the three hydroxyphenyl-1,3-dithianes **1** (*16*), **2** and **3** (Scheme 1).



1 **2** **3**

Scheme 1. Hydrogen-bond sites (A = acceptor, *D* = donor).

2. Results and discussion

We reported earlier in our publication (*15*) that contacts in crystals between divalent sulfur and other atoms X can be divided into two general types, depending on the nature of the second atom as described by Rosenfield *et al.* (*17*). The two types are distinguished by the direction of the S· · ·X vector relative to the C—S—C plane (Figure 1). Electrophiles tend to approach from above and below the plane, approximately along the directions corresponding to the electron lone pairs of an S atom. These are denoted as Type I contacts. In contrast, nucleophiles tend to approach within the C—S—C plane, close to the posterior extensions of the S—C bonds. These are shown as Type II contacts and are interpreted as interactions between the nucleophile and σ^* orbitals of S—C bonds. A comprehensive database study by Allen *et al.* (*18*) has demonstrated that divalent sulfur, particularly as part of a C—S—C unit, is a poor but adequate acceptor for conventional hydrogen bond donors such as O—H and N—H. We previously reported the crystal structures of three isomeric hydroxyphenyl-1,3-dithianes, ortho-, meta- and para-$HO{-}C_6H_4{-}C_4H_7S_2$, where both non-bonded O· · ·S contacts and O—H· · ·S hydrogen bonds play an important role in the packing within their crystals (*15*).

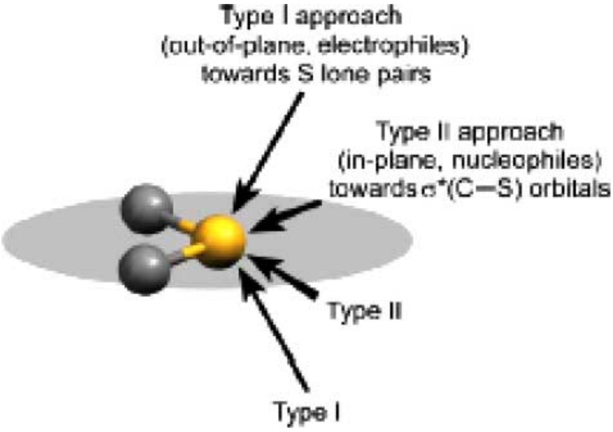


Figure 1. Geometry of non-bonded S· · ·X contacts for divalent sulfur.

2.1. *Crystal structure of 1*

Among the three dithiane compounds **1–3**, the ortho isomer **1** (*16*) adopts a chair conformation expected for a six-membered saturated ring and its disposition about the central C−C bond joining the dithiane and phenyl rings is such that one C−S bond lies approximately perpendicular to the plane of the phenyl ring (Figure S1). This structural aspect allows for the formation of an intramolecular C−H · · · O hydrogen bond between the slightly acidic carbon atom of the dithiane group and the oxygen atom O1 of the hydroxyl moiety. In the network, the phenolic OH group is also involved in an intermolecular O−H · · · S hydrogen bond (Table 1), linking the molecules into chains along the crystallographic *b*-direction (Figure S2). The geometry at the S acceptor is consistent with the expected Type I approach. The chains propagate with approximate 120° turns, imposed by the relative rotations of the phenyl and dithiane rings within the molecules themselves (Figure S2). Adjacent chains are arranged to form sheets in the *ab* plane (Figure S3) involving both the dithiane and phenyl rings. In the packing, no S· · ·S or S· · ·O contacts are observed.

2.2. *Crystal structure of 2*

With more than one OH group in the ring along with one and two dithiane rings (**2**, **3**), respectively, the packing arrangement possibilities are becoming more diverse. Similar to compound **1**, the dithiane ring in **2** adopts the expected chair conformation (Figure 2(a)) and exhibits an intramolecular C−H· · ·O hydrogen bond between the slightly acidic carbon atom C7 of the dithiane group and the oxygen atom O1 of the neighboring hydroxyl moiety. In **2**, however, the hydrogen bonding is not limited to O−H· · ·S interactions, but there is also a strong intermolecular hydrogen bond formed between the hydroxyl group O2−H2 para to the dithiane group and the oxygen O1 of a neighboring molecule (Figure 2(b)). The para hydroxyl group is also hydrogen bonded to the sulfur atom S2 of a nearer dithiane group consistent with Type I as described by Rosenfield *et al.* The hydrogen bonding interactions are completed by a strong hydrogen bond between O1−H1 and O2. In addition, a hydrogen atom of one of the dithiane methylene groups points toward the centroid of the adjacent phenyl ring, forming a relatively short contact (H10B· · ·centroid = 2.72 Å, C10−H10B· · ·centroid = 133°) that might be described as a complementary C−H· · ·π interaction. This interaction occurs on one side of the phenyl ring, the other side is π-stacked with another phenyl ring. The π-stacking and hydrogen bonds observed in **2** and especially the strong interaction between O2−H2 and O1 do not allow for an effective packing, but large voids filled with water molecules are found in the unit cell, forming channels parallel to

Table 1. Crystallographic data for **2** and **3**.

	Compound **2**	Compound **3**
Empirical formula	C_{10} H_{12} $O_{3.39}$ S_2	C_{14} H_{18} S_4 O_2
Moiety formula	C_{10} H_{12} O_2 S_2, $O_{1.39}$	
Formula weight	250.32	346.52
Temperature	100(2) K	100(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$	$P2_1/c$
Unit cell dimensions	$a = 28.3902(17)$ Å,	$a = 12.8728(6)$ Å,
	$b = 11.2221(7)$ Å,	$b = 11.3313(5)$ Å,
	$c = 7.3345(4)$ Å, $\alpha = 90°$,	$c = 10.9195(5)$ Å, $\alpha = 90°$,
	$\beta = 96.9960(10)°$, $\gamma = 90°$	$\beta = 93.9350(10)°$, $\gamma = 90°$
Volume	2319.4(2) Å^3	1589.02(13) Å^3
Z	8	4
Density (calculated)	1.434 Mg/m^3	1.448 Mg/m^3
Absorption coefficient	0.447 mm^{-1}	0.595 mm^{-1}
$F(000)$	1048	728
Crystal size	0.42 × 0.36 × 0.25 mm	0.42 × 0.35 × 0.30 mm
Crystal shape	Block	Block
Color	Yellow	Colorless
θ range for data collection	1.45–28.27°	1.59–28.27°
Limiting indices	$-37 \leq h \leq 37$, $-14 \leq k \leq 14$,	$-17 \leq h \leq 17$, $-15 \leq k \leq 15$,
	$-9 \leq l \leq 9$	$-14 \leq l \leq 14$
Reflections collected	11,628	16,089
Independent reflections	2875 (R(int) = 0.0188)[a]	3926 (R(int) = 0.0161)
Completeness to $\theta = 28.27°$	99.9%	99.7%
Absorption correction	Multi-scan	Multi-scan
Max. and min. transmission	0.890 and 0.675	0.840 and 0.721
Refinement method	Full matrix least squares on F^2	Full matrix least squares on F^2
Data/restraints/parameters	2875/25/151[a]	3926/0/253
Goodness of fit on F^2	1.102[a]	1.044
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0411, wR2 = 0.1325[a]	R1 = 0.0248, wR2 = 0.0674
R indices (all data)	R1 = 0.0424, wR2 = 0.1341[a]	R1 = 0.0253, wR2 = 0.0678
Largest diff. peak and hole	1.155 and −0.272e × Å^{-3}[a]	0.440 and −0.214e × Å^{-3}

Notes: [a]Refinement values after application of the Squeeze procedure to correct for electron density associated with disordered water molecules: R(int): 0.0176; data/restraints/parameters: 2875/0/129; goodness of fit: 1.095; final R indices [$I > 2\sigma(I)$]: R1 = 0.0337, wR2 = 0.0871; R indices (all data): R1 = 0.0353, wR2 = 0.0882; largest diff. peak and hole: 0.423 and −0.254e × Å^{-3}.

the c-axis of about 16% of the total unit cell volume (2 × 8%) (Figure 3). The water molecules are encapsulated by a layer of dithiane molecules thus not allowing for effective hydrogen bonding with the phenolic OH groups. It is worthy to be mentioned that sulfur-based compounds with different structural features show inclusion capabilities. In this regard, recently Alshahateet *et al.* (*19*) nicely described the inclusion phenomena of some sulfur-containing diquinoline host. However, in the present case, water molecules are severely disordered – they seem to be not forming hydrogen bonds with any of the sulfur atoms – and have been omitted from the structural model (see experimental details). The crucial factor for the kind of packing observed in **2** seems to be the ability to form a strong hydrogen bond between O2—H2 and O1 in combination with the π-stacking of the aromatic rings. The intramolecular C—H···O and the intermolecular O—H···S contacts, which are in common for **1** and **2**, seem to be of less importance. The hydrogen bonding data for **2** are shown in Table 2.

2.3. *Crystal structure of 3*

With an additional dithiane ring, *ortho* to the other —OH group, compound **3** crystallizes in the space group $P2_1/c$. Figure 4(a) shows an ORTEP (Oak Ridge Thermal Ellipsoid Plot Program)

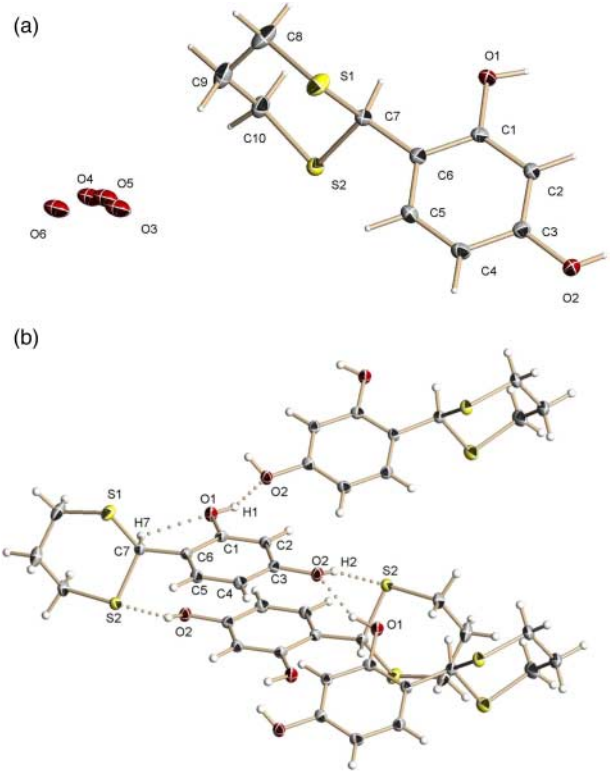


Figure 2. (a) ORTEP plot of **2** with 50% probability ellipsoids and (b) hydrogen bonding scheme of **2**.

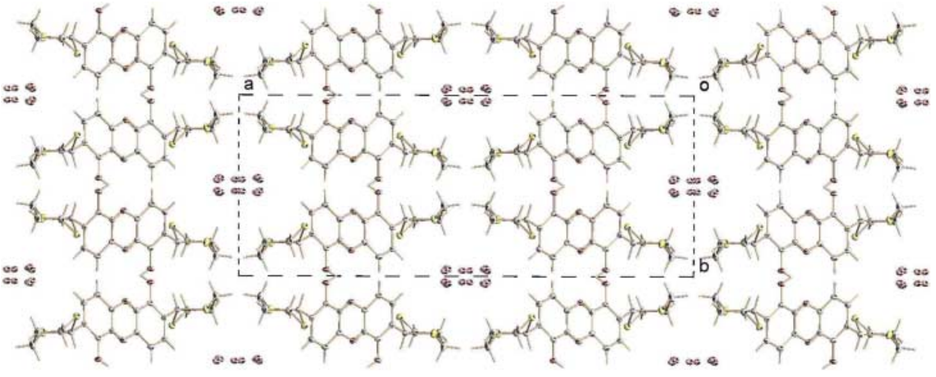


Figure 3. Packing diagram for **2** (hydrogen interactions are omitted for clarity) showing the channels along the *c*-axis at $x = 0.5$.

Table 2. Hydrogen bond distances (Å) and angles (°) for compound **2**.

D−H···A	*d* (D−H)	*d* (H···A)	*d* (D···A)	<(DHA)
O(2)−H(2)···S(2)#2	0.84	2.44	3.2417 (13)	159.2
O(2)−H(2)···O(2)#3	0.84	2.65	3.047 (2)	110.4
O(1)−H(1)···O(2)#4	0.84	1.93	2.7040 (17)	153.0
C(7)−H(7)···O(1)	1.00	2.27	2.7737 (20)	110.07

Note: Symmetry transformations used to generate equivalent atoms: #1: $-x + 1, y, -z + 3/2$; #2: $-x + 1/2, -y + 1/2, -z$; #3: $-x + 1/2, -y + 1/2, -z - 1$; #4 $-x + 1/2, y + 1/2, -z - 1/2$.

plot with the atom-numbering scheme. Similar to both **1** and **2**, the dithiane rings are in a chair conformation and orientated in such a way as to allow for a hydrogen bond between the dithiane C−H groups and the neighboring phenol oxygen atom to be formed. Three significant hydrogen bonding interactions are observed for **3** (Figure 4(b)): one strong O−H· · ·O interaction and two weaker O−H · · · S interactions. The strong hydrogen bond is formed between O2−H2 as the donor and O1 of a neighboring molecule as the acceptor. The two weaker interactions are between O1−H1 as the donor and two of the four sulfur atoms (S2 and S4). O1 is thus both acceptor for one O−H· · ·O and donor for two O−H· · ·S hydrogen bonds. The O1−H1· · ·S2 and O1−H1· · ·S4 interactions observed in the network are consistent with Type I as described by Rosenfield *et al.* H1, being hydrogen bonded to both S2 and S4, bridges the two S atoms in a Y shape. This brings the two dithiane rings into close contact so that there is a meaningful S· · ·S interaction between S2 and S4. Similar to **2**, a hydrogen atom of one of the dithiane methylene groups points toward the centroid of the adjacent phenyl ring, forming a relatively short contact (C10−H10B· · ·centroid = 2.544 Å, 16°). The other side of the phenyl ring is π-stacked with another aromatic ring. The hydrogen bonding data related to structure **3** are represented in Table 3. Figure 5 represents the packing view of the compound **3** where the weak non-covalent forces as indicated in Figure 4(b) play a

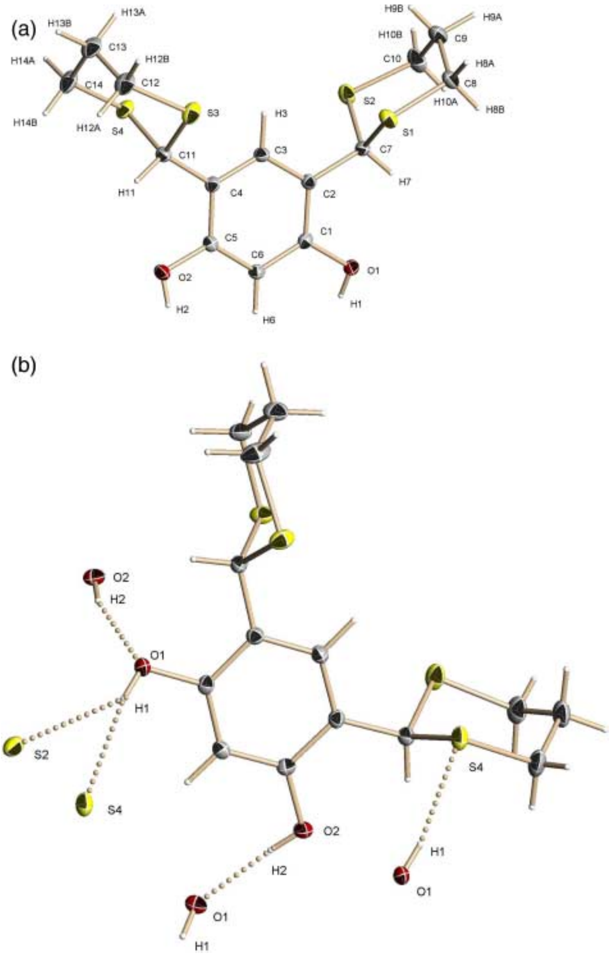


Figure 4. (a) ORTEP plot of **3** with 50% probability ellipsoids and (b) hydrogen bonding interaction scheme in **3**.

Table 3. Hydrogen bond distances (Å) and angles (°) for compound **3**.

D−H	*d* (D−H)	*d* (H···A)	*d* (D···A)	<(DHA)
O(2)−H(2)···O(1)#1	0.775(19)	2.112 (19)	2.8521 (12)	159.8 (17)
O(1)−H(1)···S(2)#2	0.761(18)	2.955 (17)	3.3910 (9)	119.1 (15)
O(1)−H(1)···S(4)#3	0.761(18)	2.529 (18)	3.2718 (8)	165.6 (17)

Note: Symmetry transformations used to generate equivalent atoms: #1: x, $-y + 3/2$, $z + 1/2$; #2: $-x + 1$, $y - 1/2$, $-z + 1/2$; #3: $-x + 1$, $-y + 2$, $-z + 1$.

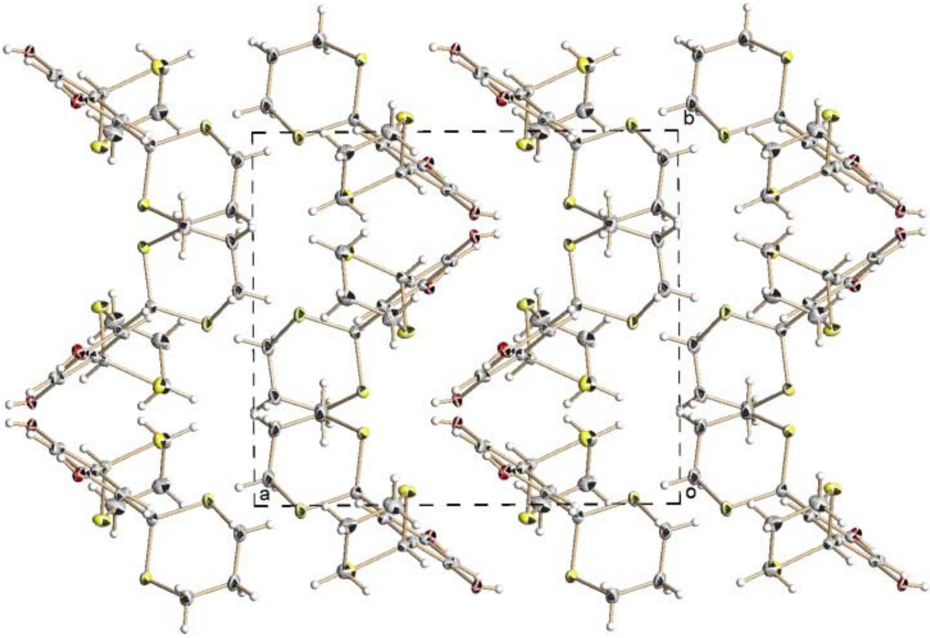


Figure 5. Packing plot of compound **3**.

decisive role. This packing plot is quite different from Figure 3 for compound **2**. No hollow space is filled in by water molecules.

3. Conclusions

Thus, the occurrence of O−H···S hydrogen bonds in **1**, **2** and **3** in preference to O−H···O hydrogen bonds appears at first sight to be at odds with the relative strengths and frequencies of the two types of interaction. This, however, is not the relative strength of two interactions, but rather the prospects for their occurrence within the constraints of an overall efficient packing arrangement. In **2** and **3**, with an increase in the number of dithiane rings, the −OH groups lie close to the long edges of the molecules and are brought by these packing arrangements into the proximity of dithiane rings thus leading to O−H···S interactions.

Importantly, the orientation of the dithiane groups with respect to the aromatic ring is so that a C−H···O interaction can be formed. This is consistent for all three compounds and seems to be a favorable interaction. Extremely important are the strong O−H···O bonds. If they can form at all, they are dominating the molecular packing. For **2**, they force it into a packing arrangement with large hydrophobic channels filled with water, which would usually be seen as quite unfavorable.

Still, the O—H···O interactions seem to be able to make up energetically for the loss in favorable interactions along these channels. π-Interactions and the π-stacking interactions also seem to play an important role. O—H···S interactions, on the other hand, seem to have no large influence on the packing.

4. Experimental

All commercially available chemicals were reagent grade and used without further purification. ^{1}H NMR spectra were recorded using a Bruker 300 MHz spectrometer. IR spectra were recorded as KBr pellets at 25°C using a Perkin Elmer L120-00A spectrophotometer.

4.1. *Synthesis*

The hydroxyphenyl-1,3-dithianes **2** and **3** were obtained from the corresponding hydroxybenzaldehydes via dithiane protection of the aldehyde functionalities, according to the following general procedure: to a solution of hydroxybenzaldehyde (18.7 mmol) in 1,3-propanedithiol (30.9 mmol), boron trifluoride etherate (2 ml) was added with stirring at 0°C for 5 h. After completion of the reaction, the mixture was poured onto a saturated aqueous solution of sodium hydrogen carbonate (50 ml) and was extracted three times (3 × 50 ml) with ethyl acetate. The organic layer was washed repeatedly with aqueous sodium hydrogen carbonate. Finally, the organic layer was dried over anhydrous sodium sulfate. The solvent was removed from the filtrate under vacuum and the product was isolated by column chromatography with chloroform as the eluent.

4.1.1. *2-(1,3-Dithian-2-yl)phenol 1*

Mp 126°C, yield 87%. ^{1}H NMR ($CDCl_3$, 300 MHz): 7.28 (m, 1H), 7.21 (m, 1H), 6.89 (d, 2H, $J = 6$ Hz,), 6.35 (s, 1H), 5.41 (s, 1H), 3.12–3.03 (m, 4H), 2.94–2.90 (m, 2H), 2.21–2.17 (m, 1H), 2.00–1.87 (m, 1H). FT–IR (KBr) ν_{max} (cm^{-1}): 3319, 2950, 2893, 1604, 1592, 1499, 1455, 1421, 1408, 1349, 1270, 1250, 1236, 1196, 1183, 1153, 1087, 1040, 790, 758. Elemental analysis: C: 56.55, H: 5.67%. Calcd for $C_{10}H_{12}OS_2$: C: 56.56, H: 5.69%.

4.1.2. *4-(1,3-Dithian-2-yl)-1,2-benzenediol 2*

Mp 162–164°C, yield 80%. ^{1}H NMR (d_6-DMSO, 300 MHz): 9.71 (s, 1H), 9.38 (s, 1H), 7.10 (d, 1H, $J = 9$ Hz), 6.27 (s, 1H), 6.22 (dd, 1H, $J_1 = 2.1$ Hz, $J_2 = 2.1$ Hz), 5.47 (s, 1H), 3.02 (t, 2H, $J = 12$ Hz), 2.83–2.78 (m, 2H), 2.09–2.05 (m, 1H), 1.72–1.60 (m, 1H). FT–IR (KBr) ν_{max} (cm^{-1}): 3122, 1631, 1498, 1443, 1329, 1230, 1163, 1129.

4.1.3. *4,6-Di(1,3-dithian-2-yl)-1,3-benzenediol 3*

Mp 232–234°C, yield = 70%. ^{1}H NMR (d_6-DMSO, 300 MHz): 9.85 (s, 2H), 7.40 (s, 1H), 6.36 (s, 1H), 5.45 (s, 2H), 3.03 (t, 4H, $J = 12$ Hz), 2.84–2.79 (m, 4H), 2.10–2.06 (m, 2H), 1.76–1.63 (m, 2H). FT–IR (KBr) ν_{max} (cm^{-1}): 3407, 3253, 2923, 2890, 1614, 1519, 1431, 1421, 1362, 1274, 1190, 1175.

4.2. *X-ray crystallography*

Diffraction data for **2** and **3** were collected on a Bruker AXS SMART APEX CCD diffractometer at 100(2) K using the monochromatic Mo Kα radiation with omega scan technique. The unit cells were determined using SMART and SAINT+. ((a) Bruker Advanced X-ray Solutions *SMART for WNT/2000* (Version 5.628), Bruker AXS Inc., Madison, Wisconsin, USA, 1997–2002 and (b) Bruker Advanced X-ray Solutions *SAINT* (Version 6.45), Bruker AXS Inc., Madison, Wisconsin, USA, 1997–2003.) The structure was solved by direct methods and refined by full matrix least squares against F^2 with all reflections using SHELXTL. (Bruker Advanced X-ray Solutions *SHELXTL* (Version 6.10), Bruker AXS Inc., Madison, Wisconsin, USA, 2000.) Refinement of an extinction coefficient was found to be insignificant. All non-hydrogen atoms were refined anisotropically.

In the crystal structure of **2**, channels parallel to the *c*-axis are filled with severely dynamically disordered water molecules. The channels make up about 16% (2 × 8%) of the unit cell volume of **2**. In a first approach, the disordered water molecules O3–O6 were refined as partially occupied and the associated hydrogen atoms were omitted from the model. The oxygen atoms O3−O5 are close to each other and their occupancies were constrained to sum up to 1.2 (to take the electron density of the missing hydrogen atoms into account). Occupancy ratios refined to 0.51(3):0.48(1):0.25(3) for O3, O4 and O5, respectively. O6 refined to have occupancy of 0.152(4). All water oxygen atoms have been restrained to have the same anisotropic displacement parameters, which have been kept isotropic within a standard deviation of 0.01. In a second approach, the electron density associated with the disordered water molecules was corrected for using the Squeeze procedure implemented in the program Platon for Windows (A.L. Spek, Delft, the Netherlands, 2003). *R*-values and structure quality indicators improved significantly (see footnote in Table 1), indicating the inadequacy of the disorder model used.

For **2**, all hydrogen atoms were placed in calculated positions and were refined with an isotropic displacement parameter 1.2 times (C−H bonds) or 1.5 times (O−H) that of the adjacent carbon atom. Hydrogen atoms of **3** were located in the difference density Fourier map and were isotropically refined. Crystal data and experimental details for **2** and **3** are listed in Table 1.

5. Supporting information

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC 777286-777288. Copies of data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax int. code +44 1223 336033, email: deposit@ccdc.cam.ac.uk). In addition, the single-crystal X-ray figures for structure **1** are presented.

Acknowledgements

We thank DST, New Delhi, India, for providing infrastructural support under DST FIST program. We also sincerely thank Dr Kumaresh Ghosh, University of Kalyani, for his helpful suggestions to prepare this manuscript.

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