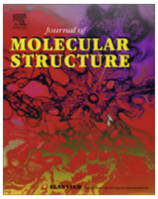
Journal of Molecular Structure 1004 (2011) 296–302

Contents lists available at SciVerse ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc



Thione vs. ketone: The influence of the chalcogenide on weak intermolecular interactions in crystal packing of 4,5-bis(bromomethyl)-1,3-dithiole-2-thione and 4,5-bis(bromomethyl)-1,3-dithiol-2-one

Vladimir A. Azov [a,*], Matthias Zeller [b], Michèle-Laure Lieunang Watat [a], Ying Xin [a]

[a] *University of Bremen, Department of Chemistry, Leobener Strasse NW 2C, D-28359 Bremen, Germany*
[b] *Youngstown State University, One University Plaza, Youngstown, OH 44555-3663, USA*

ARTICLE INFO

Article history:
Received 1 June 2011
Received in revised form 11 August 2011
Accepted 12 August 2011
Available online 23 August 2011

Keywords:
Crystallography
Non-covalent interactions
Weak hydrogen bonds
Halogen–halogen contacts
Hirshfeld surfaces
Fingerprint plots

ABSTRACT

Crystal structures of 4,5-bis(bromomethyl)-1,3-dithiole-2-thione (**1**) and 4,5-bis(bromomethyl)-1,3-dithiol-2-one (**2**) were determined and analyzed. Both compounds pack in the same *C*2/*c* space group and adopt very similar molecular geometries. Patterns of intermolecular contacts, analyzed with the help of Hirshfeld surfaces and fingerprint plots, on the other hand, are remarkably different. The dominant interactions in the packing of **1** are short Br···Br contacts and non-classical C—H···Br hydrogen bonds. For **2**, the packing is governed by short C—H···O═C hydrogen bonds, and longer C—H···Br and S···Br contacts play only a secondary role.

1. Introduction

The study of noncovalent interactions plays an increasingly important role in modern chemical research [1]. They are considered nowadays keystones in supramolecular chemistry, materials science, and even biochemistry. The importance of such interactions, which include weak hydrogen bonds [2], halogen bonds [3], and various types of interactions involving π-systems [4], in shaping the formation of crystal lattices of organic compounds is now fully recognized, which makes deeper investigations into the nature of these weak H-bonds and halogen interactions in crystalline materials an area of current interest.

Herein we analyze the molecular structures and crystal packing of two five-membered heterocyclic derivatives, 4,5-bis(bromomethyl)-1,3-dithiole-2-thione (**1**) and 4,5-bis(bromomethyl)-1,3-dithiol-2-one (**2**). Both compounds were used as intermediates for the preparation of various pyrrolo-tetrathiafulvalene derivatives [5–7]. Packing motifs for the two reported compounds show an interesting interplay of C—H···O═C and C—H···Br non-classical hydrogen bonds and Br···Br and Br···S soft–soft close contacts. Despite the similarity of molecular architectures, packing motifs for **1** and **2** are strikingly different. Hirshfeld surface analysis [8] is used to decipher the intermolecular interactions in the crystal packing of **1** and **2**.

2. Experimental

2.1. Synthesis and crystallization

4,5-Bis(bromomethyl)-1,3-dithiole-2-thione **1** was prepared by bromination of the corresponding diol, 4,5-bis(hydroxymethyl)-1,3-dithiole-2-thione, using phosphorous tribromide, as described before [5]. Large X-ray quality yellow transparent crystals were grown by slow evaporation of a chloroform/heptane solution. Mp: 128–128.5 °C; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 4.33$ (s, 4H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 20.3$, 139.4, 208.3.

4,5-Bis(bromomethyl)-1,3-dithiol-2-one **2** was prepared by radical bromination of 4,5-dimethyl-1,3-dithiol-2-one with N-bromo succinimide (NBS) as described elsewhere [6]. Large X-ray quality colorless transparent crystals were grown by slow evaporation of a chloroform solution in an NMR tube. Mp: 153–154 °C; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 4.38$ (s, 4H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 21.5$, 130.0, 187.4.

2.2. X-ray data collection and refinement

X-ray diffraction measurements were performed on a Bruker AXS SMART APEX CCD diffractometer with graphite monochroma-

---

* Corresponding author. Tel.: +49 421 218 63126; fax: +49 421 218 63120.
E-mail address: vazov@uni-bremen.de (V.A. Azov).

doi:10.1016/j.molstruc.2011.08.026

Table 1
Crystal data, collection and refinement details for compounds **1** and **2**.

	1	**2**
Formula	$C_5H_4Br_2S_3$	$C_5H_4Br_2OS_2$
M_r	320.09	304.03
Crystal system, space group	Monoclinic, *C*2/c	Monoclinic, *C*2/c
a (Å), *b* (Å), *c* (Å)	7.510(2), 16.984(5), 7.532(2)	14.910(5), 7.894(3), 7.414(3)
β (°)	111.234(4)	104.974(4)
V (Å^3)	895.5(4)	843.0(5)
Z	4	4
D_{calc} (g cm^{-3})	2.374	2.395
μ (mm^{-1})	9.673	10.039
F(000)	608	576
Crystal color, habit	Yellow, block	Colorless, block
Crystal size (mm)	0.40 × 0.45 × 0.55	0.39 × 0.47 × 0.52
Temperature (K)	100	100
Radiation type, wavelength (Å)	Mo Kα, 0.71073	Mo Kα, 0.71073
Θ range (°)	2.4–30.9	2.8–30.9
Index range	$-10 \leqslant h \leqslant 10$	$-21 \leqslant h \leqslant 21$
	$-24 \leqslant k \leqslant 24$	$-11 \leqslant k \leqslant 11$
	$-10 \leqslant l \leqslant 10$	$-10 \leqslant l \leqslant 10$
Absorption correction	Multi-scan, Bruker APEX2 [9]	
T_{min}, T_{max}	0.376, 0.746	0.411, 0746
Reflections collected/unique/observed [$I > 2.0\sigma(I)$]	4390/1338	4028/1257
R_{int}	0.024	0.035
Data/restraints/parameters	1338/0/48	1257/0/48
$R[F^2 > 2\sigma(F^2)]$	0.0210	0.0225
$wR(F^2)$	0.0527	0.0566
Goodness-of-fit, *S*	1.03	1.04
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	−0.62, 1.19	−0.71, 0.60

tized Mo Kα radiation at 100 K using APEX2 software [9] for data collection. Cell refinement, data reduction and absorption correction employing the multi-scan method were performed using SAINT [9]. The structure was solved by direct methods with the help of SIR92 [10], refinements were carried out by full-matrix least-square techniques using CRYSTALS [11]. All non hydrogen atoms were refined anisotropically. The H atoms were located from a difference map and initially refined with soft restraints on the bond lengths and angles to regularize their geometry (C—H in the range 0.93–0.98 Å) and U_{iso}(H) (in the range 1.2–1.5 times U_{eq} of the parent atom), after which the positions were refined with riding constraints [12]. Crystal data together with collection and refinement details for compounds **1** and **2** are presented in Table 1.

ORTEP diagrams were drawn using Ortep-3 for Windows [13]. Crystal structures were analyzed using the PLATON package [14]. Packing diagrams were prepared with the help of Mercury v. 2.2 [15].

2.3. Hirshfeld surface analysis

Molecular Hirshfeld surfaces in crystal structures are based on the electron distribution calculated as the sum of spherical atom electron densities of a molecule [16]. The Hirshfeld surface enclosing a molecule is defined by points where the contribution to the electron density from the molecule of interest is equal to the contribution from all the other molecules. For each point on such an isosurface two distances are defined: d_e, the distance from the point to the nearest nucleus external to the surface, and d_i, the distance to the nearest nucleus internal to the surface. The distances d_e and d_i provide a three-dimensional picture of close intermolecular contacts in a crystal structure [8]. The normalized contact distance, d_{norm}, is a symmetric function based on both d_e and d_i, and the van der Waals (*vdW*) radii of atoms internal or external to the surface:

$$d_{norm} = (d_i - r_i^{vdW})/r_i^{vdW} + (d_e - r_e^{vdW})/r_e^{vdW}$$

The value of d_{norm} is negative/positive when intermolecular contacts are shorter/longer than *vdW* separations, enabling identification of the regions of particular interest in relation to intermolecular interactions [8b,c]. Graphical plots of the molecular Hirshfeld surfaces mapped with d_{norm} use the red–white–blue color scheme with red highlighting the shorter intermolecular contacts, white showing the contacts around the *vdW* separation, and blue being used to indicate the longer contact distances.

The combination of d_i and d_e in the form of a 2D fingerprint plot affords a concise summary of intermolecular contacts in the crystal [17]. Such plots are generated by binning of (d_i, d_e) pairs in intervals of 0.01 Å and coloring each bin (a single pixel on the plot) of the resulting 2D histogram as a function of the fraction of surface points in that bin. Color ranges from blue (few points) through green to red (many points). Resolved fingerprint plots are used to identify particular close contacts in the crystal structure, such as H-bonds or halogen–halogen interactions.

Hirshfeld surfaces became a useful tool for the analysis of intermolecular interactions in crystals and were employed in studies of phenomena such as polymorphism [18], inclusion complexes [19], pressure-induced effects [18a,20], and others. The Hirshfeld surfaces and fingerprint plots presented in this paper were prepared using the program Crystal Explorer 2.1 [21].

3. Results and discussion

3.1. Molecular structures

Both compounds **1** and **2** crystallize in monoclinic system in *C*2/c space group with crystallographically imposed twofold symmetry. For that reason, the common IUPAC numbering scheme could not be applied. The molecular structures with atom numbering schemes are shown in Fig. 1 and selected geometrical parameters are summarized in Table 2. Bond lengths and distances may be considered normal. The molecular frameworks excluding Br6 are essentially planar, with maximum and r.m.s. deviations of fitted atoms from the least-squares plane of 0.009(1) (S3) and 0.002 Å, for **1**, and of 0.025(2) (C5) and 0.002 Å for **2**, respectively. The bromine atoms are directed to the opposite sides of the ring systems, with S3—C4—C5—Br6 torsion angles of 64.63(18)° for **1** and