J Chem Crystallogr (2008) 38:867–871
DOI 10.1007/s10870-008-9450-7

COMMUNICATION

Self-Assembly of N-1, 3-Dithiolan-2-ylidene-N′-[1-furan-2-yl-meth-(E)-ylidene]-hydrazine via Left-Handed Helical Chains of S···O Short Contacts and C–H···N Inter-Molecular Hydrogen-Bonds

Yong-Hong Liu · Zhi-Gang Li · Ling-Juan Yang · Xiao-Lan Liu

Received: 18 October 2007 / Accepted: 10 July 2008 / Published online: 9 August 2008

Abstract The title compound, N-1, 3-Dithiolan-2-ylidene-N′-[1-furan-2-yl-meth-(E)-ylidene]-hydrazine was synthesized via furfural with 2-hydrazono-1, 3-dithiolane and characterized by elemental analysis, ^{1}H NMR, ^{13}C NMR, IR, UV–Vis and single crystal XRD. The crystal belongs to orthorhombic, space group $F2_12_12_1$ with unit cell parameters $a = 6.4035(9)$ Å, $b = 11.8835(16)$ Å, $c = 12.3809(17)$ Å, $V = 942.1(2)$ Å^3, $Z = 4$, $Dc = 1.497$, $Mr = 212.28$, $\mu = 0.523$ mm^{-1}, $F(000) = 440$, $R_1 = 0.0243$, and $wR_2 = 0.0602$. The molecule is the anti-rotamer of the trans-isomer and every molecule forms zig-zag C(7) chains via C–H···N inter-molecular hydrogen-bond [H···N = 2.74 Å, C···N = 3.354(3) Å and C–H···N = 142°] running parallel to the [010] direction. At the same time many molecules self-assemble the left-handed spiral C(7) chains and inverse ones via the S···O short contacts [S···O = 3.1867(13) Å] along a axis.

Keywords 2-Hydrazono-1, 3-dithiolane · Furfural · Schiff's base · Synthesis · Self-assembly · Crystal structure

Introduction

2-Hydrazono-1, 3-dithiolane and its derivatives are good synthesis agents and biological activity compounds [1–5]. Many its Schiff's bases, such as its pyruvoylhydrazone, benzoylhydrazone and salicyloylhydrazone, have good biological activities on *Escherichia coli (1,047)* and *streptococcus 1,123)* and low toxicity [6]. Furthermore the salicyloylhydrazone, as a good ligand, can coordinates with lots of metal ions and some of its complexes have important material properties [7, 8]. But its furfural-hydrazone was not reported. Here as a ongoing research for new and better biologically active agents and ligands [9–11], we report the synthesis and supramolecular structure of the title compound (I) (Fig. 1) which differs in several respects from those of 1, 2-bis(1,3-dithiolan- 2-ylidene)hydrazine (II) [12].

Experimental

C, H and N elemental analyses were determined with a Carlo-Erba 1106 elemental analyser. The IR spectrum was recorded on a Brucker Tensor 27 spectrophotometer as KBr pellets. Electronic spectrum was obtained using a Shimadzu UV-2550 spectrophotometer in $CHCl_3$. The ^{1}H NMR and ^{13}C NMR spectra were carried out on a Bruker Avance 600 NMR spectrometer using $CDCl_3$ as solvent and TMS as internal standard. Melting point was measured on a Yanagimoto instrument and uncorrected.

All chemicals were of reagent grade quality obtained from commercial sources and used without further purification. 1, 3-dithiolane were prepared by literature methods (Scheme 1) [12].

Under Ar atmosphere two drops of acetyl acid were added to a solution of ferrocene-carboxaldehyde (1.0 g,

---

Y.-H. Liu · X.-L. Liu (✉)
College of Chemistry and Chemical Engineer, Yangzhou University, Yangzhou 225002, People's Republic of China
e-mail: xiaolanliu998@yahoo.com.cn

Z.-G. Li
Tianshui Institute for Drug Control, Tianshui 741018, People's Republic of China

L.-J. Yang
College of Life and Chemistry, Tianshui Normal University, Tianshui 741001, People's Republic of China

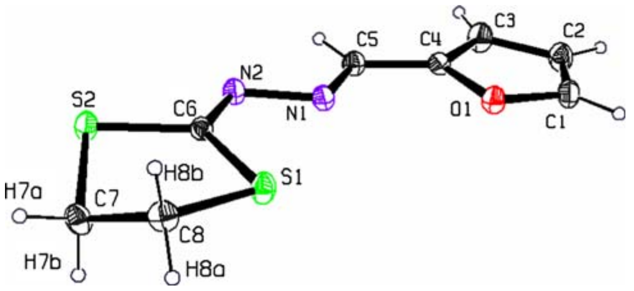
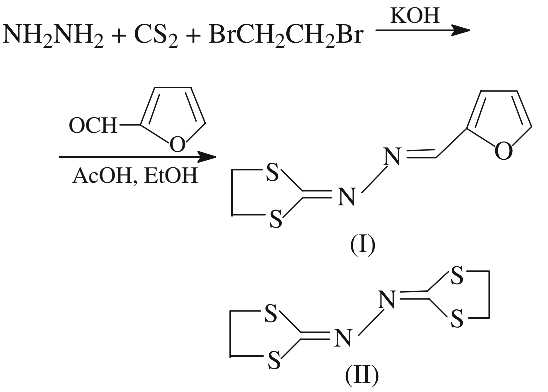


Fig. 1 The molecular structure with the atomic numbering scheme. Displacement ellipsoids are drown at the 30% probability level



Scheme 1 The synthetic process of compound I and the structure of compound II

4.5 mmol) and 2-hydrazono-1, 3-dithiolane (0.6 g, 4.5 mmol) in 95% EtOH (20 mL). The reaction mixture was stirred for 12 h at room temperature and boiled under reflux for 4 h until a precipitate formed. After concentrated to a fit volume, the mixture was set aside overnight in refrigerator and dark red crystals were obtained. After recrystallized in anhydrous ethanol, a yellowish needle crystals obtained (0.9 g, yield 94.4%, m.p. 381–382 K). Its crystal suitable for X-ray diffraction analysis was grown from methylene dichloride at room temperature over a period of several days. Analysis calculated for $C_8H_8N_2OS_2$: C, 45.29; H, 3.71; N, 13.22%; found: C, 45.26; H, 3.80; N, 13.28.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.20 (1H, *s*, N=CH); 7.59 (1H, *s*, 1-H of furan ring), 6.80 (1H, *s*, 3-H of furan ring), 6.52 (*s*, 1H, 2-H of furan ring); 3.52 (*s*, 4H, CH_2CH_2). ^{13}C NMR (600 MHz, CDCl3, δ, p.p.m.): 177.462 (Fur-C=N), 149.602 (CS2), 146.665 (4-C of furan ring) 145.462 (1-C of furan ring), 115.507 (3-C of furan ring), 112.111 (2-C of furan ring) 36.669, 35.413 (CH_2CH_2) [11]. IR (KBr, cm^{-1}): 3150 (*w*, =C–H), 1612 (*vs*, C=N), 1,546 and 1,501 (*s*, C=C), 930 (*s*, N–N), 851 (*s*, C–S). UV–Vis [λ_{max}, nm ($\varepsilon \times 10^4$), in CH_2Cl_2]: 280.0 (0.98) (B-band), 369.2 (1.29) (K-band) [13].

X-ray Crystallography

X-ray data were collected on a Bruker SMART 1000 CCD diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 294(2) K. Semi-empirical absorption corrections were applied using the SADABS program [14]. The structures were solved by direct methods and refined by full matrix least-squares methods based on F^2 with anisotropic thermal parameters for all nonhydrogen atoms. Hydrogen atoms were placed in their calculated positions, assigned fixed isotropic thermal parameters and allowed to ride on their respective parent atoms. All computations were carried out using SHELXS-97 and SHELXL-97 programs [15]. A PLATON view and ORTEP-3 view were obtained with the WinGx Program System [16]. A summary of the crystallographic data and details of the structure refinements is listed in Table 1.

Results and Discussion

The ^{1}H NMR, ^{13}C NMR, IR, UV and elemental analysis for the title compound were in good agreement with it. Figure 1 shows ORTEP-3 drawing the molecular structure, together with the numbering scheme used. Selected bond lengths and bond angles are listed in Table 2.

Compound (I) crystallizes in orthorhombic system and space group $P2_12_12_1$ with $Z = 4$, whereas (II) crystallizes in monoclinic and $P2_1/n$ with $Z = 2$ [11]. In (I) and (II) the corresponding bond distances and angles are very similar. The bond lengths S2–C6 and S1–C8 are not same in both of them, indicating differences in the electronic environments of the two S atoms (Fig. 1, Table 1). While atoms C7 and C8 deviate by −0.442(6) and 0.226(7) Å respectively from the least-squares plane in (II), those are −0.27456(5) and 0.24401(5) Å respectively in (I). It shows that the rings conformation of 1, 3-dithiolane are also in half-chair forms, but the 1, 3-dithiolane ring is more co-plane after jointed by fural, because the atoms of S1, C6, S2, N2, N1, C5, C4, C3, C2, C1 and O1 form a large π-conjugation system (for the atom deviations of them for the plane are −0.0929(16), −0.005(5), −0.0446(15), 0.054(5), 0.142(4), −0.012(5), 0.027(5), 0.068(6), 0.012 (7), −0.076(7) and −0.072(5) Å respectively). That is also indicates by that the bond length of 1.439(2) Å for C4–C5, 1.410(2) Å for N1–N2, 1.7571(18) Å for S1–C6 and 1.7520(18) Å for S2–C6 for (I) are shorter than the single band values of 1.46 Å for Csp^2–Csp^2, 1.45 Å for Nsp^2–Nsp^2 [17], 1.819 (2) Å for S1–C8 and 1.809(2) Å for S2–C7, respectively (Table 1). The length of Cg_f (centre of furan ring) to Cg_d (center of 1, 3-dithiolane ring) is 6.728(3) Å in the same molecular. The structure of

Table 1 Summary of crystallographic results

Empirical formula	$C_8H_8N_2OS_2$
CCDC deposition	620306
Color/shape	Light yellow/transparent block
Formula weight	212.28
Crystal size, mm	0.24 × 0.16 × 0.14
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions	
a (Å)	6.4035 (9)
b (Å)	11.8835 (16)
c (Å)	12.3809 (17)
V (Å^3)	942.1(2)
Z	4
Density (calculated, mg/m^3)	1.497
F(000)	440
Radiation	Mo Kα (λ = 0.71073 Å)
Temperature	294 (2) K
μ(Mo-K$_\alpha$) (mm^{-1})	0.532
Scan mode	Φ and ω
θ Range for data collection (°)	2.38 ~ 26.46
Limiting indices	$-6 \leq h \leq 8$, $-11 \leq k \leq 14$, $-15 \leq l \leq 15$
Reflections collected	5,315
Independent reflections/reflections with I > 2σ(I)	1,926/1,787
Diffractometer	Bruker SMART 1000 CCD
Absorption correction	Mult-scan SADABS
Transmission factor, T_{Max}/T_{min}	0.940643/0.903605
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1,787/0/118
$R_{(int)}$	0.0234
Goodness-of-fit on F^2	1.089
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0243$, $wR_2 = 0.0579$
R indices (all data)	$R_1 = 0.0283$, $wR_2 = 0.0602$
Flack parameter	0.02 (7)
Friedel pairs	783
Largest diff. peak and hole, (e Å^{-3})	0.171 and −0.134
Weights	$1/[\sigma^2(F_o{}^2) + (0.0279 \times P)^2 + 0.1272 \times P]$, where $P = [F_o^2 + 2F_c^2]/3$

(I) can be assigned to *E*-isomer, which is most stable configuration.

The most striking difference between (I) and (II) lies in their supramolecular aggregations. In (I), there are C(7) chains [18], which formed by short contacts of S···O and the seven atoms are in order of S1, C6, N2, N1, C5, C4 and O1 in every molecular inside, involving molecules with S···O distance of 3.1867(13) Å along a axis (Fig. 2), such as S1 and O1 at (*x, y, z*) to O1 at (−½ + *x*, ½ − *y*, −*z*) and S2 at (½ + *x*, ½ − *y*, −*z*), respectively. C6–S1···O1 angle and S1···O1–C4 angle are 164.7(2) and 152.9(3)°, respectively. The S···O distance is certainly short then the sum of the vand der Waals radii (3.32 Å) given by Bondi [19], but these are consistent with the results of a database analysis [20] (S···O distance of 3.19 Å and O···S–C angle of 163.0°). Many molecules form a *C*(7) left-handed helical spiral chain by one 2_1 screw axis along (*x*, ¼, 0). The torsion of the O1#···S1 to O1···S1* in the spiral ring is 11.2(3)° and the length of Cg_f to Cg_f (or Cg_d to Cg_d) between the two adjacent molecular layers is 6.404(2) Å, which is shorter than 6.728(3) Å, the length of Cg_f to Cg_d in the molecule itself (Table 3).

Table 2 Slected bond lengths and bond angles (Å and °)

Bond lengths			
S1–C6	1.7571(18)	N1–N2	1.410(2)
S1–C8	1.819(2)	N2–C6	1.282(2)
S2–C6	1.7520(18)	C1–C2	1.331(3)
S2–C7	1.809(2)	C2–C3	1.410(3)
O1–C1	1.356(2)	C3–C4	1.352(3)
O1–C4	1.368(2)	C4–C5	1.439(2)
N1–C5	1.271(2)	C7–C8	1.508(3)
C6–S1–C8	95.86(21)	S2–C7–C8	108.74(16)
C6–S2–C7	95.18(21)	S1–C8–C7	109.18(16)
S2–C6–N2	119.31(21)	N2–N1–C5	113.31(18)
S1–C6–N2	125.42(17)	N1–N2–C6	110.72(19)
C3–C4–C5	133.10(15)	N1–C5–C4	122.04(13)
O1–C4–C5	117.77(15)	C3–C4–O1	121.20(15)
C1–O1–C4	106.36(20)	O1–C1–C2	111.11(14)
C2–C3–C4	107.10(12)	C1–C2–C3	106.29(10)
S1–C6–S2	115.26(17)		

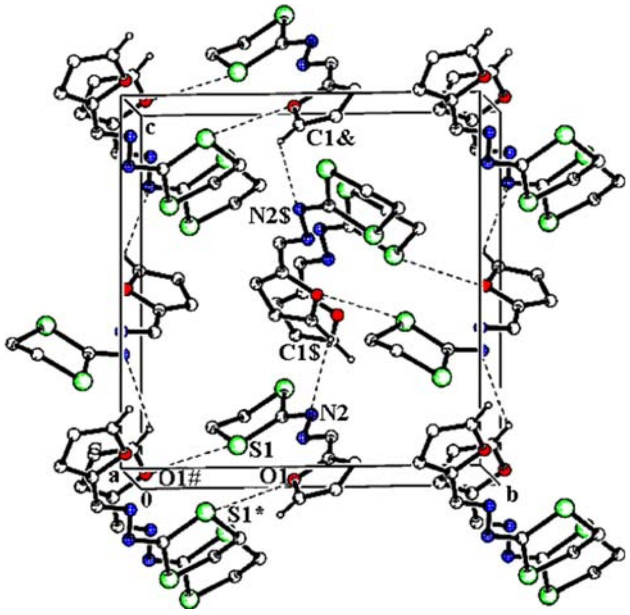


Fig. 2 A stereoview of part of compound (I), showing the formation of O···S short contact left-handed helical C(7) chain generated by the 2_1 screw axis along (*x*, ¼, 0) and an inverse one along (*x*, ¾, ½) and the formation of zig-zag chain via C(7) of C–H···N hydrogen-bonded chain in the (0, 2, 0) plane. For the sake of clarity, O···S short contacts and C–H···N inter-molecular hydrogen bonds as dashed lines, and H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (*), hash (#), dollar sign ($) or ampersand (&) are at the symmetry position (½ + *x*, ½ − *y*, −*z*), (−½ + *x*, ½ − *y*, −*z*), ($\frac{3}{2}$ − *x*, 1 − *y*, ½ + *z*) and (*x*, *y*, 1 + *z*), respectively

Table 3 Hydrogen-bond geometry (Å, °)

D–H···A	D–H	H···A	D···A	D-H···A
C1–H1[a]···N2	0.93	2.74	3.354(3)	124

[a] Symmetry code: (i) $\frac{3}{2}$ − *x*, 1 − *y*, ½ + *z*

Along c axis and around the helical spiral chains there are four inverse *C*(7) left-handed helical spiral chains which are also formed by S···O short contact and by one 2_1 screw and two is up and two is down. The seven atoms are in order of O1, C5, C4, N1, N2, C6 and S1 in every molecular inside, just in the opposite direction to the central spiral chains. Every molecule, which is made up of the five spiral chains, gives rise to zig-zag chains via *C*(7) of C–H···N inter-molecular hydrogen-bonds running parallel to the (0, 1, 0) plane. Atom C1 at ($\frac{3}{2}$ − *x*, 1 − *y*, ¼ + *z*) and C1 at (*x*, *y*, 1 + *z*) act as hydrogen-bond donors, via atom H1 at ($\frac{3}{2}$ − *x*, 1 − *y*, ½ + *z*) and H1 at (*x*, *y*, 1 + *z*), respectively, to N2 at (x, y, z) and N2 at ($\frac{3}{2}$ − *x*, 1 − *y*, ½ + *z*) with the same H···N distances of 2.74 Å and C1···N2 distance of 3.354(3) Å and C–H···N angle of 142°. The torsions of the H1&···N2$ to H1$···N2, O1#···S1 to N2···H1$ and S1*···O1 to N2···H1$ are −126, −59 and 126°, respectively.

Supplementary Material

CCDC-620306 for the title compound contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk /data_request/cif, by e-mail data_request@ ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Center, 12 Union Road, Cambridge, CB21EZ, UK; fax: +44(0)1223-336033.

Acknowledgment This work was supported financially by Tianshui Normal College (No. 2002-02) and Yangzhou University (No. 2006XJJ03).

References

1. Leml DM, Banitt EH (1964) Tetrehedron Lett 5:245–251
2. Wang Y, Li ZH, Gao N (1994) Acta Pharm Sin 29(1):78–80
3. Addor RW, Lamb GW (1973) U. S. Patent 3761492, 1973; Chem Abstr 79:137168
4. Addor RW (1964) J Org Chem 29(3):738–742
5. Gou SH, Chen HC, Fang ZP, Luo J, Wang YL (2004) Chin J Org Chem 24(2):234–238
6. Chen HC, Luo J, Cao HM, Gu JD (2002) Pesticides 43(9):10–11
7. Beghidja C, Wesolek M, Welter R (2005) Inorg Chim Acta 358:3881–3888
8. Beghidja C, Rogez G, Kortus J, Wesolek M, Welter RJ (2006) Am Chem Soc 128(10):3140–3141
9. Liu YH, Xiang QD, Liu XL, Xu W, Guo R (2007) J Chem Crystal 43:9273-y
10. Liu XL, Liu YH, Dai XQ, Zhao Y, Tong B-W (2007) Acta Cryst E63:o4019
11. Xu L-Z, Xu H-Z, Yang S-H, Li C-L, Zhou K (2005) Acta Cryst E61:o31–o32

12. Chen H-C, Luo J, Cao H-M, Gu J-D (2002) Pesticides 43(9): 10–11
13. Shi Y-C, Yang H-M, Song H-B, Liu Y-H (2004) Polyhedron 23:1541–1546
14. Sheldrick GM (1996) SADABS, program for empirical absorption correction of area detector data. University of Göttingen, Germany
15. Sheldrick GM (1997) SHELXS 97 and SHELXL 97. University of Göttingen, Germany
16. Farrugia LJ (2003) WinGx program system version 1.64. University of Glasgow, UK
17. Morrison RT, Boyd RN (1973) Organic chemistry, 3rd edn. Allyn and Bacon Inc., Boston, p 145
18. Bernstein J, Davis RE, Shimoni L, Chang N-L (1995) Angew Chem Int Ed Engl 34:1555–1573
19. Bondi A (1964) J Phys Chem 68:441–451
20. Szabó D, Kapovits I, Kucsman Á, Nagyb P, Argayb G, Kálmán A (1999) J Mol Struct 476:157–171