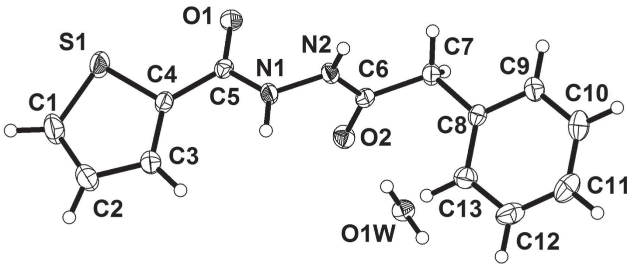
DE GRUYTER Z. Kristallogr. NCS 2017; 232(1): 69–71

Ayman El-Faham, Adel El-Merghany and Hazem A. Ghabbour*

Crystal structure of N′-(2-phenylacetyl) thiophene-2-carbohydrazide monohydrate, $C_{13}H_{14}N_2O_3S$



DOI 10.1515/ncrs-2016-0152
Received May 11, 2016; accepted October 6, 2016; available online October 29, 2016

Abstract

$C_{13}H_{14}N_2O_3S$, monoclinic, $C2/c$ (no. 15), $a = 27.9910(12)$ Å, $b = 6.5721(3)$ Å, $c = 14.2821(7)$ Å, $\beta = 92.600(3)°$, $V = 2624.6(2)$ Å^3, $Z = 8$, $R_{gt}(F) = 0.042$, $wR_{ref}(F^2) = 0.105$, $T = 100$ K.

CCDC no.: 1479028

The crystal structure is shown in the figure. Tables 1 and 2 contain details of the measurement method and a list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Colourless blocks
Size:	$0.60 \times 0.35 \times 0.11$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	2.5 cm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
$2\theta_{max}$, completeness:	66.4°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	64167, 5018, 0.059
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3921
$N(param)_{refined}$:	2188
Programs:	SHELX [17], Bruker programs [18]

Source of material

Thiophene-2-carbonyl chloride (1.6 g, 11 mmol) in 10 mL dichloromethane was added dropwise to a mixture of hydrazide (1.50 g, 10 mmol) and NaOH (0.4 g, 10 mmol) in 30 mL dichloromethane and 20 mL water at 0 °C. After complete addition of acid chloride, the reaction mixture was continued stirring at 0 °C for 2 hours and at room temperature another 2 hours. The organic layer was separated and the aqueous layer extracted with another 50 mL dichloromethane. The collected organic layer was washed with water (20 mL), saturated NaCl solution (20 mL), and then dried over anhydrous $MgSO_4$. The dichloromethane was filtered from $MgSO_4$ and then was concentered under reduced pressure to give a white solid. The crude product was recrystallized from ethanol to afford the pure product in 85% yield. (mp 220-1 °C). **^{1}H-NMR** (400 MHz, DMSO-d$_6$) δ: 3.54 (s, 2H, CH_2), 7.17 (d, $J = 4.4$ Hz, 2H, Ar), 7.19–7.36 (m, 5H, Ar), 7.83 (d, $J = 4.4$ Hz, CH-thiophene), 10.20 (s, 1H, NH), 10.41 (s, 1H, NH) ppm; **^{13}C-NMR** (100 MHz, DMSO-d$_6$) δ: 40.9, 127.2, 128.8, 128.9, 129.6, 129.7, 132.2, 136.3, 137.9, 161.2, 170.2 ppm. Anal. Cacled for $C_{13}H_{12}N_2O_2S$ (260.31): C, 59.98; H, 4.65; N, 10.76; S, 12.32; found: C, 60.06; H, 4.76; N, 10.54; S, 12.13.

Experimental details

Carbon-bound hydrogen atoms were placed in calculated positions and were included in the refinement in the riding model approximation, with U_{iso}(H) set to $1.2U_{eq}$(C).

Discussion

Bishydrazides (N,N'-diacylhydrazines) are usually obtained from esters, acid chlorides or acids [1]. They are considered as

---

***Corresponding author: Hazem A. Ghabbour,** Department of Pharmaceutical Chemistry, College of Pharmacy, King Saud, University, P.O. Box 2457, Riyadh 11451, Saudi Arabia; and Department of Medicinal Chemistry, Faculty of Pharmacy, University of Mansoura, Mansoura 35516, Egypt, e-mail: ghabbourh@yahoo.com
Ayman El-Faham: Department of Chemistry, College of Science, King Saud University, P.O. Box 2455, Riyadh 11451, Saudi Arabia; and Department of Chemistry, Faculty of Science, Alexandria University, P.O. Box 426, Ibrahimia, Alexandria 21321, Egypt
Adel El-Merghany: Department of Chemistry, College of Science, King Saud University, P.O. Box 2455, Riyadh 11451, Saudi Arabia; and Department of Chemistry, Faculty of Science, Suez University, Suez, Egypt

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
S1	0.446973(10)	0.51307(5)	0.40672(2)	0.01996(8)
O1	0.35067(3)	0.32976(13)	0.42592(6)	0.01678(17)
O2	0.25925(3)	0.53262(13)	0.27788(6)	0.01604(17)
N1	0.31011(3)	0.62900(15)	0.43446(7)	0.01299(18)
N2	0.26610(3)	0.53175(15)	0.43549(7)	0.01220(17)
C1	0.47559(4)	0.7261(2)	0.36984(10)	0.0244(3)
H1A	0.5092	0.7341	0.3633	0.029*
C2	0.44483(4)	0.8840(2)	0.35081(10)	0.0223(3)
H2A	0.4545	1.0133	0.3288	0.027*
C3	0.39675(4)	0.83209(18)	0.36783(9)	0.0166(2)
H3A	0.3705	0.9229	0.3589	0.020*
C4	0.39258(4)	0.63457(17)	0.39874(8)	0.0130(2)
C5	0.34972(4)	0.51718(16)	0.42038(8)	0.01170(19)
C6	0.24225(4)	0.49004(16)	0.35350(8)	0.01168(19)
C7	0.19405(4)	0.39035(17)	0.36177(8)	0.0136(2)
H7A	0.1942	0.3123	0.4211	0.016*
H7B	0.1888	0.2928	0.3095	0.016*
C8	0.15280(4)	0.54074(17)	0.36007(7)	0.01192(19)
C9	0.10973(4)	0.48058(18)	0.39783(9)	0.0167(2)
H9A	0.1073	0.3502	0.4259	0.020*
C10	0.07054(4)	0.6105(2)	0.39449(9)	0.0217(3)
H10A	0.0414	0.5683	0.4199	0.026*
C11	0.07387(4)	0.8015(2)	0.35426(9)	0.0231(3)
H11A	0.0469	0.8894	0.3513	0.028*
C12	0.11668(5)	0.8640(2)	0.31834(9)	0.0212(2)
H12A	0.1192	0.9959	0.2918	0.025*
C13	0.15602(4)	0.73407(18)	0.32095(8)	0.0168(2)
H13A	0.1852	0.7775	0.2959	0.020*
O1W	0.21712(3)	0.53391(13)	0.10304(6)	0.01396(16)
H1N1	0.3082(6)	0.759(3)	0.4219(12)	0.028(4)*
H1N2	0.2553(6)	0.508(2)	0.4852(12)	0.016(4)*
H2OW	0.2285(7)	0.530(3)	0.1580(15)	0.034(5)*
H1OW	0.1988(7)	0.633(3)	0.0987(14)	0.036(5)*

valuable intermediates in the synthesis of many heterocyclic compounds by employing the dehydrative cyclization method in the presence of strong acids (dehydration agents), such as H_2SO_4 [2], P_2O_5 [3], $SOCl_2$ [4], $POCl_3$ [5] or under microwave irradiation of *N,N′*-diacylhydrazines by grafting onto polymer support [6–8]. Hydrazides are considered to be an important class of compounds with various types of biological activity such as anti-bacterial [9], anti-inflammatory, anti-cancer [10], anti-microbial [11, 12], anti-fungal [9, 13] and anti-biotic [13–15].

First, 2-phenylacetohydrazide was prepared following the reported method [16]; the product was obtained as white crystals from ethanol in yield 86% (Lit. [16] 90% yield). The hydrazide was reacted with thiophene-2-carbonyl chloride using an easy two phase method (dichloromethane-water) in the presence of NaOH as HCl scavenger and help to remove the traces of acid chloride or acid remaining in the reaction medium.

The asymmetric unit of the title structure contains only one independent molecule and one molecule of water. The thiophen ring (S1/C1/-C4) is nearly parallel to the phenyl ring (C8—C13). The molecules are packed in the crystal structure with the water molecules forming three classical intermolecular hydrogen bonds N1—H1N1$\cdots$O1W^{i}, N2—H1N2$\cdots$O1W^{ii}, O1W—H1OW$\cdots$O1^{i}. The H$\cdots$$A$ distances are 1.967(19), 2.053(17), 1.92(2), respectively and the angles are 162.4(16), 170.4(16), 169(2) respectively with symmetry code: (i) $-x+1/2$, $y+1/2$, $-z+1/2$; (ii) x, $-y+1$, $z+1/2$.

Acknowledgements: The authors thank the Deanship of Scientific Research at King Saud University for funding this work through Prolific Research Group Program (PRG-1437-33; Saudi Arabia).

References

1. Dingemans, T. J.; Murthy, N. S.; Samulski, E. T.: Javelin-, Hockey Stick-, and Boomerang-shaped liquid crystals structural variations on *p*-quinquephenyl. J. Phys. Chem. B. **105** (2001) 8845–8860.
2. Short, F. W.; Long, L. N.: Synthesis of 5-aryl-2-oxazolepropionic acids and analogs antiinflammatory agents. J. Heterocycl. Chem. **6** (1969) 707–712.
3. Carlsen, P. H. J.; Jorgensen, K. B.: Synthesis of unsymmetrically substituted 4*H*-1,2,4-triazoles. J. Heterocycl. Chem. **31** (1994) 805–807.
4. Klingsberg, E.: Synthesis of carboxylic acid hydrazides and s-triazoles of the anthraquinone series. J. Am. Chem. Soc. **80** (1958) 5786–5789.
5. Kerr, V. N.; Ott, D. G.; Hayes, F. N.: Quaternary salt formation of substituted oxazoles and thiazoles. J. Am. Chem. Soc. **82** (1960) 186–189.
6. Brain, T. C.; Paul, M. J.; Loong, Y.; Oakley, J. P.: Novel procedure for the synthesis of 1,3,4-oxadiazoles from 1,2-diacylhydrazines using polymer-supported Burgess reagent under microwave conditions. Tetrahedron Lett. **40** (1999) 3275–3278.
7. Katritzky, A. R.; Mohapatra, P. P.; Huang, L.: 1,3,4-Oxadiazoles from functionalized N-acylbenzotriazoles and acyl hydrazides. ARKIVOC. **ix** (2008) 62–68.
8. Paraschivescu, C. C.; Dumitraşcu, F.; Drăghici, C.; Ruţă, L. L.; Matache, M.; Baciu, I.; Dobrotă, C.: New non-symmetrical 2,5-disubstituted 1,3,4-oxadiazoles bearing a benzo[*b*]thiophene moiety. ARKIVOC. **xiii** (2008) 198–206.
9. Mishra, A. K.; Mishra, S. B.; Tiwari, A. D.; Mamba, B. B.; Njobeh, P. B.; Dutton, M. F.; Fosso-Kankeu, E.: Synthesis, characterization, and in vitro antibacterial and antifungal studies of tin(IV) thiohydrazide complexes. J. Coord. Chem. **64** (2011) 3622–3636.

10. Ying-Xia, Z.; Rui-Fang, Y.; Cai-Ling, F.; Li-E, L.; Ben-Lai, W.; Hong-Yun, Z.: Complexes of unsymmetric bis-hydrazide ligands: crystal structures and properties. J. Coord. Chem. **65** (2012) 3133–3146.
11. Sengupta, D.; Gangopadhyay, S.; Sanchita, G.; Arnab, D.; Kumar, V.; De, S.; Gangopadhyay, P. K.: Novel low spin mixed ligand thiohydrazide complexes of iron(III): synthesis, spectral characterization, molecular modeling, and antibacterial activity. Int. J. Inorg. Chem. **2014** (2014) 1–9.
12. Beaucage, S. L.; Iyer, R. P.: The functionalization of oligonucleotides via phosphoramidite derivatives. Tetrahedron **49** (1993) 1925–1963.
13. Salawu, O. W.; Abdulsalam, A. O.: Synthesis, characterization and biological activities of Cd(II) complexes with hydrazide ligands. Der Pharma Chem. **3** (2011) 298–304.
14. Raja, M.; Ashoka, G. S.: Substitution-modulated anticancer activity of half-sandwich ruthenium(II) complexes with heterocyclic ancillary ligands. Eur. J. Inorg. Chem. **22** (2014) 3536–3546.
15. Yadav, A. A.; Patel, D.; Hasinoff, B. B.: Chiroptical properties of anionic and cationic porphyrins and metalloporphyrins in complex with left-handed Z-DNA and right-handed B-DNA. J. Inorg. Biochem. **126** (2013) 1–6.
16. Mauri, E.; Rossi, F.; Sacchetti, A.: Simple and efficient strategy to synthesize PEG-aldehyde derivatives for hydrazine orthogonal chemistry. Polym. Adv. Technol. **26** (2015) 1456–1460.
17. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112–122.
18. Bruker. APEX2, SAINT and SADABS. Bruker AXS Inc., Madison, WI, USA, 2009.