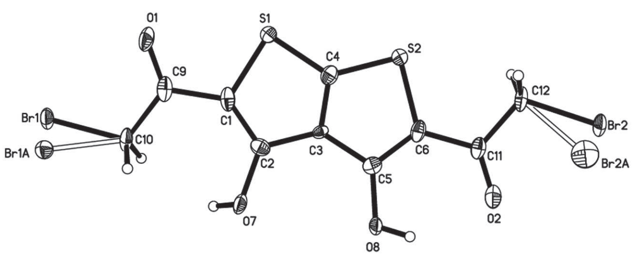
Open Access

Yahia N. Mabkhot*, Faiz A. Al-aizari, Salim Al-Showiman, Assem Barakat, Hazem A. Ghabbour and Wolfgang Frey

Crystal structure of 1,1,(3,4-dihydroxythieno [2,3-*b*] thiophene-2,5-diyl)bis(2-bromoethanone), $C_{10}H_6Br_2O_4S_2$



DOI 10.1515/ncrs-2016-0228
Received July 24, 2016; accepted January 3, 2017; available online January 20, 2017

Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	$0.37 \times 0.37 \times 0.19$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	$65.6\ \mathrm{cm}^{-1}$
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
$2\theta_{max}$, completeness:	57°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	12691, 3273, 0.041
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2522
$N(param)_{refined}$:	183
Programs:	Bruker programs [11], SHELX [12]

Abstract

$C_{10}H_6Br_2O_4S_2$, monoclinic, $P2_1/c$ (no. 14), $a = 8.1199(6)$ Å, $b = 10.4430(8)$ Å, $c = 15.4252(13)$ Å, $\beta = 96.309(3)°$, $V = 1300.08(18)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0549$, $wR_{ref}(F^2) = 0.1304$, $T = 100$ K.

CCDC no.: 1486828

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

Source of material

A solution of 1,1′-(3,4-dihydroxythieno[2,3-*b*]thiophene-2,5-diyl)diethanone [10] (2.56 g, 10 mmol) in glacial acetic acid (100 mL) was heated to 90–100 °C with stirring. To this hot solution, bromine (1.6 g, 10 mmol) in acetic acid (20 mL) was added dropwise over a period of 40 min. After complete addition of bromine, the reaction mixture was stirred vigorously at room temperature for further 1 h, then it was poured onto cold water. The solid that formed was collected, washed with water, dried and recrystallized from ethanol to give colorless crystals of the title compound.; yield 40%, mp. 120 °C; **IR** (KBr) ν (cm^{-1}) 1695(C = O), 3540(OH); **^{1}H-NMR**: δ 10.23 (s, 2H, OH), 4.82 (s, 4H, CH_2); **^{13}C-NMR**: 28.50 (CH_2), 132.3, 136.1, 140.2, 148.4 (ArCs), 186.2 (C = O). Anal. Calcd. for $C_{10}H_6Br_2O_4S_2$ (414.09): C, 29.01; H, 1.46; Br, 38.59; S, 15.49; Found: C, 29.21; H, 1.45; Br, 38.77; S, 15.65.

Experimental details

Carbon-bound H 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). The H atoms of the hydroxyl groups were allowed to rotate with a fixed angle around the C–O bond to best fit the experimental electron density (HFIX 147 [12]), with U_{iso}(H) set to $1.5U_{eq}$(O).

Discussion

Thieno[2,3-*b*]thiophene compounds have been developed for different target, in the medicinal field and have been

***Corresponding author: Yahia N. Mabkhot,** Department of Chemistry, College of Science, King Saud University, P.O. Box 2455, Riyadh 1451, Saudi Arabia, e-mail: yahia@ksu.edu.sa
Faiz A. Al-aizari, Salim Al-Showiman and Assem Barakat: Department of Chemistry, College of Science, King Saud University, P.O. Box 2455, Riyadh 1451, Saudi Arabia
Hazem A. Ghabbour: Department of Pharmaceutical Chemistry, College of Pharmacy, King Saud University, P.O. Box 2457, Riaydh 11451, Saudi Arabia; and Department of Medicinal Chemistry, Faculty of Pharmacy, Mansoura University, Mansoura 35516, Egypt
Wolfgang Frey: Institut für Organische Chemie, Universität Stuttgart, Pfaffenwaldring 55, Stuttgart 70569, Germany

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Br1[a]	0.94456(9)	0.95528(7)	0.10595(4)	0.02469(18)
Br1A[b]	0.9198(15)	1.0202(9)	0.0961(6)	0.021(3)
S1	0.88045(19)	0.79677(15)	0.44438(9)	0.0219(3)
Br2[c]	0.57022(8)	1.00955(7)	0.89881(4)	0.02441(18)
Br2A[d]	0.549(2)	1.0675(11)	0.8725(8)	0.040(4)
S2	0.7507(2)	0.84642(15)	0.62512(10)	0.0233(3)
O1	0.9897(6)	0.8105(5)	0.2765(3)	0.0304(11)
C1	0.8554(7)	0.9326(7)	0.3739(4)	0.0240(13)
C2	0.7876(7)	1.0344(6)	0.4100(4)	0.0226(12)
O2	0.5262(6)	1.1388(5)	0.7257(3)	0.0308(10)
C3	0.7521(6)	1.0039(5)	0.4975(3)	0.0148(10)
C4	0.7948(8)	0.8843(6)	0.5220(4)	0.0236(12)
C5	0.6824(7)	1.0770(6)	0.5641(4)	0.0228(12)
C6	0.6705(7)	1.0041(6)	0.6357(4)	0.0228(12)
O7	0.7505(5)	1.1521(4)	0.3695(3)	0.0239(9)
H7	0.7101	1.1398	0.3177	0.036*
O8	0.6287(6)	1.2047(4)	0.5566(3)	0.0262(10)
H8	0.6216	1.2349	0.6065	0.039*
C9	0.9145(7)	0.9092(7)	0.2875(4)	0.0247(13)
C10	0.8699(8)	1.0047(7)	0.2152(4)	0.0262(13)
H10A	0.9191	1.0887	0.2329	0.031*
H10B	0.7480	1.0153	0.2069	0.031*
C11	0.6048(7)	1.0416(6)	0.7175(4)	0.0220(12)
C12	0.6412(8)	0.9479(7)	0.7922(4)	0.0287(14)
H12A	0.7619	0.9312	0.8011	0.034*
H12B	0.5847	0.8658	0.7764	0.034*

[a]Occupancy: 0.95 ; [b]Occupancy: 0.05; [c]Occupancy: 0.96; [d]Occupancy: 0.04.

tested as prospect antitumor, antiviral, antibiotic, and antiglaucoma drugs, or as inhibitors of lamina series [1–5]. In continuation of our research [5–9] for the same platoon compounds, we have synthesized a new compound under systematic name of 1,1,(3,4-dihydroxythieno[2,3-*b*]thiophene-2,5-diyl)bis(2-bromoethanone).

The asymmetric unit cell of the title compound contains one molecule. The two Br atoms show disorder over two positions. The two thiophen rings are in the same plane with a very small deviation of 0.9°. The molecules are packed *via* at least four non-classical intermolecular hydrogen bonds C10—H10A$\cdots$O1^{i}, C10—H10B$\cdots$Br2^{ii}, C12—H12A$\cdots$Br1^{iii} and C12—H12B$\cdots$O2^{iv} the H$\cdots$A distances are 2.44, 2.91, 2.90 and 2.53 Å and the angles are 160, 151, 138 and 165°, respectively. Symmetry codes: (i) $-x+2,\ y+1/2,\ -z+1/2$; (ii) $-x+1,\ -y+2,\ -z+1$; (iii) $-x+2,\ -y+2,\ -z+1$; (iv) $-x+1,\ y-1/2,\ -z+3/2$.

Acknowledgements: The authors extend their sincere appreciation to the Deanship of Scientific Research at king Saud University for its funding this Prolific Research group (PRG-1437-29).

References

1. Jarak, I.; Kralj, M.; Piantanida, I.; Suman, L.; Zinic, M.; Pavelic, K.; Karminski-Zamola, G.: Novel cyano- and amidino-substituted derivatives of thieno[2,3-b]- and thien- o[3,2-*b*]thiophene-2-carboxanilides and thieno[3′,2′:4,5]thieno- and thieno [2′,3′:4,5] thieno[2,3-*c*]quinolones: Synthesis, photochemical synthesis, DNA binding, and antitumor evaluation. Bioorg. Med. Chem. **14** (2006) 2859–2868.
2. Peters, D.; Hornfeldt, A. B.; Gronowitz, S.: Synthesis of various 5-substituted uracils. J. Heterocycl. Chem. **27** (1990) 2165–2173.
3. Kukolja, S.; Draheim, S. E.; Graves, B. J.; Hunden, D. C.; Pfeil, J. L.; Cooper, R. D. G.; Ott, J. L.; Couter, F. T.: Structure-activity studies of bicyclic glycine derivatives of 7 aminodeacetoxy-cephalosporanic acid. J. Med. Chem. **28** (1985) 1896–1903.
4. Prugh, J. D.; Hartman, G. D.; Mallorga, P. J.; McKeever, B. M.; Michelson, S. R.; Murcko, M. A.; Schwam, H.; Smith, R. L.; Sondey, J. M.; Springer, J. P.; Surgrue, M. F.: New isomeric classes of topically active ocular hypotensive carbonic anhydrase inhibitors: 5-substituted thieno[2,3-b]thiophene-2-sulfonamides and 5-substituted thieno[3,2-b]thiophene-2-sulfonamides. J. Med. Chem. **34** (1991) 1805–1818.
5. Egbertson, M. S.; Cook, J. J.; Bednar, B.; Prugh, J. D.; Bednar, R. A.; Gaul, S. L.; Gould, R. J.; Hartman, G. D.; Homnick, C. F.; Holahan, M. A.; Libby, L. A.; Lynch, J. J., Jr.; Lynch, R. J.; Sitko, G. R.; Stranieri, M. T.; Vassallo, L. M.: Non-peptide GPIIb/IIIa inhibitors. 20. centrally constrained thienothiophene α-sulfonamides are potent, long acting in vivo inhibitors of platelet aggregation. J. Med. Chem. **42** (1999) 2409–2421.
6. Mabkhot, Y. N.; Al-Majid, A. M.; Barakat, A.; Choudhary, M. I.; Yousuf, S.: Crystal structure of 1-(5-acetyl-3,4-dimethyl-thieno[2,3-*b*]thiophen-2-yl)-ethanone, $C_{12}H_{12}O_2S_2$. Z. Kristallogr.–NCS **229** (2014) 39–40.
7. Mabkhot, Y. N.; Barakat, A.; Ghabbour, H. A.; Fun, H.-K.: Crystal structure of 2-amino-*N*-(4-methoxyphenyl)benzamide, $C_{14}H_{14}N_2O_2$. Z. Kristallogr.–NCS **231** (2016) 203–204.
8. Mabkhot, Y. N.; Al-Showiman, S. S.; Barakat, A.; Yousuf, S.; Choudhary, M. I.: Crystal structure of 1-acetylimidazolidine-2,4-dione monohydrate, $C_5H_8N_2O_4$. Z. Kristallogr.–NCS **230** (2015) 255–256.
9. Mabkhot, Y. N.; Al-Showiman, S. S.; Barakat, A.; Yousuf, S.; Choudhary, M. I.: Regioselective synthesis and crystal structure of ethyl-4-acetyl-5-((2-ethoxy-2-oxoethyl)thio)-3-hydroxythiophene-2-carboxylate, $C_{13}H_{16}O_6S_2$. Z. Kristallogr.–NCS **230** (2015) 241–242.
10. Comel, A.; Kirsch, G.: Efficient one pot preparation of variously substituted thieno[2,3-b]thiophene. J. Heterocycl. Chem. **38** (2001) 1167–1171.
11. Brucker. APEX2, SAINT and SADABS. Brucker AXS Inc., Madison, Wisconsin, USA (2009).
12. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112–122.