Crystal structure of 3-(thiophen-2-yl-carbonyl)-4-(thiophen-2-yl)-1-isopropyl-4-piperidinol, $C_{17}H_{21}NO_2S_2$

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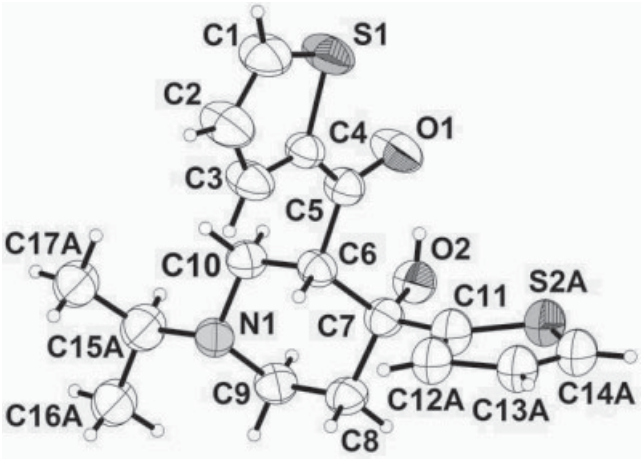

Abstract

$C_{17}H_{21}NO_2S_2$, $P\bar{1}$ (no. 2), a = 5.9254(2) Å, b = 8.9579(2) Å, c = 16.6787(4) Å, α = 92.570(1)°, β = 99.158(2)°, γ = 98.441(2)°, V = 862.4 Å^3, Z = 2, $R_{gt}(F)$ = 0.0557, $wR_{ref}(F^2)$ = 0.1477, T = 293 K.

Table 1. Data collection and handling.

Crystal:	pale yellow needles, size 0.19×0.13×0.1 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	3.15 cm^{-1}
Diffractometer, scan mode:	Rigaku R-AXIS RAPID-S,
$2\theta_{max}$:	52.76°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	18466, 3551
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2107
$N(param)_{refined}$:	265
Programs:	CrystalClear [7], SHELX [8], PLATON [9]

Source of material

A mixture of a suitable ketone, paraformaldehyde and isopropylamine hydrochloride in the 2:2:1 ratio was stirred and heated without solvent in an oil bath. Mono Mannich base type, namely 1-(thiophen-2-yl)-3-isopropylamino-1-propanone hydrochloride, and a piperidinol type compound, namely 3-(thiophen-2-yl-carbonyl)-4-(thiophen-2-yl)-1-isopropylamino-4-piperidinol hydrochloride were produced in the reaction medium at the same time. Corresponding mono Mannich base of the title compound produced in the reaction medium together with the title compound was removed from the reaction. A solution of NaOH (5%) was added on the residue. The reaction content was stirred at water bath at 313 K. Stirring was continued for 48 h observing the solidification of oily residue. Compound (I) was purified by crystallization from methanol-ether. [Yield: 11 %, mp.: 416-417 K]. ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ: 1.09 (d, J = 6.2 Hz, 6H), 2.00-2.05 (m, 2H), 2.75-2.98 (m, 5H), 4.04 (br d, J = 8.8 Hz, 1H), 5.44 (s, 1H, OH), 6.82 (dd, J = 4.6, 3.3 Hz, 1H), 6.91 (br d, J = 3.3 Hz, 1H), 7.07 (d, J = 4.6 Hz, 1H), 7.12 (dd, J = 4.8, 3.7 Hz, 1H), 7.67 (d, J = 4.8 Hz, 1H), 7.80 (d, J = 3.7 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ: 18.6, 18.8, 41.6, 44.4, 49.1, 54.4, 54.9, 72.9, 122.2, 123.9, 127.0, 128.8, 133.5, 135.8, 143.8, 153.4, 196.9; MS (EI) *m/z*: 335.2; IR (KBr,cm^{-1}): 1635 (CO). Calcd. for $C_{17}H_{21}NO_2S_2$ (335.48): C, 60.86; H, 6.31; N, 4.18; S, 19.12. Found: C, 60.55; H, 6.55; N, 4.18; S, 19.47.

Experimental details

All H atoms were positioned geometrically and treated as riding on their parent atoms, with O–H = 0.82 (hydroxyl), C–H = 0.93 (aromatic), 0.97 Å (methylene), respectively, and with U_{iso}(H) = 1.5U_{eq}(C, O) for methyl and hydroxyl and U_{iso}(H) = 1.2U_{eq}(C) for the others. One of the two thiophene rings is disordered over two positions, corresponding to rotation of approximately 180° about the single C–C bond, with site occupancy factors of 0.676(3) and 0.324(3). The atoms of the isopropyl group are also disordered over two positions [occupancies = 0.605(8):0.395(8)].

Discussion

In the title structure (Fig.) the piperidine ring (N1/C6–C10) adopts a chair conformation which is evident from the puckering parameters [1]: Q_T= 0.585(4) Å, θ = 178.0(4)° and ϕ = 162(10)°, respectively. The plane of the thiophene ring (S1/C1–C4) makes dihedral angles of and 81.9(3)° and 79.0(6)°, respectively, with the planes of the major and minor components (S2A/C11/C12A–C14A and S2B/C11/C12B–C14B) of the disordered thiophene ring, while these disordered thiophene rings form a dihedral angle of 8.0(6)° with each other. The bond lengths and angles are within normal ranges and comparable with those observed in the similar structures [2]. The C14A–S2A and C1–S1 bond lengths are 1.690(8) Å, and 1.682(5) Å, respectively. The C14A–S2A–C11 and C1–S1–C4 bond angles are 93.0(3)° and 91.9(2)°, respectively and the values are in agreement with those in [3] (1.697(2) Å, 1.704(2) Å and 93.6(1)°, 92.2(1)°), respectively. The molecular conformation is stabilized by intramolecular O2–H2A···O1 hydrogen bond, with a S(6) ring motif [4]. Semiempirical AM1 calculations of the title structure were carried out with WinMopac 7.2 software [5, 6]. The dihedral angle between the thiophene rings is 49.08° and is different from that in the x-ray result. The dipole moment, the HOMO and LUMO energy levels are calculated as about 2.530 Debye, –9.1202 and –0.0523 eV, respectively. We may state that the theoretical calcu-

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lation supports the suggestion that the present intra and intermolecular interactions influence the molecular geometry.

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	Occ.	*x*	*y*	*z*	U_{iso}
H(1)	2*i*		0.1494	0.2236	0.5746	0.101
H(2)	2*i*		0.5021	0.2836	0.5235	0.102
H(3)	2*i*		0.4431	0.3825	0.3882	0.080
H(6)	2*i*		0.2940	0.4934	0.2774	0.059
H(8A)	2*i*		0.1540	0.6725	0.0940	0.067
H(8B)	2*i*		0.3656	0.6453	0.1580	0.067
H(9A)	2*i*		0.0687	0.4145	0.0551	0.070
H(9B)	2*i*		0.3237	0.4760	0.0447	0.070
H(10A)	2*i*		0.2042	0.2364	0.2326	0.066
H(10B)	2*i*		–0.0033	0.2703	0.1686	0.066
H(12A)	2*i*	0.676	0.3769	0.7630	0.3246	0.106
H(13A)	2*i*	0.676	0.2968	0.9913	0.3765	0.109
H(14A)	2*i*	0.676	–0.0597	1.0511	0.3204	0.099
H(12B)	2*i*	0.324	–0.3051	0.7870	0.1829	0.119
H(13B)	2*i*	0.324	–0.1636	1.0220	0.2915	0.083
H(14B)	2*i*	0.324	0.2181	1.0431	0.3816	0.082
H(15A)	2*i*	0.605	0.1698	0.1473	0.0737	0.062
H(16A)	2*i*	0.605	0.3875	0.3047	–0.0074	0.122
H(16B)	2*i*	0.605	0.4342	0.1370	–0.0122	0.122
H(16C)	2*i*	0.605	0.6147	0.2620	0.0417	0.122
H(17A)	2*i*	0.605	0.3361	0.0830	0.1896	0.195
H(17B)	2*i*	0.605	0.5789	0.1361	0.1655	0.195
H(17C)	2*i*	0.605	0.4089	0.0021	0.1147	0.195
H(15B)	2*i*	0.395	0.4661	0.2642	0.0528	0.114
H(16D)	2*i*	0.395	0.0749	0.1736	–0.0006	0.171
H(16E)	2*i*	0.395	0.0630	0.0745	0.0742	0.171
H(16F)	2*i*	0.395	0.2231	0.0425	0.0111	0.171
H(17D)	2*i*	0.395	0.5943	0.1543	0.1931	0.109
H(17E)	2*i*	0.395	0.5189	0.0212	0.1254	0.109
H(17F)	2*i*	0.395	0.3485	0.0562	0.1841	0.109
H(2A)	2*i*		–0.2573	0.4896	0.1812	0.090

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	Occ.	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	2*i*		0.1587(6)	0.2619(4)	0.5241(2)	0.084(2)	0.118(3)	0.062(2)	0.028(2)	0.027(2)	0.043(2)
C(2)	2*i*		0.3583(6)	0.2961(4)	0.4953(2)	0.062(2)	0.139(3)	0.060(2)	0.028(2)	0.013(2)	0.038(2)
C(3)	2*i*		0.3241(5)	0.3533(4)	0.4172(2)	0.054(2)	0.098(2)	0.052(2)	0.015(2)	0.014(1)	0.023(2)
C(4)	2*i*		0.0988(4)	0.3608(3)	0.3895(2)	0.052(2)	0.055(2)	0.047(2)	0.008(1)	0.017(1)	0.006(1)
C(5)	2*i*		–0.0111(5)	0.4125(3)	0.3136(2)	0.050(2)	0.058(2)	0.050(2)	0.008(1)	0.011(1)	0.006(1)
C(6)	2*i*		0.1370(4)	0.4541(3)	0.2492(1)	0.046(2)	0.059(2)	0.043(1)	0.010(1)	0.009(1)	0.008(1)
C(7)	2*i*		0.0532(4)	0.5779(3)	0.1958(2)	0.049(2)	0.055(2)	0.050(2)	0.009(1)	0.006(1)	0.008(1)
C(8)	2*i*		0.2108(5)	0.6015(3)	0.1315(2)	0.057(2)	0.061(2)	0.050(2)	0.010(1)	0.010(1)	0.016(1)
C(9)	2*i*		0.2217(5)	0.4558(3)	0.0843(2)	0.068(2)	0.067(2)	0.043(2)	0.015(2)	0.012(1)	0.011(1)
C(10)	2*i*		0.1500(5)	0.3118(3)	0.1975(2)	0.059(2)	0.058(2)	0.053(2)	0.013(1)	0.015(1)	0.012(1)
C(11)	2*i*		0.0608(6)	0.7235(3)	0.2462(2)	0.067(2)	0.056(2)	0.054(2)	0.005(2)	0.018(2)	0.008(1)
C(12A)	2*i*	0.676	0.240(4)	0.800(3)	0.307(1)	0.09(1)	0.09(1)	0.10(1)	0.035(8)	0.039(9)	0.032(9)
C(13A)	2*i*	0.676	0.194(5)	0.929(2)	0.336(1)	0.16(2)	0.045(8)	0.075(5)	0.000(7)	0.046(8)	–0.010(5)
C(14A)	2*i*	0.676	–0.003(3)	0.964(2)	0.3058(9)	0.12(2)	0.040(4)	0.09(1)	0.015(9)	0.05(1)	–0.004(6)
S(2A)	2*i*	0.676	–0.1451(7)	0.8265(4)	0.2346(3)	0.088(2)	0.062(2)	0.098(2)	0.026(2)	0.030(2)	0.011(2)
C(12B)	2*i*	0.324	–0.170(6)	0.810(4)	0.221(2)	0.06(1)	0.08(2)	0.14(2)	0.02(1)	–0.04(1)	–0.05(1)
C(13B)	2*i*	0.324	–0.072(6)	0.947(5)	0.287(2)	0.05(1)	0.08(2)	0.07(1)	–0.001(9)	0.002(8)	0.02(1)
C(14B)	2*i*	0.324	0.153(9)	0.965(5)	0.342(3)	0.10(2)	0.05(2)	0.06(1)	0.01(1)	0.02(1)	–0.01(1)
S(2B)	2*i*	0.324	0.273(3)	0.799(1)	0.3159(7)	0.081(4)	0.067(4)	0.063(3)	0.008(3)	–0.004(3)	–0.004(3)
C(15A)	2*i*	0.605	0.328(3)	0.195(2)	0.096(1)	0.079(6)	0.042(6)	0.046(5)	0.017(4)	0.036(4)	0.009(5)
C(16A)	2*i*	0.605	0.453(1)	0.2279(6)	0.0226(4)	0.117(5)	0.073(4)	0.070(4)	0.024(3)	0.052(4)	0.007(3)
C(17A)	2*i*	0.605	0.419(3)	0.097(2)	0.145(1)	0.18(2)	0.12(1)	0.12(1)	0.07(1)	0.09(1)	0.005(9)
C(15B)	2*i*	0.395	0.353(5)	0.225(3)	0.087(2)	0.14(2)	0.06(1)	0.08(1)	0.02(1)	0.02(1)	0.031(7)
C(16B)	2*i*	0.395	0.162(2)	0.120(1)	0.0387(6)	0.126(9)	0.117(8)	0.089(7)	0.044(7)	–0.025(6)	–0.034(6)
C(17B)	2*i*	0.395	0.467(4)	0.100(2)	0.155(1)	0.088(7)	0.053(7)	0.084(9)	0.038(6)	0.007(6)	0.026(6)
N(1)	2*i*		0.3066(4)	0.3452(3)	0.1389(1)	0.062(2)	0.058(2)	0.046(1)	0.016(1)	0.017(1)	0.009(1)
O(1)	2*i*		–0.2189(3)	0.4187(3)	0.3020(1)	0.050(1)	0.123(2)	0.065(1)	0.018(1)	0.016(1)	0.027(1)
O(2)	2*i*		–0.1745(3)	0.5321(2)	0.1514(1)	0.053(1)	0.069(1)	0.056(1)	0.012(1)	0.0029(9)	0.0105(9)
S(1)	2*i*		–0.0716(1)	0.2961(1)	0.45887(5)	0.0636(6)	0.1149(8)	0.0657(5)	0.0161(5)	0.0275(4)	0.0292(5)

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