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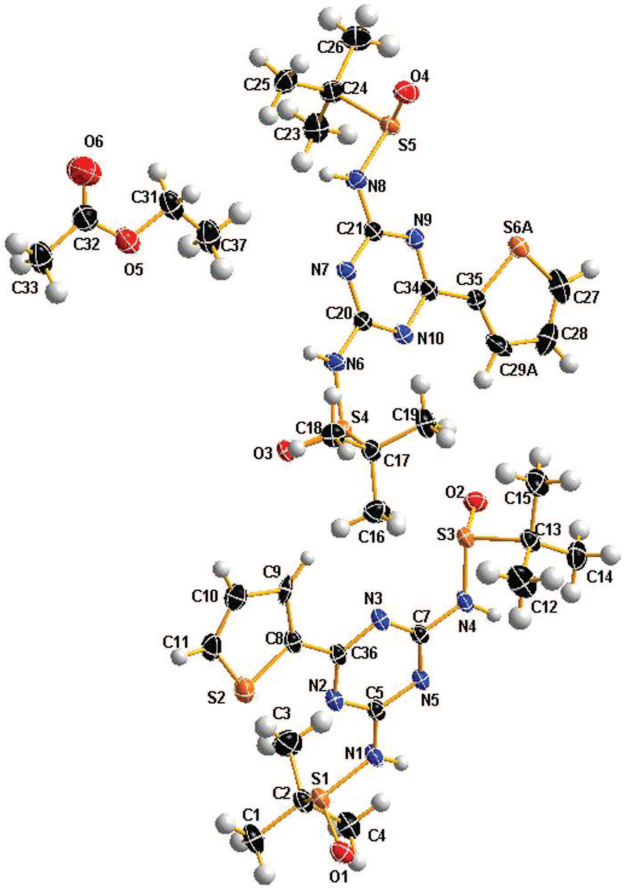
The crystal structure of *N*,*N*′-(6-(thiophen-2-yl)-1,3,5-triazine-2,4-diyl)bis(2-methylpropane-2-sulfonamide) – ethyl acetate(2/1), $C_{34}H_{54}N_{10}O_6S_6$



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Abstract

$C_{34}H_{54}N_{10}O_6S_6$, monoclinic, $P2_1$ (no. 4), $a = 11.8434(5)$ Å, $b = 11.2298(6)$ Å, $c = 17.0706(8)$ Å, $\beta = 94.661(2)°$, $V = 2262.86(19)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0287$, $wR_{ref}(F^2) = 0.0809$, $T = 150(2)$ K.

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Table 1: Data collection and handling.

Crystal:	Stripe, colorless
Size:	0.13 × 0.05 × 0.04 mm
Wavelength:	Cu $K\alpha$ radiation (1.54184 Å)
μ:	3.22 mm^{-1}
Diffractometer, scan mode:	Bruker SMART, φ and ω-scans
θ_{max}, completeness:	63.8°, >97%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	17958, 6789, 0.027
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 6602
$N(param)_{refined}$:	539
Programs:	Bruker programs [1], SHELX [2]

The asymmetric unit of the title crystal structure is shown in the figure (The disorder of the thiophen-2-yl moiety is omitted for clarity). 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

Under the protection of N_2, Mg (4.80 g, 0.20 mol) and I_2 (1.02 g, 0.004 mol) were added to the solution of tetrahydrofuran (150 mL). After 10 min 2-bromothiophene (32.60 g, 0.20 mol) was added to the suspension mixture dropwisely. When Mg disappeared, the reaction mixture was cooled to −15 °C. A solution of 2,4,6-trichloro-1,3,5-triazine (36.88 g, 0.20 mol) in tetrahydrofuran was added to the above solution of thiophen-2-yl magnesium bromide within 5 min. After 5 h, the mixture was filtered and the filtrate was evaporated to get a yellow solid, which was purified by chromatography on silica gel to get 2,4-dichloro-6-(thiophen-2-yl)-1,3,5-triazine (26.0 g, yield 56%) as a yellow solid. To a suspension of NaH (1.92 g, 0.08 mol) in 60 mL of tetrahydrofuran was added *tert*-butanesulfinamide (9.70 g, 0.08 mol). The mixture was stirred at room temperature for 30 min. Then a solution of 2,4-dichloro-6-(thiophen-2-yl)-1,3,5-triazine (4.64 g, 0.02 mol) in 20 mL of tetrahydrofuran was added slowly (about in 5 min). After stirring at reflux for 12 h, the reaction was quenched with 2 mL of MeOH and evaporated to get a yellow solid

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
O1	−0.1052(2)	−1.5389(2)	−0.42997(13)	0.0337(5)
O2	−0.61088(19)	−1.0627(2)	−0.18856(13)	0.0319(5)
O3	−0.35966(17)	−0.6373(2)	−0.31603(13)	0.0300(5)
O4	−0.8434(2)	−0.1386(3)	−0.06375(16)	0.0438(6)
O5	−0.2122(2)	−0.1237(3)	−0.16304(16)	0.0453(7)
O6	−0.1972(4)	0.0745(4)	−0.1535(3)	0.0902(14)
S1	−0.09513(6)	−1.44643(7)	−0.36826(4)	0.02623(18)
S2	−0.09269(7)	−1.04271(9)	−0.44628(5)	0.0376(2)
S3	−0.59102(6)	−1.05917(7)	−0.27347(4)	0.02476(17)
S4	−0.48283(6)	−0.64982(7)	−0.30672(4)	0.02339(17)
S5	−0.76661(6)	−0.23224(8)	−0.02997(5)	0.02979(19)
S6B[a]	−0.7619(4)	−0.8060(4)	−0.1217(3)	0.0329(10)
S6A[b]	−0.8900(3)	−0.6345(3)	−0.04373(16)	0.0299(7)
N1	−0.2257(2)	−1.4272(3)	−0.33706(17)	0.0294(6)
H1	−0.2613	−1.4884	−0.3182	0.035*
N2	−0.2199(2)	−1.2266(3)	−0.36863(15)	0.0265(6)
N3	−0.3769(2)	−1.1035(3)	−0.34428(16)	0.0257(6)
N4	−0.5319(2)	−1.1924(3)	−0.29274(17)	0.0276(6)
H4	−0.5710	−1.2578	−0.2862	0.033*
N5	−0.3813(2)	−1.3116(3)	−0.31532(15)	0.0243(6)
N6	−0.5204(2)	−0.5172(3)	−0.27089(16)	0.0284(6)
H6	−0.4926	−0.4530	−0.2918	0.034*
N7	−0.6018(2)	−0.3882(3)	−0.18881(15)	0.0238(5)
N8	−0.6758(2)	−0.2640(3)	−0.09939(15)	0.0289(6)
H8	−0.6329	−0.2069	−0.1162	0.035*
N9	−0.7260(2)	−0.4629(3)	−0.09735(15)	0.0258(6)
N10	−0.6434(2)	−0.5971(3)	−0.18516(15)	0.0245(6)
C1	0.0955(3)	−1.5356(4)	−0.3028(3)	0.0453(10)
H1A	0.0941	−1.5903	−0.3476	0.068*
H1B	0.1419	−1.5698	−0.2582	0.068*
H1C	0.1279	−1.4592	−0.3173	0.068*
C36	−0.2725(2)	−1.1229(3)	−0.36833(17)	0.0240(6)
C2	−0.0251(3)	−1.5162(3)	−0.2798(2)	0.0320(8)
C3	−0.0282(4)	−1.4259(5)	−0.2133(2)	0.0507(11)
H3A	−0.0104	−1.3466	−0.2327	0.076*
H3B	0.0278	−1.4481	−0.1703	0.076*
H3C	−0.1039	−1.4252	−0.1941	0.076*
C4	−0.0782(3)	−1.6351(4)	−0.2619(2)	0.0371(8)
H4A	−0.1573	−1.6228	−0.2508	0.056*
H4B	−0.0364	−1.6711	−0.2159	0.056*
H4C	−0.0753	−1.6882	−0.3072	0.056*
C5	−0.2768(3)	−1.3183(3)	−0.34064(19)	0.0255(7)
C7	−0.4252(2)	−1.2020(3)	−0.31812(17)	0.0236(7)
C8	−0.2132(3)	−1.0207(3)	−0.39833(19)	0.0259(7)
C9	−0.2482(3)	−0.8959(3)	−0.39191(19)	0.0269(7)
H9	−0.3114	−0.8659	−0.3673	0.032*
C10	−0.1638(3)	−0.8276(4)	−0.4320(2)	0.0382(8)
H10A	−0.1668	−0.7433	−0.4367	0.046*
C11	−0.0803(3)	−0.8949(4)	−0.4621(2)	0.0382(8)
H11	−0.0211	−0.8613	−0.4893	0.046*
C12	−0.7077(4)	−1.0887(5)	−0.4143(2)	0.0581(13)
H12A	−0.6710	−1.1649	−0.4242	0.087*
H12B	−0.6580	−1.0232	−0.4275	0.087*
H12C	−0.7795	−1.0833	−0.4469	0.087*
C13	−0.7302(3)	−1.0807(3)	−0.32801(19)	0.0297(7)
C14	−0.7906(3)	−1.1882(4)	−0.2998(3)	0.0438(9)
H14A	−0.7981	−1.1812	−0.2433	0.066*
H14B	−0.7471	−1.2600	−0.3101	0.066*
H14C	−0.8660	−1.1937	−0.3278	0.066*
C15	−0.7941(3)	−0.9660(4)	−0.3109(3)	0.0489(10)
H15A	−0.8694	−0.9676	−0.3393	0.073*
H15B	−0.7517	−0.8971	−0.3281	0.073*
H15C	−0.8019	−0.9601	−0.2543	0.073*
C16	−0.5190(3)	−0.7508(4)	−0.4478(2)	0.0404(9)
H16A	−0.5350	−0.8203	−0.4158	0.061*
H16B	−0.4377	−0.7476	−0.4549	0.061*
H16C	−0.5618	−0.7570	−0.4993	0.061*
C17	−0.5539(3)	−0.6381(3)	−0.40671(18)	0.0276(7)
C18	−0.5149(3)	−0.5273(3)	−0.4475(2)	0.0338(8)
H18A	−0.5444	−0.5284	−0.5028	0.051*
H18B	−0.4319	−0.5254	−0.4442	0.051*
H18C	−0.5430	−0.4565	−0.4218	0.051*
C19	−0.6796(3)	−0.6360(4)	−0.3966(2)	0.0419(9)
H19A	−0.6998	−0.5597	−0.3736	0.063*
H19B	−0.6985	−0.7011	−0.3618	0.063*
H19C	−0.7219	−0.6459	−0.4480	0.063*
C20	−0.5907(3)	−0.5012(3)	−0.21180(18)	0.0236(6)
C21	−0.6680(3)	−0.3749(3)	−0.12933(18)	0.0244(6)
C23	−0.5845(4)	−0.2591(4)	0.0738(2)	0.0463(10)
H23A	−0.6290	−0.3243	0.0939	0.069*
H23B	−0.5328	−0.2274	0.1165	0.069*
H23C	−0.5407	−0.2889	0.0317	0.069*
C24	−0.6636(3)	−0.1613(4)	0.04210(19)	0.0354(8)
C25	−0.6014(3)	−0.0582(4)	0.0067(2)	0.0394(8)
H25A	−0.5486	−0.0894	−0.0296	0.059*
H25B	−0.5591	−0.0134	0.0488	0.059*
H25C	−0.6563	−0.0054	−0.0218	0.059*
C26	−0.7379(4)	−0.1168(5)	0.1052(2)	0.0559(12)
H26A	−0.7883	−0.0539	0.0833	0.084*
H26B	−0.6897	−0.0851	0.1498	0.084*
H26C	−0.7832	−0.1830	0.1231	0.084*
C27	−0.9234(3)	−0.7734(4)	−0.0364(3)	0.0473(10)
H27A[b]	−0.9838	−0.7981	−0.0068	0.057*
H27[a]	−0.9875	−0.7900	−0.0082	0.057*
C28	−0.8621(4)	−0.8522(4)	−0.0738(3)	0.0481(10)
H28[b]	−0.8786	−0.9349	−0.0716	0.058*
H28A[a]	−0.8705	−0.9363	−0.0745	0.058*
C29B[a]	−0.8705(16)	−0.6535(17)	−0.0478(12)	0.040(6)
H29B[a]	−0.8929	−0.5812	−0.0248	0.048*
C29A[b]	−0.7815(11)	−0.7838(14)	−0.1124(9)	0.046(4)
H29A[b]	−0.7310	−0.8200	−0.1458	0.055*
C31	−0.3151(3)	−0.1191(5)	−0.1233(2)	0.0471(10)
H31A	−0.3764	−0.0810	−0.1574	0.057*
H31B	−0.3029	−0.0725	−0.0741	0.057*
C32	−0.1605(4)	−0.0196(4)	−0.1728(2)	0.0460(10)
C33	−0.0528(3)	−0.0354(5)	−0.2107(3)	0.0536(11)
H33A	0.0061	−0.0645	−0.1717	0.080*
H33B	−0.0294	0.0411	−0.2317	0.080*
H33C	−0.0643	−0.0932	−0.2536	0.080*
C34	−0.7123(2)	−0.5695(3)	−0.12818(17)	0.0235(6)
C35	−0.7806(3)	−0.6656(3)	−0.09926(19)	0.0271(7)
C37	−0.3462(4)	−0.2460(5)	−0.1054(3)	0.0557(12)
H37A	−0.3566	−0.2913	−0.1545	0.084*
H37B	−0.4167	−0.2468	−0.0791	0.084*
H37C	−0.2853	−0.2821	−0.0709	0.084*

Occupancies: [a] = 0.417(6), [b] = 0.583(6).

which was dissolved in the mixture of CH_2Cl_2 and water. The organic layer was separated, washed with water, dried by anhydrous Na_2SO_4 and then filtered. The filtrate was evaporated to get a yellow solid, which was purified by chromatography on silica gel (PE:EA = 6:1) to afford 2,4-bis(*R*-tertbutylsulfonamido)-6-(thiophen-2-yl)-1,3,5-triazine (3.05 g, yield 38%). **^{1}H NMR**: (400 MHz, chloroform-*d*) δ9.99 (s, 2H), 8.13 (s, 1H), 7.60 (d, J = 8 Hz, 1H), 7.17 (t, J = 3.4 Hz, 1H), 1.37 (s, 18*H*). Crystals were obtained by recrystallization with ethyl acetate at room temperature.

Experimental details

The data were scaled and corrected for absorption using SADABS-2016/2 (Bruker, APEX-II). The hydrogen atoms were placed at calculated positions and refined as riding atoms with isotropic displacement parameters. The structure was refined as an inversion twin giving a Flack parameter of 0.024(14). The disorder of the thiophen-2yl moiety is handled with an aproximately 1/1 ratio.

Discussion

As an important aromatic unit, thiophene ring was widely used in constructing many novel heterocyclic compounds. Due to its unique pharmacological activity [3, 4], high catalytic activity [5] and good photoelectric property [6] thiophene derivatives were widely used in the areas of pharmacy, chemical industry, agriculture [7] and organic semiconductor materials [8, 9]. Developing novel chiral compounds containing thiophene rings and studying its properties have drawn more and more attentions of researchers in recent years. In this paper, 2,4-bis(*R*-tertbutylsulfonamido)-6-(thiophen-2-yl)-1,3,5- triazine was synthesized using 1,3,5-triazine as starting material. Its structure was characterized by ^{1}H NMR and X-ray diffraction.

There are two cystallographically independent molecules ($2(C_{15}H_{23}N_5O_2S_3)$) and one solvent molecule ($C_4H_8O_2$) in the asymmetric unit, in which all bond lengths are in normal ranges [10]. In one of independent molecule ($C_{15}H_{23}N_5\ O_2\ S_3$), the typical bond length of S1—N1, S1—O1, N1—C5 and S2—C8 are 1.690(3) Å, 1.477(3) Å, 1.364(5) Å, 1.720(3) Å respectively. The angle of C11—S2—C8 is 91.23(18)°, which is smaller than that of C11—C10—C9 is 115.0(4)°. The torsion angle of C9—C8—C36—N3 is 11.318°, which demonstrated that thiophene ring and the 1,3,5-triazine ring were not coplanar. In molecular packing, classical (i) and non-classical (ii) hydrogen bonds were observed as following: (i) N1—H1···O3′ hydrogen bond (d(H1···O3′) = 2.04 Å), N4—H4···N7′ hydrogen bond (d(H4···N7′) = 2.27 Å), N6—H6···N5″ hydrogen bond (d(H6···N5″) = 2.12 Å), N8—H8···O2″ hydrogen bond (d(H8···O2″) = 2.07 Å); (ii) C4—H4A···O3′ hydrogen bond (d(H4A···O3′) = 2.56 Å), C10—H10A···O1″ hydrogen bond (d(H10A···O1″) = 2.41 Å), C12—H12C···O1‴ hydrogen bond (d(H12C···O1‴) = 2.46 Å), C28—H28A···O4′ hydrogen bond (d(H28A···O4′) = 2.30 Å), (′ = x, $y-1$, z; ″ = x, $y+1$, z; ‴ = $-x-1$, $y+0.5$, $-z-1$).

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