Zhenyu Zuo*, Fuhou Lei, Yang Dai and Lu Wang

The crystal structure of 2-phenyl-4,6-bis(*R*-tert-butylsulfonamido)-1,3,5-triazine – ethyl acetate (2/1), C₃₈H₅₈N₁₀O₆S₄

Table 1: Data collection and handling.

Crystal:	Clear light colourless
Size:	0.5 × 0.4 × 0.3 mm
Wavelength:	Cu K α radiation, $\lambda = 1.54178 \text{ \AA}$
μ :	2.30 mm ⁻¹
Diffractometer, scan mode:	Bruker APEX-II CCD diffractometer, φ and ω scans
θ_{max} , completeness:	68.2°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	30293, 8431, 0.046
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 8224
$N(\text{param})_{\text{refined}}$:	537
Programs:	Bruker programs [1], SHELX[2]

<https://doi.org/10.1515/ncrs-2017-0292>

Received February 6, 2018; accepted April 25, 2018; available online May 18, 2018

Abstract

C₃₈H₅₈N₁₀O₆S₄, monoclinic, $P2_1$ (no. 4), $a = 11.9542(5) \text{ \AA}$, $b = 11.4057(5) \text{ \AA}$, $c = 17.2763(8) \text{ \AA}$, $\beta = 96.380(1)^\circ$, $V = 2340.97(18) \text{ \AA}^3$, $Z = 4$, $R_{\text{gt}}(F) = 0.0325$, $wR_{\text{ref}}(F_2) = 0.0836$, $T = 200 \text{ K}$.

CCDC no.: 1563249

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 N₂, Mg (3.84 g, 0.160 mol) and I₂ (1.02 g, 0.004 mol) were added to the solution of tetrahydrofuran (150 mL). After 10 mins bromobenzene (25 g, 0.160 mol)

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.40769(5)	0.78248(6)	0.23155(4)	0.03064(15)
S2	0.89296(5)	0.39931(6)	0.13515(4)	0.03306(16)
S3	0.51085(5)	0.20116(5)	0.19187(3)	0.02871(14)
S4	0.23671(6)	0.60015(6)	0.46966(4)	0.03319(15)
O1	0.87458(19)	0.3043(2)	0.07720(12)	0.0419(5)
O2	0.38248(18)	0.7759(2)	0.31350(12)	0.0398(5)
O3	0.63326(16)	0.21359(18)	0.18538(12)	0.0354(4)
O4	0.16248(18)	0.6952(2)	0.43785(13)	0.0432(5)
N1	0.61810(19)	0.7383(2)	0.16220(13)	0.0301(5)
N2	0.61384(19)	0.5339(2)	0.19061(13)	0.0303(5)
N3	0.77421(19)	0.6182(2)	0.14149(14)	0.0315(5)
N4	0.4665(2)	0.6523(2)	0.21369(15)	0.0342(5)
H4	0.4287	0.5879	0.2212	0.041*
N5	0.7682(2)	0.4212(2)	0.17092(15)	0.0362(5)
H5	0.7356	0.3622	0.1924	0.043*
N6	0.2794(2)	0.3762(2)	0.40077(13)	0.0317(5)
N7	0.35589(19)	0.2500(2)	0.31097(13)	0.0286(5)
N8	0.39602(19)	0.45497(19)	0.31038(13)	0.0288(5)
N9	0.3257(2)	0.5732(2)	0.40131(14)	0.0360(5)
H9	0.3674	0.6305	0.3860	0.043*
N10	0.4738(2)	0.3315(2)	0.22706(14)	0.0340(5)
H10	0.4994	0.3953	0.2066	0.041*
C1	0.7386(2)	0.9358(3)	0.11704(18)	0.0369(6)
H1	0.6739	0.9487	0.1432	0.044*
C2	0.7924(3)	1.0297(3)	0.0864(2)	0.0438(7)
H2	0.7640	1.1069	0.0912	0.053*
C3	0.8877(3)	1.0114(3)	0.0488(2)	0.0446(7)

*Corresponding author: Zhenyu Zuo, College of Pharmacy, Shaanxi University of Chinese Medicine, Xi'an, Shaanxi 712046, P.R. China; and Medical University of the Air Force, Xi'an 710032, P.R. China, e-mail: 123263064@qq.com

Fuhou Lei: Guangxi Key Laboratory of Chemistry and Engineering of Forest Products, Nanning 530006, China

Yang Dai: College of Pharmacy, Shaanxi Institute of International, Trade&Commerce, Xi'an, Shaanxi 712046, China

Lu Wang: College of Pharmacy, Shaanxi University of Chinese Medicine, Xi'an, Shaanxi 712046, China

Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
H3	0.9245	1.0761	0.0279	0.054*
C4	0.9290(3)	0.8998(3)	0.04158(18)	0.0404(7)
H4A	0.9940	0.8877	0.0156	0.048*
C5	0.8758(2)	0.8047(3)	0.07226(17)	0.0347(6)
H5A	0.9051	0.7278	0.0678	0.042*
C6	0.7795(2)	0.8223(2)	0.10949(15)	0.0289(5)
C7	0.7205(2)	0.7205(2)	0.13985(15)	0.0280(5)
C8	0.5705(2)	0.6422(2)	0.18811(15)	0.0284(5)
C9	0.7176(2)	0.5281(2)	0.16715(16)	0.0296(5)
C10	0.2725(3)	0.7653(3)	0.17097(17)	0.0395(7)
C11	0.3002(4)	0.7561(5)	0.0870(2)	0.0684(12)
H11A	0.3503	0.8205	0.0761	0.103*
H11B	0.2305	0.7608	0.0515	0.103*
H11C	0.3375	0.6810	0.0797	0.103*
C12	0.2108(3)	0.8793(4)	0.1831(3)	0.0595(9)
H12A	0.1960	0.8852	0.2376	0.089*
H12B	0.1394	0.8805	0.1492	0.089*
H12C	0.2573	0.9457	0.1702	0.089*
C13	0.2083(3)	0.6615(4)	0.1965(3)	0.0587(10)
H13A	0.2500	0.5895	0.1884	0.088*
H13B	0.1343	0.6581	0.1658	0.088*
H13C	0.1986	0.6694	0.2518	0.088*
C14	0.9727(3)	0.3355(3)	0.22198(19)	0.0430(7)
C15	1.0885(3)	0.3141(5)	0.1945(3)	0.0626(10)
H15A	1.0818	0.2550	0.1531	0.094*
H15B	1.1408	0.2862	0.2383	0.094*
H15C	1.1168	0.3875	0.1745	0.094*
C16	0.9213(3)	0.2210(4)	0.2450(2)	0.0563(9)
H16A	0.8450	0.2354	0.2585	0.084*
H16B	0.9676	0.1876	0.2900	0.084*
H16C	0.9181	0.1658	0.2013	0.084*
C17	0.9803(4)	0.4273(5)	0.2855(3)	0.0775(14)
H17A	1.0045	0.5020	0.2648	0.116*
H17B	1.0350	0.4022	0.3288	0.116*
H17C	0.9063	0.4371	0.3041	0.116*
C18	0.1408(2)	0.1975(3)	0.44344(17)	0.0366(6)
H18	0.1279	0.2756	0.4592	0.044*
C19	0.0760(3)	0.1064(3)	0.46787(19)	0.0454(7)
H19	0.0179	0.1221	0.4997	0.055*
C20	0.0964(3)	−0.0071(3)	0.4456(2)	0.0486(8)
H20	0.0520	−0.0693	0.4624	0.058*
C21	0.1804(3)	−0.0312(3)	0.3993(2)	0.0443(7)
H21	0.1944	−0.1098	0.3849	0.053*
C22	0.2443(3)	0.0594(3)	0.37380(17)	0.0363(6)
H22	0.3014	0.0430	0.3412	0.044*
C23	0.2249(2)	0.1742(2)	0.39578(16)	0.0302(6)
C24	0.2915(2)	0.2722(2)	0.36819(15)	0.0273(5)
C25	0.4062(2)	0.3445(2)	0.28556(15)	0.0275(5)
C26	0.3333(2)	0.4644(2)	0.36991(15)	0.0283(5)
C27	0.4399(2)	0.2135(3)	0.09162(16)	0.0354(6)
C28	0.3145(3)	0.2173(4)	0.0993(2)	0.0555(9)
H28A	0.2952	0.1541	0.1338	0.083*
H28B	0.2721	0.2072	0.0478	0.083*
H28C	0.2954	0.2931	0.1211	0.083*
C29	0.4718(3)	0.1009(4)	0.0521(2)	0.0510(8)
H29A	0.5532	0.0996	0.0494	0.077*

Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
H29B	0.4324	0.0974	−0.0007	0.077*
H29C	0.4503	0.0332	0.0821	0.077*
C30	0.4811(3)	0.3208(3)	0.05165(18)	0.0465(7)
H30A	0.4561	0.3917	0.0768	0.070*
H30B	0.4504	0.3205	−0.0034	0.070*
H30C	0.5635	0.3197	0.0556	0.070*
C31	0.3405(3)	0.6655(3)	0.54442(18)	0.0449(7)
C32	0.4022(3)	0.7682(3)	0.5129(2)	0.0518(8)
H32A	0.4505	0.7398	0.4746	0.078*
H32B	0.4485	0.8069	0.5558	0.078*
H32C	0.3474	0.8242	0.4879	0.078*
C33	0.2672(4)	0.7051(5)	0.6066(2)	0.0721(12)
H33A	0.2179	0.7691	0.5860	0.108*
H33B	0.3155	0.7326	0.6527	0.108*
H33C	0.2214	0.6391	0.6212	0.108*
C34	0.4188(4)	0.5665(4)	0.5745(2)	0.0639(10)
H34A	0.3740	0.4985	0.5871	0.096*
H34B	0.4659	0.5924	0.6215	0.096*
H34C	0.4669	0.5447	0.5344	0.096*
O6	0.7875(2)	0.7031(3)	0.34262(15)	0.0596(7)
O5	0.8043(5)	0.8988(6)	0.3534(5)	0.149(2)
C35	0.6573(4)	0.5825(6)	0.3969(3)	0.0823(16)
H35A	0.6548	0.5364	0.3489	0.123*
H35B	0.5835	0.5799	0.4166	0.123*
H35C	0.7143	0.5497	0.4361	0.123*
C36	0.6866(4)	0.7067(6)	0.3805(2)	0.0740(14)
H36A	0.6248	0.7442	0.3462	0.089*
H36B	0.6992	0.7520	0.4295	0.089*
C37	0.8379(4)	0.8076(4)	0.3325(2)	0.0633(10)
C38	0.9444(4)	0.7926(5)	0.2967(3)	0.0691(11)
H38A	1.0050	0.7708	0.3371	0.104*
H38B	0.9637	0.8664	0.2723	0.104*
H38C	0.9348	0.7308	0.2572	0.104*

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 (31.75 g, 0.175 mol) in tetrahydrofuran was added to the above solution of PhMgBr in 5 min. After 2 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 the 2,4-dichloro-6-phenyl-1,3,5-triazine (27.85 g, yield 77%) as a white solid.

To a suspension of NaH (1.2 g, 0.05 mol) in 60 mL of tetrahydrofuran was added *tert*-butanesulfinamide (6.06 g, 0.05 mol). The mixture was stirred at room temperature for 30 mins. Then a solution of 2,4-dichloro-6-phenyl-1,3,5-triazine (3.77 g, 0.0167 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 which was dissolved in the mixture of CH₂Cl₂ and water. The organic layer was separated, washed with water, dried by anhydrous Na₂SO₄ and then filtered. The filtrate was evaporated to get a yellow solid, which

was purified by chromatography on silica gel (PE:EA = 4:1) to afford 2-phenyl-4,6-bis(*R*-tertbutylsulfonamido)-1,3,5-triazine (3.43 g, yield 52%). 1H NMR (400 MHz, chloroform-*d*) δ 9.93 (s, 4H), 8.52–8.40 (m, 4H), 7.59–7.48 (m, 6H), 4.14 (dd, J = 8 Hz, 2H), 2.07 (s, 3H), 1.40 (s, 36H), 1.29 (t, J = 8 Hz, 3H). 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 CCD). The hydrogen atoms were placed at calculated positions and refined as riding atoms with isotropic displacement parameters.

Discussion

Chiral compounds, which was synthesized mainly by catalytic asymmetric synthesis in organic chemistry, have widely applications in functional materials, pharmaceuticals, agricultural chemicals, biological reagents and so on [3]. In the field of asymmetric synthesis, sulfinamides have attracted attentions owing to its significant enantioselectivity in several transition-metal-catalyzed asymmetric reactions (such as asymmetric allylic substitutions [4], asymmetric addition of arylboronic acids to cycloalkenones [5], asymmetric reduction of aldehydes, asymmetric Michael addition [6] and so on). Therefore, design and synthesis of new chiral sulfinamides becomes an important subject in asymmetric catalysis. In this paper, a new chiral sulfinamide 2-phenyl-4,6-bis(*R*-tert-butylsulfonamido)-1,3,5-triazine was synthesized using *R*-tert-butylsulfenamide as starting materials. This chiral sulfinamide can be used as chiral ligands in transition-metal-catalyzed asymmetric reactions [7]. The structure of 2-phenyl-4,6-bis(*R*-tert-butylsulfonamido)-1,3,5-triazine was characterized by 1H NMR and X-ray diffraction.

There are two crystallographically independent molecules (2 $C_{17}H_{25}N_5O_2S_2$) and one solvent molecule ($C_4H_8O_2$) in the asymmetric unit, in which all bond lengths are in normal ranges. In one of independent molecule ($C_{17}H_{25}N_5O_2S_2$), the bond length of N1–C7 is 1.339(3) Å, which is a little shorter than that of C2–C3 1.390(5) Å. The bond length of

N5–C9, S2–N5, S2–O1 and S2–C14 are 1.360(4) Å, 1.695(2) Å, 1.475(2) Å and 1.836(3) Å, respectively. The angles of C1–C2–C3, C8–N1–C7, C9–N5–S2 and O1–S2–N5 are 120.2(3)°, 114.2(2)°, 121.32(19)° and 106.56(13)°, respectively. The torsion angle of C1–C6–C7–N1 is 11.17°, which demonstrated that phenyl moiety and the 1,3,5-triazine ring were not on the same plane. The two independent molecules can form dimers mainly by four intermolecular hydrogen bonds as following: N4–H4...N8 ($d(H4...N8) = 2.23$ Å), N5–H5...O3 ($d(H5...O3) = 2.09$ Å), N9–H9...O2 ($d(H9...O2) = 2.10$ Å) and N10–H10...N2 ($d(H10...N2) = 2.13$ Å).

Acknowledgements: We acknowledge the supports by Key Project of Shaanxi Provincial Education Department (17JS029), Natural Science Basic Research Program of Shaanxi (2017JM8070). China Postdoctoral Science Foundation funded project (2016M602994).

References

1. Bruker. APEX2, SAINT and SADABS. Bruker AXS Inc., Madison, Wisconsin, USA (2009).
2. Sheldrick, G. M.: A short history of SHELX. *Acta Crystallogr.* **A64** (2008) 112–122.
3. Belfrage, A. K.; Wakchaure, P.; Larhed, M.; Sandström, A.: Palladium-catalyzed carbonylation of aryl iodides with sulfinamides. *Eur. J. Org. Chem.* **2015** (2015) 7069–7074.
4. Mistico, L.; Ay, E.; Huynh, V.; Bourderioux, A.; Chemla, F.; Ferreira, F.; Oble, J.; Perez-Luna, A.; Poli, G.; Prestat, G.: Reactivity of tert-butanedisulfinamides in palladium-catalyzed allylic substitutions. *J. Organomet. Chem.* **760** (2014) 124–129.
5. Revu, O.; Uphade, M. B.; Prasad, K. R.: Synthesis and evaluation of C2-symmetric bis-sulfinamides as effective ligands in rhodium catalyzed addition of arylboronic acids to cycloalkenones. *Tetrahedron* **72** (2016) 5355–5362.
6. Reyes-Rangel, G.; Vargas-Caporalí, J.; Juaristi, E.: Asymmetric Michael addition reaction organocatalyzed by stereoisomeric pyrrolidine sulfinamides under neat conditions. A brief study of self-disproportionation of enantiomers. *Tetrahedron* **73** (2017) 4707–4718.
7. Yağci, N. K.; Güven, K.; Yildiz, G. D.: Crystal structure of aquadichlorido-(2,4,6-tri-2-pyridyl-1,3,5-triazine- k^3N,N',N'') nickel(II) monohydrate, $C_{18}H_{16}Cl_2N_6NiO_2$. *Z. Kristallogr. NCS* **232** (2017) 485–487.