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Crystal structure of 1-((*R*)-(2'-(dimethylamino)-[1,1'-binaphthalen]-2-yl))-3-((*S*)-2-hydroxy-1-phenylethyl)thiourea, C₃₁H₂₉N₃OS

Table 1: Data collection and handling.

Crystal:	Colorless block
Size:	0.15 × 0.14 × 0.13 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.15 mm ⁻¹
Diffractometer, scan mode:	Bruker APEX-II, φ and ω -scans
$\theta_{\max}$, completeness:	27.5°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	26545, 5937, 0.165
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2546
$N(\text{param})_{\text{refined}}$:	328
Programs:	Bruker programs [1], SHELX [2, 3]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.68888(18)	0.77208(9)	0.36710(8)	0.0544(4)
C1	0.0765(7)	0.7103(4)	0.3104(3)	0.0612(18)
H1	0.0234	0.7175	0.3525	0.073*
N1	0.4382(5)	0.6787(3)	0.3853(2)	0.0519(13)
H1B	0.4021	0.6312	0.4006	0.062*
O1	0.1738(5)	0.6867(3)	0.46570(19)	0.0714(12)
H1A	0.1631	0.6891	0.5086	0.107*
N2	0.6590(4)	0.6044(3)	0.3724(2)	0.0456(11)
H2A	0.7574	0.6036	0.3748	0.055*
C2	-0.0015(8)	0.6862(4)	0.2515(4)	0.075(2)
H2	-0.1067	0.6773	0.2540	0.090*
N3	0.9251(5)	0.4690(3)	0.4083(2)	0.0481(13)
C3	0.0736(10)	0.6749(4)	0.1882(4)	0.080(2)
H3	0.0206	0.6569	0.1483	0.096*
C6	0.2329(7)	0.7243(3)	0.3089(3)	0.0481(16)
C5	0.3069(8)	0.7149(4)	0.2449(3)	0.0669(18)
H5	0.4117	0.7250	0.2423	0.080*
C4	0.2293(10)	0.6909(4)	0.1853(4)	0.079(2)
H4	0.2815	0.6853	0.1428	0.094*
C7	0.3273(6)	0.7474(3)	0.3733(3)	0.0518(15)
H7	0.3854	0.7990	0.3618	0.062*
C8	0.2399(8)	0.7648(4)	0.4409(3)	0.0640(18)
H8A	0.3088	0.7878	0.4762	0.077*
H8B	0.1597	0.8064	0.4322	0.077*
C9	0.5893(7)	0.6821(3)	0.3750(3)	0.0438(14)
C10	0.5829(6)	0.5241(3)	0.3662(3)	0.0403(13)
C11	0.4944(6)	0.5092(4)	0.3047(2)	0.0456(15)
H11	0.4883	0.5506	0.2697	0.055*
C12	0.4184(7)	0.4338(4)	0.2972(3)	0.0509(16)
H12	0.3608	0.4242	0.2567	0.061*

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Abstract

C₃₁H₂₉N₃OS, orthorhombic, $P2_12_12_1$, (no. 19), $a = 8.7252(5)$ Å, $b = 15.6732(8)$ Å, $c = 18.9746(9)$ Å, $V = 2594.8(2)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0689$, $wR_{\text{ref}}(F^2) = 0.1179$, $T = 276(2)$ K.

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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

(*R*)-2'-Isothiocyanato-*N,N*-dimethyl-[1,1'-binaphthalen]-2-amine (0.56 mmol) was dissolved in tetrahydrofuran (10 mL) and heated to 50 °C. (*S*)-2-Amino-2-phenylethan-1-ol (0.67 mmol) was added to the solution, then the mixture was stirred for 4 h at 50 °C. After removal of the solvent, the residue was separated and purified by column chromatogra-

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Table 2 (continued)

Atom	x	y	z	U_{iso}^*/U_{eq}
C13	0.4252(6)	0.3710(4)	0.3487(3)	0.0417(14)
C14	0.3439(7)	0.2931(4)	0.3416(3)	0.0585(18)
H14	0.2839	0.2834	0.3019	0.070*
C15	0.3537(7)	0.2328(4)	0.3922(4)	0.069(2)
H15	0.2982	0.1824	0.3875	0.083*
C16	0.4460(8)	0.2450(4)	0.4517(3)	0.0695(19)
H16	0.4541	0.2023	0.4855	0.083*
C17	0.5236(7)	0.3194(4)	0.4600(3)	0.0531(16)
H17	0.5835	0.3269	0.5001	0.064*
C18	0.5163(6)	0.3852(3)	0.4100(2)	0.0381(13)
C19	0.5973(6)	0.4633(3)	0.4181(2)	0.0318(13)
C20	0.6966(6)	0.4799(3)	0.4805(3)	0.0377(13)
C21	0.6244(6)	0.5008(3)	0.5464(3)	0.0369(14)
C22	0.4624(7)	0.5080(3)	0.5540(3)	0.0469(15)
H22	0.3995	0.4953	0.5158	0.056*
C23	0.3984(7)	0.5329(4)	0.6156(3)	0.0618(18)
H23	0.2927	0.5391	0.6191	0.074*
C24	0.4924(9)	0.5494(4)	0.6746(3)	0.0677(19)
H24	0.4481	0.5657	0.7170	0.081*
C25	0.6446(8)	0.5417(4)	0.6699(3)	0.0575(18)
H25	0.7047	0.5523	0.7094	0.069*
C26	0.7155(7)	0.5180(3)	0.6064(3)	0.0459(15)
C27	0.8756(7)	0.5173(3)	0.5981(3)	0.0547(18)
H27	0.9375	0.5288	0.6368	0.066*
C28	0.9425(7)	0.5004(3)	0.5346(3)	0.0518(16)
H28	1.0488	0.5013	0.5309	0.062*
C29	0.8543(6)	0.4816(3)	0.4744(3)	0.0385(14)
C30	1.0844(7)	0.4977(4)	0.4014(3)	0.082(2)
H30A	1.0944	0.5540	0.4208	0.123*
H30B	1.1125	0.4987	0.3525	0.123*
H30C	1.1506	0.4593	0.4263	0.123*
C31	0.9028(6)	0.3867(3)	0.3738(3)	0.0578(16)
H31A	0.9884	0.3502	0.3839	0.087*
H31B	0.8949	0.3950	0.3238	0.087*
H31C	0.8104	0.3608	0.3910	0.087*

phy (petroleum ether/ethyl acetate = 10/1) to afford a white solid. Crystals were obtained by slow evaporation from the a mixture of petroleum ether and ethyl acetate (2:1 by volume) at room temperature.

Experimental details

Hydrogen atoms were placed in calculated position using a riding model. Aromatic C—H distances were set to 0.93 Å and N—H to 0.86 Å and their U_{iso} set to 1.2 times the U_{eq} for the atoms to which they are bonded. The weak diffracting crystal results in a high R^1 (all reflections) factor. The determination of absolute structure was concluded from the synthesis.

Discussion

In recent decades, chiral thiourea organocatalysts have attracted much attention due to their powerful catalytic

activity [4–7]. Meanwhile, C2 symmetric compounds represented by binaphthylamine is an important class of chiral ligands [8, 9], resolving agents [10] and catalysts [11]. Thus, the thiourea catalysts based on the binaphthyl skeleton own an efficient catalytic effect in many asymmetric synthesizes [12–14]. So we surmised that the bifunctional BINAM-thiourea derivatives bearing a chiral amino alcohol might have high catalytic activity.

The crystal structure of the title compound is only built up by the C₃₁H₂₉N₃OS molecules. Too far the molecules are linked by at least C30—H30...O1, O1—H1...S1 intermolecular hydrogen bonds. In the crystal structure, bond lengths and angles of all moieties are in their normal ranges and excellently fit with those of related compounds.

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References

1. Bruker. APEX2, SAINT and SADABS. Bruker AXS Inc., Madison, WI, USA (2014).
2. Sheldrick, G. M.: SHELXT – Integrated space-group and crystal-structure determination. *Acta Crystallogr.* **A71** (2015) 3–8.
3. Sheldrick, G. M.: Crystal structure refinement with SHELXL. *Acta Crystallogr.* **C71** (2015) 3–8.
4. Taylor, M. S.; Jacobsen, E. N.: Highly enantioselective catalytic acyl-pictet-spengler reactions. *J. Am. Chem. Soc.* **126** (2004) 10558–10559.
5. Wang, C. J.; Zhang, Z. H.; Dong, X. Q.; Wu, X. J.: Chiral amine-thioureas bearing multiple hydrogen bonding donors: highly efficient organocatalysts for asymmetric Michael addition of acetylacetone to nitroolefins. *Chem. Commun.* **12** (2008) 1431–1433.
6. Brown, A. R.; Uyeda, C.; Brotherton, C. A.; Jacobsen, E. N.: Enantioselective thiourea-catalyzed intramolecular Cope-type hydroamination. *J. Am. Chem. Soc.* **135** (2013) 6747–6749.
7. Bai, Z. S.; Ji, L.; Ge, Z. M.; Wang, X.; Li, R. T.: Asymmetric Michael addition reactions of nitroalkanes to 2-furanones catalyzed by bifunctional thiourea catalysts. *Org. Biomol. Chem.* **13** (2015) 5363–5366.
8. Sluijter, S. N.; Jongkind, L. J.; Elsevier, C. J.: Synthesis of BINAM-based chiral di-1,2,3-triazolylidene complexes and application of the Di-NHC Rh catalyst in enantioselective hydrosilylation. *Eur. J. Inorg. Chem.* **2015** (2015) 2948–2955.
9. Shi, M.; Duan, W. L.: Synthesis of an axially chiral Ir-NHC complex derived from BINAM. *Appl. Organometal. Chem.* **19** (2005) 40–44.
10. Wang, C.; Wu, E.; Pu, L.: Enantioselective fluorescent recognition by using a 1,1'-binaphthyl-2,2'-diamine derivative. *Eur. J. Org. Chem.* **2017** (2017) 4736–4739.
11. Wang, J.; Li, H.; Zu, L. S.; Wang, W.: Chiral binaphthyl-derived amine-thiourea organocatalyst-promoted asymmetric Morita-Baylis-Hillman reaction. *Org. Lett.* **7** (2005) 4293–4296.

12. Fleming, E. M.; McCabe, T.; Connon, S. J.: Novel axially chiral bis-arylthiourea-based organocatalysts for asymmetric Friedel-Crafts type reactions. *Tetrahedron Lett.* **47** (2006) 7037–7042.
13. Rabalakos, C.; Wulff, W. D.: Enantioselective organocatalytic direct addition of nitroalkanes to nitroalkenes promoted by unique bifunctional DMAP-thiourea. *J. Am. Chem. Soc.* **130** (2008) 13524–13525.
14. Moon, H. W.; Kim, D. Y.: Asymmetric conjugate addition of 1-fluoro-1-nitro(phenylsulfonyl) method to chalcones catalyzed by binaphthyl-derived organocatalyst. *Bull. Korean. Chem. Soc.* **33** (2012) 2845–2846.