Zeng-Bing Xu, Jing-Yuan He and Da-Bin Shi*

Crystal structure of 6,6'-((1*E*, 1'*E*)-(((1*R*, 2*R*)-1,2-diphenylethane-1,2-diyl) bis(azanylylidene)) bis(methanylylidene))bis(2-ethylphenol), $C_{32}H_{32}N_2O_2$

Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	0.13 × 0.12 × 0.10 mm
Wavelength:	Cu K α radiation (1.54184 Å)
μ :	0.59 mm ⁻¹
Diffractometer, scan mode:	SuperNova, ω
$\theta_{\max}$, completeness:	73.8°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	12,561, 5133, 0.024
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 5044
$N(\text{param})_{\text{refined}}$:	329
Programs:	CrysAlis ^{PRO} [1], SHELX [2, 3], Olex2 [4]

The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

A solution of 2-ethylphenol (2.4 g, 20 mmol), $MgCl_2$ (5.7 g, 60 mmol), paraformaldehyde (9.0 g, 0.1 mol), triethylamine (15 g 149 mmol) in acetonitrile (50 mL) was refluxed until full consumption of 2-ethylphenol (as indicated by TLC). The mixture was quenched with HCl (1 M) and extracted with ethyl acetate. The combined organic layers were washed with brine, dried with $MgSO_4$ and evaporated under reduced pressure. The crude residue was purified by column chromatography to obtain 3-ethyl-2-hydroxybenzaldehyde (2.2 g, 73% yield) as a yellow oil.

Synthesis of the title compound [5]: 3-ethyl-2-hydroxybenzaldehyde (1 g, 6.7 mmol) was dissolved in 30 mL of ethanol and (1*R*, 2*R*)-(-)-1,2-diphenylethane-1,2-diamine (0.71 g, 3.35 mmol) was added to the solution. The solution was heated to reflux for 4 h. The solvent was removed in vacuo and 1.48 g of the product was obtained as yellow solid (95% yield). Crystals were obtained by slow evaporation of an ethanol solution at room temperature over a period of seven days, yield: 0.72 g (93%). **M.p.:** 105–107 °C. **Elemental analysis** – found: C,

<https://doi.org/10.1515/ncrs-2021-0060>

Received February 10, 2021; accepted February 26, 2021;
published online March 12, 2021

Abstract

$C_{32}H_{32}N_2O_2$, orthorhombic, $P2_12_12_1$ (no. 19), $a = 9.78920(12)$ Å, $b = 12.71913(14)$ Å, $c = 20.9423(3)$ Å, $V = 2607.53(5)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0535$, $wR_{\text{ref}}(F^2) = 0.1365$, $T = 149.99(10)$ K.

CCDC no.: 2052199

*Corresponding author: Da-Bin Shi, School of Pharmaceutical Sciences, Zunyi Medical University, Zunyi 563000, P. R. China, E-mail: sdb007.student@sina.com. <https://orcid.org/0000-0002-2787-9524>

Zeng-Bing Xu and Jing-Yuan He, School of Pharmaceutical Sciences, Zunyi Medical University, Zunyi 563000, P. R. China

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

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
O1	0.6789 (3)	0.32760 (18)	0.83208 (10)	0.0439 (6)
H1	0.639420	0.351668	0.800779	0.066*
O2	0.7564 (2)	0.24223 (15)	0.68175 (9)	0.0322 (4)
H2	0.713378	0.297399	0.684240	0.048*
N1	0.5336 (2)	0.46340 (18)	0.76594 (10)	0.0246 (5)
N2	0.6306 (2)	0.40912 (18)	0.64151 (10)	0.0256 (5)
C1	0.3444 (3)	0.4322 (2)	0.69217 (12)	0.0273 (6)
C2	0.2207 (3)	0.4771 (3)	0.67516 (14)	0.0353 (6)
H2A	0.211018	0.549854	0.675520	0.042*
C3	0.1104 (3)	0.4138 (3)	0.65749 (16)	0.0445 (8)
H3	0.027836	0.444509	0.645943	0.053*
C4	0.1236 (3)	0.3059 (3)	0.65709 (16)	0.0441 (8)
H4	0.049815	0.264019	0.645477	0.053*
C5	0.2459 (3)	0.2599 (3)	0.67386 (15)	0.0404 (7)
H5	0.254620	0.187130	0.673122	0.048*
C6	0.3562 (3)	0.3220 (2)	0.69188 (13)	0.0316 (6)
H6	0.438045	0.290510	0.703796	0.038*
C7	0.4638 (3)	0.5024 (2)	0.70887 (12)	0.0260 (5)
H7	0.428554	0.572972	0.718036	0.031*
C8	0.5647 (3)	0.5104 (2)	0.65175 (12)	0.0250 (5)
H8	0.511601	0.527226	0.613415	0.030*
C9	0.6702 (3)	0.5964 (2)	0.66101 (12)	0.0258 (5)
C10	0.6379 (3)	0.6985 (2)	0.64190 (14)	0.0338 (6)
H10	0.551544	0.713166	0.625636	0.041*
C11	0.7340 (4)	0.7783 (2)	0.64705 (16)	0.0426 (8)
H11	0.712019	0.846188	0.634143	0.051*
C12	0.8614 (4)	0.7572 (3)	0.67116 (15)	0.0421 (7)
H12	0.925849	0.810646	0.674337	0.051*
C13	0.8941 (3)	0.6565 (3)	0.69071 (15)	0.0392 (7)
H13	0.980550	0.642483	0.707092	0.047*
C14	0.7985 (3)	0.5762 (2)	0.68602 (13)	0.0314 (6)
H14	0.820708	0.508760	0.699676	0.038*
C15	0.5159 (3)	0.5141 (2)	0.81800 (13)	0.0262 (5)
H15	0.465318	0.575987	0.816969	0.031*
C16	0.5716 (3)	0.4789 (2)	0.87885 (12)	0.0266 (5)
C17	0.6504 (3)	0.3873 (2)	0.88375 (13)	0.0344 (6)
C18	0.7057 (5)	0.3569 (3)	0.94287 (17)	0.0556 (9)
C19	0.6700 (5)	0.4170 (3)	0.99639 (16)	0.0583 (11)
H19	0.699968	0.395120	1.036385	0.070*
C20	0.5925 (4)	0.5070 (3)	0.99227 (15)	0.0464 (8)
H20	0.572640	0.545837	1.028721	0.056*
C21	0.5447 (3)	0.5388 (3)	0.93344 (14)	0.0356 (6)
H21	0.494133	0.600447	0.930036	0.043*
C22	0.8091 (5)	0.2626 (4)	0.9480 (2)	0.0645 (10)
H22A	0.855318	0.251761	0.907563	0.077*
H22B	0.877170	0.276721	0.980547	0.077*
C23	0.7290 (6)	0.1703 (5)	0.9649 (3)	0.0855 (16)
H23A	0.663891	0.156148	0.931702	0.128*
H23B	0.681683	0.182998	1.004286	0.128*
H23C	0.788601	0.110925	0.969793	0.128*
C24	0.6364 (3)	0.3722 (2)	0.58495 (12)	0.0270 (5)
H24	0.595413	0.409393	0.551853	0.032*
C25	0.7054 (3)	0.2731 (2)	0.57068 (12)	0.0268 (5)
C26	0.7155 (4)	0.2385 (2)	0.50772 (13)	0.0360 (7)
H26	0.675961	0.277889	0.475200	0.043*

Table 2: (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
C27	0.7833 (4)	0.1468 (3)	0.49300 (15)	0.0422 (8)
H27	0.789439	0.124098	0.450882	0.051*
C28	0.8424 (3)	0.0887 (2)	0.54176 (15)	0.0364 (7)
H28	0.888045	0.026869	0.531477	0.044*
C29	0.8360 (3)	0.1193 (2)	0.60534 (13)	0.0290 (6)
C30	0.7651 (3)	0.2123 (2)	0.61966 (12)	0.0256 (5)
C31	0.9035 (4)	0.0582 (3)	0.65828 (16)	0.0396 (7)
H31A	0.840309	0.004905	0.673357	0.048*
H31B	0.921679	0.105529	0.693570	0.048*
C32	1.0362 (4)	0.0051 (3)	0.6391 (2)	0.0479 (8)
H32A	1.018357	−0.045495	0.606058	0.072*
H32B	1.074920	−0.029840	0.675442	0.072*
H32C	1.099145	0.056967	0.623522	0.072*

80.68%; H, 6.72%; N, 5.84%; calculated for C₃₂H₃₂N₂O₂: C, 80.64%; H, 6.77%; N, 5.88%.

Experimental details

Data were collected via CrysAlis^{PRO} 1.171.39.7e [1], the structure of crystal was determined by SHELXT [2] and refined by OLEX2 [4] and SHELXL [3].

The absolute structure determination succeeded as the derived Flack parameter is found to be near zero with a low standard uncertainty [−0.02(9) from 2090 selected quotients] using Parsons' method [6]. There is a small disorder of one ethyl group (C22, C23) which was not included in the refinement.

Comment

Hugo Schiff described the condensation between an aldehyde and an amine leading to a Schiff base in 1864 [7]. Schiff base ligands are privileged ligands, as they are easily prepared by the condensation between aldehydes and imines. Stereogenic centres can be introduced in the synthetic design. Schiff base ligands are able to coordinate many different metals, and to stabilize them in various oxidation states, enabling the use of Schiff base metal complexes for a large variety of useful catalytic transformations [8–10]. When two equivalents of salicylaldehyde are combined with a diamine, a particular chelating Schiff base is obtained – known as salen – with four coordinating sites and two axial sites open to ancillary ligands. Here, we report a new chiral salen compound.

The asymmetric unit of the title structure contains one 6,6'-((1*E*, 1'*E*)-(((1*R*, 2*R*)-1,2-diphenylethane-1,2-diyl)

bis(azanylylidene))bis(methanylylidene))bis(2-ethylphenol). In the crystal structure, bond lengths and bond angles within the molecule are in agreement with the values reported [11]. The bond lengths of C15–N1 and C24–N2 are 1.278(3) and 1.275(3) Å, respectively. As a result of the conjugation of the benzene moiety and adjacent carbon-nitrogen double bond, the bond lengths of C15–C16 and C24–C25 are 1.457(4) and 1.461(4) Å respectively, which is shorter than that of typical C–C bond. Furthermore, the bond lengths of C17–O1 and C30–O2 are 1.351(3) and 1.358(3) Å, respectively. The bond angles (C15–N1–C7) and (C24–N2–C8) are 117.5(2)° and 118.8(2)°, respectively. There are two intramolecular hydrogen bonds (d D...A 2.63 Å; H...A 1.904 Å) between H1 and N1 atom and (d D...A 2.594 Å; H...A 1.864 Å) between H2 and N2 atom, which stabilize the crystal structure [11, 12]. In the crystal packing, dipole-dipole and van der Waals interactions are effective besides an intermolecular hydrogen bond in the molecular packing.

Author contributions: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

Research funding: National Natural Science Foundation of China (grant no. 21861045) and Technology University Students Science and Technology Innovation and Entrepreneurship Training Program Project in Zunyi Medical University (No. ZYDC2020038).

Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

References

1. Rigaku Corporation. CrysAlis^{PRO}; Yarnton, Oxfordshire, England, 2015.
2. Sheldrick G. M. *SHELXTL* – integrated space-group and crystal-structure determination. *Acta Crystallogr.* 2015, *A71*, 3–8.
3. Sheldrick G. M. Crystal structure refinement with SHELXL. *Acta Crystallogr.* 2015, *C71*, 3–8.
4. Dolomanov O. V., Bourhis L. J., Gildea R. J., Howard J. A. K., Puschmann H. OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* 2009, *42*, 339–341.
5. Reiss H., Shalit H., Vershinin V., More N. Y., Forckosh H., Pappo D. Cobalt [salen]-catalyzed selective aerobic oxidative cross-coupling between electron-rich phenols and 2-naphthols. *J. Org. Chem.* 2019, *84*, 7950–7960.
6. Parsons S., Flack H. D., Wagner T. Use of intensity quotients and differences in absolute structure refinement. *Acta Crystallogr.* 2013, *B69*, 249–259.
7. Schiff H. The syntheses and characterization of Schiff base. *Ann. Chem. Pharm. Suppl.* 1864, *3*, 343–349.
8. Belokon Y. N., North M., Parsons T. Vanadium-catalyzed asymmetric cyanohydrin synthesis. *Org. Lett.* 2000, *2*, 1617–1619.
9. Zeng X. P., Cao Z. Y., Wang X., Chen L., Zhou F., Zhu F., Wang C. H., Zhou J. Activation of chiral (salen)AlCl complex by phosphorane for highly enantioselective cyanosilylation of ketones and enones. *J. Am. Chem. Soc.* 2016, *138*, 416–425.
10. Kunisu T., Oguma T., Katsuki T. Aerobic oxidative kinetic resolution of secondary alcohols with naphthoxide-bound iron(salen) complex. *J. Am. Chem. Soc.* 2011, *133*, 12937–12939.
11. Jiao L., Tan H., Sun J., Zhang L., Wu Q. Crystal structure of *rac-trans*-N,N'-bis(3,5-dibromosalicylidene)-1,2-cyclohexanediamine, $C_{20}H_{18}Br_4N_2O_2$. *Z. Kristallogr. NCS* 2020, *235*, 847–848.
12. Wu Q., Tang Y., Li J., Li Y., Fang Y. Crystal structure of *rac-trans*-N,N'-bis(3,5-diiodosalicylidene)-1,2-cyclohexanediamine, $C_{20}H_{18}I_4N_2O_2$. *Z. Kristallogr. NCS* 2019, *234*, 69–70.