# Crystal structure of *N*,*N*′-bis(3-ethoxy-2-hydroxybenzylidene)-phenylene-1,3-diamine, $C_{24}H_{24}N_2O_4$

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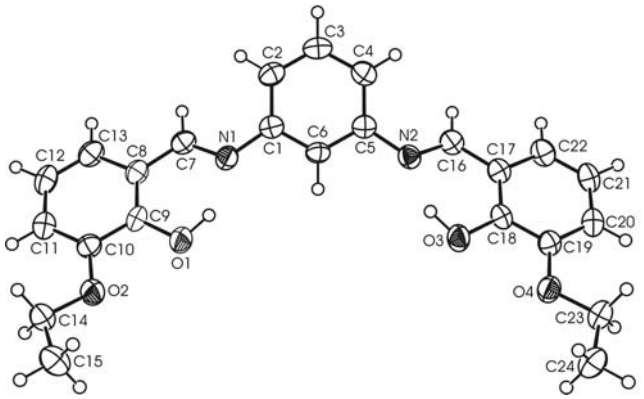


**Abstract**

$C_{24}H_{24}N_2O_4$, orthorhombic, $P2_12_12_1$ (no. 19), $a$ = 6.9103(8) Å, $b$ = 15.503(2) Å, $c$ = 19.304(2) Å, $V$ = 2068.0 Å$^3$, $Z$ = 4, $R_{gt}(F)$ = 0.049, $wR_{ref}(F^2)$ = 0.125, $T$ = 200 K.

**Source of material**

1,3-Phenylenediamine (0.7565 g, 6.995 mmol) and 3-ethoxy-salicylaldehyde (2.3270 g, 14.003 mmol) in EtOH (20 ml) were stirred for 5 h at room temperature. After evaporation of the solvent, the residue was recrystallized from a mixture of acetone/ether/pentane at –85 °C, to give an orange-red solid (2.3365 g). Crystals suitable for X-ray diffraction analysis were obtained by slow evaporation from a toluene solution.

**Experimental details**

Hydrogen atoms were positioned geometrically and allowed to ride on their parent atoms with $d$(C—H) = 0.95 Å (CH), 0.99 Å ($CH_2$) or 0.98 Å ($CH_3$) and $U_{iso}$(H) = 1.2 $U_{eq}$(C) or 1.5 $U_{eq}(C_{methyl})$. The hydroxy H atoms were located from Fourier difference maps and refined isotropically: $d$(O—H) = 0.92(4) Å and 0.96(3) Å. The highest peak (0.24 e·Å$^{-3}$) and the deepest hole (–0.21 e·Å$^{-3}$) in the difference Fourier map are located 0.89 Å and 1.51 Å from the atoms H15A and C17, respectively. The Flack parameter is –0.4(13) in the refinement. Because the compound is a weak anomalous scatterer, the parameter is meaningless and the absolute crystal structure cannot be determined reliably.

**Discussion**

The title compound is a tetradentate Schiff-base, which can act as a dibasic ligand, i.e. the N and O donor atoms can coordinate one or two metal ions. In the crystal structure, the three benzene rings are not parallel: the dihedral angles between the central benzene ring and the two lateral benzene rings are 28.0(1)° and 31.4(1)°, respectively, and the dihedral angle between the lateral benzene rings is 12.2(1)°. Two ethoxy groups are located approximately parallel to their respective carrier benzene rings. The N—C bond lengths and the C–N–C bond angles indicate that the imino N atoms (N1, N2) are $sp^2$-hybridized with $d$(N=C) = 1.285(3), 1.289(3) Å and $d$(N—C) = 1.423(3), 1.423(3) Å; ∠C–N–C = 122.3(2)° and 121.2(2)°, respectively.

The Schiff base displays strong intramolecular O–H···N hydrogen bonding between the hydroxy O atoms and the imino N atoms with $d$(O···N) = 2.593(3) - 2.605(3) Å thus forming a nearly planar six-membered ring. In addition, several intermolecular $\pi$-$\pi$ interactions between the adjacent benzene rings are present. The centroid-centroid distance between Cg1 (the centroid of ring C8-C13) and Cg2$^i$ (ring C17-C22, symmetry code i: –½+$x$,½–$y$, –$z$) is 4.708(2) Å, and the dihedral angle between the ring planes is 54.3(1)°.

**Table 1.** Data collection and handling.

| | |
|---|---|
| Crystal: | orange stick, size 0.22 × 0.29 × 0.43 mm |
| Wavelength: | Mo $K_\alpha$ radiation (0.71073 Å) |
| $\mu$: | 0.89 cm$^{-1}$ |
| Diffractometer, scan mode: | Bruker SMART 1000 CCD, $\varphi/\omega$ |
| $2\theta_{max}$: | 56.6° |
| $N(hkl)_{measured}$, $N(hkl)_{unique}$: | 15482, 5141 |
| Criterion for $I_{obs}$, $N(hkl)_{gt}$: | $I_{obs} > 2\,\sigma(I_{obs})$, 3144 |
| $N(param)_{refined}$: | 281 |
| Programs: | SHELXS-97, SHELXL-97 [1], ORTEP-III [2], PLATON [3] |

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

| Atom | Site | $x$ | $y$ | $z$ | $U_{iso}$ |
|---|---|---|---|---|---|
| H(1O) | 4*a* | 0.476(5) | 0.489(2) | –0.011(2) | 0.11(1) |
| H(3O) | 4*a* | 0.493(4) | 0.214(2) | 0.192(2) | 0.08(1) |
| H(2) | 4*a* | 1.0889 | 0.4207 | –0.0105 | 0.050 |
| H(3) | 4*a* | 1.2553 | 0.3301 | 0.0645 | 0.058 |
| H(4) | 4*a* | 1.0932 | 0.2332 | 0.1359 | 0.051 |
| H(6) | 4*a* | 0.5853 | 0.3198 | 0.0584 | 0.043 |
| H(7) | 4*a* | 0.8902 | 0.4671 | –0.0913 | 0.046 |
| H(11) | 4*a* | 0.3662 | 0.7229 | –0.1903 | 0.051 |
| H(12) | 4*a* | 0.6692 | 0.6850 | –0.2335 | 0.057 |
| H(13) | 4*a* | 0.8453 | 0.5746 | –0.1832 | 0.053 |
| H(14A) | 4*a* | 0.0352 | 0.7268 | –0.1488 | 0.058 |
| H(14B) | 4*a* | 0.1852 | 0.7792 | –0.1012 | 0.058 |
| H(15A) | 4*a* | –0.1582 | 0.7000 | –0.0511 | 0.085 |
| H(15B) | 4*a* | –0.1324 | 0.8016 | –0.0623 | 0.085 |
| H(15C) | 4*a* | –0.0092 | 0.7530 | –0.0040 | 0.085 |
| H(16) | 4*a* | 0.8929 | 0.1195 | 0.1535 | 0.048 |
| H(20) | 4*a* | 0.3958 | –0.0485 | 0.3451 | 0.052 |
| H(21) | 4*a* | 0.6941 | –0.0939 | 0.3024 | 0.056 |

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**Table 2.** Continued.

| Atom | Site | $x$ | $y$ | $z$ | $U_{iso}$ |
|---|---|---|---|---|---|
| H(22) | 4*a* | 0.8590 | –0.0107 | 0.2224 | 0.053 |
| H(23A) | 4*a* | 0.2023 | 0.0431 | 0.4066 | 0.057 |
| H(23B) | 4*a* | 0.0703 | –0.0082 | 0.3519 | 0.057 |
| H(24A) | 4*a* | –0.0179 | 0.1583 | 0.4051 | 0.079 |
| H(24B) | 4*a* | –0.1267 | 0.0714 | 0.4271 | 0.079 |
| H(24C) | 4*a* | –0.1488 | 0.1079 | 0.3500 | 0.079 |

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

| Atom | Site | $x$ | $y$ | $z$ | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| O(1) | 4*a* | 0.3815(3) | 0.5245(1) | –0.02828(9) | 0.045(1) | 0.049(1) | 0.048(1) | 0.0025(9) | 0.0099(9) | 0.0139(9) |
| O(2) | 4*a* | 0.1846(3) | 0.6516(1) | –0.08299(9) | 0.044(1) | 0.041(1) | 0.053(1) | 0.0061(9) | 0.0065(9) | 0.0071(8) |
| O(3) | 4*a* | 0.3938(3) | 0.1876(1) | 0.21964(9) | 0.047(1) | 0.040(1) | 0.047(1) | 0.0112(9) | 0.0088(9) | 0.0101(8) |
| O(4) | 4*a* | 0.2053(2) | 0.0944(1) | 0.31135(8) | 0.046(1) | 0.043(1) | 0.0422(9) | 0.0017(9) | 0.0078(8) | 0.0071(8) |
| N(1) | 4*a* | 0.7008(3) | 0.4371(1) | –0.0214(1) | 0.040(1) | 0.034(1) | 0.042(1) | –0.002(1) | 0.004(1) | 0.0023(9) |
| N(2) | 4*a* | 0.7063(3) | 0.2125(1) | 0.1468(1) | 0.039(1) | 0.040(1) | 0.034(1) | 0.004(1) | 0.001(1) | 0.0017(9) |
| C(1) | 4*a* | 0.8199(3) | 0.3795(2) | 0.0171(1) | 0.036(1) | 0.034(1) | 0.038(1) | 0.000(1) | 0.002(1) | –0.006(1) |
| C(2) | 4*a* | 1.0199(4) | 0.3820(2) | 0.0186(1) | 0.039(2) | 0.047(2) | 0.040(1) | –0.006(1) | 0.005(1) | –0.004(1) |
| C(3) | 4*a* | 1.1180(4) | 0.3277(2) | 0.0631(1) | 0.031(1) | 0.058(2) | 0.056(2) | –0.002(1) | 0.003(1) | –0.003(1) |
| C(4) | 4*a* | 1.0226(4) | 0.2698(2) | 0.1056(1) | 0.041(2) | 0.047(2) | 0.040(1) | 0.004(1) | –0.004(1) | –0.002(1) |
| C(5) | 4*a* | 0.8213(3) | 0.2661(2) | 0.1034(1) | 0.036(1) | 0.037(1) | 0.033(1) | 0.003(1) | 0.003(1) | –0.006(1) |
| C(6) | 4*a* | 0.7227(4) | 0.3215(2) | 0.0595(1) | 0.029(1) | 0.042(1) | 0.037(1) | 0.001(1) | 0.004(1) | –0.003(1) |
| C(7) | 4*a* | 0.7641(4) | 0.4791(2) | –0.0741(1) | 0.038(1) | 0.040(1) | 0.038(1) | –0.002(1) | 0.007(1) | –0.004(1) |
| C(8) | 4*a* | 0.6467(4) | 0.5445(2) | –0.1081(1) | 0.043(2) | 0.036(1) | 0.034(1) | –0.005(1) | 0.002(1) | –0.002(1) |
| C(9) | 4*a* | 0.4640(3) | 0.5663(1) | –0.0823(1) | 0.044(2) | 0.031(1) | 0.031(1) | –0.007(1) | 0.006(1) | 0.003(1) |
| C(10) | 4*a* | 0.3586(4) | 0.6344(2) | –0.1128(1) | 0.038(1) | 0.037(1) | 0.039(1) | –0.003(1) | 0.001(1) | –0.002(1) |
| C(11) | 4*a* | 0.4369(4) | 0.6774(2) | –0.1691(1) | 0.052(2) | 0.037(1) | 0.040(1) | –0.003(1) | –0.000(1) | 0.003(1) |
| C(12) | 4*a* | 0.6175(4) | 0.6549(2) | –0.1949(1) | 0.062(2) | 0.043(2) | 0.036(1) | –0.010(1) | 0.006(1) | 0.006(1) |
| C(13) | 4*a* | 0.7218(4) | 0.5895(2) | –0.1651(1) | 0.047(2) | 0.045(2) | 0.040(1) | –0.005(1) | 0.010(1) | –0.003(1) |
| C(14) | 4*a* | 0.0906(4) | 0.7313(2) | –0.1016(1) | 0.046(2) | 0.042(2) | 0.057(2) | 0.005(1) | –0.004(1) | 0.006(1) |
| C(15) | 4*a* | –0.0656(4) | 0.7479(2) | –0.0504(2) | 0.054(2) | 0.055(2) | 0.062(2) | 0.014(2) | –0.002(2) | –0.000(1) |
| C(16) | 4*a* | 0.7702(4) | 0.1394(2) | 0.1689(1) | 0.042(1) | 0.043(2) | 0.035(1) | 0.006(1) | 0.002(1) | –0.002(1) |
| C(17) | 4*a* | 0.6597(4) | 0.0866(2) | 0.2168(1) | 0.042(1) | 0.037(1) | 0.032(1) | 0.003(1) | –0.002(1) | –0.002(1) |
| C(18) | 4*a* | 0.4787(4) | 0.1134(2) | 0.2414(1) | 0.041(1) | 0.031(1) | 0.030(1) | 0.006(1) | –0.004(1) | –0.001(1) |
| C(19) | 4*a* | 0.3801(4) | 0.0630(2) | 0.2901(1) | 0.042(1) | 0.038(1) | 0.032(1) | 0.003(1) | 0.003(1) | –0.001(1) |
| C(20) | 4*a* | 0.4622(4) | –0.0139(2) | 0.3122(1) | 0.054(2) | 0.038(2) | 0.037(1) | –0.001(1) | –0.002(1) | 0.005(1) |
| C(21) | 4*a* | 0.6400(4) | –0.0410(2) | 0.2869(1) | 0.059(2) | 0.037(1) | 0.043(2) | 0.009(1) | –0.004(1) | 0.007(1) |
| C(22) | 4*a* | 0.7376(4) | 0.0083(2) | 0.2397(1) | 0.051(2) | 0.040(2) | 0.041(1) | 0.010(1) | 0.000(1) | –0.003(1) |
| C(23) | 4*a* | 0.1116(4) | 0.0499(2) | 0.3672(1) | 0.053(2) | 0.047(2) | 0.043(2) | –0.006(1) | 0.009(1) | 0.006(1) |
| C(24) | 4*a* | –0.0602(4) | 0.1013(2) | 0.3893(1) | 0.056(2) | 0.053(2) | 0.049(2) | –0.005(2) | 0.014(1) | –0.001(1) |

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