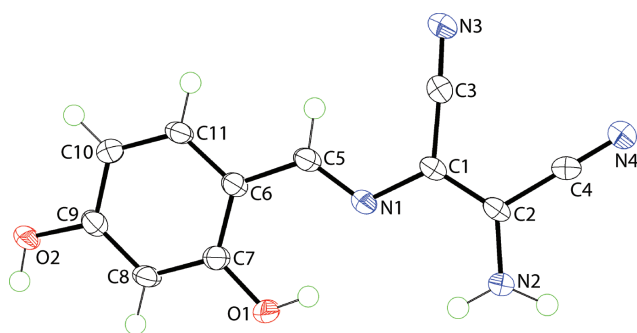


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Crystal structure of (2Z)-2-amino-3-[(E)-[(2,4-dihydroxyphenyl)methylidene]-amino]but-2-enedinitrile, C₁₁H₈N₄O₂



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Abstract

C₁₁H₈N₄O₂, triclinic, $P\bar{1}$ (no. 2), $a = 6.9017(4)$ Å, $b = 6.9496(2)$ Å, $c = 11.2372(7)$ Å, $\alpha = 88.218(4)^\circ$, $\beta = 76.489(5)^\circ$, $\gamma = 77.575(4)^\circ$, $V = 511.69(5)$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.0417$, $wR_{\text{ref}}(F^2) = 0.1200$, $T = 100(2)$ K.

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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

Diaminomaleonitrile (Fluka, 0.54 g, 5 mmol) and 2,4-dihydroxybenzaldehyde (Merck, 0.69 g, 5 mmol) were dissolved in 95% ethanol (100 mL) and the mixture was refluxed for 3 h. The resulting brown solution was filtered and allowed to evaporate at room temperature until a brown crystalline solid was formed. Yield: 0.85 g (74.5%). **M. pt** (Stuart SMP30

Table 1: Data collection and handling.

Crystal:	Brown prism
Size:	0.11 × 0.04 × 0.03 mm
Wavelength:	Cu K α radiation (1.54184 Å)
μ :	0.90 mm ⁻¹
Diffractometer, scan mode:	XtaLAB Synergy, ω
θ_{max} , completeness:	67.1°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	11895, 1830, 0.051
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 1616
$N(\text{param})_{\text{refined}}$:	166
Programs:	CrysAlis ^{PRO} [1], SHELX [2, 3], WinGX/ORTEP [4]

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

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.72280(17)	0.19693(13)	0.59053(10)	0.0211(3)
H1O	0.646(3)	0.263(3)	0.6526(13)	0.032*
O2	1.09585(16)	0.25151(14)	0.18078(9)	0.0201(3)
H2O	1.105(3)	0.1304(15)	0.1785(19)	0.030*
N1	0.53641(18)	0.54728(15)	0.71649(11)	0.0161(3)
N2	0.3002(2)	0.41733(16)	0.94232(11)	0.0211(3)
H1N	0.358(3)	0.334(2)	0.8804(13)	0.025*
H2N	0.234(3)	0.390(3)	1.0171(11)	0.025*
N3	0.4234(2)	1.04589(17)	0.80062(12)	0.0254(3)
N4	0.1541(2)	0.85921(17)	1.09948(12)	0.0260(3)
C1	0.4271(2)	0.67326(18)	0.81602(13)	0.0161(3)
C2	0.3220(2)	0.6042(2)	0.92146(13)	0.0168(3)
C3	0.4230(2)	0.8807(2)	0.80957(13)	0.0191(3)
C4	0.2266(2)	0.74616(19)	1.02039(14)	0.0191(3)
C5	0.6141(2)	0.62745(19)	0.61626(14)	0.0158(3)
H5	0.589850	0.767242	0.614718	0.019*
C6	0.7347(2)	0.51992(19)	0.50686(13)	0.0152(3)
C7	0.7869(2)	0.31172(19)	0.49633(13)	0.0159(3)
C8	0.9082(2)	0.21909(18)	0.38826(13)	0.0168(3)
H8	0.944870	0.079337	0.381885	0.020*
C9	0.9756(2)	0.3331(2)	0.28932(13)	0.0167(3)
C10	0.9243(2)	0.53861(19)	0.29702(13)	0.0176(3)
H10	0.970579	0.615217	0.229059	0.021*
C11	0.8057(2)	0.62796(19)	0.40481(14)	0.0166(3)
H11	0.770611	0.767811	0.410302	0.020*

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digital melting point apparatus; uncorrected): >573 K. **IR** (Bruker Vertex 70v FTIR Spectrometer; cm⁻¹): 3401, 3308 (m) ν (N—H), 3201 (b) ν (O—H), 2239 (w), 2211 (w) ν (C—N), 1626 (s) ν (C≡N), 1604 (s) ν (C=C), 1125 (m) ν (C—O). **¹H NMR** (Bruker Ascend 400 MHz NMR spectrometer; CD₃COCD₃): δ 6.36–7.54 (m, 3H, Ph—H), 8.52 (s, 1H, N=CH), 9.42 (b, 2H, NH₂), 11.13 (s, 1H, OH), 11.49 (s, 1H, OH). **¹³C{¹H} NMR** (as for ¹H NMR): 102.2, 102.5 (C=C), 105.4, 108.7 (C≡N), 113.0, 114.3, 123.8, 136.2, 159.9, 164.4 (Ph—C), 194.8 (C=N).

Experimental details

The C-bound H atoms were geometrically placed (C—H = 0.95 Å) and refined as riding with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The O- and N-bound H atoms were refined with O—H = 0.84 ± 0.01 Å and N—H = 0.88 ± 0.01 Å, and with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$ or $1.2U_{\text{eq}}(\text{N})$.

Comment

During the course of investigations of metal Schiff base compounds [5, 6], the reaction of diaminomaleonitrile and 2,4-dihydroxybenzaldehyde was attempted in order to prepare the potentially multidentate Schiff base molecule 2,3-bis{[(2,4-dihydroxyphenyl)methylidene]amino}but-2-enedinitrile, LH₄ [7]. Interesting luminogenic behaviour is observed when [LH₂]²⁻ is complexed to zinc(II) [7]. The title compound represents the “half-way” stage of the reaction in that only one of the amine groups of diaminomaleonitrile has been condensed with 2,4-dihydroxybenzaldehyde. Herein, the crystal and molecular structures of (2,4-(OH)₂C₆H₃)C(H)=NC(CN)=C(CN)NH₂, (I), are described.

The molecular structure of (I) is shown in the figure (70% displacement ellipsoids) which shows the *Z*-configuration about the C1=C2 [1.369(2) Å] ethene bond and the *E*-configuration about the C5=N1 [1.294(2) Å] imine bond. Deviations from co-planarity are apparent with the major twist in the molecule of nearly 7° occurring about the C1—N1 bond as seen in the C5—N1—C1—C2 torsion angle of 173.23(13)°, suggesting limited conjugation throughout the molecule. The proximate hydroxyl-O—H atom and one of the amine-N—H atoms each forms an intramolecular hydrogen bond with the imine-N atom [O1—H1o...N1: H1o...N1 = 2.05(2) Å, O1...N1 = 2.7572(14) Å with angle at H1o = 141.0(17)° and N2—H1n...N1: H1n...N1 = 2.581(16) Å, N2...N1 = 2.9105(17) Å with angle at H1n = 103.2(11)°] to close S(6) and S(5) loops, respectively.

The most closely related structure to (I) in the literature is of the analogue where the phenyl ring carries methoxy substituent in the 2-, 3- and 4- positions [8]. The overall conformation of the literature structure matches closely that described here for (I).

In the crystal, several conventional hydrogen bonding interactions are apparent. Thus, the hydroxyl-O—H atom connects to a cyano-N atom [O2—H2o...N4ⁱ: H2o...N4ⁱ = 2.036(13) Å, O2...N4ⁱ = 2.8179(15) Å with angle at H2o = 157(2)° for symmetry operation (i) 1 + x, -1 + y, -1 + z] as does an amine-N—H atom [N2—H1n...N3ⁱⁱ: H1n...N3ⁱⁱ = 2.133(14) Å, N2...N3ⁱⁱ = 2.9326(17) Å with angle at H1n = 150.7(14)° for (ii) x, -1 + y, z], indicating the N1—H1n atom is bifurcated as H1n also forms an intramolecular N—H...N interaction. The second amine-N—H connects to a hydroxyl-O atom [N2—H2n...O2ⁱⁱⁱ: H2n...O2ⁱⁱⁱ = 2.164(15) Å, N2...O2ⁱⁱⁱ = 3.0396(16) Å with angle at H2n = 166.1(18)° for (iii) -1 + x, y, 1 + z]. The result of the aforementioned hydrogen bonds is the formation of a supramolecular layer, parallel to (1 0 1), whereby three molecules contribute to a non-symmetric, 11-membered {...NC₄N...HO...HNH} synthon. Centrosymmetric layers are connected by π (phenyl)... π (phenyl) [Cg(C6—C11)...Cg(C6—C11)^{iv} = 3.6851(9)° for (iv) 2 - x, 1 - y, 1 - z] stacking to form double layers that stack along the *a*-axis in an ...ABAB... pattern without directional interactions between them.

A more complete analysis of the molecular packing was performed by calculating the Hirshfeld surface as well as the full- and delineated two-dimensional fingerprint plots, employing standard protocols [9] and Crystal Explorer 17 [10]. The fingerprint plots delineated into the H...O/O...H and H...N/N...H contacts exhibited the characteristic sharp spikes due to the strong hydrogen bonding interactions. Overall, these contacts contributed 14.7 and 31.0%, respectively, to the Hirshfeld surface. Significant contributions are also made by H...H [16.7%] and H...C/C...H [16.1%] contacts with reduced contributions from C...C [9.7%], N...C/N...C [4.5%], O...C/C...O [3.2%] and N...N [3.0%] contacts.

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