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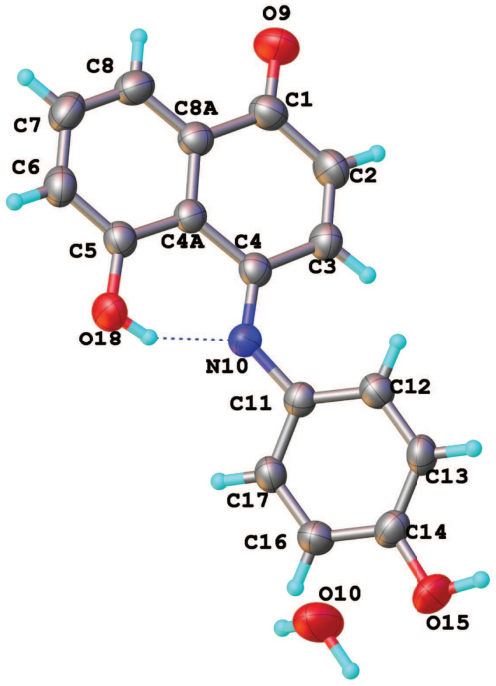
Crystal structure of 5-hydroxy-4-((4-hydroxyphenyl)imino)naphthalen-1(4H)-one monohydrate, $C_{16}H_{11}NO_3 \cdot 0.5H_2O$



DOI 10.1515/ncrs-2015-0086
Received May 4, 2015; accepted December 8, 2015; available online January 8, 2016

Abstract

$C_{16}H_{11}NO_3 \cdot H_2O$, triclinic, $P\bar{1}$ (no. 2), $a = 7.4445(3)$ Å, $b = 13.7846(7)$ Å, $c = 14.0875(9)$ Å, $\alpha = 109.945(5)°$, $\beta = 101.686(4)°$, $\gamma = 101.735(4)°$, $V = 1271.15(13)$ Å^3, $Z = 2$, $R_{gt}(F) = 0.034$, $wR_{ref}(F^2) = 0.093$, $T = 293(2)$ K.

CCDC no.: 1015027

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Table 1: Data collection and handling.

Crystal:	Brown, block, size 0.23×0.29×0.31 mm
Wavelength:	Cu K_α radiation (1.5418 Å)
μ:	8.44 cm^{-1}
Diffractometer, scan mode:	SuperNova, Dual, Cu at zero, Atlas, ω scans
$2\theta_{max}$:	123.17°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	6849, 3883
$N(param)_{refined}$:	388
Programs:	SHELXT [5], SHELXL [6], OLEX2 [7]

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

Atom	Site	x	y	z	U_{iso}
H(18)	2*i*	0.3571	0.0839	0.4801	0.092(8)
H(6)	2*i*	0.0883	−0.0760	0.2365	0.058
H(7)	2*i*	0.0645	−0.0310	0.0931	0.063
H(8)	2*i*	0.2306	0.1391	0.1127	0.060
H(2)	2*i*	0.6479	0.4508	0.3970	0.060
H(3)	2*i*	0.6760	0.4093	0.5378	0.052
H(12)	2*i*	0.5472	0.4255	0.6665	0.051
H(13)	2*i*	0.6573	0.5060	0.8478	0.054
H(16)	2*i*	0.7911	0.2406	0.8544	0.057
H(17)	2*i*	0.6769	0.1594	0.6742	0.049
H(218)	2*i*	1.1052	0.3809	0.4289	0.096(8)
H(26)	2*i*	1.0118	0.3703	0.1859	0.068
H(27)	2*i*	0.8105	0.2252	0.0383	0.078
H(28)	2*i*	0.6622	0.0677	0.0513	0.070
H(22)	2*i*	0.6357	−0.0422	0.3286	0.059
H(23)	2*i*	0.8223	0.0993	0.4750	0.051
H(212)	2*i*	1.1180	0.1575	0.5832	0.048
H(213)	2*i*	1.2200	0.2000	0.7618	0.050
H(216)	2*i*	1.1597	0.4957	0.8211	0.056
H(217)	2*i*	1.0649	0.4548	0.6437	0.050
H(10A)	2*i*	0.377(5)	0.190(3)	0.955(3)	0.160(2)
H(10B)	2*i*	0.381(4)	0.270(2)	1.065(3)	0.130(1)
H(15)	2*i*	0.775(3)	0.490(2)	1.002(2)	0.102(8)
H(215)	2*i*	1.283(3)	0.327(2)	0.934(2)	0.095(7)

The crystal structure is shown in the figure, Tables 1–3 contain details of the measurement method and a list of the atoms including atomic coordinates and displacement parameters.

Table 3: Atomic displacement parameters (Å^2).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(15)	2*i*	0.7941(2)	0.4226(1)	0.97681(9)	0.108(1)	0.0588(8)	0.0336(6)	0.0277(7)	0.0124(6)	0.0093(6)
O(9)	2*i*	0.4510(2)	0.3329(1)	0.2073(1)	0.0967(9)	0.0632(8)	0.0523(7)	0.0163(7)	0.0180(7)	0.0355(6)
O(18)	2*i*	0.2851(2)	0.03406(9)	0.42557(9)	0.0742(7)	0.0384(6)	0.0462(7)	0.0061(6)	0.0136(6)	0.0185(6)
N(10)	2*i*	0.5119(2)	0.22013(9)	0.54190(9)	0.0464(7)	0.0365(6)	0.0357(7)	0.0133(5)	0.0124(5)	0.0133(5)
C(5)	2*i*	0.2727(2)	0.0659(1)	0.3450(1)	0.0447(8)	0.0357(8)	0.0427(8)	0.0143(6)	0.0141(7)	0.0152(7)
C(6)	2*i*	0.1568(2)	−0.0075(1)	0.2453(1)	0.0489(9)	0.0360(8)	0.0501(9)	0.0094(7)	0.0100(7)	0.0110(7)
C(7)	2*i*	0.1418(2)	0.0194(1)	0.1595(1)	0.0530(9)	0.0475(9)	0.0420(9)	0.0120(8)	0.0038(7)	0.0066(7)
C(8)	2*i*	0.2412(2)	0.1213(1)	0.1711(1)	0.0560(9)	0.054(1)	0.0385(8)	0.0189(8)	0.0092(7)	0.0176(7)
C(8A)	2*i*	0.3567(2)	0.1966(1)	0.2700(1)	0.0425(8)	0.0419(8)	0.0399(8)	0.0172(6)	0.0130(6)	0.0169(7)
C(1)	2*i*	0.4606(2)	0.3060(1)	0.2824(1)	0.0554(9)	0.0481(9)	0.0467(9)	0.0190(7)	0.0178(7)	0.0252(8)
C(2)	2*i*	0.5806(2)	0.3821(1)	0.3881(1)	0.0553(9)	0.0395(8)	0.055(1)	0.0079(7)	0.0157(8)	0.0229(8)
C(3)	2*i*	0.5978(2)	0.3576(1)	0.4722(1)	0.0443(8)	0.0362(8)	0.0426(8)	0.0072(6)	0.0101(7)	0.0128(7)
C(4)	2*i*	0.4959(2)	0.2508(1)	0.4637(1)	0.0383(7)	0.0347(7)	0.0387(8)	0.0146(6)	0.0130(6)	0.0139(6)
C(4A)	2*i*	0.3755(2)	0.1709(1)	0.3594(1)	0.0386(7)	0.0355(7)	0.0367(8)	0.0157(6)	0.0121(6)	0.0130(6)
C(11)	2*i*	0.5998(2)	0.2833(1)	0.6502(1)	0.0388(7)	0.0343(7)	0.0358(8)	0.0091(6)	0.0129(6)	0.0122(6)
C(12)	2*i*	0.5953(2)	0.3880(1)	0.7042(1)	0.0484(8)	0.0391(8)	0.0423(8)	0.0154(7)	0.0144(7)	0.0176(7)
C(13)	2*i*	0.6612(2)	0.4361(1)	0.8127(1)	0.0549(9)	0.0331(8)	0.0438(9)	0.0130(7)	0.0179(7)	0.0089(7)
C(14)	2*i*	0.7335(2)	0.3812(1)	0.8700(1)	0.0550(9)	0.0428(8)	0.0349(8)	0.0098(7)	0.0127(7)	0.0104(7)
C(16)	2*i*	0.7405(2)	0.2775(1)	0.8167(1)	0.0605(9)	0.0438(8)	0.0403(8)	0.0183(7)	0.0129(7)	0.0194(7)
C(17)	2*i*	0.6734(2)	0.2294(1)	0.7090(1)	0.0503(8)	0.0327(7)	0.0406(8)	0.0129(6)	0.0153(7)	0.0141(6)
O(215)	2*i*	1.2566(2)	0.3815(1)	0.91593(8)	0.101(1)	0.0590(8)	0.0324(6)	0.0353(7)	0.0136(6)	0.0148(5)
O(29)	2*i*	0.5777(2)	−0.0613(1)	0.1384(1)	0.088(1)	0.0525(8)	0.0603(8)	−0.0020(7)	0.0002(7)	−0.0015(6)
O(218)	2*i*	1.0982(2)	0.39245(9)	0.37509(9)	0.0772(8)	0.0417(6)	0.0517(7)	0.0034(6)	0.0084(6)	0.0209(6)
N(210)	2*i*	1.0277(2)	0.28834(9)	0.48727(9)	0.0464(7)	0.0376(7)	0.0353(7)	0.0123(5)	0.0097(5)	0.0125(6)
C(25)	2*i*	0.9809(2)	0.3043(1)	0.2912(1)	0.0495(9)	0.0415(8)	0.0452(9)	0.0161(7)	0.0119(7)	0.0190(7)
C(26)	2*i*	0.9505(3)	0.3080(2)	0.1924(1)	0.067(1)	0.062(1)	0.054(1)	0.0253(9)	0.0191(9)	0.0348(9)
C(27)	2*i*	0.8313(3)	0.2210(2)	0.1040(1)	0.076(1)	0.085(1)	0.045(1)	0.034(1)	0.0167(9)	0.035(1)
C(28)	2*i*	0.7414(2)	0.1269(2)	0.1117(1)	0.060(1)	0.067(1)	0.0376(9)	0.0199(9)	0.0040(7)	0.0133(8)
C(28A)	2*i*	0.7698(2)	0.1211(1)	0.2095(1)	0.0429(8)	0.0469(9)	0.0384(8)	0.0175(7)	0.0086(6)	0.0116(7)
C(21)	2*i*	0.6759(2)	0.0198(1)	0.2173(1)	0.0476(9)	0.0414(9)	0.051(1)	0.0105(7)	0.0074(7)	0.0068(8)
C(22)	2*i*	0.7005(2)	0.0195(1)	0.3223(1)	0.0442(8)	0.0384(8)	0.060(1)	0.0069(7)	0.0129(7)	0.0177(8)
C(23)	2*i*	0.8117(2)	0.1036(1)	0.4097(1)	0.0424(8)	0.0425(8)	0.0457(9)	0.0132(7)	0.0138(7)	0.0200(7)
C(24)	2*i*	0.9174(2)	0.2028(1)	0.4052(1)	0.0372(7)	0.0358(7)	0.0368(8)	0.0145(6)	0.0110(6)	0.0125(6)
C(24A)	2*i*	0.8897(2)	0.2097(1)	0.3019(1)	0.0407(8)	0.0389(8)	0.0370(8)	0.0171(6)	0.0111(6)	0.0138(6)
C(211)	2*i*	1.0769(2)	0.3008(1)	0.5935(1)	0.0384(7)	0.0377(8)	0.0341(8)	0.0098(6)	0.0103(6)	0.0133(6)
C(212)	2*i*	1.1261(2)	0.2256(1)	0.6309(1)	0.0440(8)	0.0344(7)	0.0386(8)	0.0127(6)	0.0125(6)	0.0101(6)
C(213)	2*i*	1.1866(2)	0.2508(1)	0.7377(1)	0.0464(8)	0.0403(8)	0.0411(8)	0.0157(7)	0.0132(7)	0.0190(7)
C(214)	2*i*	1.1979(2)	0.3517(1)	0.8097(1)	0.0502(8)	0.0444(8)	0.0332(8)	0.0155(7)	0.0120(6)	0.0139(7)
C(216)	2*i*	1.1515(2)	0.4277(1)	0.7732(1)	0.0594(9)	0.0373(8)	0.0375(8)	0.0173(7)	0.0124(7)	0.0081(7)
C(217)	2*i*	1.0937(2)	0.4029(1)	0.6673(1)	0.0484(8)	0.0353(8)	0.0414(8)	0.0129(6)	0.0109(7)	0.0151(7)
O(10)	2*i*	0.3213(3)	0.2358(2)	0.9856(1)	0.178(2)	0.087(1)	0.0517(9)	0.063(1)	0.026(1)	0.0335(8)

Source of material

A suspension of 1,5-dihydroxynaphthalene (1.25 mmol), rose bengal (20 mg), 4-hydroxyphenylamine (1.25 mmol) and water (150 mL), into a round bottom flask, was vigorously stirred at room temperature. Then, the solution was irradiated by solar light or Light Emitting Diode lamps (LED: InGaN, 0.768 W, 42.24 lm, 530 nm) for 5 h at the same time a gently stream of air is bubbled through the solution. The reaction mixture was extracted with ethyl acetate (2×20 mL), the dry extract was evaporated under vacuum and the residue was chromatographed on silica gel (3:1 petroleum ether/ethyl acetate) to give 5-hydroxy-4-((4-hydroxyphenyl)imino)naphthalen-1(4*H*)-one, as brown crystals with 98 and 80° yield by using solar light and green LEDs respectively. Analysis: Solid crystalline **m.p.** 149–151 °C. **IR** (KBr) ν cm^{-1}: 3568 (O—H), 1647 (C = O), 1638 (C = N). **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 5.16 (s, 1H, OH), 6.72 (d, 1H, $J = 10.4$ Hz, 3-H), 6.95 (dd, 4H, $J = 8.8$, 8.8 Hz, 2′-H + 3′-H + 5′-H + 6′-H), 7.31 (d, 1H, $J = 8.3$ Hz, 6-H), 7.37 (d, 1H, $J = 10.4$ Hz, 2-H), 7.53 (dd, 1H, $J = 7.8$, 8.0 Hz, 7-H), 7.71 (d, 1H, $J = 7.3$ Hz, 8-H), 14.20 (s, 1H, OH); **^{13}C-NMR** (100 MHZ $CDCl_3$): δ 114.6, 116.1 (2C), 118.3, 123.7, 124.3 (2C), 130.2,

131.5, 132.9, 135.1, 138.8, 154.7, 159.3, 160.7, 185.2; HRMS (APCI): $[M+H]^+$ calcd for $C_{16}H_{11}NO_3$: 266.082 $[M+H]^+$; found 266.081.

Experimental details

H atoms were located in the difference Fourier map, but refined with fixed individual displacement parameters, using a riding mode with C—H distances of 0.93 Å with U_{iso} (H) value of $1.2U_{eq}$(C). H atom attached to O15 was located from Fourier map and was refined isotropically, giving O—H distance of 0.92(2) Å. H atom attached to O18 was located in the difference Fourier map and refined with fixed individual displacement parameters, using a riding mode with O—H distance of 0.82 with U_{iso} (H) value of $1.2U_{eq}$(O).

Discussion

The *N*-phenyl quinone imines are considered as an important class of compounds because of their properties as dyes for optical devices, antioxidants, anticarcinogenic and precursors of liquid crystalline materials [1–3]. Our group have developed a green procedure for the synthesis of *N*-phenyl-1,4-naphthoquinone monoimines, in excellent yields [4], from 1-hydroxynaphthalenes and 4-hydroxyphenylamine using air, sunlight and green LEDs, rose bengal as sensitizer "on water". This method offers operational simplicity, mild conditions and environmental friendliness as the features of this protocol.

There are two organic molecules and one water molecule in the asymmetric unit (figure, for clarity only one organic molecule is shown). The 4-hydroxyphenyl fragment make angles of 41.88(4) and 40.69(4)° with the naphthalenyl fragment, respectively. One intramolecular O–H···N hydrogen bond is observed in both molecules. The crystal packing is stabilized by hydrogen bonding interactions between water molecules and hydroxy carbonyl groups; O(215)—H(215)···O^{i}(10) and O(10)—H(10A)···O(9)^{ii}(10) respectively [symmetry code: (i) 1+x, y, z; (ii) 2−x, −y, 1−z] which links the molecules into centrosymmetric dimer with the graph-set notation $R^4_4(28)$ [8]. Further π-π stacking interactions are observed between the hydroxyphenyl fragment and between naphthalenyl fragment, ranging from 3.771–3.852 Å. All other distances and angles are in the normal range.

Acknowledgements: This work was supported by Fondo Nacional de Ciencia y Tecnología (Grant N° 1120050).

References

1. Sheldon, R. A.: Green solvents for sustainable organic synthesis: state of the art. Green Chem. **7** (2005) 267–278.
2. Sheldon, R. A.: Green chemistry: Frontiers in beningn chemical synthesis and processes. Nature **399** (1999) 33–33.
3. Tobiszewski, M.; Mechlińska, A.; Namiesnik J.: Green analytical chemistry-theory and practice. Chem. Soc. Rev. **39** (2010) 2869–2878.
4. Benites, J.; Meléndez, J.; Estela, C.; Rios, D.; Espinoza, L.; Brito, I.; Valderrama, J. A.: Oxidative phenylamination of 5-substituted 1-hydroxy-naphthalenes to N-phenyl-1,4-naphthoquinone monoimines by air and light "on water". Beilstein J. Org. Chem. **10** (2014) 2448–2452.
5. Sheldrick, G. M.: Crystal structure refinement with SHELXL. Acta Cryst. **A71** (2015) 3–8.
6. Sheldrick, G. M.: A short history of SHELXTL. Acta Cryst. **A64** (2008) 112–122.
7. 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. Cryst. **42** (2009) 339–341.
8. Bernstein, J.; Davis, R. E.; Shimoni, L.; Chang, N.-L.: Patterns in hydrogen bonding: functionality and graph set analysis in crystals. Angew. Chem. Int. Ed. **34** (1995) 1555–1573.