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6-(2-Hydroxyanilinomethylene)-4-nitrocyclohexa-2,4-dien-1-one

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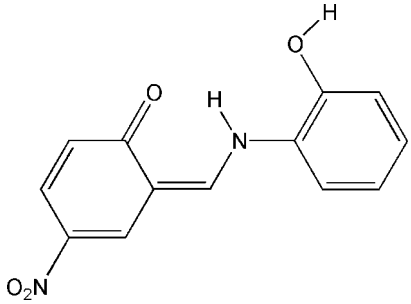
Key indicators: single-crystal X-ray study; T = 303 K; mean σ(C–C) = 0.003 Å; R factor = 0.042; wR factor = 0.115; data-to-parameter ratio = 13.1.

The molecule of the title compound, $C_{13}H_{10}N_2O_4$, is nearly planar with a dihedral angle between the two aromatic rings of 2.24 (9)°. The NH group forms an intramolecular hydrogen bond with the carbonyl O atom. The molecules form dimers about inversion centers in the crystal structure *via* intermolecular O—H···O hydrogen bonds.

Related literature

Aromatic Schiff-bases with *ortho*-hydroxy groups are useful as acyclic polydentate ligands for the preparation of chelate complexes with a wide variety of metal ions (Freeman & White, 1956; Calligaris & Randaccio, 1987; Pettinari *et al.*, 2001; Hernández-Molina & Mederos, 2004). For related literature, see: Böhme & Günther (2006, 2007); Böhme, Wiesner & Günther (2006); Dubs *et al.* (2000); Hopfl *et al.* (1998); Nazir *et al.* (2000); Pradeep (2005).



Experimental

Crystal data

$C_{13}H_{10}N_2O_4$
M_r = 258.23
Monoclinic, $P2_1/n$
a = 6.3445 (3) Å
b = 23.7378 (10) Å
c = 7.8450 (3) Å
β = 93.79 (1)°
V = 1178.90 (9) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.11 mm^{-1}
T = 303 (2) K
0.3 × 0.25 × 0.12 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: none
9006 measured reflections
2273 independent reflections
1523 reflections with $I > 2\sigma(I)$
R_{int} = 0.025

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.115
S = 1.05
2273 reflections
174 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.13 e Å^{-3}
$\Delta\rho_{min}$ = −0.17 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H2···O1	0.86	1.92	2.613 (2)	137
O2—H9···O1^{i}	0.82	1.80	2.573 (2)	157

Symmetry code: (i) $-x, -y, -z+2$.

Data collection: *SMART* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 2004); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: PV2054).

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6-(2-Hydroxyanilinomethylene)-4-nitrocyclohexa-2,4-dien-1-one

Uwe Böhme and Sabine Fels

S1. Comment

We have been working on silicon and titanium complexes with tridentate O,*N*,*O*-ligands (Böhme & Günther, 2006; Böhme, Wiesner & Günther, 2006; Böhme & Günther, 2007). The title compound, (I), was prepared in order to extend the series of available ligands. The preparation of (I) was performed according to the methods described in the literature for the parent compound salicyclidene-*o*-aminophenol ("salopH_2") (Freeman & White, 1956; Pettinari *et al.*, 2001). The molecule of (I) is nearly planar with a dihedral angle between the two aromatic rings of 2.24 (9)°. The atom H2 forms an intramolecular hydrogen bond between the phenolic oxygen atom O1 and N1 of the azomethine unit. The hydrogen atom H2 is localized at N1. This hints to the presence of the keto-amine form. The presence of a quinoidal structure is further supported by the shortening of the bond O1—C3 to 1.276 (2) Å and the lengthening of the adjacent C—C bonds in the phenyl ring [C2—C3 1.443 (2), C3—C4 1.423 (2) Å] (Nazir *et al.*, 2000). There are few structure reports of Schiff-bases with oxygen in *ortho*-position where the intramolecular bridging hydrogen atom is localized at the nitrogen atom (*e.g.* Pradeep, 2005; Dubs *et al.*, 2000; Hopfl *et al.*, 1998). The molecules form dimers about inversion centers in the crystal lattice *via* intermolecular O2—H9···O1 hydrogen bonds. Unconventional hydrogen bonds of the type C—H···O are also present in the structure.

S2. Experimental

To 2-aminophenol (2.12 g, 19.4 mmol) dissolved in ethanol (100 ml) was added 2-hydroxy-5-nitrobenzaldehyde (3.24 g, 19.4 mmol) in ethanol (50 ml). The resulting yellow suspension was refluxed for 1 h. The precipitate was filtered off and washed with ethanol. After drying, the product was purified by recrystallization from ethanol afforded yellow crystals of (I) (3.81 g, 76.2%, m.p. 528 K).

S3. Refinement

Hydrogen atoms bonded to C, N, and O were positioned geometrically and allowed to ride on their parent atoms, with C—H = 0.93, O—H = 0.82, and N—H = 0.86 Å and U_{iso}(H) values of 1.2U_{eq}(C/N) and 1.5U_{eq}(O).

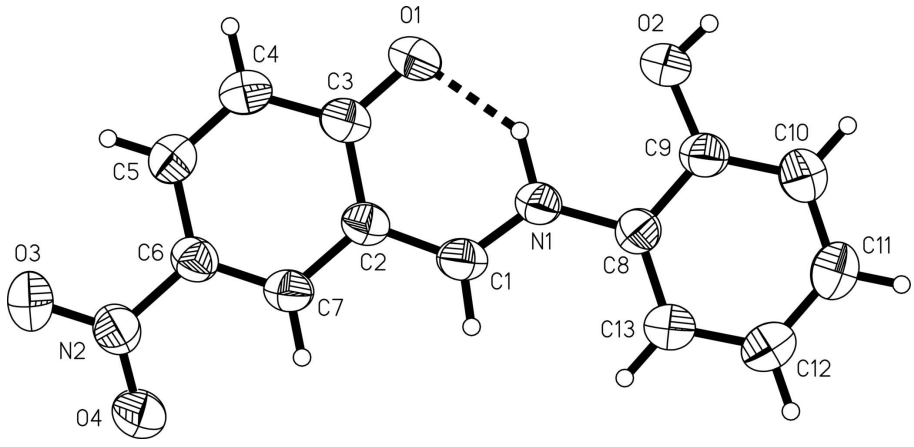

Figure 1

The molecular structure of (I) drawn with 50% probability displacement ellipsoids.

6-(2-Hydroxyanilinomethylene)-4-nitrocyclohexa-2,4-dien-1-one

Crystal data

$C_{13}H_{10}N_2O_4$
$M_r = 258.23$
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
$a = 6.3445$ (3) Å
$b = 23.7378$ (10) Å
$c = 7.8450$ (3) Å
$\beta = 93.79$ (1)°
$V = 1178.90$ (9) Å^3
$Z = 4$
$F(000) = 536$
$D_x = 1.455$ Mg m^{-3}
Melting point: 528 K
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 3470 reflections
$\theta = 3.3$–28.2°
$\mu = 0.11$ mm^{-1}
$T = 303$ K
Prism, yellow
0.3 × 0.25 × 0.12 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Radiation source: sealed tube
Graphite monochromator
φ and ω scans
9006 measured reflections
2273 independent reflections
1523 reflections with $I > 2\sigma(I)$
$R_{int} = 0.025$
$\theta_{max} = 26.0°$, $\theta_{min} = 1.7°$
$h = -7 \rightarrow 7$
$k = -29 \rightarrow 29$
$l = -8 \rightarrow 9$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.115$
$S = 1.05$
2273 reflections
174 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0575P)^2 + 0.0914P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.13$ e Å^{-3}
$\Delta\rho_{min} = -0.17$ e Å^{-3}

Special details

Experimental. NMR (DMSO, 300 K, TMS): ^{1}H: δ=15.73, 10.38 (s, OH, 2H), 9.31 (s, CH—N, 1H), 8.18–6.89 (m, $CH_{aromatic}$, 7H); ^{13}C: 172.3 (C3), 159.2 (C1), 150.4 (C9), 136.7 (C6), 130.3, 129.8, 129.2, 128.6, 120.4, 119.8, 118.7, 116.5, 116.4 (9 signals for aromatic C).

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.2616 (2)	−0.05887 (5)	0.83707 (17)	0.0600 (4)
O2	0.0255 (2)	0.06605 (5)	0.94717 (17)	0.0584 (4)
H9	−0.0597	0.0732	1.0184	0.088*
O3	1.0149 (2)	−0.17158 (6)	0.5016 (2)	0.0762 (5)
O4	1.0816 (2)	−0.08467 (6)	0.45149 (17)	0.0632 (4)
N1	0.3820 (2)	0.04592 (6)	0.81241 (17)	0.0432 (4)
H2	0.2899	0.0216	0.8403	0.068 (6)*
N2	0.9733 (2)	−0.12137 (7)	0.51253 (19)	0.0513 (4)
C1	0.5465 (3)	0.02556 (7)	0.7441 (2)	0.0449 (4)
H1	0.6502	0.0506	0.7131	0.054*
C2	0.5767 (3)	−0.03237 (7)	0.7143 (2)	0.0409 (4)
C3	0.4260 (3)	−0.07387 (7)	0.7635 (2)	0.0447 (4)
C4	0.4701 (3)	−0.13107 (8)	0.7250 (2)	0.0524 (5)
H4	0.3761	−0.1589	0.7549	0.063*
C5	0.6451 (3)	−0.14622 (7)	0.6460 (2)	0.0501 (5)
H5	0.6701	−0.1840	0.6228	0.060*
C6	0.7890 (3)	−0.10481 (7)	0.5989 (2)	0.0427 (4)
C7	0.7560 (3)	−0.04926 (7)	0.6329 (2)	0.0435 (4)
H7	0.8532	−0.0225	0.6018	0.052*
C8	0.3340 (3)	0.10296 (7)	0.8472 (2)	0.0425 (4)
C9	0.1443 (3)	0.11220 (7)	0.9216 (2)	0.0452 (4)
C10	0.0879 (3)	0.16669 (8)	0.9629 (2)	0.0572 (5)
H10	−0.0386	0.1734	1.0130	0.069*
C11	0.2198 (3)	0.21088 (8)	0.9297 (3)	0.0672 (6)
H11	0.1823	0.2474	0.9584	0.081*
C12	0.4076 (3)	0.20149 (8)	0.8538 (3)	0.0676 (6)
H12	0.4950	0.2317	0.8312	0.081*
C13	0.4653 (3)	0.14742 (8)	0.8116 (3)	0.0563 (5)
H13	0.5908	0.1410	0.7600	0.068*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0501 (8)	0.0584 (8)	0.0747 (9)	−0.0075 (6)	0.0276 (7)	−0.0052 (7)
O2	0.0563 (8)	0.0520 (8)	0.0701 (10)	−0.0084 (6)	0.0275 (7)	−0.0030 (6)
O3	0.0705 (10)	0.0513 (8)	0.1096 (13)	0.0168 (7)	0.0280 (9)	0.0042 (8)
O4	0.0589 (8)	0.0617 (9)	0.0722 (9)	0.0009 (7)	0.0275 (7)	0.0066 (7)
N1	0.0419 (8)	0.0442 (8)	0.0447 (9)	−0.0064 (7)	0.0113 (7)	−0.0019 (6)
N2	0.0481 (9)	0.0522 (10)	0.0544 (10)	0.0065 (7)	0.0089 (8)	0.0050 (7)
C1	0.0409 (10)	0.0492 (10)	0.0452 (10)	−0.0066 (8)	0.0090 (8)	0.0009 (8)
C2	0.0395 (9)	0.0459 (10)	0.0376 (9)	−0.0025 (7)	0.0056 (8)	0.0008 (7)
C3	0.0409 (10)	0.0514 (11)	0.0423 (10)	−0.0053 (8)	0.0062 (8)	−0.0015 (8)
C4	0.0474 (11)	0.0470 (10)	0.0634 (13)	−0.0100 (8)	0.0090 (9)	0.0008 (9)
C5	0.0507 (11)	0.0416 (10)	0.0583 (12)	−0.0012 (8)	0.0056 (9)	−0.0007 (8)
C6	0.0406 (9)	0.0481 (10)	0.0400 (10)	0.0018 (8)	0.0072 (8)	0.0035 (8)
C7	0.0401 (9)	0.0465 (10)	0.0447 (10)	−0.0045 (7)	0.0077 (8)	0.0043 (8)
C8	0.0454 (10)	0.0401 (9)	0.0426 (10)	−0.0027 (7)	0.0058 (8)	−0.0017 (7)
C9	0.0435 (10)	0.0468 (10)	0.0460 (10)	−0.0032 (8)	0.0076 (8)	0.0031 (8)
C10	0.0534 (12)	0.0527 (11)	0.0665 (13)	0.0060 (9)	0.0124 (10)	−0.0029 (9)
C11	0.0737 (14)	0.0431 (11)	0.0862 (16)	0.0043 (10)	0.0163 (12)	−0.0049 (10)
C12	0.0694 (14)	0.0470 (11)	0.0883 (16)	−0.0121 (10)	0.0195 (12)	−0.0014 (10)
C13	0.0525 (11)	0.0510 (11)	0.0675 (13)	−0.0068 (9)	0.0183 (10)	−0.0023 (9)

Geometric parameters (Å, º)

O1—C3	1.276 (2)	C4—H4	0.9300
O2—C9	1.352 (2)	C5—C6	1.408 (2)
O2—H9	0.8200	C5—H5	0.9300
O3—N2	1.225 (2)	C6—C7	1.364 (2)
O4—N2	1.226 (2)	C7—H7	0.9300
N1—C1	1.298 (2)	C8—C13	1.384 (2)
N1—C8	1.418 (2)	C8—C9	1.389 (2)
N1—H2	0.8600	C9—C10	1.386 (3)
N2—C6	1.444 (2)	C10—C11	1.378 (3)
C1—C2	1.410 (2)	C10—H10	0.9300
C1—H1	0.9300	C11—C12	1.385 (3)
C2—C7	1.399 (2)	C11—H11	0.9300
C2—C3	1.443 (2)	C12—C13	1.381 (3)
C3—C4	1.423 (2)	C12—H12	0.9300
C4—C5	1.356 (2)	C13—H13	0.9300
C9—O2—H9	109.5	C7—C6—N2	119.64 (15)
C1—N1—C8	128.60 (15)	C5—C6—N2	119.49 (16)
C1—N1—H2	115.7	C6—C7—C2	120.42 (16)
C8—N1—H2	115.7	C6—C7—H7	119.8
O3—N2—O4	122.35 (15)	C2—C7—H7	119.8
O3—N2—C6	118.86 (15)	C13—C8—C9	120.92 (16)
O4—N2—C6	118.79 (15)	C13—C8—N1	123.32 (16)

N1—C1—C2	123.60 (16)	C9—C8—N1	115.76 (14)
N1—C1—H1	118.2	O2—C9—C10	124.47 (16)
C2—C1—H1	118.2	O2—C9—C8	116.19 (15)
C7—C2—C1	118.58 (16)	C10—C9—C8	119.34 (16)
C7—C2—C3	119.95 (15)	C11—C10—C9	119.77 (18)
C1—C2—C3	121.46 (16)	C11—C10—H10	120.1
O1—C3—C4	122.72 (16)	C9—C10—H10	120.1
O1—C3—C2	120.43 (16)	C10—C11—C12	120.64 (18)
C4—C3—C2	116.85 (15)	C10—C11—H11	119.7
C5—C4—C3	121.92 (17)	C12—C11—H11	119.7
C5—C4—H4	119.0	C13—C12—C11	120.12 (18)
C3—C4—H4	119.0	C13—C12—H12	119.9
C4—C5—C6	119.99 (17)	C11—C12—H12	119.9
C4—C5—H5	120.0	C12—C13—C8	119.19 (18)
C6—C5—H5	120.0	C12—C13—H13	120.4
C7—C6—C5	120.86 (16)	C8—C13—H13	120.4

C8—N1—C1—C2	−179.49 (15)	N2—C6—C7—C2	179.08 (15)
N1—C1—C2—C7	177.23 (16)	C1—C2—C7—C6	−178.79 (16)
N1—C1—C2—C3	−1.9 (3)	C3—C2—C7—C6	0.3 (3)
C7—C2—C3—O1	−179.67 (16)	C1—N1—C8—C13	−0.5 (3)
C1—C2—C3—O1	−0.6 (3)	C1—N1—C8—C9	179.91 (17)
C7—C2—C3—C4	−0.1 (2)	C13—C8—C9—O2	178.46 (16)
C1—C2—C3—C4	179.00 (15)	N1—C8—C9—O2	−1.9 (2)
O1—C3—C4—C5	179.64 (17)	C13—C8—C9—C10	−1.0 (3)
C2—C3—C4—C5	0.1 (3)	N1—C8—C9—C10	178.64 (16)
C3—C4—C5—C6	−0.3 (3)	O2—C9—C10—C11	−179.28 (18)
C4—C5—C6—C7	0.5 (3)	C8—C9—C10—C11	0.1 (3)
C4—C5—C6—N2	−179.10 (16)	C9—C10—C11—C12	0.6 (3)
O3—N2—C6—C7	171.10 (16)	C10—C11—C12—C13	−0.4 (3)
O4—N2—C6—C7	−9.5 (2)	C11—C12—C13—C8	−0.4 (3)
O3—N2—C6—C5	−9.3 (2)	C9—C8—C13—C12	1.1 (3)
O4—N2—C6—C5	170.09 (16)	N1—C8—C13—C12	−178.47 (17)
C5—C6—C7—C2	−0.5 (3)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H2···O1	0.86	1.92	2.613 (2)	137
O2—H9···O1^{i}	0.82	1.80	2.573 (2)	157
C1—H1···O4^{ii}	0.93	2.35	3.220 (2)	156

Symmetry codes: (i) −*x*, −*y*, −*z*+2; (ii) −*x*+2, −*y*, −*z*+1.