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ISSN 2414-3146

6-[(2-Hydroxy-5-methylanilino)methylidene]-4-nitrocyclohexa-2,4-dien-1-one

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Received 15 October 2020
Accepted 16 October 2020

Edited by W. T. A. Harrison, University of Aberdeen, Scotland

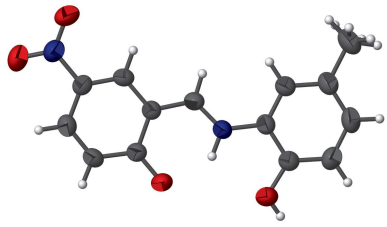
Keywords: crystal structure; Schiff base; tridentate ligand.

CCDC reference: 2038926

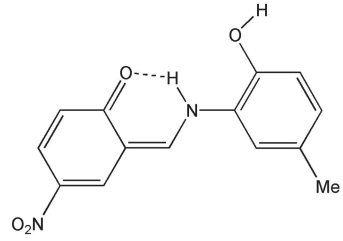
Structural data: full structural data are available from iucrdata.iucr.org

The title compound, $C_{14}H_{12}N_2O_4$, is nearly planar with a dihedral angle between the aromatic rings of 1.41 (8)°. The phenolic O atom is deprotonated and the N atom of the azomethine unit carries the proton, thereby forming an intramolecular N—H···O hydrogen bond. In the crystal, the molecules form inversion dimers *via* pairwise O—H···O hydrogen bonds.

3D view



Chemical scheme



Structure description

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). We are working on silicon, tin, and titanium complexes with tridentate *O*,*N*,*O*-ligands (Böhme & Günther, 2006, 2007; Böhme *et al.*, 2006; Paul *et al.*, 2014; Warncke *et al.*, 2012, 2016; Schwarzer *et al.*, 2018).

The title compound was prepared in order to extend the series of available ligands. Its preparation was performed according to methods described in the literature for the parent compound salicyclidene-*o*-aminophenol (salopH_2; Freeman & White, 1956; Pettinari *et al.*, 2001) by the reaction of 2-hydroxy-5-nitrobenzaldehyde and 2-amino-4-methylphenol in ethanol.

The molecule is nearly planar with a dihedral angle between the aromatic rings of 1.41 (8)°. Atom H2 forms an intramolecular hydrogen bond (Table 1, Fig. 1) between the phenolic oxygen atom O1 and N1 of the azomethine unit: the hydrogen atom is localized at a distance of 0.93 (2) Å from N1, indicating the presence of the keto–amine form. The presence of a quinoidal structure is further supported by the shortening of the bond C3—O1 to 1.2734 (19) Å and the lengthening of the adjacent C—C bonds in the phenyl ring [C2—C3 = 1.446 (2), C3—C4 = 1.420 (2) Å] (Nazır *et al.*, 2000; Warncke *et al.*, 2016). There are several structure reports of Schiff bases with an oxygen atom in the *ortho*-

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H2···O1	0.93 (2)	1.84 (2)	2.6065 (18)	138.1 (17)
O2—H9···O1^{i}	0.79 (3)	1.81 (3)	2.5817 (18)	163 (3)
C1—H1···O4^{ii}	0.93	2.32	3.220 (2)	162

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

position where the intramolecular bridging hydrogen atom is localized at the nitrogen atom (*e.g.* Pradeep, 2005; Dubs *et al.*, 2000; Höpfl *et al.*, 1998; Böhme & Fels, 2008*a*,*b*). The stabilization of salicylidene-imines by 'resonance-assisted hydrogen bonding' has been discussed previously (Hökelek *et al.*, 2004).

In the crystal, the molecule forms dimers *via* pairwise O2—H9···O1 hydrogen bonds. An intermolecular C—H···O short contact (H···O = 2.32 Å) to one of the O atoms of the nitro group is also present.

Synthesis and crystallization

To 2-amino-4-methylphenol (1.13 g, 9.18 mmol) dissolved in ethanol (80 ml) was added 2-hydroxy-5-nitrobenzaldehyde (1.53 g, 9.18 mmol) in ethanol (20 ml). An orange precipitate appeared after addition. The resulting suspension was heated at reflux temperature for 2 h. The precipitate was filtered off and washed with ethanol. After drying, the product was purified by recrystallization from ethanol solution. Yellow solid (2.21 g, 88.4%, m.p. 536 K). NMR (DMSO, 300 K, TMS): ^{1}H: δ = 15.76, 10.17 (*s*, OH, NH, 2H), 9.31 (*s*, CH—N, 1H), 8.59–6.86 (*m*, CH_{ar} (ar = aromatic) 6H), 2.28 (*s*, Ar—CH_3, 3H); ^{13}C: 172.8 (C3), 158.9 (C1), 148.1 (C9), 136.6 (C6), 130.4, 129.8, 129.1, 128.7, 128.6, 120.6, 118.8, 116.4, 116.3 (9 signals for aromatic C), 20.1 (C14).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The methyl group at C14 is rotationally disordered over two orientations in a 0.59 (5):0.41 (5) ratio.

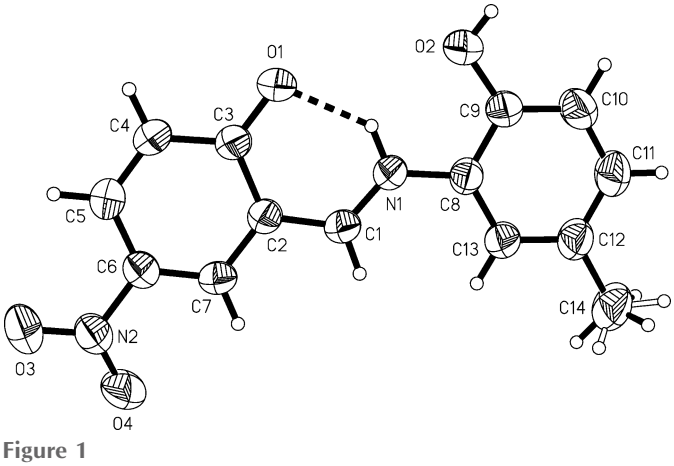


Figure 1
The molecular structure of the title compound, drawn with 50% probability displacement ellipsoids.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{14}H_{12}N_2O_4$
M_r	272.26
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	303
a, b, c (Å)	6.5499 (3), 7.6232 (3), 25.6211 (11)
β (°)	96.216 (1)
V (Å^3)	1271.77 (9)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.11
Crystal size (mm)	0.47 × 0.38 × 0.12
Data collection	
Diffractometer	Bruker SMART CCD
Absorption correction	–
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	11875, 2504, 1776
R_{int}	0.023
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.617
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.041, 0.114, 1.04
No. of reflections	2504
No. of parameters	191
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.16, −0.17

Computer programs: *SMART* and *SAINT* (Bruker, 2004), *SHELXS* (Sheldrick, 2008), *SHELXL2017/1* (Sheldrick, 2015) and *ORTEP-3 for Windows* (Farrugia, 2012).

Funding information

Funding for this research was provided by: Open Access Funding by the Publication Fund of the TU Bergakademie Freiberg.

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full crystallographic data

IUCrData (2020). **5**, x201384 [https://doi.org/10.1107/S241431462001384X]

6-[(2-Hydroxy-5-methylanilino)methylidene]-4-nitrocyclohexa-2,4-dien-1-one

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Crystal data

$C_{14}H_{12}N_2O_4$
M_r = 272.26
Monoclinic, $P2_1/c$
a = 6.5499 (3) Å
b = 7.6232 (3) Å
c = 25.6211 (11) Å
β = 96.216 (1)°
V = 1271.77 (9) Å^3
Z = 4
$F(000)$ = 568
D_x = 1.422 Mg m^{-3}
Melting point: 536 K
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 5292 reflections
θ = 2.7–30.2°
μ = 0.11 mm^{-1}
T = 303 K
Prism, yellow
0.47 × 0.38 × 0.12 mm

Data collection

Bruker SMART CCD diffractometer
Radiation source: sealed tube
Graphite monochromator
phi and ω scans
11875 measured reflections
2504 independent reflections
1776 reflections with $I > 2\sigma(I)$
R_{int} = 0.023
θ_{max} = 26.0°, θ_{min} = 2.8°
h = −5→8
k = −9→9
l = −31→27

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.114
S = 1.04
2504 reflections
191 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0502P)^2 + 0.2714P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.16 e Å^{-3}
$\Delta\rho_{min}$ = −0.17 e Å^{-3}

Special details

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

Refinement. Hydrogen atoms bonded to C were positioned geometrically and allowed to ride on their parent atoms, with C—H = 0.93 Å for Csp^2, and 0.96 Å for CH_3. U_{iso}(H) = xU_{eq}(C), where x = 1.2 for Csp^2 and 1.5 for CH_3. The hydrogen atoms at N1 and O2 (H2 and H9) were located by difference Fourier synthesis and freely refined.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
O1	0.19636 (18)	0.85732 (19)	−0.05759 (5)	0.0666 (4)	
O2	0.5013 (2)	0.9258 (2)	0.05845 (5)	0.0669 (4)	
H9	0.596 (4)	0.991 (3)	0.0647 (10)	0.093 (9)*	
N1	0.1333 (2)	0.79690 (18)	0.03950 (5)	0.0468 (4)	
H2	0.215 (3)	0.835 (3)	0.0143 (8)	0.077 (6)*	
N2	−0.5557 (2)	0.5515 (2)	−0.11991 (6)	0.0576 (4)	
O3	−0.6215 (2)	0.5556 (2)	−0.16650 (6)	0.0845 (5)	
O4	−0.6495 (2)	0.48027 (19)	−0.08672 (6)	0.0740 (4)	
C1	−0.0438 (2)	0.7351 (2)	0.02029 (6)	0.0481 (4)	
H1	−0.133979	0.696628	0.043493	0.058*	
C2	−0.1063 (2)	0.7235 (2)	−0.03427 (6)	0.0447 (4)	
C3	0.0234 (2)	0.7870 (2)	−0.07240 (6)	0.0479 (4)	
C4	−0.0523 (3)	0.7664 (3)	−0.12613 (7)	0.0563 (5)	
H4	0.027853	0.804716	−0.151711	0.068*	
C5	−0.2369 (3)	0.6928 (2)	−0.14126 (7)	0.0541 (5)	
H5	−0.282485	0.681930	−0.176767	0.065*	
C6	−0.3600 (2)	0.6328 (2)	−0.10331 (7)	0.0471 (4)	
C7	−0.2971 (2)	0.6483 (2)	−0.05097 (7)	0.0478 (4)	
H7	−0.381007	0.608690	−0.026386	0.057*	
C8	0.2130 (2)	0.8135 (2)	0.09270 (6)	0.0456 (4)	
C9	0.4090 (3)	0.8863 (2)	0.10173 (7)	0.0510 (4)	
C10	0.4949 (3)	0.9106 (3)	0.15292 (7)	0.0634 (5)	
H10	0.624875	0.960150	0.159624	0.076*	
C11	0.3879 (3)	0.8614 (3)	0.19404 (7)	0.0684 (6)	
H11	0.446815	0.879703	0.228288	0.082*	
C12	0.1941 (3)	0.7851 (3)	0.18568 (7)	0.0599 (5)	
C13	0.1080 (3)	0.7624 (2)	0.13445 (6)	0.0526 (4)	
H13	−0.021705	0.712381	0.127863	0.063*	
C14	0.0811 (4)	0.7261 (4)	0.23108 (8)	0.0869 (7)	
H14A	0.169804	0.653676	0.254283	0.130*	0.59 (5)
H14B	−0.038512	0.660356	0.217905	0.130*	0.59 (5)
H14C	0.040213	0.826966	0.249852	0.130*	0.59 (5)
H14D	0.141816	0.780054	0.262897	0.130*	0.41 (5)
H14E	0.090280	0.600890	0.234441	0.130*	0.41 (5)
H14F	−0.060592	0.760054	0.224701	0.130*	0.41 (5)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0548 (7)	0.0944 (10)	0.0521 (8)	−0.0311 (7)	0.0125 (6)	−0.0061 (7)
O2	0.0594 (8)	0.0874 (10)	0.0547 (8)	−0.0275 (8)	0.0103 (6)	0.0008 (7)
N1	0.0490 (8)	0.0530 (9)	0.0390 (8)	−0.0094 (7)	0.0082 (6)	−0.0016 (6)
N2	0.0509 (8)	0.0630 (10)	0.0572 (10)	−0.0064 (7)	−0.0016 (7)	−0.0013 (8)
O3	0.0695 (9)	0.1175 (13)	0.0616 (10)	−0.0193 (8)	−0.0147 (7)	0.0000 (8)
O4	0.0583 (8)	0.0872 (10)	0.0757 (10)	−0.0265 (7)	0.0040 (7)	0.0075 (8)

C1	0.0475 (9)	0.0534 (10)	0.0446 (10)	−0.0096 (8)	0.0108 (7)	−0.0013 (8)
C2	0.0462 (9)	0.0476 (10)	0.0411 (9)	−0.0056 (7)	0.0074 (7)	−0.0032 (7)
C3	0.0466 (9)	0.0539 (10)	0.0446 (9)	−0.0076 (8)	0.0107 (7)	−0.0055 (8)
C4	0.0561 (10)	0.0722 (12)	0.0427 (10)	−0.0119 (9)	0.0145 (8)	−0.0019 (9)
C5	0.0567 (10)	0.0636 (12)	0.0414 (10)	−0.0032 (9)	0.0036 (8)	−0.0037 (8)
C6	0.0439 (8)	0.0481 (10)	0.0487 (10)	−0.0033 (7)	0.0021 (7)	−0.0025 (8)
C7	0.0453 (9)	0.0518 (10)	0.0476 (10)	−0.0073 (7)	0.0111 (7)	0.0024 (8)
C8	0.0514 (9)	0.0459 (9)	0.0393 (9)	−0.0042 (7)	0.0044 (7)	−0.0007 (7)
C9	0.0520 (9)	0.0543 (11)	0.0470 (10)	−0.0077 (8)	0.0064 (8)	0.0025 (8)
C10	0.0543 (10)	0.0788 (14)	0.0546 (12)	−0.0118 (10)	−0.0058 (8)	0.0012 (10)
C11	0.0759 (13)	0.0842 (15)	0.0423 (11)	−0.0087 (11)	−0.0059 (9)	0.0016 (10)
C12	0.0717 (12)	0.0652 (12)	0.0428 (10)	−0.0087 (10)	0.0062 (8)	0.0012 (9)
C13	0.0566 (10)	0.0566 (11)	0.0452 (10)	−0.0116 (8)	0.0081 (8)	−0.0013 (8)
C14	0.1101 (18)	0.1055 (18)	0.0469 (12)	−0.0257 (15)	0.0171 (12)	0.0029 (12)

Geometric parameters (Å, º)

O1—C3	1.2734 (19)	C6—C7	1.365 (2)
O2—C9	1.353 (2)	C7—H7	0.9300
O2—H9	0.79 (3)	C8—C13	1.389 (2)
N1—C1	1.298 (2)	C8—C9	1.394 (2)
N1—C8	1.411 (2)	C9—C10	1.383 (3)
N1—H2	0.93 (2)	C10—C11	1.379 (3)
N2—O3	1.225 (2)	C10—H10	0.9300
N2—O4	1.2280 (18)	C11—C12	1.392 (3)
N2—C6	1.446 (2)	C11—H11	0.9300
C1—C2	1.416 (2)	C12—C13	1.382 (2)
C1—H1	0.9300	C12—C14	1.513 (3)
C2—C7	1.399 (2)	C13—H13	0.9300
C2—C3	1.446 (2)	C14—H14A	0.9600
C3—C4	1.420 (2)	C14—H14B	0.9600
C4—C5	1.351 (2)	C14—H14C	0.9600
C4—H4	0.9300	C14—H14D	0.9600
C5—C6	1.405 (2)	C14—H14E	0.9600
C5—H5	0.9300	C14—H14F	0.9600
C9—O2—H9	112.4 (18)	C13—C8—N1	123.79 (15)
C1—N1—C8	128.37 (14)	C9—C8—N1	115.70 (14)
C1—N1—H2	114.1 (13)	O2—C9—C10	125.12 (16)
C8—N1—H2	117.6 (13)	O2—C9—C8	115.95 (15)
O3—N2—O4	122.47 (16)	C10—C9—C8	118.92 (15)
O3—N2—C6	118.86 (15)	C11—C10—C9	119.98 (17)
O4—N2—C6	118.67 (15)	C11—C10—H10	120.0
N1—C1—C2	123.24 (14)	C9—C10—H10	120.0
N1—C1—H1	118.4	C10—C11—C12	121.78 (18)
C2—C1—H1	118.4	C10—C11—H11	119.1
C7—C2—C1	118.74 (14)	C12—C11—H11	119.1
C7—C2—C3	120.10 (14)	C13—C12—C11	118.04 (17)

C1—C2—C3	121.17 (14)	C13—C12—C14	120.65 (18)
O1—C3—C4	122.77 (14)	C11—C12—C14	121.31 (18)
O1—C3—C2	120.57 (15)	C12—C13—C8	120.75 (16)
C4—C3—C2	116.67 (14)	C12—C13—H13	119.6
C5—C4—C3	122.11 (15)	C8—C13—H13	119.6
C5—C4—H4	118.9	C12—C14—H14A	109.5
C3—C4—H4	118.9	C12—C14—H14B	109.5
C4—C5—C6	119.96 (16)	H14A—C14—H14B	109.5
C4—C5—H5	120.0	C12—C14—H14C	109.5
C6—C5—H5	120.0	H14A—C14—H14C	109.5
C7—C6—C5	121.13 (15)	H14B—C14—H14C	109.5
C7—C6—N2	119.33 (15)	C12—C14—H14D	109.5
C5—C6—N2	119.53 (15)	C12—C14—H14E	109.5
C6—C7—C2	120.03 (14)	H14D—C14—H14E	109.5
C6—C7—H7	120.0	C12—C14—H14F	109.5
C2—C7—H7	120.0	H14D—C14—H14F	109.5
C13—C8—C9	120.51 (15)	H14E—C14—H14F	109.5

C8—N1—C1—C2	−179.40 (16)	C1—C2—C7—C6	−178.99 (16)
N1—C1—C2—C7	177.42 (16)	C3—C2—C7—C6	0.7 (3)
N1—C1—C2—C3	−2.3 (3)	C1—N1—C8—C13	0.4 (3)
C7—C2—C3—O1	179.29 (16)	C1—N1—C8—C9	−179.56 (17)
C1—C2—C3—O1	−1.0 (3)	C13—C8—C9—O2	177.63 (16)
C7—C2—C3—C4	−0.8 (2)	N1—C8—C9—O2	−2.4 (2)
C1—C2—C3—C4	178.95 (16)	C13—C8—C9—C10	−1.5 (3)
O1—C3—C4—C5	−179.43 (18)	N1—C8—C9—C10	178.44 (16)
C2—C3—C4—C5	0.6 (3)	O2—C9—C10—C11	−178.40 (19)
C3—C4—C5—C6	−0.4 (3)	C8—C9—C10—C11	0.7 (3)
C4—C5—C6—C7	0.4 (3)	C9—C10—C11—C12	0.7 (3)
C4—C5—C6—N2	−178.90 (16)	C10—C11—C12—C13	−1.2 (3)
O3—N2—C6—C7	171.96 (17)	C10—C11—C12—C14	177.9 (2)
O4—N2—C6—C7	−8.3 (2)	C11—C12—C13—C8	0.4 (3)
O3—N2—C6—C5	−8.8 (3)	C14—C12—C13—C8	−178.81 (19)
O4—N2—C6—C5	170.98 (16)	C9—C8—C13—C12	1.0 (3)
C5—C6—C7—C2	−0.5 (3)	N1—C8—C13—C12	−178.96 (17)
N2—C6—C7—C2	178.75 (15)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H2···O1	0.93 (2)	1.84 (2)	2.6065 (18)	138.1 (17)
O2—H9···O1^{i}	0.79 (3)	1.81 (3)	2.5817 (18)	163 (3)
C1—H1···O4^{ii}	0.93	2.32	3.220 (2)	162

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