

2-[(*E*)-[(4-Methylphenyl)imino]methyl]-4-nitrophenol–2-[(*E*)-[(4-methylphenyl)iminio]methyl]-4-nitrophenolate (0.60/0.40)

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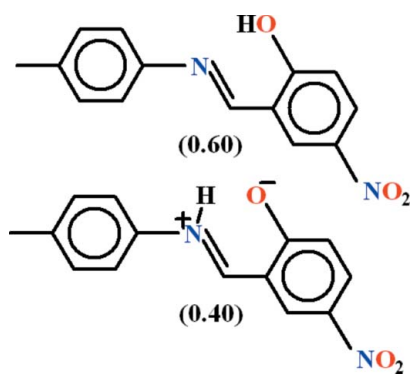
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Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.049; wR factor = 0.133; data-to-parameter ratio = 12.4.

The crystal of the title compound, $0.6\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_3 \cdot 0.4\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_3$, contains a mixture of its neutral (OH containing) and zwitterionic (NH containing) forms, in a 0.60 (4):0.40 (4) ratio. The former generates an $S(6)$ loop via an intramolecular $\text{O}-\text{H} \cdots \text{N}$ hydrogen bond and the latter generates an $S(6)$ loop via an $\text{N}-\text{H} \cdots \text{O}$ hydrogen bond. The aromatic rings are oriented at a dihedral angle of 42.52 (10)°. In the crystal, $\text{C}-\text{H} \cdots \pi$ interactions occur and aromatic $\pi-\pi$ stacking interactions [centroid-centroid separations = 3.7106 (12) and 3.9177 (13) Å] consolidate the packing.

Related literature

For related structures, see: Hijji *et al.* (2009); Kılıç *et al.* (2009). For graph-set notation, see: Bernstein *et al.* (1995).



Experimental

Crystal data

$0.6\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_3 \cdot 0.4\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_3$

$M_r = 256.26$

Monoclinic, $P2_1/c$
 $a = 14.0623$ (6) Å
 $b = 14.1723$ (8) Å
 $c = 6.2357$ (3) Å
 $\beta = 95.400$ (2)°
 $V = 1237.23$ (11) Å³

$Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.10$ mm⁻¹
 $T = 296$ K
 $0.25 \times 0.22 \times 0.20$ mm

Data collection

Bruker Kappa APEXII CCD diffractometer
 Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
 $T_{\min} = 0.976$, $T_{\max} = 0.985$

9733 measured reflections
 2238 independent reflections
 1395 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.041$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.049$
 $wR(F^2) = 0.133$
 $S = 1.03$
 2238 reflections
 181 parameters

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.20$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.18$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$Cg1$ and $Cg2$ are the centroids of the $C1-C6$ and $C9-C14$ rings, respectively.

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$O1-H1 \cdots N1$	0.80 (6)	1.86 (6)	2.566 (3)	147 (6)
$N1-H1A \cdots O1$	0.97 (8)	1.71 (7)	2.566 (3)	146 (6)
$C5-H5 \cdots Cg1^i$	0.93	2.84	3.515 (2)	130
$C11-H11 \cdots Cg2^{ii}$	0.93	2.82	3.490 (2)	130

Symmetry codes: (i) $x, -y + \frac{3}{2}, z + \frac{1}{2}$; (ii) $x, -y + \frac{3}{2}, z - \frac{1}{2}$.

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT* (Bruker, 2009); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *PLATON* (Spek, 2009); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PLATON* (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB6352).

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supplementary materials

Acta Cryst. (2011). E67, o2319 [doi:10.1107/S1600536811032028]

2-*{(E)-[(4-Methylphenyl)imino]methyl}*-4-nitrophenol-2-*{(E)-[(4-methylphenyl)iminio]methyl}*-4-nitrophenolate (0.60/0.40)

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Comment

The crystal structures of 2-((4-methoxyphenyl)iminomethyl)-4-nitrophenol (Kılıç *et al.*, 2009) and 2-(((*E*)-(2-hydroxy-5-nitrophenyl) methylidene)ammonio)-4-nitrophenolate (Hijji *et al.*, 2009) have been published which are related to the title compound (I), (Fig. 1). The title compound consists of two isomers with 0.60:0.40 ratio.

In (I), the 4-methylanilinic group A (C1—C7/N1) and the 2-hydroxy-5-nitrobenzaldehyde group B (C8—C14/N2/O1/O2/O3) are almost planar with r.m.s. deviations of 0.0283 and 0.0222 Å, respectively. The dihedral angle between A/B is 41.86 (4)°. There exist intramolecular hydrogen bonds of O—H...N and N—H...O type completing S(6) (Bernstein *et al.*, 1995) ring motifs (Table 1, Fig. 2). In the crystal, there exist π - π interaction between the centroids of the benzene rings of 4-methylaniline with a separation of 3.9177 (13) Å and a slippage of 1.333 Å. Similarly, π - π interaction between the centroids of the benzene rings of 2-hydroxy-5-nitrobenzaldehyde also exist with a separation of 3.7106 (12) Å and a slippage of 1.452 Å. In consolidating the crystal structure, C—H... π bonds (Table 1) also play role.

Experimental

Equimolar quantities of 2-hydroxy-5-nitrobenzaldehyde and 4-methylaniline were refluxed in ethanol for 30 min resulting in a yellow solution. The solution was kept at room temperature which afforded yellow prisms of (I) after three days.

Refinement

The coordinates of hydrogen atoms of O—H and N—H were refined. The occupancy factor of both H-atoms was refined and therefore, the two isomers are of 0.60:0.40 ratio. The H-atoms were positioned geometrically (C—H = 0.93 Å) and refined as riding with $U_{\text{iso}}(\text{H}) = xU_{\text{eq}}(\text{C, N, O})$, where $x = 1.2$ for all H-atoms.

Figures

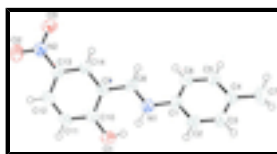


Fig. 1. View of the title compound with displacement ellipsoids drawn at the 50% probability level. The dotted line represents the minority H-atom.

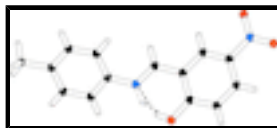


Fig. 2. Overlapped intramolecular hydrogen bonds forming two S(6) ring motif.

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Crystal data

$0.6\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_3 \cdot 0.4\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_3$

$M_r = 256.26$

Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

$a = 14.0623$ (6) Å

$b = 14.1723$ (8) Å

$c = 6.2357$ (3) Å

$\beta = 95.400$ (2)°

$V = 1237.23$ (11) Å³

$Z = 4$

$F(000) = 536$

$D_x = 1.376$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 1395 reflections

$\theta = 2.0$ – 25.3 °

$\mu = 0.10$ mm⁻¹

$T = 296$ K

Prism, yellow

$0.25 \times 0.22 \times 0.20$ mm

Data collection

Bruker Kappa APEXII CCD
diffractometer

Radiation source: fine-focus sealed tube
graphite

Detector resolution: 8.10 pixels mm⁻¹
 ω scans

Absorption correction: multi-scan
(*SADABS*; Bruker, 2005)

$T_{\min} = 0.976$, $T_{\max} = 0.985$

9733 measured reflections

2238 independent reflections

1395 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.041$

$\theta_{\max} = 25.3$ °, $\theta_{\min} = 2.0$ °

$h = -16 \rightarrow 16$

$k = -17 \rightarrow 17$

$l = -7 \rightarrow 7$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.049$

$wR(F^2) = 0.133$

$S = 1.03$

2238 reflections

181 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 atoms treated by a mixture of independent and
constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0558P)^2 + 0.2667P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.20$ e Å⁻³

$\Delta\rho_{\min} = -0.18$ e Å⁻³

Extinction correction: *SHELXL97* (Sheldrick, 2008),

$F_c^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.0052 (14)

Special details

Geometry. Bond distances, angles *etc.* have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles

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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
O1	0.18732 (12)	0.66637 (13)	0.3141 (3)	0.0536 (6)	
O2	-0.21627 (11)	0.59616 (18)	0.6085 (3)	0.0928 (9)	
O3	-0.13153 (11)	0.55621 (14)	0.8965 (3)	0.0676 (7)	
N1	0.28626 (12)	0.62025 (13)	0.6653 (3)	0.0406 (6)	
N2	-0.13922 (12)	0.58577 (15)	0.7115 (3)	0.0499 (7)	
C1	0.37651 (14)	0.62162 (15)	0.7884 (3)	0.0379 (7)	
C2	0.45601 (14)	0.59352 (16)	0.6902 (4)	0.0452 (8)	
C3	0.54536 (15)	0.59847 (17)	0.8003 (4)	0.0507 (9)	
C4	0.55810 (15)	0.63374 (16)	1.0085 (4)	0.0465 (8)	
C5	0.47796 (15)	0.66189 (16)	1.1032 (3)	0.0453 (8)	
C6	0.38783 (14)	0.65645 (16)	0.9965 (3)	0.0429 (8)	
C7	0.65595 (16)	0.6427 (2)	1.1264 (4)	0.0708 (10)	
C8	0.20829 (14)	0.60487 (15)	0.7508 (3)	0.0394 (7)	
C9	0.11702 (14)	0.61460 (15)	0.6278 (3)	0.0353 (7)	
C10	0.11017 (15)	0.64786 (15)	0.4120 (3)	0.0392 (7)	
C11	0.01983 (15)	0.66214 (15)	0.3029 (3)	0.0431 (8)	
C12	-0.06138 (15)	0.64214 (15)	0.3987 (3)	0.0431 (8)	
C13	-0.05334 (14)	0.60742 (15)	0.6096 (3)	0.0382 (7)	
C14	0.03375 (13)	0.59379 (15)	0.7226 (3)	0.0365 (7)	
H1	0.234 (4)	0.652 (3)	0.390 (10)	0.0643*	0.60 (4)
H2	0.44905	0.57122	0.54928	0.0542*	
H3	0.59813	0.57782	0.73398	0.0608*	
H5	0.48500	0.68523	1.24322	0.0544*	
H6	0.33496	0.67605	1.06375	0.0515*	
H7A	0.65363	0.62414	1.27390	0.1061*	
H7B	0.67695	0.70705	1.12087	0.1061*	
H7C	0.69974	0.60270	1.05983	0.1061*	
H8	0.21077	0.58713	0.89483	0.0472*	
H11	0.01490	0.68561	0.16300	0.0517*	
H12	-0.12117	0.65149	0.32459	0.0517*	
H14	0.03733	0.57065	0.86269	0.0438*	
H1A	0.274 (5)	0.641 (4)	0.518 (13)	0.0487*	0.40 (4)

supplementary materials

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0503 (10)	0.0696 (13)	0.0423 (10)	-0.0045 (9)	0.0123 (8)	0.0082 (8)
O2	0.0349 (10)	0.171 (2)	0.0711 (13)	0.0043 (12)	-0.0028 (9)	0.0236 (13)
O3	0.0485 (10)	0.1043 (16)	0.0511 (11)	-0.0035 (9)	0.0110 (8)	0.0189 (10)
N1	0.0362 (10)	0.0452 (12)	0.0407 (11)	0.0013 (8)	0.0053 (8)	0.0002 (9)
N2	0.0361 (10)	0.0681 (14)	0.0454 (12)	-0.0001 (10)	0.0039 (9)	0.0003 (10)
C1	0.0328 (11)	0.0393 (13)	0.0417 (13)	0.0008 (9)	0.0045 (9)	0.0027 (10)
C2	0.0424 (12)	0.0507 (15)	0.0435 (13)	0.0027 (11)	0.0094 (10)	-0.0063 (11)
C3	0.0354 (12)	0.0554 (16)	0.0627 (16)	0.0073 (11)	0.0127 (11)	-0.0019 (12)
C4	0.0390 (12)	0.0473 (15)	0.0524 (14)	0.0023 (10)	0.0008 (10)	0.0044 (12)
C5	0.0457 (13)	0.0513 (15)	0.0391 (12)	0.0015 (11)	0.0044 (10)	-0.0016 (11)
C6	0.0387 (12)	0.0489 (14)	0.0424 (13)	0.0016 (10)	0.0100 (10)	-0.0003 (11)
C7	0.0458 (14)	0.086 (2)	0.0776 (19)	0.0041 (14)	-0.0102 (13)	-0.0008 (16)
C8	0.0398 (12)	0.0403 (14)	0.0383 (12)	0.0014 (10)	0.0053 (10)	0.0032 (10)
C9	0.0350 (11)	0.0356 (12)	0.0351 (12)	-0.0005 (9)	0.0030 (9)	0.0003 (9)
C10	0.0432 (12)	0.0378 (13)	0.0372 (12)	-0.0030 (10)	0.0077 (10)	-0.0014 (10)
C11	0.0537 (14)	0.0440 (14)	0.0309 (11)	-0.0015 (11)	0.0005 (10)	0.0046 (10)
C12	0.0427 (12)	0.0441 (14)	0.0406 (13)	0.0014 (10)	-0.0067 (10)	-0.0023 (10)
C13	0.0351 (11)	0.0422 (14)	0.0378 (12)	-0.0019 (9)	0.0055 (9)	-0.0025 (10)
C14	0.0392 (11)	0.0394 (13)	0.0308 (11)	-0.0002 (10)	0.0029 (9)	0.0007 (9)

Geometric parameters (\AA , $^\circ$)

O1—C10	1.320 (3)	C9—C10	1.421 (3)
O2—N2	1.215 (2)	C10—C11	1.398 (3)
O3—N2	1.223 (3)	C11—C12	1.367 (3)
O1—H1	0.80 (6)	C12—C13	1.399 (3)
N1—C1	1.420 (3)	C13—C14	1.368 (3)
N1—C8	1.282 (3)	C2—H2	0.9300
N2—C13	1.449 (3)	C3—H3	0.9300
N1—H1A	0.96 (8)	C5—H5	0.9300
C1—C2	1.383 (3)	C6—H6	0.9300
C1—C6	1.384 (3)	C7—H7A	0.9600
C2—C3	1.376 (3)	C7—H7B	0.9600
C3—C4	1.387 (3)	C7—H7C	0.9600
C4—C5	1.380 (3)	C8—H8	0.9300
C4—C7	1.503 (3)	C11—H11	0.9300
C5—C6	1.377 (3)	C12—H12	0.9300
C8—C9	1.439 (3)	C14—H14	0.9300
C9—C14	1.392 (3)		
C10—O1—H1	110 (4)	N2—C13—C12	119.32 (18)
C1—N1—C8	122.22 (18)	N2—C13—C14	119.13 (17)
O2—N2—O3	122.38 (18)	C12—C13—C14	121.55 (18)
O3—N2—C13	118.87 (17)	C9—C14—C13	119.96 (18)
O2—N2—C13	118.74 (18)	C1—C2—H2	120.00

C8—N1—H1A	111 (4)	C3—C2—H2	120.00
C1—N1—H1A	126 (4)	C2—C3—H3	119.00
N1—C1—C2	118.38 (18)	C4—C3—H3	119.00
N1—C1—C6	122.00 (18)	C4—C5—H5	119.00
C2—C1—C6	119.45 (19)	C6—C5—H5	119.00
C1—C2—C3	120.2 (2)	C1—C6—H6	120.00
C2—C3—C4	121.1 (2)	C5—C6—H6	120.00
C3—C4—C5	117.8 (2)	C4—C7—H7A	109.00
C3—C4—C7	121.3 (2)	C4—C7—H7B	109.00
C5—C4—C7	120.9 (2)	C4—C7—H7C	109.00
C4—C5—C6	121.92 (19)	H7A—C7—H7B	109.00
C1—C6—C5	119.51 (18)	H7A—C7—H7C	109.00
N1—C8—C9	121.13 (18)	H7B—C7—H7C	109.00
C8—C9—C14	119.82 (17)	N1—C8—H8	119.00
C8—C9—C10	120.96 (18)	C9—C8—H8	119.00
C10—C9—C14	119.20 (18)	C10—C11—H11	119.00
O1—C10—C9	121.23 (19)	C12—C11—H11	119.00
O1—C10—C11	119.66 (18)	C11—C12—H12	120.00
C9—C10—C11	119.11 (18)	C13—C12—H12	120.00
C10—C11—C12	121.02 (18)	C9—C14—H14	120.00
C11—C12—C13	119.13 (19)	C13—C14—H14	120.00
C8—N1—C1—C2	149.4 (2)	C4—C5—C6—C1	0.2 (3)
C8—N1—C1—C6	-35.4 (3)	N1—C8—C9—C10	-4.4 (3)
C1—N1—C8—C9	172.72 (19)	N1—C8—C9—C14	177.4 (2)
O2—N2—C13—C12	1.9 (3)	C8—C9—C10—O1	3.4 (3)
O2—N2—C13—C14	-178.5 (2)	C8—C9—C10—C11	-175.9 (2)
O3—N2—C13—C12	-179.4 (2)	C14—C9—C10—O1	-178.4 (2)
O3—N2—C13—C14	0.3 (3)	C14—C9—C10—C11	2.3 (3)
N1—C1—C2—C3	176.6 (2)	C8—C9—C14—C13	176.8 (2)
C6—C1—C2—C3	1.3 (3)	C10—C9—C14—C13	-1.4 (3)
N1—C1—C6—C5	-175.7 (2)	O1—C10—C11—C12	178.9 (2)
C2—C1—C6—C5	-0.5 (3)	C9—C10—C11—C12	-1.8 (3)
C1—C2—C3—C4	-1.7 (4)	C10—C11—C12—C13	0.4 (3)
C2—C3—C4—C5	1.3 (3)	C11—C12—C13—N2	-179.76 (19)
C2—C3—C4—C7	-177.7 (2)	C11—C12—C13—C14	0.6 (3)
C3—C4—C5—C6	-0.6 (3)	N2—C13—C14—C9	-179.70 (19)
C7—C4—C5—C6	178.4 (2)	C12—C13—C14—C9	0.0 (3)

Hydrogen-bond geometry (Å, °)

Cg1 and Cg2 are the centroids of the C1—C6 and C9—C14 rings, respectively.

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1—H1...N1	0.80 (6)	1.86 (6)	2.566 (3)	147 (6)
N1—H1A...O1	0.97 (8)	1.71 (7)	2.566 (3)	146 (6)
C5—H5...Cg1 ⁱ	0.93	2.84	3.515 (2)	130
C11—H11...Cg2 ⁱⁱ	0.93	2.82	3.490 (2)	130

Symmetry codes: (i) $x, -y+3/2, z+1/2$; (ii) $x, -y+3/2, z-1/2$.

Fig. 1

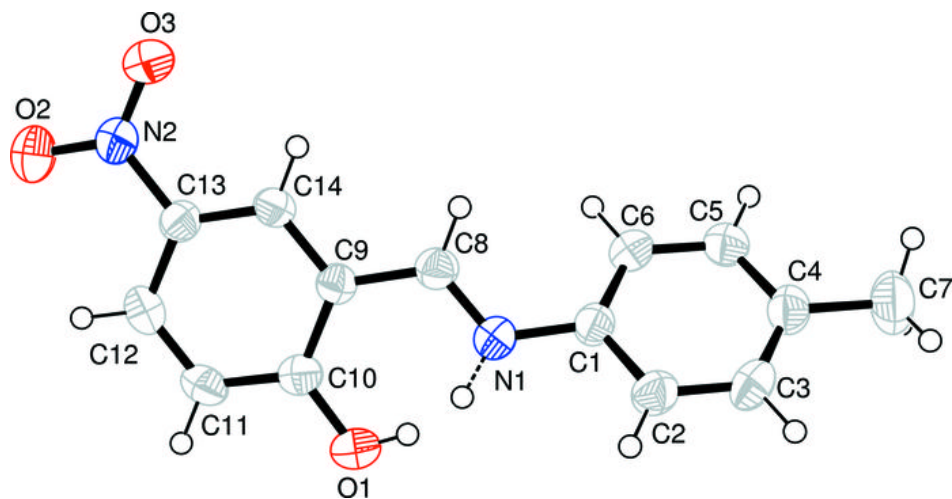


Fig. 2

