

3-[(2-Oxo-1-naphthylidene)methyl-  
amino]benzoic acidGordana Pavlović<sup>a\*</sup> and Julija Matijević Sosa<sup>b</sup><sup>a</sup>Chemistry Department, Laboratory of General and Inorganic Chemistry, Faculty of Science, University of Zagreb, Ul. kralja Zvonimira 8, 10000 Zagreb, Croatia, and<sup>b</sup>Department of Biochemistry and Molecular Biology, Faculty of Pharmacy and Biochemistry, University of Zagreb, Ante Kovačića 1, 10000 Zagreb, Croatia

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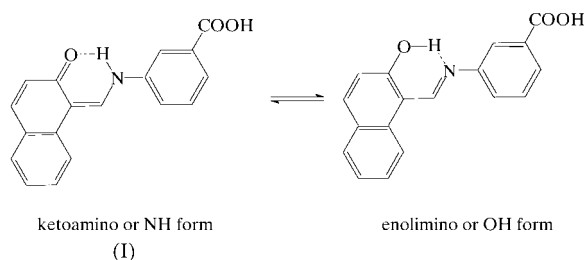
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The title compound,  $C_{18}H_{13}NO_3$ , exists as a ketoamino tautomer implying a fairly short  $N-H\cdots O$  intramolecular hydrogen bond between the 2-naphthalenone and amino moieties [ $N\cdots O$  2.531 (3) Å] which is enhanced by the  $\pi$ -electron delocalization effect. The naphthaldimine and 3-carboxyphenyl fragments are inclined at an angle of 4.41 (7)°, so the molecule is almost planar. The molecules are connected by intermolecular  $O-H\cdots O$  hydrogen bonds between the carboxy and keto O atoms, forming infinite chains around the twofold screw axes parallel to **b**.

## Comment

Schiff bases derived from 2-hydroxy-1-naphthaldehyde with various alkyl or aryl N-substituents, apart from excellent donor abilities (Calligaris & Randaccio, 1987), exhibit interesting photo- and thermochromic features. Such characteristics are strongly influenced by the crystal structures of the compounds, *i.e.* the  $\pi$ - $\pi$  intermolecular interactions could be sufficiently strong to promote the proton-transfer reversible process and self-isomerization of the molecule (Inabe *et al.*, 1991, 1994). Contrary to the case in salicylaldimine derivatives, for which the enol tautomer has been exclusively established, 2-hydroxy-1-naphthaldehyde Schiff base derivatives (containing an extended aromatic ring on the aldehyde side of the Schiff base compared with a benzene ring in the salicylaldimine derivatives) exhibit both ketoamino and enolimino tautomeric forms in the crystalline state. The tautomerization induced by intramolecular proton transfer is accompanied by a  $\pi$ -electron configurational change (Inabe *et al.*, 1991, 1994). The population of the NH form is expected to be larger for 2-hydroxy-1-naphthaldehyde Schiff base derivatives than for *N*-salicylideneaniline derivatives, since the process of proton transfer from the hydroxyl oxygen to the imine nitrogen retains the particular  $D_{2h}$  symmetry of the naphthalene ring (Pavlović, 1998), while in *N*-salicylideneanilines, this process leads to a loss of the benzene-ring aromaticity.

The X-ray structure analyses revealed the NH forms of *N*-*n*-propyl-2-oxo-1-naphthylidene-methylamine (Kaitner & Pavlović, 1996), *N*-( $\alpha$ -naphthyl)- and *N*-( $\beta$ -naphthyl)-2-oxo-1-naphthaldimines (Gavranić *et al.*, 1996), the *N*-4-methyl-2-pyridyl derivative (Elerman *et al.*, 1998) and *N*-(2-hydroxyethyl)-2-oxo-1-naphthaldimine (Kaitner & Pavlović, 1999), while the OH tautomers have been observed in the crystals of *N*-*o*-tolyl-2-hydroxy-1-naphthaldimine (Kaitner *et al.*, 1998), *N*-(2-bromo-4-methylphenyl)naphthaldimine (Elmali, Elerman & Kendi, 1998), *N*-(3,5-dichlorophenyl)naphthaldimine (Elmali, Elerman, Svoboda & Fuess, 1998) and 1-[(3-nitrophenylimino)methyl]-2-naphthol (Yeap *et al.*, 1998). In the crystals of *N*-(2-hydroxy-1-naphthylmethylene)-1-pyrenamine, the H-atom position is disordered over the oxygen and nitrogen sites even at 120 K (Inabe *et al.*, 1994), suggesting that both tautomeric forms are present in the crystal.



In the title compound, (I), the most sensitive bond distance for deciding the tautomer type is the  $Csp^2-O$  bond distance. The  $O1-C2$  bond length of 1.290 (2) Å is significantly shorter than those of phenols (1.362 Å) indicating significant  $\pi$ -character (Allen *et al.*, 1987). The  $O-C$  bond distances observed in the ketoamino tautomers cited above are 1.277 (2)–1.302 (3) Å, and those in the enol tautomers 1.320 (3)–1.323 (3) Å. The  $N1-C11$  bond distance of 1.319 (3) Å corresponds to the values observed in the crystals of the NH tautomers, 1.294 (5)–1.322 (4) Å, and is longer than those in the OH tautomers, 1.290 (3)–1.291 (4) Å (Fig. 1).

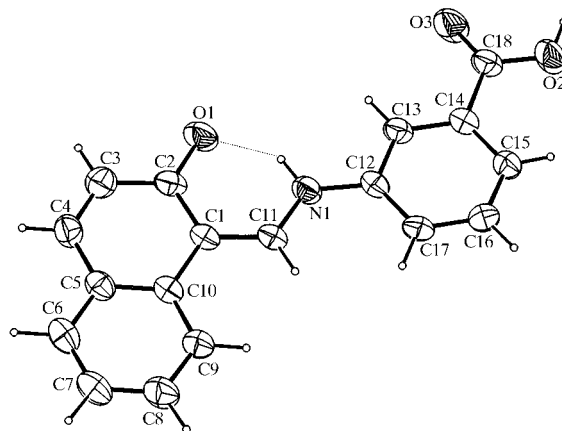
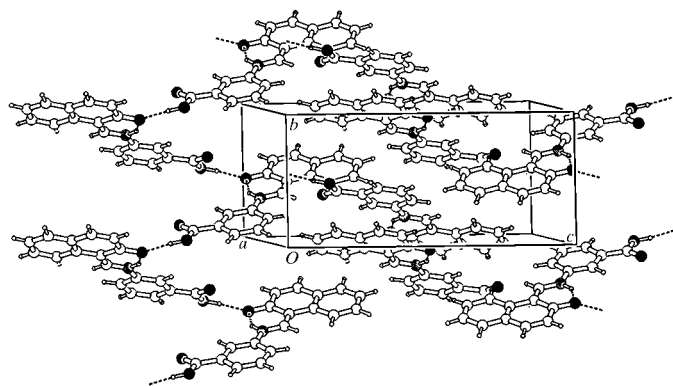


Figure 1

The molecular structure of (I) showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are drawn as small circles of arbitrary radii. The hydrogen bond is indicated by a dashed line.



**Figure 2**  
The crystal packing of (I). Hydrogen bonds are shown by dashed lines.

The shortened C3—C4 naphthalene ring bond distance of 1.341 (3) Å suggests a quinoidal effect and confirms that the O1—C2 bond is not a pure single bond. The imine N1 atom is  $sp^2$  hybridized and displays coplanarity of the naphthalimine fragment. The dihedral angle between the naphthalimine and 3-carboxyphenyl moieties amounts to 4.41 (7)°. The rather short N1···O1 value of 2.531 (3) Å is enhanced by the  $\pi$ -electron delocalization effect within the heterodienic moiety (resonance-assisted hydrogen bonding; Bertolasi *et al.*, 1993). A survey of the Cambridge Structural Database (Version 5.18; Allen & Kennard, 1993) confirmed that the N···O distances in the intramolecular hydrogen bond in Schiff bases derived from 2-hydroxy-1-naphthaldehyde are in the range 2.5–2.6 Å. The stronger intramolecular hydrogen bond indicates the H-atom position to be towards the nitrogen site (Wozniak *et al.*, 1995), since tautomerization causes energetically small but structurally remarkable changes (*i.e.* bond-order changes).

Neighbouring molecules are joined *via* an intermolecular O2—H···O1 hydrogen bond (Table 2) to form infinite chains around  $2_1$  screw axes parallel to **b** (Fig. 2). The antiparallel stacking of nearly planar molecules maximizes  $\pi$ – $\pi$  interactions, and intermolecular C—H···O close contacts further stabilize the crystal structure.

## Experimental

The title compound was prepared by condensation of equimolar quantities of 2-hydroxy-1-naphthaldehyde and 3-aminobenzoic acid in methanol. After stirring briefly, a yellow precipitate separated and was washed with water; yield 91%. After recrystallization from dioxane, the melting point was measured as 551–552 K (literature 554 K; Senier & Clarke, 1911). Pale-orange crystals were obtained from a methanol–water mixture by slow evaporation.

### Crystal data

$C_{18}H_{13}NO_3$	$D_x = 1.423 \text{ Mg m}^{-3}$
$M_r = 291.29$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 28 reflections
$a = 11.665$ (2) Å	$\theta = 9.1$ – $16.9^\circ$
$b = 7.4718$ (11) Å	$\mu = 0.098 \text{ mm}^{-1}$
$c = 16.2794$ (15) Å	$T = 293$ (2) K
$\beta = 106.666$ (14)°	Plate, pale orange
$V = 1359.3$ (3) Å <sup>3</sup>	$0.55 \times 0.24 \times 0.04 \text{ mm}$
$Z = 4$	

**Table 1**  
Selected geometric parameters (Å, °).

O1—C2	1.290 (2)	N1—C12	1.411 (3)
N1—C11	1.319 (3)	C3—C4	1.341 (3)
C11—N1—C12		129.2 (2)	

**Table 2**  
Hydrogen-bonding geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1N···O1	0.90 (2)	1.74 (2)	2.531 (3)	144.3 (2)
O2—H2O···O1 <sup>i</sup>	0.92 (3)	1.71 (3)	2.626 (2)	173.7 (3)

Symmetry code: (i)  $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$ .

### Data collection

Philips PW1100 diffractometer	$\theta_{\max} = 26.9^\circ$
upgraded by Stoe	$h = -14 \rightarrow 14$
$\omega$ scans	$k = 0 \rightarrow 9$
2968 measured reflections	$l = 0 \rightarrow 20$
2866 independent reflections	3 standard reflections
1374 reflections with $I > 2\sigma(I)$	frequency: 90 min
$R_{\text{int}} = 0.014$	intensity decay: 6.8%

### Refinement

Refinement on $F^2$	All H-atom parameters refined
$R[F^2 > 2\sigma(F^2)] = 0.046$	$w = 1/[\sigma^2(F_o^2) + (0.0551P)^2]$
$wR(F^2) = 0.117$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.944$	$(\Delta/\sigma)_{\max} < 0.001$
2866 reflections	$\Delta\rho_{\max} = 0.17 \text{ e \AA}^{-3}$
251 parameters	$\Delta\rho_{\min} = -0.17 \text{ e \AA}^{-3}$

All H atoms were located on difference syntheses and their parameters refined. The N—H and O—H distances are 0.90 (2) and 0.92 (3) Å, respectively, and the C—H distances are in the range 0.91 (2)–1.03 (3) Å.

Data collection: *STADIA* (Stoe & Cie, 1995); cell refinement: *STADIA*; data reduction: *X-RED* (Stoe & Cie, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON98* (Spek, 1998); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1032). Services for accessing these data are described at the back of the journal.

## References

- Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 31–37.  
 Allen, F. H., Kennard, O., Watson, D. G., Brammer, L. & Orpen, A. G. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.  
 Bertolasi, V., Ferretti, V., Gilli, P., Gilli, G., Issa, Y. M. & Sherif, O. E. (1993). *J. Chem. Soc. Perkin Trans. 2*, pp. 2223–2228.  
 Calligaris, M. & Randaccio, L. (1987). *Comprehensive Coordination Chemistry*, Vol. 2, edited by G. Wilkinson, pp. 715–738. London: Pergamon Press.  
 Elerman, Y., Kabak, M., Elmali, A. & Svoboda, I. (1998). *Acta Cryst.* **C54**, 128–130.

- Elmali, A., Elerman, Y. & Kendi, E. (1998). *Acta Cryst.* **C54**, 1137–1139.
- Elmali, A., Elerman, Y., Svoboda, I. & Fuess, H. (1998). *Acta Cryst.* **C54**, 974–976.
- Gavranić, M., Kaitner, B. & Meštrović, E. (1996). *J. Chem. Crystallogr.* **26**, 23–28.
- Inabe, T., Gautier-Luneau, I., Hoshino, N., Okaniwa, K., Okamoto, H., Mitani, T., Nagashima, U. & Maruyama, Y. (1991). *Bull. Chem. Soc. Jpn.* **64**, 801–810.
- Inabe, T., Luneau, I., Mitani, T., Maruyama, Y. & Takeda, S. (1994). *Bull. Chem. Soc. Jpn.* **67**, 612–621.
- Kaitner, B., Meštrović, E. & Pavlović, G. (1998). *J. Chem. Crystallogr.* **28**, 77–82.
- Kaitner, B. & Pavlović, G. (1996). *Acta Cryst.* **C52**, 2573–2575.
- Kaitner, B. & Pavlović, G. (1999). *Croat. Chem. Acta*, **72**, 607–620.
- Pavlović, G. (1998). PhD thesis, University of Zagreb, Croatia. (Abstract in English.)
- Senier, A. & Clarke, R. (1911). *J. Chem. Soc.* **99**, 2081–2084.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Spek, A. L. (1998). *PLATON98 for Windows*. University of Utrecht, The Netherlands.
- Stoe & Cie (1995). *STADI4* and *X-RED*. Stoe & Cie, Darmstadt, Germany.
- Wozniak, K., He, H., Klinowski, J., Jones, W., Dziembowska, T. & Grech, E. (1995). *J. Chem. Soc. Faraday Trans.* **91**, 77–85.
- Yeap, G. Y., Teoh, S. G., Teo, S. B., Valle, G. & Calogero, S. (1998). *Z. Kristallogr. New Cryst. Struct.* **213**, 489–490.