Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

4-{[(1*E*)-(2-Hydroxyphenyl)methylidene]amino}-1,5-dimethyl-2-phenyl-2,3-dihydro-1*H*-pyrazol-3-one

Tuncer Hökelek,[a]* Muhammed Işıklan[b] and Zeynel Kılıç[b]

[a]Hacettepe University, Department of Physics, 06532 Beytepe, Ankara, Turkey, and [b]Ankara University, Department of Chemistry, 06100 Tandoğan, Ankara, Turkey
Correspondence e-mail: merzifon@hacettepe.edu.tr

Received 25 August 2000
Accepted 27 October 2000

In the title compound, $C_{18}H_{17}N_3O_2$, a strong intramolecular O—H···N hydrogen bond [N···O 2.607 (3), O—H 0.97 (3) and H···N 1.71 (3) Å, and O—H···N 153 (2)°] was observed, which leads to a unique phenol–imine tautomerism in the solid state. The C=N imine bond distance and the C—N—C bond angle [1.287 (2) Å and 121.7 (1)°, respectively] indicate the existence of this phenol–imine tautomer. In solution, the phenol–imine tautomer of the title free Schiff base ligand is dominant in both polar and non-polar solvents, as supported by ^{1}H NMR and UV–visible spectroscopic data.

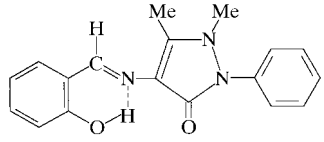
Comment

2-Hydroxy Schiff base ligands and their transition-metal complexes derived from the reactions of hydroxyaldehyde derivatives with various amines have been extensively studied (Hökelek, Akduran *et al.*, 2000; Hökelek, Işıklan & Kılıç, 2000; Hökelek, Kılıç *et al.*, 2000; Hökelek *et al.*, 1995*a*,*b*; Yıldız *et al.*, 1998; Gavranić *et al.*, 1996) and a number of them have been used as models for biological systems (Chen & Martell, 1987; Pyrz *et al.*, 1985; Costamagna *et al.*, 1992). The Schiff base ligand of salicylaldehyde with 4-amino-1,2-dihydro-1,5-dimethyl-2-phenyl-3*H*-pyrazol-3-one (4-aminophenazone, 4-AAP) has been prepared and various transition-metal complexes of this ligand have been synthesized (Nair & Prabhakaran, 1998; Barton *et al.*, 1987). 4-Aminophenazone and its derivatives are very important compounds in pharmacology and biochemistry (El-Naggar *et al.*, 1981; Lenarcik *et al.*, 1980). They are especially used as anti-inflammatory drugs (Lodzinska *et al.*, 1989).

Aldimine Schiff base ligands are of interest mainly due to the existence of O—H···N and O···H—N intramolecular hydrogen bonds and tautomerism between phenol–imine and keto–amine forms (Yıldız *et al.*, 1998; Costamagna *et al.*, 1992; Salman *et al.*, 1991). In these types of ligands, short hydrogen bonds are observed between the 2-hydroxy group and the imine N atom. In some instances, the H atom from the phenol group is completely transferred to the imine N atom (Hökelek, Akduran *et al.*, 2000; Kaitner & Pavlovic, 1996; Gavranić *et al.*, 1996).

In the solid state, salicylaldimine and naphthaldimine ligands tend to form N···H—O and N—H···O hydrogen bonds, respectively (Hökelek, Işıklan & Kılıç, 2000; Hökelek, Kılıç *et al.*, 2000). In solution, both forms have been observed. Tautomerism in Schiff base ligands is very important for distinguishing their photochromic (Barbara *et al.*, 1980; Hadjoudis, 1981; Higelin & Sixl, 1983; Dürr, 1989; Hadjoudis, 1990) and thermochromic (Cohen *et al.*, 1964; Moustakali *et al.*, 1978) characteristics.

Although the oxomolybdenum(V) and dioxomolybdenum(VI) complexes of the title compound, (I), have been reported (Nair & Prabhakaran, 1998), the free ligand has not been studied crystallographically. The present structure determination of (I) was undertaken in order to determine the type of hydrogen bonding and to compare the results obtained with those reported previously. The crystallographic atom numbering of (I) is different from that in the IUPAC name; the latter is not suitable, due to the duplicate C2 atom labels in the salicylidene and phenazone moieties.



(I)

The molecule of (I) (Fig. 1) contains the bulky 4-aminophenazone-N substituent. It includes a short intramolecular O—H···N hydrogen bond [O1—H1 0.97 (3), H1···N1 1.71 (3) and N1···O1 2.607 (3) Å, and O—H···N 153 (2)°], which means that the ligand is in the phenol–imine form, as in 1,8-di(*N*-2-oxyphenylsalicylidene)-3,6-dioxaoctane [O—H 1.154 (3), H···N 1.488 (3) and O···N 2.578 (3) Å; Yıldız *et al.*, 1998] and 1,5-di(*N*-2-oxyphenylsalicylidene)-3-oxapentane [O1—H1 0.864 (4), H1···N1 1.865 (3) and N1···O1 2.587 (4), and O5—H5 1.056 (3), H5···N2 1.603 (4) and N2···O5 2.542 (4) Å; Hökelek, Akduran *et al.*, 2000]. The ^{1}H NMR data for (I) illustrate that the phenol–imine form dominates in $CDCl_3$ solution (δ_{CH} = 9.63 and δ_{OH} = 13.33 p.p.m., both singlets), supporting the location of the H atom on the O atom.

The C=N imine bond distance and the C—N—C bond angle in (I) [1.287 (3) Å and 121.7 (1)°, respectively] can be compared with the values of 1.270 (3) Å and 123.5 (2)° in 1,8-di(*N*-2-oxyphenylsalicylidene)-3,6-dioxaoctane (Yıldız *et al.*, 1998), and the values of 1.288 (4) Å and 121.3 (3)°, and 1.277 (4) Å and 124.3 (3)° in 1,5-di(*N*-2-oxyphenylsalicylidene)-3-oxapentane (Hökelek, Akduran *et al.*, 2000).

As expected, rings *A* (C1–C6) and *D* (C13–C18) are planar, while rings *B* (N1/H1/O1/C1/C6/C7) and *C* (N2/N3/C10/C8/C9) are not, with maximum deviations of 0.023 (1) and 0.040 (2) Å from the best least-squares planes, respectively. The dihedral angles between the best planes of the rings are

A/*C* 5.7 (6), *A*/*D* 131.6 (1), *B*/*C* 4.3 (7), *B*/*D* 132.8 (1) and *C*/*D* 136.4 (1)°. The Φ_{CN} torsion angle (C6—C7—N1—C8) is 177.6 (1)°, which shows that the conformation about the C7—N1 bond is *anti* (1*E*). The Φ_{CN} (C11—C10—N3—C12) and Φ_{NN} (C13—N2—N3—C12) torsion angles are −36.9 (3) and 55.7 (2)°, respectively, showing that the conformations about C10—N3 and N2—N3 are *gauche*. The sums of the bond angles about atoms N2 and N3 are 355.0 (1) and 345.2 (1)°, respectively. In the five-membered ring, the puckering parameter, *i.e.* the angle between the best planes (N3/C8/C9/C10 and N2/N3/C9), is 7.1(1.5)°. The displacements of atoms C12 and C13 from the best plane of the five-membered ring are 0.710 (5) and −0.324 (4) Å, respectively, showing that the methyl group bonded to N3 and the phenyl group are on opposite sides of ring *C*.

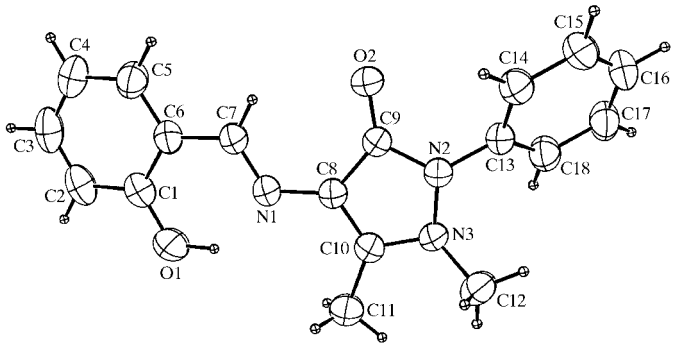


Figure 1
An *ORTEP*II (Johnson, 1976) drawing of (I) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

The close contact H123(C12)···H181(C18) [2.45 Å] may cause steric hindrance between the methyl and phenyl groups.

Experimental

Compound (I) was prepared from a mixture of salicylaldehyde (1.16 g, 9.50 mmol) and 4-aminophenazone (1.93 g, 9.50 mmol) in boiling methanol (100 ml). The precipitate was filtered and the residue was then dissolved in $CHCl_3$–MeOH (3:1) and set aside for crystallization (yield 2.58 g, 88%; m.p. 474 K).

Crystal data

$C_{18}H_{17}N_3O_2$
M_r = 307.35
Monoclinic, $P2_1/n$
a = 7.5950 (10) Å
b = 7.4980 (10) Å
c = 27.277 (2) Å
β = 95.332 (7)°
V = 1546.6 (3) Å^3
Z = 4
D_x = 1.320 Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 20–43°
μ = 0.713 mm^{-1}
T = 293 (2) K
Rod, yellow
0.30 × 0.20 × 0.15 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
3226 measured reflections
3079 independent reflections
2463 reflections with $I > 2\sigma(I)$
R_{int} = 0.033
θ_{max} = 74.24°
$h = 0 \rightarrow 9$
$k = 0 \rightarrow 9$
$l = -33 \rightarrow 33$
3 standard reflections
frequency: 120 min
intensity decay: 1%

Table 1
Selected geometric parameters (Å, °).

N2—C9	1.3963 (19)	C8—N1	1.3916 (19)
N2—N3	1.4034 (18)	C9—O2	1.230 (2)
N2—C13	1.4194 (19)	C7—N1	1.287 (2)
C1—O1	1.351 (2)	N3—C10	1.369 (2)
C9—N2—N3	110.14 (12)	N2—C9—C8	104.45 (13)
C9—N2—C13	124.66 (13)	N1—C7—C6	120.71 (15)
O1—C1—C6	121.60 (16)	C10—N3—N2	106.21 (12)
C10—C8—N1	121.89 (14)	N2—N3—C12	117.22 (14)
N1—C8—C9	129.95 (14)	C8—C10—N3	110.51 (13)
O2—C9—C8	131.53 (14)	C7—N1—C8	121.70 (14)
O1—C1—C6—C7	0.9 (3)	N2—N3—C10—C11	−174.68 (17)
C13—N2—N3—C10	−164.32 (15)	C12—N3—C10—C11	−36.9 (3)
C9—N2—N3—C12	−148.16 (15)	C6—C7—N1—C8	177.55 (14)
C13—N2—N3—C12	55.7 (2)		

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.066
$wR(F^2)$ = 0.180
S = 0.802
3079 reflections
231 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.1629P)^2 + 0.3199P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.29 e Å^{-3}
$\Delta\rho_{min}$ = −0.31 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0068 (12)

The hydroxy H1 atom was positioned from a difference map and refined isotropically [O1—H1 0.97 (3) Å]; the positions of the remaining H atoms were calculated geometrically, at distances of 0.93 (CH) and 0.96 Å (CH_3) from the corresponding C atoms, and a riding model was used during the refinement process.

Data collection, cell refinement and data reduction: *MolEN* (Fair, 1990); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976).

The authors wish to acknowledge the purchase of the CAD-4 diffractometer under Grant DPT/TBAG1 of the Scientific and Technical Research Council of Turkey.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS1128). Services for accessing these data are described at the back of the journal.

References

Barbara, P. F., Rentzepis, P. M. & Brus, L. E. (1980). *J. Am. Chem. Soc.* **102**, 2786–2791.
Barton, R. J., Johnson, K. E., Robertson, B. E., Yerhoff, F. W. & Hu, S. (1987). *Can. J. Chem.* **65**, 2082–2088.
Chen, D. & Martell, A. E. (1987). *Inorg. Chem.* **26**, 1026–1030.
Cohen, M. D., Schmidt, G. M. J. & Flavin, S. (1964). *J. Chem. Soc.* pp. 2041–2051.
Costamagna, J., Vargas, J., Latorre, R., Alvarado, A. & Mena, G. (1992). *Coord. Chem. Rev.* **119**, 67–68.
Dürr, H. (1989). *Angew. Chem. Int. Ed. Engl.* **28**, 413–431.

El-Naggar, A. M., Ahmed, F. S. M. & Badie, M. F. (1981). *J. Heterocycl. Chem.* **18**, 91–94.
Fair, C. K. (1990). *MolEN*. Enraf–Nonius, Delft, The Netherlands.
Gavranić, M., Kaitner, B. & Meštrović, E. (1996). *J. Chem. Crystallogr.* **26**, 23–28.
Hadjoudis, E. (1981). *J. Photochem.* **17**, 355–367.
Hadjoudis, E. (1990). *Studies in Organic Chemistry – Photochromism, Molecules and Systems*, Vol. 40, edited by H. Dürr & H. Bouas-Laurent, pp. 631–653. Amsterdam: Elsevier.
Higelin, D. & Sixl, H. (1983). *Chem. Phys.* **77**, 391–395.
Hökelek, T., Akduran, N., Yıdız, M. & Kılıç, Z. (2000). *Anal. Sci.* **16**, 553–554.
Hökelek, T., Gündüz, N., Hayvalı, Z. & Kılıç, Z. (1995*a*). *Acta Cryst.* C**51**, 880–884.
Hökelek, T., Gündüz, N., Hayvalı, M. & Kılıç, Z. (1995*b*). *J. Chem. Crystallogr.* **25**, 827–832.
Hökelek, T., Işıklan, M. & Kılıç, Z. (2000). *Anal. Sci.* **16**, 99–100.
Hökelek, T., Kılıç, Z., Işıklan, M. & Toy, M. (2000). *J. Mol. Struct.* **523**, 61–69.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Kaitner, B. & Pavlovic, G. (1996). *Acta Cryst.* C**52**, 2573–2575.
Lenarcik, B., Wisniewski, M. & Gabryszewski, M. (1980). *Pol. J. Chem.* **54**, 1869–1874.
Lodzinska, A., Golinska, F. & Rozploch, F. (1989). *Pol. J. Chem.* **63**, 355–364.
Moustakali-Mavridis, I., Hadjoudis, E. & Mavridis, A. (1978). *Acta Cryst.* B**34**, 3612–3615.
Nair, M. L. H. & Prabhakaran, C. P. (1998). *Indian J. Chem. Ser. A*, **37**, 452–455.
Pyrz, J. W., Roe, A. L., Stern, L. J. & Que, L. Jr (1985). *J. Am. Chem. Soc.* **107**, 614–620.
Salman, S. R., Farrant, R. D. & Lindon, J. C. (1991). *Spectrosc. Lett.* **24**, 1071–1078.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.
Yıldız, M., Kılıç, Z. & Hökelek, T. (1998). *J. Mol. Struct.* **441**, 1–10.