Instrumental Achievements

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

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In 2-hydroxy aldimine Schiff bases, two types of hydrogen bonds [either N–H···O (*keto*-amine tautomer) or N···H–O (phenol-imine tautomer)] can exist. It is claimed that the hydrogen-bond type depends neither on the stereochemistry of the molecule nor on the sort of substituent bonded to the N imino atom, but on the kind of aldehyde used.[1]

In the solid state, it is also claimed that only an intramolecular N–H···O type hydrogen bond is present in naphthaldimines regardless of the kind of N-substituents, aryl or alkyl.[2] However, our crystallographic studies have shown an intramolecular (N···H–O (phenol-imine tautomer) hydrogen bond, which is in contrast to observations reported in the literature.[2,3] The title ligand was prepared from a mixture of 2-hydroxy-1-naphthaldehyde (0.60 g, 3.5 mmol) and 4-aminophenazone (4-AAP) (0.71 g, 3.5 mmol) in boiling methanol (100 ml). After the precipitate was filtered, the residue was dissolved in $CHCl_3$–EtOH (3:1) and set aside for crystallization (yield 0.80 g, 64%; m.p. 491 K). 4-AAP and its derivatives are very important compounds in pharmacology and biochemistry. They are especially used as anti-inflammatory drugs.[4]

The results of X-ray structure determinations are given in Tables 1 – 3. The hydrogen atoms were located by a difference Fouirer synthesis and a geometrical calculation, with the parameters of 4 hydrogen atoms (H1, H71, H111, H181) (out of 19) being refined.

The title molecule (Fig. 2) has a short intramolecular N···H–O hydrogen bond [O1–H1 0.953(3), H1···N1 1.497(3), N1···O1

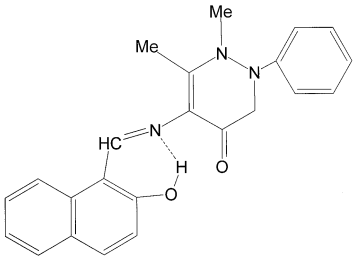

Fig. 1 Chemical diagram.

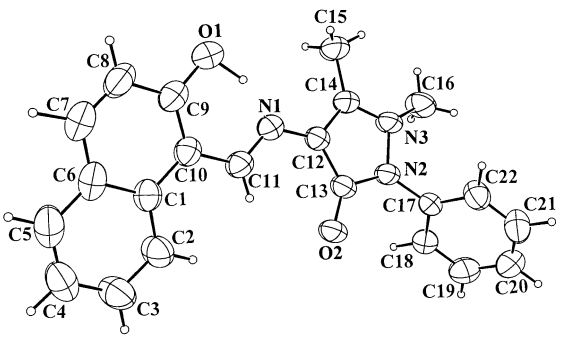

Fig. 2 Molecular structure of the title compound along with the atom-numbering scheme. The thermal ellipsoids are drawn at the 50% probability level.

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Table 1 Crystal and experimental data

Formula: $C_{22}H_{19}N_3O_2$	
Formula weight = 357.42	
Crystal system: orthorhombic	
Space group: $P2_12_12_1$	$Z = 4$
a = 8.717(2)Å	
b = 14.561(3)Å	
c = 14.690(2)Å	
V = 1864.7(5)Å^3	
D_X = 1.273 g/cm^3	
μ(Cu K$_\alpha$) = 0.63 mm^{-1}	
T = 293 K	
Orange	
Crystal size: 0.15 × 0.20 × 0.30 mm	
λ(Cu K$_\alpha$) = 1.54184	
R = 0.051	
wR = 0.061	
No. of reflections measured = 2201	
No. of reflections used = 1577	
[F >3.0 $\sigma(F)$]	
No. of parameters = 260	
Goodness-of-fit = 0.84	
$(\Delta/\sigma)_{max}$ = 0.01	
$(\Delta\rho)_{max}$ = 0.20 eÅ^{-3}	
$(\Delta\rho)_{min}$ = –0.32 eÅ^{-3}	
$2\theta_{max}$ = 148.7°	
Measurements: Enraf-Nonius CAD-4 diffractometer	
Program system: CAD-4 EXPRESS Software	
Structure determination: MolEN	
Refinement: full matrix least-squares	

Table 2 Final atomic coordinates and equivalent isotropic thermal parameters

Atom	*x*	*y*	*z*	B_{eq}/Å^2
O1	0.8175(4)	0.3734(3)	0.6973(2)	5.09(8)
O2	0.3430(4)	0.5300(2)	0.4960(2)	4.48(7)
N1	0.5681(4)	0.4278(3)	0.6282(2)	3.82(7)
N2	0.2064(4)	0.5472(3)	0.6301(2)	3.83(8)
N3	0.2293(4)	0.5242(3)	0.7217(2)	3.92(8)
C1	0.8411(5)	0.3673(3)	0.4465(3)	3.95(9)
C2	0.7571(6)	0.3828(4)	0.3656(3)	5.1(1)
C3	0.8183(7)	0.3640(5)	0.2816(4)	6.0(1)
C4	0.9670(7)	0.3300(4)	0.2746(4)	5.9(1)
C5	1.0523(7)	0.3157(4)	0.3497(4)	5.8(1)
C6	0.9944(6)	0.3344(3)	0.4375(4)	4.6(1)
C7	1.0814(6)	0.3190(4)	0.5178(4)	5.5(1)
C8	1.0232(6)	0.3316(4)	0.6003(4)	5.3(1)
C9	0.8707(5)	0.3628(3)	0.6113(3)	4.3(1)
C10	0.7790(5)	0.3831(3)	0.5359(3)	3.78(9)
C11	0.6259(5)	0.4195(3)	0.5481(3)	3.84(9)
C12	0.4249(5)	0.4675(3)	0.6422(3)	3.44(8)
C13	0.3297(5)	0.5148(3)	0.5787(3)	3.62(9)
C14	0.3592(5)	0.4729(3)	0.7270(3)	3.85(9)
C15	0.4110(7)	0.4311(4)	0.8139(3)	5.4(1)
C16	0.1000(6)	0.5279(4)	0.7843(3)	5.1(1)
C17	0.0978(5)	0.6150(3)	0.6042(3)	3.36(8)
C18	-0.0133(6)	0.5914(3)	0.5418(3)	4.2(1)
C19	-0.1179(7)	0.6570(4)	0.5152(4)	5.9(1)
C20	-0.1137(7)	0.7439(4)	0.5510(4)	6.0(1)
C21	-0.0019(7)	0.7660(4)	0.6129(4)	5.9(1)
C22	0.1043(6)	0.7024(3)	0.6406(3)	4.6(1)

$B_{eq} = (8\pi^2/3)\,\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* (\boldsymbol{a}_i \cdot \boldsymbol{a}_j)$.

Table 3 Bond distances (Å) and angles with torsion angles (°)

O1-C9	1.343(5)	N2-C17	1.422(5)
O1-H1	0.953(3)	N3-C14	1.362(6)
O2-C13	1.239(5)	N3-C16	1.452(6)
N1-C11	1.285(5)	C10-C11	1.455(6)
N1-C12	1.394(6)	C12-C13	1.426(6)
N2-N3	1.399(4)	C12-C14	1.369(6)
N2-C13	1.395(5)	C14-C15	1.487(6)
C9-O1-H1	118.5(3)	O2-C13-C12	132.3(4)
C11-N1-C12	121.4(4)	N2-C13-C12	104.8(3)
N3-N2-C13	109.4(3)	N3-C14-C12	109.2(4)
C13-N2-C17	127.1(3)	N3-C14-C15	121.7(4)
N2-N3-C14	107.5(3)	O1-C9-C10	122.2(4)
N2-N3-C16	119.6(3)	N1-C11-C10	120.4(4)
C14-N3-C16	128.9(4)	N1-C12-C13	128.8(3)
O2-C13-N2	122.9(4)	N1-C12-C14	122.0(4)
C12-N1-C11-C10	176.2(4)	C17-N2-C13-O2	-13.8(7)
C13-N2-N3-C16	-163.4(4)	N2-N3-C14-C15	-175.4(4)
C17-N2-N3-C14	-167.5(4)	C16-N3-C14-C15	-18.7(8)
C17-N2-N3-C16	33.1(6)	O1-C9-C10-C11	2.5(7)

2.527(4)Å, N1··H1–O1 155.7(4)°], which means that the compound is in the phenol-imine form, as in 4-{[(1*E*)-(2-hydroxyphenyl)methylidene]amino}-1,5-dimethyl-2-phenyl-2,3-dihydro-1*H*-pyrazol-3-one[5] [O–H 0.97(3), H··N 1.71(3), N··O 2.607(3)Å, N··H–O 153(2)°]. These results are clear evidence of the importance of the *N*-substituent in 2-hydroxy naphthaldimine Schiff bases. The rings, (N1, H1, O1, C9, C10, C11) and (N2, N3, C12, C13, C14), are essentially planar with maximum deviations of H1 [0.08(9)] and N3 [–0.022(4)Å] from the best least-squares planes, respectively.

The ϕ_{CN} torsion angle (C10–C11–N1–C12) is 176.2(4)°, which shows that the configuration about the C11–N1 bond is *anti* (1*E*).

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