Instrumental Achievements

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

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

Our crystallographic studies indicated that the title compound has neither *keto*-amine nor phenol-imine form, (Fig. 2), which is in contrast to the observations reported in the literature.[1,2] The title ligand was prepared from a mixture of 3,5-dinitrosalicylaldehyde (0.50 g, 2.50 mmol) and 4-aminophenazone (4-AAP) (0.51 g, 2.50 mmol) in boiling methanol (100 ml). The precipitate was filtered and the residue was dissolved in CH_3CN and set aside for crystallization (yield 0.87 g, 91%; m.p. 506 K). 4-AAP and its derivatives are used as anti-inflammatory drugs and are very important compounds in pharmacology and biochemistry.[3]

The results of X-ray structure determination are given in Tables 1 – 3. The hydrogen atoms were located by a difference synthesis and a geometrical calculation, with the parameters of 8 hydrogen atoms (H2A, H2B, H4A, H4B, H5B, H6A, H6B, H7A) (out of 33) being refined.

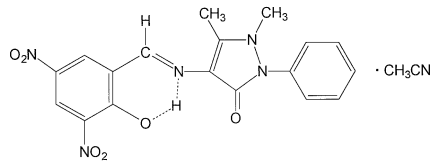

Fig. 1 Chemical diagram.

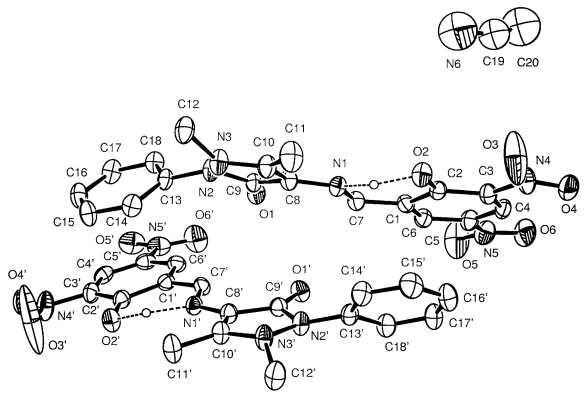

Fig. 2 Molecular structure of the title compound along with atom-numbering scheme. The thermal ellipsoids are drawn at the 50% probability level.

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Table 1 Crystal and experimental data

Formula:	$C_{38}H_{33}N_{11}O_{12}$
Formula weight:	835.75
Crystal system:	monoclinic
Space group:	$P2_1$ $Z = 4$
a =	11.260(1)Å
b =	21.332(2)Å
c =	16.375(2)Å
β =	102.49(1)°
V =	3840.1(8)Å^3
D_x =	1.446 g/cm^3
μ(Mo K$_\alpha$) =	0.111 mm^{-1}
T =	296 K
F(0 0 0) =	1736
Color:	red
Crystal size:	0.20 × 0.20 × 0.30 mm
λ(Mo K$_\alpha$) =	0.71073 Å
$R(F^2)$=	0.0587 $wR(F^2)$= 0.1471
No. of reflections measured=	7069
No. of reflections used=	3628
[$I > 2\sigma(I)$]	
No. of parameters =	570
Goodness-of-fit =	0.918
$(\Delta/\sigma)_{max}$ =	0.001
$(\Delta\rho)_{max}$ =	0.287
$(\Delta\rho)_{min}$ =	– 0.324
$2\theta_{max}$ =	52.6°
Measurements:	Enraf-Nonius CAD-4 diffractometer
Program system:	CAD-4 EXPRESS Software
Structure determination:	SHELXS97
Refinement:	full matrix least-squares (SHELXL97)

Table 2 Final atomic coordinates and equivalent isotropic thermal parameters

Atom	*x*	*y*	*z*	U_{iso}/Å^2
N1	0.61055(2)	0.0934(1)	0.6054(1)	0.0496(5)
N1'	0.9129(2)	0.10839(9)	0.9097(1)	0.0453(5)
N2	0.5600(2)	0.13540(9)	0.8076(1)	0.0511(5)
N2'	0.9584(2)	0.14775(8)	0.7058(1)	0.0506(5)
N3	0.5468(2)	0.19266(9)	0.7641(1)	0.0563(6)
N3'	0.9871(2)	0.20431(9)	0.7510(1)	0.0550(6)
N4	0.6077(2)	0.0539(1)	0.2894(2)	0.0648(7)
N4'	0.9134(3)	0.0624(1)	1.2257(2)	0.0818(9)
N5	0.7348(3)	-0.1409(1)	0.4328(2)	0.0734(7)
N5'	0.7541(2)	-0.1230(1)	1.0714(2)	0.0694(7)
N6	0.2531(5)	0.1996(3)	0.3076(4)	0.178(2)
O1	0.6186(2)	0.03460(7)	0.7796(1)	0.0515(4)
O1'	0.8817(2)	0.05108(8)	0.7336(1)	0.0541(5)
O2	0.5885(2)	0.10640(8)	0.4496(1)	0.0592(5)
O2'	0.9497(2)	0.11514(8)	1.0690(1)	0.0595(5)
O3	0.5544(5)	0.1030(1)	0.2873(2)	0.175(2)
O3'	0.9466(8)	0.1132(2)	1.2276(2)	0.317(5)
O4	0.6273(2)	0.0293(1)	0.2270(2)	0.0818(7)
O4'	0.9021(3)	0.0361(1)	1.2872(1)	0.0897(7)
O5	0.7525(4)	-0.1716(1)	0.4969(2)	0.1348(13)
O5'	0.7425(2)	-0.1458(1)	1.1382(2)	0.0896(8)
O6	0.7371(2)	-0.1628(1)	0.3644(2)	0.0924(8)
O6'	0.7341(3)	-0.1521(1)	1.0059(2)	0.0995(8)
C1	0.6562(2)	0.0111(1)	0.5196(2)	0.0454(6)
C1'	0.8541(2)	0.0278(1)	0.9941(2)	0.0443(6)
C2	0.6258(2)	0.0492(1)	0.4454(2)	0.0437(5)
C2'	0.8974(2)	0.0620(1)	1.0699(2)	0.0480(6)
C3	0.6370(2)	0.0206(1)	0.3681(2)	0.0483(6)
C3'	0.8806(2)	0.0317(1)	1.1454(2)	0.0542(6)
C4	0.6744(2)	-0.0406(1)	0.3640(2)	0.0494(6)
C4'	0.8334(2)	-0.0269(1)	1.1457(2)	0.0526(7)
C5	0.7013(2)	-0.0754(1)	0.4378(2)	0.0539(6)
C5'	0.7976(2)	-0.0586(1)	1.0712(2)	0.0534(7)
C6	0.6931(2)	-0.0506(1)	0.5136(2)	0.0501(6)
C6'	0.8056(2)	-0.0316(1)	0.9962(2)	0.0512(6)
C7	0.6462(2)	0.0358(1)	0.5995(2)	0.0472(6)
C7'	0.8653(2)	0.0533(1)	0.9142(2)	0.0449(6)
C8	0.5922(2)	0.1202(1)	0.6785(2)	0.0481(6)
C8'	0.9328(2)	0.1345(1)	0.8365(2)	0.0468(6)
C9	0.5939(2)	0.0891(1)	0.7566(2)	0.0426(5)
C9'	0.9192(2)	0.1039(1)	0.7571(2)	0.0446(6)
C10	0.5614(3)	0.1815(1)	0.6862(2)	0.0542(6)
C10'	0.9761(2)	0.1942(1)	0.8301(2)	0.0526(6)
C11	0.5439(4)	0.2316(1)	0.6200(2)	0.081(1)
C11'	1.0100(3)	0.2420(1)	0.8978(2)	0.0737(9)
C12	0.4693(3)	0.2405(1)	0.7886(2)	0.0661(8)
C12'	1.0753(3)	0.2462(1)	0.7280(2)	0.0716(9)
C13	0.5813(2)	0.1343(1)	0.8962(2)	0.0457(6)
C13'	0.9368(2)	0.1465(1)	0.6179(2)	0.0475(6)
C14	0.6492(2)	0.1805(1)	0.9443(2)	0.0543(7)
C14'	0.8822(3)	0.1967(1)	0.5700(2)	0.0599(7)
C15	0.6659(3)	0.1793(1)	1.0298(1)	0.0618(7)
C15'	0.8641(3)	0.1945(1)	0.4849(2)	0.0696(8)
C16	0.6162(3)	0.1307(1)	1.0679(2)	0.0625(7)
C16'	0.8965(3)	0.1425(1)	0.4450(2)	0.0687(8)
C17	0.5512(3)	0.0848(1)	1.0200(2)	0.0595(7)
C17'	0.9478(3)	0.0920(1)	0.4927(2)	0.0642(8)
C18	0.5307(2)	0.0864(1)	0.9330(2)	0.0518(6)
C18'	0.9694(3)	0.0936(1)	0.5782(2)	0.0556(7)
C19	0.2556(4)	0.1559(3)	0.2610(3)	0.116(2)
C20	0.2266(7)	0.0971(5)	0.2271(7)	0.191(3)

Table 3 Selected bond distances (Å) and angles (°)

C7-C1	1.437(4)	C1'-C7'	1.448(3)
C10-C8	1.365(3)	C8'-C10'	1.375(3)
C8-N1	1.382(3)	N1'-C8'	1.384(3)
N1-C7	1.304(3)	C7'-N1'	1.300(3)
O2-C2	1.298(3)	C2'-O2'	1.279(3)
C9-O1	1.235(3)	O1'-C9'	1.236(3)
C20-C19	1.383(10)	N6-C19	1.209(7)
C3-C2-C1	117.1(2)	C1'-C2'-C3'	115.6(2)
C7-N1-C8	124.2(2)	C7'-N1'-C8'	123.9(2)
N1-C7-C1	120.0(2)	N1'-C7'-C1'	120.5(2)
C6-C5-C4	122.3(2)	C4'-C5'-C6'	121.5(3)
C2-C3-C4	122.1(2)	C2'-C3'-C4'	122.6(2)
N6-C19-C20	156.6(7)		

The title molecule (Fig. 2) has short intramolecular N–H··O hydrogen bonds [N1··O2 2.525(3), N1–H2A 1.30(4), O2··H2A 1.35(4)Å, N1–H2A··O2 144.6(3.4)° and N1′··O2′ 2.555(3), N1′–H2B 1.38(5), O2′··H2B 1.30(5)Å, N1′–H2B··O2′ 144.5(3.8)°], which means that the compound is neither in *keto*-amine nor in phenol-imine form. This behavior is surprisingly different from the determinations observed in similar compounds.[4,5]

The results clearly reflect the importance of the stereochemistry of the molecule and the kind of *N*-substituents in salicylaldimine Schiff bases. The rings (N1, H2A, O2, C1, C2, C7), (N2, N3, C8, C9, C10) and (N1′, H2B, O2′, C2′, C1′, C7′), (N2′, N3′, C8′, C9′, C10′) are essentially planar, with maximum deviations of H2A = 0.23(4), N3 = 0.027(3) and H2B = 0.20(4), N3′ = 0.026(3)Å from the best least-square planes.

The C=N imine bonds and C–N–C bond angles can be compared with 1.270(3)Å and 123.5(2)° values in 1,8-di[*N*-2-oxyphenyl-salcylidene]-3,6-dioxaoctane.[6]

The ϕ_{CN} torsion angles C1–C7–N1–C8 and C1′–C7′–N1′–C8′ are 176.6(2) and 176.3(2)°, respectively, which show the configurations about the C7–N1 and C7′–N1′ bonds are anti (1*E*).

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