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X-ray Structure Analysis Online

Crystal Structure of *N*-2-Methoxyphenyl-2-oxo-5-nitro-1-benzylidene-methylamine

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The crystal structure of the title compound, $C_{14}H_{12}N_2O_4$, was determined by a single-crystal X-ray diffraction technique, (Fig. 1). The title compound crystallizes in the orthorhombic space group $Pca2_1$ with the following unit-cell parameters: a = 18.4391(15)Å, b = 4.2710(2)Å, c = 32.2187(16)Å and V = 2537.3(3)Å^3. The crystal data were solved with a final R = 0.062 using 2394 independent reflections. There are two molecules in the asymmetric unit. The title compound adopts the keto-amine tautomeric form. In the structure, there are N–H···O and C–H···O intramolecular hydrogen bonds and C–H···O intermolecular hydrogen bonds.

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Schiff bases are of interest because they are known to show photochromism and thermochromism in the solid state; this may involve reversible proton transfer from the hydroxyl-O atom to the imine-N atom. Interest in studies on photochromic compounds has been increasing ever since the potential application of photochromic materials was realized in various areas, such as control and measurement of the radiation intensity, optical computers and display systems.[1]

The compound *N*-2-methoxyphenyl-2-oxo-5-nitro-1-benzylidene-methylamine was prepared by refluxing a mixture of a solution containing 5-nitrosalicylaldehyde (0.034 g 0.20 mmol) in 20 ml of ethanol and a solution containing *o*-anisidine (0.025 g 0.20 mmol) in 20 ml of ethanol. The reaction mixture was stirred for 1 h under reflux. Crystals of *N*-2-methoxyphenyl-2-oxo-5-nitro-1-benzylidene-methylamine suitable for X-ray analysis were obtained from ethyl acetate by slow evaporation (yield %, 71; m.p., 461 – 465 K).

The molecular data were collected on a Stoe IPDS II diffractometer using Mo K_α radiation at room temperature. For the title compound data collection, X-AREA; cell refinement, X-AREA; data reduction, X-RED32; program used to solve the structure, SHELXS97;[2] program used to refine the structure, SHELXL97;[2] molecular figures, ORTEP III;[3] publication software, WinGX[4] and PARST.[5] The structure was solved by direct methods with SHELXS-97 and refined by full-matrix least-squares procedures on F^2, using the program SHELXL-97, a computer program belonging to the WinGX software package. Atoms H1A1 and H1B1, bonded to N1A and N1B and involved in hydrogen bonding, were found in a difference Fourier map and refined freeyl. All other H atoms were placed at calculated positions and refined as a riding model. The R_{int} value was obtained to be slightly high because of the intensity data

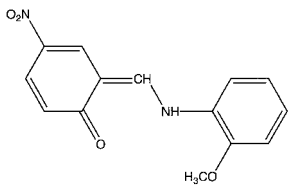

Fig. 1 Schematic diagram of the title compound.

Table 1 Crystal and experimental data

Formula: $C_{14}H_{12}N_2O_4$
Formula weight: 272.26
Crystal system: orthorhombic
Space group: $Pca2_1$
Z = 8
a = 18.4391(15)Å
b = 4.2710(2)Å
c = 32.2187(16)Å
V = 2537.3(3)Å^3
No. of reflections used = 9972
$2\theta_{max}$ = 60° Mo K_α
R = 0.063
(Δ/σ)max = 0.000
$(\Delta\rho)$ = 0.177 eÅ^{-3}
$(\Delta\rho)$ = –0.209 eÅ^{-3}
F(0 0 0)= 1136
μ = 0.106 mm^{-1}
Measurement: STOE IPDS II
Program system: STOE X-RED
Structure determination: direct methods
Refinement: full matrix
CCDC Number: 688257

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Table 2 Selected geometric parameters (Å, °)

C11A-O2A	1.280(9)	N1A-C14A	1.307(8)
C11B-O2B	1.274(9)	N1B-C14B	1.321(8)
C5A-N1A-C14A	124.7(7)	C5B-N1B-C14B	125.3(7)

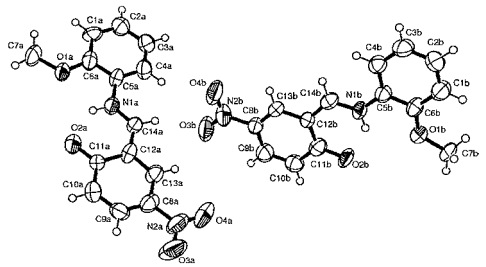

Fig. 2 Structure of the title compound showing a 50% probability displacement ellipsoids and the atom numbering scheme.

collected for the title structure was generally weak. Friedel pairs (1218) were averaged before the final refinement, because the absolute value could not be determined unambiguously.[6]

There are two independent molecules (A and B) in an asymmetric unit. The dihedral angles between the aromatic rings are 1.90(3)° and 1.51(3)° for molecules A and B, respectively. This shows that both molecules are almost planar, but the dihedral angle between the A and B molecules are 70.85(2)°. The imine H atom forms a strong intramolecular hydrogen bond with the hydroxyl O atom. The H atoms in the compound are located on atom N1, thus confirming a preference for the *keto*-amine tautomer in the solid state. Also, it is known that Schiff bases may exhibit thermochromism, depending on the planarity or non-planarity, respectively.[7] The C11–O2 and N1–C14 bond lengths show that the *keto*-amine forms the title compound (Table 2). These values are in good agreement with the 2-hydroxy-6-[(1-napthylamino)methylene]-cyclohexa-2,4-dien-1-one.[8]

The title compound is stabilized by inter and intra molecular hydrogen bonds, namely, C4B–H4B···O4A^{i} (symmetry code: i = *x*–1/2, –*y*+1, *z*), C14B–H14B···O3A^{i} (symmetry code: *i* = *x*–1/2, –*y*+1, *z*) graph set $R_2^2(9)$, N1A–H1A1···O1A and N1B–H1B1···O1B graph set S(5), N1A–H1A1···O2A and N1B–H1B1···O2B graph set S(6), and finally C14A–H14A···O3B. The

Table 3 Hydrogen-bonds geometry (Å, °)

D-H···A	D-H	H···A	D···A	D-H···A
C4B-H4B...O4A	0.93	2.42	3.242(9)	146.5
C14B-H14B...O3A	0.93	2.56	3.397(11)	149.5
C14A-H14A...O3B	0.93	2.51	3.397(11)	159.2
N1A-H1A1...O1A	0.86	2.21	2.600(8)	107.3
N1A-H1A1...O2A	0.86	1.92	2.604(9)	135.3
N1B-H1B1...O1B	0.86	2.25	2.633(7)	106.9
N1B-H1B1…O2B	0.86	1.89	2.585(9)	136.4
C13A-H13A…O4A	0.93	2.37	2.698(10)	100.1

details of the hydrogen bonds are given in Table 3. π-π stacking interactions are present in the molecule, between Cg(1)–Cg(2)^{ii} and Cg(3)–Cg(4)^{ii} [Cg(1) is C1A–C2A–C3A–C4A–C5A–C6A, Cg(2) is C8A–C9A–C10A–C11A–C12A–C13A, Cg(3) is C1B–C2B–C3B–C4B–C5B–C6B, Cg(4) is C8B–C9B–C10B–C11B–C12B–C13B, symmetry code: ii = *x*, 1+*y*, *z*]. In both molecules, phenyl ring systems align in an anti-parallel manner. In closest interaction [with a perpendicular separation of 3.3 Å between Cg(2) and Cg(1)], the lateral offset is small, while a longer interaction [with a perpendicular separation of 3.35 Å between Cg(4) and Cg(3)] has a larger lateral offset.

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