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Crystal structure analysis of Schiff's base derivatives

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Abstract: Compound 1 ((E)-N-benzylideneaniline) crystallizes in monoclinic $P2_1/n$ space group with four molecules in the asymmetric unit. Compound 2 ((E)-5-(diethylamino)-2-((phenylimino)methyl)phenol) crystallizes in orthorhombic P $2_12_12_1$ with eight molecules in the asymmetric unit. Crystal data were collected using BRUKER SMART APEX II CCD X-ray diffractometer. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares procedures to the final R_1 of 0.0481 and 0.0366, respectively using SHELXL programs.
Key Words: Schiff's base, Crystal structure.

Introduction:

Schiff bases are considered important compound because of their wide range of biological activities, and also because of their use as ligands in conjunction with transition metals. Schiff base ligands usually coordinate to a metal ion through the imine nitrogen atom, but coordination *via*, other functional groups, e.g. through oxygen or carbon, has also been reported[1,2]. Schiff's bases derived from salicyladehyde and fluoroaniline, specifically, have been considered as potential pharmaceutically interesting compounds as several of the members of this family of molecules have shown antitumor, antimicrobial or antiviral activities[3-5]. Schiff base compounds are a class of important materials used as pharmaceuticals and in various medicinal fields of interest[6-8]. Schiff bases have also been used as versatile ligands in coordination chemistry[9-11].During the last few decades, there has been a considerable interest in the chemistry of Schiff base compounds[12-13]. Schiff bases, containing different donor atoms, also find use in analytical applications and metal coordination[14-16]. Since manycompounds containing sulfur and nitrogen atoms are antihypertensive[17-21], analgesic, anti-inflammatory, sedative, or fungicidal, synthesis of the corresponding heterocyclic compounds could be of interest from the viewpoint of chemical reactivity and biological activity. As an extension of our work on the structural characterization of Schiff's base compounds, the solid state structure of two compounds is reported here.

Experimental

X-ray crystal determination: single crystal of the compound 1 and compound 2 suitable for x-ray diffraction were obtained by slow evaporation method. Three dimensional intensity data were collected on Bruker[22] SMART APEX II CCD diffractometer using graphite monochromatized Mo-Kα radiation (λ= 0.71073 Å) at CAS in Crystallography and Biophysics, University of Madras, Chennai. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares procedures using the SHELXL[23] programs. All the non-hydrogen atoms were refined using isotropic and later anisotropic thermal parameters. The hydrogen atoms

were included in the structure factor calculation at idealized positions by using a riding model, but not refined. Images were created with ORTEP[24]. The Crystallographic data for the two compounds were listed in Table 1and 2, respectively.

Table 1: Crystal data for compound 1

Parameters	**Compound 1**
Empirical formula	C_{13} H_{11} N
Formula weight	181.23
Temperature	293(2) K
Wavelength	0.71073 **Å**
Crystal system, space group	Monoclinic, P 21/c
Unit cell dimensions	a=11.9456(7) Å b=7.9219(5) Å β(º)=118.438(2)º c=12.1612(7)Å
Volume	1011.97(10)A^3
Z, Calculated density	4, 1.190 Mg/m^3
Absorption coefficient	0.070 mm^-1
F(000)	384
Crystal size	0.30 x 0.25 x 0.20 mm
Theta range for data collection	1.94 to 28.34 deg
Limiting indices	-15<=h<=15, -10<=k<=10, -16<=1<=16
Reflections collected / unique	9374 / 2525 [R(int) = 0.0248]
Completeness to theta = 28.34 º	99.8 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full –matrix-least-squares on F^2
Data / restraints / parameters	2525 / 0 / 127
Goodness-of-fit on F^2	1.003
Final R indices [I>2sigma(I)]	R1=0.0481, wR2=0.1363
R indices (all data)	R1=0.0706, wR2=0.1578
Largest diff. peak and hole (e.A^-3)	0.185 and -0.216

Synthesis of Compound 1:

The general procedure for the synthesis of Schiff's bases aniline (1.82 ml, 0.02 mol) and prepared in 30 ml of dry ethanol treated with (2.03 ml, 0.02 mol) of benzaldehyde with vigorous stirring. The reaction mixture was left standing at room temperature for 10 minutes, and then adds distilled water starring few minus after one hour put in refrigerator. The crystals were collected and were washed several times in ethanol. Recrystalization using 85% ethanol was done several time get pure benzalaniline product.

Synthesis of Compound 2:

The general procedure for the synthesis of Schiff bases aniline (0.03mol) and few drop of dilute sulfuric acid pH4-5 range prepared in 30 ml of dry ethanol treated with (0.036 mol) of 4-(diethylamino) salicyladehyde with stirring in a flask than was refluxed 70°C overnight at Argon atmosphere of condition. The reaction mixture was left standing at room temperature for 10 minutes, and then adds distilled water starring few minus after one hour put in refrigerator. The crystals were collected and were washed several times in ethanol. Recrystalization using 85% ethanol was done several times.

Results and Discussion

Compound 1:

The phenyl ring (C1-C6) makes a dihedral angle 64.74 (8)° with the other phenyl ring (C8-C13). The molecule adopts an extended conformation about N1-C7 bond which is evident from the torsional angle (C4-

N1-C7-C8= 179.55 (2)°). No classical hydrogen bond is found in the structure. The selected bond lengths and bond angles are given in table 3 and 4, respectively. The ORTEP of compound is given in Fig 1.

Table 2: Crystal data for compound 2

Parameters	**compound 2**
Empirical formula	C_{17} H_{20} N_2 O
Formula weight	268.35
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, P 2_1 2_1 2_1
Unit cell dimensions	a=6.450(5) Å b=13.985(5) Å c=16.644(5)Å
Volume	1501.3(14) A^3
Z, Calculated density	4, 1.187 Mg/m^3
Absorption coefficient	0.075 mm^-1
F(000)	576
Crystal size	0.30 x 0.25 x 0.20 mm
Theta range for data collection	1.94 to 28.34 deg
Limiting indices	-4<=h<=8, -18<=k<=12, -22<=1<=14
Reflections collected / unique	8317 / 3541 [R(int) = 0.0181]
Completeness to theta = 28.34 º	100.0%
Absorption correction	Semi-empirical from equivalents
Refinement method	Full–matrix-least-squares on F^2
Data / restraints / parameters	3541 / 0 /185
Goodness-of-fit on F^2	1.030
Final R indices [I>2sigma(I)]	R1=0.0366, wR2=0.0903
R indices (all data)	R1=0.0491, wR2=0.0977
Largest diff. peak and hole (e.A^-3)	0.161 and -0.121

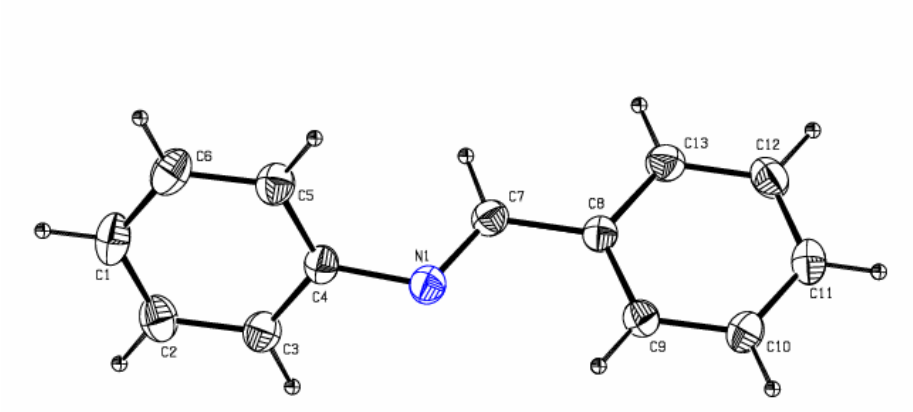

Fig 1: Molecular Structure of compound 1. Displacement ellipsoids are drawn at 30% probability.

Table 3: Selected bond length for compound 1 (Å)

Atom	Length
C(3)-C(4)	1.377(2)
C(4)-C(5)	1.381(2)
C(4)-N(1)	1.4235(16)
C(5)-C(6)	1.382(2)
C(7)-N(1)	1.2479(19)
C(7)-C(8)	1.4625(18)
C(8)-C(13)	1.3880(19)
C(8)-C(9)	1.3882(19)
C(9)-C(10)	1.3774(19)
C(10)-C(11)	1.376(2)
C(11)-C(12)	1.365(2)
C(12)-C(13)	1.379(2)

Table 4: Selected bond angle for compound 1 (°)

Atom	Angle
C(2)-C(1)-C(6)	119.78(14)
C(1)-C(2)-C(3)	120.19(16)
C(4)-C(3)-C(2)	120.70(14)
C(3)-C(4)-C(5)	119.03(13)
C(3)-C(4)-N(1)	117.87(12)
C(5)-C(4)-N(1)	123.01(13)
C(4)-C(5)-C(6)	120.08(16)
C(1)-C(6)-C(5)	120.21(15)
N(1)-C(7)-C(8)	122.30(13)
C(13)-C(8)-C(9)	118.77(12)
C(13)-C(8)-C(7)	119.56(12)
C(9)-C(8)-C(7)	121.67(12)
C(10)-C(9)-C(8)	120.30(13)
C(11)-C(10)-C(9)	120.10(14)
C(12)-C(11)-C(10)	120.23(13)
C(11)-C(12)-C(13)	120.22(14)
C(12)-C(13)- C(8)	120.36(14)
C(7)-N(1)-C(4)	119.72(12)

Compound 2:

The dihedral angle between the two phenyl rings is 42.90 (1)°**.** The hydroxyl oxygen atom attached with the phenyl ring deviate by 0.0103 (1)Å. The diethylamino groups attached with the phenyl ring makes a dihedral angle of 77.93 (1)° and 82.66 (1)°,respectively. The compound lacks hydrogen bond functionality. The selected bond lengths and bond angles are given in table 5 and 6, respectively. The ORTEP of compound is given in Fig 2.

Table 5: Selected bond length for compound 2 (Å)

Atom	Length
C(1)-C(2)	1.381(2)
C(1)-C(6)	1.395(2)
C(1)-N(1)	1.4109(18)
C(2)-C(3)	1.388(2)
C(3)-C(4)	1.370(3)
C(4)-C(5)	1.366(3)
C(5)-C(6)	1.381(2)
C(7)-N(1)	1.2859(17)
C(7)-C(8)	1.4311(18)
C(8)-C(9)	1.3986(18)
C(8)-C(13)	1.4196(19)
C(9)-C(10)	1.3627(19)
C(10)-C(11)	1.419(2)
C(11)-N(2)	1.3658(17)
C(11)-C(12)	1.4033(19)
C(12)-C(13)	1.3776(19)
C(13)-O(1)	1.3462(16)
C(14)-N(2)	1.455(2)
C(14)-C(15)	1.505(2)
C(16)-N(2)	1.460(2)
C(16)-C(17)	1.502(3)

Table 6: Selected bond angle for compound 2 (°)

Atom	Angle
C(2)-C(1)-C(6)	118.81(15)
C(2)-C(1)-N(1)	118.09(15)
C(6)-C(1)-N(1)	122.94(14)
C(1)-C(2)-C(3)	120.24(19)
C(4)-C(3)-C(2)	120.37(19)
C(5)-C(4)-C(3)	119.81(18)
C(4)-C(5)-C(6)	120.7(2)
C(5)-C(6)-C(1)	120.04(17)
N(1)-C(7)-C(8)	122.19(12)
C(9)-C(8)-C(13)	116.79(12)
C(9)-C(8)-C(7)	121.27(12)
C(13)-C(8)-C(7)	121.90(12)
C(10)-C(9)-C(8)	122.79(12)
C(9)-C(10)-C(11)	120.73(12)
N(2)-C(11)-C(12)	121.45(12)
N(2)-C(11)-C(10)	121.55(13)
C(12)-C(11)-C(10)	117.01(12)
C(13)-C(12)-C(11)	121.99(12)
O(1)-C(13)-C(12)	118.35(12)
O(1)-C(13)-C(8)	120.97(12)
C(12)-C(13)-C(8)	120.68(12)
N(2)-C(14)-C(15)	114.80(14)
N(2)-C(16)-C(17)	114.11(14)
C(7)-N(1)-C(1)	120.76(12)
C(11)-N(2)-C(14)	120.84(13)
C(11)-N(2)-C(16)	121.51(13)
C(14)-N(2)-C(16)	116.93(12)

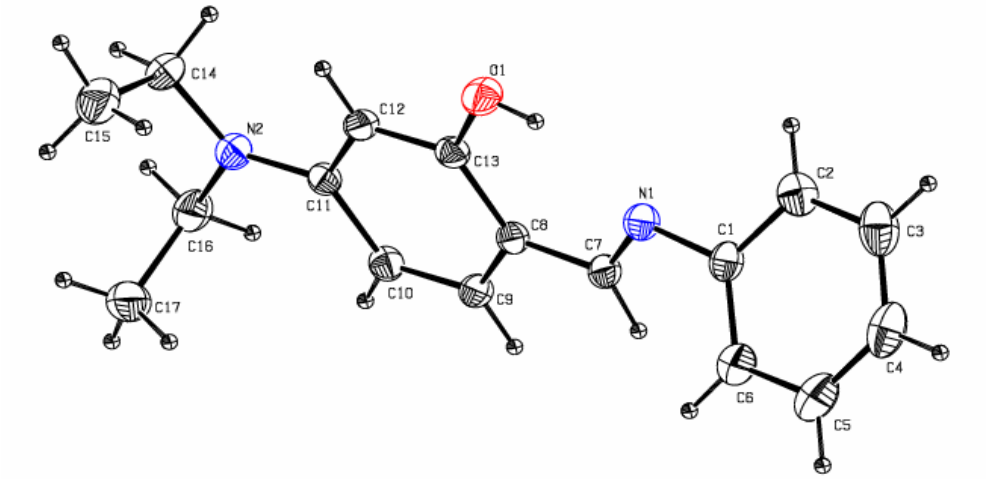

Fig 2: Molecular Structure of compound 2. Displacement ellipsoids are drawn at 30% probability.

Crystallographic data for the structures reported here have been deposited with CCDC (Deposition No's. CCDC **1005223 & 1005222**). These data can be obtained free of charge via http: // www. ccdc. cam. ac. uk/conts/ retrieving.html or from CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, E-mail:deposit@ ccdc.cam.ac.uk.

Conclusion

The crystal structure analysis of two novel Schiff's base derivatives were studied using x-ray diffraction and the structural aspects were discussed.

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