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SYNTHESIS AND CHARACTERIZATION OF SOME NOVEL ASYMMETRIC TETRADENTATE SCHIFF BASES OF 2,4-DIAMINO -6-PHENYL-1,3,5- TRIAZINE

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ABSTRACT:
The present work involves synthesis of some novel asymmetric tetradentate Schiff bases derived from 2,4-diamino-6-phenyl-1,3,5-triazine and Dehydroacetic acid in two steps. First step of scheme involves preparation of mono Schiff base by condensation of 2,4-diamino-6-phenyl-1,3,5-triazine and Dehydroacetic acid. The second step involves preparation of some novel asymmetric tetradentate Schiff bases from condensation of mono Schiff bases with substituted aromatic aldehydes. Prepared ligands were characterized by spectral analysis i.e. FT-IR, LCMS, ^{1}HNMR.
KEYWORDS: Tetradentate ligand, mono Schiff bases 2,4-diamino-6-phenyl-1,3,5-triazine, Dehydroacetic acid.

1.INTRODUCTION:

Schiff bases play an important role as chelating ligand used in coordination chemistry [i-ii]. They form stable complexes with transition metal elements [iii]. Schiff bases are generally formed by condensation of an aldehyde or ketone with a primary amine [iv]. It is represented by azomethine group with general formula RHC=NR1 [Where R and R1 are alkyl, aryl, cycloalkyl or heterocyclic group] is common structural feature of these compounds [v]. These compounds are also known as anils, imines or azomethine [vi].

Literature survey reveals that a number of Schiff bases containing the imine group shows wide variety of biological activities including antibacterial [vii], antifungal [viii], antiviral [ix], anti-inflammatory [x], antitumor [xi], anticancer activities [xii], insecticides [xiii] and herbicidal activities [xiv]. These compounds also shows an important properties i.e. their ability to reversibly bind oxygen [xv], catalytic properties [xvi], transfer of an amino group [xvii], photochromic property [xviii] and

complexing ability towards some toxic metals [xix]. The biological activity is related to the hydrogen bonding through the imine group of Schiff bases with active centers of the all constituents like donor atoms such as N, O, S [xx]. Literature survey manifest that some work has been done on Schiff bases derived from dehydroacetic acid with aliphatic amines, hydrazides, semicarbazides, thiosemicarbazides and studied intensively [xxi-xxii]. However very less work is reported on the synthesis of an asymmetric Schiff bases derived from aromatic heterocyclic diamine triazine, dehydroacetic acid and substituted aromatic aldehydes [xxiii].

In present work Schiff bases of dehydroacetic acid are synthesized. It is a biological active compound, finds biological and industrial application including fungicide, herbicide, bactericide activity [vii-viii-xiv]. Also, it is used as food preservatives and additives [xxiv-xxv]. Dehydroacetic acid is significant class of compounds in organic synthesis, particularly as starting material for preparation of various heterocycles like Schiff bases, chalcone etc [xxvi-xxviii]. Dehydroacetic acid Schiff bases and its metal complexes shows anticancer activity [xii]. So in future it can be used as a medicine against anticancer diseases.

By considering the importance of dehydroacetic acid we have reported the synthesis of asymmetric tetradentate Schiff bases derived from condensation of dehydroacetic acid, 2,4-diamino-6-phenyl-1,3,5-triazine and various aromatic substituted aldehydes. The Schiff bases synthesized were characterized by FT-IR, LCMS and ^{1}HNMR spectra.

2.EXPERIMENTAL:

2.1 Material:

All reagents used for the preparation of ligand were of analytical grade available and were used without further purification. Dehydroacetic acid and 2,4-diamono-6-phenyl-1,3,5-triazine were provided from SIGMA ALDRICH company (assay>_98%), various aldehydes were provided from Toronto Research Chemicals, absolute ethanol (assay>_99.8%).

2.2 Instrumentation and measurements:

IR spectra of solid ligand were recorded on FT-IR Bruker with KBr disc. NMR spectrum were recorded on Bruker Spectro spin avance DPX-400 ultrashield (400 and 300 MHz). Mass by LCMS spectrophotometer. Melting point were determined by open capillary method. All reactions were monitored by Thin Layer Chromatography (TLC). TLC confirmed the purity of all prepared compounds.

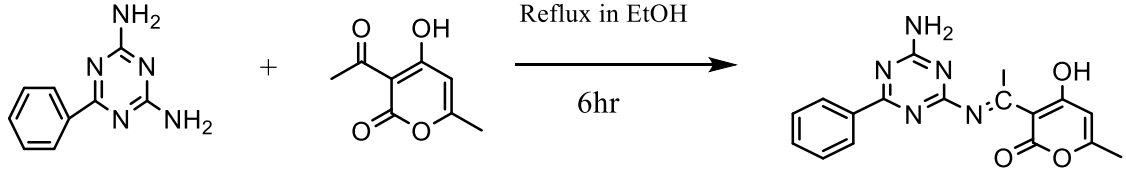
The ligand was prepared by a modification of reported methods. Asymmetric tetradentate Schiff base ligand has been synthesized via a stepwise approach.

2.3.a. Scheme I

Procedure for the synthesis of (*E*) -3-(1-(4-amino-6-phenyl-1,3,5-triazine-2-yl) imino) ethyl)-4-hydroxy-6-methyl-2H-pyran-2-one

In a round bottom flask (10 mmol) of DHA and (10 mmol) of 2,4-diamino-6-phenyl-1,3,5-triazine were taken. In this reaction mixture 50 ml super dry ethanol was added as a solvent and 2-3 drops of acetic acid was added as an acid catalyst. The reaction mixture was refluxed on water bath for 5-6 hours. Progress of the reaction was checked by TLC. After completion the reaction mixture was poured in ice cold water. The precipitate was filtered & recrystallized from ethanol and recorded the melting point and yield of the product.

Step I:



1 2 3

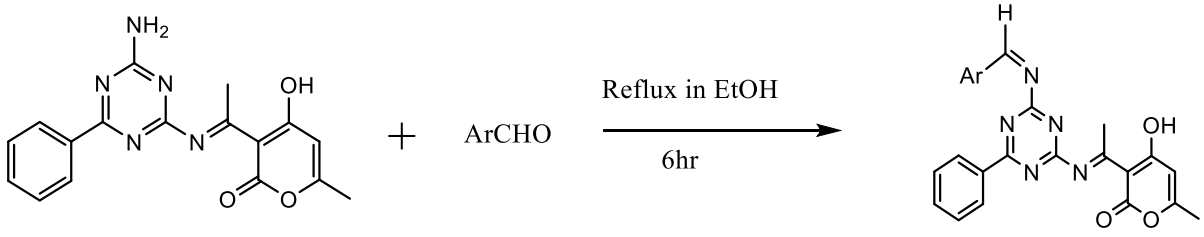
2.3.b: Scheme II

Synthesis of asymmetric tetradentate Schiff base

Synthesis of derivatives of 3-((*E*)-1-((4-(((*Z*)-benzylidene) amino)-6- phenyl-1,3,5-triazine-2-yl) imino) ethyl)-4-hydroxy-6-methyl-2H-pyran-2-one :

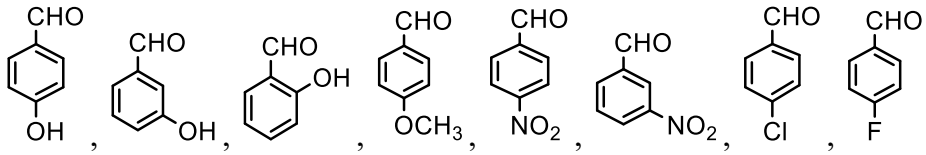
In a round bottom flask (10 mmol) of (*E*) -3-(1-(4-amino-6-phenyl-1,3,5-triazine-2-yl) imino)ethyl)-4-hydroxy-6-methyl-2H-pyran-2-one and (10 mmol) of aromatic aldehyde were taken. In this reaction mixture 50 ml super dry ethanol was added as a solvent and 2-3 drops of acetic acid was added as an acid catalyst. The reaction mixture was refluxed on water bath for 5-6 hours. After completion, the reaction mixture was poured in ice cold water. The precipitate was filtered and recrystallized from ethanol.

Step II:



3 4 5

Where Ar =

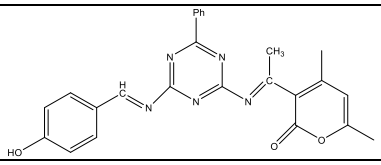
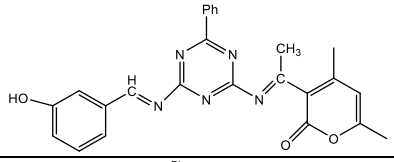
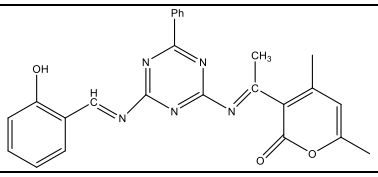


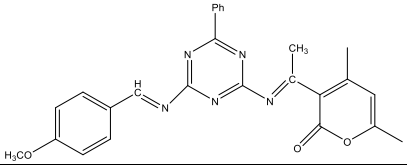
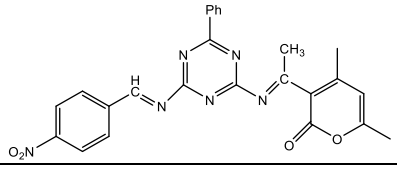
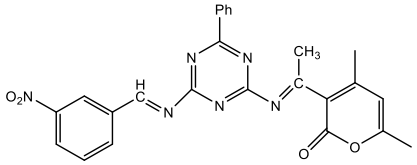
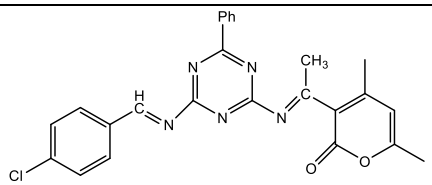
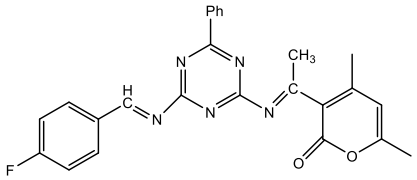
RESULT AND DISCUSSION:

All the synthesized Schiff bases are white to yellow coloured solids, stable to air and non hygroscopic. They are insoluble in water and soluble in hot ethanol. Their physical characteristics data are summarized in Table 1.

Table 1.

Analytical and Physical properties data of synthesized Schiff base Ligands

Sr. No.	Compound Structure	M.F.	Mol. Wt.	R	Color	M.P.
L1		$C_{24}H_{19}N_5O_4$	441.14	4-OH	Pale yellow	212^{0}C
L2		$C_{24}H_{19}N_5O_4$	441.14	3-OH	Pale yellow	244^{0}C
L3		$C_{24}H_{19}N_5O_4$	441.14	2-OH	Pale yellow	252^{0}C

L4		$C_{25}H_{21}N_5O_4$	455.45	4-OCH_3	White	234^{0}C
L5		$C_{24}H_{18}N_6O_5$	470.44	4-NO_2	Pale yellow	268^{0}C
L6		$C_{24}H_{18}N_6O_5$	470.44	3-NO_2	Pale yellow	258^{0}C
L7		$C_{24}H_{18}ClN_5O_3$	459.88	4-Cl	White	238^{0}C
L8		$C_{24}H_{18}FN_5O_3$	419	4-F	White	242^{0}C

SPECTRAL ANALYSIS:

FTIR analysis:

The absorption peak pattern in IR spectra exhibited complex nature due to various vibrational modes. However, with few objectives, only characteristic peaks which were specific to all Schiff bases related to enolic O-H, aromatic C=C, azomethine >C=N, aryl azomethine, lactone carbonyl C=O and enolic C-O/C=O of Schiff bases were taken into consideration for characterization.

In all the synthesized DHA Schiff bases the characteristic O-H stretching frequencies were observed as broad weak band at 3454 to 3368 cm^{-1} due to strong intermolecular hydrogen bonding between enolic O-H and N of azomethine group.

Azomethine >C=N stretching frequency is dependent on its substituent and mostly causes resonance interaction and H-bonding. In the present work azomethine (>C=N-) depicted strong absorption stretching vibration band in the region 1644-1634 cm^{-1}.

The peak in the region 1708 to1685 cm^{-1} appeared due to >C=O lactone carbonyl stretching vibrations; peak in the region 1388 to 1333 cm^{-1} appeared due to aryl/aliphatic (C-N) stretching vibrations and the peak in the region 1256 to 1214 cm^{-1} appeared due to (C-O) enolic stretching vibrations.

^{1}HNMR Spectra:

^{1}HNMR Spectra of all the compounds were recorded in DMSO at room temperature. The following signals, chemical shift value δ(ppm) relative to TMS as internal standard were observed;

Singlet signal a δ value 2.1-2.28 for the methyl group at C_6, singlet signal at δ value 14.72-16.00 of enolic O-H group which is highly deshielded, singlet signal at δ value 5.00-5.94 belonging to H atom at C_5 and singlet signal at δ value 2.57-2.75 for the methyl group attached to azomethine C atom of DHA moiety and different signals of amine moiety.

SPECTRAL DATA:

Intermediate: (*E*)-3-(1-((4-amino-6-phenyl-1,3,5-triazin-2-yl)imino)ethyl)-4-hydroxy-6-methyl-2H-pyran-2-one : -

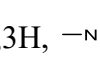
I.R.(KBr) Cm^{-1}: 3388.28(OH), 1614.44(-C=N), 1706.26(-C=O lactone), 1394.59(-C-N), 1252.95(C-O enolic)

^{1}HNMR (DMSO) ppm: δ(ppm) 2.213 (S,3H, ), δ 2.525 (S,3H, ), δ 6.091 (S, 1H pyrone), δ 6.533 (S, 2H,-NH_2), δ 7.342-7.414 (M, 5H), δ 15.88 (S,1H, -O-H)

MS: m/z [M+1] 337

1. 4-hydroxy-3-(*E*)-1-((4-(((*Z*)-4-hydroxybenzylidene)amino)-6-phenyl-1,3,5-triazin-2-yl)imino)ethyl)-6-methyl-2H-pyran-2-one:

I.R.(KBr) Cm^{-1}: 3081.48(OH), 1668.31(-C=N), 1712.91(-C=O lactone), 1389.64(-C-N), 1289.93(C-O enolic)

^{1}HNMR (DMSO) ppm: δ(ppm) 2.26 (S,3H, ), δ 2.56 (S,3H, ), δ 6.25 (S,1H,-OH), δ 6.80 (S,1H, pyrone), δ 6.96 (dd,2H) , δ 7.50-53 (M,5H), δ 7.732 (dd, 2H), δ 9.80 (S,1H ,-N=C-H), δ 15.85(S,1H,-O-H)

MS: m/z [M+1] 441.14

2.3-(E)-1-((4-(((-*E)*-4-methoxybenzylidene)amino)-6-phenyl-1,3,5-triazin-2-yl)imino)ethyl)-6-methyl-2H-pyran-2-one:

I.R.(KBr) Cm^{-1}: 3287.17(OH), 1614.82(C=N), 1393.08(C-N), 1254.35(C-O enolic), 3126.47(OCH_3)

^{1}HNMR (DMSO) ppm: δ(ppm) 2.29 (S,3H, ), δ 2.60 (S,3H, ), δ 3.90 (S,3H,-OCH_3), δ 6.82 (S,1H, pyrone), δ 7.20(dd,2H), δ 7.54(dd,2H),δ 7.54-7.58(M,5H, aromatic), δ 9.52(S,1H, -N=CH-), δ 15.85(S,1H,-O-H)

MS: m/z [M+1] 455.45

3. 4,6-dimethyl-3-((*E*)-1-((4-(((*E*)-4-nitrobenzylidene) amino)-6- phenyl-1,3,5-triazin-2-yl)imino)ethyl)-6-methyl-2H-pyran-2-one:

I.R.(KBr) Cm^{-1}: 3388.19(OH), 1614.67(C=N), 1716.60(C=O lactone), 1394.08(C-N), 1256.16(C-O enolic), 1588.78(NO_2)

^{1}HNMR (DMSO) ppm: δ(ppm) 2.24 (S,3H, ), δ 2.66 (S,3H, ), δ 6.28(S,1H, pyrone) , δ 7.60 (dd,2H), δ 7.52-8.40(M,5H, aromatic), δ 8.40(dd,2H),δ 9.75 (S,1H, -N=CH-), δ 15.95(S,1H,-O-H)

MS: m/z [M+1] 470.44

CONCLUSION:

A novel asymmetric tetradentate Schiff base ligands have been prepared by condensation of dehydroacetic acid, 2,4-diamino-6-phenyl-1,3,5-triazine and various aromatic substituted aldehydes by two step reaction. All the synthesized Schiff bases are white to yellow colored solids, stable to air and non-hygroscopic. They are insoluble in water and soluble in hot ethanol. The structure of all synthesized Schiff bases was determined by IR and ^{1}HNMR.

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