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Research article

Synthesis, spectral studies, antioxidant and antibacterial evaluation of aromatic nitro and halogenated tetradentate Schiff bases

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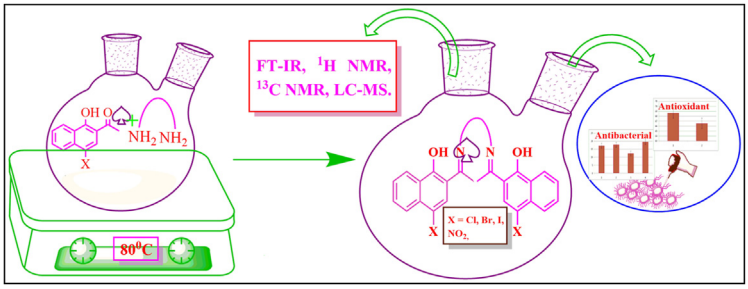
GRAPHICAL ABSTRACT



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ABSTRACT

Herein, we report the synthesis, characterization, and biological properties of eleven **(3a-3k)** novel Schiff bases. The spectral data of FT-IR, ^{1}H NMR, ^{13}C NMR, and LC-MS are associated with these synthesized compounds. From the FT-IR analysis, we confirmed the azomethine (-C=N-) group and from ^{1}H NMR data, the phenolic –OH proton is appeared at range δ 13.92–14.09ppm due to hydrogen bonding. The LC-MS analysis agreed with molecular ion peaks of synthesized Schiff bases. To evaluate the antibacterial activity of newly synthesized compounds were screened against *b. licheniformis*, *b. species*, *e. coli*, and *s. aureus*. Furthermore, the antioxidant activity was investigated by two methods 2,2-diphenyl-1-picryl hydrazyl (DPPH) and hydroxyl radical scavenging methods. The (-NO_2,-Cl,-Br,-I) substituted compounds have shown good antibacterial activity against tested organisms. Also, these compounds were exhibited higher antioxidant activity by given methods.

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Specifications Table

Subject area	Organic Chemistry
Compounds	4- halo/nitro substituted 2,2'-((alkane-1, 3-diylbis(azanylylidene))bis (ethan-1-yl-1-ylidene))bis(naphthalen-1-ol)
Data category	Synthesized, Spectral and Biological data.
Data acquisition format	FT-IR, ^{1}H NMR, ^{13}C NMR, Mass spectra, Elemental analysis
Data type	Experimental
Procedure	A series of substituted 4- halo/nitro substituted 2,2'-((alkane-1,3-diylbis (azanylylidene))bis(ethan-1-yl-1-ylidene)) bis(naphthalen-1-ol) derivatives have been synthesized and Characterized by spectral data. Also screened for their biological potential.
Data accessibility	Data is with this article.

1. Introduction

The Schiff bases synthesized by the condensation of the active carbonyl group and primary amines with azomethine (-C=N-) linkage may have numerous applications. Some Schiff bases were reported to possess antibacterial [1, 2], antioxidant [1, 2, 3], antifungal [4, 5], anti-HIV [6], antitumor [7], anti-inflammatory [8], anticancer [9], antimalarial [10, 11] antiproliferative activities [11]. Phenolic Schiff base derivatives with one or more halo groups (-Cl, -Br, –I) or nitro group in the aromatic ring may show biological activities like antibacterial [12] and antiviral [12] activities. Some isatin Schiff base derivatives were applicable for docking study [13], some Schiff bases were supposed to be adsorbed on the metal surface by its characteristic imine group [14]. Schiff bases were known to be a sort of ligands with strong coordinative ability due to the intra-hydrogen bonding [15, 16]; hence mostly all Schiff Bases can form 1:1 complexes with transition metal ions. Metal complexes of Schiff bases having O-hydroxy aromatic tetradentate Schiff bases exhibit various bioactivities like antibacterial [17, 18], antioxidant [17, 18, 19, 20], antifungal [20], DNA damage assays [20], antitumor [21], anticancer [22], antiviral [23], anti-inflammatory [24] activities. It is also used for homogeneous catalysis [25], electrocatalytic reduction [26], catalytic oxidation [27], fluorescent chemosensor for detection of Fe^{2+} ions [28], potentiometric sensor [29], catalytic used in heck [30] & Suzuki reaction [30], dyes [31], polymers [31], phenoxazinone synthase mimicking activity [32], and catalase mimic activity [33]. The prolongation of our research work on Schiff bases [34]; herein we report a synthesis of eleven tetradentate Schiff Bases. The structure elucidation of synthesized Schiff bases had done with spectroscopic techniques (FT-IR, ^{1}H NMR, ^{13}C NMR, and LC-MS). The result of this article will be useful for the upcoming researchers to gain more information about the antibacterial and antioxidant activities of Schiff bases (see Scheme 1).

2. Experimental

2.1. Chemical material and instrumentation

For the experimental work, the chemicals were purchased by aura, spectrochem & TCI and without further purification. In the laboratory, thin layer chromatography (TLC) took by 0.25-mm e merck gel Plates (60F-254). Synthesized compounds were dissolved in a minimum amount of acetic acid, spotted on the given TLC plate, and ran through a solution of ethyl acetate and benzene. The melting point determination of compounds was done by digital apparatus koefler banc. The elemental analysis of the synthesized compounds was carried out through perkin-elmer 240 elemental analyzer. The structure of unknown compounds was agreed upon by different spectral characterization. FT-IR spectrometer was recorded KBr pellets on a perkin-elmer 2000 at 8 cm^{-1} resolution in the region 4000-400 cm^{-1}. ^{1}H NMR spectra were carried out with bruker avance III HD 300/400 operating at 300/400 MHz using $CDCl_3$ solution with TMS at internal standard. ^{13}C NMR spectra obtained with bruker avance III HD 300 operating at 300 MHz using $CDCl_3$ solution with TMS at internal standard. Mass spectra recorded on LC-MS (ESI) mass spectrometer at 70 ev.

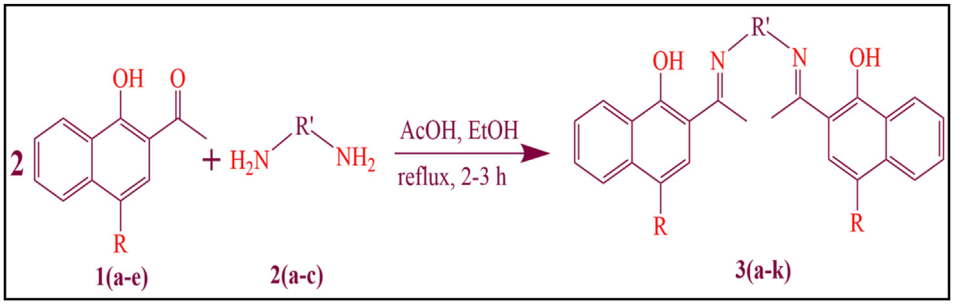
2.2. Synthesis

2.2.1. General synthesis of schiff base compounds (3a-3k)

Schiff bases had been synthesized by mixing of warm absolute ethanolic solution of substituted 1-(1-hydroxynaphthalen-2-yl)ethan-1-one (2 mmol) with ethane-1,2-diamine (1 mmol) **(3a-3e)** as well as with propane-1,3-diamine (1 mmol) **(3f-3h)** and also with pentane-1,3-diamine (1 mmol) **(3i-3k)**. In each reaction mixture catalytic amount of acetic acid (2–3 drops) was added and refluxed for 3–4 h (Scheme-1). The progress of the reaction mixture was monitored on TLC using pet-ether: ethyl acetate (8:2V/V) as eluent. After completion, the reaction mixture was kept overnight at room temperature. The crystalline compound was filtered, washed with cold water, and re-crystallized from absolute ethanol. The purity of the product was checked by using TLC and the physical data were tabulated in Table 1.

2.2.2. Procedure for antibacterial activity

The given compounds were screened for antibacterial activity against the bacteria *bacillus licheniformis*, *bacillus species*, *escherichia coli*, and *staphylococcus aureus* by using well diffusion method. The microbial



Scheme 1. Synthesis of Schiff Bases **(3a-3k).**
1a. R = -H, **1b.** R = -Cl, **1c.** R = -Br, **1d.** R = -I, **1e.** R = $-NO_2$.
2a. R'= $-CH_2-CH_2-$, **2b.** R'= $-CH_2-CH_2-CH_2-$, **2c.** R' = $-CH(C_2H_5)-CH_2-CH_2-$.
3a. R = -H, R' = $-CH_2-CH_2-$, **3b.** R = -Cl, R'= $-CH_2-CH_2-$, **3c.** R = -Br, R' = $-CH_2-CH_2-$, **3d.** R = -I, R' = $-CH_2-CH_2-$, **3e.** R = $-NO_2$, R' = $-CH_2-CH_2-$, **3f.** R = -Br, R'= $-CH_2-CH_2-CH_2-$, **3g.** R = -I, R' = $-CH_2-CH_2-CH_2-$, **3h.** R = $-NO_2$, R' = $-CH_2-CH_2-CH_2-$, **3i.** R = -Cl, R' = $-CH(C_2H_5)-CH_2-CH_2-$, **3j.** R = -I, R' = $-CH(C_2H_5)-CH_2-CH_2-$, **3k.** R = $-NO_2$, R' = $-CH(C_2H_5)-CH_2-CH_2-$.

Table 1. Physical properties of Schiff bases **(3a-3k)**.

compound	molecular formula	color	yield%	M.P. (°C)
3a	$C_{26}H_{24}O_2N_2$	yellow	88	128–130
3b	$C_{26}H_{22}O_2N_2Cl_2$	yellow	85	158–160
3c	$C_{26}H_{22}O_2N_2Br_2$	brown	90	172–174
3d	$C_{26}H_{22}O_2N_2I_2$	pale yellow	92	182–184
3e	$C_{26}H_{22}O_6N_4$	yellow	82	205–207
3f	$C_{27}H_{24}O_2N_2Br_2$	brown	92	135–137
3g	$C_{27}H_{24}O_2N_2I_2$	yellow	88	195–197
3h	$C_{27}H_{24}O_6N_4$	green	78	220–222
3i	$C_{29}H_{28}O_2N_2Cl_2$	yellow	80	192–194
3j	$C_{29}H_{28}O_2N_2\ I_2$	yellow	90	205–207
3k	$C_{29}H_{28}O_6N_4$	brown	81	235–237

suspension (100uL) having 108 CFU mL^{-1} of bacteria was carried out with the help of Mueller-Hinton agar (MHA) medium. The extracts were diluted by 100% dimethyl sulphoxide at the concentrations of 5 mg/mL and the given medium was melted and cooled to 48–50 °C. The solid plates were formed by the addition of standardized inoculums (1.5 × 108C FU/mL, 0.5McFarland) to the molten agar which was poured into sterile petri dishes. The well diffusion method was used to prepare product which was in the seeded agar plate; the compound activity had checked, and that was put into the well (6 mm). The plates were incubated in the incubator at 37 °C for overnight. The antibacterial zone of inhibition of the extract had determined for the bacterial species in zone sizes around each well. The compounds produced diameters of the zone of inhibition as compared to standard ciprofloxacin [35, 36].

2.2.3. Determination of minimum inhibitory concentration (MIC)

The broth dilution method is applicable for the minimum inhibitory concentration of given compounds. The concentration of compounds was prepared 8 mg/mL in the first tube containing 1mL of broth. The conduits were vortexes to make the initial standard concentration. These were serially diluted to other cannulas. Finally, 1mL compound was discarded from the last tube and prepared the dilution of 0.25, 0.50, 0.75, 1.0 mg/mL. To all these tubes, 0.1mL of the log phase culture of target microorganisms were added separately and incubated at 37 °C for 24–48 h for bacteria. After incubation, the lowest concentration of tube solution with no detectable bacterial growth was considered a minimum inhibitory concentration.

2.2.4. Antioxidant activity

2.2.4.1. Procedure for 2, 2-diphenyl-1-Picryl hydrazyl (DPPH) assay. DPPH (2, 2, diphenyl-1-picryl hydrazyl) radical scavenging assay was carried out [37] with slight modifications. The 1mL ethanolic solution had different concentrations of synthesized compounds. It was added with an equal volume of 0.1mm ethanolic solution of DPPH. The prepared solution settled for incubation at room temperature. The decreases in the concentration of DPPH were measured by noting the absorbance at 517nm. A similar test was performed with ascorbic acid, as an internal standard, instead of Schiff's base. The percentage scavenging of DPPH free radical for each concentration of test compounds had calculated the absorbance of negative control using Eq. (1).

$$\%\ \text{scavenging} = \frac{\text{absorbance of control} - \text{absorbance of test sample}}{\text{absorbance of control}} \times 100 \quad (1)$$

2.2.4.2. Procedure for hydroxyl radical scavenging assay. Hydroxyl radical scavenging activities of given compounds were determined by using the earlier reported method [37]. The reaction cocktail included 60μL of 1mm $FeCl_3$, 90μL of 1mm 1,10 phenanthroline, 2.4mL of 0.2M phosphate buffer (pH 7.8), 150μL of 0.17 M H_2O_2, and 1.5mL of various concentrations of each compound. The prepared solutions of given compounds were kept at room temperature for 5min incubation, and absorbance was measured at 560 nm with the help of spectrophotometer. The α-tocopherol was used as the reference compound for hydroxyl radical scavenging assay.

3. Result and discussion

All the synthesized Schiff bases are in different colors and they are stable in air and moisture at room temperature. They are soluble in methanol, dimethyl sulphoxide, dimethylformamide, dichloromethane, chloroform, and partially soluble in ethanol. The spectral data of FT-IR, ^1H NMR, ^{13}C NMR, and LCMS confirmed their structure.

3.1. FT-IR analysis

FT-IR spectra of given compounds performed with the KBr pellet technique, and the observed results are in Table 2. The stretching bands are observed at 3444-3403 cm^{-1} due to the phenolic –OH group and 1665-1622 cm^{-1} due to the (–C=N) stretching mode of the imine group. The IR absorption peak at 1278–1263 cm^{-1} shows the phenolic ν(C–O) group with the presence of the keto-amine group having (N–O···H) intramolecular hydrogen bonding only in the solid-state [38]. The Schiff bases have shown two C–X stretching vibrations in the range of 794–760 cm^{-1} which confirms that the halogen groups are presented at the para position to the aromatic –OH group [38, 39]. Even two stretching vibrations have been observed in the range 1573–1523 cm^{-1} and

Table 2. FT-IR values of Schiff bases**(3a-3k)**.

compound	ν(O–H) cm^{-1}	ν(−C=N−) cm^{-1}	ν(C=C) cm^{-1}	ν(C–N–C) cm^{-1}	ν(C−X) cm^{-1}	ν(N–O) cm^{-1}
3a	3434	1629	1452	1018	–	–
3b	3444	1640	1457	1076	788,761	–
3c	3419	1630	1440	1068	788,763	–
3d	3440	1646	1457	1070	794,760	–
3e	3413	1636	1467	1081	–	1573, 1413
3f	3403	1622	1450	1072	790,765	–
3g	3407	1635	1450	1076	790,765	–
3h	3417	1650	1455	1076	–	1527, 1384
3i	3444	1640	1452	1078	790,769	–
3j	3440	1647	1457	1018	786, 760	–
3k	3430	1630	1450	1027	–	1523, 1388

Table 3. Antibacterial activity of Schiff bases (in mm) **(3a-3k).**

sample	*B. Lichenifermis*	*Bacillus Sp.*	*E.coli*	*S.aureus*
3a	08	07	07	08
3b	24	19	16	20
3c	17	20	11	21
3d	23	13	09	16
3e	09	16	18	20
3f	10	22	10	27
3g	16	12	11	13
3h	19	25	08	26
3i	25	23	19	28
3j	12	15	17	19
3k	26	24	10	18
ciprofloxacin	27	26	20	30
DMSO	00	00	00	00
average	17.18	17.81	12.36	19.63

1413–1384 cm^{-1} due to the $–NO_2$ group. Table 2 and the supplementary file (Fig. No. S1 to S11) represents spectroscopic data (IR) of given Schiff bases **(3a-3k)** (see Table 3).

3.2. ^1H NMR analysis

^1H NMR spectral data of Schiff bases analyzed in $CDCl_3$ solvent, from the data, the presence of multiplets at δ value between 6.78–8.53ppm is due to aromatic protons. The appearance of the singlet at δ 13.92–14.09ppm shows the existence of the phenolic –OH proton having (N–O···H) intramolecular hydrogen bonding. In compounds **(3a-3h)** $–CH_3$ groups have appeared singlet at range δ 2.45–2.49ppm of 6H indicating that they are symmetrically equivalent. The compounds **(3i, 3j, 3k)**, $–CH_3$ groups have shown two singlets at range δ 2.44–2.47ppm, which indicates that they are symmetrically non-equivalent. The spectral data of ^1H NMR is represented in the supplementary file (Fig. No.S12 to S22) of synthesized Schiff bases **(3a-3k).**

3.3. ^{13}C NMR analysis

In ^{13}C NMR spectra, the peaks are observed at the range of δ value from 105 to 140ppm is due to aromatic and olefinic carbon. The signal present at δ 175.1–175.5ppm confirms azomethine (-C=N-) group, and the phenolic C–OH carbon atom showed a sharp peak at δ 170.6–171.7ppm. The Schiff bases **(3e, 3h, 3k)** display signal at δ 165.1–164.5ppm due to a $C–NO_2$ bond. Schiff bases **(3b-d, 3f, 3g, 3i, 3j)** have exhibited a peak at δ 132.1–135.0ppm stipulates the presence of a C–X bond and the signal present at δ 14.3–14.6ppm due to $–N=C–CH_3$ group. The spectral data of ^{13}C NMR is represented in the supplementary file (Fig. No. S23 to S33) of given Schiff bases **(3a-3k).**

3.4. LC-MS analysis

The LC-MS spectra of the Schiff bases exhibited different fragmentation patterns as expected, and results were getting to be in good agreement with their molecular formulae. –Cl and–Br containing Schiff bases gave different molecular ion peaks due to its isotopic effect. The molecular ion peak of the Schiff bases is displayed at $[M + H]^+$ peak. Especially the aromatic nitro Schiff bases **(3e, 3h, 3k)** lose $–NO_2$ radical and give molecular ion peak (M – NO_2) [39]. The spectral analysis (FT-IR, ^1H NMR, ^{13}C NMR, and LC-MS) confirmed that the synthesized compounds are Schiff bases. The mass spectrometry data of synthesized Schiff bases **(3a-3k)** is represented in the supplementary file (Fig. No. S34 to S44).

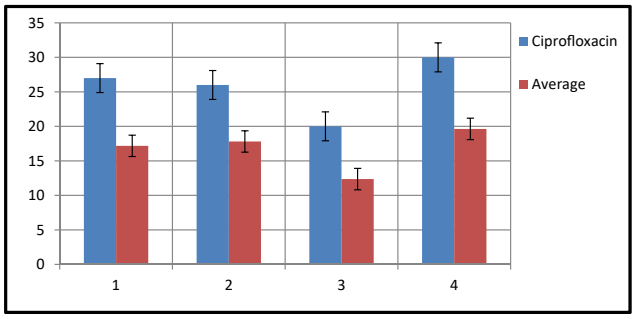


Figure 1. Antibacterial activity of Schiff bases **(3a-3k)** against gram positive and gram negative error bars represents the standard deviation of triplicate measurements.

3.5. Antibacterial activity

The experimental details and zone of inhibition of Schiff bases concerning the antibacterial activity against the bacterial strains is illustrated in table no.3. Among the eleven Schiff bases, the compound **3i** has more potent against tested all four micro-organisms. The Schiff bases **3b, 3d, 3k** are more effective against b. Licheniformis and the compounds **3b, 3e, 3j** show the higher activity against e. coli. Also, the compounds **3f, 3j** are more potent against Bacillus sp., and compounds 3f, 3h give promising activity against s. aureus. The synthesized Schiff bases with the electron-withdrawing group such as [-Cl, -Br, -I, and $-NO_2$] and extended carbon chain of diamines suggest more potent in antibacterial activities. The impact of electronegative groups like -Cl,-Br, and $–NO_2$ is more effective than the –H and –I group on synthesized compounds. The antibacterial activity of these compounds is represented graphically in Figure 1.

The minimum inhibitory concentration was done at 0.25, 0.50, 0.75, and 1.0 mg/mL; the observed results are presented in Table 4. The Schiff base 3i has a good inhibition character at minimum concentration against referred microorganisms. It indicates the -Cl group and extended carbon chain of diamine which gives more potent biological activity. The Schiff bases **3b, 3d, 3k** have shown good inhibition against b. licheniformis (gram-positive), and compounds **3f, 3h, 3k** show high potent against b. species (gram-positive). The compounds **3e, 3j** against e. coli (gram-negative) strain, and compounds **3f, 3h** against s. aureus (gram-positive) organisms have conveyed good inhibition at a minimum concentration (0.25 mg/mL).

Table 4. MIC of Schiff bases (In Mg/mL) **(3a-3k).**

sample	bacterial pathogens			
	B.Licheniformis Mg/mL	Bacillus sp. Mg/mL	E.coli. Mg/mL	S.aureus Mg/mL
3a	0.638	0.792	0.792	0.653
3b	0.172	0.261	0.267	0.256
3c	0.267	0.272	0.272	0.291
3d	0.229	0.642	0.690	0.667
3e	0.531	0.267	0.192	0.269
3f	0.639	0.218	0.609	0.235
3g	0.351	0.739	0.752	0.761
3h	0.279	0.162	0.713	0.169
3i	0.149	0.140	0.149	0.138
3j	0.632	0.275	0.172	0.329
3k	0.153	0.158	0.571	0.269
ciprofloxacin	0.107	0.107	0.097	0.112
average	0.367273	0.356909	0.470818	0.367

Table 5. Antioxidant activity of Schiff bases **(3a-3k).**

sample	DPPH (%)	OH (%)
3a	55.89 ± 0.55	62.93 ± 0.25
3b	75.19 ± 0.15	72.50 ± 0.15
3c	72.99 ± 0.15	56.12 ± 0.51
3d	59.91 ± 0.89	47.80 ± 0.76
3e	62.89 ± 0.55	61.93 ± 0.15
3f	52.24 ± 0.03	57.17 ± 0.53
3g	78.56 ± 0.45	73.28 ± 0.17
3h	78.28 ± 0.36	77.77 ± 0.91
3i	67.99 ± 0.51	78.25 ± 0.1
3j	72.29 ± 0.45	70.55 ± 0.78
3k	79.28 ± 0.36	73.77 ± 0.31
ascorbic acid	85.42 ± 0.78	–
α- tocopherol	–	82.50 ± 0.84
average	68.68	66.55

3.6. Antioxidant activity

The antioxidant activity is one of the prime activities for the Schiff bases by using DPPH and hydroxyl radical scavenging assay. Ascorbic acid is used as a control compound for the DPPH method whereas α-tocopherol is used for the hydroxy method; the observed results are illustrated in Table 5. The compounds (**3b, 3g, 3h, 3k**) containing an electron-withdrawing group at the para position to phenolic –OH group were shown more potent with antioxidant activity by both methods. The results of both techniques reveal that the electron-withdrawing substitution with an extended carbon chain of diamines perform alternating antioxidant activity. The obtained data of compounds is mean graphically in Figure 2.

3.7. Spectral data

[E]-2,2'-((ethane-1,2-diylbis(azanylylidene))bis(ethan-1-yl-1-ylidene)) bis(naphthalen-1-ol) (3a)

Yield – 349.53 mg, 88%, Color -Yellow, M.P. 128–130 °C.

FT-IR (KBr, cm^{-1}): 3434(νOH),1629(νC = N),1452(νC = C-), 1018 (νC-N-C).

^{1}H NMR (400MHz,$CDCl_3$):δ 14.02 (s,2H,Ar-OH),8.48–6.82 (m,12H, Ar-H),4.05 (s,4H,-CH_2), 2.49(s,6H-CH_3).

^{13}C NMR (300MHz,CDCl3):δ 175.2(−C=N−),171.6(C–O),137.2–108.8(Ar-C-),35.2(−N-CH_2-), 14.5(-N=C-CH_3).

ESIMS (m/z): 397.40.

Anal. Cal. For $C_{26}H_{24}O_2N_2$: C 78.78, H 6.60, N 7.07; found C 78.60, H 6.82, N 7.72.

[E]-2,2'-((ethane-1,2-diylbis(azanylylidene))bis(ethan-1-yl-1-ylidene)) bis(4-chloronaphthalen-1-ol) (3b)

Yield – 395.34 mg, 85%, Color -Yellow, M.P. 158–160 °C.

FT-IR(KBr,cm^{-1}):3444(νOH),1640(νC = N),1457(νC = C-),1076 (νC−N−C),788(νC-Cl),761(νC-Cl) cm^{-1};

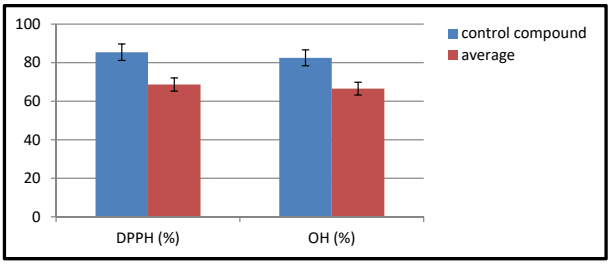


Figure 2. Antioxidant activity of Schiff bases **(3a-3k)** error bars represents the standard deviation of triplicate measurements.

^{1}H NMR (300MHz,$CDCl_3$):δ 13.93 (s,2H,Ar-OH),8.50–6.79 (m,10H,Ar-H),4.09 (s,4H,-CH_2), 2.45 (s, 6H, -CH_3).

^{13}C NMR (300MHz,$CDCl_3$):δ 175.3(−C=N−),171.7(C−O),137.1–108.2(Ar-C-),132.6(-C-Cl), 35.1(−N-CH_2-),14.5(-N=C-CH_3).

ESIMS(m/z): 465.70.

Anal. Cal. For $C_{26}H_{22}O_2N_2Cl_2$: C 67.24, H 4.74, N 6.03; found C 67.03, H 4.93, N 6.65.

[E]-2,2'-((ethane-1,2-diylbis(azanylylidene))bis(ethan-1-yl-1-ylidene)) bis(4-bromonaphthalen-1-ol) (3c)

Yield – 496.80 mg, 90%, Color -Brown, M.P. 172–174 °C.

FT-IR(KBr,cm^{-1}): 3419(νOH),1630(νC = N),1440(νC = C-),1068 (νC−N−C),788(νC-Br),763(νC-Br) cm^{-1}.

^{1}H NMR (400MHz,$CDCl_3$):δ 14.02 (s,2H,Ar-OH),8.50–6.90 (m,10H, Ar-H),4.04 (s,4H,-CH_2) 2.48 (s,6H,-CH_3).

^{13}C NMR (300MHz,$CDCl_3$):δ 175.2(−C=N−),171.7(C−O),137.1–108.2(Ar-C-),132.4(-C-Br),35.1(−N-CH_2-),14.4(-N=C-CH_3).

ESIMS(m/z): 556.10.

Anal. Cal. For $C_{26}H_{22}O_2N_2Br_2$: C 56.31, H 3.09, N 5.05; found C 56.11, H 3.31, N 5.78.

[E]-2,2'-((ethane-1,2-diylbis(azanylylidene))bis(ethan-1-yl-1-ylidene)) bis(4-iodonaphthalen-1-ol) (3d)

Yield– 597.06 mg, 92%, Color–Pale Yellow, M.P. 182–184 °C.

FT-IR(KBr, cm^{-1}): 3440(νOH),1646(νC = N),1457(νC = C-),1070 (νC−N−C),794(νC-I),760(νC-I) cm^{-1}.

^{1}H NMR (300MHz,$CDCl_3$):δ 13.92 (s,2H,Ar-OH),8.50–6.79 (m,10H,Ar-H),4.09 (s,4H,-CH_2), 2.46 (s,6H,-CH_3).

^{13}C NMR (300MHz,$CDCl_3$):δ 175.2(−C=N−),171.7(C−O),137.1–108.1(Ar-C-),132.4(-C-I), 35.0(−N-CH_2-),14.3(-N=C-CH_3).

ESIMS(m/z): 649.80.

Anal. Cal. For $C_{26}H_{22}O_2N_2I_2$: C 48.14, H 3.39, N 4.42; found C 48.03, H 3.69, N 4.64.

[E]-2,2'-((ethane-1,2-diylbis(azanylylidene))bis(ethan-1-yl-1-ylidene)) bis(4-nitronaphthalen-1-ol) (3e)

Yield – 399.47 mg, 82%, Color-Yellow, M.P. 205–207 °C.

FT-IR(KBr,cm^{-1}): 3413(νOH),1636(νC = N),1467(νC = C-),1573(νC-NO_2),1413(νC-NO_2),1081(νC−N−C) cm^{-1}.

^{1}H NMR (400MHz,$CDCl_3$):δ 14.02 (s,2H,Ar-OH),8.47–6.87 (m,10H, Ar-H),4.04 (s,4H,-CH_2),2.48 (s,6H,-CH_3).

^{13}C NMR (300MHz,$CDCl_3$):δ 175.2(−C=N−),171.7(C−O),137.1–108.2(Ar-C-),133.2(-C-NO_2), 35.1(−N-CH_2-),14.4(-N=C-CH_3).

ESIMS(m/z): 487.70.

Anal. Cal. For $C_{26}H_{22}O_6N_4$: C 64.19, H 4.52, N 11.52; found C 64.06, H 4.74, N 11.86.

[E]-2,2'-((propane-1,3-diylbis(azanylylidene))bis(ethan-1-yl-1-ylidene)) bis(4-bromonaphthalen-1-ol) (3f)

Yield – 520.73 mg, 92%, Color- Brown, M.P.135-137 °C.

FT-IR(KBr,cm^{-1}): 3403(νOH),1622(νC = N),1450(νC = C-),1076 (νC−N−C),790(νC-Br),765(νC-Br) cm^{-1}.

^{1}H NMR (400MHz,$CDCl_3$):δ 14.02 (s,2H,Ar-OH),8.45–7.26 (m,10H, Ar-H),3.81 (t,4H,J = 4.5Hz,-CH_2),2.47 (s,6H,-CH_3),2.32 (m,2H,J = 4.5Hz,-CH_2).

^{13}C NMR (300MHz,$CDCl_3$):δ 175.2(−C=N−),171.7(C−O),137.1–108.2(Ar-C-),132.4(-C-Br), 42.1(−N-CH_2-),29.2(HC-C-CH_2-),14.4(-N=C-CH_3).

ESIMS(m/z): 566.40.

Anal. Cal. For $C_{27}H_{24}O_2N_2Br_2$: C 57.04, H 4.25, N 4.92; found C 56.84, H 4.51, N 5.09.

[E]-2,2'-((propane-1,3-diylbis(azanylylidene))bis(ethan-1-yl-1-ylidene)) bis(4-iodonaphthalen-1-ol) (3g)

Yield – 583.44 mg, 88%, Color - Yellow, M.P.195-197 °C.

FT-IR(KBr,cm^{-1}): 3407(νOH),1635(νC = N),1450(νC = C-),1076 (νC−N−C),790(νC-I),765(νC-I) cm^{-1}.

^{1}H NMR (400MHz,$CDCl_3$): δ 14.02 (s,2H,Ar-OH),8.45–7.26 (m,10H, Ar-H),3.81 (t,4H,J = 4.5Hz,-CH_2),2.47 (s,6H,-CH_3),2.32 (m,2H,J = 4.5Hz,-CH_2).

^{13}C NMR (300MHz,$CDCl_3$): δ 175.1(−C=N−),171.6(C−O),137.1–108.2(Ar-C-),132.1(-C-I),42.1(−N-CH_2-),29.2(HC-C-CH_2-),14.4(-N=C-CH_3).

ESIMS(m/z): 662.92.

Anal. Cal. For $C_{27}H_{24}O_2N_2I_2$: C 48.94, H 3.39, N 4.32; found C 48.72, H 3.68, N 4.56.

[E]-2,2'-((propane-1,3-diylbis(azanylylidene))bis(ethan-1-yl-1-ylidene)) bis(4-nitronaphthalen-1-ol) (3h)

Yield – 436.01 mg, 87%, Color - Green, M.P.220–222 °C.

FT-IR(KBr,): 3417(νOH),1650(νC=N),1455(νC=C-),1527(νC-NO_2), 1384(νC-NO_2),1076(νC−N−C) cm^{-1}.

^{1}H NMR (400MHz,$CDCl_3$):δ 14.02 (s,2H,Ar-OH,),8.50–6.82 (m,10H, Ar-H),3.82 (t,4H,J=4.5Hz,-CH_2),2.47 (s,6H,-CH_3),2.32 (m,2H,J=4.5Hz,-CH_2).

^{13}C NMR (300MHz,$CDCl_3$):δ 175.5(−C=N−),171.9(C–O),137.1–108.4(Ar-C-),133.6(-C-NO_2),42.1(−N-CH_2-),29.3(HC-C-CH_2-),14.6(-N=C-CH_3).

ESIMS(m/z): 500.52.

Anal. Cal. For $C_{27}H_{24}O_6N_4$: C 64.08, H 4.08, N 11.02; found C 63.83, H 4.32, N 11.53.

[E]-2,2'-((pentane-1,3-diylbis(azanylylidene))bis(ethan-1-yl-1-ylidene)) bis(4-chloronaphthalen-1-ol) (3i)

Yield- 406.52 mg, 80%, Color- yellow, M.P. 192–194 °C.

FT-IR(KBr,cm^{-1}): 3444(νOH),1640(νC = N),1452(νC=C-),1078 (νC−N−C),790(νC-Cl),769(νC-Cl) cm^{-1}.

^{1}H NMR (400MHz,$CDCl_3$): δ 14.03 (s,2H,Ar-OH),8.53–6.80 (m,10H,Ar-H),4.11 (t,2H,J=4.5Hz,-CH_2),3.70 (m,1H,J=4.6Hz,-CH),2.47 (s,3H,-CH_3),2.45 (s,3H,-CH_3),2.25 (q,2H,J=4.3Hz,-CH_2),1.86 (m,2H, J=4.1Hz,-CH_2),1.03 (t,3H,J=4.1Hz,-CH_3).

^{13}C NMR (300MHz,$CDCl_3$):δ 175.2(-C=N-),170.7(C-O),137.1–105.9(Ar-C-),135.0(-C-Cl),54.1(-N-C-H),41.7(-N-CH_2-),34.6(HC-C-CH_2-),29.4(H_3C-C-CH-),14.4(-N=C-CH_3),10.2(-C-CH_2-CH-);

ESIMS(m/z): 508.51.

Anal. Cal. For $C_{29}H_{28}O_2N_2Cl_2$: C 68.77, H 5.53, N 5.53; found C 68.60, H 5.81, N 5.72.

[E]-2,2'-((pentane-1,3-diylbis(azanylylidene))bis(ethan-1-yl-1-ylidene)) bis(4-iodonaphthalen-1-ol) (3j)

Yield – 621.92 mg, 90%, Color - yellow, M.P. 205–207 °C.

FT-IR(KBr,cm^{-1}): 3440(νOH),1647(νC=N),1457(νC=C-),1088 (νC−N–C),786(νC-I),760(νC-I)cm^{-1}.

^{1}H NMR (300 MHz,$CDCl_3$): δ 14.09 (s,2H,Ar-OH),8.50–6.79 (m,10H,Ar-H),4.09 (t,2H,J=4.5Hz,-CH_2),3.65 (m,1H,J=4.6Hz,-CH),2.46 (s,3H,-CH_3),2.35 (s,3H,-CH_3),2.24 (q,2H,J=4.3Hz,-CH_2),1.84 (m,2H, J=4.1Hz,-CH_2),1.04 (t,3H,J=4.1Hz,-CH_3).

^{13}C NMR (300MHz,$CDCl_3$):δ 175.2(-C=N-),170.6(-C-O),137.0–105.8 (Ar-C-),134.9(-C-I),54.1(-N-C-H),41.7(-N-CH_2-),34.6(HC-C-CH_2-),29.4(H_3C-C-CH-),14.4(-N=C-CH_3),10.2(-C-CH_2-CH-).

ESIMS(m/z): 691.20.

Anal. Cal. For $C_{29}H_{28}O_2N_2I_2$: C 50.43, H 4.05, N 4.05; found C 50.20, H 4.27, N 4.35.

[E]-2,2'-((pentane-1,3-diylbis(azanylylidene))bis(ethan-1-yl-1-ylidene)) bis(4-nitronaphthalen-1-ol) (3k)

Yield -428.65 mg, 81%, Color - Brown, M.P. 235–237 °C.

FT-IR (KBr, cm^{-1}): 3430(νOH),1665(νC=N),1450(νC=C-),1523(νC-NO_2),1388(νC-NO_2), 1027(νC-N-C) cm^{-1}.

^{1}H NMR (400MHz,$CDCl_3$):δ 14.01 (s,2H,Ar-OH),8.50–6.78 (m,10H, Ar-H),4.12 (t,2H,J=4.5Hz,-CH_2),3.66 (m,1H,J=4.6Hz,-CH),2.44 (s,3H,-CH_3),2.33 (s,3H,-CH_3),2.35 (q,2H,J=4.3Hz,-CH_2),1.90 (m,2H,J=4.1Hz,-CH_2),1.07 (t,3H,J=4.1Hz,-CH_3).

^{13}C NMR (300MHz,$CDCl_3$):δ 175.5(-C=N-),170.9(C-O),137.4–106.0(Ar-C-),136.2(-C-NO_2),54.3(-N-C-H),41.7(-N-CH_2-),34.7(HC-C-CH_2-),29.5(H_3C-C-CH-),14.5(-N=C-CH_3),10.2(-C-CH_2-CH-).

ESIMS (*m/z*): 528.70.

Anal. Cal. For $C_{27}H_{24}O_6N_4$ C 65.90, H 5.30, N 10.60; found C 65.72, H 5.68, N 10.96.

4. Conclusion

The current study describes the synthesis of new eleven Schiff bases having an electronegative group (-Cl, -Br, –I, and –NO_2) located at para position to the phenolic –OH group. They are confirmed by using instrumental techniques viz. FT-IR, ^{1}H NMR, ^{13}C NMR, and LCMS analysis, also evaluated biologically by antibacterial and antioxidant activities. From the FT-IR analysis, we confirm the azomethine (-C=N-) group, and the ^{1}H NMR peaks of the phenolic –OH proton are shown at δ 13.92–14.09ppm due to hydrogen bonding. The LC-MS analysis agrees with molecular ion peaks of synthesized Schiff bases. The screening data for antibacterial activity shows that electronegative-substituted Schiff bases are more potent against the tested gram-positive and gram-negative bacteria. Among these Schiff bases, compound 3i shows the best Antibacterial activity against all tested pathogens. From this, it is concluded that the influence of the –Cl group and extended carbon chain of diamines on synthesized compounds is more effective than other substituent's. The comparative determination of the total antioxidant capacity also shows the highest value for the electronegative Schiff bases with an extended carbon chain of diamines by DPPH and the hydroxyl radical scavenging method.

Declarations

Author contribution statement

Bhagwat Vhanale: Performed the experiments; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Digambar Kadam: Analyzed and interpreted the data.

Avinash Shinde: Conceived and designed the experiments.

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The authors declare no conflict of interest.

Additional information

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