Available online at www.scholarsresearchlibrary.com

Scholars Research Library

Archives of Applied Science Research, 2010, 2 (2):356-363
(http://scholarsresearchlibrary.com/archive.html)

ISSN 0975-508X
CODEN (USA) AASRC9

Synthesis and characterization of new schiff′s bases containing an azo group

V. Padmini

Department of Chemistry, Periyar Maniammai University, Tamil Nadu, India

---

Abstract

In the present study, a series of Schiff's bases: ***1a-1g****; 5-((4-n-methoxyphenyl) azo)-N-(4′-n-alkoxyphenyl)salicylaldimine homologues have been synthesized and characterized by IR, NMR spectroscopy and elemental analyses. The mesomorphic character of these compounds was mainly studied by using polarizing microscope equipped with a heating and cooling stage. These homologues series do not exhibit liquid crystalline property. Electrochemical reductions were studied by use of Cyclic-Voltammetric technique. These compounds gave one peak and are irreversible in nature in presence of Tetra butyl ammonium bromide (TBAB) as supporting electrolyte. The electrochemical reductions of imines group were found to be diffusion controlled. All compounds are showing very good anti microbiol activity.*

Keywords: Azo compounds; Schiff′s bases; Salicylaldimine; Cyclic-Voltammety, Biological activities

---

INTRODUCTION

Schiff′s bases are used extensively as ligands in coordination chemistry [1, 2]. Schiff′s bases have thermochromic properties in their solid state [3-5]. Thermochromism is due to change in л-electron configuration induced by proton transfer, which can occur in the ground state, and requires a planar molecular system. Azo benzene is one of the representative photochromic molecules with two geometric isomers, a trans form and a cis form [6, 7].

Aromatic Schiff′s bases containing a hydroxyl group in the ortho position may have two tautomeric forms, namely phenol imine and keto-imine structures [8-13]. It was revealed that while the keto-imine the existence of the tautomers has been demonstrated by X-ray crystallographic, which was the predominant form in polar solvents, the phenol-imine form was predominant in apolar solvents. There are a number of studies indicating that amines are the product of the electrochemical reduction of imines in protic solvents. There are a number of studies indicating that amines are the product of the electrochemical reduction of imines in protic solvents [14-16]. Andriex *etal* [17], in Cyclic Voltammetric study of various imines in acetonitile

and DMF media claimed that the reduction was either a two-electron transfer resulting in a saturated amine or two one electron transfer leading to a dimerised product depending upon the compound and solvents employed. They stated that reduction irreversible in both cases.

Azo compounds are important due to their applications in dyes, pigments, and functional materials. For example, azo-containing photochromic organic compounds especially with many attentions recently because of their possible applications in the area of photon-mode high density information storage, photo-switching devices and optical computing liquid crystalline character and azo-conjugated metal complexes have been attracting [18]. Because of the importance of azo-containing liquid crystalline dyes and in continuance of interest of scientist in synthesis of azo-based liquid crystalline compounds [19, 20], Schiff's base and their metal complexes have been reported to possess important biological, catalytic activity and also oxygen carriers. Schiff's base and their metal complexes have been reported to possess important biological [21-23], catalytic activity [24, 25] and also oxygen carriers [26-28]. For the purpose of antimicrobial and antifungal screening four bacterial strains and one fungus i.e., Staphylococcus aureus, Bacillus subtilis, Proteus vulgaris, Pseudomonas aruginosa and Candida albicans were chosen. *Staphylococcus aureus, Bacillus subtilis* are a gram-positive organism while *Proteus vulgaris, Pseudomonas aeruginosa* are a gram negative one. A wide range of techniques can test antimicrobial and antifungal activity of a drug or a test compound. Essentially a concentration gradient of the drug /test compound is produced in a nutrient medium and the growth or inhibition of the growth of the organism taking place when the medium is seeded with test organism and incubated is observed. Many factors such as the kind of microorganism, the physiological state of the organism, the temperature and the environment that includes the physical and chemical properties of the medium or substrate carrying the organism are important. The environmental factors must be considered in the application of any chemical agent to inhibit or destroy microbial populations. we report herein the syntheses and study the liquid crystalline character, electrochemical and biological behaviour of a series of azo-linked salicylidenic Schiff′s bases named 5-((4-n-methoxyphenyl) azo)-N-(4′-n-alkoxyphenyl)salicylaldimine (alkoxy = octyloxy, decyloxy, undecyloxy, dodecyloxy, tetradecyloxy, hexadecyloxy, octadecyloxy) homologues.

MATERIALS AND METHODS

All homologue materials were prepared similarly. The related amine (4-n-alkoxyaniline, 1 equivalent) and 1 equivalent of 5-(4-n-methoxyphenylazo) salicylaldehyde were dissolved in 20 ml absolute ethanol with a few drops of glacial acetic acid as a catalyst. The solution was then refluxed for 1 h. The solution was left at room temperature and after cooling; the compounds were obtained as yellow micro-crystals (**1a-1g**). The micro-crystals were filtered off, washed with 20ml of cold absolute ethanol and then recrystallized for several times from ethanol/chloroform.

*5-((4-n-methoxyphenyl) azo)-N-(4′-n-octyloxyphenyl)salicylaldimine***(1a)**

Yellow; Yield 80%; IR(KBr Pellet): ν_{max} in cm^{-1} 1624 and 1215; UV-VIS: λ_{max} = 346.1 nm, ε = 3.44 x 10^4 L mol^{-1} cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$), 13.99 (s, 1H), 8.76 (s, 1H), 8.01 (d, J = 2.8 Hz, 1H), 7.98 (dd, J = 2.7, 9.8 Hz, 1H),7.81 (d, J = 9.6 Hz,2 H), 7.39 (d, J = 9.7 Hz, 2H), 7.14(d, J = 8.9 Hz, 1H), 6.93 (d, J = 9.9 Hz, 2H), 6.90 (d, J = 9.8 Hz, 2H), 4.02 (t, J = 9.1 Hz, 1H), 3.95 (t, J = 8.6 Hz, 1H), 1.83-0.84 (m, 12H). IR(KBr Pellet): Elemental analysis: $C_{28}H_{33}N_3O_3$, Calculated(%).C 73.18, H 7.24, N 9.14. Found(%). C 73.18, H 7.24, O 9.14.

5-((4-n-methoxyphenyl) azo)-N-(4'-n-decyloxyphenyl)salicylaldimine **(1b)**
Yellow; Yield 87%; IR(KBr Pellet): ν_{max} in cm^{-1} 1624 and 1215; UV-VIS: λ max = 348.61nm, ε =2.38 x 10^4 L mol^{-1} cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$), 13.99 (s, 1H), 8.76 (s, 1H), 8.01 (d, J = 2.8 Hz, 1H), 7.98 (dd, J = 2.7, 9.8 Hz, 1H),7.81 (d, J = 9.6 Hz,2 H), 7.39 (d, J = 9.7 Hz, 2H), 7.14(d, J = 8.9 Hz, 1H), 6.93 (d, J = 9.9 Hz, 2H), 6.90 (d, J = 9.8 Hz, 2H), 4.02 (t, J = 9.1 Hz, 1H), 3.95 (t, J = 8.6 Hz, 1H),1.83-0.84 (m, 16H); Elemental analysis: $C_{30}H_{37}$ N_3O_3, Calculated(%).C, 73.89; H,7.65, N, 8.62; Found(%). C, 73.89; H, 7.65; N, 8.62;

*5-((4-n-methoxyphenyl) azo)-N-(4'-n-undecyloxyphenyl)salicylaldimine***(1c).**
Yellow; Yield 89%; IR(KBr Pellet): ν_{max} in cm^{-1} 1624 and 1215; UV-VIS: λ max = 348.61nm, ε =2.38 x 10^4L mol^{-1} cm^{-1} ^{1}H NMR (400 MHz, $CDCl_3$), 13.99 (s, 1H), 8.76 (s, 1H), 8.01 (d, J = 2.8 Hz, 1H), 7.98 (dd, J = 2.7, 9.8 Hz, 1H),7.81 (d, J = 9.6 Hz,2 H), 7.39 (d, J = 9.7 Hz, 2H), 7.14(d, J = 8.9 Hz, 1H), 6.93 (d, J = 9.9 Hz, 2H), 6.90 (d, J = 9.8 Hz, 2H), 4.02 (t, J = 9.1 Hz, 1H), 3.95 (t, J = 8.6 Hz, 1H), 1.83-0.84(m, 18H); Elemental analysis: $C_{31}H_{39}$ N_3 O_3, Calculated(%). C, 74.22; H, 7.84; N,9.57; Found (%): C, 74.22; H, 7.84; N, 9.57;

5-((4-n-methoxyphenyl) azo)-N-(4'-n-dodecyloxyphenyl)salicylaldimine **(1d)**
Yellow; Yield 88%; IR(KBr Pellet): ν_{ax} in cm^{-1} 1624 and 1215; UV-VIS: λ max = 348.78 nm, ε = 2.59 x 10^4L mol^{-1} cm^{-1} ^{1}H NMR (400 MHz, $CDCl_3$), 13.99 (s, 1H), 8.76 (s, 1H), 8.01 (d, J = 2.8 Hz, 1H), 7.98 (dd, J = 2.7, 9.8 Hz, 1H),7.81 (d, J = 9.6 Hz,2 H), 7.39 (d, J = 9.7 Hz, 2H), 7.14(d, J = 8.9 Hz, 1H), 6.93 (d, J = 9.9 Hz, 2H), 6.90 (d, J = 9.8 Hz, 2H), 4.02 (t, J = 9.1 Hz, 1H), 3.95 (t, J = 8.6 Hz, 1H), 1.83-0.84(m, 20H); Elemental analysis: $C_{32}H_{41}$ N_3 O_3, Calculated(%). C 74.53, H 8.01, N 9.37. Found(%). C 74.53, H 8.01, N 9.37.

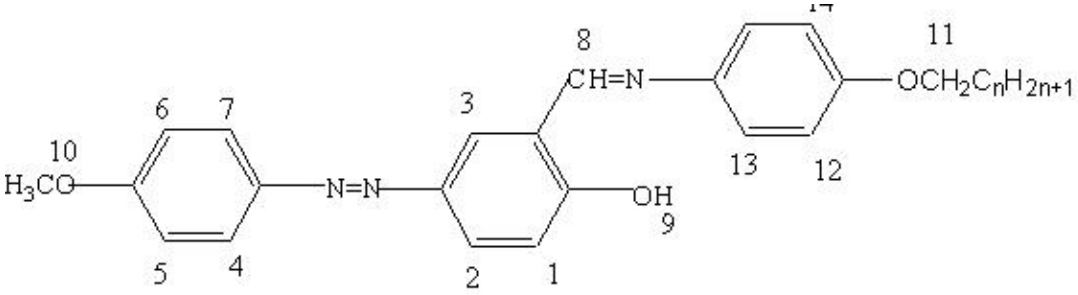
5-((4-n-methoxyphenyl) azo)-N-(4'-n- tetradecyloxyphenyl)salicylaldimine **(1e)**
Yellow; Yield 90%; IR(KBr Pellet): ν_{ax} in cm^{-1} 1624 and 1215; UV-VIS: λ max=348.31nm, ε =2.35 x 10^4 L mol^{-1} cm^{-1} ^{1}H NMR (400 MHz, $CDCl_3$), 13.99 (s, 1H), 8.76 (s, 1H), 8.01 (d, J = 2.8 Hz, 1H), 7.98 (dd, J = 2.7, 9.8 Hz, 1H),7.81 (d, J = 9.6 Hz,2 H), 7.39 (d, J = 9.7 Hz, 2H), 7.14(d, J = 8.9 Hz, 1H), 6.93 (d, J = 9.9 Hz, 2H), 6.90 (d, J = 9.8 Hz, 2H), 4.02 (t, J= 9.1 Hz, 1H), 3.95 (t, J= 8.6 Hz, 1H), 1.83-0.84(m, 14H); Elemental analysis: $C_{34}H_{45}N_3O_3$, Calculated(%).C 75.10, H 8.34, N 7.73. Found(%). C 75.10, H 8.34, N 7.73.

5-((4-n-methoxyphenyl) azo)-N-(4'-n-hexadecyloxyphenyl)salicylaldimine **(1f)**
Yellow; Yield 87%; IR(KBr Pellet): ν_{max} in cm^{-1} 1624 and 1215; UV-VIS: λ max=348.3nm, ε =2.32X10^4 L mol^{-1} cm^{-1} ; ^{1}H NMR (400 MHz, $CDCl_3$), 13.99 (s, 1H), 8.76 (s, 1H), 8.01 (d, J= 2.8 Hz, 1H), 7.98 (dd, J= 2.7, 9.8 Hz, 1H),7.81 (d, J= 9.6 Hz,2 H), 7.39 (d, J= 9.7 Hz, 2H), 7.14(d, J= 8.9 Hz, 1H), 6.93 (d, J= 9.9 Hz, 2H), 6.90 (d, J= 9.8 Hz, 2H), 4.02 (t, J= 9.1 Hz, 1H), 3.95 (t, J= 8.6 Hz, 1H), 11.83-0.84(m, 28H). Elemental analysis: $C_{36}H_{49}N_3O_3$, Calculated(%). C 75.62, H 8.64, N 7.35. Found(%). C 75.62, H 8.64, N 7.35

5-((4-n-methoxyphenyl) azo)-N-(4'-n-octadecyloxyphenyl)salicylaldimine **(1g)**
Yellow; Yield 80%; IR(KBr Pellet): ν_{max} in cm^{-1} 1625 and 1215; UV-VIS: λ max = 348.56nm, ε =2.47 x 10^4 L mol^{-1} cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$), 13.99 (s, 1H), 8.76 (s, 1H), 8.01 (d, J= 2.8 Hz, 1H), 7.98 (dd, J= 2.7, 9.8 Hz, 1H),7.81 (d, J= 9.6 Hz,2 H), 7.39 (d, J= 9.7 Hz, 2H), 7.14(d, J= 8.9 Hz, 1H), 6.93 (d, J= 9.9 Hz, 2H), 6.90 (d, J= 9.8 Hz, 2H), 4.02 (t, J= 9.1 Hz, 1H), 3.95 (t, J= 8.6 Hz, 1H), 1.83-0.84(m, 32H); Elemental analysis: $C_{38}H_{53}$ N_3O_3, Calculated(%). C 76.09, H 8.91, N 7.01. Found(%). C 76.09, H 8.91, N 7.01.

Schiff base dyes **1a-1g**, were synthesized in a four step process, in which the hydroxyl group in 4-acetamidophenol is first replaced by an alkoxy chain followed by hydrolysis of acetamido

group to amine. In the third step, salicylaldehyde coupled with the diazonium chloride obtained from the 4-n-alkoxyaniline (n-alkoxy = Octyloxy, Undecyloxy, Decyloxy, Dodecyloxy, Tetradecyloxy, Hexadecyoxy, Octadecyloxy) and finally the Schiff base dyes were obtained by reaction of 5-(4-n-methoxy phenylazo) salicylaldehyde **1** with an appropriate aromatic amine (**Scheme 1**) by refluxing in absolute ethanol using a few drops of acetic acid as catalyst. The Schiff's bases, **1a-1g**, were purified by repeated recrystallisation in the ethanol/chloroform mixture.



1a-1g

Compound no	n
1a	7
1b	9
1c	10
1d	11
1e	13
1f	15
1g	17

Scheme 1

The 5-(4-n-methoxyphenylazo) salicylaldehyde **1** and Schiff's bases dyes, **1a-1g**, were characterized by ^{1}H NMR, IR, UV and elemental analyses. The IR spectral frequencies of synthesized compounds, **1a-1g**, were carried out using KBr pellets as described in experimental section. In the compound 1, the hydroxyl group was observed at 3210 cm^{-1} because the intramolecular hydrogen bonding between OH and formyl group in compound **1** leads to decrease in the stretching frequency of OH. In the compounds **1a-1g**, the OH group was found at 3420-3450 cm^{-1} because of the poor intramolecular hydrogen bonding between OH and C=N. The carbonyl group in the compound **1** was formed at 1666 cm^{-1}, but in the compounds **1a-1g** the C=O stretching disappeared and a sharp strong peak at 1619-1925 cm^{-1} due to C=N was appeared. Physical and characterization data for compounds **1** and **1a-1g** are given in experimental section and some selected IR data are given in **Table 1**.

Table 1. Antimicrobial Activity of compounds against *S.aureus, B.subtilis, P.vulgaris, P.aeruginosa and C.albicans* (Zone of inhibition in mm)

Compound	*S.aureus*	*B.subtilis*	*P.vulgaris*	*P.aeruginosa*	*C.albicans*
1a	13	15	16	15	14
1b	14	12	12	10	15
1c	16	15	15	15	15
1d	12	14	15	13	14
1e	12	12	12	12	13
1f	9	9	8	11	10
1g	10	13	13	12	13
Standard	30	30	30	30	30

RESULTS AND DISCUSSION

The mesomorphic properties of 5-(4-n-methoxyphenylazo) salicylaldehyde **1** and azo Schiff′s bases; **1a-1g** have been studied by polarizing optical microscopy observations using a heating-cooling stage. 5-(4-n-methoxyphenylazo) salicylaldehyde **1** and Schiff′s bases **1a-1g**; did not show any liquid crystalline character on heating or cooling stage. In the heating cycle, the compounds show a crystal-to-crystal transition and then clearly melted to isotropic liquid as seen the polarizing microscope. Under examination by polarizing microscopy in the cooling scan the compounds **1** and **1a-1g** were found to crystallize directly from isotropic liquid. On the basis of the literature data we propose that this behaviour results from the transoid N, N′ conformation of Schiff′s bases ligands which stabilizes a stepped molecular geometry that prevents mesomorphism [21]. This behaviour is similar to that of the tetradentate Schiff base ligands N, N′-bis [5-(4′-n-alkoxy-5′fluoro) salicylidene] ethylenedimines reported by Iolinda asello and co-workers [21].

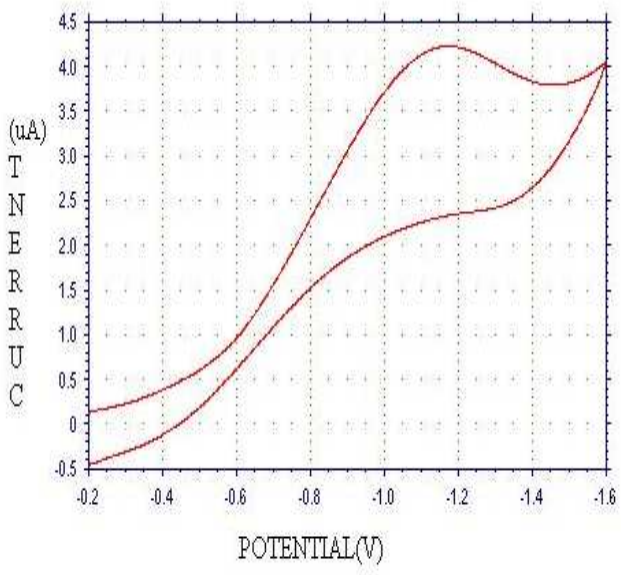
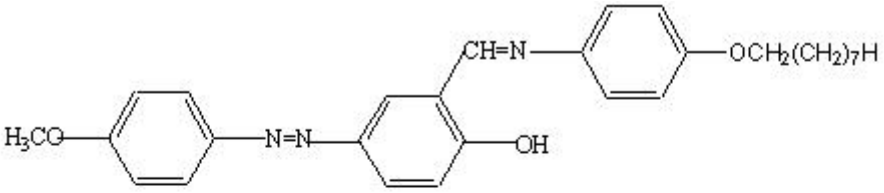


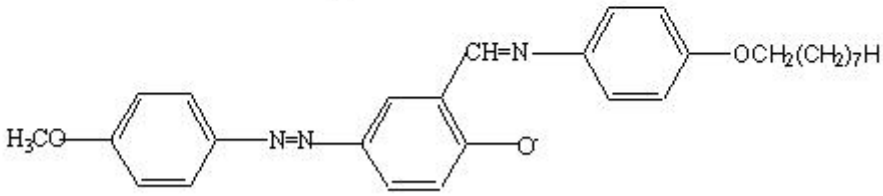
Figure 1. Cyclic Voltammogram of 1d at C=0.003M, scan rate=0.1V\s and pH=6.5

All the synthesized Schiff′s bases **1a-1g;** exhibits in fact only one irreversible cathodic peak with Ep = -1.00 to 1.30 V at ν = 0.1 V/s and C = 0.003 M as shown in **Table 1** and **Figure1**. The

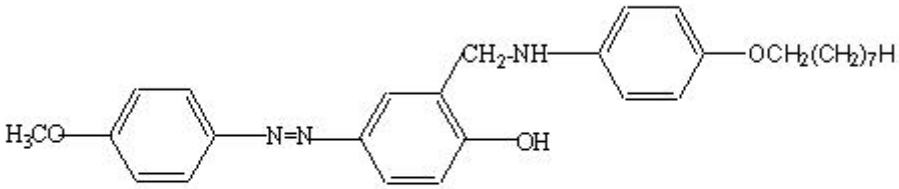
current function, Ip/√ν is independent of the scan rate. It confirms the diffusion-controlled nature of the electrochemical reduction of **1a-1g**. In the presence of acetic acid pre-peak appeared which is more positive than the main reduction potential. The appearance of a prepared in the presence of acetic acid may also relate to its basic properties. In the presence of acetic acid protonation of the imine may take place to give an iminium ion, the reduction of which is expected to be more positive than that of the starting imine. The observed pre-peak may be attributed to the reduction of the iminum ion. The addition of 1 equivalent Bu_4NOH the original peaks move towards more –ive potential side. This peak is to be attributed to the reduction of the monodissociated conjugated base. Addition of a further equivalent of base eliminates this peak. The reduction mechanism of **1a** is given in **Scheme 2**. The same is applicable to other Schiff bases.



1a



1a$^-$



1a 2H

2 **1a**+e$^-$ ⟶ **1a** 2H + **1a**$^-$

Scheme 2

The antimicrobial activity of synthesized compounds namely **1a-1g** is given in the **table 1.** It shows most of the synthesized compounds were found to be good antibacterial and antifungal agents due to aromaticity and conjugation of molecules. It shows most of the synthesized compounds were found to be good antibacterial and antifungal agents due to aromaticity and conjugation of molecules. The activity of synthesized compounds compared with standard was shown in **figure 2** and **table 1.**

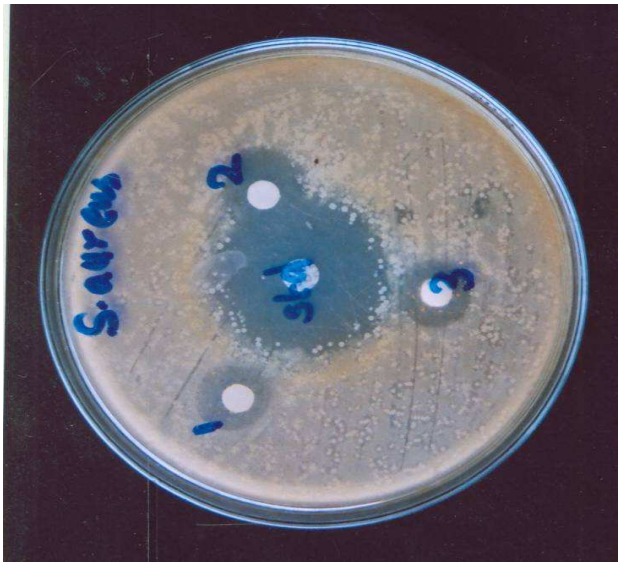


Fig.2 Anticrobial activity of synthesized compounds (1,2 and 3) against S. aureus

CONCLUSION

We have synthesized a series of 5-((4-n-methoxyphenyl)azo)-N-(4-n-alkoxyphenyl) salicylaldimine derived from 5-(4-n-methoxyphenylazo) salicylaldehyde **1** and 4-n-alkoxyanilines. All the synthesized compounds were characterized by IR NMR, Differential scanning calorimetry, Polarising microscopy and Cyclic-Voltammetry. All these Schiff′s bases did not show any liquid crystalline phases except crystal-crystal transition. The Schiff′s bases **1a-1g** were electrochemically active and gave one irreversible cathodic peak and found to be diffusion-controlled .It is observed that alky chain with lower homologues facilitates the reduction process when compared to higher homologues. All synthesized compounds are showing good antimicrobial activity.

REFERENCES

[1] Unver. H.;.Zengin. D.M.; Durlu.T.N. *Anal.Sci*. **2001**, 17, 102.
[2] Unver. H.; Zengin. D.M; Given. K. *J.Chem.Crystallography*. **2000**, 30, 359.
[3] Cochen. M.D.; Scmidt. G.M.; Flavan S.J.; *J.Chem.Soc.B*. **1964**, 16, 2041.
[4] Hadjoudis. E.; Vitterakis. M.; Maustakali-Marridis. T.; *Tetrahedran*. **1987**, 43, 1345.
[5] Kletskii. M.E.;Millov. A.A.;Metlitsa. A.V.; .Knyazhansky. M.I.; *J.Photochem. Photobiol. A.Chem.*, **1997**, 110, 267.
[6] Chen. D.;E.Martel. A.; *Inorg.Chem*. **1987**, 26,1026.
[7] Hamilton. D.E.; Dragu. R.S.;Zonbeck. A.; *J.Amer.Chem.Soc*. **1987**, 109, 374.
[8] Herfelda. R; Nagy. P.; *Curr.Org.Chem*. **2001**, 5, 373.
[9] Gavranic. M.; Kaitner. B.; Mestrovic. E.; *J.Chem.Crys*, **1996**, 26, 23.
[10] Kaitner. B.; .Pavlonic. R.H.; *Acta.Cryst.C*. **1996**, 52, 2573.
[11] Dudek. G.; Holm. R.H,; *J.Amer.Chem.Soc*. **1964**, 1 86, 4283.
[12] Salman .S.R, Shawkat. S.H.;.AL-Obaidi. G.M.; *Can.J.Spectrosc*. **1990**, 35, 27.
[13] Salman S.R.;Farrant R.D., Lindan. J.C.; *Spectrosc.Lett*., **1994**, 24, 1071.
[14] Lund. H.; *Acta.Chem.Sci*, **1959,** 13, 246.
[15] Paspalaev. E.; Wolva. A.P.; Acad. C.R.; *Bulg.Sci*. **1965**, 18, 533.
[16] Dmitrieva. V.N.; Kononenko. L.V.V.D.Beuglyi, *Thor.Eksp.Khim*. **1965**, 1, 456.
[17] Andreiex C.P.; Saveant. J.M.; *Electroanal.Chem*. **1971**, 33, 453.

[18] Murata. M.; Aoki. M.; Nishi. T.;.Ikeda. A.; Shinkai .S. *Chem.Commun*, **1715**, 4, 544.
[19] Huge T.; Holland. N.B.; Cattani. A.; Moroder. L.; Seitz.; Gaub H.E.; *Science*. **2002**, 286, 1103.
[20] D.Demus, H.Demus and H.Zaschke, *Flussige Kristalle in Tabellen* **1974**.
[21] Aello. I.;.Ghedini. M; Neve. F.; Pucci. *Chem.Mater*., **1997**, 9, 733.
[22] Mishra. L.; Sharma. R.C.; Parashar. R.K.; Polish *J.Chem.* **1992**, 66, 929.
[23] Mishra. L.; Jha. A.; Yadv. A.K.; *Trans. Met. Chem.* **1997**, 22,929.
[24] Parashar.R.K, Sharma. R.C.; Kumar. A.; Mohan. G.; *Inorg Chim. Acta.***1988**, 151, 201.
[25] EL.Hendawy.A.M.; Albubaisi. H.; Kourashy. A.; Shanab. M.; *Polyhedron*, **1993**, 12, 2343.
[26] Bhowon M.G.; Li Kam Wah.; Narayan. R.; Polyhedron, **1998,** 18,3 41.
[27] Niswander R.H.;Martell. A.E .; *Inorg Chem*. **1978**, 17, 2341.
[28] Padmin tamilenthi.V, *Archives of Applied Science Research*, **2010**, 2 (1) 57-65.