

Vol 6 Issue 4 Jan 2017

ISSN No : 2249-894X

---

*Monthly Multidisciplinary  
Research Journal*

*Review Of  
Research Journal*

Chief Editors

---

**Ashok Yakkaldevi**  
A R Burla College, India

**Ecaterina Patrascu**  
Spiru Haret University, Bucharest

**Kamani Perera**  
Regional Centre For Strategic Studies,  
Sri Lanka

Review Of Research Journal is a multidisciplinary research journal, published monthly in English, Hindi & Marathi Language. All research papers submitted to the journal will be double - blind peer reviewed referred by members of the editorial Board readers will include investigator in universities, research institutes government and industry with research interest in the general subjects.

**Regional Editor**

Dr. T. Manichander

*Advisory Board*

Kamani Perera Regional Centre For Strategic Studies, Sri Lanka	Delia Serbescu Spiru Haret University, Bucharest, Romania	Mabel Miao Center for China and Globalization, China
Ecaterina Patrascu Spiru Haret University, Bucharest	Xiaohua Yang University of San Francisco, San Francisco	Ruth Wolf University Walla, Israel
Fabricio Moraes de Almeida Federal University of Rondonia, Brazil	Karina Xavier Massachusetts Institute of Technology (MIT), USA	Jie Hao University of Sydney, Australia
Anna Maria Constantinovici AL. I. Cuza University, Romania	May Hongmei Gao Kennesaw State University, USA	Pei-Shan Kao Andrea University of Essex, United Kingdom
Romona Mihaila Spiru Haret University, Romania	Marc Fetscherin Rollins College, USA	Loredana Bosca Spiru Haret University, Romania
	Liu Chen Beijing Foreign Studies University, China	Ilie Pinteau Spiru Haret University, Romania
Mahdi Moharrampour Islamic Azad University buinzahra Branch, Qazvin, Iran	Nimita Khanna Director, Isara Institute of Management, New Delhi	Govind P. Shinde Bharati Vidyapeeth School of Distance Education Center, Navi Mumbai
Titus Pop PhD, Partium Christian University, Oradea, Romania	Salve R. N. Department of Sociology, Shivaji University, Kolhapur	Sonal Singh Vikram University, Ujjain
J. K. VIJAYAKUMAR King Abdullah University of Science & Technology, Saudi Arabia.	P. Malyadri Government Degree College, Tandur, A.P.	Jayashree Patil-Dake MBA Department of Badruka College Commerce and Arts Post Graduate Centre (BCCAPGC), Kachiguda, Hyderabad
George - Calin SERITAN Postdoctoral Researcher Faculty of Philosophy and Socio-Political Sciences Al. I. Cuza University, Iasi	S. D. Sindkhedkar PSGVP Mandal's Arts, Science and Commerce College, Shahada [ M.S. ]	Maj. Dr. S. Bakhtiar Choudhary Director, Hyderabad AP India.
REZA KAFIPOUR Shiraz University of Medical Sciences Shiraz, Iran	Anurag Misra DBS College, Kanpur	AR. SARAVANAKUMAR LAGAPPA UNIVERSITY, KARAIKUDI, TN
Rajendra Shendge Director, B.C.U.D. Solapur University, Solapur	C. D. Balaji Panimalar Engineering College, Chennai	V. MAHALAKSHMI Dean, Panimalar Engineering College
Awadhesh Kumar Shirotriya	Bhavana vivek patole PhD, Elphinstone college mumbai-32	S. KANNAN Ph.D , Annamalai University
	Awadhesh Kumar Shirotriya Secretary, Play India Play (Trust), Meerut (U.P.)	Kanwar Dinesh Singh Dept. English, Government Postgraduate College , solan

More.....



## SYNTHESIS AND CHARACTERISATION OF NOVEL POLYBENZIMIDAZOLES CONTAINING TETRA-PHENYLTHIOPHENE GROUPS

P. H. Basutkar

Department of Chemistry , D. B. F. Dayanand College of Arts & Science, Solapur (Maharashtra State). India.

### ABSTRACT:

The preparation of a novel aromatic tetraamine monomer 2,5-bis-(3,4-diaminophenyl)-3,4-diphenyl thiophene (X), its characterisation and the solution polycondensation of (X) tetrahydrochloride with aromatic dicarboxylic acid in polyphosphoric acid co give high molecular weight polybenzimidazoles (PBI) are described. Physical characteristics, such IR, solutions viscosity, solubility and thermal properties of a series of new aromatic co-PBI containing tetraphenylthiophene units are studied.

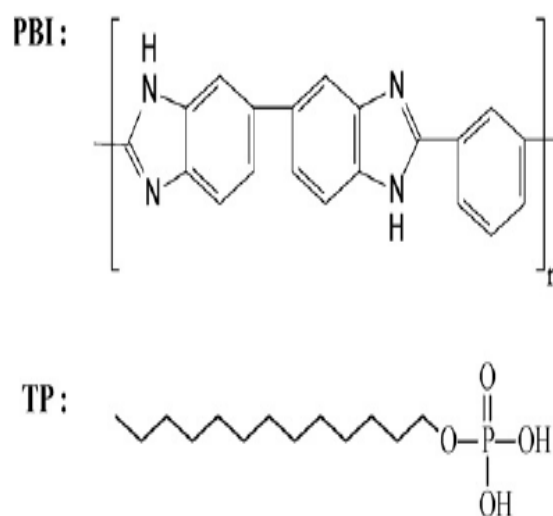
**KEYWORDS:** novel aromatic tetraamine , high molecular , solutions viscosity, solubility.

### INTRODUCTION:

Aromatic polybenzimidazoles (PBI) are known for their excellent high thermo-oxidative stability mechanical and adhesive properties. Melt condensation (1) of suitable aromatic tetramines, such as 3,3-diaminobenzidine (DAB) (I) with the diphenylesters of aromatic dicarboxylic acids or

derivatives (II) thereof produced linear, high molecular weight polybenzimidazoles. Imai et al. (2) reported solution polymerization of DAB. 4 HCl in polyphosphoric acid with aromatic. The aromatic polybenzimidazoles have remarkable thermal stability but they dissolved only in solvents such as concentrated sulfuric acid. The disiloxanebenzimidazole and aliphatic moiety containing polymers reported by Mulvaney and Marvel (3) were soluble in a rather wide range of solvents including sulfuric acid, formic acid, dimethylformamide, dimethylsulfoxide and ethanol, however polymers melted at 215-220°C and had an inherent viscosity of 0.12 dL/g in ethanol. Srinivasan et al. (4) investigated polybenzimidazoles containing cardo groups which dissolved in dimethyl, formamide and chlorinated solvents like tetrachloroethane. Solution polymerisation technique was reported by Ueda et al. to yield high molecular weight PBI utilising P<sub>2</sub>O<sub>5</sub> alongwith methanesulfonic acid (5)

We have reported the synthesis of modified polyamide, polyimide (6,7) by introducing phenyl or bulky groups (8) as the side chain/substituent to improve the solubility and processability with some success, thereby polymers dissolved in wide range of the organic solvents. However, there is no report on the synthesis of polybenzimidazole containing pendant phenyl group. We now report the synthesis of new aromatic tetraamine 2,5-



bis – (3,4- diaminophenyl) -3, 4 diphenylthiophene (X) from benzyl chloride. Further we describe the characterization of (VII-IX) intermediates and tetramine (X) and polycondensation of (X) tetrahydrochloride, in combination with DAB.4HCl, with aromatic diacid viz. isophthalic acid to synthesize novel copolybenzimidazoles containing tetraphenylthiophene units in main polymer chain providing phenyl groups as pendant substituents. These polybenzimidazoles were characterized by solution viscosity, IR spectroscopy, and other properties to investigate the structure property relationships with a view to study the improvement in solubility of polymers in organic solvents. Model compounds of X and XI with monobasic acids are also reported.

#### EXPERIMENTAL:

**Monomers:** 3, 3'- Diaminobenzidine tetrahydrochloride (DAB.4 HCL): DAB tetrahydrochloride dihydrate was prepared starting from benzidine in four steps (1). Phenylated tetramine (X) was synthesised as described below.

a) 2,5-bis-4-aminophenyl-3,4-diphenylthiophene (VI) : compound (VI) was obtained as per procedure in literature (6).

b) 2,5-bis-(4-aminoacetyl phenyl)-3,4-diphenylthiophene (VIII) : In a 500mL flask were placed 24.418 g (0.06081 mol) of VI and 210mL of glacial acetic acid. 15.2mL. (0.147 mol) of acetic anhydride was added maintaining temperature at 50-60°C over a period of 1.5 h and stirred at 100°C for 1.5 h. The solid was filtered recrystallised from glacial acetic acid.

c) 2, 5-bis- (3-nitro, 4-amino acetyl phenyl)-3, 4-diphenylthiophene (VIII): in a 500mL flask 14.73 g (0.249 mol) of compound (VII), 12 mL glacial acetic acid, 15.63mL of distilled water and 1.1mL of acetic anhydride were added. 5.58mL concentrated nitric acid (63% HNO<sub>3</sub>, d. 1.42) was added and stirred for 10 minutes at 45°C and 10 minutes at 75°C. bright yellow solid was filtered, washed with cold glacial acetic acid and dried. Yield 7.4 g (50%) M.P. 2140C, NMR H-1 10.5 (s, 1H, exchange with D<sub>2</sub>O) 6.7-8.7 (m, Aromatic 8H), 2.2 (s, CH<sub>3</sub>)

IR: 3340 cm (-NH), 1700 cm (c=O), 1540, 1350 cm (-NO<sub>2</sub>) Mass: (m/e) 592 M

d) 2, 5-bis-(3-Nitro, 4-aminophenyl)-3,4- diphenylthiophene (IX) : 7.41g (0.0125 mol) of VIII, 50mL methyl alcohol, 1.25 g of solid potassium hydroxide stirred for 1 h. after one hour additional 1 g of potassium hydroxide was added and stirring continued for 16 h. the volatile solvent was removed and the solid was treated with water, filtered, washed with distilled water and dried, yield 6.2 g (97.6%) M.P. 220-222°C, IR 3520-3480, 3300-3260 (NH<sub>2</sub>), 1420 and 1350 cm (No<sub>2</sub> Mass: (m/e) 508 (M), NMR H1 : (6) 8.0 (d, 1H) 7.2-6.7 (m, 6H), 6.5 (d, 2H), 5.95 (s, NH<sub>2</sub>, 2H)

e) 2, 5-bis-(3,4-diaminophenyl)-3, 4-diphenylthiophene (X): in a 250mL flask was placed solution of 68.7 g of stannous chloride dehydrate (0.3045 mol) dissolved in 143mL concentrated hydrochloride acid and 11.45 g (0.225 mol) of (IX) were added, and heated at 75-80°C for 15 h. The reaction mixture was cooled to 25°C and poured into water. (X) hydrochloride was insoluble in water. The product was filtered, washed with cold water and dried under vacuum to yield (XI) in almost quantitative yields, compound (X) was obtained by adding sodium hydroxide solution to (XI) and extracting the liberated tetramine (X) with dichloromethane, and removing a solvent under nitrogen to produce (X), M.P. 250°C IR (Nujol) 3400, 3370, 3350, 3220 cm (NH<sub>2</sub>), NMR C-13, (d DMSO) 138.24, 137.60, 137.47, 135.03, 130.99, 128.00 126.64, 123.11, 118.77, 115.40, 114.43, 114.04. Mass: (m/e) 448 (M+)

**Model Compounds:** Two Model compounds [MC-1 and MC-2) were prepared from (X) and (XII) by reacting with formic acid and benzoic acid, respectively.

**Polymerisation:** One typical example of polymerisation follows. In a 100mL flask 28.5 g of PPA (116%) was prepared. To this 1 g (0.002525 mol) of DAB. 4 HCL was added and stirred at 140°C under nitrogen to effect the dehydrochlorination. Isophthalic acid 0.419 g (0.002525 mol) was added and the mixture was stirred 6 h at 100°C, 18 h at 140°C and at 240°C/4 h. Viscous mass was poured in about 200mL distilled water and methyl alcohol. The product was dried under vacuum. at 100°C for 6 h. Yield 0.771 g (91%).  $\eta_{inh} = 0.77$  dL/g.

Similarly other polymers reported in table I was prepared.

**Measurements:** The IR spectra were recorded on Perkin-Elmer 883 spectrophotometer. The <sup>1</sup>H NMR and C-13 spectra were recorded on a Varian FT-80A instrument. The viscosity measurements were made in Formic acid/concentrated sulfuric acid at 30°C using an Ubbelohle viscometer at 0.2% polymer concentration. The

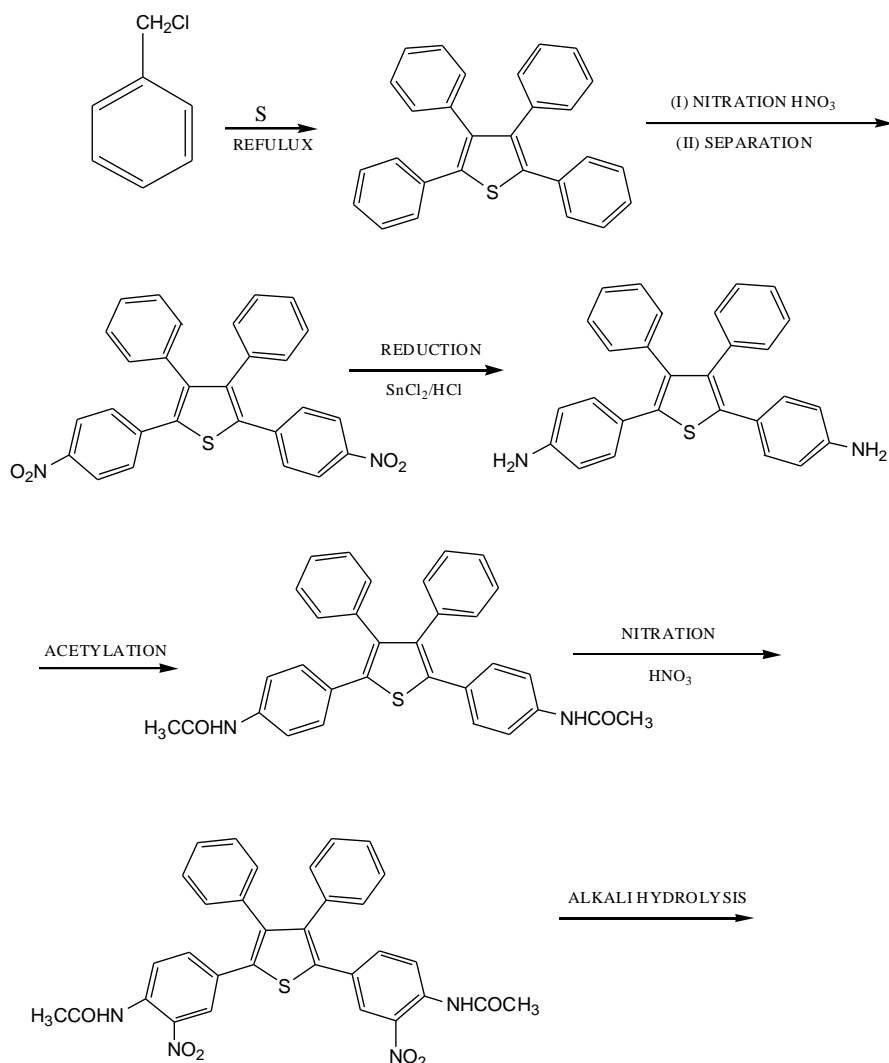
thermogravimetric analysis and differential scanning calorimetry were made with Rigaku TG-DSC thermal analyser. The mass spectra were run on A-IMS-30 double beam mass spectrometer.

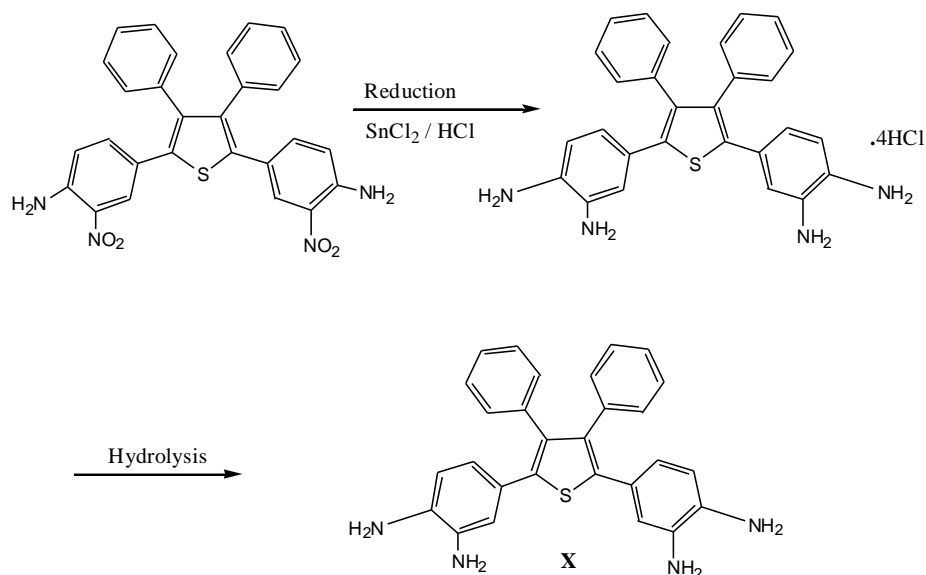
## RESULTS AND DISCUSSION

Synthesis of tetramine X: The methodology adopted to synthesise (X) is shown in scheme-1. Diamine (VI) was obtained as described previously (6). Acetylation of (VI) with acetic anhydride afforded diacetyl compound (VII) which was purified by recrystallisation from glacial acetic acid. Nitration of (VII) gave (VIII) and other isomers. The desired dinitro compound (VIII) was separated and purified by washings with cold acetic acid and then methanol. Alkali hydrolysis of (VIII) at ambient- temperature gave orange red (IX) in stannous chloride and hydrochloric acid to give amine, hydrochloride (XI) which was purified by washing with cold concentrated hydrochloric acid, The overall yield of (XI) starting from (VI) was 41.7%. (XI) on treatment with dichloromethane and evaporation of solvent gave (X). All these manipulations were performed using oxygen free solutions and in inert atmosphere.

All intermediates (VII-IX) and (X) were single spot on TLC, had sharp mps and showed characteristics absorptions in the IR spectra, and  $^1\text{H}$  NMR signals. C-13 NMR of (X) and mass spectra of (VII-X) agreed well with theoretically predicted values.

Scheme 1: Synthesis of tetramine (X)





**Model Compounds:** The synthesis of PBI by the reaction of X or XI with diacid has not been reported so far. Therefore we first studied the reaction of X/XI with formic acid / benzoic acid respectively, to determine if the method gave the desired model compound. These preliminary experiments revealed that condensation was complete to give imidazole as evidenced by IR spectra.

**Polymer Synthesis:** Aromatic polybenzimidazoles were synthesised by polycondensation of XI and DAB.4 HCl with IPA using solution polymerization in polyphosphoric acid as in 3 schene-2. The results of the preparation of aromatic co-PBI series are summarized in Table-I. These polymers were obtained in (72-100%) yields with inherent viscosities of 0.22-0.77 dL/g which imply the formation of high molecular weight polymers. It was observed that the polymerisation of DAB.4 HCL with IPA in polyphosphoric acid proceeded in about 0.77 dL/g, while copolymerisation with XI led to the polymer precipitation on therefore somewhat lower inherent viscosities obtained for these PBI-II to IV. Polymerization involved formation of polyamide-amine and subsequent cyclodehydration by polyphosphoric acid ( $\text{P}_2\text{O}_5$ ) when heated at  $140^\circ\text{C}$  and finally  $200^\circ\text{C}$  under nitrogen; thereby the polyamide-amines formed initially were converted to the corresponding PBI.

TABLE I: Synthesis of Copolybenzimidazoles

Tetramine hydrochloride		Polymer		
DAB: 4 HCL (mol %)	XI	Code	Yield%	$\eta_{inh}$ (dL/g)
100	--	I	91	0.77
75	25	II	72	0.50 c
50	50	III	99.8	0.30 c
25	75	IV	74	0.22 c

(a) For Polymer I, condensation at  $200^\circ\text{C}/24$  h. (b) Measured at a concentration of 0.2 g/dL in concentrated sulfuric acid at  $30^\circ\text{C}$  (c) in formic acid (90%). The structure of the PBI thus formed was confirmed by characteristic absorptions in the IR spectra. Thus the IR spectra of PBI-I showed, characteristic absorption at 3250-2750  $\text{cm}^{-1}$  (imidazole), 1595  $\text{cm}^{-1}$  aromatic  $\text{C}=\text{C}$ , where as copolybenzimidazoles containing tetraphenylthiophene in addition to above absorptions show 1380  $\text{cm}^{-1}$  absorption IR absorptions are similar to those for model compound-2 obtained from XI and benzoic acid. There is also complete disappearance of absorptions due to acid ( $\text{C}=\text{O}$ ) and amine ( $\text{NH}$ ) functional groups of monomers, suggesting that high molecular weight polymers were produced. Polybenzimidazole I from DAB. 4 HCl dissolved in concentrated sulphuric acid, NMP and DMAC at room temperature. It is soluble in formic acid on heating, however did not dissolve in m-cresol or DMSO4.

Copolybenzimidazole II-IV dissolved readily soluble in amide solvents such as NMP, DMSO4 and DMAC. They also dissolved readily in formic acid. The solubility of copolybenzimidazole II-IV may be attributed to the non linear chain, the distortion of the phenyl groups in the tetraphenylthiophene unit and copolymerisation technique. All the polymers are insoluble in benzene, acetone, methanol and water. PBI (II-IV) gave red color solutions in concentrated sulfuric acid. It is interesting to note that as percentage of X units increased in PBI, solubility increased relatively for polymers II to IV. Thermal behavior of the polymers evaluated by means of TGA will be discussed to illustrate remarkable thermal stability of these PBI. The further work is aimed at utilizing these new polybenzimidazoles in making membranes or hollow filmforming used for R.O. sea water desalination and for gas separations.

**CONCLUSIONS:** The main outcome of the present study can be summarized as given below

1) Novel Polyfunctional monomer aromatic tetramine, 2, 5-bis- (3,4-diaminophenyl) -3, 4-diphenylthiophene, has been synthesized and utilized as co monomer to obtain fully aromatic PBI. 2) We have obtained new types of soluble high temperature polybenzimidazoles by the introduction of bulky pendant phenyl groups along the polymer backbone. 3) The solubility properties of the co-PBI can be explained by the characteristics pendant phenyl groups. 4) Some of these aromatic polybenzimidazole are promising candidates for soluble, high temperature engineering plastic materials that can find many useful high performance applications and as reverse osmosis membranes.

#### ACKNOWLEDGEMENT

This work was partly funded by Department of Atomic Energy (BRNS) Bombay through grants No. 37/15/92-G

#### REFERENCES

- 1) Vogel H and Marvel C S (1961) J. Polym. Sci. L 511; (1963) J. Polym. Sci. (part A) 1, 1531; (1964) 1, 2559.
- 2) Iwamura Y, Uno K and Imai Y (1964) J. Polym. Sci. (Part-A), 2, 2605.
- 3) Mulvaney J E and Marvel C S (1961) J. Polym. Sci. 1, 541.
- 4) Srinivasan P R Mahadevan V and Srinivasan M (1982) J. Polym. Sci. (Polym. Chem. Ed.) 20, 3095.
- 5) Ueda M Sato M and Mochizuki A (1985) Macromolecules, 18, 2723.
- 6) Imai Y Maldar N N and Kakimoto M (1984) J. Polym. Sci. (Polym. Chem. Ed.) 22, 2189.
- 7) Imai Y Maldar N N Kakimoto M (1985) J. Polym. Sci. (Polym. Chem. Ed.) 23, 1797, Mohite S S, Maldar N N and Marvel C S (1988) *ibid* 26, 2777.
- 8) Jadhav A S, Vernekar S P and Maldar N N (1993) Polym. Internat. 32, 5.

# Publish Research Article

## International Level Multidisciplinary Research Journal For All Subjects

Dear Sir/Mam,

We invite unpublished Research Paper, Summary of Research Project, Theses, Books and Books Review for publication, you will be pleased to know that our journals are

### Associated and Indexed, India

- ★ Directory Of Research Journal Indexing
- ★ International Scientific Journal Consortium Scientific
- ★ OPEN J-GATE

### Associated and Indexed, USA

- DOAJ
- EBSCO
- Crossref DOI
- Index Copernicus
- Publication Index
- Academic Journal Database
- Contemporary Research Index
- Academic Paper Database
- Digital Journals Database
- Current Index to Scholarly Journals
- Elite Scientific Journal Archive
- Directory Of Academic Resources
- Scholar Journal Index
- Recent Science Index
- Scientific Resources Database

Review Of Research Journal  
258/34 Raviwar Peth Solapur-  
413005, Maharashtra  
Contact-9595359435

E-Mail-ayisrj@yahoo.in/ayisrj2011@gmail.com