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QUALITATIVE STUDIES OF REACTIONS OF FURYL-SUBSTITUTED PYRAZINE AND QUINOXALINE LIGANDS TOWARDS SOME METAL IONS

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Five new reagents, 2, 3-bis (2′-furyl)-5-methyl-5, 6-dihydropyrazine (I) 2, 3-bis (2′-furyl)-5-methyl-pyrazine (III), 2, 3-bis (2′-furyl)-5, 6-dihydropyrazine (II), 2, 3-bis (2′-furyl)-5, 6-diphenylpyrazine (IV) and 2, 3-bis (2′-furyl)-quinoxaline (V) have been prepared. The reagents have been characterized using IR, U.V. and mass spectroscopic techniques. Iron (II) develops brown and iron (III), copper (I), copper (II), cobalt (II) and nickel (II) develop yellow colour or turbidity within 1-4 hr. at room temperature. The colour reactions have also been studied spectrophotometrically.

Key words: Furyl, Methye pyrazine; dihydropyrazine; diphenyl pyrazine; Quinoxaline; Reagents.

INTRODUCTION

Pyridyl-substituted pyrazine and quinoxaline have proved quite interesting due to their close resemblance to 1, 10-phenanthroline and related compounds [1-5]. Recently the furyl groups have been substituted in pyrazine ring and the reagents react slowly to form coloured metal complexes. In the present work five ligands have been synthesized to explore their complexing properties towards metal ions and to investigate the effect of furyl substitution in quinoxaline on complexation.

EXPERIMENTAL

Preparation of the reagents

2, 3-Bis (2′-furyl)-5, 6-dihydropyrazine (I). The solution of furil (3.8g) in ethanol was added 1, 2-diaminopropane (1.48g) in ethanol. The mixture was heated for 10 min. and then the solvent removed. The solid mass was extracted several times with ether and then diluted with equal volume of petroleum spirit (40-60°). The solvent was partially evaporated and the precipitate so obtained was recrystallised twice from petroleum spirit (40-60°), m.p. = 88°C. IR shows υ_{max} cm^{-1} at 3110(s), 2990(m), 2940(m), 2860(w) for C–H stretching, 1605(s) 1575(s), 1540(m), 1480(s) for ring stretching, 780(s), 765(s), 755(s) for C–H deformation, 600(s), 535(m), 450(m) for ring deformation vibrations. Mass spectrum shows molecular ion peak at m/e 228(31.8 %) and at *m/e* 199(8.2 %), 185 (12.7 %), 158 (4.5 %) 126(57 %), 97(100 %). Calculated for $C_{13}H_{12}N_2O_2$ requires % C = 68.42, H = 5.26, N = 12.28; found % 68.18, H = 5.31, N-12.14.

2, 3-Bis (2′-furyl)-dl-5, 6-diphenyl-5, 6-dihydropyrazine (II). To the refluxing solution of furil (1.6g) in ethanol was added a solution of freshly prepared dl-stilbenediamine (2.1g) in ethanol. The mixture heated for 10 min and most of the solvent was distilled off and the residue cooled at 0°. The precipitate was filtered and recrystallised from *n*-hexane, m.p., 190-2. IR shows υ_{max} cm^{-1} at 3150(m), 3100(s) 3100(s), 3025(w), 3000(w), for C–H, 1600(m), 1570(s), 1543(s), 1495(s), 1480(s), 1450(s), 1395(m), 1385(m) for ring stretching vibrations, 905(m), 980(m), 860(m), 770(s), 750(s), 700(s) for C–H out of plane deformation and 590(m), 540(m), 500(m), 440(m) for ring deformation. Mass spectrum shows molecular ion peak at *m/e* 360(100 %) and at m/e 337 (22.7 %), 289(30 %), 261 (32.7 %), 158 (27.2 %) 129(13.6 %), 103(15.5 %), 31(32.6 %). Calculated for $C_{24}H_{18}N_2O_2$, requires % C = 78.68, H = 4.91, N = 6.65; found % C = 78.58, H = 5.04, N = 7.67.

2, 3-Bis (2′-furyl)-5-methylpyrazine (III). Palladium-charcoal (0.1g, 10%) was added to the solution of 2, 3-bis (2′-furyl)-5-methyl-5, 6-dihydropyrazine (1g) in mesitylene (20 ml) and mixture refluxed for 36 hr. The mixture was readily filtered and concentrated to 5 ml. The remaining solvent was evaported and residue was dissolved in ether and equal amount of petroleum spirit was added. The precipitate was filtered and recrystallised from petroleum ether (40-60°C); m.p. 70. IR shows bands at υ_{max} cm^{-1} at 3150(m), 3110(s), 2925(w), 2900(w) for C–H stretching; 1595(s), 1545(m), 1512(m), 1485(s) for ring stretching; 940(s), 880(s), 850(m), 830(w), 815(w), 750(s) for C–H out of plane deformation and 590(m), 490(m), for ring deformation vibrations. Mass spectrum shows molecular ion peak at m/e 226(100 %) and at m/e, 209(25.5 %), 197(23.6 %) 172(8.2 %), 93(28.2 %), 79(10 %). Calcualted for $C_{13}H_{10}N_2O_2$ requires % C = 69.02, H = 4.42, N = 12.38; found % C = 68.81, H = 4.54, N = 12.23.

2, 3-Bis (2'-furyl)-5, 6-diphenylpyrazine (IV). Palladium charcoal (0.1g, 10 %) and 2, 3-bis (2'-furyl)-5, 6-diphenyl-5, 6-dihydropyrazine (1.0) in 20ml mesitylene was refluxed for 36 hr. The mixture was filtered and concentrated to 5ml and remaining solvent was evaporated at room temperature. The residue was dissolved in ether and equal amount of the petroleum spirit was added. The precipitate was recrystallized from n-hexane; m.p., 160-62. IR shows υ_{max} cm^{-1} at 3155(w), 3120(w), 3055(w) for CH stretching; 1595(m), 1575(s), 1510(w), 1485(m), 1475(s), 1445(m), 1400(s), 1380(s), 1370(s) for ring stretching, 940(m), 910(m), 885(m), 775(s), 750(s), 715(s), 700(s), for C–H out of plane deformation and 595(s), 542(m), 400(s) for ring deformation vibrations. Mass spectrum shows M$^+$ at m/e 364(100 %) and peaks at m/e 335(16.3 %), 307(10 %), 270(4 %), 178(9 %), 158(22.7 %), 129(11.8 %), 102(29 %). Calculated for $C_{24}H_{16}N_2O_2$ requires % C = 79.12, H = 4.39, N = 7.69; found % C = 78.46, H = 4.65, N = 7.54.

2, 3-Bis (2'-furyl)-quinoxaline (V). 1, 2-Diaminobenzene (1.1g) dissolved in ethanol was added to the solution of Furil (1.9g) in 15ml of ethanol. The solution was heated for 30 min and sufficient amount of water was added. Precipitate was filtered and recrystallised from n-hexane; m.p., 125° IR shows υ_{max} cm^{-1} at 3140(w), 3115(w), 3060(w) for C–H stretching; 1575(s), 1540(w), 1490(w), 1480(s), 1450(m), 1400(s) for ring streatching, 905(s), 880(w), 820(w), 760(s), 745(s) for C–H out of plane deformation and 595(s), 495(s) for ring deformation vibrations. Mass spectrum shows M$^+$. at m/e 262(100 %) and peaks at m/e 233(15.4 %), 199(2 %), 169(10 %), 153(1.8 %), 131(10.9 %), 114(7.3 %), 89(10 %) 76(13.6 %). Calculated for $C_{16}H_{10}N_2O_2$; requires C = 73.20, H = 3.81, N = 10.68; found %, C = 72.90, H = 3.81, N = 10.74.

Solutions. Solutions (0.2 %) of organic reagents were prepared in ethanol. A few drops of dilute hydrochloric acid were added if required to facilitate dissolution. Conventional buffer solutions in pH range 1-10 were used [6]. Qualitative and spectrophotometric studies were carried out, following the procedure as reported earlier [6].

IR in KBr was recorded on Hitachi 250-30 IR Spectrophotometer in the 4000-250 cm^{-1} region. Spectrophotometric studies were carried out on Hitachi 220 Spectrophotometer. Microanalysis was carried out by Elemental Microanalysis Ltd., U.K. Mass spectra were recorded at HEJ Research Institute of Chemistry, University of Karachi.

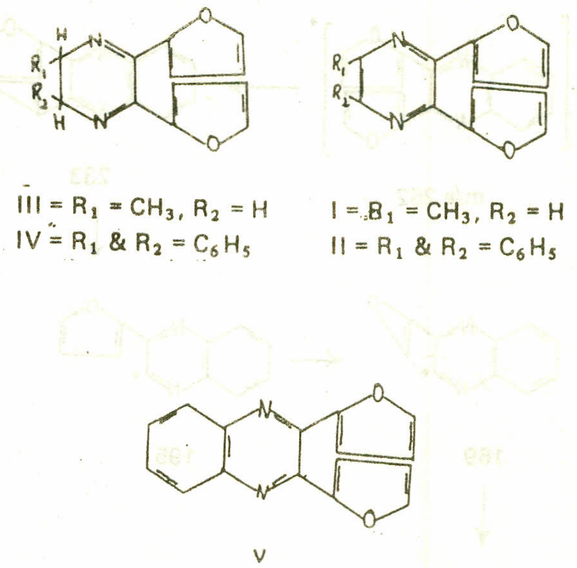

Fig. 1. Structural diagrams of the reagents.

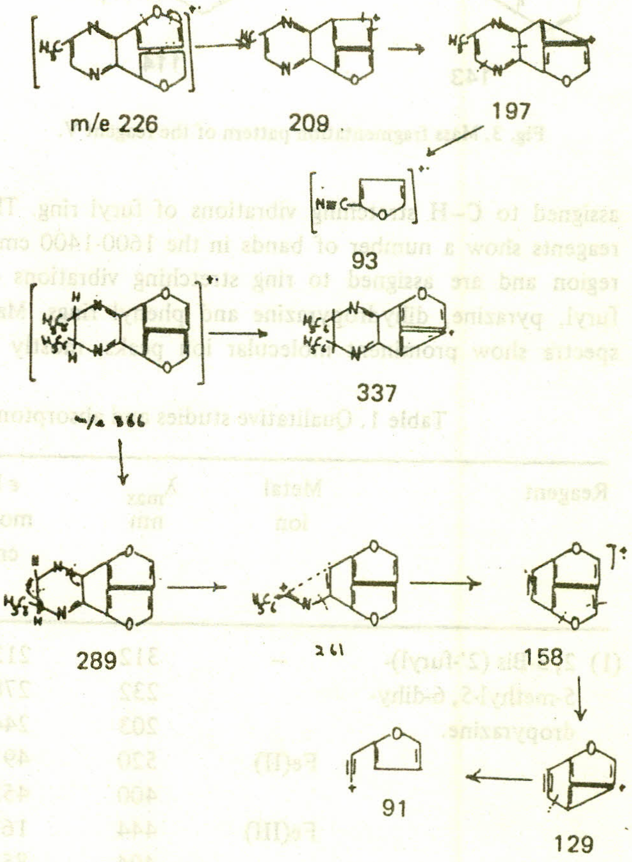

Fig. 2. Mass fragmentation pattern of the reagents II and III.

RESULTS AND DISCUSSION

The IR of the furyl substituted pyrazine and quinoxaline are quite complex, but the bands near 3100 cm^{-1} are

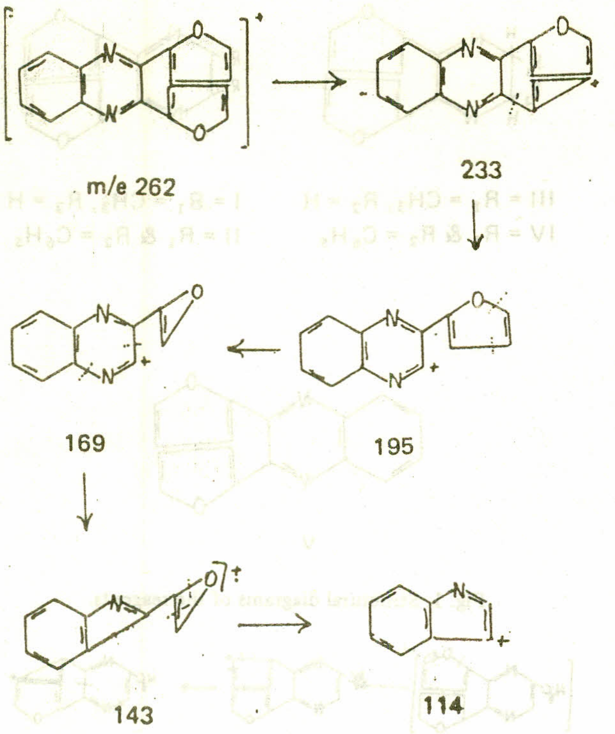

Fig. 3. Mass fragmentation pattern of the reagent V.

assigned to C–H stretching vibrations of furyl ring. The reagents show a number of bands in the 1600-1400 cm^{-1} region and are assigned to ring stretching vibrations of furyl, pyrazine, dihydropyrazine and phenyl rings. Mass spectra show prominent molecular ion peaks, mostly as base peak, except in case of 1 with base peak at m/e 97, and indicate a characteristic of heteroaromatic systems. The mass spectrum of the reagent III indicates a loss of CHO from furyl ring, followed by the opening of the pyrazine ring with a main fragment at m/e 93 corresponding to C_4H_3CN. Reagent II shows loss of phenyl group, followed by peak at m/e 158 corresponding to $C_{10}H_8O_2$ and subsequent loss of furyl group with a peak at m/e 91. Reagent IV loses CHO and CO from furyl rings with a peaks at m/e 335 and 307, followed by the opening of the pyrazine ring with a peak at m/e 178 corresponding to $C_{14}H_{10}$ and subsequent loss of C_6H_4 to give a fragment at m/e 102. The mass fragmentation pattern of V (Fig. 3) shows the losses of CHO and HC-CH fragment from furyl group, followed by the opeing of quinoxaline ring.

The results of qualitative and spectrophotometric studies are summarized in Table 1. All the reagents react in similar fashion in slightly acidic to natural media (pH 4-7) to form coloured complexes. Iron (II) develops brown colour, but iron (III), copper (I), copper (II), and cobalt (II) complexes are yellow in colour. The rate of complex formation is slow at room temperature, except in the case of iron (II) in ethanolic media and reaches the maximum within 1-4 hr. The complexes precipitate out or are changed in turbid solution within 24 hr. Attempt to extract the precipitate in chloroform or 1, 2-dichloroethane indicate that the complexes are only partially extractable in non-aqueous solvent. The variation of the reagent concentration exercised little effect on the extraction of the precipitate.

Table 1. Qualitative studies and absorptometric data of the reagents and their metal complexes.

Reagent	Metal ion	λ_{max} nm	ε l. $mole^{-1}$ cm^{-1}	Absorbence measured after preparation of solution	Colour	Reaction after 24 hr.
(1) 2, 3-Bis (2'-furyl)-5-methyl-5, 6-dihydropyrazine.	–	312	21390			
		232	27844	–	–	–
		203	24453			
	Fe(II)	520	4915	2 hr	Brown	Dark brown ppt
		400	4524			
	Fe(III)	444	1675	2 hrs	Yellow	Yellow ppt.
		404	8517			
	Cu(II)	380	4765	1 hr	Yellow	Yellow ppt.
	Co(II)	450	3005	5 hr	Yellow	Yellow ppt.
		402	3388			
	Ni(II)	452	2348	5 hr	Yellow	Yellow ppt.
		410	3126			

(continued.....)

(Table 1, continued)

(2) 2, 3-Bis (2'-furyl)-	–	310	33194			
5-methylpyrazine		270	30368	–	–	–
		228	28250			
		205	34606			
	Fe(II)	510	8126	2 hr	Brown	Brown ppt.
		402	8237			
	Fe(III)	414	2932	1 hr	Yellow	Dark Yellow ppt.
	Cu(II)	472	1747	5 hr	Yellow	Yellow Turbid.
		402	3812			
	Cu(II)	404	1429	1 hr	Yellow	Yellow Turbid.
	Co(II)	456	3417	2 hr	Yellow	Yellow ppt.
	Ni(II)	452	2319	2 hr	Yellow	Yellow ppt.
(3) 2, 3-Bis (2'-furyl)-dl-	–	310	6176			
5, 6-diphenyl-5, 6-di-		245	10522	–	–	–
hydropyrazine		210	12800			
	Fe(II)	508	5878	2 hr	Brown	Brown ppt.
	Fe(III)	488	1675	15 min	Yellow	Yellow turbid.
	Cu(I)	458	1270	1 hr	Yellow	Yellow ppt.
		402	715			
	Cu(II)	420	238	1 hr	Yellow	Yellow turbid.
	Co(II)	450	589	1 hr	Yellow	Yellow turbid.
	Ni(II)	438	4682	5 hr	Yellow	Yellow turbid.
(4) 2, 3-Bis (2'-furyl)-	–	–	–	–	–	–
5, 6-diphenylpyrazine	Fe(II)	508	6004	2 hr	Brown	Brown ppt.
	Fe(III)	470	2025	1 hr	Yellow	Yellow turbid.
	Cu(I)	402	2494	1 hr	Yellow	Yellow turbid.
	Cu(II)	460	1767	2 hr	Yellow	Yellow ppt.
	Ni(II)	458	1614	2 hr	Yellow	Yellow ppt.
(5) 2, 3-Bis (2'-furyl)-	–	380	23743			
quinoxaline		290	45031	–	–	–
		255	46669			
		218	36846			
		208	35206			
	Fe(II)	508	6144	2 hr	Brown	Brown ppt.
	Fe(III)	428	2499	2 hr	Yellow	Yellow turbid
	Cu(I)	432	362	1 hr	Yellow	Yellow turbid
	Cu(II)	432	357	1 hr	Yellow	Yellow turbid
	Co(II)	482	2499	2 hr	Yellow	Yellow turbid.
	Ni(II)	480	1174	2 hr	Yellow	Yellow turbid.

Iron (II) readily reacts with the reagents in ethanolic media to develop brown turbid solution. However the reactions are fairly slow in water ethanol (1:1) medium to enable to measure the absorbence within 1-2 hr. The colour reaction absorbs maximally in visible region between 500-525 nm with molar absorptivities in the range of 4×10^3 to 8×10^3 l. mole^{-1} cm^{-1}.

Yellow colour of iron (III), copper (I), copper (II), cobalt (II), and nickel (II) is relatively less sensitive spectrophotometrically.

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