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Synthesis, IR and ^{13}C-NMR Spectral Studies of Some 2-Pyrazolin-5-One Derivatives

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4-Formyloxime-3-methyl-1-(2′,4′-dinitrophenyl)-2-pyrazolin-5-one, 4-formyloxime - 3-phenyl - 1-(2′,4′-dinitrophenyl - pyrazolin-5-one, 4-formyl-oxime-1-3-diphenyl-2-pyrazolin-5-one, 4-acetyloxime-3-phenyl-1-(2′,4′-dinitrophenyl)-2-pyrazolin-5-one, 4-benzoyloxime-3-methyl-1-(2′,4′-di-nitrophenyl)-2-pyrazolin-5-one, 4-oximino-3-methyl-1-(2′,4′-dinitro-phenyl)-2-pyrazolin-5-one, 4-oximino-3-phenyl-1-(2′,4′-dinitrophenyl)-2-pyrazolin-5-one have been synthesized. The elemental analysis, m.p., yield (%) FT-IR and ^{13}C-NMR spectral studies of all compounds have been reported.

Key Words: Synthesis, Infrared, NMR, 2-Pyrazolin-5-one, Derivatives

INTRODUCTION

In continuation of our earlier work[1–6] on transition metal complexes of 2-pyrazolin-5-one base heterocyclic-β-diketones and their derivatives, we report here the synthesis, IR and ^{13}C-NMR spectral studies of (a) 4-formyloxime-3-methyl-1-(2′,4′-dinitrophenyl)-2-pyrazolin-5-one [FMNPPZ], (b) 4-formyloxime-3-phenyl-1-(2′,4′-dinitrophenyl)-2-pyrazolin-5-one [FPNPPZ], (c) 4-formyloxime-1,3-diphenyl-2-pyrazolin-5-one [FDPPZ], (d) 4-acetyloxime-3-phenyl-1-(2′,4′-dinitrophenyl-2-pyrazolin-5-one [APNPPZ] (e) 4-benzoyloxime-3-methyl-1-(2′,4′-dinitrophenyl)-2-pyrazolin-5-one [BMNPPZ], (f) 4-oximino-3-methyl-1-(2′,4′- dinitrophenyl)-2-pyrazolin-5-one [OMNPPZ], (g) 4-oximino-3-phenyl-1-(2′,4′- dinitrophenyl)-2-pyrazolin-5-one [OPNPPZ]. The use of above 2-pyrazolin-5-ones for the preparation of transition metal complexes is in progress[1, 2].

EXPERIMENTAL

All chemicals used were of reagent grade (BDH). Melting points of all the compounds were taken in open glass capillary on Tempo melting point apparatus. The ligands were analyzed for carbon, hydrogen and nitrogen on a Carlo-Erba-1108 micro analyzer. The FT-IR spectra were recorded on a Shimadzu-8201 PC FT-IR spectrophotometer in KBr pellets. The ^{13}C-NMR spectra were recorded on a Bruker DRX-300 FT-NMR spectrophotometer. The physical and analytical data of all the 2-pyrazolin-5-ones are listed in Table-1.

Synthesis of 2-pyrazolin-5-one derivatives

[I] 3-Methyl-1-(2′,4′-dinitrophenyl)-2-pyrazolin-5-one (m.p. found : 92°C, reported[7] : 92°C), **[II]** 3-phenyl-1-(2′,4′-dinitrophenyl)-2-pyrazolin-5-one (m.p. found: 160°C; reported[8]: 160°C), **[III]** 4-formyl-3-methyl-1-(2′,4′-dinitrophenyl)

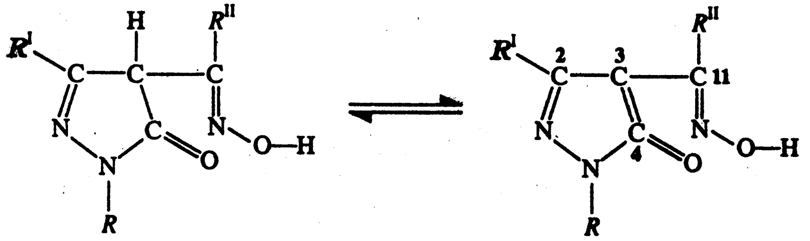
-2-pyrazolin-5-one (m.p. found 130°C), **[IV]** 4-formyl-3-phenyl-1-(2′,4′-dinitrophenyl)-2-pyrazolin-5-one (m.p. found 90°C), **[V]** 4-formyl- 1,3-diphenyl-2-pyrazolin-5-one (m.p. found: 141°C, reported: 140–143°C), **[VI]** 4-acetyl-3-phenyl-1-(2′,4′-dinitrophenyl)-2-pyrazolin-5-one (m.p. found: 140°C), **[VII]** 4-benzoyl-3-methyl-1-(2′,4′-dinitrophenyl)-2-pyrazolin-5-one (m.p. found 157°C) were synthesized according to the reported methods[10].

The following general literature[11] procedure is used for the preparation of oximes of **III, IV, V, VI** and **VII.** A mixture of ethanolic solution (20 mL) of 4-acyl-2-pyrazolin-5-one (0.01 mole), hydroxylamine hydrochloride (0.01 mole) and sodium acetate (1 g) was refluxed for 1-2 h on a water bath. The resulting solution was then poured into ice-water (500 mL) with constant stirring. The isolated solid was filtered, washed several times with water then with ethanol and finally dried in air. The crude product was then recrystallized in ethanol. The oximino derivative of [I] and [II] were prepared according to the reported methods[10].

RESULTS AND DISCUSSION

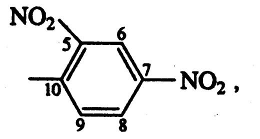
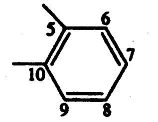
Infrared Spectra

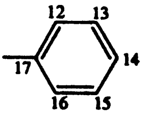
The ligands FMNPPZ, FPNPPZ, FDPPZ, APNPPZ and BMNPPZ used in the present study may have the following tautomeric forms (A) and (B):

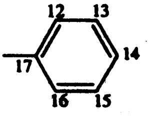


[A] [B]

Where,

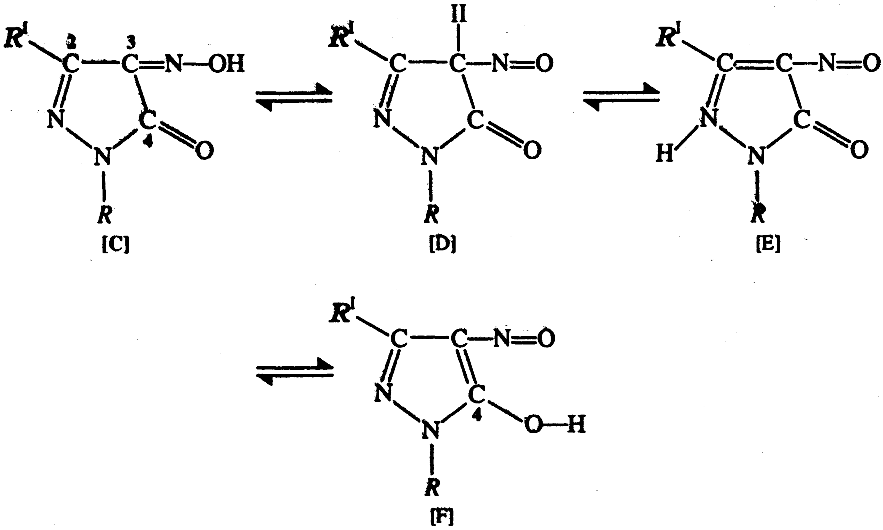
R =  , 

R^I = $-{}^1CH_3$, 

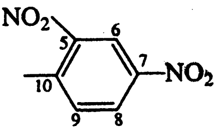
R^{II} = —H, $-{}^{18}CH_3$, 

The IR spectra of the compoundss FMNPPZ, FPNPPZ, FDPPZ, APNPPZ and BMNPPZ show medium broad band with some fine structures in the region 3500–3100 cm^{-1}, which may be due to ν(O—H) of oxime +ν(O—H) of 5-(OH) group of pyrazolin ring[2,11,12]. The observed low value of ν(O—H) suggests the presence of intramolecular or intermolecular hydrogen bonding[2,11,12] in ligands and also suggests the presence of enol form (structure B) of ligands at least in the solid state. The IR spectra of ligands show bands in the region 1422–1220 cm^{-1}, which may be due ν(C—O)[11,13,14]. The IR spectra of ligands show bands in the region 1137–1028 cm^{-1}, which may be due to ν(N—O) of oximino group[11-13]. The infrared spectra of ligands show bands in the region 1689–1670 cm^{-1}, which may be due to ν(C=N) (oxime)[12,13]. The IR spectra of ligands show band in the region 1620–1600 cm^{-1}, which may be due to ν(C=N) (pyrazolin ring)[15]. The IR spectra of ligands FMNPPZ, FPNPPZ, APNPPZ and BMNPPZ show bands in the region 1340–1330 cm^{-1}, which may be assigned to $\nu(NO_2)$[1,16].

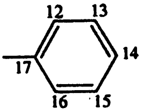
The possible resonance structures of ligands OMNPPZ and OPNPPZ studied in the present work are:



Where, R =



R' = —¹CH_3 ,



The IR spectra of OMNPPZ and OPNPPZ show bands in the region 3390–3380 cm^{-1}, which may be due to ν(O—H) of oximino group[17-19]. The observed low value of ν(O—H) suggest the presence of intramolecular or intermolecular hydrogen bonding in ligands. These observations suggest that ligands OMNPPZ and OPNPPZ studied in the present work may have tautomeric form [C].

The IR spectra of OMNPPZ and OPNPPZ show a strong band in the region 1740–1735 cm^{-1}, which may be due to ν(C=O) (pyrazolin ring)[20]. Infrared spectra of OMNPPZ and OPNPPZ show bands in the region 1622–1618 cm^{-1}, which may be due to ν(C=N) of oximino group[20]. The IR spectra of OMNPPZ and OPNPPZ show ν(C=N) (cyclic) frequencies[15, 21] of pyrzolin ring at 1590 cm^{-1}. The (N—O) stretching frequencies observed in the IR spectra of OMNPPZ and OPNPPZ in the range[20] 1024–922 cm^{-1}. Infrared spectra of ligands OMNPPZ and OPNPPZ show bands in the range 1336–1334 cm^{-1}, which may be assigned to ν(NO_2)[1, 16].

TABLE-1
PHYSICAL AND ANALYTICAL DATA OF COMPOUNDS

Compound	m.f.	Colour	m.p. (°C)	Yield (%)	% Analysis, Found (Calcd.)		
					C	H	N
FMNPPZ	$C_{11}H_9N_5O_6$	Orange	87	67	43.06 (43.00)	3.05 (2.93)	23.06 (22.80)
FPNPPZ	$C_{16}H_{11}N_5O_6$	Reddish orange	140	65	52.63 (52.03)	2.34 (2.98)	18.14 (18.97)
FDPPZ	$C_{16}H_{13}N_3O_2$	Turmeric yellow	101	72	69.09 (68.81)	4.76 (4.66)	15.15 (15.05)
APNPPZ	$C_{17}H_{13}N_5O_6$	Brown	97	61	53.57 (53.26)	3.29 (3.39)	18.56 (18.27)
BMNPPZ	$C_{17}H_{13}N_5O_6$	Light brown	177	59	53.17 (53.26)	3.47 (3.39)	18.47 (18.27)
OMNPPZ	$C_{10}H_7N_5O_6$	Yellow	245	71	41.48 (40.95)	2.47 (2.38)	22.99 (23.89)
OPNPPZ	$C_{15}H_9N_5O_6$	Orange	142	63	50.77 (50.70)	2.67 (2.53)	19.66 (19.72)

The important infrared vibrational frequencies of all the compounds are listed in Table-2.

^{13}C-NMR Spectra

An attempt has been made to characterize ligands by ^{13}C-NMR spectral studies. The assignment of ^{13}C-NMR shift has been made using reported values for 2-pyrazolin-5-one derivatives[17,22–24]. The ^{13}C-NMR spectral data of 2-pyrazolin-5-one derivatives are presented in Table-3.

TABLE-2
INFRARED VIBRATIONAL FREQUIENCY (cm^{-1}) OF COMPOUNDS

FMNPPZ	FPNPPZ	FDPPZ	APNPPZ	BMNPPZ	OMNPPZ	OPNPPZ	AssignmentS [25, 26]
3400–3100	3480–3250	3450–3100	3300–3100	3480–3200	—	—	ν(O—H) (oxime + 5-OH group)
—	—	—	—	—	3382	3390	ν(O—H) (oximino)
3040	3037	3058	3030	3080	3025	3015	Aryl ν(C—H)
2940	—	—	2910	2945	2943	—	Saturated ν(C—H)
—	—	—	—	—	1736	1740	ν(C=O) (Pyrazolin ring)
1675	1680	1689	1670	1676	1618	1622	ν(C=N) (oxime)
1620	1620	1600	1612	1612	1590	1590	ν(C=N) (Pyrazolin ring)
1570	1535	1565	1531	1531	1570	1565	Pyrazolin ring stretch
1514	1490	1492	1510	1510	1512	1512	Phenyl ring ν(C=C)
1450	1452	1452	1450	1455	1425	1450	Pyrazolin ring stretch
1410	1420	1332	1420	1422	—	—	ν(C—O) (enol)
1330	1330	—	1336	1340	1336	1334	ν(NO$_2$)
1267	—	—	1300	1265	1303	—	β$_S$(CH$_3$)
1200	1168	1172	1175	1200	1136	1136	β(C—H)
1124	1105	1028	1028	1137	1024	922	ν(N—O) (oxime)
1100	1120	1118	1107	1115	1110	1110	Pyrazolin ring breathing
1005	—	—	1010	1004	986	—	CH$_3$ rocking
—	965	916	962	960	—	940	C—C$_6$H$_5$ stretch
923	—	—	914	916	905	—	C—CH$_3$ stretch

TABLE-3

^{13}C-NMR SPECTRAL DATA OF LIGANDS (δ) ppm

Ligand	Types of carbon atoms														
	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12} C_{16}	C_{13} C_{15}	C_{14}	C_{17}	C_{18}
FMNPPZ	12.3	148.2	99.3	153.7	129.6	128.6	140.8	117.3	123.2	139.5	164.8	—	—	—	—	—
FPNPPZ	—	144.4	116.8	149.0	137.8	130.1	143.4	126.6	128.7	140.7	167.5	125.0	121.5	122.8	136.3	—
FDPPZ	—	139.8	116.5	145.5	127.4	118.5	125.3	118.5	127.4	128.8	163.6	128.0	119.7	126.0	129.0	—
APNPPZ	—	148.5	114.3	157.0	136.0	127.7	145.2	123.5	124.6	139.0	164.9	120.0	117.5	119.0	128.7	12.6
BMNPPZ	12.6	152.6	104.0	160.4	139.6	129.4	142.1	126.9	128.8	140.6	164.1	124.0	119.8	121.0	137.8	—
OMNPPZ	14.3	135.1	148.2	177.0	137.1	123.1	141.4	114.2	120.0	140.0	—	—	—	—	—	—
OPNPPZ	—	141.0	149.2	179.4	134.3	128.5	140.0	125.1	127.2	139.4	—	123.5	120.8	122.5	130.0	—

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