Indian Journal of Chemistry
Vol. 37B, November 1998, pp. 1180-1183

Note

N, N'-Ethylenebis(1-phenyl-3-methyl-4-acylpyrazoloneimine) derivatives: Synthesis and UV, IR, ^{1}H and ^{13}C NMR spectral studies

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Received 10 March 1997; accepted 30 September 1997

N, N'-Ethylenebis(1-phenyl-3-methyl-4-acylpyrazoloneimine) derivatives have been synthesised and characterised using UV, IR, ^{1}H and ^{13}C NMR spectroscopy, where the substituents R(R')=CH_3(H); $CH_3(CH_3)$; CH_3CH_2(H); $CH_3CH_2CH_2$(H). The spectral data show that the compounds behave in solution as quadridentate ligands and the bis(hydroxyimine) tautomer is the most stable tautomeric form in solution. The UV, IR, ^{1}H and ^{13}C NMR spectral assignments have been reported.

In continuation of our work on the synthesis and characterisation of derivatives of 1-phenyl-3-methyl-4-acylpyrazolone, we report here the synthesis and spectroscopic characterisation of some schiff bases from 4-acylpyrazolones. Application of β-ketoamines as potential extraction and spectrophotometric reagents[1] and in the synthesis of interesting tetradentate β-ketoamine complexes with metals[2-4] has been reported. Some workers have reported the synthesis of some β-ketoamines which they characterised in solution as bidentate and tridentate[5-7] ligands, and this includes some schiff bases synthesised from 4-acylpyrazolone[8].

In this note we report the synthesis and spectroscopic characterisation of β-ketoamine bases of 4-acylpyrazolone which behave in solution as quadridentate β-hydroxyimines.

Experimental Section

Synthesis of ligands. The 4-acetyl, 4-propionyl and 4-butyryl derivatives of 1-phenyl-3-methylpyrazolone were synthesised according to the method reported in literature[9], using acyl chlorides of acetic, propionic and butyric acids, respectively. The schiff bases were prepared as follows:

***N, N'*-Ethylenebis(1-phenyl-3-methyl-4-acetylpyrazoloneimine) (H_2AEtP).** An ethanolic solution of 1-phenyl-3-methyl-4-acetylpyrazolone (HAP) was refluxed with ethylenediamine (Et) in the mole ratio of HAP:Et=2:1 for 1 hr. After 35 min. of refluxing a white precipitate was observed coming out from the solution. Refluxing was continued for another 25 min. The white suspension was poured into cold distilled water. The bone white precipitate that came out was filtered and washed several times by making a suspension in hot ethanol to get 68% yield of a bone white solid product, mp 306°C. Anal. Calcd for $C_{26}H_{28}O_2N_6$: C, 68.4; H, 6.2; N, 18.4. Found: C, 68.2; H, 6.3; N, 18.4%. Insoluble in ethanol, petroleum ether; slightly soluble in methanol, $CHCl_3$, acetone and benzene.

***N, N'*-Bis(1-phenyl-3-methyl-4-acetylpyrazoloneimine)-1, 2-propane (H_2ADPP).** An ethanolic solution of 1-phenyl-3-methyl-4-acetylpyrazolone (HAP) was refluxed with 1,2-diaminopropane (DP) for 2 hr in the mole ratio of HAP:DP=2:1. The resultant wine red solution was poured into distilled water. On acidification of the milky solution a white precipitate appeared that was filtered and recrystallized from aqueous ethanol to obtain a grey-white product (47% yield), mp 198°C. Anal. Calcd for $C_{27}H_{30}O_2N_6$: C, 68.9; H, 6.4; N, 17.9. Found: C, 68.5; H, 6.4; N, 17.6%. Insoluble in petroleum ether; slightly soluble in ethanol and methanol, soluble in $CHCl_3$, acetone, CH_2Cl_2 and benzene.

***N, N'*-Ethylenebis(1-phenyl-3-methyl-4-propionylpyrazoloneimine) (H_2PrEtP).** An ethanolic solution of 1-phenyl-3-methyl-4-propionylpyrazolone (HPrP) was refluxed with ethylenediamine (Et) in the mole ratio of HPrP:Et=2:1 for 2 hr. The resultant pink ethanolic solution was left overnight in a fume cupboard. Thereafter, the white deposit was filtered and recrystallized from ethanol to obtain a white product (75% yield), mp

214°C. Anal. Calcd. For $C_{28}H_{32}O_2N_6$: C, 69.4; H, 6.7; N, 17.3. Found: C, 69.3; H, 6.5; N, 17.3%. Slightly soluble in ethanol and methanol; soluble in $CHCl_3$, acetone, CH_2Cl_2 and benzene.

***N, N'*-Ethylenebis(1-phenyl-3-methyl-4-butyrylpyrazoloneimine) (H_2BuEtP).** The ligand was synthesised and purified following the procedure described above for H_2PrEtP to obtain a white product, 70% yield, mp 235°C. Anal. Calcd for $C_{30}H_{36}O_2N_6$: C, 70.3; H, 7.1; N, 16.4. Found: C, 70.1; H, 7.1; N, 16.5%. Slightly soluble in ethanol; soluble in methanol, $CHCl_3$, acetone, CH_2Cl_2 and benzene.

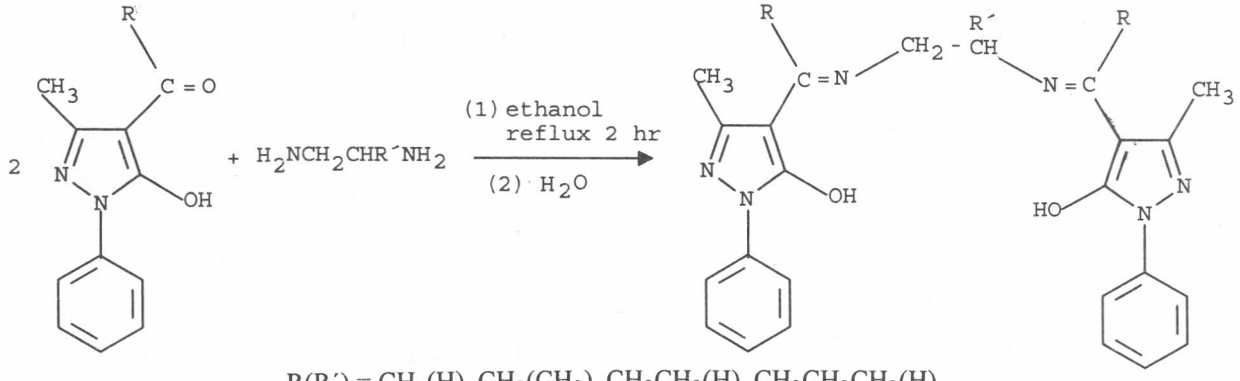
Physical measurement. The UV spectra were recorded in chloroform on a Perkin-Elmer UV-vis spectrophotometer. IR spectra were obtained in chloroform on a Heydon and Sons infrared spectrometer using NaCl windows. ^1H and ^{13}C NMR spectra were measured on a Bruka Data systems spectrometer in DMSO-d_6 (chemical shifts are reported in δ, ppm relative to TMS).

Results and Discussion

Synthesis of the 4-acylpyrazolone schiff bases was carried out by the reaction between a 4-acylpyrazolone and a diaminoalkyl derivative. This can be represented by the reaction shown in **Scheme I**. Elemental analyses and spectral data show that the compounds were formed from 4-acylpyrazolone and diaminoalkyl derivative in a mole ratio of 2:1 as shown in **Scheme I**. The schiff bases can exist in several tautomeric forms represented in **Figure 1**.

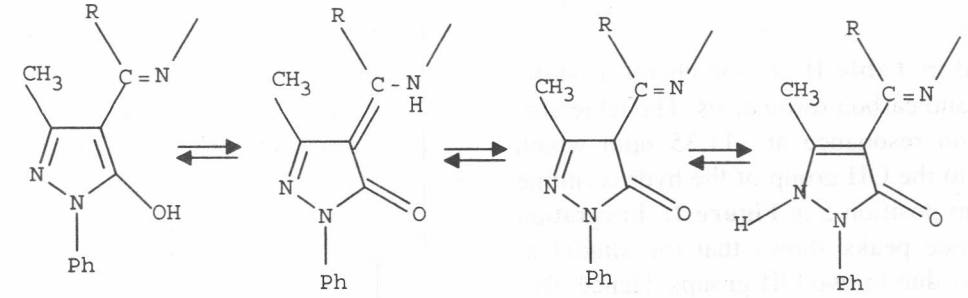
The ultraviolet spectra of the schiff bases in chloroform solutions showed absorption maxima (**Table I**) at 260 nm ($\varepsilon=2\times10^4$ $l.mol^{-1}.cm^{-1}$) and 303 nm ($\varepsilon=2.2\times10^4$). The absorption maximum at 303 nm results from a bathochromic shift by ~30 nm of similar absorption maximum in UV spectrum of the corresponding 4-acylpyrazolone. The absorption maxima were assigned to $\pi\rightarrow\pi^*$ transition.

Bands in the 3400-3600 cm^{-1} region of IR spectra (**Table I**) of the compounds were assigned to the stretching vibrations of OH involved in C=N...H-O hydrogen bonding. This indicates that all the schiff baes existed as 1,3-hydroxyimine shown in **Figure 1** as the most stable tautomer. The very strong vibrational frequency band[8] at 1628 cm^{-1} was assigned to ν_{as} C=N. The NMR



R(R´) = CH_3(H), CH_3(CH_3), CH_3CH_2(H), $CH_3CH_2CH_2$(H)

Scheme I



1,3-Hydroxyimine 1,3-Ketoamine 1,3-Ketoimine forms

Figure 1 Tautomeric forms of 4-acylpyrazolone schiff bases

Table I—UV and infrared (cm^{-1}) spectral data of the ligands

	H_2AEtP	H_2ADPP	H_2PrEtP	H_2BuEtP
λ_1 max (nm)	260	260	261	261
ε_1	2.0×10^4	2.1×10^4	2.2×10^4	1.9×10^4
λ_2 max (nm)	303	301	304	301
ε_2	2.2×10^4	2.3×10^4	2.4×10^4	20×10^4
νOH	3600w	3600w	3244w	2296b
ν_{as}C=N	1628vs	1628vs	1628vs	1624vs
phenyl ring νC=C	1596s	1592vs	1592vs	1592vs
pyrazole ring stretch	1536s	1536s	1536vs	1536s
ν_{as}C=C=C	1500s	1500s	1500vs	1500vs
phenyl ring νC=C	1456s	1456m	1456s	1456s
pyrazole ring stretch	1396s	1396m	1396vs	1400vs
ν_sC=N	1364s	1368s	1368s	1368s

w, weak; vs, very strong; s, strong; m, medium; b, broad

Table II—^{1}H and ^{13}C NMR specral data of the ligands in δ ppm relative to TMS

^1H; (^{13}C)	H_2AEtP	H_2ADPP	H_2PrEtP	H_2BuEtP
1	2.31 (s,6H); (16.73)	2.26 (s, 6H)	2.31 (s,6H); (16.51)	2.34 (s,6H); (16.54)
2	— (146.81)	—	— (146.30)	— (146.26)
3	— (97.44)	—	— (96.97)	— (97.40)
4	— (166.24)	—	— (165.45)	— (165.35)
5	11.38 (b, 2H); —	11.35 (s,2H)	11.35 (s,2H) —	11.42 (s, 2H) —
6, 10	7.34 (m,4H); (128.39)	7.35 (m,4H)	7.35 (m,4H); (128.52)	7.38 (m,4H); (128.54)
7, 9	8.00 (m,4H); (117.65)	7.98 (m,4H)	7.98 (m, 4H); (117.83)	8.01 (m,4H); (117.75)
8	7.10 (m,2H); (123.16)	7.10 (m,2H)	7.10 (m,2H); (123.37)	7.12 (m,2H); (123.31)
11	— (139.24)		— (139.28)	— (139.25)
12	2.40 (s,6H); (15.50)	2.49 (s,6H)	1.21 (t,6H); (12.17)	1.06 (t,6H); (13.87)
13	— —		2.77 (m, 4H); (21.45)	1.62 (m, 4H); (21.41)
14	— —	—	— —	2.72 (b,4H); (29.73)
15	— (166.74)	—	— (171.12)	— (169.69)
16	3.45 (t,2H); (45.51)	4.35 (b,2H)	3.84 (s,2H); (42.28)	3.49 (b, 2H); (45.38)
17	R′=H	1.36 (d, 3H)	R′=H	R′=H
18		3.78 (b, H)		

data presented in **Table II** are the chemical shifts of the proton and carbon resonances. The table also shows a proton resonance at ~11.35 ppm which was assigned to the OH group of the hydroxyimine tautomer (atom position 5 in **Figure 2**). Integration of the resonance peaks shows that the singlet at 11.35 ppm was due to two OH groups. Hence, this further indicates the presence of C–C=N....HO bonding rather than C=C–NH....O bonding in the ligands.

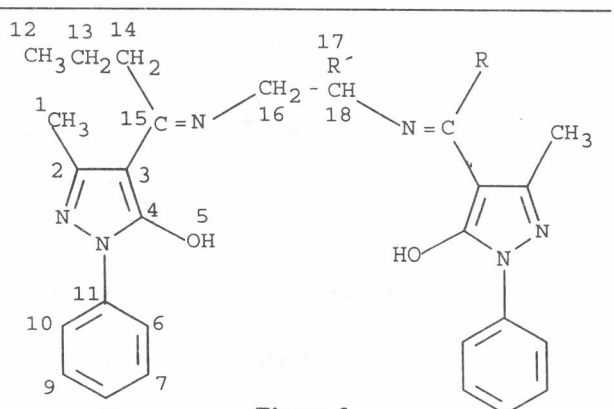


Figure 2

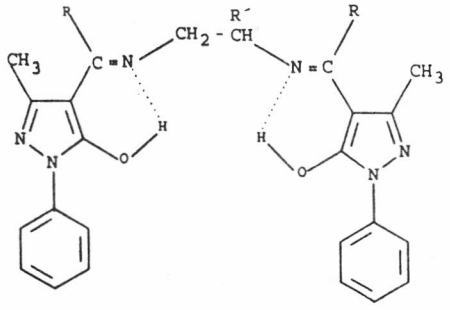


Figure 3

The proton resonance absorptions for positions 16 and 18 were recorded at 4.35 ppm and 3.84 ppm, respectively in H_2ADPP. This was attributed to the chiral centre at position 18. Hence, the structure of the 4-acylpyrazoloneimine schiff bases can be represented as shown in **Figure 3**.

Acknowledgement

The authors wish to thank Alexander von-Humboldt Foundation for support to BAU for this work.

References

1 Okafor E C, *Talanta,* 27, **1980,** 887.

2 Belcher R, Blessel K, Cardwell T, Praica M, Stephen W I & Uden P C, *J Inorg Nucl Chem,* 35, **1973,** 1127.

3 Rao S N, Jaiswal M N, Mishra D D, Maurya R C & Rao N N, *Polyhedron,* 12, **1993,** 2045.

4 Holm R H, Everett G W & Chakravorty A, *Prog Inorg Chem,* 7, **1966,** 83.

5 Donia A M & El-Saied F A, *Polyhedron,* 7, **1988,** 2149.

6 El-Saied F A, *Inorg Chim Acta,* 165, **1989,** 147.

7 Kuncheria B & Indrasenan P, *Polyhedron,* 7, **1988,** 143.

8 Rao S N, Mishra D D, Maurya R C & Rao N N, *Bull Chem Soc Japan,* 68, **1995,** 1589.

9 Jensen B S, *Acta Chem Scand,* 13, **1959,** 1668.