

SHORT COMMUNICATION**SYNTHESIS AND SPECTROSCOPIC STUDIES OF 4-ADIPOYL-BIS (1-PHENYL-3-METHYL-PYRAZOLONE-5) AS A BIS-(1,3-DIKETONE)**B.A. UZOUKWU^{1*}, H. DUDDECK¹ and S.I. OKEKE²¹*Institut für Organische Chemie, Universität Hannover, Schneiderberg 1B, Hannover, Germany.*²*Environmental Study Unit, Evergreen University, Los Angeles, USA.**(Received: 16 January 1997; accepted: 12 June 1998)*

Abstract: 4-Adipoylbis (1-phenyl-3-methylpyrazolone-5) has been synthesised and characterised spectroscopically using UV, IR, NMR and mass spectroscopy. The compound was synthesised through a condensation reaction between pyrazolone and adipoyl chloride. The spectral data showed that the compound existed as a bis (1,3-diketone). Assignments of the IR, NMR, and mass spectral results are reported.

Key Words: Adipoyl pyrazolone, chelating agents, pyrazolone, spectroscopic data

INTRODUCTION

1-phenyl-3-methyl-4-acylpyrazolones-5 have been found to possess valuable spectroscopic¹⁻³ and extraction⁴⁻⁶ properties for metal ions from aqueous media. Synthesis of derivatives of the ligand and their application in the extraction of Mn(II)⁶, Cu(II) [†] alkaline earth and alkali earth metals⁸ from aqueous media and in the separation of metal ions^{4,9} from one another have been carried out. However, the search for new derivatives of this ligand for better selective extraction and chemico-spectrographic analysis of metal ions continues. Some of the different methods tried included increasing the acidity of the chelating ring by introducing electron withdrawing substituents¹⁰ at the 4-acyl position or increasing the number of the carbon atoms of the 4-acyl substituent. 4-Acylpyrazolones have been characterized as bidentate ligands existing in solution as the ketoenol^{1,2,3} tautomer.

The present study reports the synthesis of the 4-adipoyl derivative which is quadridentate, though a modified method described by Jensen.¹¹ Characterization of the ligand spectroscopically showed that unlike other derivatives of 4-acylpyrazolone, it existed as the bis(1,3-diketone) shown in Fig 1.

METHODS AND MATERIALS**Experimental:**

Synthesis of 4-adipoylbis (1-phenyl-3-methylpyrazolone-5) : The ligand was synthesised by dissolving 10 g (57.4 mmol) of 1-phenyl-3-methyl-pyrazolone in 100 ml of dioxane in a one-litre 3-neck quick-fit flask carrying a reflux condenser

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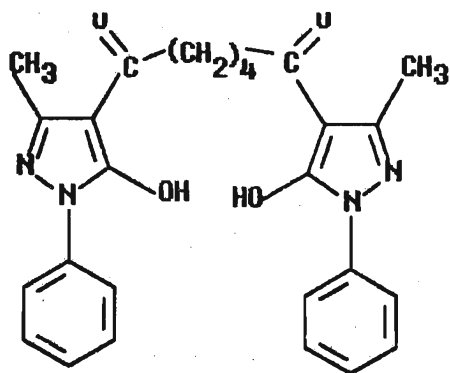


Figure 1: The molecular structure of 4-adipoylbis (1-phenyl-3-methyl-pyrazolone-5).

by warming. Calcium hydroxide (5.g) was added to the solution and the temperature of the suspension raised to 100°C before 4.5 ml (31 mmol) of adipoyl chloride was added dropwise within 5 min with stirring. After 20 min of stirring, the exothermic reaction mixture changed from green to dull orange. The temperature of the oil bath heating the reaction mixture was raised to 125°C and stirring continued for another 15 min when the product became a clay brown thick paste.

The thick paste was poured into 400 ml of 4 M HCl solution. Some pieces of ice were added to assist precipitation. The brown solid that settled was filtered off and washed in a suspension of hot ethanol to obtain 83% yield of a light pink fluffy product, m.p=193 ° C Anal. Cal.for $C_{26}H_{26}N_4O_4$:C, 68.1; H,5.7; N,12.2 found C,68.0;H,5.7;N, 12.0%. When the experiment was carried out at temperatures below 80°C, stickily brown products with low yield and of low quality were obtained.

Physical measurements:

The IR spectrum was recorded on a Heydon and Sons Infrared spectrophotometer, dispersed in chloroform and NaCl windows. The NMR spectrum was obtained from Bruker Data Systems spectrometer using $CDCl_3$ as solvent and reported as δ ppm relative to TMS.

UV (assignment): CHCl_3 , $\lambda = 270 \text{ nm}$, $\epsilon = 7.8 \times 10^4 (\pi \rightarrow \pi^*)$.

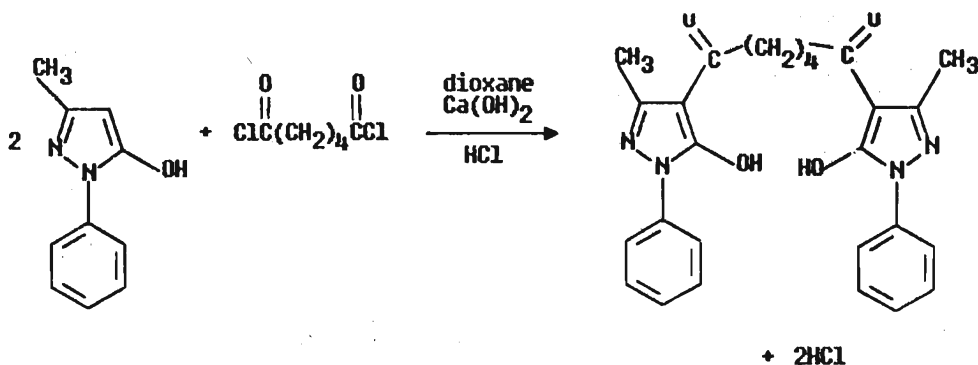
IR (assignment): 1620s ($\nu_{\text{as}} \text{C=O}$); 1596s, 1460m (phenyl ring $\nu \text{C=C}$); 1564s, 1392m; (pyrazole ring stretch); 1500m ($\nu_{\text{as}} \text{C-C-C}$); 1428m ($\beta_{\text{as}} \text{CH}_3$); 1364m ($\nu_{\text{s}} \text{C=O}$); 1304m ($\nu_{\text{s}} \text{C-C-C}$); 1192m, 1076s, 1028m (C-H in-plane deformation); 644w, 604w, cm^{-1} (chelate ring vibration).

NMR, δ (assignment): 1.88 (b, 4H, $-\text{CH}_2-\text{CH}_2\text{CO}-$); 2.49 (s, 6H, $-\text{CH}_3$); 2.83 (b, 4H, $-\text{CO}-\text{CH}_2-\text{CH}_2-$); 7.29 (s, 2H, pyrazole ring); 7.30 (t, 2H, $J = 7.45 \text{ Hz}$, p-Ph); 7.45 (t, 4H, $J = 8.0 \text{ Hz}$, m-Ph); 7.83 ppm (d, 4H, $J = 7.72 \text{ Hz}$, o-Ph).

MS, m/e (% assignment): 458 (6, M^+); 457 (25, M^+-1); 439 (13, $(\text{M}^+-1)-\text{H}_2\text{O}$); 229 (26, $\text{M}^+/2$); 201 ($\text{M}^+/2-\text{C}_2\text{H}_4$); 175 (79); 91 (37, $\text{C}_6\text{H}_5\text{N}^+$); 77 (75, C_6H_7^+).

DISCUSSION

The synthesis of 4-adipoylbis (1phenyl-3-methyl-pyrazolone-5) can be represented by the condensation reaction shown below.



The chelating agent can exist in the tautomeric forms given in Fig 2, already reported for 4-acylpyrazolones^{1,2,3}.

The ketoenol structures I and II presented in Fig. 2 are eliminated among the possible structures because the IR data did not have vibrational frequencies near 3100 cm^{-1} and 2700 cm^{-1} that are assigned¹¹ to νOH and $\nu \text{OH} \cdots \text{O}$ of ketoenol respectively. Proton NMR data presented also do not have any resonance signal near 11 ppm usually assigned¹¹ to OH group of the ligand. Absence of vibrational frequency bands in the $3100-4000 \text{ cm}^{-1}$ region which could be due to νNH also eliminates the diketone structure IV. That leaves the diketone structure III as the form in which 4-adipoylbis (1-phenyl-3-methyl-pyrazolone-5) is existing.

Structure III is supported by the very strong CO absorption band at 1620 cm^{-1}

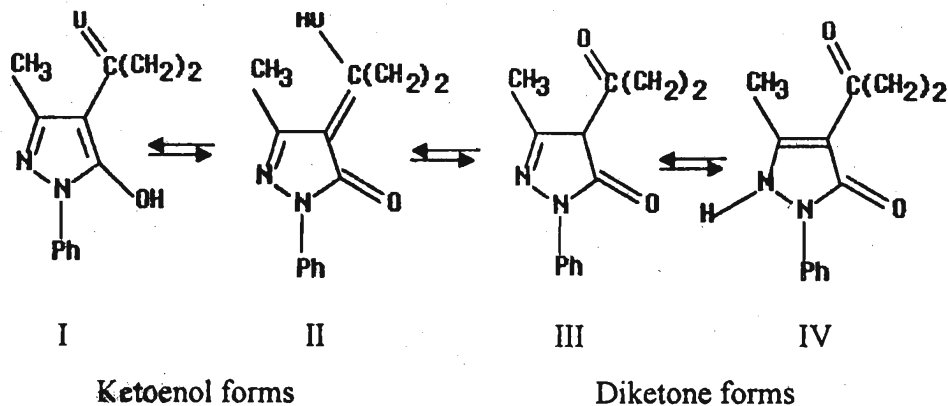


Figure 2 : Tautomeric forms of the ligand.

and another strong absorption band of equal intensity at 1564 cm^{-1} assigned to the pyrazole ring stretch. The chemical shift assignments, spectral integration and multiplicity of the resonance peaks all supported the bis(diketone) structure III presented in Fig 2. Further evidence of bis(diketone) structural form of 4-adipoylbis(1-phenyl-3-methylpyrazolone-5) is the presence of proton resonance signal as 7.29 ppm (integrated for 2H) due to the two CH- protons of the two pyrazole ring moieties of the ligand.

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