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APPLICATIONS OF SPECTROSCOPIC METHODS
TO PROBLEMS IN PYRROLE CHEMISTRY.

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CONTENTS

	Page.
<u>CHAPTER 1 - INTRODUCTION.</u>	
1.1. General	1
1.2. Infrared Spectroscopy and Hydrogen bonding	2
1.3. Electronic Absorption Spectra and Steric Effects	8
1.4. Colour and Constitution	12
<u>CHAPTER 2 - PYRROLES WITH ACYL SUBSTITUENTS.</u>	
2.1. Introduction	16
2.2. Preparation of Compounds	21
2.3. Results and Discussion	25
<u>CHAPTER 3 - PYRROLES WITH PHENYL SUBSTITUENTS.</u>	
3.1. Introduction	37
3.2. Preparation of Compounds	37
3.3. Results and Discussion	39
<u>CHAPTER 4 - THE NH STRETCHING FREQUENCIES AND ELECTRONIC SPECTRA OF ALKYL- AND ETHOXYCARBONYL-DIPYRRROMETHENES.</u>	
4.1. Introduction	43
4.2. Synthesis of Compounds	46
4.3. Measurement of the Spectra	50
4.4. Results and Discussion	52
<u>CHAPTER 5 - THE NH STRETCHING FREQUENCIES AND ELECTRONIC SPECTRA OF PHENYLDIPYRRROMETHENES.</u>	
5.1. Introduction	60

5.2.	Synthesis of Compounds	61
5.3.	Results and Discussion	63

CHAPTER 6 - 3,5,3',5'-TETRAARYLAZADIPYRROMETHENES.

6.1.	Introduction	72
6.2.	Preparation of Compounds	73
6.3.	Results and Discussion	75

CHAPTER 7 - A PRELIMINARY STUDY OF DIPYRROMETHENES WITH
meso-SUBSTITUENTS.

7.1.	Introduction	85
7.2.	Synthesis of <u>meso</u> -Substituted Dipyrromethenes.	86
7.3.	Results and Discussion	91

CHAPTER 8 - EXPERIMENTAL.

8.1.	Physical Measurements	99
8.2.	General	100
8.3.	Pyrroles	101
8.4.	Alkyl- and Ethoxycarbonyl- dipyrromethenes	134
8.5.	Phenyldipyrromethenes	144
8.6.	3,5,3',5'-Tetraarylazadipyrro- methenes	157
8.7.	Dipyrromethenes with <u>meso</u> - Substituents	164
8.8.	Miscellaneous	167

<u>REFERENCES.</u>	169
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SUMMARY.

The infrared spectra of a number of acylpyrroles have been examined in the NH and carbonyl stretching region under high resolution in carbon tetrachloride. Analysis of the data show that the effect of each group on the NH stretching frequency is independent of other substituents and additive, and for pyrroles containing methyl and acyl groups the NH stretching frequencies may be obtained from the following equations:

Acetyl Pyrroles

$$\nu_{\text{NH}} (\text{cm}^{-1}) = 3496 - 9n_{\alpha}\text{CH}_3 + 2n_{\beta}\text{CH}_3 - 45n_{\alpha}\text{COCH}_3 - 18n_{\beta}\text{COCH}_3$$

Benzoyl Pyrroles

$$\nu_{\text{NH}} (\text{cm}^{-1}) = 3496 - 9n_{\alpha}\text{CH}_3 + 2n_{\beta}\text{CH}_3 - 42n_{\alpha}\text{COPh} - 18n_{\beta}\text{COPh}$$

where n_{α} and n_{β} are the number of α and β substituents respectively. Pyrroles with β -acyl substituents show two concentration-independent bands and the weak lower frequency band is assumed to arise from interaction with the out-of-plane deformation of the NH group, producing a hot band. The carbonyl stretching frequency of an α -acylpyrrole is lower than the corresponding β -acylpyrrole and this is attributed to intramolecular hydrogen bonding with the NH group.

The NH stretching frequencies and electronic absorption spectra of pyrroles with phenyl substituents have also been examined, and the infrared data show that the NH stretching

frequency of a pyrrole with methyl and phenyl groups may be represented by the equation:

$$\nu_{\text{NH}} (\text{cm}^{-1}) = 3496 - 9n_{\alpha}\text{CH}_3 + 2n_{\beta}\text{CH}_3 - 12n_{\alpha}\text{Ph} - 7n_{\beta}\text{Ph}$$

In the NH stretching region a second band was observed for the majority of phenylpyrroles and is assumed to be a hot band by analogy with the β -acylpyrroles. Deviations from the calculated NH frequencies are small and suggest that steric interactions between adjacent phenyl groups are accommodated by slight deviation of the phenyl rings from coplanarity with the pyrrole ring, and the electronic spectra indicate that some rotation of adjacent phenyl groups occurs.

The NH stretching frequencies and electronic spectra of twenty-one alkyl- and ethoxycarbonyl-dipyrromethenes and twenty-two phenyldipyrromethenes have been measured and the results correlated with the electronic and steric effects of the substituents. It is suggested that there is some steric interaction between the two ethoxycarbonyl groups of 3,3'-diethoxycarbonyl-4,5,4',5'-tetramethyldipyrromethene, that interaction between two phenyl groups in the 3,3'-positions is accommodated by twisting of the phenyl rings with little or no distortion of the dipyrromethene skeleton. The effect of unsymmetrical substitution on the NH frequency is also discussed.

Twenty-one tetraarylazadipyrromethenes have been prepared and their electronic spectra measured. The spectra

indicate that protonation of the tetraarylazadipyrromethenes occurs on the heterocyclic nitrogen atom and not the meso-nitrogen atom. In addition, the spectra show that steric interaction of 3- and 3'-aryl substituents does not result in distortion of the azadipyrromethene skeleton, although this may occur when 3,3'-p-dimethylaminophenyl substituents are present.

Finally, a preliminary investigation of meso-substituted dipyrromethenes has been made. The spectra of the meso-phenyldipyrromethenes suggest that the protonated species is more crowded than the base, and it is postulated that the strain is relieved by reducing the central methine bond angle in the bases and twisting around the methine bridge bonds in the salts. The accurate measurement of the spectra of meso-alkyldipyrromethene bases is difficult due to the ease with which they tautomerize to the ethylenic form.
