

chelating sulfato groups—around the linear OUO group.

Registry No. $\text{UO}_2(\text{phen})\text{SO}_4$, 42565-88-8; $\text{UO}_2(2,2'\text{-bpy})\text{SO}_4$, 40415-75-6; $\text{UO}_2(2,2'\text{-bpyO}_2)\text{SO}_4$, 50989-29-2; $\text{UO}_2(4,4'\text{-bpy})\text{SO}_4$, 51024-41-0; $\text{UO}_2(2,2'\text{-bpyA})_2\text{SO}_4$, 63162-30-1; $\text{UO}_2(4,4'\text{-bpyO}_2)_2\text{SO}_4$, 96789-83-2; $\text{UO}_2(\text{MP})\text{SO}_4$, 76772-31-1; $\text{UO}_2(\text{Q})_2\text{SO}_4$, 73689-28-8; $\text{UO}_2(\text{DMQ})_2\text{SO}_4$, 73700-17-1; $\text{UO}_2(\text{HMTA})_2\text{SO}_4$, 71769-14-7; $\text{UO}_2(\text{DPP})\text{SO}_4$, 60647-93-0; $\text{UO}_2(\text{MBT})\text{SO}_4$, 68229-42-5; $\text{UO}_2(\text{NA})_2\text{SO}_4$, 67799-02-4.

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Spectroscopic Study of Some New *N*-Aryl Pyrroles

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A series of new 2,5-dimethyl-*N*-substituted pyrroles (I) were obtained by condensation of 2,5-hexanedione with different amines. The UV data show that about 11.7% of the total electronic density of the nitrogen of pyrrole ring is conjugated with the aryl group. A correlation between the UV and NMR results has been established, and the mass spectra of these derivatives have also been measured and discussed.

Introduction

It is well-known that alkylated and *N*-alkylated pyrroles were obtained from condensation between 2,5-hexanedione and amines (1). The UV (1, 2), IR, and NMR spectra (1, 3) and mass fragmentation (1, 4, 5) of pyrrole and some of its derivatives have been investigated previously. Our *N*-substituted pyrroles series allows us to establish a correlation study between the UV and NMR, a study not previously attempted on pyrroles. The mass spectra of these derivatives have also been measured.

Results and Discussion

The position of CH_3 groups in the NMR spectra (Table I) of Ib ($\delta = 2.008$) and Id ($\delta = 1.930$) are shifted to a higher field compared with that of Ia ($\delta = 2.090$) owing to the conjugation of the nitrogen electron pair with the π -conjugated system of the phenyl ring. *N*-Aryl substitution causes a red shift of the long UV band (Table I) by about the same amount, 28 ± 3 nm, which probably means that only $28/240 = 0.117$ or 11.7% of the total electronic density of the nitrogen electrons is conjugated with the aryl ring.

The long UV bands of all compounds are red-shifted in concentrated sulfuric acid by the same amount (Table I); in this medium withdrawal of the nitrogen electron lone pair should

Table I. ^1H NMR Data and UV Absorption Bands of 2,5-Dimethyl-*N*-substituted Pyrroles in Ethanol and Concentrated Sulfuric Acid

molecule	NMR data			UV bands [λ_{max} , nm (log ϵ , $\text{m}^2 \text{mol}^{-1}$)]	
	δ , ppm	intens	multipl	EtOH	concd H_2SO_4
pyrrole ^a				240 (2.48) 210 (3.70)	
Ia	0.84 1.61 2.09 3.55 5.62	3 2 6 2 2	triplet sextet singlet triplet singlet	226 (2.10) ^b 208 (2.30)	242 (2.46) 202 (2.21)
Ib	2.008 5.88 7.20-7.33	6 2 5	singlet singlet complex	264 (2.31) 230 (3.05) ^b 213 (2.23)	284 (2.73) 240 (2.86) 205 (3.12)
Ic	2.010 3.85 5.87 6.91-7.23	6 3 2 4	singlet singlet singlet complex	271 (2.04) ^b 234 (3.03) 209 (3.02)	294 (2.51) 235 (2.64) ^b 222 (2.70)
Id	1.93 5.79 6.88-6.98 7.23-7.32	6 2 2 2	singlet singlet doublet doublet	266 (2.40) 243 (3.03) 218 (3.28)	288 (2.72) 242 (2.83) 219 (3.07)
Ie				270 (3.23) 204 (3.16)	291 (3.35) 208 (2.90)

^aFrom ref 2. ^bShoulder.

occur and the spectrum may represent a charged aminodiene (6).

The mass spectra of compounds Ia-e are shown in Table II in the form of relative intensities vs. m/z .

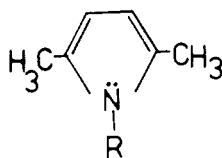
Experimental Section

Compound Ia (Figure 1) was prepared by refluxing, for 90 min equimolar amounts of *n*-propylamine and 2,5-hexanedione;

Table II. *m/z* of Major Peaks with Their Relative Intensities Observed in the Mass Spectra of Compounds Ia-e^a

Ia		Ib		Ic		Id		Ie			
<i>m/z</i>	rel intens	<i>m/z</i>	rel intens	<i>m/z</i>	rel intens	<i>m/z</i>	rel intens	<i>m/z</i>	rel intens	<i>m/z</i>	rel intens
39	14	51	15	39	5	39	7	39	18	121	9
41	24	77	23	63	5	50	5	41	14	128	11
42	21	115	5	64	5	51	10	42	11	129	5
43	7	128	9	65	5	52	6	50	6	130	10
51	8	129	6	77	8	53	7	51	26	131	7
52	8	130	5	92	5	72	5	52	7	132	5
										141	6
53	14	154	10	100	8	75	15	53	16	143	6
54	13	156	11	117	6	77	6	55	5	144	18
55	6	168	5	145	22	83	14	56	5	146	58
65	7	170	100	154	6	84	7	63	7	147	10
66	6	171 ^c	79	156	5	111	14	65	9	154	24
67	14	172	10	159	7	113	5	66	5	155	5
77	7			160	5	127	5	67	5	156	18
79	7			186	20	128	7	76	5	157	9
80	9			200	65	129	26	77	48	158	21
92	7			201 ^c	100	154	25	78	10	159	5
93	9			202	16	155	10	79	9	167	33
94	71					167	8	80	5	168	68
95	24					168	13	81	13	169	16
106	6					169	17	83.5 ^b	14	170	26
107	8					170	5	89	8	171	5
108	100					190	10	90	8	172	21
109	37					204	100	90.5 ^b	9	180	9
120	6					205 ^c	95	91	11	181	10
122	23					206	45	91.5 ^b	8	182	48
136	35					207	34	92	8	183	22
137 ^c	82									184	11
138	11									186	43
										187	5
										196	24
										200	37
										201 ^c	100
										202	38
										100	8
										103	5
										104	5
										105	29
										115	11
										116	5
										117	9
										118	10
										119	8

^a Peaks less than 5% are not included. ^b Doubly charged ion. ^c Parent peak.



Ia: R = n-C₃H₇

b: R = C₆H₅

c: R = C₆H₄(p-OCH₃)

d: R = C₆H₄(p-Cl)

e: R = C₆H₄(o-CH₂OH)

Figure 1. Structure of 2,5-dimethyl-N-substituted pyrroles.

the mixture was then fractionally distilled twice under reduced pressure and the fraction which boiled at 40 °C/0.3 torr was collected.

The other compounds, Ib-e, were prepared by refluxing equimolar amounts of the corresponding amine and the dione for 6 h. On freezing, a colorless to light brown crystalline product precipitated in every case; the precipitate was filtered and purified by sublimation under reduced pressure. Ib had mp

48-49 °C; Ic, 60-61 °C; Id, 46-48 °C; Ie, 105-107 °C. All the compounds gave satisfactory elemental analyses. The measurements of the spectra are discussed elsewhere (7, 8).

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Registry No. Ia, 20282-39-7; Ib, 83-24-9; Ic, 5044-27-9; Id, 5044-23-5; Ie, 97690-10-3.

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