Dielectric Relaxation and Dipole Moments of Substituted Pyrroles

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The electric permittivities of 17 pyrroles have been measured in benzene and 1,4-dioxan solutions at one radio and two microwave frequencies. Their dielectric relaxation is discussed in terms of the size and possible internal rotations of the solute molecules. One conclusion drawn, that internal rotation in 2-acylpyrroles is negligible, is supported by n.m.r. evidence. Their electric dipole moments in benzene solutions at 25·0 °C are analysed in terms of component moments and it is concluded that 2-acylpyrroles and similar molecules exist in a *syn*-conformation. In 1,4-dioxan solutions the apparent increments in the electric dipole moments of pyrroles with a free N–H indicate the presence of hydrogen bonding to the solvent.

DIELECTRIC relaxation in solution occurs by overall molecular tumbling and also, with some molecules, by an internal relaxation process. Appropriate dielectric measurements on solutions of substituted pyrroles can show if a polar substituent is rotating around the bond linking it to the pyrrole ring. This information, together with an analysis of their electric dipole moments, can then indicate the molecular conformations in solution. A comparison between the results obtained in benzene and 1,4-dioxan solutions further shows if there is hydrogen bonding to dioxan molecules.

EXPERIMENTAL AND RESULTS

For each solute measurements were made at 25·0 °C upon seven dilute solutions in the relevant solvent. Electric permittivities at a radiofrequency (0·5 MHz), refractive indices to Na(D) radiation (5×10^8 MHz), and specific volumes of the solutions were measured as described previously.[1] The range of weight fractions employed was generally 0·001 to 0·016. Table 1 lists the slopes † α_0, α_D, and β respectively of the linear graphs of electric permittivity, refractive index squared, and specific volume against weight fraction and in Table 2 are the polarization data and the dipole moments (μ_R) computed by standard methods.[1]

Electric permittivities of the solutions at *X*- and *K*-band frequencies were obtained from the absorption of microwave radiation by the solutions placed in a length of waveguide. The method used was as described [2] with one improvement. An amplifier of much greater sensitivity was employed so that the residual standing-wave ratio (s_0), when the short circuit plunger was in contact with the mica window, could be measured directly. This was subtracted from the ratio measured with the plunger set to an integral number of half-wavelengths in the liquid and its ε' and ε'' values were computed for this particular length of solution. This was repeated for 7 different depths of each solution and the mean of the experimental ε' and ε'' values taken. The accuracy and reproducibility of the results was increased significantly compared with the previous procedure. The slopes of the linear graphs of ε' and ε'' for each solution against its weight fraction, α' and α'' respectively, are also in Table 1. For low-loss compounds maximum weight fractions as high as 0·02 (*X*-band) and 0·05 (*K*-band) were employed but with higher-loss materials they did not exceed 0·01. Dielectric relaxation times (τ_K and τ_X), Debye behaviour being assumed, and electric dipole moments (μ_K and μ_X) were evaluated by the various methods already described [2] and the most likely values are in Table 2.

Pyrrole-2-carbaldehyde and 2-benzoylpyrrole associated slightly in dilute benzene solution so that the plot of radiofrequency electric permittivity against weight fraction was not quite linear. The limiting gradients at infinite dilution were employed in the calculations; this procedure was not adopted with the literature values quoted in Table 2 which accounts for the 0·3 D difference between the dipole moments.

Preparation and Purification of Compounds.—The purification of the two solvents has been described.[3] Each compound was finally purified immediately before its solutions were prepared and physical measurements made. Their purity was checked by t.l.c. or g.l.c. and only accepted if >99·9% pure. Pyrrole (B.D.H.), purified *via* its potassium salt and dried and fractionated, had b.p. 130°/760 mmHg. 1-Methylpyrrole (Koch–Light) was refluxed over potassium hydroxide and then fractionated, and had b.p. 113°/760 mmHg. 2-Methylpyrrole from the reduction of pyrrole-2-carbaldehyde semicarbazone [4] was dried ($CaSO_4$) and fractionated and had b.p. 148°/760 mmHg. The aniline salt of mucic acid was pyrolysed [5] to give 1-phenylpyrrole which was purified by steam distillation and recrystallised from light petroleum to m.p. 62°. Heating of this compound over a red-hot wire to 230—275° gave 2-phenylpyrrole [6] which was fractionated and repeatedly crystallised

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† Detailed experimental results are available from the authors or from the Ph.D. Thesis of J. W. M. Wood, London University, 1970.

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from aqueous alcohol and precipitated from toluene with light petroleum; it had m.p. 130°. 2,3,4,5-Tetraphenylpyrrole, prepared by condensation of benzoin, ammonia, and benzyl phenyl ketone,[7] was precipitated with water and recrystallised (m.p. 214°) from ethanol. 1,2,4-Triphenylbutane-1,4-dione, from benzoin and acetophenone, was condensed with aniline [8] and the product, 1,2,3,5-tetraphenylpyrrole, recrystallised from glacial acetic acid, had m.p. 197°. 2,3,4,5-Tetraiodopyrrole [9] was recrystallised from alcohol and from aqueous acetone. The purity was checked by t.l.c. since it decomposes on heating. Pyrrole was nitrated with fuming nitric acid in acetic anhydride at −50° to give 2-nitropyrrole [10] which was chromatographed over alumina and recrystallised from light petroleum and from chloroform–light petroleum and had m.p. 66·5°. Pyrrole-2-aldehyde [11] (m.p. 45°), 1-methylpyrrole-2-carbaldehyde [11] (b.p. 75°/11 mmHg), 2-acetylpyrrole [11] (m.p. 90°), methyl pyrrole-2-carboxylate [12] (m.p. 71°), and 2-benzoylpyrrole [12] (m.p. 79°) were prepared by methods in the literature. Methyl pyrrole-2-carboxylate was hydrolysed and allowed to react with phosphorus pentachloride to give pyrrole-2-carbonyl chloride and then with anhydrous dimethylamine to form NN-*dimethylpyrrole*-2-*carboxamide*. The amide was recrystallised from light petroleum to m.p. 100° (Found: C, 60·9; H, 7·2; N, 20·5. $C_7H_{10}N_2O$ requires C, 60·9; H, 7·3; N, 20·3%).

3-*Acetylpyrrole*.—Pyrrolemagnesium bromide reacts with acetyl chloride to give the 2-isomer and a small quantity of 3-acetylpyrrole which can be separated by fractionation;[13] 2-acetylpyrrole, b.p. 122—132°/24 mmHg; 3-acetylpyrrole, b.p. 184—189°/24 mmHg. The product was recrystallised from benzene and had m.p. 115°. Methyl pyrrole-3-carboxylate was obtained by the condensation of *N*-ethoxycarbonylglycine ethyl ester with ethyl acrylate [14] followed by methylation, hydrolysis, and methylation with diazomethane.[15] The product was sublimed under vacuum and recrystallised from carbon tetrachloride and had m.p. 87°.

TABLE 1

Slopes of the graphs of electric permittivities (α) and specific volumes (β) against solute weight fraction at 25·0°

		Waveband							
		X-band			*K*-band				
Pyrrole	Radio α_0	GHz	α_X'	α_X''	GHz	α_K'	α_K''	Optical α_D	β
Benzene solution									
Pyrrole	$5{\cdot}37_9$	9·82	5·00	1·37	24·30	3·59	2·46	0·060	−0·123
1-Methyl-	$5{\cdot}09_2$	9·89	4·60	1·55	24·23	2·87	2·61	−0·030	−0·039
2-Methyl-	$5{\cdot}12_5$	9·83	4·33	1·87				0·036	−0·078
1-Phenyl-	$1{\cdot}64_9$	9·82	0·73	0·63				0·276	−0·199
2-Phenyl-	$2{\cdot}44_1$	9·81	2·28	1·00				0·361	−0·240
2,3,4,5-Tetraphenyl-	$1{\cdot}36_5$	9·78	0·65	0·12				0·617	−0·319
1,2,3,5-Tetraphenyl-	$1{\cdot}72_3$							0·524	−0·321
2,3,4,5-Tetraiodo-	$1{\cdot}49_7$	9·79	0·52	0·45				0·272	−0·893
2-Nitro-	$18{\cdot}4_5$	9·81	11·0	8·51	24·00	4·88	7·06	0·260	−0·379
-2-carbaldehyde	$5{\cdot}61_8$	9·83	4·33	2·11				0·228	−0·293
2-Acetyl-	$3{\cdot}51_8$	9·82	2·46	1·44				0·255	−0·253
2-Benzoyl-	$2{\cdot}50_8$	9·79	1·41	0·85	23·91	0·91	0·50	0·438	−0·291
1-Methylpyrrole-2-carbaldehyde	$8{\cdot}10_5$	9·82	5·77	3·28	24·19	2·58	3·25	0·131	−0·232
Methyl pyrrole-2-carboxylate	$2{\cdot}76_9$	9·83	1·91	1·04	24·22	1·06	0·81	0·075	−0·309
NN-Dimethylpyrrole-2-carboxamide	$3{\cdot}50_9$	9·82	2·47	1·19	24·22	1·54	0·85	0·170	−0·280
3-Acetyl-	$25{\cdot}6_6$	9·84	12·56	8·71	24·19	6·06	6·59	0·263	−0·320
Methyl pyrrole-3-carboxylate	$11{\cdot}4_4$	9·84	5·60	4·17	24·19	2·46	2·70	0·218	−0·370
1,4-Dioxan solution									
Pyrrole	$8{\cdot}49_2$	9·83	6·13	3·64				0·292	0·064
1-Methyl-	$6{\cdot}27_4$	9·81	4·69	2·72				0·218	0·127
2-Methyl-	$7{\cdot}86_3$	9·92	3·73	3·58				0·290	0·070
1-Phenyl-	$2{\cdot}06_5$	9·82	0·71	0·48				0·538	−0·047
2-Phenyl-	$3{\cdot}71_2$	9·82	1·05	0·99				0·646	−0·079
2,3,4,5-Tetraphenyl-	$2{\cdot}07_3$							0·823	−0·124
2,3,4,5-Tetraiodo-	$2{\cdot}36_0$	9·79	0·61	0·43				0·332	−0·719
2-Nitro-	$23{\cdot}5_7$	9·82	6·71	9·02	23·90	2·94	4·45	0·532	−0·286
-2-carbaldehyde	$8{\cdot}83_0$	9·79	2·92	3·74				0·465	−0·120
2-Acetyl-	$4{\cdot}68_7$	9·78	1·32	1·65				0·395	−0·053
2-Benzoyl-	$3{\cdot}12_9$	9·78	1·22	0·61	24·15	1·05	0·30	0·606	−0·135
Methyl pyrrole-2-carboxylate	$3{\cdot}79_7$	9·79	1·23	1·03				0·299	−0·148
NN-Dimethylpyrrole-2-carboxamide	$4{\cdot}78_9$	9·82	2·25	1·33	24·08	1·61	0·89	0·375	−0·103
3-Acetyl-	$31{\cdot}2_2$							0·448	−0·135
Methyl pyrrole-3-carboxylate	$14{\cdot}7_5$							0·350	−0·158

RESULTS AND DISCUSSION

I. *Dielectric Relaxation in Benzene and* 1,4-*Dioxan Solutions*.—The experimental relaxation times are compared in Table 3 with estimated values for overall mole-

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TABLE 2

Polarization data and electric dipole moments (μ) at radiofrequencies and dipole moments and relaxation times at microwave frequencies and 25·0 °C

	Radio frequency †			Microwave frequencies				Dipole moment (ref. 28)
Pyrrole	$_\infty P_2$/cm^3	R_D/cm^3	μ_R/D	μ_X/D	μ_K/D	τ_X/ps	τ_K/ps	
Benzene solution								
Pyrrole	88·25	20·85	1·82	1·81	1·80	4·5	4·6	1·80, 1·85
1-Methyl-	104·4	25·82	1·96	1·96	1·98	5·4	5·8	1·92
2-Methyl-	103·9	25·91	1·95	1·96		7·0		1·89
1-Phenyl-	84·76	47·29	1·36	1·32		22·5		1·32
2-Phenyl-	104·3	47·82	1·66	1·63		16·3		
2,3,4,5-Tetraphenyl-	186·7	133·5	1·61	1·59		78		
1,2,3,5-Tetraphenyl-	211·5	126·8	2·04					
2,3,4,5-Tetraiodo-	203·4	71·70	2·54	2·46		33·3		2·52
2-Nitro-	414·2	30·69	4·33	4·25	4·22	13·1	12·8	
-2-carbaldehyde	124·6	27·87	2·18	2·12		8·2		1·88
2-Acetyl-	101·2	33·84	1·82	1·64		10·8		
2-Benzoyl-	124·2	57·10	1·81	1·64	1·66	21·0	21·2	1·52
1-Methylpyrrole-2-carbaldehyde	196·7	31·90	2·84	2·77	2·63	11·1	11·2	
Methyl pyrrole-2-carboxylate	92·28	32·41	1·77	1·56	1·55	13·5	13·9	1·70
NN-Dimethylpyrrole-2-carboxamide	126·7	39·48	2·07	1·75	1·72	14·2	15·2	
3-Acetyl-	553·0	31·84	5·03	4·22	3·65	10·8	8	
Methyl pyrrole-3-carboxylate	297·9	33·63	3·60	3·16	3·51	12·5	8·0	3·63
1,4-Dioxan solution								
Pyrrole	113·8	21·12	2·13	2·09		10·2		1·97, 2·15
1-Methyl-	109·4	25·80	2·02	2·01		9·6		
2-Methyl-	129·3	26·68	2·25	2·16		16·0		
1-Phenyl-	86·80	47·58	1·39	1·32		43		
2-Phenyl-	124·3	49·20	1·92	1·84		44		
2,3,4,5-Tetraphenyl-	217·4	135·4	2·00					
2,3,4,5-Tetraiodo-	263·4	71·13	3·07	3·00		70		
2-Nitro-	457·0	30·31	4·57	4·42	4·41	30·2	30·9	
-2-carbaldehyde	161·6	38·58	2·55	2·50		24·8		2·42
2-Acetyl-	113·1	33·26	1·98	1·83		29		1·79
2-Benzoyl-	129·5	55·16	1·91	1·70	1·71	51	46	
Methyl pyrrole-2-carboxylate	108·0	32·96	1·92	1·73		40		
NN-Dimethylpyrrole-2-carboxamide	143·4	39·87	2·25	1·80	1·95	30	24	
3-Acetyl-	587·2	32·02	5·21					
Methyl pyrrole-3-carboxylate	333·2	33·77	3·83					

† $_\infty P_2$ = molar polarization of solute at infinite dilution. R_D = molar refraction of solute.

TABLE 3

Structure factor (f), calculated Fischer relaxation time in benzene solution (τ_F), and experimental results

		Benzene soln.		Dioxan soln.	
Pyrrole	f	τ_F	τ_{exp}	τ_{exp}	$\tau_{dioxan} : \tau_{benzene}$
Pyrrole	1·09	4·5	4·5	10·2	2·26
1-Methyl-	1·12	5·3	5·6	9·6	1·71
2-Methyl-	1·11	5·6	7·0	16·0	2·29
1-Phenyl-	1·15	15	22·5	43	1·91
2-Phenyl-	1·17	12	16·3	44	2·70
2,3,4,5-Tetraphenyl-	1·19	38	78		
2,3,4,5-Tetraiodo-	1·30	19	33	70	2·12
2-Nitro-	1·24	11	13·0	30·2	2·31
-2-carbaldehyde	1·20	9·6 *	8·2	24·8	3·02
2-Acetyl-	1·21	12 *	10·8	29	2·68
2-Benzoyl-	1·13	21 *	21·1	48	2·28
1-Methylpyrrole-2-carbaldehyde	1·20	10 *	11·1		
Methyl pyrrole-2-carboxylate	1·20	12·5 *	13·7	40	2·92
NN-Dimethylpyrrole-2-carboxamide	1·10	14·5	14·7	(27)	(1·84)
3-Acetyl-	1·24	12·5	†		
Methyl pyrrole-2-carboxylate	1·37	15	†		

* Calculated on the assumption that the mesomeric moment acts midway between C=O and the C–C bond attaching the group to the pyrrole ring and with the conformations suggested in Part II. The calculated relaxation times are not very sensitive to the molecular conformation. † Large departures from Debye behaviour.

cular tumbling as given by the Fischer equation [16] ($\tau_F = 4\pi\eta fabc/kT$), it being assumed that the microscopic viscosity η is 0·23 times the macroscopic value for the solvent.[17] The lengths of the semiaxes *a*, *b*, and *c* of the molecules' enveloping ellipsoid were obtained from molecular models and the values of the structure factor *f* obtained from them [18] are recorded. For many of the pyrroles the agreement between these values is reasonable, indicating that the molecules are relatively rigid.

Benzene solution. The Fischer relaxation time for 2,3,4,5-tetraphenyl- and -tetraiodo-pyrroles is only about half the experimental value because the empirical factor of 0·23 is too small for solute molecules so much larger than those of the solvent. The predicted relaxation times for 1- and 2-phenylpyrroles are also slightly low; for all the phenylpyrroles the structure factors *f* in Table 3, and hence the τ_F values, are probably low since the molecules are unlikely to be planar (*cf.* structures of biphenyl and bipyridyl [19]).

The agreement for all the compounds with polar substituents in the 2-position is good, implying that any contribution from a second (internal) relaxation process is small. Such contributions would have been expected had the substituent been capable of rotation around the bond linking it to the pyrrole ring. The energy barrier inhibiting such a rotation is evidently sufficiently high effectively to prevent its occurring and the molecules probably exist in only one of the two possible planar molecular conformations. This is to be contrasted with the behaviour displayed by the last two compounds in Table 3 which have substituents in the 3-position; their dielectric characteristics show such large departures from Debye behaviour that single relaxation times cannot be calculated. Evidently dielectric relaxation is occurring by an internal rotation mechanism in addition to molecular tumbling. Analogous conclusions have been obtained [20] from dielectric studies on some benzene and pyridine compounds with polar substituents. Of the compounds investigated only for pyridine-2-carbaldehyde and 2-acetylpyridine was it possible to analyse the results in terms of a single relaxation process; the remainder of the compounds had two distinct relaxation times, one of *ca.* 12 ps for overall molecular rotation and the other of *ca.* 1 ps for an internal process.

Confirmation of the above conclusions is provided by Table 4 which gives the results from a Cole–Cole plot of the data for 9 of the compounds. The accuracy is not high since three points are only just sufficient to fix the positions of the arcs, but only for 3-acetylpyrrole and methylpyrrole-3-carboxylate was there definitely a non-zero value for the Cole distribution parameter γ. A finite value for γ shows that the relaxation cannot be described by a single mechanism. In many cases the extrapolated ε_∞ value from the Cole–Cole curve, though very approximate, is significantly greater than the ε_D value measured directly with Na(D) light. This could arise from a higher-frequency absorption, as would ensue from an internal relaxation, or from the presence of a particularly high atom polarization as almost certainly exists in 2-nitropyrrole. There was no evidence in either solvent for a high-frequency internal relaxation in 2-benzoylpyrrole of the type present in benzophenone.[21] *NN*-Dimethylpyrrole-2-carboxamide exhibited Debye behaviour in benzene solution but the extrapolated ε_∞ value seems to be too large; it is suspected that there may be a second absorption region at higher frequencies associated with a very short relaxation time, owing to inversion of the nitrogen atom, which is known to occur in many amides. The ^{1}H n.m.r. spectra at 40° (Varian A60A spectrometer) of the 2-substituted pyrroles in CCl_4 or $CDCl_3$ solution gave no indication that alternative molecular conformations were present. With methylpyrrole-3-carboxylate (5% solution in $CDCl_3$ at −40 to +40°) the chemical shifts of the pyrrole hydrogen atoms adjacent to the ester groups are temperature-dependent indicating that there is an inhibited rotation of this group; the proton on C(5) is sufficiently remote from the ester substituent for its signal to be independent of temperature. Unlike dimethylformamide [22] only one n.m.r. signal is given by the methyl groups in *NN*-dimethylpyrrole-2-carboxamide; it is unlikely that this arises from a rapid rotation about the C–N bond but another possibility, that the methyls are symmetrically situated on either side of the C_4H_4N–CO–N molecular plane would not have been expected.

TABLE 4

Cole–Cole equation: extrapolated α_0 value, mean relaxation time (τ_0), and distribution parameter (γ)

Pyrrole	Optical α_D	Cole–Cole equation α_∞	τ_0	γ
Benzene solution				
Pyrrole	0·060	0·30	4·8	0
1-Methyl-	−0·030	−0·18	5·6	0
2-Nitro-	0·260	1·15	12·7	0
2-Benzoyl	0·438	0·75	21	0
1-Methyl pyrrole-2-carbaldehyde	0·131	0·05	11	0·02
Methyl pyrrole-2-carboxylate	0·075	0·69	14	0
NN-Dimethylpyrrole-2-carboxamide	0·170	1·21	15	0
3-Acetyl-	0·263	0·86	(21)	0·22
Methyl pyrrole-3-carboxylate	0·218	0·93	(24)	0·14
1,4-Dioxan solution				
2-Nitro-	0·532	2·06	30·6	0
2-Benzoyl	0·606	0·99	48	0·02
NN-Dimethylpyrrole-2-carboxamide	0·375	1·14	26	0·14

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1,4-Dioxan solution. The empirical equation $\tau = A\eta^x$ has been found [23] to express the variation of relaxation time with viscosity η. In general the power x increases with the size of the solute molecule to a limiting value of unity for large solute molecules, when the relationship becomes equivalent to the Debye expression. The viscosities of benzene and dioxan at 25·0 °C are 0·599 and 1·170 cP respectively so that the ratio τ_{dioxan} : τ_{benzene} should be <2. For the compounds studied this was only the case (Table 3) for three solutes, two of which were substituted at the nitrogen atom. In the remaining 9 cases examined this ratio was significantly greater owing to hydrogen bonding between the pyrrolic hydrogen atom and 1,4-dioxan solvent molecules. This association might increase the effective size of the rotating unit in solution but the effect is more likely due to a ' time lag ' in breaking the hydrogen bonds which thereby reduces the angular velocity of the solute molecules. Similar results have been reported for amines [24] though with these compounds the situation is complicated by the existence of two dispersion regions.

The $\tau_{\text{dioxan}} : \tau_{\text{benzene}}$ ratio of 1·84 for *NN*-dimethylpyrrole-2-carboxamide is based on a relaxation time in dioxan given by the Cole–Cole equation. In benzene solution a second absorption was suspected at higher frequencies and in dioxan there was definite evidence of this. The relaxation time for molecular tumbling in dioxan is consequently greater than 27 ps and the above ratio is too low. There was no measurable absorption by 2,3,4,5-tetraphenylpyrrole in 1,4-dioxan at the frequencies employed because the relaxation time (*ca.* 2 × 78 ps) was too long.

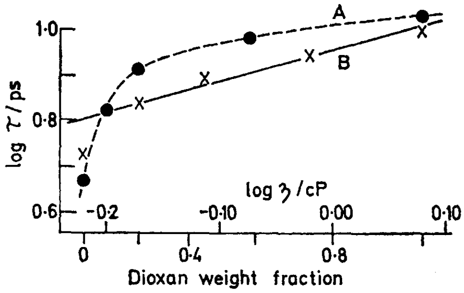

FIGURE 1 Relaxation times of A, pyrrole; and B, 1-methylpyrrole as a function of the viscosity of benzene–1,4-dioxan solutions at 25·0 °C

Confirmation of a solute solvent interaction in 1,4-dioxan was obtained from measurements made in mixed benzene–dioxan solvents. For 1-methylpyrrole, where there is no specific interaction, all the results were of the Debye type, indicating one dispersion region, and the plot of log τ against log η (Figure 1) was linear with slope $x \approx 0{\cdot}6$. For pyrrole itself, however, the Cole–Cole plots in each mixed solvent indicated fairly large distribution parameters with a range of relaxation times and the plot of log τ_0 against log η was far from being linear.

II. *Electric Dipole Moments and Molecular Conformations in Benzene Solution.*—The dipole moments determined at the radiofrequency (μ_{R} in Table 2) are used in this discussion. The geometrical structure of the gaseous pyrrole molecule has been determined by microwave spectroscopy [25] and will be employed in the following analysis, substituted pyrroles being considered to have a bond in the same direction as the replaced C–H or N–H bond.

It is not possible to predict the dipole moment of pyrrole itself since the N–H and C–N bond moments are sensitive to the hybridization of the nitrogen atom and the π-electron moment cannot be predicted accurately. One scheme of bond moments [26] leads to a calculated σ bond moment of 0·32 D, in which case that due to π-bonding would be 1·5 D.

Bond moments quoted in the following discussion are positive in the sense A $\leftarrow\!\!\!+$ B and act along the bond direction unless stated otherwise. The dipole moment of pyrrole itself acts along its symmetry axis in the H–N direction.

Methylpyrroles. If the replacement of the C(2)–H bond by C–Me introduces a group moment of −0·30 D [26] the predicted dipole moment of 2-methylpyrrole is 1·95 D, in exact agreement with the experimental value. If the N–H and N–Me moments are taken as −1·28 D (from NH_3) and −0·83 D (from NMe_3) [26] the predicted dipole moment of 1-methylpyrrole is 1·82 − (1·28 − 0·83) = 1·37 D, 0·59 less than the experimental value. This could be due to the component moments not being appropriate to a planar nitrogen atom but the result is not inappropriate for an increase in the π-electron moment of the molecule (*cf.* toluene has a dipole moment [27] of 0·37 D).

Phenylpyrroles. The two rings in biphenyl and bipyridyls are not coplanar [19] in solution, mainly owing to steric interactions. Geometrical considerations show that analogous steric interactions would be less important in 1- and 2-phenylpyrroles and the dihedral angle between the two rings smaller. Significant mesomeric moments, acting *into* the phenyl rings, would be expected. Vector analysis of the experimental dipole moments requires an extra component of either 0·62 to 0·85 D in the C(2)–Ph direction in 2-phenylpyrrole and of 0·46 D in the N–Ph direction in 1-phenylpyrrole. In the latter molecule one factor contributing to these values is the difference between N–H and N–C bond moments but in both compounds there must be a mesomeric moment.

At first sight the dipole moments of the two tetraphenylpyrroles are unexpected. There are considerable steric interactions twisting the phenyl residues out

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[23] K. Chitoku and K. Higasi, *Bull. Chem. Soc. Japan*, 1963, **36**, 1064.

[24] K. Chitoku and K. Higasi, *Bull. Chem. Soc. Japan*, 1966, **39**, 2160.

[25] B. Bak, D. Christensen, L. Hansen, and J. Rastrup-Andersen, *J. Chem. Phys.*, 1956, **24**, 720.

[26] C. W. N. Cumper, *Tetrahedron*, 1969, **25**, 3131.

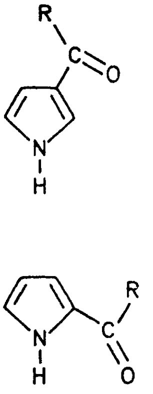
[27] C. W. N. Cumper, A. I. Vogel, and S. Walker, *J. Chem. Soc.*, 1957, 3640.

of the pyrrole plane, particularly for those sandwiched between adjacent phenyl rings. If, because of this, the mesomeric moments associated with the phenyl groups in the 3- and 4-positions in 2,3,4,5-tetraphenylpyrrole are negligible compared with those for the 2- and 5-positions it is understandable that its dipole moment (1·61 D) is less than that of pyrrole itself (1·82 D). Likewise, in 1,2,3,5-tetraphenylpyrrole steric effects reduce the mesomeric moments associated with the phenyl groups in positions 1 and 2 to a greater extent than those in positions 3 and 5. The shape of a pyrrole molecule being considered the phenyl on C(3) would increase the resultant moment more that that on C(5) decreases it. In agreement with this the experimental value (2·04 D) is 0·22 D greater than that of pyrrole.

In 2,3,4,5-tetraiodopyrrole no complication is likely to arise from non-planarity of the molecule and its dipole moment (2·54 D) requires contributions of 0·90 D from each C–I bond, it being assumed that each makes the same contribution (*cf.* 1·30 D in iodobenzene [26] and 1·28 and 0·98 D for *m*- and *o*-di-iodobenzene respectively [28]).

Acylpyrroles. Various structures have been suggested to explain the chemical properties of these compounds but there seems to be no reason to consider them as existing other than in a keto-form, possibly with a tendency to associate in solution.[29] Conjugation between the carbonyl group and the pyrrole ring prevents free rotation about the C–C bond to the pyrrole ring. Analysis of dielectric relaxation and n.m.r. data in Part I failed to provide evidence for any rotation about this bond with substituents on C(2) but rotation did occur when they were attached to C(3). In other words, it seems that 2-acylpyrroles exist almost exclusively in either the planar *syn* (I) or the *anti* (II) forms, whilst the 3-acylpyrroles comprise a mixture of the two forms.

The dipole moments calculated for these molecules,[26] that of the C=O bond being taken 2·34 D and Me–C$\leqslant$ as 0·30 D, are in Table 5. Also in Table 5 are values for an interaction moment Δμ necessary to give the experimental value on the assumption (1) that it is directed along the C=O bond, (2) that it acts in the direction of the C–C bond linking the group to the pyrrole ring, and (3) that the interaction moment acts equally in these two directions. When no value is quoted the solutions of the relevant quadratic equation are imaginary. This interaction moment must be mainly due to a mesomeric shift in the π-electron distribution but there will also be lesser contributions from inductive effects. The experimental dipole moment of each 2-acylpyrrole lies between the values calculated for structures (I) and (II) but it is only possible to calculate an interaction moment for the *syn*-forms (I); for 3-acylpyrroles the calculated moments for both structures (I) and (II) are less than the experimental value and an interaction moment can be calculated for each structure. It is clear that if there is no rotation of the acyl groups the magnitudes of these extra moments are higher than the corresponding values for benzaldehyde ($\Delta\mu_1 = 0{\cdot}95$, $\Delta\mu_2 = 0{\cdot}57$, $\Delta\mu_3 = 0{\cdot}64$ D) and acetophenone ($\Delta\mu_1 = 0{\cdot}87$, $\Delta\mu_2 = 0{\cdot}44$, $\Delta\mu_3 = 0{\cdot}53$ D), but this would be expected as the pyrrole system is the stronger π-electron donor. In view of the inductive effect of a methyl group it is not surprising that the interaction moments are greater in aldehydes than in the corresponding methyl ketones. If it is accepted that 2-acylpyrroles have one predominant conformation then it must be the *syn*-form (I).


(I)

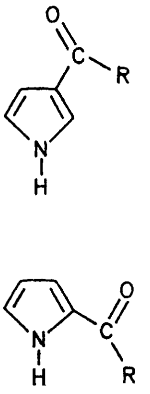

(II)

TABLE 5

Calculated dipole moments and interaction moments in benzene solution

Pyrrole	Conformation	$\mu_{\text{calc.}}$	μ_{R}	Interaction moments $\Delta\mu_1$	$\Delta\mu_2$	$\Delta\mu_3$
-2-carbaldehyde	(I)	0·63	2·18	1·61	1·55	1·59
	(II)	3·64		—	—	—
2-Acetyl-	(I)	0·71	1·82	1·11	1·28	1·14
	(II)	3·90		—	—	—
2-Benzoyl	(I)	0·90	1·81	0·94	1·29	1·05
	(II)	4·18		—	—	—
1-Methylpyrrole-2-carbaldehyde	(I)	0·53	2·84	2·42	2·32	2·32
	(II)	3·76		—	—	—
Methyl pyrrole-2-carboxylate	(I)	0·20	1·77	1·80	1·61	1·72
	(II)	3·20		—	—	—
3-Acetyl-	(I)	2·88	5·03	2·39	2·27	2·18
	(II)	3·97		1·10	1·37	1·11
Methyl pyrrole-3-carboxylate	(I)	2·39	3·60	1·55	1·22	1·23
	(II)	3·51		0·09	0·13	0·09

2-Nitropyrrole can only have the one planar conformation and its calculated moment of 3·08 D (taking that of the $-NO_2$ group as 3·32 D [26]) requires an interaction moment of 1·41 D in the $C-NO_2$ direction. This is greater than the corresponding interaction moments for nitrobenzene (0·67) and 2-nitropyridine (0·20) but the sequence is as expected for the mesomeric moments in this series of compounds.

III. *Electric Dipole Moments in* 1,4-*Dioxan Solution.*—It is well established that dipole moments derived from measurements made in solution depend slightly upon the

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[28] A. L. McClellan, 'Tables of Experimental Dipole Moments,' Freeman, San Francisco, 1963.

[29] M. K. A. Khan and K. J. Morgan, *J. Chem. Soc.*, 1964, 2579.

solvent. One equation expressing this dependence, that of Buckingham and Le Fèvre,[30] predicts that dipole moments in 1,4-dioxan solution should exceed those determined in benzene by 0·09 D for 2-nitropyrrole, 0·08 D for 3-acetylpyrrole, and 0·01—0·05 D for the other compounds listed in Table 6. It is evident that this normal solvent effect only explains the results for the two pyrroles substituted on the nitrogen atom. For the remaining compounds there is a specific solute 1,4-dioxan interaction through hydrogen-bonding of the type well established for aromatic amines [31] and aminopyridines.[32] If we accept the component moments discussed when analysing the results in benzene solution, the dioxan increment, acting in the direction of the H–N bond, required to increase the dipole moment to that found in 1,4-dioxan solution is shown in Table 6; the three values for the acyl compounds correspond to the three interaction (mesomeric) moments discussed in Part II. As expected, the electron-withdrawing substituents in tetraphenyl- and tetraiodo-pyrroles result in larger dioxan increments than for pyrrole itself. In the former molecule steric effects involving the dioxan molecule might reduce the mesomeric moments of the 2- and 5-phenyl groups thereby giving an additional contribution to the increment. The increment for 2-nitropyrrole is ambiguous and unexpectedly large.

TABLE 6

Dipole moment increments in dioxan solution resolved in direction of N–H bond

Pyrrole	Increment	Pyrrole	Increment
Pyrrole	0·31	2-Phenyl-	0·30
		2-Nitro-	1·55 or
1-Methyl-	0·06		−1·38
2-Methyl-	0·30	2,3,4,5-Tetraphenyl-	0·39
1-Phenyl-	0·03	2,3,4,5-Tetraiodo-	0·53

Pyrrole	Conformation	Increment *		
		$\Delta\mu_1$	$\Delta\mu_2$	$\Delta\mu_3$
-2-carbaldehyde	(I)	−0·39	−0·62	−0·46
2-Acetyl-	(I)	−0·16	−0·23	−0·18
2-Benzoyl-	(I)	−0·10	−0·13	−0·11
Methyl pyrrole-2-carboxylate	(I)	−0·16	−0·39	−0·21
3-Acetyl-	(I)	0·69	0·28	0·39
	(II)	0·20	0·19	0·19
Methyl pyrrole-3-carboxylate	(I)	0·51	0·31	0·37
	(II)	0·23	0·23	0·23

* Interaction moments resolved in three directions: $\Delta\mu_1$, along the C=O bond; $\Delta\mu_2$, along the (C_4H_4N)–COR bond; $\Delta\mu_3$, equally in the previous two directions.

The increments for 2-acylpyrrole and methyl pyrrole-2-carboxylate are most unusual in being negative. One explanation is that some of the complexes have the substituent in the *anti*-form (II) but this is unlikely in view of their dielectric relaxations discussed in Part I and because steric hinderance to association would be greater in this form. The substituents could, however, be forced a few degress out of planarity with the pyrrole ring. An alternative explanation is that the mesomeric moment in the substituent is enhanced as a consequence of hydrogen-bonding to the N–H.

Association constant of complex. Several attempts have been made to evaluate solute–solvent association constants from dielectric measurements. One of the more satisfactory procedures is that suggested by Few and Smith [33] which involves determinations of apparent solute polarizations in a series of mixed solvents. Their method was successfully applied to pyrrole in mixtures of benzene and 1,4-dioxan as solvent. The results obtained were that the pyrrole–1,4-dioxan complex had a dipole moment of 2·20 D, an association constant of about 260 mol⁻¹ cm³ and that at infinite dilution in pure dioxan 78% of the pyrrole is complexed. The corresponding result obtained by Few and Smith for the more basic aniline indicated that in this case only 65% was complexed. Finally, the plots in Figure 2, of dipole moment of pyrrole and 1-methylpyrrole against composition of a benzene–dioxan mixed solvent shows clearly the difference between solutes which do and do not form hydrogen bonds to 1,4-dioxan.

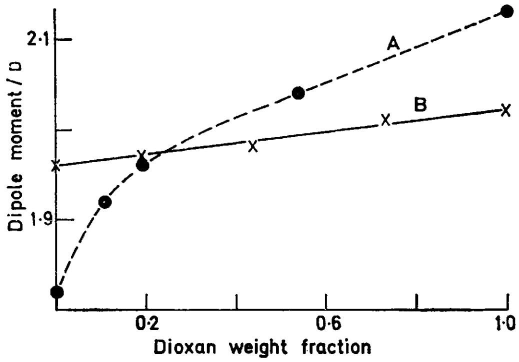

FIGURE 2 Apparent dipole moments of A, pyrrole; and B, 1-methylpyrrole in benzene–1,4-dioxan at 25·0 °C

[1/252 *Received, March* 11*th*, 1971]

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[30] A. D. Buckingham and R. J. W. Le Fèvre, *J. Chem. Soc.*, 1952, 1932.

[31] J. W. Smith and S. M. Walshaw, *J. Chem. Soc.*, 1957, 3217; 1959, 3784.

[32] C. W. N. Cumper and A. Singleton, *J. Chem. Soc.* (*B*), 1967, 1100; 1968, 645.

[33] A. V. Few and J. W. Smith, *J. Chem. Soc.*, 1949, 2781.