

269. *The Molecular Structure of Pyrrole and Some of its Simple Derivatives, from Electric Dipole Moment Measurements.*

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Seventeen pyrrole derivatives have been investigated. The electric dipole moments are consistent with the conclusions about ring structure from other physical methods. They indicate that the extra-annular nitrogen valency is not more than 7° out of the symmetry axis of the ring. The direction of the π -electron moment of pyrrole has been determined. It agrees with deductions from organic chemical evidence, and from theoretical considerations, in having its positive pole towards the nitrogen and its negative one towards the remainder of the ring.

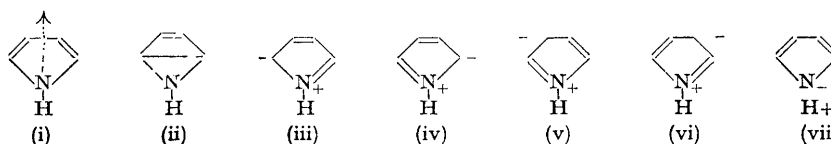
Resonance phenomena and the steric inhibition thereof have been studied in a series of *N*-phenylpyrrole derivatives. The π -moment due to interannular conjugation has been estimated to be *ca.* 0.5 D, antiparallel to the main moment of phenylpyrrole.

A series of indole derivatives measured by Janetsky and Lebreton has been included in the discussion. These and all the reported pyrrole derivatives fit into a general pattern.

Electronic Structure and Geometry of the Pyrrole Ring : Previous Information from Other Methods.

PYRROLE has benzene-like aromatic character. The language used to account for this has changed from time to time, but the essential idea remains the same. The aromaticity is now generally attributed to a sextet of unlocalized π -electrons, the nitrogen providing by its lone pair the two electrons necessary to complete the sextet. According to the molecular-orbital treatment (Coulson and Longuet-Higgins, *Trans. Faraday Soc.*, 1947, **43**, 87) the delocalization of the lone pair is so effective as to leave the nitrogen with a formal positive charge in spite of the fact that its electronegativity is higher than that of carbon. A corresponding negative charge is distributed over the carbon atoms in the ring. The pyrrole ring will therefore possess an electric dipole moment due to the π -electron distribution (often referred to as the π -moment), apart from the resultant of the σ -bond moments.

In the terms of the valence-bond method the electron distribution may be described by the resonating structures shown below. From the formally charged structures (iii)—(vii) contributing to the resonance hybrid it is to be expected that the π -moment will have its negative pole uppermost in the formulæ written as below. Further, since (iii) and (iv) have the same weight, likewise (v) and (vi), the π -moment should be parallel to the symmetry axis which the ring itself may be presumed to have.



By an electron-diffraction examination, Pauling and Schomaker (*J. Amer. Chem. Soc.*, 1939, **61**, 1778) found dimensions for pyrrole which agreed with the ring's being planar. The bonds 2–3 and 4–5 are slightly shorter, 1.35 Å, than the other bonds, 1.42 Å, showing that the classical structure (i) contributes most to the hybrid. No one of the intra-annular valency angles deviates from 108° by more than the experimental error. It is therefore sufficient for the present purpose to regard the pyrrole ring as a coplanar regular pentagon having a side of length 1.4 Å.

The electron-diffraction method cannot place the hydrogen atoms in pyrrole. Garach

and Lecomte (*Bull. Soc. chim.*, 1946, 415; *Compt. rend.*, 1946, **222**, 74) report that the infra-red absorption spectrum of pyrrole is readily explained by a model having all bonds, including the C-H bonds, coplanar; but there seems still to be some doubt about the direction of the N-H bond relatively to the ring plane. The above authors conclude that this bond is inclined to the ring plane, but others differ: *e.g.*, Lord and Miller (*J. Chem. Physics*, 1942, **10**, 339) conclude that the Raman and infra-red spectra strongly support a coplanar structure, although a non-coplanar one is not definitely ruled out. If, as is supposed in the theoretical treatment (Coulson and Longuet-Higgins, *loc. cit.*), the three σ -bonds of the nitrogen are formed by hybridization of one *s*- and two *p*-orbitals, it would be expected that they would be coplanar. The establishment of this point would therefore be a useful verification of the said treatment.

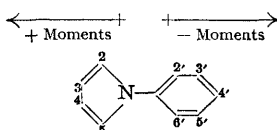
The present investigation fails to provide conclusive evidence as to the direction of the N-H bond; but it gives limits to the degree of non-coplanarity.

Calculation of the Electric Dipole Moment of Pyrrole.—Neither the moment due to the electrons in the σ -bonds nor that due to those in the π -bonds of pyrrole can be accurately calculated *a priori*, but a rough estimate may be attempted. Taking values of 0.4 D for H-C, 1.3 D for H-N, and 0.5 D for C-N (*cf.*, *e.g.*, Hill and Sutton, *J.*, 1949, 746; Everard and Sutton, *J.*, 1949, 2320) * and assuming the geometry of pyrrole to be as outlined above, we get a resulting σ -moment of about +0.4 D.† The π -moment may be approximately calculated from the π -electron densities obtained by Coulson and Longuet-Higgins (*loc. cit.*). The result is +1.97 D. However, owing to certain approximations, such molecular-orbital treatments are prone to exaggerate the π -electron moment (see Orgel, Cottrell, Dick, and Sutton, *Trans. Faraday Soc.*, 1951, **47**, 113 ‡). Pauling and Schomaker (*loc. cit.*) derived an experimental value of the π -moment and used this to assess the importance of contributions by structures (iii)–(vi). They found that the results agreed quite reasonably with those obtained from the bond lengths. A σ -moment of +0.4 D being taken, it follows that if the observed moment, 1.80 D, is positive, the π -moment is +1.40 D. Pauling and Schomaker (*loc. cit.*) give a value, similarly derived, of 1.5 D.

TABLE 1. *Electric dipole moments of pyrrole derivatives in benzene solution at 25°.*
(Debye units.)

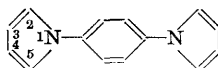
<i>Pyrroles.</i>			
(I) Unsubstituted	1.80 \pm 0.01	(IV) 1 : 2 : 5-Trimethyl	2.07 \pm 0.01
(II) 1-Methyl	1.92 \pm 0.02	(V) 3 : 4-Di-iodo-2 : 5-dimethyl	4.00 \pm 0.01
(III) 2 : 5-Dimethyl	2.08 \pm 0.03	(VI) 2 : 3 : 4 : 5-Tetraiodo	2.52 \pm 0.04

1-Phenylpyrroles.



(VII) Unsubstituted	1.32 \pm 0.04	(XII) 2 : 5 : 4'-Trimethyl	2.34 \pm 0.02
(VIII) 2 : 5-Dimethyl	2.00 \pm 0.04	(XIII) 4'-Chloro	<i>ca.</i> 0.03
(IX) 2 : 5 : 2' : 5'-Tetramethyl	2.07 \pm 0.02	(XIV) 4'-Chloro-2 : 5-dimethyl ...	0.50 \pm 0.04
(X) 2 : 5 : 2' : 4' : 6'-Penta-		(XV) 4'-Bromo-2 : 5-dimethyl...	0.54 \pm 0.03
methyl	2.06 \pm 0.04	(XVI) 2 : 5-Dimethyl-4'-nitro ...	2.48 \pm 0.02
(XI) 4'-Methyl	1.79 \pm 0.04		

p-Di-1-pyrrolylbenzene.



(XVII) <i>p</i> -Bis-(2 : 5-dimethyl-1-pyrrolyl)benzene	0.77 \pm 0.03
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* The convention used here is that the right-hand atom bears the negative dipolar charge.

† A plus sign denotes a moment parallel to the symmetry axis of pyrrole and with its negative end upwards in the formulæ written as in (i)–(vii), whereas a minus sign shows a moment in the opposite direction.

‡ These authors did not calculate an independent value for the moment of pyrrole but used the observed value to derive a parameter for nitrogen.

DISCUSSION

(A) *The Monocyclic Compounds* (I) —(VI) (Table 1).—Two of the compounds in Table 1 were measured in 1933 by one of us (J. J.), namely, pyrrole (I) and 1-methylpyrrole (II), and the results were briefly reported (Sutton, *Trans. Faraday Soc.*, 1934, **30**, 789). The moments have been recalculated from the observations by the method of Halverstadt and Kumler (*J. Amer. Chem. Soc.*, 1942, **64**, 2988), which has been used throughout this paper. No other records of the moment of 1-methylpyrrole have been found. Other values reported for pyrrole are 1.83 at 20° (Cowley and Partington, *J.*, 1933, 1259); 1.80 at 20° (Robles, *Rec. Trav. chim.*, 1939, **58**, 111); 2.2—2.0 at 20°, 1.8 at 22°, and 1.7 at 23° (Hückel, Datow, and Simmersbach, *Z. physikal. Chem.*, 1940, *A*, **186**, 166). The figures from the last reference are each based on only one solution and are hence deemed less reliable.

For considering the moments of many of the other compounds the group moment of $\text{Me}-\text{C}_{\text{ar}}$ is needed, *i.e.*, the extra moment produced when a hydrogen atom attached to carbon in the pyrrole ring is replaced by a methyl group. In view of the similarity of the aromatic systems of pyrrole and benzene, we shall assume this group moment to be equal in magnitude and direction to the moment of toluene 0.35 D, *i.e.*, $\text{CH}_3-\bar{\text{C}}_{\text{ar}}$. Some support for this assumption comes from the moments of alkylindoles. Indole is assumed to contain an undistorted regular pyrrole ring and the entire molecule is taken as coplanar. From the practically identical experimental values 2.11 and 2.08 found for indole and 3-methylindole (Janetzky and Lebet, *Rec. Trav. chim.*, 1944, **63**, 123), it follows that either the $\text{Me}-\text{C}_{\text{ar}}$ moment is vanishingly small, which is very unlikely, or it is oriented almost orthogonally to the main moment of indole. This means, however, that in 2-methylindole the main moment and the $\text{Me}-\text{C}_{\text{ar}}$ moment are practically parallel. We should therefore be able to get a reliable value for the latter as the difference between the moment of 2-methylindole, 2.47 (*loc. cit.*), and that of indole 2.11, *i.e.*, 0.36. Hence the value chosen, 0.35 D, seems to be reasonable.

The moment calculated for 2:5-dimethylpyrrole (III) on the assumptions already given and the moment of pyrrole being taken as 1.80 D, is +2.02 D. The observed moment is 2.08 ± 0.03 D. This agreement confirms that the pyrrole moment is positive. The fact that the agreement is so good furthermore suggests that the H—N bond is at least roughly coplanar with the ring, as the calculated moment of any reasonable non-coplanar molecule would be *lower* than 2.02 D.

Similarly, the moment of 1:2:5-trimethylpyrrole (IV) derived from the value 1.92 D observed for 1-methylpyrrole (II) is 2.14 D (cf. 2.07 D observed).

The reasonably good vector additivity found for these compounds is obviously no rigorous proof of coplanarity, for the contribution of a substituent moment of only 0.35 D to the final moment is too small compared with the probable error in the values (0.02—0.05 D). It was therefore hoped that a clearer answer might be obtained by using a substituent with a somewhat higher moment, and so the iodo-derivatives (V) and (VI) were used. In order to be able to compare these with the parent compounds (III) and (I), the difference of the moments of $\text{C}_{\text{ar}}-\text{I}$ and $\text{H}-\text{C}_{\text{ar}}$ is needed. It will be taken as the moment of iodobenzene, thus making an empirical allowance for the π -moment in *C*-iodopyrrole by assuming it to be equal to the one in iodobenzene. The value taken is 1.42 D (Mr. M. J. Saxby, private communication); earlier values varying from 1.25 to 1.38 D are given by Walden and Werner (*Z. physikal. Chem.*, 1929, *B*, **2**, 10), Bergmann *et al.* (*ibid.*, 1930, *B*, **10**, 106), and Tiganik (*ibid.*, 1931, *B*, **13**, 425). Assuming the simple ring geometry already described, and making no allowance for the various induced moments, we obtain 4.38 D for 3:4-di-iodo-2:5-dimethylpyrrole. When allowance is made for induced moments ($\text{C}_{\text{ar}}-\text{I}$ moment on iodine and pyrrole moment on iodine) by Hampson and Weissberger's method (*J.*, 1936, 393) we obtain 4.24 D. The agreement with the observed value 4.00 D is only fair and may possibly indicate some non-coplanarity of the N—H bond; but the corrections for induced moments are not very precise. For 2:3:4:5-tetraiodopyrrole (VI), a similar basis being used and without corrections for induced moments, a value of 3.22 D is obtained. When corrected, this becomes 2.48 D, which agrees well with the observed value of 2.52 D; but in view of the previous result we regard this agreement as

somewhat fortuitous. These results for the iodo-derivatives obviously confirm the previous conclusions about the direction of the pyrrole moment but do not provide decisive evidence for a coplanar N-H bond.

From the moments of pyrrole (1.80) and of 1-methylpyrrole (1.92) it appears that the effective moment of Me-N exceeds that of H-N by 0.12 D, whereas the σ -moment of Me-N is *lower* than that of H-N by about 0.5 D (H-N 1.3 against Me-N 0.85 D from ammonia and trimethylamine, respectively). Hence we have to explain an extra moment of +0.6 superimposed upon the normal σ -moment in Me-N. As for the toluene moment, we can put forward several hypotheses all having the feature in common that they are formal "explanations" in different languages expressing our ignorance rather than our knowledge (see, e.g., Hurdis and Smyth, *J. Amer. Chem. Soc.*, 1943, **65**, 89; Baker *J.*, 1939, 1150; Le Fèvre, Le Fèvre, and Robertson, *J.*, 1935, 480). Some explanations can, however, be ruled out.

It is, for instance, unlikely to be due to solvent effect, which should be much the same in pyrrole and in 1-methylpyrrole; nor is it due to association. Hydrogen bonding, giving head-to-head association between a pair of pyrrole molecules, would admittedly reduce the observed moment of pyrrole and could thus account for the discrepancy. But, although the relatively high boiling point is some indication of this, the total polarization of pyrrole in benzene solution varies very little with concentration and in any case no more than does that of 1-methylpyrrole (see p. 1475).

The apparent extra moment of Me-N in methylpyrrole may be explained by the greater electronegativity of the nitrogen atom in pyrrole than in the aliphatic compounds, owing to the formal positive charge given by π -electron redistribution. The effect of the increased electronegativity would be more marked in 1-methylpyrrole than in pyrrole because of the greater polarizability of the methyl group.

The anomaly may also originate from the different hybridization of the nitrogen atom in the aliphatic and in the cyclic state. Further light might be thrown upon this problem by the dipole moments of other *N*-alkyl-pyrroles.

(B) *Collinearity of Ring Axes in the 1-Phenylpyrroles* (VII)—(XVI).—These compounds were investigated with the aim of studying the interaction between the two aromatic rings, and the steric and electronic influence on this interaction of substituents introduced in either ring.

In 1-phenylpyrrole itself a certain degree of interannular conjugation is to be expected. It may be visualized from a series of resonating structures having a positive charge on the nitrogen atom, a negative one on the benzene ring (*o*- or *p*-position), and an interannular double bond.

The resonance energy in 1-phenylpyrrole due to the interannular conjugation has been estimated by Pauling and Schomaker (*loc. cit.*) from combustion data as 6 kcal./mol. In diphenyl the conjugation energy is 8 kcal./mol. (Pauling and Sherman, *J. Chem. Physics*, 1933, **1**, 606, 679). It is reasonable that the interannular conjugation energy is lower in 1-phenylpyrrole, since the nitrogen atom is already involved in *intra*annular conjugation.

In order that the conjugation energy may be as large as possible, the two rings will tend to be more or less coplanar. Bastiansen (*Acta Chim. Scand.*, 1949, **3**, 408) concludes from an electron-diffraction examination that, in the vapour state, diphenyl is linear with the two ring planes mutually twisted $45^\circ \pm 10^\circ$ round the interannular bond. Neither the coplanar nor the orthogonal configuration is satisfactory. In the crystalline state, on the other hand, diphenyl is found to be linear and coplanar (Dhar, *Indian J. Physics*, 1932, **7**, 43). The structure of the molecule will probably not differ very much in the vapour state and in dilute solutions. The angle 45° suggested agrees in this case with the conclusions from a scale diagram (Fig. 1). There is an appreciable steric interference between the hydrogen atoms in *o*-positions to the interannular bond. In *N*-phenylpyrrole (Fig. 2), however, the steric interference is considerably less (0.3 Å overlap compared with 0.6 Å in diphenyl) because, although the Ph-N bond is shorter than the Ph-Ph bond, the pentagonal pyrrole ring increases the clearance of the *o*-hydrogen atoms. This molecule may therefore well be coplanar or nearly so in spite of the interannular resonance energy being smaller than in the non-coplanar diphenyl.

The interannular conjugation will manifest itself in an extra π -moment probably of negative sign (negative pole towards phenyl nucleus). This direction will be shown to be correct, and the magnitude estimated by using the device of steric inhibition of resonance (Section C). To effect this demonstration properly, however, we need information about the inclination of the N-Ph link relatively to the pyrrole ring axis both in the conjugated (VII, XI, XIII) and in the non-conjugated 1-phenylpyrroles (VIII, IX, X, XII, XIV, XV, XVI). Whereas the former are *a priori* almost certainly axially collinear, it is less certain that the latter are. The facts are the following.

The observed moment of 1-phenylpyrrole (VII) is 1.32 D. Adding the moment of toluene 0.35 D, we get 1.67 D as the expected value for 1-tolylpyrrole (XI). The fairly

FIG. 3. The pyrrole and benzene rings are shown orthogonally. The broken lines indicate the two modes of oscillation suggested for each pyrrol group and the bond attaching it to benzene.

FIG. 1.

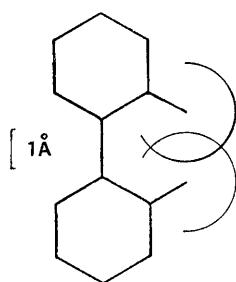
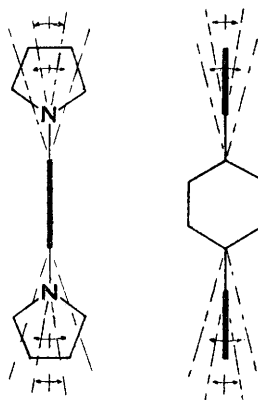
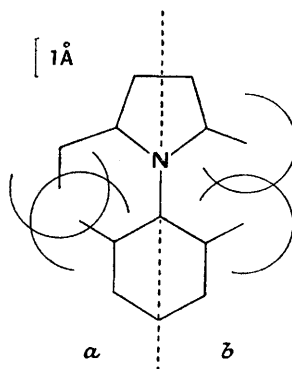


FIG. 2.



good agreement with the observed value 1.79 D shows that the resultant moment of 1-phenylpyrrole is positive and further suggests that the assumed collinearity of both compounds is correct. Non-collinearity would make the predicted value even smaller.

The moment calculated for 1-*p*-chlorophenylpyrrole (XIII) by a similar procedure, chlorobenzene being taken as 1.60 D, is -0.28 D. If allowance be made for the moments induced in chlorine by the pyrrol dipole and in the pyrrole ring by the C-Cl dipole this value becomes -0.31 D. The experimental figure is 0.3 D. Non-collinearity is therefore unlikely in the conjugated compounds.

Collinearity in the non-conjugated series may be tested by comparison of (VIII) with (XII). The value predicted for (XII) from that of (VIII) and the assumed extra moment 0.35 D of Me-C_{ar.} is 2.35 D, collinearity being assumed. The observed value is 2.34 D. The component moment of Me-C is, however, too small for this test to be reliable. For this reason (XIV) and (XV), with the more polar halogen substituents, were investigated. From the observed moments of (VIII) and with chlorobenzene taken as 1.60 D, we get $+0.40$ D as the expected value for (XIV) if this be collinear. When allowance is made for induced moments, this value is reduced to $+0.36$. The observed value is 0.50 D, *i.e.*, it is larger than the predicted one. The same is true for the bromo-derivative (XV), where the respective values, the moment of bromobenzene being taken as 1.57 D, are $+0.43$ (uncorrected), $+0.41$ (corrected), and 0.54 D (observed). The discrepancy in the last two cases could arise from a small departure, about 6–7°, from collinearity.

The nitro-compound (XVI) has a moment of 2.48 D. The uncorrected calculated value, the moment of nitrobenzene being taken as 4.00 D, is -2.00 D, and the corrected one is 2.09 D. The discrepancy provides no evidence for non-collinearity, because electronic shifts involving the π -electrons of the nitro-group and of the pyrrole ring may well occur.

Because these results gave no clear answer, it was hoped that a direct test might be

made by measuring (XVII), which evidently would be non-polar if it were collinear. The observed moment is, however, 0.77 D. This may be real, *i.e.*, due to permanent non-collinearity of the molecule, or it may be an apparent moment due to atom polarization, which has been shown to reach considerable magnitudes in other *p*-disubstituted benzenes, or it may be due to each factor in part. It is possible that the 2 : 5-dimethylpyrryl groups oscillate as a whole owing to bending of the Ph-N valencies relatively to the axis of the benzene ring (Fig. 3), and further that the pyrrole rings themselves either (*a*) oscillate relatively to the N-Ph bonds or (*b*) are permanently bent relatively to them. Alternative (*a*) would give rise to two atom polarizations, and alternative (*b*) to an atom polarization and an orientation polarization, although the distinction in such cases is not an absolute one (cf. Sutton, *Ann. Reports*, 1940, **37**, 57 *et seq.*).

The first contribution may be estimated by assuming that each pyrrol group is a two-dimensional oscillator, that the oscillating moment μ_i is 2.0 D [that of compound (VIII)], and that the force constant is $V_i = 3 \times 10^{-12}$ erg/radian²/molecule. From the relation ${}_A P = 4\pi N \mu_i^2 / 9V_i$ for each dimension of oscillation of each oscillator, we get an atom polarization ${}_A P = 4.5$ c.c. The apparent orientation polarization, corresponding to the moment 0.77 D, which we have to explain is 12.1 c.c. The remaining 7.6 c.c. must then be due either to the second atom polarization or to the permanent bending about the ring nitrogen atom. In the former case we can calculate the force constant, by applying the same relation, regarding each pyrrole ring as a two-dimensional oscillator and taking the moment μ_i as 0.8 D [*i.e.*, that of compound (III) less an estimated 1.3 for the H-N bond]. This gives $V_i = 0.28 \times 10^{-12}$ erg/radian²/molecule, which is a very small value. In the latter case we can derive the angle θ of permanent bend relatively to the axis of the pyrrole ring, from the relation $2\mu_i \sin \theta = \sqrt{2} \mu_T$ where μ_T is the moment (0.6 D) corresponding to 7.6 c.c. of orientation polarization. This gives $\theta = 32^\circ$. We conclude, therefore, either that there is an unusually small force constant of bending for the N-Ph bond relatively to the pyrrole ring, or that this bond is up to 32° permanently out of line with the axis of the pyrrole ring. Lord and Miller (*J. Chem. Physics*, 1942, **10**, 339) consider that there is spectroscopic evidence for a flattened potential curve for energy as a function of the inclination of the N-H bond in pyrrole to the ring plane. This would agree with the former of our alternative conclusions, which therefore we favour. For further elucidation the moment of *p*-phenylenedi-1-pyrrolbenzene (XVII without the methyl groups) should be useful. If this conjugated compound were to have moment of the same order of magnitude as that of (XVII) it would support the explanation on grounds of atom polarization only. If, on the other hand, the moment be decidedly smaller or zero, then the apparent moment of (XVII) is likely to be due to permanent bend. An attempt is being made to prepare the new compound.

The general conclusions from the tests carried out are that in 1-phenylpyrrole the ring axes are very probably collinear, but that in the compounds with sterically hindered conjugation (VIII, etc.) they probably are not more than 7° out of line, as judged from the values of the *p*-substituted derivatives. Even if the N-Ph bond in these is out of plane to this extent, this still means that there is clear evidence of a large degree of separation of the orbitals of the nitrogen atom into an sp^2 set used for σ -bonds and a *p*-orbital which participates in π -bonding within the pyrrole ring. The problem is the same as that which arises in the sydnones (cf. Hill and Sutton, *loc. cit.*).

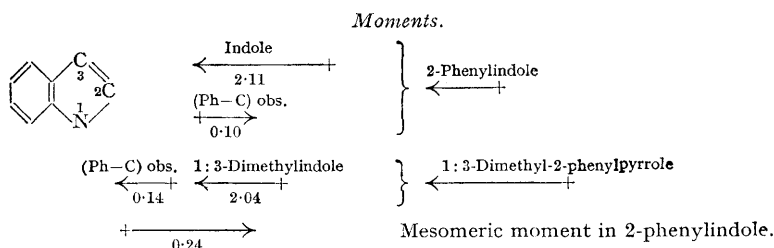
(C) *Steric Inhibition of Interannular Conjugation in the 1-Phenylpyrrole Series.*—In the series (VII)—(X) because of the increasing number of methyl groups in the positions *ortho* to the interannular link, the steric interference (cf. Fig. 3) should cause the benzene ring to be twisted about the N-Ph link out of the plane of the hetero-ring and thus inhibit the interannular conjugation more and more in the order given. The moments of (VIII), (IX), and (X) are directly comparable because the moments of the methyl groups in the benzene ring cancel; but in (VII) we must allow for the absence of the methyl groups in the 2 : 5-positions of the pyrrole ring. If we do this, on the basis of the substitution moments used previously, we obtain 1.54 D as the comparable value [*i.e.*, the moment predicted for (VIII) if it had been coplanar].

In (VII), with least if any steric influences, the positive moment of 1-phenylpyrrole

may be opposed by a negative π -moment, due to the interannular conjugation. The π -moment should progressively diminish in (VIII) and (IX). It probably vanishes in (IX) as shown by the near equality of the observed moments of (IX) and (X). The magnitude of the π -moment may be calculated, as the difference of the corrected moment of (VII), *i.e.*, 1.54 D, and the moment of (IX) or (X), to be -0.53 D. In this calculation we have assumed collinearity of all the compounds involved. A check on this value is obtained from the pair (VII) and (II), which should differ only by the π -moment, which therefore is -0.60 D.

The observed moments of (IV) and (IX) are identical, which is to be expected if the conjugation is completely inhibited in (IX) and if the effective σ -moments of Me-N and Ph-N are similar.

It would be interesting to compare the derived π -moment of *ca.* -0.5 D with that created by interannular conjugation when the benzene ring is attached to a *carbon* atom in pyrrole and not to the nitrogen. The present investigation does not include C-phenylpyrroles but results for indoles reported by Janetsky and Lebet (*loc. cit.*) permit of a rough calculation. The direction of the indole moment being taken to be approximately parallel to the radial bond from C₍₂₎ and in the sense shown in Fig. 1 (see p. 1471) the contribution of the Ph-C link is the difference between 2.11 D and 2.01 D, *i.e.*, $\mu_{O-Ph} = 0.10$. The Ph-C moment can also be calculated from 1 : 3-dimethylindole (2.04 D) and 1 : 3-dimethyl-2-phenylindole (2.18 D), to be $\mu_{Ph-C} = 0.14$ D, which is in the opposite direction. The reason for the difference in magnitude and direction of the two derived values is probably that 1 : 3-dimethyl-2-phenylpyrrole is similar to 2 : 5-dimethyl-1-phenylpyrrole in that steric influences twist the benzene ring out of the normal plane and inhibit the conjugation. The latter value, $\mu_{Ph-C} = 0.14$ D, may give the order of magnitude and direction of the extra σ -moment (relative to H-C) of the group Ph-C in indole and pyrrole. We conclude, therefore, that in the coplanar, conjugated compounds a π -moment of about 0.24 D in the opposite direction, C-Ph, is superimposed on it. These relations are shown in the vector diagram below.



(The direction of the mesomeric moment is that which would be expected from the increase of negative charge in the pyrrole ring.)

Conclusions.—The main conclusions we derive from the results are the following :

(i) The moments of pyrrole and of 1-methylpyrrole are certainly *positive*, *i.e.*, they have the positive pole toward the nitrogen atom and the negative one toward the rest of the ring atoms. This agrees with current explanations of the aromatic character of the pyrrole ring.

(ii) The observed moment of pyrrole agrees fairly well in magnitude with that calculated by a molecular-orbital procedure: the π -moment derived therefrom is $+1.40$ D. The moment of 1-methylpyrrole indicates that the Me-N group moment is larger than in a tertiary aliphatic amine.

(iii) The N-H and N-Me bonds in pyrrole and 1-methylpyrrole are probably not much inclined to the plane of the ring. This also agrees with current theory.

(iv) The ring axes in 1-phenylpyrrole are very probably collinear, but in 2 : 5-dimethyl-1-phenylpyrrole they may be up to 7° out of line.

(v) *p*-Bis-(2 : 5-dimethyl-1-pyrrolyl)benzene (XVII) has a small apparent moment of 0.77 D. If this is due to atom polarization the force constant for the bending of the pyrrolyl

group relatively to the benzene ring must be abnormally small. If it is a real moment, the pyrrole and the phenyl axes are about 32° out of line. The former alternative agrees with the spectroscopic evidence for the structure of pyrrole itself.

(vi) In 1-phenylpyrrole there is a π -moment of about -0.5 D, due to interannular conjugation. It is reduced by substituting methyl groups for hydrogen in the 2:5-positions of the pyrrole ring and in the *o*-positions of the benzene ring. Methyl groups in the 2:5-positions stop it almost completely, and one more methyl group in an *o*-position does so quite completely.

(vii) There are small induced moments in 2:5-dimethyl-1-*p*-nitrophenylpyrrole and probably a considerable electromeric interaction moment.

EXPERIMENTAL

Physical Measurements.—All measurements were made at 25° . The electric dipole moment was obtained from the equation $\mu = 0.2212(\tau P - R_D)^{\frac{1}{2}}$. No correction was made for atom polarization apart from that implied in using R_D to give the distortion polarization. The total polarization τP was computed from the observed values of dielectric constant, and the specific volume for benzene solutions by Halverstadt and Kumler's procedure (*J. Amer. Chem. Soc.*, 1942, **64**, 2988). Symbols have the same significance as in that paper. The dielectric constants ϵ were measured with a heterodyne beat capacity meter designed by R. A. W. Hill and L. E. Sutton in conjunction with a condenser similar to that described by Jenkins and Sutton (*J.*, 1935, 609). Specific volumes were measured with a modified Sprengel–Ostwald pyknometer. The molar refractions R_D were computed from the refractive indices and specific volumes usually only from the most concentrated solutions, as most of the compounds have refractive indices close to that of benzene itself.

The refractive index n_D of the solution relative to that of the benzene used for preparing it was measured with a Pulfrich refractometer fitted with a centrally divided cell. The standard dielectric constant of pure dry benzene was taken as 2.2727 (Hartshorn and Oliver, *Proc. Roy. Soc.*, 1929, **123**, A, 664).

The results are given in Table 2, all dipole moments being in Debye units.

Preparation and Purification of Materials.—*Benzene.* Analytical-grade benzene was frozen out three times, about one-fifth being poured off and rejected each time, dried over phosphoric oxide, distilled just before use, and stored under dry air; it had f. p. 5.2° .

Pyrrole (preparation by J. JACKSON). Commercial pyrrole was distilled in a coal-gas atmosphere under reduced pressure. The middle fraction distilling at $31\text{--}32^\circ/17$ mm. was converted into the potassium salt. Pyrrole was recovered from the purified salt by treatment with water and finally dried and redistilled in a coal-gas atmosphere, the middle fraction being used for the measurements.

1-Methylpyrrole (preparation by J. JACKSON). Potassium pyrrole was boiled for 6 hours with 2 equivalents of methyl iodide and an equal volume of dry ether. The product was isolated by fractional distillation and, after a final treatment with metallic sodium, was redistilled in a coal-gas atmosphere under reduced pressure; it had b. p. $20^\circ/17$ mm. (yield 40%) (Found: N, 17.4. Calc. for C_5H_7N : N, 17.3%).

2:5-Dimethylpyrrole. This was prepared by refluxing acetylacetone with ammonium carbonate (*Org. Synth.*, Coll. Vol. II, p. 219). After isolation the product was distilled under reduced nitrogen pressure. The constant-boiling middle fraction distilled at $74^\circ/19$ mm. It was twice frozen out in a nitrogen atmosphere, one-fourth being poured off and rejected each time. The product was stored in a glass container which was sealed off, after being filled with nitrogen. It had n_D^{25} 1.4980 (n_D^{25} 1.500, *loc. cit.*), and remained colourless until exposed to air. The measurements were carried out in a nitrogen atmosphere.

1:2:5-Trimethylpyrrole. An attempt was made to prepare this compound by refluxing acetylacetone with methylammonium chloride at 100° . The mixture turned green, and no condensation took place in neutral conditions. A successful preparation was carried out as follows. Acetylacetone and methylammonium chloride (0.2 mole each) in water (20 ml.), were treated with aqueous sodium hydroxide (0.4 mole in 20 ml.) dropwise, at $<0^\circ$. The reaction mixture was finally heated for a few minutes, and the oily layer isolated, washed with water, dried and distilled. The substance, b. p. $68^\circ/17$ mm., was stored in a sealed tube. It is more stable to air and light than the previous compound. Knorr (*Annalen*, 1886, **236**, 304) gives b. p. $170^\circ/760$ mm., $169^\circ/746$ mm.

TABLE 2. (Roman numerals refer to Table 1).

Pyrrole (I)					2 : 5 : 2' : 5'-Tetramethyl-1-phenylpyrrole (IX)				
$10^5\omega$	ε	ν	τP	$10^5\Delta n_{25}^D$	$10^5\omega$	ε	ν	τP	$10^5\Delta n_{25}^D$
157	2.2800	—	—	—	212	2.2780	1.14485	—	—
320	2.2898	—	87.4	—	351	2.2812	1.14460	—	—
716	2.3111	1.14360	87.0	—	829	2.2930	1.14438	—	—
1028	2.3268	1.14328	85.9	—	1443	2.3078	1.14374	—	57
1487	2.3514	—	85.4	—	$\varepsilon = 2.2728 + 2.429\omega$; $\nu = 1.41505 - 0.0937\omega$; $\tau P = 153.4$ c.c.; $R_D = 66.2$ c.c.; $\mu = 2.07 \pm 0.02$ D				
2033	2.3812	1.14185	85.5	—	2 : 5 : 2' : 4' : 6'-Pentamethyl-1-phenylpyrrole (X)				
$\varepsilon = 2.2720 + 5.376\omega$; $\nu = 1.14456 - 0.1323\omega$; $\tau P = 88.0$ c.c.; $R_D = 21.7$ c.c.; $\mu = 1.80 \pm 0.01$ D					273	2.2786	1.14496	—	—
1-Methylpyrrole (II)					684	2.2875	1.14460	—	—
258	2.2896	1.14390	104.5	—	837	2.2917	1.14450	—	—
492	2.2977	1.14380	103.6	—	1316	2.3019	1.14402	—	44
742	2.3103	1.14371	103.1	—	$\varepsilon = 2.2725 + 2.241\omega$; $\nu = 1.14523 - 0.0916\omega$; $\tau P = 156.8$ c.c.; $R_D = 70.2$ c.c.; $\mu = 2.06 \pm 0.04$ D				
1480	2.3468	1.14336	101.5	—	1-p-Tolylpyrrole (XI)				
2309	2.3895	1.14300	101.6	—	80	2.2752	1.14489	—	—
$\varepsilon = 2.2747 + 4.929\omega$; $\nu = 1.14401 - 0.0428\omega$; $\tau P = 101.7$ c.c.; $R_D = 26.7$ c.c.; $\mu = 1.92 \pm 0.02$ D					370	2.2815	1.14446	—	—
2 : 5-Dimethylpyrrole (III)					418	2.2828	1.14444	—	—
283	2.2849	1.14539	—	—	874	2.2940	1.14345	—	55
560	2.3003	1.14513	—	—	$\varepsilon = 2.2730 + 2.388\omega$; $\nu = 1.14510 - 0.182\omega$; $\tau P = 115.6$ c.c.; $R_D = 50.1$ c.c.; $\mu = 1.79 \pm 0.04$ D				
856	2.3134	1.14500	—	—	2 : 5 : 4'-Trimethyl-1-phenylpyrrole (XII)				
1468	2.3438	1.14446	—	00	69	2.2746	1.14526	—	—
$\varepsilon = 2.2717 + 4.918\omega$; $\nu = 1.14563 - 0.0802\omega$; $\tau P = 118.2$ c.c.; $R_D = 29.8$ c.c.; $\mu = 2.08 \pm 0.03$ D					311	2.2827	1.14500	—	—
1 : 2 : 5-Trimethylpyrrole (IV)					662	2.2943	1.14459	—	30
189	2.2809	1.14511	—	—	$\varepsilon = 2.2723 + 3.328\omega$; $\nu = 1.14532 - 0.107\omega$; $\tau P = 173.3$ c.c.; $R_D = 61.2$ c.c.; $\mu = 2.34 \pm 0.02$ D				
446	2.2921	1.14502	—	—	1-p-Chlorophenylpyrrole (XIII)				
568	2.2970	1.14496	—	—	114	2.2731	1.14503	—	—
1196	2.3238	1.14478	—	00	180	2.2736	1.14485	—	—
$\varepsilon = 2.2730 + 4.254\omega$; $\nu = 1.14517 - 0.0328\omega$; $\tau P = 123.5$ c.c.; $R_D = 35.8$ c.c.; $\mu = 2.07 \pm 0.01$ D					422	2.2742	1.14427	—	—
3 : 4-Di-iodo-2 : 5-dimethylpyrrole (V)					722	2.2745	1.14333	—	36
116	2.2789	1.14433	—	—	$\varepsilon = 2.2732 + 0.207\omega$; $\nu = 1.14540 - 0.2857\omega$; $\tau P = 52.4$ c.c.; $R_D = 50.2$ c.c.; $\mu = 0.50 \pm 0.03$ D				
375	2.2922	1.14243	—	—	1-p-Chlorophenyl-2 : 5-dimethylpyrrole (XIV)				
540	2.3008	1.14129	—	32	105	2.2728	1.14492	—	—
1143	2.3322	1.13679	—	76	275	2.2734	1.14450	—	—
$\varepsilon = 2.2727 + 5.199\omega$; $\nu = 1.14518 - 0.7311\omega$; $\tau P = 382.2$ c.c.; $R_D = 55.5$ c.c.; $\mu = 4.00 \pm 0.01$ D					674	2.2749	1.14332	—	44
2 : 3 : 4 : 5-Tetraiodopyrrole (VI)					1046	2.2756	1.14203	—	66
109	2.2748	1.14421	—	—	$\varepsilon = 2.2726 + 0.310\omega$; $\nu = 1.14530 - 0.306\omega$; $\tau P = 63.4$ c.c.; $R_D = 58.2$ c.c.; $\mu = 0.50 \pm 0.04$ D				
238	2.2759	1.14288	—	—	1-p-Bromophenyl-2 : 5-dimethylpyrrole (XV)				
586	2.2815	1.13986	—	50	163	2.2733	1.14450	—	—
1091	2.2887	1.13566	—	86	229	2.2733	1.14420	—	—
$\varepsilon = 2.2729 + 1.443\omega$; $\nu = 1.14502 - 0.864\omega$; $\tau P = 202.7$ c.c.; $R_D = 72.7$ c.c.; $\mu = 2.52 \pm 0.04$ D					557	2.2743	1.14278	—	38
1-Phenylpyrrole (VII)					1057	2.2759	1.14074	—	67
80	2.2745	1.14489	—	—	$\varepsilon = 2.2727 + 0.309\omega$; $\nu = 1.14514 - 0.414\omega$; $\tau P = 69.0$ c.c.; $R_D = 62.9$ c.c.; $\mu = 0.54 \pm 0.03$ D				
191	2.2771	1.14471	—	20	2 : 5-Dimethyl-1-p-nitrophenylpyrrole (XVI)				
435	2.2808	1.14442	—	—	136	2.2774	1.14459	—	—
773	2.2859	1.14363	—	76	331	2.2834	1.14410	—	—
$\varepsilon = 2.2736 + 1.610\omega$; $\nu = 1.4508 - 0.180\omega$; $\tau P = 84.1$ c.c.; $R_D = 48.7$ c.c.; $\mu = 1.32 \pm 0.04$ D					472	2.2883	1.14344	—	38
2 : 5-Dimethyl-1-phenylpyrrole (VIII)					884	2.3022	1.14242	—	73
104	2.2759	1.14532	—	—	$\varepsilon = 2.2727 + 3.321\omega$; $\nu = 1.14500 - 0.299\omega$; $\tau P = 189.5$ c.c.; $R_D = 64.1$ c.c.; $\mu = 2.48 \pm 0.02$ D				
288	2.2812	1.14501	—	—	p-Bis-(2 : 5-dimethyl-1-pyrrolyl)benzene (XVII)				
699	2.2920	1.14444	—	41	173	2.2731	1.14475	—	—
$\varepsilon = 2.2732 + 2.691\omega$; $\nu = 1.14545 - 0.145\omega$; $\tau P = 137.6$ c.c.; $R_D = 56.1$ c.c.; $\mu = 2.00 \pm 0.04$ D					377	2.2747	1.14451	—	—
					648	2.2751	1.14379	—	47
					964	2.2771	1.14315	—	73
					$\varepsilon = 2.2725 + 0.456\omega$; $\nu = 1.14523 - 0.218\omega$; $\tau P = 95.6$ c.c.; $R_D = 83.5$ c.c.; $\mu = 0.77 \pm 0.03$ D				

2 : 3 : 4 : 5-Tetraiodopyrrole. This was prepared according to Ciamician and Silber (*Ber.*, 1885, 18, 1766) by iodination of pyrrole in alkaline aqueous solution. It is essential in order to avoid formation of tar that the iodine solution be added dropwise no faster than it is consumed : even then the product is strongly coloured. It was recrystallized (charcoal) several times. The final product was slightly yellow; it decomposed without melting at 150—160° [Found : N, 2.6; I, (82.2), 88.7. Calc. for C_4HNI_4 : N, 2.5; I, 89.0%].

3 : 4-Di-iodo-2 : 5-dimethylpyrrole. On attempted direct iodination in neutral aqueous solution, partial decomposition and precipitation of a heavy brown oil occurred. In an alkaline medium (1.9 g. of 2 : 5-dimethylpyrrole, 2 g. of sodium hydroxide in 50 ml. of 50% ethanol) the substance readily takes up the calculated amount of iodine, and white heavy crystals appear. (Undoubtedly the hydrogen iodide set free during iodination in initially neutral solution causes the coloration.) Recrystallized several times from 50% alcohol, the compound had m. p. 123—124° (decomp.) (Found : N, 4.0; I, 73.5. $C_6H_7NI_2$ requires N, 4.0; I, 73.2%).

2 : 5-Dimethyl-1-phenylpyrrole. Ethyl diacetylsuccinate was prepared as described by Fischer ("Anleitung zur Darstellung Organischer Präparate," 1920, 48). It was condensed with aniline in glacial acetic acid (Knorr, *Annalen*, 1886, 236, 305). The ethyl 2 : 5-dimethyl-1-phenylpyrrole-3 : 4-dicarboxylate was hydrolysed and decarboxylated. The product, recrystallized twice from alcohol, had m. p. 49—50° (Knorr, *loc. cit.*, gives 51°).

1-Phenylpyrrole. This was prepared by Köttnitz's method (*J. pr. Chem.*, 1873, 6, 143), *i.e.*, by pyrolysis of anilinium mucate. On being twice recrystallized from alcohol, it was obtained as white leaflets, m. p. 60—61° (Köttnitz, *loc. cit.*, gives 62°).

1-p-Tolylpyrrole. This was prepared similarly and recrystallized from alcohol as white crystals, m. p. 82—82.5° (Pictet, *Ber.*, 1904, 37, 2795, gives 82°).

1-p-Chlorophenylpyrrole. By the same method, this compound was prepared; recrystallized twice from alcohol, it had m. p. 87—88° (Wibaut and Dhont, *Rec. Trav. chim.*, 1933, 62, 272, report 88—89°).

2 : 5 : 2' : 5'-Tetramethyl-1-phenylpyrrole. This and the following compounds were prepared according to Hazlewood, Hughes, and Lions's method (*J. Proc. Roy. Soc. New South Wales*, 1937, 71, 92), *i.e.*, condensation of the appropriate amine with acetylacetone, catalysed by a few drops of 5N-hydrochloric acid. Commercial *p*-xylidine, free from *m*-4-xylidene, was distilled at 214°/760 mm., and condensed with acetylacetone. The product distilled at 148—149°/45 mm. (Hazlewood *et al.*, *loc. cit.*, give 121°/9 mm.).

2 : 5 : 2' : 4' : 6'-Pentamethyl-1-phenylpyrrole. Nitromesitylene, prepared essentially according to *Org. Synth.*, Coll. Vol. II, p. 449, by nitration of commercial mesitylene, was reduced with tin and hydrochloric acid. A complex was precipitated as dark red crystals. It was decomposed by alkali, and the amine isolated by steam-distillation as a slightly yellow product and dried. The b. p. was 233°/760 mm. This product was then condensed with acetylacetone, the reaction proceeding smoothly at 100°. The product was obtained in good yield as a colourless liquid which distilled constantly at 134—135°/11 mm. (Found : C, 84.4; H, 9.0. $C_{15}H_{19}N$ requires C, 84.5; H, 8.9%).

2 : 5-Dimethyl-*p*-tolylpyrrole. Prepared from *p*-toluidine, this formed white crystals, m. p. 45—46° (Knorr, *loc. cit.*, gives 45—46°).

1-*p*-Chlorophenyl-2 : 5-dimethylpyrrole, similarly prepared from *p*-chloroaniline, formed white crystals, m. p. 49—50° (Hazlewood *et al.*, *loc. cit.*, give 50°); the *p*-bromo-compound, from *p*-bromoaniline, formed white crystals, m. p. 74.5—75° (74—75°, *loc. cit.*); and the *p*-nitro-compound, from *p*-nitroaniline, formed yellow crystals, m. p. 145° (145°, *loc. cit.*).

***p*-Bis-(2 : 5-dimethyl-1-pyrrolyl)benzene,** from *p*-phenylenediamine, recrystallized from benzene as white crystals, m. p. 255—257° (Hazlewood *et al.*, *loc. cit.*, give 245—253°) (Found : C, 81.9; H, 7.4. Calc. for $C_{18}H_{20}N_2$: C, 81.8; H, 7.6%).

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