11. *Studies in Dielectric Polarisation. Part XV. The Dipole Moments of Five-membered Nitrogen Ring Compounds: Indole, Skatole, Carbazole, Isatin, Phthalimide, and Succinimide.*

By ERIC G. COWLEY and JAMES R. PARTINGTON.

ALTHOUGH numerous determinations of the moments of six-membered nitrogen ring compounds have been made, the only existing data for five-membered rings containing nitrogen are those for pyrrole and *N*-methylpyrrole (Part XI, J., 1933, 1259; Jackson, *Trans. Faraday Soc.*, 1934, **30**, 800). We have therefore determined the moments of the analogous compounds indole, skatole, and carbazole, and also those of isatin, phthalimide, and succinimide for comparison. We find that the dipole moment increases from pyrrole to indole, but there is then a smaller increase to carbazole. The values of the dipole moments found (in Debye units) are summarised below, together with relevant data of other authors.

Compound.	μ.	Compound.	μ.
Pyrrole	1·83,[1] 1·78[2]	Pyridine	2·11,[4] 2·21,[5] 2·26[8]
N-Methylpyrrole	1·94[2]	*iso*Quinoline	2·53,[5] 2·52,[7] 2·54[8]
Indole	2·05[3]	Quinoline	2·25,[6] 2·14,[5] 2·18,[7] 2·16[8]
Skatole	2·08[3]	—	—
Carbazole	2·09[3]	Acridine	1·95[5]
Isatin	5·72[3]	Succinimide	1·54[3]
		Phthalimide	2·10[3]

References: [1] Cowley and Partington, J., **1933**, 1259 (solvent, benzene). [2] Jackson, *loc. cit.* (solvent not stated). [3] Present research (indole and skatole in benzene; other compounds in dioxan). [4] Lange, *Z. Physik*, 1925, **33**, 169 (solvent, benzene). [5] Bergmann, Engel, and Meyer, *Ber.*, 1932, **65**, 446 (solvent, benzene). [6] Rolinski, *Physikal. Z.*, 1928, **29**, 658 (solvent, benzene). [7] Le Fèvre and Smith, J., **1932**, 2810 (solvent, benzene). [8] Rau and Narayanaswamy, *Z. physikal. Chem.*, 1934, *B*, **26**, 23 (solvent, benzene).

The three compounds pyrrole, indole, and carbazole are very similar in general properties. Chemically, they all exhibit both acidic and basic properties, and the stability increases as the series is ascended. These five-membered nitrogen rings present a comparatively simple case for consideration of the dipole moments, for the regular five-membered ring is flat and the intervalency angles are nearly tetrahedral. This will be approximately the case in the above compounds, the hydrogen atom of the imino-group lying out of the plane of the ring. An approximate calculation of the moment of pyrrole can be made from the following data. In the ammonia molecule the distances are (Mecke, " Structure of Molecules," ed. Debye, 1932, 30) : N–H 0·977, H–H 1·43, height of pyramid 0·517 Å.; hence it follows that the angle between one of the N–H bonds and the plane of the other two is 96° 30′. If the moment of the $\overset{+\!\!\longrightarrow}{\mathrm{C—N}}$ bond is taken as 0·6, from that of trimethylamine 0·6 (Steiger, *Physikal. Z.*, 1931, **32**, 425; vapour measurement) with no allowance for the methyl group, and the angle of the C–N–C bonds is taken as 108° in pyrrole, the resultant moment of the two C–N moments is vectorially added to that of the $\overset{\longleftarrow\!\!+}{\mathrm{N—H}}$ moment, taken as 1·5 from that of ammonia (Watson, *Proc. Roy. Soc.*, 1927, *A*, **117**, 43; vapour measurement). This gives the moment of pyrrole as 1·58, which can be considered as reasonably near the experimental value 1·83, in view of the fact that the influence of the double bonds and the ring has not been allowed for, and also of the uncertainty in the angles. It can be shown that the moment of pyrrole will act in the line joining the nitrogen nucleus and the mid-point of the opposite side of the ring at an angle of about 70° to the plane of the ring.

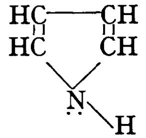
The higher moment of indole than of pyrrole reflects the influence of the benzene ring. The further increase from indole to carbazole is much smaller. These results are compared in the above table with those for the six-membered rings. It is seen that this change in moment is paralleled by the results for pyridine and quinoline. In view of the results of von Auwers and Kraul (*Ber.*, 1925, **58**, 543), which indicate that the acridine molecule contains seven double links, the structure with a para-bond can be eliminated, and the lower moment of acridine than of pyridine and quinoline is therefore unexpected. The fact that the moment of skatole (β-methylindole) differs but little from that of indole would be expected.

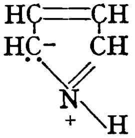
Isatin is generally regarded as being diketonic in the free state and in acid solution. Its structure cannot be definitely deduced from the available data for the absorption spectra of this compound and its *N*- and *O*-ethers, since the conclusions of Hartley and Dobbie, (J., 1899, **75**, 640) and Dabrowski and Marchlewski, (*Bull. Soc. chim.*, 1933, **53**, 946) have not been supported by other authors (Morton and Rogers, J., 1925, **127**, 2698; Ault, Hirst, and Morton, J., 1935, 1653), although the spectrum of isatin resembles that of its *N*-methyl ether rather than that of its *O*-methyl ether. The large value of the dipole moment, however, can be most easily explained by the diketonic formula. From a consideration of the moment of indole, 2·05, and of the keto-group, 3·0 (from the moment of benzophenone; Fuchs and Donle, *Z. physikal. Chem.*, 1933, *B*, **22**, 1), and their respective positions on the ring, it can be calculated that the moment of isatin would be large, and that of the isomeric phthalimide much smaller : the values now found, *viz.*, 5·72 and 2·10 respectively, are in agreement with this calculation.

Succinimide has a lower moment than phthalimide, and this leads to the conclusion that the five-membered ring containing nitrogen and also the two keto-groups has a large polarising influence on the benzene ring. Rau and Narayanaswamy (*loc. cit.*) find that the moments of the derivatives of pyridine and quinoline, calculated on the assumption that the C–N bond has a moment of 1·3, are in good agreement with the observed figures for these compounds. Since the C–N moment was deduced from the nitrile group moment, however, these calculations are open to objection, for it has been shown (*e.g.*, Sidgwick, " The Covalent Link in Chemistry," 1933, p. 153) that the increase of the moment of a multiple link over that of the corresponding single link is greater than would be expected from the number of links.

The energies of the pyrrole, indole, and carbazole molecules have been examined by Pauling and Sherman (*J. Chem. Physics*, 1933, **1**, 606), who compared the heats of formation *E* of the various possible electronic structures of different molecules with the heat of formation *E*′ calculated for the usual structure. The difference *E* — *E*′ may be interpreted as the resonance energy of the molecule among these electronic structures. The differences are for pyrrole 0·98, indole 2·34, and carbazole 3·93 volt-electrons. Pauling and Sherman, therefore, postulate that the large resonance energy requires that, in addition to the ordinary form of pyrrole (I), other structures contribute strongly to the normal state of the molecule, the four of the type (II) being the most reasonable, since a negative carbon atom, with three shared and one unshared pair of electrons, occurs in other structures. The resonance energies of indole and carbazole are both a little lower respectively than the energies of (i) pyrrole plus benzene and (ii) pyrrole plus twice that of benzene, as would be expected since the sharing of atoms by both rings partially inhibits resonance.

(I.)





(II.)

The effect of these excited structures on the dipole moment of pyrrole has been considered by Sutton (*Trans. Faraday Soc.*, 1934, **30**, 799), but further work on the substituted pyrroles is necessary in order to obtain more definite evidence on this question.

EXPERIMENTAL.

The apparatus and method of calculation were those of the previous paper.

Materials.—All the compounds used were obtained from Kahlbaum and had the following m. p.'s : indole 52·5°, skatole 95·1°, carbazole 245·0°, isatin 201·0°, phthalimide 238·0°. Succinimide was heated in a vacuum and twice recrystallised from anhydrous acetone; m. p. 125·0°.

Kahlbaum's " thiophen-free " benzene, which had been dried by sodium and fractionated, was used as solvent for indole and skatole. The solubility of the other compounds in benzene was too low to allow moments to be measured, so these were determined in dioxan. The dioxan (B.D.H.), which had been purified by treatment with sodium wire until no further action took place, was fractionated several times and finally frozen out. It was always dried and fractionated before each measurement. The dielectric constants of the specimens of dioxan used were little different from that of benzene, so that the comparison of the moments in the two solvents is justifiable. All the measurements were made at 20°.

Measurements in benzene solution.

Indole.

f_2.	ϵ.	$D_{4^\circ}^{20^\circ}$.	P_{12}.	P_2.
0	2·279	0·8786	26·56	—
0·006295	2·320	0·8804	27·18	125·1
0·014449	2·375	0·8830	27·99	125·5
0·023030	2·433	0·8855	28·83	125·1
0·028441	2·469	0·8871	29·34	124·3

$P_{2\infty} = 125·7$ c.c.; $P_E = 36·5$ c.c.;
$P_{2\infty} - P_E = 89·2$ c.c.; $\mu = 2·05$.

Skatole.

f_2.	ϵ.	$D_{4^\circ}^{20^\circ}$.	P_{12}.	P_2.
0	2·279	0·8786	26·56	—
0·006850	2·324	0·8806	27·27	130·2
0·015841	2·379	0·8832	28·14	126·3
0·024339	2·430	0·8858	28·92	123·5
0·027826	2·450	0·8868	29·23	122·5

$P_{2\infty} = 132·5$ c.c.; $P_E = 41·1$ c.c.;
$P_{2\infty} - P_E = 91·4$ c.c.; $\mu = 2·08$.

Measurements in dioxan solution.

Carbazole.

0	2·237	1·0325	24·90	—
0·007559	2·293	1·0345	25·80	144·0
0·016210	2·355	1·0365	26·82	144·3
0·021625	2·395	1·0375	27·45	142·8
0·027953	2·440	1·0391	28·18	142·2

$P_{2\infty} = 144·6$ c.c.; $P_E = 51·8$ c.c.;
$P_{2\infty} - P_E = 92·8$ c.c.; $\mu = 2·09$.

Isatin.

0	2·237	1·0328	24·90	—
0·006209	2·550	1·0355	29·10	701·3
0·010335	2·768	1·0374	31·70	682·9
0·012977	2·908	1·0388	33·25	668·4
0·017953	3·177	1·0407	36·02	644·3

$P_{2\infty} = 731·9$ c.c.; $P_E = 40·4$ c.c.;
$P_{2\infty} - P_E = 691·5$ c.c.; $\mu = 5·72$.

Phthalimide.

0	2·243	1·0324	24·99	—
0·005255	2·280	1·0342	25·56	133·5
0·008962	2·307	1·0359	25·96	133·2
0·014725	2·349	1·0381	26·58	133·0
0·018699	2·378	1·0395	27·00	132·5

$P_{2\infty} = 133·7$ c.c.; $P_E = 40·4$ c.c.;
$P_{2\infty} - P_E = 93·3$ c.c.; $\mu = 2·10$.

Succinimide.

0	2·244	1·0326	25·00	—
0·005860	2·266	1·0342	25·29	75·6
0·012737	2·292	1·0362	25·63	74·5
0·017458	2·310	1·0375	25·86	74·3
0·022599	2·330	1·0389	26·16	74·1

$P_{2\infty} = 76·0$ c.c.; $P_E = 25·6$ c.c.;
$P_{2\infty} - P_E = 50·4$ c.c.; $\mu = 1·54$.

SUMMARY.

The following moments (in *D*) have been measured and the results discussed : indole 2·05, and skatole 2·08, in benzene; carbazole 2·09, isatin 5·72, phthalimide 2·10, and succinimide 1·54, in dioxan.

We thank the Chemical Society and the Dixon Fund for grants, and one of us (E. G. C.) is indebted to the University of London for the award of a Postgraduate Studentship.

QUEEN MARY COLLEGE, LONDON, E. 1.

[*Received, October* **22*nd*, 1935.**]