# 327. *The Dipole Moment of Pyrrole measured in the Dissolved and in the Gaseous State.*

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The apparent dipole moment of pyrrole dissolved in benzene is slightly lower than that as a gas. Such a relationship is qualitatively predicted by equations (1) and (2) of Buckingham and Le Fèvre (*J.*, 1952, 1932).

IT is well known that small dipole moments are difficult to determine with accuracy. Hence the numerical quotients $\mu_{\text{solution}}/\mu_{\text{gas}}$, obtained by dividing values from experiment, are likely to be more certain the larger the polarity of the molecule considered. From this viewpoint, pyrrole ($\mu$ = *ca.* 1·8 D) should be a better compound to study than either furan ($\mu$ = *ca.* 0·7 D) or thiophen ($\mu$ = 0·5 D) (see preceding paper). An examination of this base is therefore now reported.

*Present Work.*—Pyrrole was obtained by heating ammonium mucate (cf. *Org. Synth.*, Coll. Vol. 1, 1941, p. 473); it was redistilled over potassium hydroxide before use.

Polarisations of vaporised pyrrole at five temperatures were recorded relatively to carbon dioxide. Essential readings are in Table 1.

TABLE 1. *Polarisation–temperature relation for gaseous pyrrole.*

| $T$, °K | No. of obs. | Press. range (cm. Hg) | $x/x'$ | $P$ (obs.) | $P$ (calc.) * |
|---|---|---|---|---|---|
| 391·3 | 9 | 3—10 | $10{\cdot}03_5$ | 73·67 | 73·58 |
| 413·8 | 11 | 9—19 | $9{\cdot}59_5$ | 70·44 | 70·71 |
| 426·9 | 10 | 7—16 | $9{\cdot}39_5$ | 68·97 | 69·16 |
| 452·0 | 7 | 9—20 | $9{\cdot}19_4$ | 67·49 | 66·48 |
| 465·7 | 9 | 10—28 | $8{\cdot}78_1$ | 64·46 | 65·13 |

* Calibrating equation used: $(\delta C/p)_{CO_2} = -0{\cdot}157 + 2229{\cdot}5/T$.

The dielectric constants of solutions of pyrrole in benzene were determined with a circuit newly constructed to replace that used previously (cf. *J.*, 1948, 1949), which suffered from " drifts " as the batteries gradually became discharged. Details are shown in the Figure. Only miniature valves are employed so that a conventional power-pack, stabilised by voltage-regulator tubes, is sufficient to provide both heater current and high-tension supply. The (Franklin) oscillator, with its filaments connected in series, is followed by a " buffer " R.F. amplifier, which in turn is coupled through a mounted quartz-crystal-containing condenser to a valve voltmeter. The dielectric cell and standard variable capacity are joined in parallel across the inductance $L$. The reference point is taken as the centre of the sigmoid curve exhibited by $M$ as the oscillation frequency passes through the natural frequency of the quartz crystal. Measurements obtained, and equations fitted thereto by the method of least squares, are given in Table 2. Quoting standard errors, we find from Table 1 : $(P)_T = (20{\cdot}8 \pm 5{\cdot}2) + (20{,}636 \pm 2232)/T$, whence $\mu_{gas} = 1{\cdot}84 \pm 0{\cdot}08$ D; and from Table 2: $(\alpha\varepsilon_1)_{w_2=0} = 5{\cdot}282 \pm 0{\cdot}014$, and $(\beta d_1)_{w_2=0} = 0{\cdot}0947 \pm 0{\cdot}0001$, so that ${}_{\infty}P_2$ becomes 87·04 ± 0·17 c.c. With a distortion polarisation of 20·8 ± 5·2 c.c., the dipole moment of pyrrole in benzene follows as 1·80 ± 0·07 D. These results are in harmony with others in the literature (see Table 3).

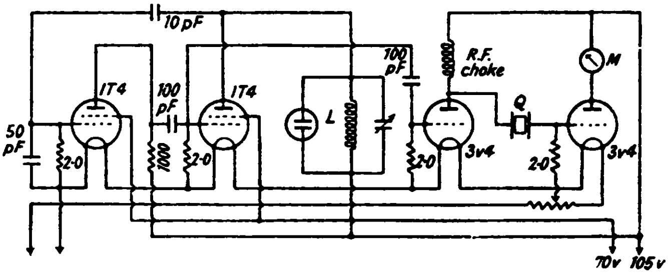

TABLE 2. *Pyrrole in benzene at 25°.*

| | | | | | |
|---|---|---|---|---|---|
| $10^6 w_2$ | 0 | 12,450 | 26,350 | 31,635 | 36,748 |
| $\varepsilon_{25}$ | 2·2725 | 2·3385 | 2·4146 | 2·4440 | 2·4711 |
| $d_4^{25}$ | 0·87378 | 0·87493 | 0·87614 | 0·87654 | 0·87697 |

whence $\delta\varepsilon = (\varepsilon_{12} - \varepsilon_1)_{w_2} = 5{\cdot}282\, w_2 + 3{\cdot}8\, w_2^2$
and $\delta d = (d_{12} - d_1)_{w_2} = 0{\cdot}0947\, w_2 - 0{\cdot}22\, w_2^2$

| | | | | |
|---|---|---|---|---|
| $10^4\delta\varepsilon$ (obs.) | 660 | 1421 | 1715 | 1986 |
| ,, (calc.) | 663 | 1418 | 1709 | 1992 |
| $10^5\delta d$ (obs.) | 115 | 236 | 276 | 319 |
| ,, (calc.) | 115 | 234 | 277 | 318 |

TABLE 3. *Dipole-moment values recorded for pyrrole.*

| Moment, D | Method | Authors |
|---|---|---|
| 1·80 ± 0·07 | In benzene at 25° | This paper. |
| 1·84 ± 0·08 | Gas | ,, ,, |
| 1·80 | In benzene at 25° | Kofod, Sutton, and Jackson, *J.*, 1952, 1467. |
| 1·80 | ,, ,, 20° | Robles, *Rec. Trav. chim.*, 1939, **58**, 111. |
| 1·83 | ,, ,, ,, | Cowley and Partington, *J.*, 1933, 1259. |

*Predicted Values of* $\mu_{solution}/\mu_{gas}$.—Scale drawings based on the dimensions of the pyrrole molecule quoted by Allen and Sutton (*Acta Cryst.*, 1950, **3**, 46), together with Stuart's " Wirkungsradien," give—if the N–H bond is taken as lying in the $C_4$-plane—$A = 5{\cdot}83_5$, $B = 6{\cdot}12$, and $C = 2{\cdot}90$, whence $\exp x^2 = 0{\cdot}504_5$. For the Na-D line $n^{25}_{pyrrole}$ is 1·5051 and $n^{25}_{benzene}$ is 1·4976. The volume polarisation of benzene at 25° is 0·2978. Accordingly, we would predict the ratio $\mu_{C_6H_6}/\mu_{gas}$ as $0{\cdot}92_5$ or 0·93 respectively by the equations (1) or (2) of *J.*, 1952, 1932. The value now found is 0·98 ± 0·08. The Ross–Sack equation [*i.e.* (4) in the same paper] forecasts 0·92 (using a ξ factor of 0·24, cf. Osborn, *Phys. Review*, 1945, **67**, 351). All three relations, therefore, correctly require the " solvent effect " (*viz.*, $\pm\,\delta\mu = \mu_{soln.} - \mu_{gas}$) to be negative in sign, in accordance with experiment. As with furan, however, the *observed* $-\delta\mu$ is somewhat smaller than that calculated. Remembering the uncertainties underlying the " Wirkungsradien " used to produce $A$, $B$, and $C$, we view the result, on the whole, as satisfactory.

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