## *The Electric Moment of* 1-*Methylpyrrolid*-2-*one.*

By Ernst Fischer.

[Reprint Order No. 5677].

In a recent paper (*J.*, 1952, 4525; 1953, 2836) a comparison was made between calculated and "experimental" dipole moments of pyrrolid-2-one, and conclusions were drawn regarding the contribution of dipolar mesomers to the structure of this compound. At that time no reliable data were available for the dipole moment of this ketone, and the value for piperid-2-one was used instead. The moments of pyrrolid-2-one and its 1-methyl derivative have now been measured, the results corroborating the conclusions reached in the previous paper.

Pyrrolid-2-one, like oxazolid-2-one described previously, is strongly associated in benzene solution, as shown by the fact that the slope of the curve of dielectric increment against concentration increases with decreasing concentration even at weight fractions below $10^{-3}$. With the methylated compound, on the other hand, this curve is rectilinear up to weight fractions above $8 \times 10^{-3}$, proving that the *N*-hydrogen atom is responsible for the association. From the tangent of the plot of dielectric increment against weight fractions up to $10^{-3}$ the moment calculated for pyrrolid-2-one is 3·7 D. Because of the pronounced association this value is probably still too low, and is mentioned here only because the value of 2·3 D reported by Devoto (*Gazzetta*, 1933, **63**, 495) appears to be much too low as it is based on measurements at much higher concentrations, where association is of course considerable. For 1-methylpyrrolid-2-one the moment found was $4{\cdot}09 \pm 0{\cdot}04$ D, to be compared with 4·0 D observed for 1-methylpiperidone. Comparison with the calculated moment of 2·8 D leads to a contribution by dipolar mesomers of about 16%, thus corroborating earlier results with open amides (Kumler, *J. Amer. Chem. Soc.*, 1952, **74**, 261).

*Experimental.*—Pyrrolid-2-one and 1-methylpyrrolid-2-one were kindly given by Messrs. General Aniline and Film Corporation, New York, and purified by vacuum distillation immediately before use. Pyrrolid-2-one had $n_D^{25}$ 1·486, $d_4^{25}$ 1·107; 1-methylpyrrolid-2-one had $n_D^{25}$ 1·469, $d_4^{25}$ 1·027. The resulting molar refractions $R_D$ for the sodium-*D* line are 22·0 and 26·9 ml., in good agreement with the values calculated from bond refractions (Vogel *et al.*, *J.*, 1952, 514).

The dipole moment was calculated from the slopes of the rectilinear plots of dielectric constant increment $\Delta\varepsilon(= \varepsilon_{sol.} - \varepsilon_{solv.})$ and density increment $\Delta d(= d_{sol.} - d_{solv.})$ against weight fraction $w$ in benzene at 30° (cf. Bergmann, Weizmann, and Fischer, *J. Amer. Chem. Soc.*, 1950, **72**, 5009, where the symbols and the method of extrapolation used are explained). Experimental figures for 1-methylpyrrolid-2-one are given in the Table.

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $10^5w$ ..... | 27 | 45·5 | 63·5 | 81·5 | 109 | 145 | 172·5 | 1783 |
| $10^4\Delta\varepsilon$ ..... | 49 | 82 | 115 | 148 | 197 | 262 | 310 | — |
| $10^5\Delta d$ ..... | — | — | — | — | — | — | — | 291 |

$C\alpha\varepsilon_0 = 3{\cdot}415$, $\beta = 0{\cdot}188$, $P_\infty = 366$ ml., $1{\cdot}05R_D = 28$ ml., $P_\infty - 1{\cdot}05R_D = 338$ ml., $\mu = 4{\cdot}09 \pm 0{\cdot}04$ D.

WEIZMANN INSTITUTE OF SCIENCE, REHOVOTH, ISRAEL. [*Received, August 23rd*, 1954.]