286. *The Dipole Moments of Pyridine, Quinoline, and* isoQuinoline
as Vapours and as Solutes.

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Determinations of the polarisations of the substances named in the title
as vapours reveal limitations in accuracy of the conventional experimental
arrangements. New measurements of the dipole moments of these liquids
as solutes in light petroleum, carbon tetrachloride, or benzene show that
quinoline and *iso*quinoline conform within $\pm 3\%$ to an empirical equation
advanced by Buckingham and Le Fèvre, the second liquid doing so more
satisfactorily than the first. The $\mu_{soln.}/\mu_{gas}$ ratios found for pyridine are
notably higher than expected. This behaviour may be attributed in part to
association with the solvents : thus pyridine and carbon tetrachloride could
tend to form a quaternary polar complex; alternatively $_A P_{C_5 H_5 N}$ might be
increased as an effect of solvation. In either case the moment—and hence
the quotient $\mu_{soln.}/\mu_{gas}$—recorded by use of the refractivity method applied to
solutions would appear to be larger than that forecast by previously adequate
relations.

The measurements here recorded, commenced several years ago, were to provide critical
data for the comparison of various equations by which the " true " or gas-phase dipole
moments of molecules could be predicted from experiments on solutions. It seemed that
three solutes—pyridine, quinoline, and *iso*quinoline—offered interesting differences in
shape-factors although their polarities were roughly the same.

As no figures for the three " gas " moments were available, determinations of the
polarisations of the vapours at temperatures from 90° to 315° were undertaken. The
observations listed below were made by several of the authors at widely separated intervals.

The order of their accuracy is not so high as it was hoped to achieve. The technical difficulties incurred in making the polarisation measurements at high temperatures, and the uncertainties inherent in the calibration of the apparatus, are considered in detail below.

In addition, earlier determinations of the electric moments of the three substances in benzene have been supplemented; and new ones have been made in light petroleum and carbon tetrachloride. These results are summarised in Table 1.

TABLE 1. *Dipole moments and* $\mu_{soln.}/_{gas}$ *ratios for pyridine, quinoline, and* isoquinoline.*

Substance	$\mu_{l.p.}$†	μ_{CCl_4}	$\mu_{C_6H_6}$	μ_{gas}	$\mu_{l.p.}/\mu_{gas}$	μ_{CCl_4}/μ_{gas}	$\mu_{C_6H_6}/\mu_{gas}$
Pyridine	2·27	2·37	2·25	2·23 (0·02)	1·02 (0·02)	1·06 (0·02)	1·01 (0·02)
Quinoline	2·17	2·27	2·24	2·29 (0·05)	0·95 (0·06)	0·99 (0·06)	0·98 (0·06)
isoQuinoline	2·60	2·65	2·61	2·73 (0·03)	0·95 (0·04)	0·97 (0·04)	0·96 (0·04)

* Figures in parentheses following μ_{gas} are standard deviations calculated from observations. Estimates of the standard deviations of the quotients have been made by assuming those of the solution moments to be $\pm 1\%$ of the values tabulated.
† " l.p." = light petroleum.

EXPERIMENTAL

Polarisations of Vapours.—For the vapours of pyridine, quinoline, and isoquinoline we used the high-temperature oven–Franklin oscillator–wavemeter combination.[1] For one series of measurements on pyridine, the apparatus was calibrated with sulphur dioxide. The quantity $x' = (\partial C/p)_{p\to 0}$ for this substance at any temperature was obtainable from an experimental curve, $x' = (241\cdot15/T - 0\cdot2095)$, and the polarisation [2] $P_{SO_2} = 10\cdot9 + 16160/T$.

For the other two substances, and for a second sequence of measurements on pyridine, benzene was taken as the standard gas. Using dry air with $_TP = 4\cdot344$ c.c. as a primary standard,[3] we found the average polarisation of benzene vapour at those temperatures to be $27\cdot2 \pm 0\cdot2$ c.c. The standard deviations of the constants in the Debye equations were computed.[4]

TABLE 2. *Polarisations of vapours.*

Temp. (°K)	x/x'	No. of obsns.	Press. range (cm. Hg)	P (c.c.) (msd.)	P (c.c.) (calc.)	μ *	Temp. (°K)	x/x'	No. of obsns.	Press. range (cm. Hg)	P (c.c.) (msd.)	P (c.c.) (calc.)	μ *
							Pyridine †						
414·7	1·868	13	16—60	93·2	93·4	—	539	1·866	15	18—60	76·3	76·1	—
428·1	1·847	14	15—62	89·8	91·0	—	562	1·841	15	19—62	73·1	73·7	—
477·4	1·902	19	14—62	85·2	83·5	—	588	1·831	19	15—59	70·3	71·3	—
518	1·891	16	20—61	79·6	78·4	—							

whence $P = (18\cdot4 \pm 3\cdot6) + (31,090 \pm 1630)/T$; $\mu = 2\cdot26 \pm 0\cdot06$ D.

Pyridine ‡ ($R_D = 24\cdot1$ c.c.)							Quinoline ‡ ($R_D = 41\cdot9$ c.c.)						
365	3·863	5	6—13	105·1	104·7	2·20	482	3·945	10	5—7	107·3	110·1	2·27
431	3·374	5	6—11	91·8	92·0	2·19	498	3·961	11	7—8	107·8	107·1	2·32
439	3·319	6	6—11	90·3	90·7	2·18	499	3·999	9	3—7	108·8	106·9	2·34
499	3·036	6	6—8	82·6	82·5	2·19	521	3·832	11	5—10	104·4	103·0	2·31
542·5	2·864	5	14—21	77·9	77·6	2·19	572	3·447	15	4—9	93·8	95·1	2·21

whence $P = (22\cdot0 \pm 1\cdot3) + (30,175 \pm 590)/T$; $\mu = 2\cdot23 \pm 0\cdot02$ D (For pyridine).
Debye equation : $P = (14\cdot2 \pm 17\cdot7) + (46,270 \pm 9100)/T$; $\mu = 2\cdot8 \pm 0\cdot3$ D (For quinoline).
Refractivity method : $\mu = 2\cdot29 \pm 0\cdot05$ D (For quinoline).

isoQuinoline ‡ ($R_D = 41\cdot5$ c.c.)													
448	5·246	9	1—2	142·6	144·3	2·73	513	4·774	11	4—8	129·9	130·0	2·73
469	5·247	9	4—6	142·7	139·2	2·79	513	4·737	9	1—9	128·8	130·0	2·71
492	4·980	6	4—7	135·5	134·2	2·76	547	4·667	11	5—10	126·9	123·8	2·77
494	4·800	8	1—3	130·6	133·7	2·69	565	4·459	11	8—13	121·3	120·9	2·71
497	4·974	12	5—8	135·3	133·1	2·76	567	4·368	11	7—20	118·8	120·9	2·68

Debye equation : $P = (31\cdot6 \pm 32\cdot6) + (50,650 \pm 16,540)/T$; $\mu = 2\cdot9 \pm 0\cdot5$ D.
Refractivity method : $\mu = 2\cdot73 \pm 0\cdot03$ D.

* By refractivity method. † Standard vapour : SO₂. ‡ Standard vapour : benzene.

[1] Freeman, Le Fèvre, Rao, and Ross, *J.*, 1955, 3840.
[2] Le Fèvre, Ross, and Smythe, *J.*, 1950, 267.
[3] Le Fèvre, " Dipole Moments," Methuen, London, 3rd edn., 1953, p. 45.
[4] Cf., *e.g.*, Youden, *Analyt. Chem.*, 1947, **19**, 946.

The results are shown in Table 2. For pyridine, the two series of determinations gave Debye equations which were compatible with each other within the standard errors of their A and B terms. The measurements with benzene as standard were more self-consistent and hence the value $\mu = 2 \cdot 23 \pm 0 \cdot 02$ D will be taken for the true dipole moment of pyridine.

From the experimental standpoint, the temperature ranges over which the measurements could be made were limited by the b. p.s of the substances on the one hand and by the instability of vacuum-greases, glass diaphragms, and electric connections on the other. For quinoline and isoquinoline, these conditions restricted measurements to ranges of *ca.* 100° : extrapolation from such short temperature ranges gave standard deviations of $_{\mathrm{D}}P$, in the Debye equations,

TABLE 3. *Dielectric constants and densities of solutions.*

$10^5 w_2$	ε_{25}	d_4^{25}	$10^5 w_2$	ε_{25}	d_4^{25}	$10^5 w_2$	ε_{25}	d_4^{25}
			Pyridine in light petroleum					
1043	1·9805	0·6981	1883	2·0212	0·7004	3940	2·1307	0·7037
1248	1·9913	0·6982	1958	2·0273	0·6995	4247	—	0·7041
1411	2·0017	0·6985	2444	2·0522	0·7006			
			Pyridine in carbon tetrachloride					
543	2·3024	1·57955	1127	2·3845	1·57429	1858	2·4843	1·56755
1002	2·3658	1·57523	1702	2·4641	1·56882	2029	1·5078	1·56554
			Pyridine in benzene					
993	2·3420	0·87384	2891	2·4749	0·87684	6081	2·6982	0·88019
1361	2·3660	0·87529	4988	2·6217	0·87904	6935	2·7579	0·88108
1877	2·4039	0·87578						
			Quinoline in light petroleum					
931	1·9583	0·6982	1581	1·9767	0·6999	3201	2·2076	0·7042
1087	1·9626	0·6985	1965	1·9896	0·7008	3575	2·0409	0·7052
1151	1·9659	0·6986	2625	2·0109	0·7027	3893	2·0507	0·7061
			Quinoline in carbon tetrachloride					
859	2·2986	1·57829	1261	2·3313	1·57575	1663	2·3645	1·57293
892	2·3011	1·57818	1422	2·3430	1·57487	1789	2·3738	1·57184
			Quinoline in benzene					
561	2·2980	0·8747	1875	2·3585	0·8773	3106	2·4161	0·8794
797	2·3070	0·8755	1952	2·3585	0·8775	3169	2·4165	0·8799
898	2·3143	0·8753	1954	2·3656	0·8776	3506	2·4092	0·8802
1041	2·3208	0·8756	2926	2·4055	0·8794	3557	2·4353	0·8805
			isoQuinoline in light petroleum					
914	1·9705	0·6983	1946	2·0118	0·7010	4230	2·1103	0·7073
1511	1·9943	0·6998	2133	2·0180	0·7015	4293	2·1096	0·7074
1813	2·0065	0·7006	2150	2·0185	0·7016	5261	2·1539	0·7100
			isoQuinoline in carbon tetrachloride					
797	2·3144	1·58398	1261	2·3660	1·58371	1659	2·4104	1·57352
853	2·3206	1·58394	1365	2·3774	1·57594	2430	2·4951	1·56806
			isoQuinoline in benzene					
610	2·3089	0·87504	896	2·3264	0·87558	1017	2·3338	0·87588
780	2·3204	0·87538	989	2·3320	0·87579	2233	2·4087	0·87830

TABLE 4. *Calculation of results from solutions.*

Solute	Solvent	$\alpha\varepsilon_1$ (mean)	β (mean)	$_\infty P_2$ (c.c.)	R_D (c.c.)	μ (D)
Pyridine	L. p.	4·99	0·284	129·3	24·1	$2 \cdot 2_7$
,,	CCl$_4$	13·84	−0·583	138·8	,,	$2 \cdot 3_7$
,,	C$_6$H$_6$	6·99	0·117	127·8	,,	$2 \cdot 2_5$
Quinoline	L. p.	$3 \cdot 06_5$	0·367	138·3	41·9	$2 \cdot 1_7$
,,	CCl$_4$	$8 \cdot 25$	−0·443	147·1	,,	$2 \cdot 2_7$
,,	C$_6$H$_6$	4·48	0·214	144·4	,,	$2 \cdot 2_4$
isoQuinoline	L. p.	4·22	0·382	179·3	41·5	$2 \cdot 6_0$
,.	CCl$_4$	11·01	−0·424	184·4	,,	$2 \cdot 6_5$
,,	C$_6$H$_6$	6·06	0·233	181·0	,,	$2 \cdot 6_1$

which exceeded the numerical values of $_DP$ obtained. For these compounds, the dipole moments were calculated *via* the orientation polarisations, taken as $(_TP - R_D)$.

Solution Measurements.—A new apparatus for the measurement of the dielectric constants of liquids has been constructed to replace those described in *J.*, 1948, 1949, and *J.*, 1953, 1626. Circuit details are shown in the Figure. The arrangement is a less sensitive version of that developed for gases by Le Fèvre, Ross, and Smythe (ref. 2, Fig. 3). The test cells and standard (Sullivan 50—250 μμF) variable condenser C, used formerly, have been retained. The reference
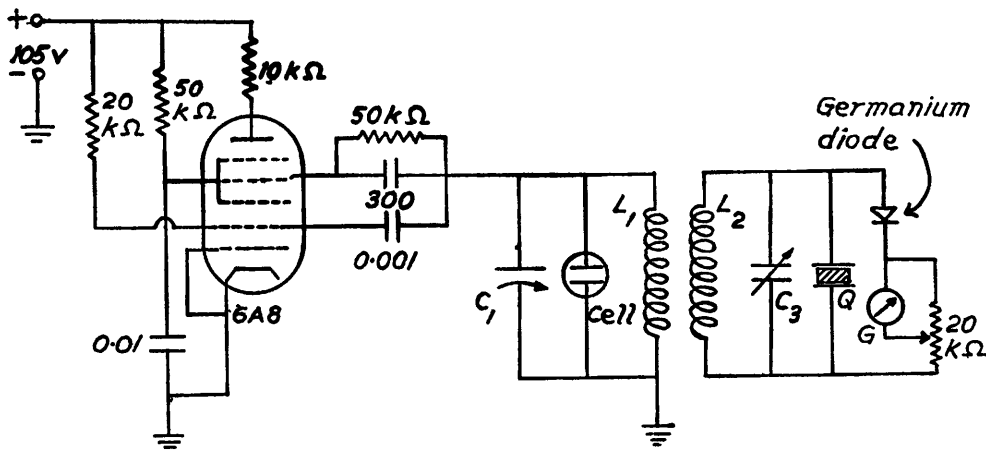
TABLE 5. *Comparison of present data with those from earlier literature.*

Solvent	Temp.	$_∞P_2$ (c.c.)	$_DP$ (c.c.)	$μ(D)$	No. of solns. examined	Ref.	Solvent	Temp.	$_∞P_2$ (c.c.)	$_DP$ (c.c.)	$μ(D)$	No. of solns. examined	Ref.
					Pyridine								
C_6H_6	24°	*ca.* 23 114 *	2·11	6 †	a		CCl_4	20°	139·3	?	2·33	?	⎫
							C_6H_6	20	132·6	?	2·26	?	
C_6H_6	15·1	$∞(_oP)$ = 104·5	2·21	4	b		C_6H_5Me	20	131·0	?	2·25	?	e
							CS_2	20	117·8	?	2·10	?	⎭
C_6H_6		$P = 31·3 +$ $31,420/T$	2·26	?	c		C_6H_6	25	125·4	26·5	2·20	3	⎫ f
							Dioxan	25	127·8	26·5	2·22	4	⎭
C_6H_6	17	130·7	24·54	2·23	?	d	L. p.	25	129·3	24·1	2·27	8	⎫
	(From P at 3 temperatures)	2·34	—				CCl_4	25	139·1	24·1	2·37	6	g
C_6H_{14} *cyclo-*	20	127·7	?	2·21	?	⎫	C_6H_6	25	127·8	24·1	2·25	5	⎭
Hexane	20	126·5	?	2·20	?	⎭ e							
					Quinoline								
C_6H_6	25	*ca.* 150 *	?	2·25	9 †	h	C_6H_6	25	141·1	41·9	2·19	4	j
							?	?	?	?	2·18	?	k
C_6H_6	14·2	$∞(_oP)$ = 97·4	2·14	4	b		L. p.	25	138·3	41·9	2·17	9	⎫
C_6H_6	25	141	41·9	2·18	3	i	CCl_4	25	147·1	41·9	2·27	6	g
C_6H_6		$P = 39·0 +$ $28,980/T$	2·16	?	c		C_6H_6	25	144·4	41·9	2·24	12	⎭
					*iso*Quinoline								
C_6H_6	14·2	$∞(_oP)$ = 137·5	2·53	4	b		C_6H_6	25	175·8	41·5	2·55	4	j
							L. p.	25	179·3	41·5	2·60	9	⎫
C_6H_6	25	173·7	41·5	2·52	3	i	CCl_4	25	184·4	41·5	2·65	6	g
C_6H_6		$P = 41·2 +$ $39,770/T$		2·54	?	c	C_6H_6	25	181·0	41·5	2·61	6	⎭

References. (a) Lange, *Z. Physik*, 1925, **33**, 169. (b) Bergmann, Engel, and Meyer, *Ber.*, 1932, **65**, 446. (c) Rau and Narayanaswamy, *Z. phys. Chem.*, 1934, *B*, **26**, 23. (d) Goethals, *Rec. Trav. chim.*, 1935, **54**, 299. (e) Middleton and Partington, *Nature*, 1938, **141**, 516. (f) Leis and Curran, *J. Amer. Chem. Soc.*, 1945, **67**, 79. (g) Present work. (h) Rolinski, *Physikal. Z.*, 1928, **29**, 658. (i) Le Fèvre and Smith, *J.*, 1932, 2810. (j) Le Fèvre and Le Fèvre, *J.*, 1935, 1470. (k) Topchiev, Yakshin, and Shindel, *Chem. Abs.*, 1943, **37**, 290.

? = Not stated in source quoted.
* = Estimated by present authors.
† = Complete concentration range from 0—100% covered.

point is the sharp minimum of a current " crevasse."[5] For this reason it is desirable to choose by trial a mounted quartz crystal which exhibits one " crevasse " which is notably deeper than others usually accompanying it. Performance has proved most satisfactory, drift being negligible during several hours.

Observations are tabulated under the usual headings in Table 3. For the three solvents, the necessary physical properties are listed below Table 6. Table 4 shows the calculations of the moments in solution, and Table 5 summarises data from the literature.

Materials.—B.D.H. pyridine was purified *via* the zinc chloride double salt (twice recrystallised from alcohol), and distilled over sodium hydroxide pellets just before use; it had b. p. 115—115·5°/760 mm (Biddiscombe, Coulson, Handley, and Herington[6] give b. p. 115·256°/760 mm.; cf. also Heap, Hones, Speakman[7]). Quinoline (B.D.H. " synthetic ") was treated with a diazotising mixture[8] and steam-distilled to remove all volatile material. The mixture was then made alkaline and again steam-distilled. The quinoline after separation was dried (KOH) and fractionated through a 24″ column, packed with Fenske helices, under adiabatic conditions. Collection for use was made at 140—143°/*ca.* 50 mm. or 124—125°/25—26 mm. *iso*Quinoline (B.D.H.) was solid at room temperature; it was twice fractionated through the column used for quinoline, the portion with b. p. 117°/15 mm. being retained. Benzene and carbon tetrachloride were purified by methods often described previously.[9] Light petroleum, b. p. *ca.* 80°, was used without further treatment other than drying with sodium.

DISCUSSION

In order to test the several empirical relations between $\mu_{\text{soln.}}$ and μ_{gas}, scale drawings were made as described before.[10] They were based on the published dimensions of pyridine

(I)   (II)   (III)
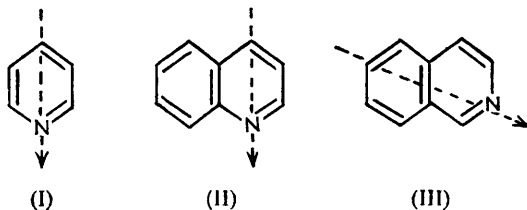
and naphthalene.[11] The molecular dimensions, together with the assumption[12] that the molecular resultant moments act as indicated in (I), (II), and (III), yielded the geometrical part of the data in Table 6, which shows the ratios $\mu_{\text{soln.}}/\mu_{\text{gas}}$ predicted by the relations of Barclay and Le Fèvre and of Buckingham and Le Fèvre.[10] Ross and Sack's equation[13] has also been applied since this seems the most satisfactory yet produced of those which rest upon *a priori* theory;[14] the internal field functions ζ have been read from Osborn's graphs of demagnetising factors.[15] Comparison with the predictions of $\mu_{\text{soln.}}/\mu_{\text{gas}}$ in Table 6 shows the Buckingham–Le Fèvre formula to be applicable within $\pm 3\%$ to quinoline and *iso*quinoline; the three cases involving pyridine display ratios from 6 to 14% larger than those forecast.

We have accordingly considered whether our figures for μ_{gas} of pyridine are too low, or those for $\mu_{\text{soln.}}$ too high. The former is improbable : $_DP$ usually exceeds R_D, so that the use of the correct $_DP$'s—were they more satisfactorily known—would yield smaller values for μ_{gas} than those of Table 2. We note in this connection that two determinations of μ_{pyridine} by Stark splitting have been recorded as 2·19 and 2·09 D.[16]

[5] See ref. 3, p. 37.
[6] Biddiscomb, Coulson, Handley, and Herington, *J.*, 1954, 1962.
[7] Heap, Hones, and Speakman, *J. Amer. Chem. Soc.*, 1921, **43**, 1936.
[8] Clarke and Davis, *Org. Synth.*, Coll. Vol. I, 2nd edn., p. 478.
[9] See, *e.g.*, Le Fèvre, ref. 3, p. 45.
[10] (*a*) Barclay and Le Fèvre, *J.*, 1950, 556; (*b*) Angyal, Barclay, and Le Fèvre, *J.*, 1950, 3370; (*c*) Buckingham and Le Fèvre, *J.*, 1952, 1932.
[11] Schomaker and Pauling, *J. Amer. Chem. Soc.*, 1939, **61**, 1769; Mathieson, Robertson, and Sinclair, *Acta Cryst.*, 1950, **3**, 245, 257.
[12] Le Fèvre and Le Fèvre, *J.*, 1935, 1470.
[13] Ross and Sack, *Proc. Phys. Soc.*, 1950, **63**, 693.
[14] Cf. Le Fèvre, ref. 3, Chap. III.
[15] Osborn, *Phys. Rev.*, 1945, **67**, 351.
[16] De More, Wilcox, and Goldstein, *J. Chem. Phys.*, 1954, **22**, 876.

Alternatively, our estimates of $\mu_{soln.}$ may be too high. It is seen from Table 5 that the $_\infty(P_2)$'s now presented are greater than those of previous authors : this could in part be due to the method of extrapolation used[17] which often leads to higher figures at infinite dilution

TABLE 6. *Predicted values of the ratio* $\mu_{soln.}/\mu_{gas}$.

Solute	Pyridine			Quinoline			isoQuinoline		
$\left.\begin{array}{l}A\\B\\C\end{array}\right\}$Geom. factors ...	6·1			6·1			7·7		
	6·2			8·7			7·3		
	2·9			2·9			2·9		
$(n_2)_D^{25}$	1·5074			1·6247			1·6229		
Solvent	l.p.	CCl$_4$	C$_6$H$_6$	l.p.	CCl$_4$	C$_6$H$_6$	l.p.	CCl$_4$	C$_6$H$_6$
μ_s/μ_g [10a]	0·954	0·928	0·918	0·995	0·982	0·975	0·963	0·943	0·934
μ_s/μ_g [13]	0·952	0·918	0·912	0·994	0·966	0·961	0·944	0·908	0·903
μ_s/μ_g [10c]	0·962	0·934	0·920	0·979	0·969	0·964	0·984	0·968	0·956
μ_s/μ_g (Exptl.)	1·02	1·06	1·01	0·95	0·99	0·98	0·95	0·97	0·96
	±0·03	±0·03	±0·03	±0·06	±0·06	±0·06	±0·04	±0·04	±0·04

For the above, where necessary, the following properties of the solvents at 25° have been used :

Solvent	d_4^{25}	$(n_1^2)_D$	ε_1	$(\varepsilon_1 - 1)/(\varepsilon_1 + 2)$
Light petroleum	0·6959	1·9182	1·9300	0·2366
Carbon tetrachloride	1·58454	2·1243	2·2270	0·2903
Benzene	0·87378	2·2419	2·2725	0·2978

than does the older (and less certain) graphical procedure; in this connection it is relevant that the actual experimental observations by Le Fèvre and Smith are, at their concentrations, concordant with those now found.

Real exaltations of *apparent* moments in solution could arise from at least two causes : association of solute and solvent giving a polar complex, or solute–solvent interactions causing the atomic polarisation of the dissolved molecule to be greater than that of the gaseous molecule. Partington and Middleton [18] reported, without practical details, the moments of pyridine in carbon tetrachloride and benzene as 2·33 and 2·26 D, respectively; in other media results were lower (cf. Table 5) and the suggestion was made that pyridine forms an adduct with carbon tetrachloride; evidence was cited that this substance undergoes some kind of association with benzene and toluene (in which the apparent moment was given as 2·26 D); however, the fact (Table 6) that $\mu_{soln.}/\mu_{gas}$ (exptl.) is 1·02 in light petroleum, 1·06 in carbon tetrachloride, and 1·01 in benzene does not offer much support for a hypothesis that a polar complex C_5H_5N,CCl_4 is formed. Nevertheless solvation in general might alter the force constants for the various bending modes of the dissolved molecule (stretching frequencies seem to be reduced by solvents, cf. Bayliss, Cole, and Little [19]) and thus (cf. Le Fèvre and Rao [20]) affect the atomic contribution $_AP$ to the distortion polarisation $_DP$. The literature contains much evidence [21] which suggests that atom polarisations of polar species may sometimes be unexpectedly greater in solutions than in gases. In the particular case of pyridine, $_DP_{pyridine} = 24·1$ c.c. is likely to be an underestimate : since pyridine possesses two polar links (C–N) and benzene none, $_AP_{pyridine}$ should exceed $_AP_{benzene}$, which [20] is *ca.* 1 c.c. From Goethals's finding [22] that P minus R for 4 : 4'-dipyridyl is $6·9 ± 2·0$ c.c., a reasonable value for $_AP_{pyridine}$ might well lie between 3·5 and 4·5 c.c. If this is added to R_∞ (23·3 c.c. calculated from refractivities given in Landolt-Börnstein's " Tabellen," 1912 edn.), then $_DP$ becomes 26·8—27·8 c.c.

This is not far from the value $1·1R_D = 26·5$ c.c. assumed by Leis and Curran.[23] Further, from the temperature dependence of the polarisations of solutions of pyridine in benzene, Rau and Narayanaswamy [24] calculated an A term of $31·3 ± 1·2$ c.c. Use of this figure, in

[17] Cf. Le Fèvre, *Trans. Faraday Soc.*, 1950, **46**, 1.
[18] Partington and Middleton, *Nature*, 1938, **141**, 516.
[19] Bayliss, Cole, and Little, *Austral. J. Chem.*, 1955, **8**, 26.
[20] Le Fèvre and Rao, *Austral. J. Chem.*, 1954, **7**, 135; 1955, **8**, 39.
[21] *E.g.*, Smythe and Walls, *J. Amer. Chem. Soc.*, 1930, **52**, 2234; Morgan and Lowry, *J. Phys. Chem.*, 1930, **34**, 2385; Jenkins, *Trans. Faraday Soc.*, 1934, **30**, 739; Sugden, *ibid.*, p. 734.
[22] Goethals, *Rec. Trav. chim.*, 1935, **54**, 299.
[23] Leis and Curran, *J. Amer. Chem. Soc.*, 1945, **67**, 79.
[24] Rau and Naraswamy, *Z. phys. Chem.*, 1934, *B*, **26**, 23.

conjunction with $_\infty P_2 = 127 \cdot 8$ c.c. (Table 5), leads to moments of $2 \cdot 17 \pm 0 \cdot 01$ D, which do not exceed $\mu_{gas} = 2 \cdot 19$ D obtained *via* the refractivity method (with $R_D = 24 \cdot 1$ c.c.) or $\mu_{gas} = 2 \cdot 23$ D, *via* the vapour polarisation–temperature relation (see Table 2). It is relevant that Rau and Narayanaswamy found that the *A* terms for quinoline–benzene and *iso*quinoline–benzene systems were much closer to R_D than was that for pyridine.

We conclude, therefore, that the apparent alterations of polarity by solution of these bases, particularly of pyridine, may be due to causes other than the physical solvent effects for which the equations used in Table 6 were devised.

Finally, we have considered the moments deducible from the ε_{25} and d_4^{25} of the same heterocycles in the liquid state.[25] These are set out in Table 7; the dielectric constants

TABLE 7. *Calculations of* μ_{gas} *from data on the pure liquids.*

	ε_{25}	d_4^{25}	$_T P_{liquid}$ (c.c.)	μ_{liquid}	μ_{gas} (Onsager)	μ_{gas} (Buckingham and Le Fèvre)	μ_{gas} (exptl.)
Pyridine	12·01	0·978	63·5	1·39	2·1	2·5	2·2
Quinoline	8·704	1·090	85·3	1·46	1·9	2·1	2·3
*iso*Quinoline	10·71	1·099	89·8	1·54	2·2	2·7	2·7

are close to those given in the "Table of Dielectric Constants of Pure Liquids."[26] Refractive indexes and shape factors are from Table 6. Under μ_{liquid} are the apparent moments computed from the differences between the total polarisations, $(\varepsilon - 1)M/(\varepsilon + 2)d$, and the molecular refractions of the liquids. The values of μ_{gas} calculated by Onsager's equation[27] are compared with those derived from μ_{liquid} by use of Buckingham and Le Fèvre's empirical relation (5).[10c] The results favour the latter expression in two cases.

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[25] Le Fèvre, *J.*, 1935, 773.
[26] Nat. Bur. Stands. Circular 514, Washington, 1951.
[27] Onsager, *J. Amer. Chem. Soc.*, 1936, **58**, 1486.