697. *Physical Properties and Chemical Constitution. Part XXV.** (a) *Determination of the Orientation Polarization of Alkylpyridines in Benzene Solutions by Two Independent Methods.* (b) *Dipole Moments of Alkylpyridines.*

By C. W. N. Cumper, A. I. Vogel, and S. Walker.

(*a*) The orientation polarizations of twenty-two alkylpyridines have been calculated from measurements of the dielectric constants and densities of their solutions in benzene. These values are compared with Smith's and Palit's modifications of Guggenheim's method of computing the orientation polarization from the dielectric constants and refractive indices of their solutions. The results obtained agree within the experimental errors for the systems studied.

(*b*) The dipole moments of twenty-two mono- and di-alkylpyridines in benzene solution are reported. The change in moment when the hydrogen atoms in position 2, 3, and 4 are replaced by various alkyl groups have been calculated and shown to be consistent with the relative values of the π electron densities computed for the different carbon atoms in pyridine. The moments of substituents in position 4 have been analysed quantitatively in terms of primary and induced bond moments. Finally the moments of five lutidines are compared with values derived from those for the picolines.

(a) *Orientation Polarizations.*

The dipole moment of a solute in a non-polar solvent is generally obtained from experimental measurements of the dielectric constants and densities of a series of dilute solutions; solute–solute interactions are eliminated by extrapolating the results to infinite dilution in the deduction of the molecular polarization ($_{\infty}P_2$). Guggenheim [1] has demonstrated that, provided the refractive indices of the solutions are measured, accurate densities of the solutions are not required; Smith [2] has further shown that all density data of the solutions may be dispensed with in the evaluation of dipole moments (cf. also Palit [3]). Comparison of the results obtained by the " density " and the " refractive index " method is available only for a small number of compounds. In this communication the orientation polarizations (P_0) obtained by both procedures for alkylpyridines in benzene are presented and discussed. The dipole moments of these compounds will be considered in Section (b).

Experimental

Apparatus.—The dielectric constants were obtained by the heterodyne-beat method using a circuit modified from that described by Smyth.[4] The main difference was the use of a cathode-ray tube instead of a " magic eye " as the indicating device for the balance point. The amplifer output was connected to the horizontal plates of the cathode-ray tube whilst the output of a tuning fork maintained by a 1000 cycles/sec. valve (Muirhead, type D-630-C) was connected to the vertical plates. The oscillator, controlled by a quartz crystal, operated at a frequency of 5×10^5 cycles/sec. The dielectric-constant cell and precision variable condenser were connected in parallel. A small copper-wire link (dipping into mercury cups mounted in Perspex blocks to eliminate interference from the condensation of moisture) in the high-tension lead to the cell enabled it to be switched in and out of the circuit. The position of the link was such that no change was detected on the cathode-ray tube when the link was removed and then replaced in the circuit. The link was close to the cell so that the capacity of the leads, etc., was reduced to *ca.* one-twentieth of the capacity of the cell filled with air.

The factor limiting the accuracy was the Sullivan precision variable air-condenser (type No. C700 of 400 $\mu\mu$F capacity), which was the best available for use with a cell of capacity

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* Part XXIV, *J.*, 1952, 514.

[1] Guggenheim, *Trans. Faraday Soc.*, 1949, **45**, 714.

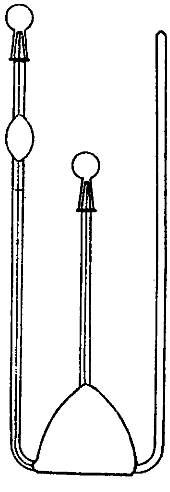
[2] Smith, *ibid.*, 1950, **46**, 394.

[3] Palit, *J. Amer. Chem. Soc.*, 1952, **74**, 3952.

[4] Smyth, in Weissberger, " Physical Methods of Organic Chemistry," Interscience Publ. Inc, New York, 1949, Vol. I, p. 1638.

ca. 100 $\mu\mu$F when filled with air. An experienced operator, taking the mean of several readings, could obtain an accuracy of 1 part in 10,000—20,000 with the cell filled with air, and a somewhat better precision when it was filled with the solutions. An auxiliary variable condenser (of 400 $\mu\mu$F capacity) permitted the capacity of the cell to be measured over different regions of the standard condenser.

The dielectric-constant cell of Sayce-Briscoe type, as modified by Few, Smith, and Witten,[5] had a volume of *ca.* 16 ml. and an annulus 1 mm. wide. A 4 cm. gold guard-ring above the silvering on the inner surface of the outer cell wall eliminated both the "edge effect" and the interference from small variations in the water-level in the thermostat; the water-level was in fact kept constant.



The densities of the solutions were measured in a specially designed pyknometer (see Figure) provided with ground-glass caps on the side arms (bore 0·2 and 0·5 mm. respectively). The weight of solution filling the pyknometer (volume 10 ml.) was reproducible to 0·1 mg. or to 1 part in 10^5. All weights were corrected for buoyancy.

The refractive indices were measured on a Bellingham and Stanley refractometer of the Pulfrich type, reading to $\pm 0{\cdot}00001$.

Materials.—Thiophen-free "Catarex" reagent benzene (Petro-Chemicals Ltd.) was fractionated twice, dried over sodium wire, and partially frozen; the solid was melted and then redistilled in a fractional-distillation apparatus of 40 theoretical plates (Griffin and Tatlock Ltd., based on designs of the Anglo-Iranian Oil Company, Ltd.). The purified benzene was stored over sodium wire in an all-glass apparatus.

The alkylpyridines were prepared and purified by Mr. C. T. Kyte, B.Sc., of this Laboratory. Experimental details, together with other physical measurements on these compounds, are reserved for Part XXVI. Freshly distilled middle fractions were used throughout.

Procedure.—Six or eight solutions of each compound in benzene were used with weight fractions between 0·001 and 0·02. They were prepared in Pyrex glass-stoppered bottles which could be fitted with special delivery heads, with ground-glass joints, for transfer of the solution to the cell or pyknometer without exposure to the atmosphere.

Measurements were made in a large thermostat maintained at 25·00° ± 0·01°. The water was circulated through the refractometer by means of an efficient pump. The dielectric cell was calibrated with air and with pure benzene, and the pyknometer with benzene, both before and after each series of measurements.

Results.—The dielectric constants (ε_{12}), densities (d_{12}) and refractive indices (n_{12}) of the solutions of weight fractions w_2 are recorded in Table 1. In each case, over the concentration range studied, ε_{12}, d_{12}, and n_{12}^2 were linear functions of the weight fraction:

$$\varepsilon_{12} = \varepsilon_1(1 + \alpha w_2) \qquad d_{12} = d_1(1 + \beta w_2) \qquad n_{12}^2 = n_1^2(1 + \gamma w_2)$$

CALCULATION OF RESULTS AND DISCUSSION

To avoid giving undue weight to results in the most dilute solutions the values of α and β were calculated from the quotients:

$$\sum(\varepsilon_{12} - \varepsilon_1')/\sum w_2 = \alpha\varepsilon_1'; \; \sum(d_{12} - d_1')/\sum w_2 = \beta d_1'$$

where ε_1' and d_1' are the dielectric constant and density, respectively, of the solvent obtained by extrapolation of the experimental results to zero weight fraction. γ was obtained directly from a graphical plot. The orientation polarization (P_{O}) of the solute at infinite dilution was calculated from the values of α, β, and γ (Table 2) in two ways. In the following calculations ε_1 has been taken as 2·2725, d_1 as 0·87378 g. cm.$^{-3}$, and n_1 as 1·49790.

(i) *Orientation Polarization from* α *and* β.—The total molecular polarization at infinite dilution is given by the formula (cf. ref. 6, p. 55):

$$_{\infty}P_2 = \frac{M_2}{d_1}\left[\frac{3\alpha\varepsilon_1}{(\varepsilon_1 + 2)^2} + \frac{\varepsilon_1 - 1}{\varepsilon_1 + 2}(1 - \beta)\right]$$

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[5] Few, Smith, and Witten, *Trans. Faraday Soc.*, 1952, **48**, 211.

[6] Smith, "Electric Dipole Moments," Butterworths, London, 1955.

TABLE 1.

Pyridine

w_2	d_{12}	ε_{12}	n_{12}
0·00183	0·87391	2·2861	1·49777
0·00378	0·87417	2·2975	1·49778
0·006398	0·87445	2·3160	1·49783
0·007889	0·87458	2·2358	1·49784
0·013451	0·87512	2·3633	1·49791
0·024696	0·87620	2·4397	1·49805

2-*Methylpyridine*

w_2	d_{12}	ε_{12}	n_{12}
0·00202	0·87394	2·2811	1·49781
0·00302	0·87398	2·2852	1·49782
0·006956	0·87425	2·3035	1·49786
0·009635	0·87441	2·3151	1·49790
0·014827	0·87473	2·3398	1·49794
0·017271	0·87487	2·3504	1·49795
0·020853	0·87512	2·3672	1·49798

3-*Methylpyridine*

w_2	d_{12}	ε_{12}	n_{12}
0·00222	0·87394	2·2890	1·49760
0·00410	0·87409	2·3009	1·49761
0·013548	0·87476	2·3645	1·49769
0·023013	0·87547	2·4282	1·49776
0·026266	0·87572	2·4490	1·49779

4-*Methylpyridine*

w_2	d_{12}	ε_{12}	n_{12}
0·00208	0·87381	2·2896	1·49764
0·00351	0·87409	2·3008	1·49770
0·007956	0·87428	2·3355	1·49771
0·015050	0·87471	2·3835	1·49777
0·021838	0·87515	2·4448	1·49781
0·026435	0·87545	2·4806	1·49786

4-*Ethylpyridine*

w_2	d_{12}	ε_{12}	n_{12}
0·00214	0·87391	2·2881	1·49771
0·00400	0·87401	2·3017	1·49774
0·00587	0·87414	2·3149	1·49772
0·011447	0·87446	2·3557	1·49775
0·016584	0·87477	2·3941	1·49778
0·020206	0·87499	2·4208	1·49780

2-n-*Propylpyridine*

w_2	d_{12}	ε_{12}	n_{12}
0·00160	0·87385	2·2773	1·49772
0·00298	0·87388	2·2815	1·49772
0·006972	0·87403	2·2943	1·49768
0·011823	0·87420	2·3098	1·49764
0·017090	0·87439	2·3272	1·49759
0·025336	0·87468	2·3539	1·49751

3-n-*Propylpyridine*

w_2	d_{12}	ε_{12}	n_{12}
0·00151	0·87384	2·2804	1·49766
0·00272	0·87395	2·2874	1·49767
0·00586	0·87405	2·3038	1·49763
0·012139	0·87436	2·3377	1·49760
0·019340	0·87469	2·3764	1·49758
0·022485	0·87486	2·3930	1·49756

4-n-*Propylpyridine*

w_2	d_{12}	ε_{12}	n_{12}
0·00139	0·87383	2·2816	1·49778
0·00240	0·87391	2·2891	1·49780
0·00529	0·87399	2·3065	1·49779
0·009154	0·87419	2·3318	1·49777
0·017327	0·87459	2·3855	1·49774
0·022906	0·87485	2·4214	1·49773

4-iso*Propylpyridine*

w_2	d_{12}	ε_{12}	n_{12}
0·00224	0·87387	2·2857	1·49777
0·00382	0·87393	2·2976	1·49775
0·007951	0·87411	2·3246	1·49770
0·013637	0·87434	2·3609	1·49767
0·017134	0·87449	2·3843	1·49765
0·030643	0·87506	2·4736	1·49753

2-n-*Butylpyridine*

w_2	d_{12}	ε_{12}	n_{12}
0·00177	0·87381	2·2771	1·49732
0·00319	0·87385	2·2810	1·49732
0·006023	0·87400	2·2891	1·49730
0·008827	0·87405	2·2927	1·49727
0·013819	0·87417	2·3113	1·49722
0·015575	0·87422	2·3158	1·49718
0·018588	0·87430	2·3267	1·49715

3-n-*Butylpyridine*

w_2	d_{12}	ε_{12}	n_{12}
0·00205	0·87385	2·2828	1·49787
0·00294	0·87389	2·2866	1·49784
0·00433	0·87393	2·2939	1·49782
0·008170	0·87408	2·3120	1·49780
0·012988	0·87428	2·3354	1·49777
0·015164	0·87436	2·3469	1·49778
0·017629	0·87446	2·3580	1·49775

4-n-*Butylpyridine*

w_2	d_{12}	ε_{12}	n_{12}
0·00177	0·87383	2·2836	1·49783
0·00356	0·87394	2·2941	1·49782
0·006127	0·87428	2·3086	1·49782
0·006779	0·87404	2·3122	1·49781
0·011302	0·87407	2·3397	1·49780
0·017345	0·87451	2·3758	1·49778
0·021843	0·87471	2·4014	1·49777

4-sec.-*Butylpyridine*

w_2	d_{12}	ε_{12}	n_{12}
0·00215	0·87387	2·2858	1·49788
0·00339	0·87395	2·2965	1·49785
0·006461	0·87406	2·3116	1·49785
0·010547	0·87424	2·3356	1·49782
0·010620	0·87425	2·3357	1·49781
0·015617	0·87445	2·3650	1·49778

4-tert.-*Butylpyridine*

w_2	d_{12}	ε_{12}	n_{12}
0·00206	0·87389	2·2846	1·49766
0·00406	0·87391	2·2965	1·49764
0·00571	—	2·3053	—
0·006718	0·87410	2·3126	1·49763
0·014916	0·87449	2·3535	1·49758
0·015554	—	2·3640	—
0·019529	0·87472	2·3886	1·49756
0·026427	0·87505	2·4302	1·49751

2-n-*Pentylpyridine*

w_2	d_{12}	ε_{12}	n_{12}
0·00203	0·87380	2·2783	1·49775
0·00328	0·87383	2·2810	1·49778
0·006180	0·87388	2·2886	1·49773
0·009279	0·87392	2·2961	1·49771
0·010395	0·87394	2·2992	1·49769
0·012189	0·87397	2·3028	1·49767

4-n-*Pentylpyridine*

w_2	d_{12}	ε_{12}	n_{12}
0·00170	0·87383	2·2808	1·49790
0·00369	0·87388	2·2918	1·49783
0·00683	0·87400	2·3085	1·49776
0·012615	0·87414	2·3389	1·49766
0·020317	0·87437	2·3800	1·49761
0·022570	0·87443	2·3910	1·49754

4-1′-*Ethylpropylpyridine*

w_2	d_{12}	ε_{12}	n_{12}
0·00195	0·87383	2·2820	—*
0·00386	0·87392	2·2926	—
0·00502	0·87394	2·3000	—
0·007437	0·87402	2·3139	—
0·014663	0·87426	2·3507	—
0·020696	0·87445	2·3855	—

2 : 3-*Lutidine*

w_2	d_{12}	ε_{12}	n_{12}
0·00203	0·87392	2·2834	1·49780
0·00254	0·87394	2·2862	1·49780
0·00621	0·87417	2·3035	1·49783
0·012719	0·87456	2·3352	1·49787
0·019032	0·87495	2·3666	1·49791
0·024004	0·87524	2·3908	1·49792

2 : 4-*Lutidine*

w_2	d_{12}	ε_{12}	n_{12}
0·00135	0·87382	2·2798	1·49775
0·00264	0·87389	2·2883	1·49775
0·00600	0·87402	2·3049	1·49776
0·011313	0·87427	2·3327	1·49778
0·016209	0·87448	2·3592	1·49770
0·021885	0·87424	2·3886	1·49776

2 : 5-*Lutidine*

w_2	d_{12}	ε_{12}	n_{12}
0·00187	0·87388	2·2811	1·49770
0·00385	0·87396	2·2902	1·49772
0·008380	0·87418	2·3107	1·49770
0·012816	0·87440	2·3318	1·49772
0·014327	0·87446	2·3391	1·49770

2 : 6-*Lutidine*

w_2	d_{12}	ε_{12}	n_{12}
0·00128	0·87381	2·2771	1·49782
0·00261	0·87387	2·2820	1·49775
0·007078	0·87404	2·2931	1·49772
0·009633	0·87412	2·3002	1·49770
0·014343	0·87429	2·3127	1·49769
0·020564	0·87454	2·3302	1·49767

3 : 5-*Lutidine*

w_2	d_{12}	ε_{12}	n_{12}
0·00177	0·87387	2·2855	1·49777
0·00241	0·87391	2·2888	1·49774
0·00683	0·87414	2·3176	1·49780
0·013609	0·87450	2·3638	1·49782
0·021144	0·87492	2·4136	1·49783
0·027560	0·87527	2·4578	1·49784

* The refractive indices of the solutions of 4-1′-ethylpropylpyridine were measured at different weight fractions from those used above. The values of w_2 and n_{12} respectively were : 0·00127, 1·49781; 0·00356, 1·49779; 0·00725, 1·49777; 0·009729, 1·49775; 0·016860, 1·49769; 0·021793, 1·49766.

Allowance for the electron and atom polarization was made by subtracting the molar refraction R_D, *i.e.*, $P_o = {}_{\infty}P_2 - R_D$.

In order to compare the results for P_O with those deduced by method (ii), we have preferred to use a value of R_D derived from the refractive indices and densities of the dilute solutions, rather than use the value for the pure solute. It was assumed that $r_{12} = w_1r_1 + w_2r_2$, or $\delta r_{12}/\delta w_2 = r_2 - r_1$, where the r's are the specific refractions. From the linear graph of r_{12} against w_2 the specific, and hence the molar, refraction of the solute was obtained. In some cases this value of R_D was slightly greater, but in others slightly smaller, than the value determined directly, the mean difference being 0·19 ± 0·11 cm.³.

(ii) *Orientation Polarization from α and γ.*—In this method the orientation polarization is given (cf. ref. 2) by :

$$P_O = \frac{M_2}{d_1}\left[\frac{3\alpha\varepsilon_1}{(\varepsilon_1 + 2)^2} - \frac{3\gamma n_1{}^2}{(n_1{}^2 + 2)^2}\right] + C$$

$$= P + C$$

where C is a small correction, seldom greater than unity, the value of which depends on the assumption made regarding the atom polarization. If the electron and atom polarizations are assumed to be equal to R_D, then Smith [2] (equation 10 on p. 398) finds that the value of C is given by the expression :

$$C\ (\text{Smith}) = \frac{M_2}{d_2}\left[\frac{\varepsilon_1 - 1}{\varepsilon_1 + 2} - \frac{n_1{}^2 - 1}{n_1{}^2 + 2}\right]$$

Palit [3] (equation 7, rearranged, on p. 3953) gives the expression

$$C\ (\text{Palit}) = \frac{M_2}{d_1}\left[\frac{\varepsilon_1 - 1}{\varepsilon_1 + 2} - \frac{n_1{}^2 - 1}{n_1{}^2 + 2}\right](1 - \beta)$$

If the rectilinear relation between d_{12} and w_2 held over the complete concentration range, then

$$d_2 = d_1(1 + \beta)$$

and

$$\frac{1}{d_2} = \frac{1}{d_1(1 + \beta)} = \frac{(1 - \beta)}{d_1(1 - \beta^2)}$$

Normally β^2 is $\ll 1$, so the two expressions for C would be virtually identical. Dr. J. W. Smith (personal communication) has pointed out that his expression assumes that the specific volumes of the solutions (v_{12}) are a linear function of w_2 and, if the behaviour of the solutions is ideal, this linearity would hold up to $w_2 = 1$: hence,

$$v_2 = v_1 + \delta v/\delta w_2$$

and

$$\frac{1}{d_2} = \frac{1}{d_1} + \frac{\delta(1/d)}{\delta w_2} = \frac{1}{d_1} - \frac{1}{d_1{}^2}\left(\frac{\delta d}{\delta w_2}\right)_{w_2 = 0}$$

$$= \frac{1 - \beta}{d_1}$$

i.e., the two expressions for C would be identical. A necessary condition for the accurate determination of dipole moments in solution is that the solutions should not depart greatly from ideal behaviour and in consequence the difference between C (Smith) and C (Palit) must be small. With the systems under investigation the extrapolated values of d_2 and v_2 differ by less than 1% from the experimental values and the two expressions for C [*i.e.*, C (Smith) and C (Palit)] give values which differ only by about 0·002 cm.³.

The values calculated for C, ${}_{\infty}P_2$, and P, and the two values of P_O $\{({}_{\infty}P_2 - R_D)$ and $(P + C)\}$ are recorded in Table 2. These values are quoted to 0·01 cm.³ solely for comparison : it is realised that the absolute values are not as accurate as this implies. It is evident that provided the factor C is included the results obtained for P_o by the

" density " and the " refractivity " method are in good agreement. The mean difference, including the sign, between the two values of P_0 is actually 0·02 with a standard deviation of 0·05. If the values of R_D determined on the pure solute are used, as is normally done in practice, this difference between the two values of P_O becomes 0·00 with a standard deviation of 0·24.

TABLE 2.

Pyridine deriv.	α *	β	γ	C (cm.^{3})	R_D (cm.^{3})	$_\infty P_2$ (cm.^{3})	P (cm.^{3})	P_O (cm.^{3})	
								$_\infty P_2 - R_\mathrm{D}$	$P + C$
Pyridine	$2{\cdot}965_4$	$0{\cdot}111_0$	$+0{\cdot}014_9$	0·38	24·17	124·23	99·75	100·06	100·13
2-Methyl	$1{\cdot}991_2$	$0{\cdot}071_0$	$+0{\cdot}012_8$	0·47	29·52	108·75	78·75	79·23	79·22
2-*n*-Propyl	$1{\cdot}416_9$	$0{\cdot}041_1$	$-0{\cdot}012_4$	0·63	38·31	112·99	74·03	74·68	74·64
2-*n*-Butyl	$1{\cdot}245_2$	$0{\cdot}031_7$	$-0{\cdot}013_6$	0·72	42·99	116·59	72·76	73·60	73·48
2-*n*-Pentyl	$1{\cdot}237_1$	$0{\cdot}017_8$	$-0{\cdot}016_1$	0·80	47·86	121·63	72·70	73·77	73·50
3-Methyl	$2{\cdot}962_4$	$0{\cdot}084_0$	$+0{\cdot}010_3$	0·46	29·04	146·99	117·51	117·95	117·97
3-*n*-Propyl	$2{\cdot}347_4$	$0{\cdot}055_0$	$-0{\cdot}005_6$	0·62	38·13	160·62	121·87	122·49	122·49
3-*n*-Butyl	$2{\cdot}127_7$	$0{\cdot}044_2$	$-0{\cdot}007_7$	0·70	42·76	167·00	123·43	124·24	124·13
4-Methyl	$3{\cdot}478_4$	$0{\cdot}073_1$	$+0{\cdot}010_0$	0·47	29·38	167·88	138·05	138·50	138·52
4-Ethyl	$3{\cdot}138_1$	$0{\cdot}068_4$	$+0{\cdot}006_0$	0·54	33·72	177·75	143·45	144·03	143·99
4-*n*-Propyl	$2{\cdot}862_9$	$0{\cdot}053_1$	$-0{\cdot}004_9$	0·62	38·24	187·39	148·53	149·15	149·15
4-*iso*Propyl	$2{\cdot}872_2$	$0{\cdot}047_6$	$-0{\cdot}010_9$	0·63	38·14	188·10	149·32	149·96	149·95
4-*n*-Butyl	$2{\cdot}597_4$	$0{\cdot}048_6$	$-0{\cdot}008_4$	0·70	42·74	193·95	150·58	151·21	151·28
4-*sec.*-Butyl ...	$2{\cdot}594_1$	$0{\cdot}050_1$	$-0{\cdot}009_6$	0·70	42·47	193·68	150·46	151·21	151·16
4-*tert.*-Butyl ...	$2{\cdot}624_3$	$0{\cdot}053_8$	$-0{\cdot}009_7$	0·70	42·32	195·26	152·21	152·94	152·91
4-*n*-Pentyl	$2{\cdot}340_2$	$0{\cdot}032_8$	$-0{\cdot}020_3$	0·78	47·14	198·47	150·56	151·33	151·34
4-1′-Ethyl-*n*-propyl	$2{\cdot}394_8$	$0{\cdot}037_6$	$-0{\cdot}009_8$	0·78	47·44	201·71	153·39	154·27	154·17
2 : 3-Lutidine ...	$2{\cdot}146_9$	$0{\cdot}069_7$	$+0{\cdot}008_4$	0·54	33·80	132·30	97·94	98·50	98·48
2 : 4-Lutidine ...	$2{\cdot}338_4$	$0{\cdot}050_5$	0·000	0·55	34·10	141·77	107·09	107·67	107·64
2 : 5-Lutidine ...	$2{\cdot}041_6$	$0{\cdot}054_5$	0·000	0·55	33·91	128·03	93·50	94·12	94·05
2 : 6-Lutidine ...	$1{\cdot}201_6$	$0{\cdot}041_0$	$-0{\cdot}008_3$	0·56	34·16	90·24	55·41	56·08	55·97
3 : 5-Lutidine ...	$2{\cdot}953_6$	$0{\cdot}061_4$	$+0{\cdot}002_3$	0·54	33·87	169·56	135·17	135·69	135·71

* The values of α have been quoted to the fourth decimal place solely to be able to express P_O to 0·01 cm.^{3}. It is not intended to imply that they have an accuracy beyond the third decimal place.

With benzene as solvent it is very unlikely that the factor C would be greater than unity for any solute. Consequently, in evaluating dipole moments by the " refractivity " method, C (and therefore d_2) need not be determined with great accuracy unless the solute has a low dipole moment (say, $<0{\cdot}7$ D). The densities of the solutions are not required in this method. With the compounds under investigation the factor C usually has a value less than 1% of P_O. Such a small value for C is only just significant in the determination of the dipole moment since the latter depends upon $\sqrt{(P_\mathrm{O}T)}$. For $C = 0{\cdot}5$, P_O must fall to 30·32 cm.^{3} (corresponding to $\mu = 1{\cdot}22$ D) before the dipole moment is changed by 0·01 D.

We conclude that, for the compounds studied, the " density " and the " refractivity " method give equally accurate results for the orientation polarization of the solute in benzene solution.

(b) *Dipole Moments.*

For the accurate determination of the small differences in dipole moment in solution produced by substituents in a ring system, the dipole moment of the latter must be reasonably large. No comprehensive study of such a system has yet been made. The influence of alkyl groups in the pyridine system ($\mu = 2{\cdot}21$ D in benzene solution) is now discussed and in a future communication the investigation will be extended to other substituents.

RESULTS

The orientation polarizations (P_O) at 25·00° of alkylpyridines dissolved in benzene have been presented above. Their dipole moments (in Debye units) have been calculated from the usual formula $\mu = 0{\cdot}01281\sqrt{(P_\mathrm{O}T)}$, where T is the absolute temperature, and are listed in Tables **3** and 5. Earlier values (where available) are also given. All the calculations in this paper have been carried out to the third decimal place in the dipole moment; the results are shown to 0·001 D only for the 4-alkylpyridines to demonstrate how closely an empirical equation can be made to agree with the measured dipole moments.

Apart from the theoretical limitations in evaluating dipole moments in solution the results are considered to be accurate to 0·01 D. (A variation of 0·01 D corresponds to a change in P_O of 0·86 cm.³ for $\mu = ca.$ 1·90 D, and of 1·12 cm. for $\mu = ca.$ 2·74 D; this is also the order of magnitude of the atom polarizations in pyridine and in α- and β-picoline.[7]) If the distortion polarization is taken as $1{\cdot}05R_D$ instead of R_D then the moment of 4-methylpyridine is reduced by 0·011 D whilst that of 4-*n*-butylpyridine is reduced by 0·019 D. These changes would not affect the arguments presented in this paper.

DISCUSSION

4-*Alkylpyridines.*—Substituents in position 4 will be considered first since any error in the bond angles of pyridine will not affect the discussion and also because the rotation of the alkyl groups is not restricted by the nitrogen atom. The dipole moment of an alkylpyridine may be expressed as:

$$\mu = \mu_{C_5H_5N} - \mu_{C-H} + \mu_R + I$$

where $\mu_{C_5H_5N}$ is the dipole moment of pyridine, μ_{C-H} the bond moment of hydrogen attached to the pyridine ring in position 4, μ_R the moment associated with the alkyl group itself, and I the small change in the moment induced in the pyridine ring when its hydrogen atom is replaced by the alkyl group R.

We find that μ_R can be expressed in terms of a primary moment and the moments this induces in the components of the side chain attached to its α-carbon atom. This primary moment we consider to be a consequence of the different states of hybridization of the carbon atoms in the ring and in the side chain, *i.e.*, to arise mainly from the bond linking the ring to the side chain. If the primary moment is " a " (irrespective of its origin) and the C–H moment in saturated aliphatic compounds is " b " then, since saturated paraffins have zero dipole moments, μ_R consists of the moment $(a - b)$ together with the moment this induces in the C_α–H bonds (μ_H) and in the other C–C bonds in the chain. We assume that the moment induced in successive C–C bonds decreases in a geometrical progression, with constant ratio " x." μ_H includes any moment arising through hyperconjugation. The moments associated with the alkyl groups are therefore:

$$3\mu_H + (a - b) \qquad \text{for } CH_3{\cdot}C_5H_4N$$

$$2\mu_H + (a - b)(1 + x + x^2) \qquad \text{for } CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}C_5H_4N$$

$$\mu_H + (a - b)(1 + 2x) \qquad \text{for } (CH_3)_2CH{\cdot}C_5H_4N\text{, etc.}$$

All of the induced moments are their components resolved in the direction of the C_5H_4N–C_α bond. The values of x will vary slightly for each C–C bond in the substituent because of their different orientations with respect to the ring, but as these induced moments fall off rapidly with increasing chain length it is permissible, as an approximation, to take a single value for x.

The following values were calculated from the experimental results:

$$(a - b) = 0{\cdot}528 \text{ D} \qquad \mu_{C-H} - I = 0{\cdot}483 \text{ D}$$

$$\mu_H = 0{\cdot}115 \text{ D} \qquad x = 0{\cdot}310$$

These were employed in calculating the figures in the last column of Table 3.

The agreement with the observed values supports the preceding interpretation of the results except for *sec.*-butyl- and 1′-ethyl-*n*-propyl-pyridine; in the last two cases the differences are probably due to restricted rotation of the terminal components of the substituent group which decreases their contributions to the moment below that calculated. The agreement for *iso*propyl- and *tert.*-butyl-pyridine indicates that the inductive effect of one methyl on another attached to the same carbon atom is very small.

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[7] Cartwright and Errara, *Acta Physicochim. U.R.S.S.*, 1935, **3**, 649; *Proc. Roy. Soc.*, 1936, *A*, **154**, 138.

The moment induced in C_α–$C_\beta H_2$ $\{(a - b)x\}$ and in the C_α–H bonds (μ_H) of the side chain have definite values but a small change in ($a - b$), together with compensating change in the values of x and of ($\mu_{C-H} - I$), is possible without materially affecting the agreement between the observed and the calculated dipole moments. Since μ_H is small the assumption that each hydrogen atom contributes equally to any hyperconjugation effect is not serious, though there should probably be a small extra moment from hyperconjugation in methylpyridine.

TABLE 3. *Dipole moments* (D) *of alkylpyridines.*

			4-Alkyl	
Alkyl	2-Alkyl	3-Alkyl	obs.	calc.
(H)	2·21 *	2·21	$2{\cdot}21_3$	—
Me	1·97 †	2·40 ‡	$2{\cdot}60_3$ ¶	$2{\cdot}60_3$
Et	—	—	$2{\cdot}65_5$	$2{\cdot}65_6$
Pr^n	1·91	2·45	$2{\cdot}70_3$	$2{\cdot}70_2$
Pr^i	—	—	$2{\cdot}70_9$	$2{\cdot}70_2$
Bu^n	1·90	2·47	$2{\cdot}72_0$	$2{\cdot}71_8$
Bu^s	—	—	$2{\cdot}72_0$	$2{\cdot}75_3$
Bu^t	—	—	$2{\cdot}73_6$	$2{\cdot}74_0$
n-C_5H_{11}	1·90	—	$2{\cdot}72_1$	$2{\cdot}72_2$
$CHEt_2$	—	—	$2{\cdot}74_8$	$2{\cdot}80_3$

Earlier values : * 2·20,[a] 2·23,[b] 2·26 [c]; † 1·96,[d] 1·92,[e] 1·72 [f]; ‡ 2·30 [f]; ¶ 2·57,[a] 2·4.[g]

[a] Leis and Curran, *J. Amer. Chem. Soc.*, 1945, **67**, 79. [b] Goethals, *Rec. Trav. chim.*, 1935, **54**, 299. [c] Middleton and Partington, *Nature*, 1938, **141**, 516. [d] Rogers and Campbell, *J. Amer. Chem. Soc.*, 1953, **75**, 1209. [e] Freiser and Glowacki, *ibid.*, 1948, **70**, 2575. [f] Rau and Narayanaswamy, *Z. phys. Chem.*, 1934, *B*, **26**, 23. [g] Huckel and Salinger, *Ber.*, 1944, **77**, 810.

The C–H moment is usually thought to be very sensitive to the hybridization of s- and p-orbitals in the carbon atom to which the hydrogen atom is attached : the C–H moments [6] suggested for the usual hybridizations are sp^3 (—0·30 D), sp^2 (0·40 D), and sp (1·05 D). If one s- and two p-type orbitals of the ring-carbon atoms in pyridine are hybridized, to give three bonds at the experimentally observed bond angles,[8] then the carbon orbitals forming bonds to the hydrogen atoms in positions 2, 3, and 4 in pyridine have the normalized wave functions (cf. ref. 9) :

$$\psi_2 = 0{\cdot}531\psi_s + 0{\cdot}848\psi_p$$
$$\psi_3 = 0{\cdot}594\psi_s + 0{\cdot}805\psi_p$$
$$\psi_4 = 0{\cdot}601\psi_s + 0{\cdot}799\psi_p$$

and the moments of the corresponding C–H bonds, interpolated in terms of the amount of s character in the carbon atomic orbital, are $C_{(2)}$–H = 0·06 D, $C_{(3)}$–H = 0·50 D, and $C_{(4)}$–H = 0·54 D. From these figures b would have a value —0·30 D (sp^3 hybridization), and a would be 0·528 + 0·30 = 0·83 D. This is 0·29 D greater than the moment of the C–H bond in position 4 in pyridine (0·54 D) and is the cause of the extra moment (I) induced in the ring when this hydrogen atom is replaced by an alkyl group. The above figures give a value of 0·06 D for I.

2-, 3-, *and* 4-*Alkylpyridines*.—The increase in moment $\Delta\mu$ ($= -\mu_{C-H} + \mu_R + I$) when a hydrogen atom in the pyridine ring is replaced by the alkyl group R has been calculated from the observed dipole moments by vector analysis. It is assumed that the resultant moment of the alkyl group acts in the direction of the original pyridine C–H bond and that the pyridine bond angles are as determined recently by Bak, Hansen, and Rastrup-Anderson [8] (*viz.*, $\angle NC_{(2)}C_{(3)} = 124°\ 00'$, $\angle C_{(2)}C_{(3)}C_{(4)} = 118°\ 36'$, $\angle C_{(3)}C_{(4)}C_{(5)} = 118°\ 06'$, $\angle NC_{(2)}H = 115°\ 44'$, and $\angle C_{(4)}C_{(3)}H = 121°\ 07'$).

The values of $\Delta\mu$ are collected in Table 4.

The most recent molecular-orbital calculations of π-electron densities at the carbon

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[8] Bak, Hansen, and Rastrup-Anderson, *J. Chem. Phys.*, 1954, **22**, 2013.
[9] Coulson, " Valence," Oxford Univ. Press, 1952, p. 194.

atoms of pyridine[10] are included in Table 4. It will be noted that the Δμ values, an indication of the tendency of electronic charge to flow from the alkyl groups into the ring, are in the expected order. The exceptionally large values of Δμ for position 2 may be connected with the small polarity calculated above for the $C_{(2)}$–H bond in pyridine (0·06 D) and with the proximity of the highly electronegative nitrogen atom. The relative electron-density values are known to be in agreement with the chemical behaviour of pyridine.[11]

In addition to the values of Δμ in the various positions the individual values of $(a - b)$ and of μ_H would also be expected to depend inversely upon the electron densities at the carbon atoms. This is borne out by the differences between the Δμ values of *n*-propyl- and methyl-pyridines shown in Table 4.

TABLE 4. *Change in group moment* Δμ *when a hydrogen atom in pyridine is replaced by an alkyl group* R.

	Position in ring				Position in ring		
R	2	3	4		2	3	4
	$\Delta\mu_2$	$\Delta\mu_3$	$\Delta\mu_4$	R	$\Delta\mu_2$	$\Delta\mu_3$	$\Delta\mu_4$
Me	0·56	0·36	0·39	Bu^t	—	—	0·52
Et	—	—	0·44	n-C_5H_{11}	0·83	—	0·51
Pr^n	0·80	0·44	0·49	$CHEt_2$	—	—	0·54
Pr^i	—	—	0·50	$\Delta\mu_{Pr^n} - \Delta\mu_{Me}$	0·24	0·08	0·10
Bu^n	0·83	0·47	0·51	π Electron density in pyridine	0·939	0·988	0·945
Bu^s	—	—	0·51				

TABLE 5. *Dipole moments of lutidines* (D).

Lutidine	2 : 6-	2 : 5-	2 : 4-	2 : 3-	3 : 5-
μ (obs.)	1·66 *	2·15	2·30	2·20	2·58
μ (calc.)	1·61	2·09	2·35	2·23	2·55

* Earlier values: 1·65,[b] 1·87[d] (for refs. *b* and *d* see Table 3).

Lutidines.—The lutidines were examined with a view to comparing their measured dipole moments with the values calculated by vector analysis from the observed moments of pyridine and the three methylpyridines; it was assumed that the geometries of pyridine and the picoline and the lutidine molecules are identical. The calculated dipole moments are included in Table 5 under μ (calc.).

The maximum difference between the calculated and the observed dipole moments is 0·06 D: a small departure from strict vector additivity would be expected in view of the above assumption and also because no account has been taken of the inductive effects round the ring.

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[10] Davies, *Trans. Faraday Soc.*, 1955, **51**, 449.

[11] Cf. Elderfield, " Heterocyclic Compounds," Wiley, New York, 1950, Vol. I, p. 546.