

920. *Physical Properties and Chemical Constitution. Part XXX.** *The Dipole Moments of Some Halogeno- and Cyano-pyridines.*

By CHARLES W. N. CUMPER and ARTHUR I. VOGEL.

The electric dipole moments of 18 chloro-, bromo-, and cyano-pyridines, together with those of chloro-, bromo-, and cyano-benzene, have been calculated from measurements of the dielectric constants, specific volumes, and refractive indices of their solutions in benzene at 25·00°. The dipole moments are considered in terms of the different "apparent bond moments" of the substituents in the α -, β -, and γ -positions in the pyridine ring. The main causes for the differences between the pyridine and benzene ring systems and discussed.

THE electric dipole moments of a very large number of mono- and poly-substituted benzenes have been measured but few systematic investigations of heterocyclic systems have been reported. Analysis of their dipole moments is frequently complicated by two factors. The parent heterocyclic molecule often has a large moment itself and the carbon atoms in the ring are no longer entirely equivalent. A detailed investigation of the dipole moments of heterocyclic compounds, however, could provide information about the electron distribution within the molecules and the electron availability at different carbon atoms in the ring.

In Part XXV¹ the dipole moments of mono-alkylpyridines and -lutidines were reported. This investigation has now been extended to the halogeno- and cyano-pyridines.

EXPERIMENTAL

The apparatus and techniques used were described in Part XXV.¹ Measurements were made of benzene solutions at 25·00° \pm 0·01°.

2-Chloropyridine and all the bromopyridines, except 4-bromopyridine, were very kindly given to us by Professor J. P. Wibaut, University of Amsterdam. The remaining compounds were high-grade commercial products. These were extensively purified before use, and all the compounds were given a final crystallisation or fractional distillation immediately before their solutions in benzene were prepared and the physical measurements taken. Their m. p.s or b. p.s agreed with published values and the consistency amongst the dipole moments found for the whole series of compounds is considered evidence of their purity.

The b. p.s of the 2-, 3-, and 4-chloropyridines were, respectively, 170°/770, 150°/769, and 147°/757 mm.; and of 2-, 3-, and 4-bromopyridine 192°/756, 173°/760, and 30°/0·4 mm. (m. p. 6°). The m. p.s of the crystalline pyridine compounds were: 2-, 3-, and 4-cyanopyridine, 26°, 50°, and 82°; 2,6- and 3,5-dichloropyridine, 87° and 65°; 2,6-, 3,5-, 3,4-, and 2,5-dibromopyridine, 119°, 111·5°, 73°, and 93°; 2,4,6-, 2,3,6-, and 3,4,5-tribromopyridine, 108°, 82°, 109°, respectively. Chlorobenzene had b. p. 132°/760 mm., bromobenzene b. p. 156°/764 mm., and benzonitrile b. p. 191°/766 mm.

Results.—The dielectric constants (ϵ_{12}), specific volumes (v_{12}), and refractive indices to sodium light (n_{12}) of benzene solutions with weight fractions (w_2) are recorded in Table 1. Over the concentration range studied, ϵ_{12} was a linear function of w_2 , and the parameters of this relation, determined by a method of least squares, are also in Table 1. Likewise v_{12} and the specific refraction (r_{12}) of the solutions were linear function of w_2 .

The total polarisation of the solutes at infinite dilution (${}_{\infty}P_2$) was evaluated. The distortion polarisation, to be subtracted from ${}_{\infty}P_2$ to give the orientation polarisation (${}_oP$), was assumed equal to the molar refraction to sodium light (R_p) and obtained from the specific refraction of the solutions.¹ The values of ${}_{\infty}P_2$, R_p , ${}_oP$, and the electric dipole moment (μ) of the compounds are given in Table 2. A large atom polarisation could result in a significant error in the dipole moment of 3,4,5-tribromopyridine.

* Part XXIX, preceding paper.

¹ Cumper, Vogel, and Walker, *J.*, 1956, 3621.

DISCUSSION

There are two main centres of polarity in these molecules. Pyridine has a dipole moment of 2.21D,¹ associated largely with the nitrogen atom itself, particularly its lone-pair electrons in a hybridised orbital. One wave-mechanical calculation² indicates that this hybridisation causes a dipole moment of 1.78D, the C₍₄₎-H bond contributing 0.20D, and the π -electron distribution 0.35D. Other calculations involve larger contributions from the π -electrons but are based on assumed values for the σ -bond moment. The second polar centre arises from the replacement of a hydrogen atom by the substituent X.

Interactions between these components of the resultant dipole moment being neglected, the contribution of the substituent relative to that of the C-H bond it replaces,* ($\Delta\mu = \mu_{C-X} - \mu_{C-H}$), may be calculated. The values for this increment in bond moment,

TABLE 1.

100w ₂	v ₁₂	ϵ_{12}	n ₁₂	100w ₂	v ₁₂	ϵ_{12}	n ₁₂	100w ₂	v ₁₂	ϵ_{12}	n ₁₂
2-Chloropyridine				3-Chloropyridine				4-Chloropyridine			
0.2362	1.14368	2.2963	1.49799	0.0566	1.14428	2.2748	1.49795	0.2000	1.14404	2.2740	1.49798
0.3061	1.14345	2.3034	1.49800	0.1292	1.14403	2.2776	1.49797	0.3607	1.14331	2.2753	1.49804
0.6665	1.14231	2.3398	1.49804	0.2796	1.14365	2.2839	1.49799	0.5751	1.14263	2.2765	1.49808
0.9174	1.14148	2.3654	1.49809	0.3041	1.14352	2.2849	1.49799	0.8604	1.14174	2.2785	1.49812
1.3036	1.14023	2.4045	1.49815	0.5777	1.14261	2.2955	1.49803	1.1564	1.14080	2.2807	1.49820
1.4033	1.13989	2.4146	1.49817	1.2499	1.14049	2.3222	1.49819	1.6104	1.13936	2.2839	1.49824
1.6134	1.13922	2.4359	1.49821	1.7966	1.13875	2.3435	1.49831	1.7328	1.13901	2.2850	1.49831
v ₁₂ = 1.14445(1 - 0.283w ₂)				v ₁₂ = 1.14445(1 - 0.277w ₂)				v ₁₂ = 1.14445(1 - 0.275w ₂)			
ϵ_{12} = 2.2723 ₆ (1 + 4.46 ₅ w ₂)				ϵ_{12} = 2.2726 ₈ (1 + 1.73 ₅ w ₂)				ϵ_{12} = 2.2724 ₃ (1 + 0.31 ₅ w ₂)			
r_{12} = 0.33543(1 - 0.258w ₂)				r_{12} = 0.33541(1 - 0.241w ₂)				r_{12} = 0.33543(1 - 0.240w ₂)			
2-Bromopyridine				3-Bromopyridine				4-Bromopyridine			
0.1010	1.14394	2.2799	1.49783	0.1139	1.14389	2.2758	1.49804	0.1864	1.14342	2.2738	1.49796
0.1977	1.14340	2.2869	1.49785	0.1969	1.14342	2.2783	1.49807	0.3020	1.14283	2.2746	1.49797
0.3841	1.14239	2.2999	1.49790	0.5676	1.14145	2.2888	1.49820	0.5359	1.14153	2.2761	1.49802
0.8068	1.14010	2.3302	1.49802	1.1187	1.13852	2.3046	1.49838	1.0691	1.13969	2.2796	1.49821
1.2089	1.13796	2.3591	1.49820	1.6077	1.13594	2.3186	1.49855	1.4683	1.13627	2.2823	1.49840
1.6224	1.13553	2.3888	1.49826	1.8021	1.13515	2.3244	1.49862	1.7376	1.13507	2.2840	1.49858
1.8178	1.13460	2.4029	1.49829	1.9730	1.13401	2.3294	1.49868	2.1900	1.13265	2.2870	1.49879
v ₁₂ = 1.14445(1 - 0.471w ₂)				v ₁₂ = 1.14445(1 - 0.462w ₂)				v ₁₂ = 1.14445(1 - 0.472w ₂)			
ϵ_{12} = 2.2725 ₆ (1 + 3.15 ₅ w ₂)				ϵ_{12} = 2.2724 ₈ (1 + 1.26 ₆ w ₂)				ϵ_{12} = 2.2726 ₅ (1 + 0.28 ₅ w ₂)			
r_{12} = 0.33538(1 - 0.423w ₂)				r_{12} = 0.33546(1 - 0.408w ₂)				r_{12} = 0.33538(1 - 0.403w ₂)			
2-Cyanopyridine				3-Cyanopyridine				4-Cyanopyridine			
0.0359	1.14439	2.2826	1.49795	0.0381	1.14435	2.2777	1.49787	0.0657	1.14433	2.2745	1.49793
0.0555	1.14435	2.2885	1.49795	0.1870	1.14401	2.2965	1.49793	0.1712	1.14408	2.2775	1.49795
0.1634	1.14408	2.3194	1.49801	0.4163	1.14343	2.3253	1.49802	0.4374	1.14344	2.2851	1.49805
0.2875	1.14383	2.3550	1.49803	0.6911	1.14275	2.3604	1.49813	0.7047	1.14279	2.2929	1.49817
0.4652	1.14340	2.4061	1.49810	1.1293	1.14172	2.4164	1.49826	1.0927	1.14188	2.3038	1.49830
0.8332	1.14253	2.5117	1.49823	1.3807	1.14108	2.4485	1.49835	1.5324	1.14081	2.3165	1.49847
1.1286	1.14191	2.5966	1.49830	1.5134	1.14075	2.4654	1.49839	1.7124	1.14040	2.3216	1.49851
v ₁₂ = 1.14445(1 - 0.196w ₂)				v ₁₂ = 1.14445(1 - 0.214w ₂)				v ₁₂ = 1.14445(1 - 0.205w ₂)			
ϵ_{12} = 2.2724 ₃ (1 + 12.65w ₂)				ϵ_{12} = 2.2726 ₃ (1 + 5.60 ₁ w ₂)				ϵ_{12} = 2.2726 ₆ (1 + 1.25 ₈ w ₂)			
r_{12} = 0.33543(1 - 0.141w ₂)				r_{12} = 0.33539(1 - 0.155w ₂)				r_{12} = 0.33541(1 - 0.145w ₂)			
2,6-Dichloropyridine				3,5-Dichloropyridine				2,6-Dibromopyridine			
0.0537	1.14421	2.2777	1.49791	0.0630	1.14421	2.2729	1.49800	0.0751	1.14397	2.2759	1.49805
0.1027	1.14405	2.2827	1.49792	0.1478	1.14389	2.2736	1.49801	0.1575	1.14341	2.2807	1.49811
0.1958	1.14369	2.2919	1.49795	0.3931	1.14293	2.2753	1.49807	0.5674	1.14064	2.3045	1.49832
0.5135	1.14244	2.3229	1.49801	0.7121	1.14170	2.2774	1.49812	0.8710	1.13858	2.3224	1.49851
0.9373	1.14079	2.3645	1.49812	0.9589	1.14076	2.2792	1.49821	1.3860	1.13502	2.3528	1.49877
1.3830	1.13906	2.4084	1.49822	1.2502	1.13961	2.2813	1.49830	1.5274	1.13412	2.3621	1.49885
1.4086	1.13896	2.4109	1.49824	1.4764	1.13875	2.2828	1.49836	1.8010	1.13225	2.3775	1.49900
v ₁₂ = 1.14445(1 - 0.341w ₂)				v ₁₂ = 1.14445(1 - 0.337w ₂)				v ₁₂ = 1.14445(1 - 0.591w ₂)			
ϵ_{12} = 2.2725 ₁ (1 + 4.32 ₁ w ₂)				ϵ_{12} = 2.2725 ₁ (1 + 0.30 ₆ w ₂)				ϵ_{12} = 2.2723 ₉ (1 + 2.58 ₈ w ₂)			
r_{12} = 0.33540(1 - 0.299w ₂)				r_{12} = 0.33544(1 - 0.305w ₂)				r_{12} = 0.33546(1 - 0.501w ₂)			

* There is reason to believe¹ that the C-H, and presumably the C-X, bond moments are somewhat reduced in the 2-position as a consequence of the smaller s character of the hybridised carbon orbital but this effect would be offset by the increased electronegativity of C₍₂₎.

² Brown and Heffernan, *Austral. J. Chem.*, 1957, **10**, 493.

TABLE 1. (Continued.)

$100w_2$	v_{12}	ϵ_{12}	n_{12}	$100w_2$	v_{12}	ϵ_{12}	n_{12}	$100w_2$	v_{12}	ϵ_{12}	n_{12}
3,5-Dibromopyridine				3,4-Dibromopyridine				2,5-Dibromopyridine			
0.1001	1.14378	2.2730	1.49789	0.0892	1.14385	2.2733	1.49790	0.1258	1.14365	2.2756	1.49794
0.1797	1.14322	2.2735	1.49794	0.1576	1.14339	2.2740	1.49793	0.1772	1.14334	2.2770	1.49795
0.5735	1.14061	2.2758	1.49809	0.4912	1.14116	2.2761	1.49809	0.4729	1.14132	2.2848	1.49809
1.0248	1.13762	2.2786	1.49830	0.8798	1.13855	2.2792	1.49827	0.9312	1.13828	2.2966	1.49831
1.6176	1.13365	2.2822	1.49854	1.2534	1.13605	2.2820	1.49846	1.3023	1.13584	2.3063	1.49846
1.7994	1.13302	2.2833	1.49859	1.6775	1.13320	2.2853	1.49867	1.6477	1.13345	2.3153	1.49863
1.9044	1.13170	2.2839	1.49868	1.8033	1.13236	2.2862	1.49874	1.8700	1.13198	2.3212	1.49872
$v_{12} = 1.14445(1 - 0.584w_2)$				$v_{12} = 1.14445(1 - 0.586w_2)$				$v_{12} = 1.14445(1 - 0.579w_2)$			
$\epsilon_{12} = 2.2723_9(1 + 0.26_8w_2)$				$\epsilon_{12} = 2.2726_0(1 + 0.33_1w_2)$				$\epsilon_{12} = 2.2724_0(1 + 1.14_6w_2)$			
$r_{12} = 0.33535(1 - 0.505w_2)$				$r_{12} = 0.33538(1 - 0.504w_2)$				$r_{12} = 0.33539(1 - 0.507w_2)$			
2,4,6-Tribromopyridine				2,3,6-Tribromopyridine				3,4,5-Tribromopyridine			
0.1031	1.14375	2.2747	1.49793	0.0922	1.14373	2.2756	1.49800	0.0972	1.14372	2.2727	1.49790
0.2418	1.14269	2.2774	1.49800	0.3321	1.14198	2.2840	1.49814	0.2503	1.14264	2.2731	1.49795
0.6625	1.13967	2.2855	1.49818	0.6998	1.13915	2.2969	1.49837	0.5228	1.14052	2.2739	1.49815
0.7812	1.13878	2.2880	1.49826	0.9256	1.13745	2.3049	1.49850	0.6961	1.13915	2.2744	1.49828
1.1440	1.13617	2.2949	1.49842	1.2669	1.13487	2.3168	1.49870	1.0959	1.13616	2.2756	1.49851
1.3664	1.13456	2.2994	1.49854	1.5294	1.13282	2.3260	1.49892	1.3477	1.13429	2.2763	1.49863
1.5391	1.13285	2.3030	1.49886	1.6274	1.13209	2.3298	1.49897	1.6607	1.13192	2.2770	1.49885
$v_{12} = 1.14445(1 - 0.641w_2)$				$v_{12} = 1.14445(1 - 0.666w_2)$				$v_{12} = 1.14445(1 - 0.659w_2)$			
$\epsilon_{12} = 2.2726_6(1 + 0.86_3w_2)$				$\epsilon_{12} = 2.2723_5(1 + 1.54_8w_2)$				$\epsilon_{12} = 2.2724_1(1 + 0.12_7w_2)$			
$r_{12} = 0.33540(1 - 0.554w_2)$				$r_{12} = 0.33542(1 - 0.556w_2)$				$r_{12} = 0.33537(1 - 0.557w_2)$			
Chlorobenzene				Bromobenzene				Benzonitrile			
0.1892	1.14399	2.2771	1.49796	0.1893	1.14357	2.2761	1.49794	0.0777	1.14432	2.2862	1.49794
0.2894	1.14377	2.2796	1.49797	0.3052	1.14298	2.2780	1.49801	0.1737	1.14420	2.3027	1.49798
0.7158	1.14273	2.2902	1.49806	0.6034	1.14160	2.2835	1.49809	0.4817	1.14371	2.3558	1.49805
1.0078	1.14204	2.2976	1.49813	1.0208	1.13958	2.2910	1.49826	0.7390	1.14331	2.4000	1.49812
1.4635	1.14093	2.3088	1.49821	1.4788	1.13742	2.2991	1.49842	1.2041	1.14256	2.4804	1.49824
1.7340	1.14027	2.3155	1.49828	1.5643	1.13702	2.3007	1.49845	1.6729	1.14183	2.5616	1.49838
1.8668	1.13993	2.3190	1.49832	1.6176	1.13680	2.3018	1.49846	1.7109	1.14175	2.5682	1.49839
$v_{12} = 1.14445(1 - 0.211w_2)$				$v_{12} = 1.14445(1 - 0.415w_2)$				$v_{12} = 1.14445(1 - 0.137w_2)$			
$\epsilon_{12} = 2.2723_8(1 + 1.09_8w_2)$				$\epsilon_{12} = 2.2726_2(1 + 0.79_1w_2)$				$\epsilon_{12} = 2.2726_6(1 + 7.59_8w_2)$			
$r_{12} = 0.33541(1 - 0.174w_2)$				$r_{12} = 0.33540(1 - 0.354w_2)$				$r_{12} = 0.33542(1 - 0.110w_2)$			

TABLE 2.

	∞P_2 (cm. ³)	R_D (cm. ³)	$\circ P$ (cm. ³)	μ (D)	Previous values for C ₆ H ₆ solutions
2-Chloropyridine	244.3	28.27	216.0	3.25	3.28 ^a
3-Chloropyridine	112.4	28.90	83.47	2.02	
4-Chloropyridine	43.33	28.96	14.37	0.84	0.84, ^b 0.9
2-Bromopyridine	241.4	30.61	210.8	3.21	2.98 ^d
3-Bromopyridine	114.5	31.39	83.10	2.02	1.93 ^d
4-Bromopyridine	47.97	31.67	16.30	0.89	
2-Cyanopyridine	591.4	30.00	561.4	5.24	
3-Cyanopyridine	274.6	29.52	245.1	3.46	
4-Cyanopyridine	84.20	29.86	54.34	1.63	1.61
2,6-Dichloropyridine	306.6	34.81	271.8	3.65	
3,5-Dichloropyridine	52.78	34.50	18.28	0.95	
2,6-Dibromopyridine	295.1	39.68	255.4	3.54	3.43 ^d
3,5-Dibromopyridine ...	60.54	39.35	21.19	1.02	0.98 ^d
3,4-Dibromopyridine ...	66.92	39.42	27.50	1.16	
2,5-Dibromopyridine ...	150.1	39.22	110.9	2.33	
2,4,6-Tribromopyridine	154.8	47.30	107.5	2.29	2.05 ^d
2,3,6-Tribromopyridine...	244.6	47.01	197.6	3.11	
3,4,5-Tribromopyridine	53.87	46.92	6.95	0.58	
Chlorobenzene	83.08	31.19	51.89	1.59	1.53—1.64, ^e 1.59, ^f 1.58, ^g 1.60
Bromobenzene	84.38	34.00	50.38	1.57	1.48—1.58, ^e 1.56, ^g 1.55 ^h
Benzonitrile	365.2	30.78	334.4	4.05	3.74—4.02, ^e 4.05 ⁱ

^a Rogers and Campbell, *J. Amer. Chem. Soc.*, 1953, **75**, 1209. ^b Leis and Curran, *ibid.*, 1945, **67**, 79. ^c Hückel and Salinger, *Ber.*, 1944, **77**, 810. ^d Goethals, *Rec. Trav. chim.*, 1935, **54**, 299. ^e Various measurements prior to 1947 from Wesson, "Tables of Electric Dipole Moments," Massachusetts Inst. Technol., 1948. ^f Le Fèvre, *Trans. Faraday Soc.*, 1950, **46**, 1. ^g Littlejohn and Smith, *J.*, 1953, 2456. ^h Brown and de Vries, *J. Amer. Chem. Soc.*, 1951, **73**, 1811. ⁱ Everard, Kumar, and Sutton, *J.*, 1951, 2807.

$\Delta\mu_a$ shown in Table 3, were evaluated on the assumption that the bond angles are as in pyridine.* In Table 4 the experimental dipole moments of some di- and tri-substituted pyridines are compared with the values (μ_a) computed from the dipole moment of pyridine and the appropriate $\Delta\mu_a$ values. In both Tables there is a close parallelism between the chloro- and bromo-derivatives, but the resultant moments cannot be explained completely by direct vector addition of bond moments.

TABLE 3.

Compound	$\Delta\mu_a$ (D)	$\Delta\mu_b$ (D)	μ_y (D)	μ_x (D)
2-Chloropyridine	1.47	1.57	0.00 *	0.08 *
3-Chloropyridine	1.54	1.39	-0.04	-0.01
4-Chloropyridine	1.37	1.40	0.00	-0.03
Chlorobenzene	1.59	—	—	—
2-Bromopyridine	1.42	1.53	0.01	0.10
3-Bromopyridine	1.53	1.31	-0.05	-0.02
4-Bromopyridine	1.32	1.36	0.00	-0.04
Bromobenzene	1.57	—	—	—
2-Cyanopyridine	3.71	3.75	0.02	0.07
3-Cyanopyridine	3.89	3.85	-0.04	-0.01
4-Cyanopyridine	3.84	3.88	0.00	-0.03
Benzonitrile	4.05	—	—	—

* Referred to the co-ordinates

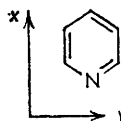


TABLE 4.

Compound	μ (D)	μ_a (D)	μ_b (D)	μ_c (D)
2,6-Dichloropyridine	3.65	3.80	3.74	3.72
3,5-Dichloropyridine	0.95	0.77	0.94	0.95
2,6-Dibromopyridine	3.54	3.74	3.66	3.65
3,5-Dibromopyridine	1.02	0.79	1.02	1.03
3,4-Dibromopyridine	1.16	1.36	1.15	1.11
2,5-Dibromopyridine	2.33	2.27	2.35	2.35
2,4,6-Tribromopyridine	2.29	2.39	2.34	2.34
2,3,6-Tribromopyridine	3.11	3.31	3.26	3.22
3,4,5-Tribromopyridine	0.58 *	0.53	0.30	0.10

* Probably high, since only partial allowance is made for atom polarisation.

In each case the $\Delta\mu$ value is less than for the corresponding benzene derivative, as might be expected for electronegative substituents. Calculations show that, relative to benzene, the carbon atoms are positively charged as a consequence of the π -electron distribution. (According to one calculation³ the charges at the C₍₂₎, C₍₃₎, C₍₄₎, and N atoms are 0.061, 0.012, 0.055, and -0.202, respectively.) The $\Delta\mu_a$ values, however, are not in the same order as these charges, and so other factors which influence the electron distribution in the molecule must be considered.

Induced moments resulting from a polarisation of part of the molecule by the electric field generated by the primary dipole moments and by the net charge on the nitrogen atom are complications. The substituent polarises the pyridine ring but, since its polarisabilities in the plane of the ring⁴ are 10.72×10^{-24} in the C₍₄₎-N direction and 10.43×10^{-24} cm.³ perpendicular to this, any induced moment would be virtually in the direction of the C-X bond and incorporated in $\Delta\mu$. Moments will, however, also be induced in the substituent and their direction may not lie along the C-X bond.

If only the moment, μ_N , resulting from hybridisation of the nitrogen atom and locating its centre at the nucleus of this atom, is considered, the dipole moment induced in a

* If the results are to be consistent, the dipole moment of 4-cyanopyridine and of 3,4,5-tribromopyridine must act in the opposite direction to that in pyridine.

³ Davies, *Trans. Faraday Soc.*, 1955, **51**, 449.

⁴ Le Fèvre, Le Fèvre, Rao, and Smith, *J.*, 1959, 1188.

substituent may be estimated approximately, following Littlejohn and Smith (cf. Hampson and Weissberger ⁵), from the equations:

$$\mu_x = \mu_N[(\epsilon_a + 2)/\epsilon_b r^3] \gamma_x (\cos^2 \theta - \frac{1}{3})$$

$$\mu_y = \mu_N[(\epsilon_a + 2)/\epsilon_b r^3] \gamma_y \cos \theta \sin \theta$$

μ_x and μ_y are the moments induced respectively parallel and perpendicular to the inducing moment μ_N , and γ_x and γ_y the corresponding polarisabilities of the polarisable group of dielectric constant ϵ_a , and distant r from μ_N ; ϵ_b is the dielectric constant of the medium between the two centres and θ the angle between the vectors μ_N and r . Unfortunately, it is difficult to assign numerical values to these quantities. The polarisation centres have been taken as at the nuclei of the halogen atoms ⁶ ($r_{\text{C-Cl}} = 1.70 \text{ \AA}$, $r_{\text{C-Br}} = 1.85 \text{ \AA}$) ⁷ and the middle of the C-N bond ($r_{\text{C-CN}} = 2.00 \text{ \AA}$). ϵ_a^* is about 2.2, but ϵ_b , which has been assumed to be the dielectric constant of the compound corresponding to the portion of the molecule between the two centres,⁵ could have a value between the dielectric constants of benzene (2.3) and pyridine (12.3),⁸ and the effective value will vary somewhat with the position of the substituent. The value of μ_N is also uncertain. Analysis of the induced moments in picolines and lutidines ⁹ indicates that μ_N/ϵ_b is about $\frac{1}{2}\text{D}$, and a slightly greater value ¹⁰ seems consistent with the dipole moments of phenyl-pyridines and -quinolines.

With the above assumptions, and Le Fèvre and Rao's ¹¹ data for polarisabilities, the moments induced in the substituent are listed in Table 3. It is obvious that the resultant moment induced in substituents in the 2- or 3-position do not lie along the C-X bond. Allowance being made for these induced moments,[†] the corrected $\Delta\mu$ values in the C-X bond direction are given under $\Delta\mu_b$ in Table 3. Although the absolute values are uncertain, the relative magnitude of the changes in $\Delta\mu$ is evident. It is most unlikely that $\Delta\mu$ is the same in the 2-, 3-, and 4-positions.

Some evidence for these modified bond-moment increments is provided by examination of the dipole moments of the di- and tri-substituted pyridines. After allowance for the above polarisation, the dipole moments μ_b (Table 4) predicted for these molecules are in better agreement with experiment, though they are still somewhat high if the molecule has substituents in both the 2- and the 6-position. Even better agreement might be expected if the mutually induced moments in the halogen atoms are considered. To estimate their importance, the primary C-X moments have been taken as $\Delta\mu_b$, operating from their polarisable centres, and ϵ_b as 4.0. The dipole moments (μ_c) calculated do not differ greatly from the μ_b values.

This apparent improvement has resulted from the assumption that the C-X moment is not exactly in the bond direction. A moment induced by a net negative charge on the nitrogen atom would also produce this effect, which would be most marked with substituents in the 2- and the 6-position. The magnitude of the effect is difficult to estimate because of lack of trustworthy values of the effective net charge on the nitrogen atom and the dielectric constant of the medium (ϵ_b).

The Relative Order of the $\Delta\mu$ Values.—When allowance is made for the induced moments, the increment in bond moment would seem to be greater in the 2- than in the 3- and

* Naturally, the appropriate value of ϵ_a will vary with the different substituents and might also differ in the x and y directions as the polarisability is anisotropic. Since it enters the formulæ for the induced moments as $(\epsilon_a + 2)$, a slight error in ϵ_a will not seriously affect the values computed for these small induced moments.

† These induced moments vary from 0.00 to about 0.10D. Those caused by the less polar centres in pyridine would be correspondingly smaller and are neglected.

⁵ Littlejohn and Smith, *J.*, 1953, 2458; Hampson and Weissberger, *J.*, 1936, 396.

⁶ Smith and Littlejohn, *J.*, 1954, 2552.

⁷ "Tables of Interatomic Distances and Configurations in Molecules and Ions," Chem. Soc. Special Publication, No. 11, 1958.

⁸ Partington, "An Advanced Treatise on Physical Chemistry," Vol. V, Longmans, Green & Co., London, 1954.

⁹ Cumper, *Chem. and Ind.*, 1958, 1628.

¹⁰ Unpublished results.

¹¹ Le Fèvre and Rao, *J.*, 1958, 1465.

4-positions with chloro- and bromo-pyridines, but somewhat less in the cyanopyridines. Some factors which can affect these "bond moments" are listed below.

(a) The positive charges on the carbon atoms, resulting both from the distribution of π -electrons and from the electronegative nitrogen atom attracting the σ -electrons, affect the availability of electrons to the substituent.

(b) The non-classical inductive effect discussed by Everard and Sutton.¹² This is a mesomeric effect in the ring initiated by the polarity of the C-X σ -bond.

(c) The mesomeric effect arising from the tendency for π -bonding between the substituent and the carbon atom to which it is linked. In the halogenopyridines this would reduce both the positive charges on the carbon atoms and $\Delta\mu$. This would be less important with cyanopyridines since the mesomeric effect increases the existing positive charges. There is evidence from nuclear quadrupole resonance spectra¹³ that π -bond conjugation is particularly great in 2-chloropyridine, though the interpretation of the results is not unambiguous in view of long-range shielding.¹⁴ A Hückel-type molecular-orbital calculation¹⁰ does indicate that the effect of conjugation in reducing the $\Delta\mu$ values in halogenopyridines is least in the 3-position and somewhat less in the 2- than in the 4-position.

(d) The bond angles might not be as in pyridine. (This might be more important in polysubstituted pyridines.) It could alter the moments of the ring, particularly that due to the lone-pair electrons on the nitrogen atom, and would also change the angle between the two primary moments. A 1° decrease in the angle between the C₍₄₎-N and C-Cl directions in the chloropyridines, for example, reduces the $\Delta\mu_b$ value in the 2-position by 0.03D and increases it in the 3-position by 0.11D.

The net effect of these factors is a reduction (by up to about 0.3D) in the apparent C-X bond moment in these pyridine compounds, compared with their benzene analogues; different bond moments in different positions round the pyridine ring; and a breakdown of strict vector additivity in the polysubstituted pyridines.

Of the various factors (c) appears the most likely to account for the difference between the order of the $\Delta\mu$ values in the halogeno- and cyano-pyridines.

Similar effects might be expected with other heterocyclic systems; this is being investigated.

The authors thank Professor Wibaut for his gift of some of the compounds studied, and the Imperial Chemical Industries Limited for a grant.

WOOLWICH POLYTECHNIC, LONDON, S.E.18.

[Received, March 17th, 1960.]

¹² Everard and Sutton, *J.*, 1951, 2821.

¹³ Dewar and Lucken, *J.*, 1959, 426.

¹⁴ Cf. Elridge and Jackman, *Proc. Chem. Soc.*, 1959, 89; Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, London, 1959.