

**876. Physical Properties and Chemical Constitution. Part XXXVII.¹
The Electric Dipole Moments of Some Phenyl-substituted 2-Phenylpyridines.**

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The electric dipole moments of the three 2-tolylpyridines and of 2-(4-biphenyl)-, 2-*p*-nitrophenyl-, and 2-*p*-aminophenyl-pyridine have been calculated from measurements of the dielectric constants, specific volumes, and refractive indices of their solutions in pure benzene at 25.00°. Information is obtained about the additivity of the component group moments in these molecules. Internal rotation is restricted, but for 2-*o*- and 2-*m*-tolylpyridine the dipole moment value does not suggest preference for a configuration with the methyl group either *cis* or *trans* to the nitrogen atom.

THE electric dipole moments of phenylpyridines were considered in the preceding paper.¹ The phenyl group itself has no primary moment, yet, in the compounds studied, there were substantial apparent phenyl group moments, the largest being that for 2-phenylpyridine (0.66 D). The question arises whether this phenyl group moment should be included in a vector analysis of the dipole moment of a substituted phenylpyridine. Another problem is whether substituents in the phenyl group of the non-planar 2-phenylpyridine molecule prefer a *cis*- or a *trans*-configuration with respect to the nitrogen atom. Some 2,2'-disubstituted biphenyls are known to have a preferred slightly *cis*-orientation,² but in 2,2'-bipyridyl³ and some 3,3'-disubstituted biphenyls² the *trans*-configuration is preferred. The dipole moments of a few substituted 2-phenylpyridines have been measured to provide some data for these problems.

EXPERIMENTAL AND RESULTS

The apparatus, experimental techniques, and method of calculation and of presenting the results are as described in previous Parts^{4,5} of this series. The measured properties of the benzene solutions at 25.00° are presented in Table 1 and the slopes of the linear graphs of dielectric constants (α) and of specific volume (β) against weight fraction, together with the polarisation data and dipole moments, are collected in Table 2.

Preparation and Purification of Compounds.—The final purification of each compound was carried out immediately before its dipole moment was measured. The infrared and ultraviolet spectra of the compounds were also determined.

2-(4-Biphenyl)pyridine. 4-Biphenyl-lithium, prepared from lithium and recrystallised 4-bromobiphenyl (m. p. 89°) in ether, was treated with a pure pyridine (b. p. 115.3°/762 mm.) in sulphur-free toluene. Water was added and the toluene layer dried and fractionated. The fraction of b. p. 180—191°/1 mm. was collected, the base was converted into the picrate, and the latter recrystallised from acetone to constant m. p. (190—191°). The regenerated base was recrystallised from alcohol to constant m. p. (142.5—143°) (Found: C, 88.4; H, 5.6; N, 5.9. Calc. for C₁₇H₁₃N: C, 88.3; H, 5.7; N, 6.1%).

2-p-Nitrophenylpyridine. *p*-Nitroaniline in hydrochloric acid was diazotised and then added to an excess of pure pyridine⁶ at 40°. An excess of water was added and the insoluble material dried in air and distilled: the fraction of b. p. 170—200°/0.8 mm. was collected. The bases were extracted as their hydrochlorides and then fractionally recrystallised from ethanol, the 2-isomer being the least soluble. The 2-*p*-nitrophenylpyridine was purified by recrystallising its hydrochloride (m. p. 185°) from hydrochloric acid, and the base itself (m. p. 130.5—131.5°) from ethanol, to constant m. p.s.

¹ Part XXXVI, Cumper, Ginman, and Vogel, preceding paper.

² Littlejohn and Smith, *J.*, 1954, 2552.

³ Cumper, Ginman, and Vogel, *J.*, 1962, 1188.

⁴ Cumper, Vogel, and Walker, *J.*, 1956, 3621.

⁵ Cumper, Redford, and Vogel, *J.*, 1962, 1176.

⁶ Haworth, Heilbron, and Hey, *J.*, 1940, 349.

TABLE 1.

$100w_2$	ϵ_{12}	ν_{12}	n_{12}	$100w_2$	ϵ_{12}	ν_{12}	n_{12}
2-(4-Biphenyl)pyridine				2-p-Aminophenylpyridine			
0.1424	2.2754	1.14395	1.49774	0.0676	2.2748	1.14425	1.49764
0.2810	2.2783	1.14360	1.49805	0.1105	2.2765	1.14413	1.49771
0.3866	2.2806	1.14366	1.49826	0.2053	2.2798	1.14381	1.49789
0.5458	2.2841	1.14289	1.49853	0.3768	2.2853	1.14323	1.49819
0.6966	2.2876	1.14247	1.49878	0.6202	2.2930	1.14249	1.49860
0.8864	2.2916	1.14188	1.49906	1.0201	2.3065	1.14121	1.49927
1.1479	2.2972	1.14113	1.49948	1.2247	2.3137	1.14058	1.49963
2-p-Nitrophenylpyridine				2-p-Tolylpyridine			
0.3297	2.3283	1.14323	1.49796	0.0431	2.2734	1.14435	1.49774
0.3948	2.3407	1.14294	1.49801	0.1362	2.2755	1.14419	1.49778
0.5704	2.3700	1.14230	1.49824	0.2960	2.2790	1.14383	1.49795
0.7952	2.4096	1.14142	1.49855	0.4635	2.2835	1.14351	1.49816
1.0219	2.4481	1.14074	1.49884	0.7442	2.2897	1.14293	1.49847
1.1527	2.4716	1.14003	1.49903	1.0118	2.2963	1.14239	1.49876
1.3716	2.5095	1.13925	1.49927	1.5388	2.3086	1.14131	1.49924
2-m-Tolylpyridine				2-o-Tolylpyridine			
0.0725	2.2748	1.14427	1.49770	0.0737	2.2749	1.14431	1.49774
0.2313	2.2786	1.14395	1.49773	0.1540	2.2773	1.14413	1.49774
0.3981	2.2829	1.14358	1.49808	0.3107	2.2820	1.14381	1.49795
0.6582	2.2887	1.14299	1.49833	0.3739	2.2835	1.14360	1.49798
0.7689	2.2923	1.14282	1.49846	0.5046	2.2874	1.14339	1.49812
0.9480	2.2970	1.14247	1.49861	0.8877	2.2982	1.14260	1.49846
1.1405	2.3018	1.14198	1.49883	1.1039	2.3046	1.14212	1.49866

TABLE 2.

Compound	α	β	∞P_2 (cm. ³)	R_D (cm. ³)	oP (cm. ³)	μ (D)
2-(4-Biphenyl)pyridine	2.18 ₂	-0.290 ₅	153.7	79.00	74.7	1.91
2- <i>p</i> -Aminophenylpyridine	3.32 ₉	-0.315 ₉	148.6	57.88	90.7	2.11
2- <i>p</i> -Nitrophenylpyridine	17.3 ₉	-0.376 ₉	700.5	59.39	641.1	5.60
2- <i>p</i> -Tolylpyridine	2.36 ₃	-0.204 ₀	122.3	57.28	65.0	1.78
2- <i>m</i> -Tolylpyridine	2.53 ₈	-0.215 ₅	127.5	56.31	71.2	1.87
2- <i>o</i> -Tolylpyridine	2.86 ₈	-0.210 ₉	138.1	54.77	83.4	2.02

2-*p*-Aminophenylpyridine. 2-*p*-Nitrophenylpyridine was reduced with tin and hydrochloric acid. The mixture was made alkaline and the precipitated base extracted with chloroform and recrystallised to constant m. p. (97°) from light petroleum (b. p. 80—100°)-benzene [picrate, plates, m. p. 220—221° (decomp.)].

2-Tolylpyridines. The three tolylpyridines were prepared by treating a solution of pyridine in toluene with ethereal solutions of *o*-, *m*-, or *p*-tolyl-lithium, prepared from lithium wire and *o*- (b. p. 178—180°/761 mm.), *m*- (b. p. 187°/750 mm.), or *p*-bromotoluene (b. p. 184°/759 mm.), respectively. Water was added and the base extracted from the toluene layer with hydrochloric acid. The tolylpyridines, isolated in the usual manner, were each fractionated three times under reduced pressure, giving 2-*o*-, b. p. 102°/1.2 mm., d_4^{20} 1.0621, n_D^{20} 1.60675 (Found: C, 84.9; H, 6.5; N, 8.3. C₁₂H₁₁N requires C, 85.2; H, 6.5; N, 8.3%), [picrate, m. p. 143° (Found: C, 54.6; H, 3.6; N, 14.1. C₁₈H₁₄O₇N₄ requires C, 54.3; H, 3.5; N, 14.1%)], 2-*m*-, b. p. 102°/0.5 mm., d_4^{20} 1.0644, n_D^{20} 1.61316 (Found: C, 85.1; H, 6.7; N, 8.3%) [picrate, m. p. 183.5° (Found: C, 54.1; H, 3.3, N, 14.7%)], and 2-*p*-tolylpyridine, b. p. 142°/10 mm., d_4^{20} 1.0572, n_D^{20} 1.61348 (Found: C, 84.6; H, 6.6; N, 8.8%) [picrate, m. p. 182.5—183.5° (Found: C, 54.6; H, 3.5; N, 14.5%)]. A mixed m. p. of the picrates of the 2-*m*- and the 2-*p*-isomer gave a depression of 20°.

The purity of the tolylpyridines was checked by gas-chromatography (Griffin and George Ltd., Mark II A apparatus). A mixture of the three isomers was readily separated but each on its own gave no indication that the other isomers were present as impurities.

DISCUSSION

The geometrical structures of 2-phenylpyridine was discussed in the preceding paper.¹ Rotation about the C-C bond joining the rings is restricted, the minimum energy of the

system occurring with the mean angle between the planes of the rings probably somewhat less than 40° . The ultraviolet spectra of the compounds investigated indicate that conjugation between the rings is very similar to that in 2-phenylpyridine, with the exception of 2-*o*-tolylpyridine where it is less and the angle between the planes of the rings probably rather greater.

In most molecules the component group moments which combine to give the resultant dipole moment are easily identified but in these substituted 2-phenylpyridines there are two possibilities: (1) The dipole moment of the substituted pyridine could be the vector sum of the moments of pyridine ⁴ (2.21 D) and of the appropriately substituted benzene; or (2) the dipole moment could be formulated as the vector sum of the moments of 2-phenylpyridine ¹ (1.94 D) and the group moment of the benzene derivative. The latter may be done in two ways: (2*a*) The phenyl group could be assumed to have a group moment of 0.66 D in the direction of the C-C bond joining the phenyl and pyridine rings.¹ (2*b*) The phenyl group moment actually acts in a direction closer to the N-C₍₄₎ direction in pyridine.¹ This is because of the moment induced in the phenyl group by the primary pyridine moment. If the methyl group moment ⁷ is taken as 0.37 D, vector analysis of the dipole moments of 2-phenylpyridine and 2-*p*-tolylpyridine requires the phenyl group moment to be 0.28 D at an angle of 12.7° to the N-C₍₄₎ direction.

TABLE 3.

Compound	μ_{exp}		μ_1 (D)	μ_{2a} (D)	μ_{2b} (D)
2- <i>p</i> -Aminophenylpyridine	2.11	<i>cis</i>	1.54	1.61	1.38
		<i>trans</i>	2.70	2.74	2.51
2- <i>p</i> -Nitrophenylpyridine	5.53		5.52	4.91	5.27
2- <i>p</i> -Tolylpyridine	1.78		2.04	1.87	1.78
2- <i>m</i> -Tolylpyridine	1.87	<i>cis</i>	1.90	1.65	1.63
		<i>trans</i>	2.36	2.16	2.10
2- <i>o</i> -Tolylpyridine	2.02	<i>cis</i>	2.12	1.77	1.84
		<i>trans</i>	2.54	2.25	2.27

In Table 3 the experimental dipole moments are compared with the values μ_1 , μ_{2a} , and μ_{2b} calculated by the above procedures. The mean angle between the plane of the rings was assumed to be 35° (cf. ref. 1) and the substituent group moments to be those of nitrobenzene ⁸ (4.01 D), aniline ⁹ (1.53 D inclined at 48.5° to the plane of the benzene ring), and toluene ⁷ (0.37 D). As the dipole moment of 2-(4-biphenyl)pyridine is only 0.03 D lower than that of 2-phenylpyridine the moments induced in the substituent of the phenyl group must be small and have been neglected.

If the molecules are equally distributed between near-*cis*- and near-*trans*-conformations, the observed values should be the root-mean-square of the values for the two forms. The root-mean-square values are collected in Table 4.

TABLE 4.

	μ_1 (D)	μ_{2a} (D)	μ_{2b} (D)
2- <i>p</i> -Aminophenylpyridine	2.19	2.25	2.04
2- <i>m</i> -Tolylpyridine	2.14	1.92	1.88
2- <i>o</i> -Tolylpyridine	2.34	2.02	2.07

The dipole moment of 2-*p*-aminophenylpyridine is approximately the root-mean-square of the values calculated with the pyridine and amino-group moments reinforcing and opposing each other. It therefore seems that this molecule spends roughly equal times in each state.

The dipole moment of 2-*p*-nitrophenylpyridine is in good agreement with the calculated moments μ_1 . In the nitrophenyl group the π -electrons will be attracted towards the nitro-group, so it is not surprising that the electron drift towards the pyridine ring present in 2-phenylpyridine is suppressed.

⁷ Cumper, Vogel, and Walker, *J.*, 1957, 3640.

⁸ Wesson, "Tables of Electric Dipole Moments," Massachusetts Inst. Technol., 1948.

⁹ Smith and Walshaw, *J.*, 1957, 3217; Smith, *J.*, 1961, 81.

The results for the tolylpyridines appear to be conflicting. The experimental values for the *ortho*- and the *meta*-isomer agree with the calculated values μ_1 if the two primary moments act in opposition; that for the *para*-isomer is, however, 0.26 D high. Since the small methyl group moment acts towards the phenyl ring it seems probable that the moment induced in the phenyl group in 2-phenylpyridine is also present in these molecules. Allowance for this induced moment (μ_{2a} and μ_{2b}) gives a reasonable explanation of the dipole moment of 2-*p*-tolylpyridine, but in this case there can be no great preference for the near-*cis*- or near-*trans*-configuration of the *ortho*- and *meta*-isomers. That the interaction between the primary dipoles and the van der Waals forces are not sufficient to favour either configuration in solution would not be surprising. There is probably little hindrance to rotation about the C-C bond joining the rings, provided the angle between the planes of the rings is greater than about 20–30°.

Neither the experimental nor the calculated dipole moments have been corrected for the solvent effect; it is unlikely that this would invalidate the conclusions drawn.

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