988. *Physical Properties and Chemical Constitution. Part XLII.** *The Electric Dipole Moments of Nitrophenylpyridines*

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The electric dipole moments of eight nitrophenylpyridines have been calculated from measurements of the dielectric constants, specific volumes, and refractive indices of their solutions in pure benzene at 25·00°. In the *para*- and *meta*-isomers the planes of the pyridine and benzene rings are probably inclined at about 40°, but this angle is greater in *o*-nitrophenylpyridines. The 2-*m*-, 3-*m*-, and 3-*o*-nitrophenylpyridines favour a *trans*-conformation but in the 2-*o*-isomer a *cis*-configuration is preferred.

THE electric dipole moments of phenylpyridines [1] and of some phenyl-substituted 2-phenylpyridines [2] have been considered previously. These molecules are not planar, and in many phenyl-substituted phenylpyridines the substituent can have a *cis*- or a *trans*-configuration with respect to the pyridine nitrogen atom. Information concerning conjugation between the pyridine and benzene rings in nitrophenylpyridines, analysed in relation to nitrobenzene and pyridine, is provided by the dipole moments; further information on the extent of conjugation is furnished by the ultraviolet (u.v.) spectra of these compounds.

EXPERIMENTAL AND RESULTS

Preparation and Purification of Nitrophenylpyridines.—The dipole moment of each compound was measured immediately it had been purified and its infrared (i.r.) and u.v. spectra recorded.

The compounds were prepared by the method of Haworth, Heilbron, and Hey,[3] in which a diazotised nitroaniline is decomposed in the presence of pyridine.

p-Nitrophenylpyridines. Pure *p*-nitroaniline in hydrochloric acid was diazotised, then added very slowly to pure pyridine at 40° and the mixture heated on a water-bath for 1 hr. The reaction mixture was poured into a large excess of water and the precipitate filtered off, washed, dried at 110°, and digested with boiling benzene. After cooling and filtering, the benzene was removed and the mixture of *p*-nitrophenylpyridines distilled under nitrogen; the fraction of b. p. 160—220°/0·8 mm. was collected.

The three isomers were dissolved in 5N-hydrochloric acid, and 0·5N-sodium hydroxide added very slowly and with vigorous stirring until the pH had risen to 1·5. After stirring for several hours, the precipitate was filtered off, washed, dried, recrystallised from ethanol, and dissolved in hot 3N-hydrochloric acid. The 2-*p*-nitrophenylpyridine hydrochloride which crystallised out on cooling was recrystallised from hydrochloric acid to a constant m. p. (186°). The remaining *p*-nitrophenylpyridines in the solution of pH 1·5 were precipitated with 5N-sodium hydroxide, filtered off, washed, and dissolved in hot 5N-hydrochloric acid. On cooling, 4-*p*-nitrophenylpyridine hydrochloride crystallised and was recrystallised from the same solvent to a constant m. p. (246°). The residual hydrochloride solution was rendered alkaline, the base filtered off, and dissolved in hot 5N-nitric acid. On cooling, 3-*p*-nitrophenylpyridine nitrate crystallised, m. p. 220° (decomp.).

Final purification of each compound was effected by regenerating the free base and recrystallising it from ethanol to a constant m. p. The picrate was formed, recrystallised from acetone to constant m. p., the free base liberated with ethanolamine, extracted with ether, and again crystallised from ethanol. Thus were obtained: 2-*p*-nitrophenylpyridine, m. p. 131°, picrate, m. p. 168°; 3-*p*-nitrophenylpyridine, m. p. 147°, picrate, m. p. 220°; 4-*p*-nitrophenyl-pyridine, m. p. 125°, picrate, m. p. 230°.

m-Nitrophenylpyridines. Pure *m*-nitroaniline in hydrochloric acid was diazotised and poured slowly into pure pyridine at 40°. The mixture was made strongly alkaline with

* Part XLI, G. B. Arrowsmith, G. H. Jeffery, and A. I. Vogel, *J.*, 1965, 2072.

[1] C. W. N. Cumper, R. F. A. Ginman, and A. I. Vogel, *J.*, 1962, 4518.
[2] C. W. N. Cumper, R. F. A. Ginman, and A. I. Vogel, *J.*, 1962, 4525.
[3] J. W. Haworth, I. M. Heilbron, and D. H. Hey, *J.*, 1940, 349.

ammonia and excess of pyridine removed by steam-distillation. The *m*-nitrophenylpyridines were extracted with benzene, washed with water, dried, the benzene distilled off, and the compounds distilled at 1 mm., the fraction of b. p. 160—190° being collected.

The mixed isomers were dissolved in 3N-hydrochloric acid, and 0·5N-sodium hydroxide added slowly until the pH rose to 1·7. The precipitated 2-*m*-nitrophenylpyridine was filtered off, washed with water, dried, and recrystallised from ethanol to constant m. p. (74°). The remaining isomers were converted into their picrates and these separated by fractional crystallisation from acetone to constant m. p. Each base was regenerated with ethanolamine, extracted with benzene, the benzene removed, and the base recrystallised to constant m. p. from acetone–light petroleum (b. p. 80—100°). Thus were obtained: 2-*m*-nitrophenylpyridine, m. p. 74°, picrate, m. p. 157°; 3-*m*-nitrophenylpyridine, m. p. 102°, picrate, m. p. 201°; 4-*m*-nitrophenylpyridine, m. p. 109°, picrate, m. p. 250°.

o-*Nitrophenylpyridines.* The mixture of isomers was prepared from pure *o*-nitroaniline as described for the *m*-nitrophenylpyridines. The fraction of b. p. 180—200°/14 mm. was collected. The picrates of the mixed isomers were formed, and were fractionally crystallised from acetone to constant m. p. The 4-*o*-nitrophenylpyridine, which was present in very small amount, was not isolated. The picrates of the other isomers were decomposed with aqueous ethanolamine, the bases extracted with ether, and the ether removed. 2-*o*-Nitrophenylpyridine was crystallised from ether to a constant m. p. 60°, picrate, m. p. 152°. 3-*o*-Nitrophenyl-pyridine was fractionally distilled at 142°/0·4 mm.; picrate, m. p. 183°.

TABLE 1

100 w_2	ε_{12}	v_{12}	n_{12}	100 w_2	ε_{12}	v_{12}	n_{12}
4-p-*Nitrophenylpyridine*				3-p-*Nitrophenylpyridine*			
0·0306	2·2759	1·14427	1·49781	0·0406	2·2770	1·14421	1·49760
0·1986	2·2796	1·14360	1·49789	0·0777	2·2820	1·14409	1·49774
0·2597	2·2810	1·14339	1·49801	0·2005	2·2902	1·14380	1·49783
0·5210	2·2868	1·14235	1·49826	0·2863	2·2974	1·14355	1·49796
0·5738	2·2883	1·14220	1·49829	0·3262	2·3010	1·14328	1·49799
0·5818	2·2886	1·14213	1·49836	0·3553	2·3030	1·14320	1·49802
0·6145	2·2901	1·14198	1·49859	0·5571	2·3198	1·14253	1·49825
2-p-*Nitrophenylpyridine*				4-m-*Nitrophenylpyridine*			
0·0691	2·2753	1·14447	1·49760	0·1678	2·2852	1·14383	1·49763
0·1464	2·3003	1·14391	1·49766	0·2627	2·2906	1·14347	1·49773
0·2201	2·3124	1·14359	1·49780	0·5807	2·3115	1·14233	1·49803
0·3442	2·3315	1·14315	1·49793	0·6763	2·3178	1·14192	1·49814
0·4253	2·3441	1·14283	1·49804	0·8061	2·3261	1·14143	1·49838
0·5683	2·3713	1·14225	1·49828	0·9213	2·3352	1·14107	1·49841
				1·0114	2·3407	1·14073	1·49849
3-m-*Nitrophenylpyridine*				2-m-*Nitrophenylpyridine*			
0·0418	2·2775	1·14416	1·49744	0·0337	2·2785	1·14419	1·49759
0·1362	2·2855	1·14356	1·49766	0·1927	2·2964	1·14351	1·49778
0·2665	2·2936	1·14211	1·49786	0·2512	2·3031	1·14326	1·39786
0·5272	2·3154	1·14112	1·49811	0·2685	2·3060	1·14321	1·49788
0·8158	2·3358	1·14112	1·49839	0·4366	2·3259	1·14259	1·49806
0·8223	2·3391	1·14081	1·49849	0·4749	2·3318	1·14237	1·49810
0·9077	2·3441	1·14050	1·49872	0·7379	2·3634	1·14120	1·49840
3-o-*Nitrophenylpyridine*				2-o-*Nitrophenylpyridine*			
0·1029	2·2847	1·14409	1·49770	0·1462	2·2965	1·14405	1·49750
0·3726	2·3155	1·14289	1·49796	0·2166	2·3020	1·14365	1·49769
0·4422	2·3202	1·14274	1·49803	0·4234	2·3191	1·14285	1·49779
0·5878	2·3357	1·14223	1·49821	0·7391	2·3499	1·14165	1·49816
0·6027	2·3375	1·14207	1·49823	1·0545	2·3856	1·14065	1·49848
0·9430	2·3737	1·14087	1·49886	1·1037	2·3881	1·14038	1·49856
1·2940	2·4113	1·13957	1·49961	1·9895	2·4796	1·13711	1·49974

The apparatus, experimental techniques, and method of calculation and of presenting the results are as described in previous Parts [4] 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 their

[4] C. W. N. Cumper, A. A. Foxton, J. Read, and A. I. Vogel, *J.*, 1964, 430.

dielectric constants (α) and their specific volumes (β) against weight fraction, together with their polarisation data and dipole moments (μ) are collected in Table 2. The u.v. spectra were measured in absolute alcohol solution with Unicam S.P. 500 and Bausch and Lomb " Spectronic 505 " spectrophotometers.

TABLE 2

Nitrophenylpyridine	α	β	$_\infty P_2$ (cm.^{3})	R_D (cm.^{3})	$_0P$ (cm.^{3})	μ (D)
4-p-	2.30_3	-0.385_2	132.0	55.83	76.14	1.93
3-p-	8.11_1	-0.327_4	353.9	59.85	294.1	3.79
2-p-	16.7_3	-0.408_3	670.5	60.50	610.0	5.51
4-m-	6.72_0	-0.366_8	295.6	57.63	238.0	3.41
3-m-	7.70_6	-0.415_2	333.5	54.69	278.8	3.69
2-m-	12.0_8	-0.421_8	497.8	55.38	442.4	4.65
3-o-	10.6_4	-0.373_6	446.3	57.88	388.4	4.36
2-o-	10.0_1	-0.367_1	423.0	57.06	366.0	4.23

DISCUSSION

The geometrical structure of pyridine has been determined by microwave spectroscopy [5] and those of phenylpyridines were discussed in a previous Communication.[1] In the gaseous phase the most probable angle (φ) between the planes of the two rings in biphenyl and in 4,4'-bipyridyl is 41.6° and 37.2°, respectively.[6] It is most unlikely that the nitrophenylpyridines are planar in solution,[7] and a value of about 40° would normally be anticipated for (φ). Molecular models and the hypsochromic effect shown by the u.v. absorption spectra of 2-o- and 3-o-nitrophenylpyridines (Table 3, cf. ref. 1) indicate that φ is increased in the *ortho*-substituted compounds as compared with the corresponding *meta*- and *para*-compounds. It is appreciated that φ will vary about its most probable value. When calculating the dipole moments of nitrophenylpyridines by the vector addition of the component group moments, the result is only dependent upon the value of φ in the 2-o-, 2-m-, 3-o-, and 3-m-isomers, and in these cases the nitro-group may either have a *cis*- or a *trans*-conformation with respect to the pyridine nitrogen atom.

TABLE 3

Nitrophenyl-pyridine	$\lambda_{max.}$ (mμ)	ε	$\lambda_{max.}$ (mμ)	ε	Nitrophenyl-pyridine	$\lambda_{max.}$ (mμ)	ε	$\lambda_{max.}$ (mμ)	ε
	Absorption maxima					Absorption maxima			
4-p-	—		300	19,000	3-m-	240	16,500	268 *	15,000
3-p-	—		292	16,500	2-m-	243	20,100	270	15,100
2-p-	—		300	19,200	3-o-	220	16,100	252	10,200
4-m-	243	19,700	—		2-o-	225	21,000	260	13,500

* Point of inflexion.

Normally the group moments which have to be combined to give a calculated value for the dipole moment of a molecule are easily identified, but in nitrophenylpyridines there are several possibilities. The obvious combination is that of the dipole moments of pyridine and nitrobenzene. Phenylpyridines, however, do not possess the same dipole moment as pyridine, and to allow for the displacement of electronic charge from the benzene to the pyridine ring it might be more appropriate in some cases to employ the phenylpyridine moments instead of that of pyridine. Alternatively, the charge displacement could be from pyridine to the nitrobenzene residue: the relevant nitrobiphenyl moment [8] could then be employed in place of that of nitrobenzene.

The dipole moments obtained by vector addition of those of pyridine [9] (2.21 D) and nitrobenzene [10] (3.99 D) are given in Table 4; the bond angles being taken as those of the

[5] B. Bak, L. Hansen-Nygaard, and J. Rastrup-Anderson, *Mol. Spectroscopy*, 1958, **2**, 361.
[6] A. Almenningen and O. Bastiansen, *Kgl. Norske Videnskab. Selskabs Skrifter*, 1958, No. 4.
[7] Cf. J. Dahr, *Indian J. Phys.*, 1932, **7**, 43; D. H. Saunder, *Proc. Roy. Soc.*, 1946, **188**A, 31; J. N. Niekerk and D. H. Saunder, *Acta Cryst.*, 1948, **1**, 44.
[8] A. C. Littlejohn and J. W. Smith, *J.*, 1953, 2456.
[9] C. W. N. Cumper, A. I. Vogel, and S. Walker, *J.*, 1956, 3621.
[10] A. L. McClellan, " Tables of Experimental Dipole Moments," Freeman, 1963.

separate benzene and pyridine [5] molecules. For those nitrophenylpyridines in which the calculated moments depend upon ϕ, the results are presented in the Figure, the angle being measured from the planar conformation in which the group moments reinforce one another.

To obtain information about the flow of electronic charge between the two rings and the nitro-groups, a Hückel molecular-orbital calculation [11] was made for each molecule. The calculations were for planar molecules, but neither this approximation nor the values chosen for the coulombic integrals (α) and resonance integrals (β) affects the general picture of the *relative* net π-electron charges associated with the benzene and pyridine rings and with the nitro-group. The results in Table 4 were obtained with the following numerical

TABLE 4

Nitrophenyl-pyridine	Charge on pyridine nitrogen	Net π-electron charges			$\mu_{calc.}$ (D)	$\mu_{obs.}$ (D)
		Pyridine ring	Benzene ring	Nitro-group		
4-p-	−0·0704	+0·0029	+0·0521	−0·0550	1·78	1·93
3-p-	−0·0712	+0·0104	+0·0461	−0·0565	3·54	3·79
2-p-	−0·0729	+0·0025	+0·0525	−0·0550	5·51	5·51
4-m-	−0·0744	−0·0090	+0·0580	−0·0491	3·46	3·41
3-m-	−0·0711	−0·0023	+0·0514	−0·0491	*	3·69
2-m-	−0·0771	−0·0096	+0·0587	−0·0491	*	4·65
4-o-	−0·0703	+0·0034	+0·0531	−0·0564	5·45	—
3-o-	−0·0712	+0·0109	+0·0470	−0·0579	*	4·36
2-o-	−0·0728	+0·0029	+0·0536	−0·0564	*	4·23
Pyridine	−0·0716	0·0000	—	—	—	2·21
Nitrobenzene	—	—	+0·0495	−0·0495	—	3·99

* See Figure.

values. The coulombic integrals were taken to be $\alpha = \alpha_c + k\beta$ where $k = 0$ for carbon, 0·2 for pyridine nitrogen, 0·6 for nitrogen in the nitro-group, and 0·4 for oxygen. In addition, the coulombic integrals of atoms bonded to those named above were increased by $\frac{1}{4} k$. The resonance integrals used for the various bonds were C–C, C–N (pyridine) $= \beta$; C–NO$_2 = 0 \cdot 8\beta$; N–O $= 0 \cdot 7\beta$. The relative values of these parameters are the same as those suggested by Streitwieser,[12] but his coulombic integrals have been reduced by 60% so that the charge distribution calculated for pyridine agrees with that obtained by an elaborate self-consistent-field calculation.[13]

p-*Nitrophenylpyridines.*—The dipole moments of 4-p-nitrophenylpyridine is 0·15 D greater than the calculated value, due largely to an increase in the moment of the nitro-group. p-Nitrobiphenyl has a dipole moment [8] 0·37 D greater than that of nitrobenzene, but the flow of charge between the two rings in this molecule is greater than in 4-p-nitrophenylpyridine, (calculated net π-electron charges in p-nitrobiphenyl are C_6H_5, +0·0128; C_6H_4, +0·0442; NO$_2$, −0·0570).

The dipole moment of 3-p-nitrophenylpyridine is 0·25 D greater than the calculated value, and Table 4 shows that this is primarily due to a significant flow of electronic charge from the pyridine ring, and an increase in that on the nitro-group. The moment calculated from those of pyridine and p-nitrobiphenyl [8] (4·36 D) is 3·86 D.

In 2-p-nitrophenylpyridine the net charges on the two rings and on the nitro-group are very similar to those of the 4-p-isomer. The phenyl group in 2-phenylpyridine, however, substantially reduces (by 0·27 D) the moment [2] of the parent pyridine molecule, and this reduction would tend to affect the enhanced moment of the nitro-group. The experimental and calculated dipole moments for this compound are actually identical.

m-*Nitrophenylpyridines.*—The dipole moment of 4-m-nitrophenylpyridine is 0·05 D less than the calculated value. In this isomer the calculated charge distribution indicates

[11] H. C. Louguet-Higgins and C. A. Coulson, *Trans. Faraday Soc.*, 1947, **43**, 87.
[12] Streitwieser, "Molecular Orbital Theory for Organic Chemists," Wiley, New York, 1961, p. 135.
[13] McWeeny and Peacock, *Proc. Phys. Soc.*, 1957, A**70**, 41.

some electron flow from the benzene into the pyridine ring, thereby increasing the component moment from the nitrobenzene residue, but decreasing that associated with the pyridine ring.

In 3-*m*-nitrophenylpyridine there is only a very small flow of charge from the benzene into the pyridine ring, which would not effect the calculated dipole moment at small values of ϕ but might increase it slightly as ϕ approaches 180°. From the Figure it is seen that the experimental dipole moment of 3·69 D corresponds to $\phi = 103°$. It seems more likely that the planes of the two rings are preferentially inclined at an angle of about 40° in which case the experimental result indicates that the molecules spend about one third of their time with $\phi \sim 40°$ and two thirds with $\phi \sim 140°$. It is interesting that 3,3'-disubstituted biphenyls preferentially adopt the *trans*-conformation.[14]

The situation in 2-*m*-nitrophenylpyridine is very similar to that in the 4-*m*-isomer, the transfer of charge from the benzene to the pyridine ring being slightly greater. If no allowance is made for this effect, then the experimental moment of 4·65 D corresponds to an average value for ϕ of about 107° or, more probably, a similar molecular distribution between the two conformations with $\phi \sim 40°$ and 140° as postulated for the 3-*m*-isomer.

Variation of dipole moment with the angle between the rings, ϕ.

(A) 2-*m*-Nitrophenylpyridine. (B) 3-*o*-Nitrophenylpyridine. (C) 3-*m*-Nitrophenylpyridine. (D) 2-*o*-Nitrophenylpyridine.
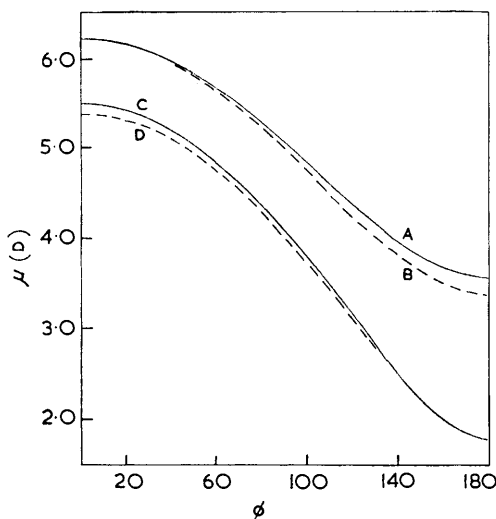
o-Nitrophenylpyridines.—4-*o*-Nitrophenylpyridine could not be prepared. Its calculated dipole moment of 5·45 D may be a little low in view of the calculated charge distribution. The conjugation between the pyridine and benzene rings in all these *ortho*-substituted compounds, however, must be small because steric repulsions will increase the angle ϕ.

In 3-*o*-nitrophenylpyridine the charge on the nitro-group would appear to be enhanced at the expense of that in the pyridine ring. The actual flow of charge will be small because of the inhibited conjugation between the rings, but what does take place would increase the component moments and the resultant dipole moment calculated for this compound may be slightly low. The experimental dipole moment of 4·36 D corresponds to an average value of ϕ greater than found for the *meta*-isomers. As the steric effects require a greater angle between the planes of the rings, it seems probable that the molecules exist largely in a single conformation with $\phi \sim 113°$.

Finally, in 2-*o*-nitrophenylpyridine the charge distribution indicates that the calculated dipole moment shown in the Figure might be slightly low, but nevertheless the average value of ϕ would seem to be less than 90°, indicating a preference for the two nitrogen

[14] A. C. Littlejohn and J. W. Smith, *J.*, 1954, 2552.

atoms in the molecule to be close together. 2,2′-Disubstituted biphenyls [14] also favour a slightly *cis*-disposition.

No allowance has been made for the effect of the benzene solvent upon the dipole moments of the nitrophenylpyridines or upon those of pyridine or nitrobenzene used in analysing the results. This would not affect the conclusions reached in the above discussion.