226. *Physical Properties and Chemical Constitution. Part XXXV.** *The Electric Dipole Moments of Some Phenanthrolines and Bipyridyls.*

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The electric dipole moments of three phenanthrolines, four bipyridyls, and 2,2′-biquinolyl have been calculated from measurements of the dielectric constants, specific volumes, and refractive indices of their solutions in pure benzene at 25·00°. They are discussed in terms of the dipole moments expected by the vector addition of the moments of two pyridine molecules and of the interaction between them.

THE electric dipole moments of substituted pyridines have been discussed earlier in this series;[1,2] this communication extends the results to molecules which may be considered to consist of two pyridine units linked together. In the phenanthrolines the two pyridine units are fixed in space and their moments provide information on the interaction between them; in the bipyridyls they can rotate about the bond linking them together and their resultant dipole moment is influenced by this rotation.

Littlejohn and Smith[3] measured the dipole moments of substituted biphenyls and this work is of importance in discussing the dipole moments of phenyl-pyridines and -quinolines.[4]

EXPERIMENTAL AND RESULTS

The apparatus, techniques, and method of calculation and of presenting the results are as described in previous Parts of this series.[1,5] The measured properties of the benzene solutions are presented in Table 1. Table 2 includes the slopes of the graphs of dielectric constant and

TABLE 1.

$100w_2$	ε_{12}	v_{12}	n_{12}	$100w_2$	ε_{12}	v_{12}	n_{12}	$100w_2$	ε_{12}	v_{12}	n_{12}
	o-*Phenanthroline*				m-*Phenanthroline*				p-*Phenanthroline*		
0·1200	2·2817	1·14395	1·49771	0·1337	2·2765	1·14398	1·49778	0·0894	2·2799	1·14427	1·49783
0·2014	2·2893	1·14364	1·49791	0·2018	2·2791	1·14377	1·49803	0·1762	2·2872	1·14375	1·49794
0·4133	2·3081	1·14275	1·49830	0·2912	2·2817	1·14349	1·49803	0·2305	2·2916	1·14367	1·49805
0·5301	2·3179	1·14218	1·49850	0·4370	2·2862	1·14295	1·49829	0·3378	2·3005	1·14337	1·49816
0·6126	2·3244	1·14202	1·49882	0·5985	2·2913	1·14243	1·49861	0·4114	2·3072	1·14305	1·49825
0·8038	2·3411	1·14128	1·49902	0·7943	2·2971	1·14164	1·49900	0·6137	2·3241	1·14236	1·49862
1·0155	2·3592	1·14056	1·49944	1·0274	2·3041	1·14068	1·49922	0·6970	2·3311	1·14205	1·49879
	2,2′-Bipyridyl				*2,4′-Bipyridyl*				*3,4′-Bipyridyl*		
0·1400	2·2731	1·14407	1·49787	0·0407	2·2769	1·14436	1·49778	0·0284	2·2736	1·14437	—
0·3526	2·2744	1·14349	1·49810	0·0515	2·2779	1·14432	1·49779	0·0883	2·2760	1·14420	—
0·5509	2·2753	1·14295	1·49847	0·0889	2·2822	1·14420	1·49780	0·0942	2·2762	1·14415	—
0·7455	2·2765	1·14239	1·49858	0·1563	2·2891	1·14402	1·49791	0·1281	2·2779	1·14410	—
1·0477	2·2784	1·14159	1·49890	0·3069	2·3048	1·14362	1·49810	0·1802	2·2799	1·14385	—
1·3731	2·2809	1·14069	1·49920	0·5164	2·3270	1·14297	1·49826				
1·7738	2·2832	1·13961	1·49963	0·6561	2·3420	1·14259	1·49851				

$100w_2$	ε_{12}	v_{12}	n_{12}	$100w_2$	ε_{12}	v_{12}	n_{12}
	4,4′-Bipyridyl				*2,2′-Biquinolyl*		
0·1887	2·2773	1·14390	1·49778	0·0849	2·2736	1·14420	1·49787
0·3910	2·2742	1·14320	1·49796	0·1041	2·2738	1·14412	1·49786
0·5314	2·2750	1·14278	1·49811	0·1572	2·2744	1·14395	1·49799
0·7705	2·2759	1·14205	1·49836	0·2287	2·2752	1·14370	1·49810
0·9591	2·2770	1·14144	1·49859	0·3357	2·2755	1·14366	1·49833
1·1738	2·2776	1·14074	1·49883	0·6107	2·2777	1·14246	1·49890
1·4865	2·2786	1·13980	1·49919	0·9047	2·2799	1·14146	1·49947

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* Part XXXIV, preceding paper.

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

[2] Cumper and Vogel, *J.*, 1960, 4723.

[3] Littlejohn and Smith, *J.*, 1953, 2456; 1954, 2552.

[4] Cumper, Ginman, and Vogel, unpublished work.

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

TABLE 2.

Compound	α	β	${}_{\infty}P_2$ (cm.^{3})	R_D (cm.^{3})	${}_0P$ (cm.^{3})	μ (D)	Previous values for C_6H_6 soln.
o-Phenanthroline	$8\cdot57_4$	$-0\cdot399_5$	330·6	60·02	270·6	3·64	4·11 [a]
m-Phenanthroline	$3\cdot04_3$	$-0\cdot343_6$	146·1	59·47	86·6	2·06	
p-Phenanthroline	$8\cdot44_2$	$-0\cdot339_2$	329·4	59·47	269·9	3·63	
2,2′-Bipyridyl ...	$0\cdot62_9$	$-0\cdot273_4$	58·99	49·15	9·84	0·69	0·91,[a] 0·68
2,4′-Bipyridyl ...	$10\cdot56_7$	$-0\cdot279_0$	350·4	49·46	300·9	3·84	
3,4′-Bipyridyl ...	$4\cdot27_2$	$-0\cdot304_4$	164·6	48·50	116·1	2·38	
4,4′-Bipyridyl ...	$0\cdot44_7$	$-0\cdot313_4$	51·80	48·07	3·73	0·31	0·55
2,2′-Biquinolyl ...	$0\cdot76_1$	$-0\cdot325_6$	99·20	89·88	9·32	0·68	

[a] Fielding and Le Fèvre, *J.*, 1951, 1811. [b] Goethals, *Rec. Trav. chim.*, 1934, **54**, 299; Goethals and Wibaut, *ibid.*, 1954, **73**, 35.

of specific volume against weight fraction, α and β respectively, together with the polarisation data and dipole moments.

Materials.—Each compound was purified immediately before its dipole moment was determined. Their infrared and ultraviolet spectra, and their m. p.s and those of their derivatives, were in good agreement with published data where available.

o-*Phenanthroline.* The compound (from Messrs. Hopkin and Williams Ltd.) was purified by recrystallising its picrate (m. p. 191°) from alcohol and then recrystallising the base itself, after drying at 78°/8 mm., from light petroleum (b. p. 80—100°) to constant m. p. 118°. (The m. p. recorded in the literature,[6] 98—100°, may refer to the hydrate.)

m-*Phenanthroline.* Prepared by a Doebner–Miller synthesis [7] from *m*-phenylenediamine, glycerol, sulphuric and arsenic acids, *m*-phenanthroline hydrate was recrystallised from hot water (m. p. *ca.* 70°), dried at 120°/10 mm. for several hours, and recrystallised from light petroleum (b. p. 60—80°) to constant m. p. 79°. The picrate had m. p. 250°.

p-*Phenanthroline.* Prepared as for *m*-phenanthroline but from *p*-phenylenediamine, the compound was extracted from the reaction mixture with hot benzene and recrystallised from hot water (m. p. *ca.* 160°). After drying, the anhydrous material was repeatedly recrystallised from light petroleum (b. p. 100—120°) and had m. p. 175°. The picrate had m. p. 234°.

2,4′- *and* 3,4′-*Bipyridyl.* Small samples of pure 2,4′-bipyridyl picrate (m. p. 215°) and 3,4′-bipyridyl dipicrate (m. p. 207°) were kindly provided by Professor Kuffner.[8] The bipyridyls were regenerated from the picrates in the usual manner and dried under a vacuum. 2,4′-Bipyridyl had m. p. 58°; 3,4′-bipyridyl was a pale yellow liquid.

4,4′- *and* 2,2′-*Bipyridyl;* 2,2′-*biquinolyl.* 4,4′-Bipyridyl, was presented by the Imperial Chemical Industries Limited, and commercial 2,2′-bipyridyl and 2,2′-biquinolyl (British Drug Houses Ltd.) were purified by digestion in chloroform with activated charcoal and repeated recrystallisation from light petroleum to constant m. p.: 4,4′-bipyridyl, m. p. 112° (picrate, m. p. 253°); 2,2′-bipyridyl, m. p. 69·5° (picrate, m. p. 155°); 2,2′-biquinolyl, m. p. 196° (picrate, m. p. 214°).

DISCUSSION

The geometrical structure of these molecules is not known. We shall consider them to consist of two pyridine molecules, whose structure in the vapour phase is well established,[9] joined through an undistorted benzene ring (the phenanthrolines) or by a C–C single bond (the bipyridyls).

Phenanthrolines.—In Table 3 the experimental dipole moments are compared with the values, μ_1, obtained by vector addition of the dipole moment of two pyridine molecules.[1] The values in parentheses were computed by vector addition of the moments of two quinoline molecules.[5] These calculated dipole moments are slightly high and would be further increased by the first two of the following factors.

(*a*) Theories of the solvent effect (*e.g.*, as expressed in Buckingham and Le Fèvre's

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[6] Smith and Getz, *Chem. Rev.*, 1935, **16**, 113; Willink and Wibaut, *Rec. Trav. chim.*, 1935, **54**, 275.

[7] Smith, *J. Amer. Chem. Soc.*, 1930, **52**, 400.

[8] Kuffner and Straberger, *Monatsh.*, 1957, **88**, 793.

[9] Bak, Hansen-Nygaard, and Rastrup-Andersen, *Mol. Spectroscopy*, 1958, **2**, 361; cf. Cumper, *Trans. Faraday Soc.*, 1958, **54**, 1266.

TABLE 3.

Compound	$\mu_{(\mathrm{exp.})}$ (D)	μ_1 (D)	μ_2 (D)
o-Phenanthroline	3·64	3·74 (3·63)	3·65
m-Phenanthroline	2·06	2·21 (2·15)	2·23
p-Phenanthroline	3·63	3·92 (3·81)	3·70
2,2′-Bipyridyl	0·69	*cis* * 3·73	3·35
		trans * 0	0
2,4′-Bipyridyl	3·84	3·88	3·93
3,4′-Bipyridyl	2·38	2·28	2·30
4,4′-Bipyridyl	(0·31)	0	0
2,2′-Biquinolyl	0·68	*cis* * 3·63	3·21
		trans * 0	0

* Planar configuration.

equation [10]) indicate that polarisation of the solvent molecules reduces the true dipole moment of pyridine to a greater extent than that of the larger phenanthroline molecules.* An allowance for this would increase the calculated moments.

(*b*) A small contribution to the dipole moment of pyridine arises from the distribution of π-electrons within the molecule. A Hückel molecular-orbital calculation indicates that this contribution to the dipole moment of the phenanthrolines is greater than for two unconjugated pyridine molecules. This is illustrated by the data in Table 4, computed by the method of Longuet-Higgins and Coulson [12] with $\alpha_N = \alpha_0 + 0{\cdot}20\beta$ (α = coulombic integral, β = exchange integral).

TABLE 4.

	Resultant π-electron moment	π-Electron moment for two unconjugated pyridine molecules
o-Phenanthroline	0·96 D	0·85
m-Phenanthroline	0·61	0·51
p-Phenanthroline	0·95	0·89

(*c*) The primary moment of each pyridine residue, mainly associated with the nitrogen atom itself,[13] induces moments in the benzene and other pyridine residues. Employing an approximate estimate for these induced moments, by the method adopted previously,[5] changes the calculated moments to those given under μ_2 in Table 3. Any moment induced by the net π-electron charge on the nitrogen atom would enhance this effect. The predicted dipole moment of *meta*-phenanthroline is increased slightly by this factor but the *ortho*- and *para*-isomers have their moments appreciably reduced.

Thus it seems that the experimental dipole moments for these molecules are somewhat smaller than expected. A 5° increase in the angle between the primary dipole of the two pyridine molecules would decrease the calculated dipole moments by about 0·2 D and if the C–H bond moment varies with its position in the molecule [1] this also could reduce the estimated moment.

Bipyridyls.—In these molecules the degree of conjugation between the pyridine rings, and consequently their resultant dipole moment, will depend on the mean angle between the planes of the rings,† and in 2,2′-bipyridyl (and 2,2′-biquinolyl) the angle between the

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* Values of 2·15 and 2·23 D have been recorded for the dipole moment of pyridine in the vapour phase.[11]

† Since the polarisability of a pyridine molecule is anisotropic [14] any induced moment within these bipyridyls will also depend upon the interplanar angle; the effect on the dipole moment is, however, not of great significance.

[10] Buckingham and Le Fèvre, *J.*, 1952, 1932.

[11] DeMore, Wilcox, and Goldstein, *J. Chem. Phys.*, 1954, **22**, 876; Buckingham, Chau, Freeman, Le Fèvre, Rao, and Tardif, *J.*, 1956, 1405.

[12] Longuet-Higgins and Coulson, *Trans. Faraday Soc.*, 1947, **43**, 87.

[13] Cumper, *Chem. and Ind.*, 1958, 1628; Barassin and Lumbroso, *Bull. Soc. chim. France*, 1959, 1947.

[14] Le Fèvre, Le Fèvre, Rao, and Smith, *J.*, 1959, 1188.

primary pyridine moments will itself be affected by rotation about the bond linking the two units.

2,2′- and 4,4′-Bipyridyl are known to be planar in the crystalline state,[15] but this is not the case in the gaseous phase [16] and is unlikely to be so in solution (cf. biphenyl [17]). In 4,4′-bipyridyl the most probable angle (ϕ) between the planes of the two pyridine rings, obtained by electron diffraction in the gaseous phase, is [16] 37·2°. The experimental evidence for 2,2′-bipyridyl is not so conclusive but the scattering between N and $C_{(3)}$ corresponds to $\phi > 20°$, though the other distances, which are less reliable, correspond more closely to a planar molecule in the *trans*-configuration. Supporting evidence for different values of ϕ, and of the extent of conjugation between the rings, is furnished by their ultraviolet spectra (measured for absolute ethanol solution). They have two prominent bands at about 240 and 275 mμ which closely resemble those of the phenylpyridines (Table 5; cf. ref. 18). The second peak, in particular, seems to have a greater wavelength and intensity when steric repulsion between the hydrogen atoms is small and conjugation between the two rings consequently greater.

TABLE 5.

Compound	$\lambda_{\text{max.}}$ (mμ)	ε	$\lambda_{\text{max.}}$ (mμ)	ε	Compound	$\lambda_{\text{max.}}$ (mμ)	ε	$\lambda_{\text{max.}}$ (mμ)	ε
Biphenyl	255	18,000	—		2,2′-Bipyridyl ...	236	12,000	283	15,000
2-Phenylpyridine	245	12,700	277	10,400	2,4′-Bipyridyl ...	242	13,100	274	12,300
3-Phenylpyridine	246	17,100	270 infl.	7500	4,4′-Bipyridyl ...	241	15,700	270 infl.	6100
4-Phenylpyridine	256	16,900	—		2,2′-Biquinolyl...	314	21,200	326	24,000

Rotation about the bond joining the two pyridine units in these molecules does not occur freely and the most probable angle between the rings varies from isomer to isomer.

4,4′-Bipyridyl. Irrespective of the angle ϕ between the planes of the two rings in 4,4′-bipyridyl the moments of the two pyridyl groups should be in direct opposition and their resultant zero. The molecule, however, has an orientation polarisation of 3·7 c.c., which corresponds to a dipole moment of 0·31 D and an angle of 8° between the pyridyl group moments. Molecules possessing large opposing dipoles, particularly when these are far apart, are known to have a particularly large atom polarisation [19] and it seems that the apparent orientation polarisation of 4,4′-bipyridyl is really due to an inadequate allowance for its atom polarisation. The error would be 8% of its R_{D} value.

2,2′-Bipyridyl. The orientation polarisation of this molecule, 9·8 c.c., is small, but it cannot be attributed to an inadequate allowance for atom polarisation as this should be at a maximum in the 4,4′-isomer. The dipole moment of 0·69 D, which should be regarded as a maximum value, corresponds to an angle of 162° between the two pyridyl group moments. The dipole moment of pyridine in benzene solution was taken as 2·21 D.[1] The same mean angle of 18° between the planes of the rings is obtained for biquinolyl from its dipole moment and that of quinoline.[5]

The resonance energy and dipole–dipole interaction for the planar *trans*-forms of 2,2′-bipyridyl and 2,2′-biquinolyl are evidently insufficient to hold the molecules in this configuration in solution and in the gaseous phase. It seems likely that rotation through an appreciable angle from the planar *trans*-form occurs, but it is unlikely to pass through the planar *cis*-configuration.

2,4′- and 3,4′-Bipyridyl. In these molecules steric repulsion between the hydrogen atoms considerably reduces the probability of these molecules' existing in planar configurations. Their ultraviolet spectra indicate that π-electron conjugation increases in the order 3,4′-, 4,4′-, 2,4′-, and 2,2′-bipyridyl. Apart from the non-planarity of these

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[15] Dahr, *Indian J. Phys.*, 1932, **7**, 43; Saunder, *Proc. Roy. Soc.*, 1946, *A*, **188**, 31; Niekerk and Saunder, *Acta Cryst.*, 1948, **1**, 44.

[16] Almenningen and Bastiansen, *Kgl. Norske Videnskab. Selskabs Skrifter*, 1958, No. 4.

[17] Bastiansen, *Acta Chem. Scand.*, 1949, **3**, 408; 1950, **4**, 926; 1952, **6**, 205.

[18] Krumholz, *J. Amer. Chem. Soc.*, 1951, **73**, 3487.

[19] Finn, Hampson, and Sutton, *J.*, 1938, 1254; Coop and Sutton, *J.*, 1938, 1269.

molecules, however, the effect of conjugation between the rings upon the dipole moment will be further reduced when the C–C bond linking them is between carbon atoms which already possess a significant positive charge. This is confirmed by a Hückel molecular-orbital calculation.

The experimental dipole moments are compared in Table **3** with the values obtained by vector addition of two pyridine moments (μ_1) and with the values when approximate corrections are made for induced moments (μ_2). An allowance for the π-electron distribution would improve the agreement with the experimental results.

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