875. *Physical Properties and Chemical Constitution. Part XXXVI.* The Electric Dipole Moments of Phenyl Derivatives of Some N-Heterocyclic Molecules.*

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The electric dipole moments of three phenylpyridines, six of the phenylquinolines, 2,6-diphenylquinoline, 5-phenylacridine, and 9-phenylphenanthridine have been calculated from measurements of the dielectric constants, specific volumes, and refractive indices of their solutions in pure benzene at 25·00°. The dipole moments of acridine and phenanthridine were also determined. The apparent group moment of the phenyl substituent in these molecules is discussed in terms of conjugation between the phenyl group and heterocyclic ring and of the moments induced in the phenyl group.

The electric dipole moments of the methylpyridines [1] and methylquinolines [2] were measured and discussed in earlier papers of this series. These results are now extended to the corresponding phenyl derivatives. Replacement of a hydrogen atom in a heterocyclic ring by a phenyl group should not introduce a second primary moment into the molecule.† Consequently the difference between the dipole moments of the substituted molecule and the parent compound must arise through electron displacements within the molecule. This will be caused largely by polarisation of the phenyl substituent and by a change in the π-electron distribution. Sobczyk [3] recently discussed the dipole moments of a few of these compounds entirely in terms of the moment induced in the phenyl substituent by the primary moment of the parent heterocyclic molecule, but this factor alone cannot explain all our results.

Experimental and Results

The apparatus, experimental techniques, method of calculation, and presentation of the results are as described in previous Parts.[1,2] The measured properties of the benzene solutions at 25·00° are presented in Table 1, and the slopes of the linear graphs of dielectric constant (α) and of specific volume (β) against weight fraction, together with the polarisation data and dipole moments (μ) are in Table 2.

Preparation and Purification of Compounds.—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 picrates were in good agreement with published data where available.

Phenylpyridines. A mixture of the three monophenylpyridines was prepared by the method of Haworth, Heilbron, and Hey [4] by the action of benzenediazonium chloride on pyridine. The isomers were separated by fractional recrystallisation of their picrates from alcohol and from acetone. These had m.p.s identical with those of the same compounds obtained by the following unambiguous procedures.

2-Phenylpyridine. Evans and Allen's method [5] was employed in which phenyl-lithium, formed under anhydrous conditions from bromobenzene and lithium in ether, was treated with pyridine in sulphur-free toluene under nitrogen. The mixture was hydrolysed with water and the 2-phenylpyridine isolated from the toluene layer by fractional distillation. Purification was effected by recrystallising its picrate from acetone to a constant m. p. (177·5—178·5°) and

* Part XXXV, *J.*, 1962, 1188.

† The C–H bond moment may vary with the hybridisation of the carbon atom [1] but as these atoms are similarly hybridised in the molecules considered the resultant C–H moment should be virtually unchanged.

[1] Cumper, Vogel, and Walker, *J.*, 1956, 3621.
[2] Cumper, Redford, and Vogel, *J.*, 1962, 1176.
[3] Sobczyk, *Trans. Faraday Soc.*, 1961, **57**, 1041.
[4] Haworth, Heilbron, and Hey, *J.*, 1940, 349.
[5] Evans and Allen, *Org. Synth.*, Coll. Vol. II, 1947, p. 517; Geissman, Schlatter, Webb, and Roberts, *J. Org. Chem.*, 1941, **11**, 741.

by distillation. The product had b. p. 140°/12 mm., 98—100°/1 mm., d_4^{20} 1·0891, n_D^{20} 1·62295, R_D 50·24.

3-*Phenylpyridine*. It was prepared by the method described by Rapoport, Look, and Kelly.[6] *N*-3-Pyridylisobutyramide, b. p. 173—175/1 mm. (from isobutyric anhydride [7] and 3-aminopyridine, m. p. 65°), was caused to react with nitrosyl chloride.[8] The basic product was extracted with benzene, dried, and heated until gas evolution ceased. The 3-phenylpyridine was isolated by fractional distillation, and then redistilled; it had b. p. 144°/10 mm. and gave a picrate as needles, m. p. 163·5—164·0°.

4-*Phenylpyridine*. 1,2,3,6-Tetrahydro-4-phenylpyridine, b. p. 115—136°/1—2 mm., was prepared from redistilled α-methylstyrene (b. p. 161—162°), ammonium chloride, and aqueous formaldehyde [9] at 60—65°. The compound was then dehydrogenated with 10% palladium–charcoal in nitrobenzene; the non-basic material was removed from a hydrochloric acid solution of the product by extraction with toluene; the aqueous portion was then rendered alkaline with sodium hydroxide, and the base extracted with toluene, dried, distilled (b. p. 135—137°/3·5 mm.), and finally recrystallised from water to a constant m. p. (77—78°) (picrate, needles, m. p. 199—200°).

2-*Phenylquinoline*. Evans and Allen's method for 2-phenylpyridine [5] was applied to quinoline (b. p. 103·5—104·0°/12 mm.). The resulting 2-phenylquinoline was extracted from the toluene solution with dilute hydrochloric acid, precipitated therefrom with alkali, removed with ether, distilled, and recrystallised from light petroleum (b. p. 60—80°) to constant m. p. (82·5—83·0°) (picrate, m. p. 192·5—193·5°).

3-*Phenylquinoline*. This was prepared by the method of Kaslow and Buchner.[10] Phenylpyruvic acid (from sodium ethoxide, ethyl oxalate, and ethyl phenylacetate) was treated with isatin, to give 3-phenylquinoline-2,4-dicarboxylic acid. This was decarboxylated by copper bronze in paraffin oil at 280°. The 3-phenylquinoline was precipitated as the hydrochloride from an ethereal extract of the mixture, and the free base fractionated (b. p. 163—165°/0·9 mm.) and recrystallised from n-hexane to constant m. p. (52°) (picrate, needles, m. p. 205°).

4-*Phenylquinoline*. 2-Chloroethyl phenyl ketone (m. p. 48°) (from β-chloropropionic acid) was treated with aniline and aniline hydrochloride in ethyl alcohol to form 4-phenylquinoline, the procedure of Kenner and Statham [11] being followed. The compound was converted into the picrate which was crystallised from alcohol to constant m. p. (226°). The regenerated base was fractionated (b. p. 170°/1 mm.) and crystallised from light petroleum (b. p. 40—60°) to constant m. p. (61°).

5-*Phenylquinoline*. Attempts to prepare this compound by Case's method [12] did not yield sufficient product for an adequate sample of pure 5-phenylquinoline to be obtained. Neither could it be obtained from 5-chloroquinaldine [13] and phenyl-lithium.

6-*Phenylquinoline*. A commercial sample (Kodak) was purified by digestion in ethanol with activated charcoal and then recrystallised from ethanol to a constant m. p. (110·5—111·5°) (picrate, needles, m. p. 204°).

7-*Phenylquinoline*. A sample of 7-phenylquinoline, presented by Professor F. H. Case,[14] was digested in chloroform with activated charcoal and then recrystallised from light petroleum (b. p. 40—60°) to a constant m. p. of 59—60°.

8-*Phenylquinoline*. This was prepared by Kaslow and Hayek's method.[15] Concentrated sulphuric acid was added to a mixture of 2-aminobiphenyl and *o*-nitrophenol at 125—130°, the product decomposed with iced water, and the base extracted with benzene. Three fractional distillations gave 8-phenylquinoline, b. p. 185—186°/5·5 mm., m. p. 48·5—49·5°, d_4^{20} 1·1525, n_D^{20} 1·68133, R_D 67·07 (picrate, needles, m. p. 154°).

2,6-*Diphenylquinoline*. 6-Phenylquinoline in toluene–benzene was caused to react with ethereal phenyl-lithium (cf. refs. 5, 17), water added, and the compound extracted with benzene.

[6] Rapoport, Look, and Kelly, *J. Amer. Chem. Soc.*, 1952, **74**, 6293.
[7] Gerrard and Thrush, *J.*, 1952, 741.
[8] Morton and Wilcox, *Inorg. Synth.*, Vol. IV, 1953, p. 48.
[9] Schmilde and Mansfield, *J. Amer. Chem. Soc.*, 1956, **78**, 1702.
[10] Kaslow and Buckner, *J. Org. Chem.*, 1958, **23**, 271.
[11] Kenner and Statham, *J.*, 1935, 301.
[12] Case, *J. Org. Chem.*, 1951, **16**, 1541.
[13] Spivey and Curd, *J.*, 1949, 2656.
[14] Case and Buck, *J. Org. Chem.*, 1956, **21**, 697.
[15] Kaslow and Hayek, *J. Amer. Chem. Soc.*, 1951, **73**, 4986.

2,6-*Diphenylquinoline* was isolated as its hydrochloride and purified by crystallising its picrate from ethanol–2-ethoxyethanol to constant m. p. (235·5°) and the regenerated base successively from light petroleum (b. p. 100—120°) and alcohol–benzene; it then had m. p. 204—205° (Found: C, 89·5; H, 5·5; N, 4·9. $C_{21}H_{15}N$ requires C, 89·7; H, 5·4; N, 5·0%). [Picrate found N, 11·2. $C_{27}H_{18}N_4O_4$ requires N, 11·0%.]

Substitution with phenyl-lithium in *N*-heterocyclic compounds usually occurs in the 2-position: for this reason we regard our compound as 2,6-diphenylquinoline. This is supported by a consideration of the dipole moments: quinoline, 2·15; 6-phenylquinoline, 2·14; 2-phenylquinoline, 1·77; 4-phenylquinoline, 2·39; 2,6-diphenylquinoline, 1·73 D.

Acridine. A commercial sample was purified by precipitating it as the hydrochloride from benzene solution with hydrogen chloride, regenerating and drying the base at 110°/50 mm., and recrystallising it from ligroin to constant m. p. 111° (picrate, prisms, m. p. 256—259°).

5-*Phenylacridine.* Acridone (m. p. 350°), prepared by the action of sulphuric acid on *N*-phenylanthranilic acid, was suspended in benzene and then treated with ethereal phenyl-lithium.[16] Iced water was added and 5-phenylacridine hydrochloride precipitated from the benzene phase. The regenerated base, crystallised from aqueous alcohol and then recrystallised to constant m. p. from alcohol, had m. p. 186—187° (picrate, m. p. 234—235°).

Phenanthridine. (1) A commercial sample (Light) was purified by recrystallising it from light petroleum (b. p. 80—100°) to constant m. p. (106—106·5°) (picrate, needles, m. p. 244·5—245·5°).

(2) 2-Aminobiphenyl (Light) was purified by fractional distillation under reduced pressure in nitrogen and had m. p. 49—50°. It was converted into the formamido-compound by refluxing it for 15 min. with a slight excess of 80% formic acid and pouring the mixture into ice-cold water: the resulting solid was treated with cold ethanol to remove any 4-formamidobiphenyl present (this is sparingly soluble; the 2-formamido-compound is very soluble). Recrystallisation from dilute ethanol gave pure 2-formamidobiphenyl,[17] m. p. 75°. The latter (25 g.) and polyphosphoric acid [18] (250 ml.) were heated at 140—160° for 1 hr. with constant and vigorous stirring, then poured into water (1 l.), and the resultant milky solution was adjusted to pH 10 with concentrated sodium hydroxide solution and kept overnight. The solid which separated was collected (22 g.; m. p. 104—105°) and recrystallised from light petroleum (b. p. 80—100°) (charcoal) as needles, m. p. 106—107°. This was further purified as follows. The synthetic phenanthridine (20 g.) in hydrochloric acid (1 : 1; 100 ml.) was added to mercuric chloride solution (60 g. in 3 l. of water), the mixture was heated to the b. p. and concentrated hydrochloric acid added until all the solid had dissolved: on cooling, the mercuric chloride addition compound separated in needles (47 g.; m. p. 199—200°).[17] This was decomposed with strong sodium hydroxide solution, and the phenanthridine was extracted with ether and recrystallised as above: the yield was 16 g., and the m. p. 106—107°.

(3) 1-Benzylbenzotriazole, m. p. 115—116° (10 g.), and activated copper powder (0·1 g.) were heated in a Woods' metal bath at 360—380° under nitrogen for 6—7 hr., *i.e.*, until no more volatile material was formed. The dark product was extracted with hot dilute hydrochloric acid (100 ml.), the extract basified with sodium hydroxide, and the crude phenanthridine removed with ether, dried ($MgSO_4$), and recovered. The residual reddish liquid (*ca.* 3 ml.) was dissolved in warm acetone, and picric acid (2 g.) in acetone added: on cooling, needles of phenanthridine picrate separated. 40 g. of 1-benzylbenzotriazole yielded 3·5 g. of the picrate.[19] The latter was recrystallised from water: it softened slightly at 220° whilst changing its crystalline form from needles to cubes and then melted at 245°. The picrate was decomposed with an excess of ethanolamine and the base extracted with ether. Phenanthridine recovered from the dried ethereal solution was recrystallised from light petroleum (b. p. 80—100°) and melted at 106—107°.

(4) " Phenanthridine purum " (Fluka; 20 g.) was purified through the mercuric chloride addition compound as above and gave a product (16 g.) of m. p. 106—107°.

9-*Phenylphenanthridine.* Phenyl-lithium and phenanthridine were allowed to react in ether,[20] ice–water added, and the mixture refluxed for 3 hr. The ethereal layer was separated the ether removed, and the residue refluxed with nitrobenzene. 9-Phenylphenanthridine was

[16] Lehmstedt and Dostal, *Ber.*, 1939, **72**, 804.
[17] Pictet and Hubert, *Ber.*, 1896, **29**, 1813.
[18] Taylor and Kalenda, *J. Amer. Chem. Soc.*, 1954, **76**, 1699.
[19] Gibson, *J.*, 1956, 1076.
[20] Gilman and Nelson, *J. Amer. Chem. Soc.*, 1948, **70**, 3316.

TABLE 1.

$100w_2$	ε_{12}	v_{12}	n_{12}
	2-Phenylpyridine		
0·1345	2·2765	1·14415	—
0·2763	2·2804	1·14382	—
0·7478	2·2920	1·14271	—
1·0775	2·3036	1·14185	—
1·2418	2·3087	1·14141	—
1·7286	2·3226	1·14036	—
1·7707	2·3244	1·14019	—
	4-Phenylpyridine		
0·0759	2·2765	1·14424	1·49786
0·1711	2·2812	1·14395	1·49796
0·2816	2·2868	1·14371	1·49806
0·4824	2·2961	1·14325	1·49823
0·9217	2·3177	1·14207	1·49867
1·1849	2·3310	1·14148	1·49900
	3-Phenylquinoline		
0·1697	2·2775	1·14400	1·49787
0·2598	2·2806	1·14369	1·49792
0·2880	2·2818	1·14366	1·49796
0·5578	2·2890	1·14302	1·49843
0·9539	2·3005	1·14182	1·49901
	6-Phenylquinoline		
1·1610	2·2775	1·14398	1·49800
0·2264	2·2795	1·14375	1·49819
0·3903	2·2841	1·14328	1·49839
0·4753	2·2870	1·14300	1·49854
1·1862	2·3077	1·14101	1·49971
1·2145	2·3080	1·14085	1·49984
1·3935	2·3134	1·14038	1·50002
	8-Phenylquinoline		
0·1177	2·2759	1·14410	1·49786
0·2805	2·2798	1·14358	1·49823
0·3303	2·2811	1·14343	1·49818
0·4671	2·2847	1·14306	1·49839
0·6912	2·2903	1·14238	1·49872
1·0070	2·2990	1·14145	1·49921
1·0803	2·3013	1·14116	1·49930
	Acridine		
0·0928	2·2757	1·14413	1·49793
0·1959	2·2789	1·14385	1·49815
0·3253	2·2835	1·14345	1·49844
0·3836	2·2852	1·14331	1·49852
1·2897	3·3141	1·14059	1·50027
1·7447	2·3292	1·13917	1·50124
1·7472	2·3297	1·13923	1·50121
	Phenanthridine, specimen 1		
0·1186	2·2770	1·14416	1·49790
0·2175	2·2808	1·14377	1·49808
0·4439	2·2898	1·14309	1·49842
0·6626	2·2983	1·14236	1·49879
0·7044	2·3001	1·14226	1·49889
0·9541	2·3101	1·14150	1·49934
1·4444	2·3293	1·13993	1·50010
	Phenanthridine, specimen 3		
0·0874	2·2764	1·14410	1·49786
0·1694	2·2797	1·14391	1·49791
0·2845	2·2835	1·14355	1·49818
0·2876	2·2841	1·14347	1·49824
0·5250	2·2925	1·14242	1·49850
0·6000	2·2955	1·14235	1·49863
0·6736	2·2991	1·14217	1·49873
	3-Phenylpyridine		
0·0734	2·2754	1·14424	1·49792
0·1468	2·2785	1·14406	1·49792
0·2501	2·2825	1·14383	1·49808
0·2659	2·2834	1·14373	1·49808
0·3358	2·2855	1·14361	1·49814
0·5383	2·2938	1·14311	1·49836
0·6234	2·2971	1·14290	1·49849
	2-Phenylquinoline		
0·1196	2·2753	1·14411	1·49792
0·3222	2·2794	1·14351	1·49831
0·1689	2·2763	1·14395	1·49807
0·4969	2·2834	1·14299	1·49864
0·9550	2·2933	1·14166	1·49942
1·3698	2·3021	1·14046	1·50014
1·5712	2·3066	1·13986	1·50057
	4-Phenylquinoline		
0·0890	2·2758	1·14421	1·49776
0·1072	2·2762	1·14416	1·49778
0·1543	2·2777	1·14402	1·49784
0·2336	2·2808	1·14379	1·49793
0·3828	2·2856	1·14339	1·49823
0·5621	2·2918	1·14290	1·49845
0·8013	2·3012	1·14216	1·49882
	7-Phenylquinoline		
0·1300	2·2768	1·14411	1·49770
0·2514	2·2796	1·14375	1·49786
0·4236	2·2849	1·14324	1·49818
0·5784	2·2886	1·14279	1·49825
	2,6-Diphenylquinoline		
0·0613	2·2738	1·14429	1·49773
0·1100	2·2747	1·14415	1·49782
0·1309	2·2751	1·14406	1·49790
0·1865	2·2759	1·14383	1·49799
0·3006	2·2778	1·14352	1·49824
0·3640	2·2792	1·14335	1·49832
0·7094	2·2850	1·14235	1·49901
	5-Phenylacridine		
0·0448	2·2741	1·14428	1·49775
0·1226	2·2766	1·14403	1·49790
0·2968	2·2817	1·14348	1·49826
0·3610	2·2841	1·14315	1·49846
0·5067	2·2882	1·14281	1·49873
0·8543	2·2987	1·14174	1·49939
1·1970	2·3091	1·14069	1·50000
	Phenanthridine, specimen 2		
0·0483	2·2751	1·14433	1·49783
0·1235	2·2786	1·14410	1·49793
0·2880	2·2843	1·14357	1·49824
0·4619	2·2912	1·14302	1·49849
0·7057	2·3013	1·14229	1·49897
0·9206	2·3093	1·14157	1·49932
1·2616	2·3230	1·14050	1·49984
	9-Phenylphenanthridine		
0·0469	2·2747	1·14415	1·49789
0·2929	2·2801	1·14356	1·49824
0·3710	2·2825	1·14324	1·49840
0·5670	2·2876	1·14268	1·49879
0·7392	2·2926	1·14208	1·49907
0·9880	2·2991	1·14129	1·49963
1·2147	2·3052	1·14055	1·49993

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.
2-Phenylpyridine	$2{\cdot}92_1$	$-0{\cdot}240_6$	127·0	50·24 *	76·7	1·94	1·77 †
3-Phenylpyridine	$3{\cdot}94_0$	$-0{\cdot}253_8$	156·0	49·99	106·0	2·28	2·45 †
4-Phenylpyridine	$4{\cdot}98_6$	$-0{\cdot}256_6$	183·8	48·88	134·9	2·57	2·50 †
2-Phenylquinoline	$2{\cdot}15_9$	$-0{\cdot}292_1$	135·4	71·59	63·8	1·77	1·76 †
3-Phenylquinoline	$2{\cdot}87_8$	$-0{\cdot}271_8$	164·3	70·79	93·5	2·14	2·22 †
4-Phenylquinoline	$3{\cdot}41_3$	$-0{\cdot}279_8$	184·4	67·61	116·8	2·39	2·33 †
6-Phenylquinoline	$2{\cdot}91_2$	$-0{\cdot}295_2$	164·3	70·45	93·8	2·14	
7-Phenylquinoline	$2{\cdot}69_6$	$-0{\cdot}282_7$	156·6	69·63	87·0	2·06	
8-Phenylquinoline	$2{\cdot}64_1$	$-0{\cdot}301_7$	153·4	68·40	85·0	2·04	
2,6-Diphenylquinoline ...	$1{\cdot}72_9$	$-0{\cdot}300_6$	162·1	101·30	60·8	1·73	
Acridine	$3{\cdot}24_6$	$-0{\cdot}301_4$	154·3	65·08	89·2	2·09	1·95, ‡ 1·94 §
5-Phenylacridine	$3{\cdot}03_9$	$-0{\cdot}324_2$	208·1	90·28	117·8	2·40	
Phenanthridine	$3{\cdot}95_6$	$-0{\cdot}309_8$	177·7	60·82	116·9	2·39	1·50 ¶
9-Phenylphenanthridine	$2{\cdot}71_9$	$-0{\cdot}318_7$	193·1	88·28	104·8	2·27	

* Measured on the pure liquid. † Sobczyk, *Trans. Faraday Soc.*, 1961, **57**, 1041. ‡ Bergmann, Engel, and Meyer, *Ber.*, 1932, **65***B*, 446. § Rushkareva, Varyukhina, and Kokoshko, *Doklady Akad. Nauk S.S.S.R.*, 1953, **93**, 77. ¶ Gaouck and Le Fèvre, *J.*, 1939, 1392.

isolated by distillation under reduced pressure and recrystallised from light petroleum (b. p. 60—80°)—benzene to a constant m. p. of 104·5—105° (picrate, needles, m. p. 252—253°).

DISCUSSION

The geometrical structure of benzene [21] and of pyridine [22] has been established experimentally and it is reasonable to assume that the phenylpyridines consist of these units linked together. The structure of the other parent heterocyclic molecules (quinoline, acridine, and phenanthridine) have not been determined, so we shall assume that they consist of undistorted benzene and pyridine rings fused together. Any error this introduces into the angle between the primary moment of the molecule and the direction of the bond linking the two rings must be small in view of the small departures from 120° angles in naphthalene and anthracene.[23]

Some of the phenyl-substituted molecules may be planar in the solid phase,[24] but none is likely to be so in solution (see ref. 25). In biphenyl and 4,4′-bipyridyl the most probable angle between the planes of the two rings is 41·6° and 37·2°, respectively,[26] in the gaseous phase and an angle of about 40° would therefore be expected for 3- and 4-phenylpyridine and for 3-, 6-, and 7-phenylquinoline. For 2,2′-bipyridyl there would seem to be considerable freedom for oscillation about the planar *trans*-form, an angle of about 18° being the most likely.[26, 27] In 2-phenylpyridine and 2-phenylquinoline, however, steric repulsion between a pair of hydrogen atoms would increase this angle, though probably not to a value as large as 40°. In 4-, 5- and possibly 8-phenylquinoline, 5-phenylacridine, and 9-phenylphenanthridine there will be considerable steric hindrance and the interplanar angle is likely to be much greater than 40°. The ultraviolet spectra of these compounds were determined for absolute ethanol solutions and agreed well with the available published data.[28] There is a tendency for the absorption maxima to occur at longer wavelengths where the above discussion indicates that conjugation should be greatest (Table 3).

[21] Landseth and Stoicheff, *Canad. J. Phys.*, 1956, **34**, 350; Almenningen, Bastiansen, and Fernholt, *Kgl. norske Videnskab. Selskabs Skrifter*, 1958, No. 3.
[22] Bak, Hansen-Nygaard, and Rastrup-Andersen, *Mol. Spectroscopy*, 1958, **2**, 361; cf. Cumper, *Trans. Faraday Soc.*, 1958, **54**, 1266.
[23] Cruickshank and Sparks, *Proc. Roy. Soc.*, 1960, *A*, **258**, 270.
[24] Dahr, *Indian J. Phys.*, 1932, **7**, 43; Saunder, *Proc. Roy. Soc.*, 1946, *A*, **188**, 31; Neikerk and Saunder, *Acta Cryst.*, 1948, **1**, 44.
[25] Bastiansen, *Acta Chem. Scand.*, 1949, **3**, 408; 1950, **4**, 926; 1952, **6**, 205.
[26] Almenningen and Bastiansen, *Kgl. norske Videnskab. Selskabs Skrifter*, 1958, No. 4.
[27] Cumper, Ginman, and Vogel, *J.*, 1962, 1188.
[28] Krumholz, *J. Amer. Chem. Soc.*, 1951, **73**, 3487; Colona and Risaliti, *Atti Accad. naz. Lincei, Rend. Classe Sci. fis. mat. nat.*, 1953, **14**, 809.

TABLE 3.

Compound	μ (D)	Moment (D) of Ph group	π-Electron charge	Absorption			
				$\lambda_{max.}$ (mμ)	ε	$\lambda_{max.}$* (mμ)	ε
2-Phenylpyridine	1·94	0·66	+0·021	245·5	12,700	277	10,400
3-Phenylpyridine	2·28	0·14	+0·005	246·0	17,100	270†	7,500
4-Phenylpyridine	2·57	0·36	+0·020	256·0	16,900	—	—
2-Phenylquinoline	1·77	—‡	+0·032	256·5	39,000	322	7,300
3-Phenylquinoline	2·14	−0·02	+0·000	252·0	35,000	280	9,700
4-Phenylquinoline	2·39	0·24	+0·027	228·0	37,800	293	9,000
6-Phenylquinoline	2·14	−0·04	+0·001	252·0	46,100	—	—
7-Phenylquinoline	2·06	0·17	+0·006	252·0	46,000	322	5,800
8-Phenylquinoline	2·04	0·11	−0·003	233·5	33,300	295	7,000
5-Phenylacridine	2·40	0·31	+0·043	253·5	135,400	357·5	10,100
9-Phenylphenanthridine	2·27	0·24	+0·042	252·5	55,700	—	—

* Approximate centre of absorption band. † Point of inflexion. ‡ Expression for a group moment along the C–C bond not soluble.

In Table 3 the apparent phenyl group moments, relative to that of a C–H bond, are also presented. These were calculated by vector analysis from the dipole moment of the phenyl compound and of the unsubstituted parent compound. (The dipole moment of pyridine [1] was determined previously as 2·21 D and that of quinoline [2] 2·15 D in benzene solution.) The finite group moments, and the variation between them, seem to be due to four main factors.

(i) The moment induced in the phenyl group by the primary moment of the parent molecule, located near the nitrogen atom.[29] This falls off rapidly with increasing distance and could be estimated by the methods adopted previously.[2,30]

(ii) The phenyl group has a large polarisability [31] and its electrons would also be displaced by the net charges on the atoms of the pyridine or quinoline ring. The charge due to the π-electron distribution is greatest on the nitrogen atom, but the charge on the atom at which substitution occurs probably has the greater effect. These charges, estimated by a Hückel molecular-orbital approximation [32] (cf. ref. 33), with $\alpha_N = \alpha_C + 0{\cdot}2\ \beta$, are listed in Table 3 (α = coulombic integral, β = exchange integral; the relative order of these charges is not dependent upon the value of the numerical factor).

(iii) For planar molecules π-electron conjugation between the ring systems would make a substantial contribution to their dipole moments. This would increase with the positive charge on the substituted carbon atom in the pyridine or quinoline ring. The actual contribution in these molecules will decrease rapidly as the interplanar angle increases.

(iv) The dipole moments of all molecules are affected to some extent by the solvent; this effect may be greater for the smaller unsubstituted molecules where the surrounding solvent is rather closer to the primary dipole of the solute molecules.[34] An allowance for this factor is unlikely to have a serious effect upon the *relative* values of the phenyl group moments given in Table 3.

In view of uncertainty about the quantitative effect of some of these factors it only seems profitable to consider the results qualitatively.

If the numerical values adopted previously [2] are employed, the moments induced in the phenyl group by the primary moment associated with the nitrogen atom, and by its π-electron charge, are of real significance only for substitution in positions close to the nitrogen atom. It is important with 2-substituents and will cause the direction of the phenyl group moment to be appreciably different from the assumed direction along the C–C bond linking the rings. This is why an apparent group moment cannot be calculated

[29] Brown and Heffernan, *Austral. J. Chem.*, 1957, **10**, 493.
[30] Cumper, *Chem. and Ind.*, 1958, 1628.
[31] Le Fèvre and Le Fèvre, *J.*, 1954, 1577.
[32] Cumper, unpublished results.
[33] Longuet-Higgins and Coulson, *Trans. Faraday Soc.*, 1947, **43**, 87.
[34] Cf. Buckingham and Le Fèvre, *J.*, 1952, 1932.

for 2-phenylquinoline and is probably the reason why 2,6-diphenylquinoline has an even lower dipole moment than 2-phenylquinoline (6-phenylquinoline has a moment virtually identical with that of quinoline).

Table 3 shows a general correlation between the phenyl group moment and the net π-electron charge on the substituted carbon atom. That the resultant moment can also be influenced by conjugation of the phenyl group with the parent molecule is most clearly demonstrated with 4-phenylpyridine. The π-electron charge on the substituted carbon atom, and the moment produced in the phenyl group, increase along the series 4-phenylpyridine, 4-phenylquinoline, and 5-phenylacridine. The phenyl group moment, however, is greatest for 4-phenylpyridine as this is the only one of the three in which conjugation with the parent molecule could make a significant contribution to its value. Steric repression of conjugation is also the reason why the group moment in 9-phenylphenanthridine is appreciably lower than in 2-phenylpyridine and 2-phenylquinoline. There is some evidence, from nuclear quadrupole resonance spectra,[35] that π-electron conjugation is greater in 2-chloroquinoline than in 2-chloropyridine—this might be why the dipole moment of 2-phenylquinoline is 0·17 D lower than that of 2-phenylpyridine.

The influence of conjugation in 3-phenylpyridine and in 3- and 6-phenylquinoline must be less than in 4-phenylpyridine since, although the interplanar angles are probably similar, these positions are least affected by the nitrogen atom. 3- and 6-Phenylquinoline actually have dipole moments virtually identical with that of quinoline itself. The somewhat greater group moment in 3-phenylpyridine probably reflects the greater π-electron charge on C-3 in pyridine.

The group moment in 8-phenylquinoline seems to be rather large. The net charge on C-8 is very small and the ultraviolet spectrum appears to indicate little conjugation with the parent molecule. The moment induced in the phenyl group by the primary quinoline moment would reduce the resultant dipole moment and there is also a possibility of direct interaction between the substituent and lone pair electrons on the nitrogen atom.

There is a large difference between the dipole moment of phenanthridine (specimen 1) recorded in Table 2 (2·39 D) and the literature value of $1{\cdot}5_0$ D.[36] The physical properties of that sample of phenanthridine employed agreed well with the published data and we feel that its moment should be comparable with those of 3- and 4-phenylquinoline (2·14 and 2·39 D, respectively) and a little greater than that of 9-phenylphenanthridine (2·27 D). Gaouck and Le Fèvre's value,[36] obtained from very limited experimental work on very dilute solutions, does not seem to be consistent with any of the dipole moments reported in this paper. In view of this serious discrepancy, phenanthridine was synthesised by two independent methods (specimens 2 and 3), and a pure commercial sample (Fluka) (4) was purified through the mercuric chloride addition compound. The dipole moments obtained for these three additional samples were 2·39, 2·38, and 2·38 D. The figures (including the values of the parameters α and β) in Table 2 recorded for specimen 1 were substantially the same for specimens 2—4.

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[35] Dewar and Lucken, *J.*, 1958, 2653.
[36] Gaouck and Le Fèvre, *J.*, 1939, 1392.