

224. *Physical Properties and Chemical Constitution. Part XXXIII.**
The Electric Dipole Moments of Methylquinolines.

By C. W. N. CUMPER, D. G. REDFORD, and A. I. VOGEL.

The electric dipole moments of quinoline, the seven methylquinolines, and 2,6- and 4,8-dimethylquinoline have been calculated from measurements of the dielectric constants, specific volumes, and refractive indices of their solutions in pure benzene at 25.00°. The apparent differences between the C-Me group moments in these compounds and those previously found for toluene and the methylpyridines are discussed. The dipole moments of 1- and 2-methylnaphthalene were also determined.

THE electric dipole moments of many substituted benzenes and pyridines have been measured but there are comparatively few systematic data for other heterocyclic systems. In this and subsequent papers, the dipole moments of alkyl-, phenyl-, chloro-, nitro-, and

* Part XXXII, *J.*, 1960, 570.

amino-quinolines will be reported and discussed. Of these derivatives the methyl compounds should be the simplest because this substituent cannot conjugate with the heterocyclic ring, nor will its moment be influenced by rotation about the C-Me bond.

Comparison of the dipole moments of methyl-pyridines and -quinolines could provide information about the differences between the two systems and also on the electron distribution within these molecules, particularly as to differences between the ring carbon atoms at which substitution occurs.

EXPERIMENTAL

The apparatus and techniques employed were described in Parts XXV¹ and XXVI.² Measurements were made on solutions in pure benzene at $25.00^\circ \pm 0.01^\circ$.

Each substance was extensively purified immediately before use; its physical properties, together with the m. p. of the picrate, were in good agreement with recorded values.³ The infrared and ultraviolet spectra of each compound were determined and agreed with published data, where available. The gas-liquid chromatograms of 4- and of 8-methylquinoline were determined with a Griffin and George Ltd. Mark II A apparatus—only single peaks were obtained under the conditions employed.

Preparation of Pure Compounds.—Each compound measured was finally purified by recrystallisation of suitable derivatives to constant m. p., and the regenerated compound fractionally distilled through a column packed with glass Fenske rings (4 mm. diameter).

Quinoline. Commercial samples from (i) Hopkin and Williams Ltd. and (ii) the Yorkshire Tar Distillers were fractionated through a 30 cm. column and further purified by recrystallisation of the zinc chloride complex (m. p. variable) and of the dichromate complex to constant m. p. ($166\text{--}167^\circ$). The regenerated quinoline was fractionated twice, then having b. p. $233.0\text{--}233.2^\circ/755$ mm., $103.5\text{--}104.0^\circ/12$ mm. n_D^{20} 1.62670, d_4^{20} 1.0937 (picrate, m. p. $205\text{--}206^\circ$).

2-Methylquinoline (quinaldine). Quinaldine (Hopkin and Williams), when purified by fractional distillation and through its zinc chloride complex (variable m. p.) and picrate, m. p. $196\text{--}197^\circ$, had b. p. $239.5\text{--}240.0^\circ/750$ mm., $86\text{--}87^\circ/1$ mm. n_D^{20} 1.61210, d_4^{20} 1.0594.

3-Methylquinoline. (i) Willmott and Simpson's method⁴ was used in which *o*-nitrobenzaldehyde and propionaldehyde were condensed under the action of piperidine, and the aldol formed was reduced with stannous chloride and hydrochloric acid. The product, b. p. $138.5\text{--}139.5^\circ/21$ mm., n_D^{20} 1.61687, d_4^{20} 1.0692, gave a picrate, m. p. $190\text{--}191^\circ$. (ii) The compound was also prepared by a Skraup synthesis from aniline and α -methacraldehyde⁵ with sodium *m*-nitrobenzenesulphonate as the oxidising agent.⁶ The dichromate was recrystallised from water (m. p. $132\text{--}133^\circ$). The base, b. p. $127^\circ/12$ mm., gave a picrate, m. p. $190\text{--}191^\circ$.

4-Methylquinoline (lepidine). Lepidine (Hopkin and Williams Ltd.), purified by fractional distillation followed by recrystallisation of its dichromate complex (m. p. 138°), had b. p. $260.0\text{--}260.5^\circ/755$ mm., n_D^{20} 1.61995, d_4^{20} 1.0831 (picrate, m. p. $219\text{--}220^\circ$).

5-Methylquinoline. 6-Cyano-*m*-toluidine ($\text{NH}_2 = 1$) was prepared by von Niementowski's method⁷ and converted into 5-methylquinoline-8-carboxylic acid by a Skraup reaction with glycerol, 70% sulphuric acid, and sodium *m*-nitrobenzenesulphonate.⁸ The acid was heated with copper-bronze powder⁹ and any remaining acidic material extracted with alkali. The base, purified by fractional distillation and through the picrate (m. p. $220\text{--}221^\circ$), had b. p. $257\text{--}258^\circ/760$ mm., $141\text{--}142^\circ/28$ mm.

6-Methylquinoline. Prepared by a normal Skraup synthesis³ from *p*-toluidine and *o*-nitrophenol and purified by recrystallisation of its zinc chloride complex (m. p. 190°), this had b. p. $254^\circ/760$ mm., $84\text{--}85^\circ/1.5$ mm., n_D^{20} 1.61605, d_4^{20} 1.0668 (picrate, m. p. $234\text{--}235^\circ$).

7-Methylquinoline. (i) A commercial sample (British Drug Houses Ltd.) was purified by

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

² Cumper, Vogel, and Walker, *J.*, 1957, 3640.

³ Manske, Marion, and Leger, *Canad. J. Res.*, 1942, B, 20, 133; see also refs. 4—13.

⁴ Willmott and Simpson, *J.*, 1926, 2807.

⁵ Untermohlen, *J. Org. Chem.*, 1943, 8, 544; "Organic Reactions," Vol. VII, John Wiley, New York, 1948, p. 70.

⁶ Bradford, Elliott, and Rowe, *J.*, 1947, 437.

⁷ von Niementowski, *J. prakt. Chem.*, 1889, 40, 4.

⁸ von Yakubovskii, *Ber.*, 1910, 43, 3026.

⁹ Seibert, Norton, Benzon, and Bergstrom, *J. Amer. Chem. Soc.*, 1946, 68, 2721.

five recrystallisations of its dichromate from water (m. p. 149°), then having b. p. 255—256°/760 mm., m. p. 38° (picrate, m. p. 243—244°). (ii) The compound was also prepared by a Skraup synthesis from *m*-toluidine,⁶ iodine being the oxidising agent,¹⁰ and purified through its dichromate (m. p. 149°) and picrate (m. p. 243°). This sample had b. p. 254—256°/757 mm., 160°/40 mm., m. p. 38°, n_D^{20} 1.61481, d_4^{20} 1.0624.

8-Methylquinoline. The very pure material from British Drug Houses was further purified by fractionation and through its zinc chloride complex, then having b. p. 245—246°/760 mm., n_D^{20} 1.61631, d_4^{20} 1.0726 (picrate, m. p. 206—207°).

2,6-Dimethylquinoline. A Doebner-Miller quinaldine synthesis¹¹ from *p*-toluidine and acetaldehyde gave a base of b. p. 100°/2 mm., m. p. 59.0—59.5° (recrystallised from light petroleum) [picrate, m. p. 191—192°; dichromate, m. p. 116—117° (decomp.)].

4,8-Dimethylquinoline. This was formed by condensing *o*-toluidine and acetoacetic ester.¹² The hydroxyl group was removed by Mikhailov's method.¹³ The base had m. p. 57.0—57.5° (recrystallised from light petroleum).

1-Methylnaphthalene. Commercial 1-methylnaphthalene was purified by recrystallisation of its picrate to a constant m. p. (141—142°) followed by fractionation of the compound which was regenerated by steam-distillation from sodium hydroxide. It then had b. p. 121.5°/23 mm.

2-Methylnaphthalene. Commercial 2-methylnaphthalene, recrystallised from ethanol, had m. p. 34—35° and gave a picrate, m. p. 118—119°.

RESULTS

The dielectric constants (ϵ_{12}), specific volumes (v_{12}) and refractive indices to sodium light (n_{12}) of benzene solutions at 25.00° with weight fractions w_2 are recorded in Table I. Over the

TABLE I.

$100w_2$	ϵ_{12}	v_{12}	n_{12}	$100w_2$	ϵ_{12}	v_{12}	n_{12}
<i>Quinoline</i>				<i>2-Methylquinoline</i>			
0.1097	2.2773	1.14418	1.49790	0.0831	2.2753	1.14434	—
0.2026	2.2811	1.14402	1.49795	0.1927	2.2787	1.14408	—
0.4355	2.2909	1.14340	1.49820	0.3491	2.2840	1.14380	—
0.8411	2.3077	1.14238	1.49867	0.6550	2.2928	1.14316	—
1.2549	2.3250	1.14132	1.49924	0.9534	2.3022	1.14250	—
1.6277	2.3412	1.14039	1.49954	1.1228	2.3076	1.14218	—
1.7984	2.3491	1.13991	1.49977	1.3532	2.3151	1.14164	—
<i>3-Methylquinoline</i>				<i>4-Methylquinoline</i>			
0.2072	2.2812	1.14402	1.49782	0.2154	2.2829	1.14399	—
0.4501	2.2913	1.14347	1.49804	0.4468	2.2947	1.14342	—
0.9614	2.3132	1.14236	1.49862	0.7794	2.3121	1.14266	—
1.0769	2.3191	1.14204	1.49872	1.0235	2.3254	1.14206	—
1.5940	2.3403	1.14093	1.49926	1.2574	2.3374	1.14153	—
1.8849	2.3531	1.14022	1.49958	1.4316	2.3468	1.14109	—
2.3241	2.3715	1.13923	1.50007	1.5795	2.3546	1.14073	—
<i>5-Methylquinoline</i>				<i>6-Methylquinoline</i>			
0.1990	2.2814	1.14398	1.49773	0.0952	2.2765	1.14422	1.49783
0.5031	2.2959	1.14328	1.49805	0.2435	2.2825	1.14390	1.49797
0.8832	2.3143	1.14237	1.49848	0.3245	2.2869	1.14375	1.49801
1.4068	2.3399	1.14121	1.49907	0.6204	2.3000	1.14314	1.49832
1.6712	2.3532	1.14064	1.49933	0.8379	2.3092	1.14267	1.49859
1.9210	2.3656	1.14004	1.49957	1.3238	2.3297	1.14164	1.49906
2.0420	2.3724	1.13976	1.49968	1.9078	2.3556	1.14039	1.49967
<i>7-Methylquinoline</i>				<i>8-Methylquinoline</i>			
0.2102	2.2802	1.14395	1.49794	0.2042	2.2750	1.14426	—
0.3286	2.2849	1.14369	1.49799	0.1105	2.2775	1.14410	—
0.8236	2.3023	1.14267	1.49852	0.4295	2.2829	1.14357	—
1.1280	2.3138	1.14200	1.49883	0.9234	2.2952	1.14249	—
1.3502	2.3225	1.14146	1.49907	1.6404	2.3121	1.14091	—
1.5054	2.3288	1.14112	1.49929	1.6648	2.3139	1.14085	—
1.7595	2.3379	1.14057	1.49954	2.1287	2.3231	1.13996	—

¹⁰ Vogel, "Elementary Practical Organic Chemistry," Longmans, Green, London, 1957, p. 319.

¹¹ Mills, Harris, and Lambourne, *J.*, 1921, **119**, 1294.

¹² Ewins and King, *J.*, 1913, **103**, 107.

¹³ Mikhailov, *J. Gen. Chem. (U.S.S.R.)*, 1936, **6**, 1511.

TABLE 1. (Continued).

$100w_2$	ϵ_{12}	v_{12}	n_{12}	$100w_2$	ϵ_{12}	v_{12}	n_{12}
	2,6-Dimethylquinoline				4,8-Dimethylquinoline		
0.1054	2.2754	1.14425	1.49772	0.0510	2.2740	1.14438	1.49776
0.2585	2.2800	1.14400	1.49788	0.0980	2.2762	1.14419	1.49781
0.5219	2.2881	1.14357	1.49814	0.1665	2.2779	1.14412	1.49787
0.9866	2.3025	1.14270	1.49860	0.3690	2.2849	1.14378	1.49803
1.2058	2.3095	1.14230	1.49881	0.6372	2.2940	1.14311	1.49829
1.5060	2.3186	1.14176	1.49912	1.1097	2.3099	1.14213	1.49881
1.9511	2.3323	1.14098	1.49951				
	1-Methylnaphthalene				2-Methylnaphthalene		
0.4943	—	1.14366	1.49806	0.2619	2.2738	1.14431	1.49766
1.0580	2.2774	1.14274	1.49867	0.9156	2.2764	1.14308	1.49836
1.8694	2.2808	1.14135	1.49956	2.5520	2.2834	1.14065	1.49995
2.9230	2.2850	1.13956	1.50069	3.5275	2.2883	1.13906	1.50112
3.7185	2.2880	1.13812	1.50158	5.0067	2.2945	1.13671	1.50266
4.2952	2.2905	1.13718	1.50216	6.3582	2.3004	1.13466	1.50414
5.0007	2.2933	1.13593	1.50297	8.4953	2.3101	1.13142	1.50650

TABLE 2.

Quinoline derivative	α	β	${}_{\infty}P_2$ (cm. ³)	R_D (cm. ³)	${}_0P$ (cm. ³)	μ (D)	Previous values for C ₈ H ₈ solns.
Quinoline	4.20 ₀	-0.246 ₁	136.5	41.74	94.81	2.15	2.14—2.25, ^a 2.24 ^b
2-Methyl-	3.01 ₈	-0.201 ₈	124.2	46.99 *	77.21	1.94	1.86, ^c 2.19, ^d 1.95 ^e
3-Methyl-	4.27 ₇	-0.221 ₉	154.6	47.35	107.2	2.29	
4-Methyl-	5.26 ₈	-0.232 ₇	180.7	46.44 *	134.3	2.56	2.52 ^e
5-Methyl-	4.89 ₉	-0.230 ₈	170.6	47.11	123.6	2.46	
6-Methyl-	4.35 ₈	-0.211 ₂	157.1	47.58	110.5	2.32	1.86 ^d
7-Methyl-	3.72 ₀	-0.221 ₅	139.6	47.27	92.29	2.12	
8-Methyl-	2.38 ₈	-0.211 ₅	104.1	46.67 *	57.40	1.68	
2,6-Dimethyl-	3.09 ₁	-0.178 ₈	136.6	52.76	83.82	2.02	2.00 ^d
4,8-Dimethyl-	3.38 ₈	-0.202 ₇	144.2	51.43	92.81	2.13	
1-Methylnaphthalene	0.40 ₈	-0.168 ₈	52.08	49.32	2.76	0.37	0.28 ^f
2-Methylnaphthalene	0.44 ₈	-0.152 ₂	53.87	49.83	4.04	0.44	0.44

* R_D measured on the pure liquid.

^a Measurements prior to 1948 from Wesson "Tables of Electric Dipole Moments," Massachusetts Inst. Technol., 1948. ^b Buckingham, Chan, Freeman, Le Fèvre, Rao, and Tardiff, *J.*, 1956, 1405. ^c Rau and Narayanaswamy, *Z. phys. Chem.*, 1934, B, 26, 23. ^d Le Fèvre and Le Fèvre, *J.*, 1935, 1470. ^e Rogers and Campbell, *J. Amer. Chem. Soc.*, 1953, 75, 1209. ^f Luther and Operskalski, *Naturwiss.*, 1950, 37, 376.

concentration range studied, ϵ_{12} was a linear function of w_2 and the parameters of this relation were determined by a method of least squares. Likewise v_{12} and the specific refraction of the solutions were also linear functions of w_2 . The slopes α and β , respectively, of the ϵ_{12} - w_2 and v_{12} - w_2 graphs, are recorded in Table 2. The total polarisation of the solutes at infinite dilution (${}_{\infty}P_2$), molar refraction to sodium light (R_D) (obtained from the specific refractions of the solutions and taken as equivalent to the distortion polarisation),¹ orientation polarisation (${}_0P$), and electric dipole moment (μ) have also been collected in Table 2. The dipole moments of the methylnaphthalenes may be slightly high because of inadequate allowance for their atom polarisation.

DISCUSSION

Since this is to be the first of a series of papers comparing the electric dipole moments of quinoline compounds with corresponding derivatives of pyridine some differences between these two systems will first be considered.

(a) The geometrical structure of pyridine has been established by microwave spectroscopy¹⁴ and we assume that it is unaltered when the hydrogen atoms are replaced by other atoms or radicals. Unfortunately the bond angles in quinoline have not been established,

¹⁴ Bak, Hansen-Nygaard, and Rastrup-Andersen, *Mol. Spectroscopy*, 1958, 2, 361; cf. Cumper, *Trans. Faraday Soc.*, 1958, 54, 1266.

so we shall take them to be those of a benzene¹⁵ and a pyridine ring fused together. The error this introduces into the directions of the bond and group moments is unlikely to be large in view of the small angular distortions when naphthalene (and anthracene) are formed from regular benzene hexagons.¹⁶

(b) The different shapes of the pyridine and the quinoline molecule will give rise to different solvent effects. One of the more satisfactory relations allowing for the effect of solvent upon electric dipole moments is the semiempirical equation of Buckingham and Le Fèvre.¹⁷ This equation indicated that the dipole moment of quinoline in benzene solution is 0.972 of its value in the vapour phase, and for the methylquinolines this factor varies between 0.965 and 0.990 (Table 3); the corresponding factors for the pyridine series are about 0.05 lower, *viz.*, pyridine 0.918, 2-methylpyridine 0.933, 3-methylpyridine 0.945 and 4-methylpyridine 0.922. The apparent group moments would therefore be expected to be about 5% greater in the quinoline compounds.

(c) Moments will also be induced in the unsubstituted ring in quinolines. This problem was first considered by Hampson and Weissberger¹⁸ for chloronaphthalenes. The dipole moment induced in part of a molecule by a primary dipole of moment μ_p may be estimated, by following Littlejohn and Smith,¹⁹ from the equations:

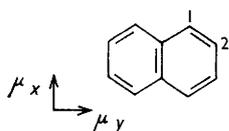
$$\mu_x = \mu_p[(\epsilon_a + 2)/\epsilon_b r^3] \gamma_x (\cos \theta - 1/3)$$

$$\mu_y = \mu_p[(\epsilon_a + 2)/\epsilon_b r^3] \gamma_y \cos \theta \sin \theta.$$
(1)

and

μ_x and μ_y are the moments induced, respectively, parallel and perpendicular to the inducing moment, γ_x and γ_y the corresponding polarisabilities of the polarisable group of dielectric constant ϵ_a and distance r from μ_p ; ϵ_b is the dielectric constant of the medium between the two centres, and θ the angle between the vectors μ_p and r .

If the dipole moments of 1- and 2-methylnaphthalene differ from that of toluene by the moments induced in the unsubstituted ring then they may be estimated from these equations. The dipole moment of toluene² (0.37 D) was used for μ_p and located at the methyl-carbon atom, and results of Le Fèvre and his co-workers²⁰ on polarisabilities were employed. The polarisation centre was taken at the centre of mass of the additional atoms of the other ring.¹⁸ On this basis the induced moments are as illustrated:

	<table border="1" style="border-collapse: collapse; text-align: center;"> <thead> <tr> <th>Posn.</th> <th>μ_x (D)</th> <th>μ_y (D)</th> </tr> </thead> <tbody> <tr> <td>1</td> <td>-0.016</td> <td>0.006</td> </tr> <tr> <td>2</td> <td>-0.074</td> <td>-0.010</td> </tr> </tbody> </table>	Posn.	μ_x (D)	μ_y (D)	1	-0.016	0.006	2	-0.074	-0.010
Posn.	μ_x (D)	μ_y (D)								
1	-0.016	0.006								
2	-0.074	-0.010								

(d) The π -electron distributions, and their contribution to the net charges on the carbon atoms, differ in the two ring systems. Theoretical estimates of these charges vary somewhat but the relative values obtained from different calculations are reasonably consistent. Those given by a Hückel molecular-orbital approximation²¹ are given on formulæ (I) and (II), relative to that on the nitrogen atom in pyridine. The net charge on the nitrogen atom²² in pyridine with $\alpha_N = \alpha_O + 0.4\beta$ is -0.142 (α = coulombic integral, β = exchange integral). This electron distribution will be modified somewhat in substituted quinolines.

¹⁵ Langseth and Stoicheff, *Canad. J. Phys.*, 1956, **34**, 350; Almenningen, Bastiansen, and Fernholt, *Det. kgl. Norske Videnskab. Selskabs Skrifter*, 1958, No. 3.

¹⁶ Cruickshank and Sparks, *Proc. Roy. Soc.*, 1960, *A*, **258**, 270.

¹⁷ Buckingham and Le Fèvre, *J.*, 1952, 1932.

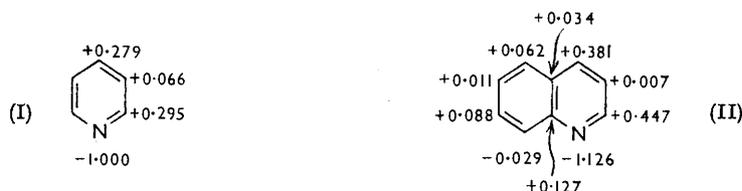
¹⁸ Hampson and Weissberger, *J.*, 1936, 393.

¹⁹ Littlejohn and Smith, *J.*, 1953, 2456.

²⁰ Le Fèvre and Le Fèvre, *J.*, 1955, 1641; Le Fèvre and Rao, *J.*, 1958, 1461; Le Fèvre, Rao, and Smith, *J.*, 1959, 1188.

²¹ Longuet-Higgins and Coulson, *Trans. Faraday Soc.*, 1947, **43**, 87; Orgel, Cottrell, Dick, and Sutton, *ibid.*, 1951, **47**, 113.

²² Cumper, unpublished results.



The greatest charge (q) is on the nitrogen atom itself but all could possibly induce moments in the substituents. These may be estimated from the formula:

$$\mu = \gamma qe/\epsilon_b r^2 \quad (2)$$

Methylquinolines.—In column 3 of Table 3 the dipole moments μ_1 are those predicted by vector addition of the moments of quinoline and toluene.² The agreement with experiment is improved by using the apparent group moments in methylpyridines for corresponding positions in the methylquinolines. This, as the results μ_2 demonstrate, has the greatest effect in 2-methylquinoline. The agreement with experiment is not satisfactory and in the other columns of Table 3 some allowance is made for the various induced moments.

TABLE 3.
Dipole moments (in D).

Quinoline derivative	μ_{exp}	μ_1	μ_2	μ_3	μ_4	μ_5	$\mu_{\text{C}_6\text{H}_5}/\mu_{\text{vapour}}$
2-Methyl-	1.94	1.97 ₄	1.90 ₈	1.91 ₈	1.90 ₈	1.90 ₈	0.987
3-Methyl-	2.29	2.34 ₈	2.34 ₉	2.36 ₈	2.34 ₈	2.36 ₉	0.988
4-Methyl-	2.56	2.52 ₈	2.54 ₀	2.53 ₄	2.53 ₄	2.52 ₈	0.967
5-Methyl-	2.46	2.52 ₈	2.52 ₈	2.51 ₇	2.51 ₉	2.51 ₈	0.967
6-Methyl-	2.32	2.34 ₇	2.34 ₇	2.36 ₈	2.34 ₈	2.36 ₈	0.990
7-Methyl-	2.12	1.97 ₆	1.97 ₆	1.97 ₉	1.96 ₈	1.96 ₈	0.988
8-Methyl-	1.68	1.77 ₇	1.77 ₇	1.78 ₃	1.81 ₉	1.82 ₄	0.965

Accepting the results obtained previously for the moments induced by the methyl group in the unsubstituted ring in methylnaphthalenes factor (c), only slightly modifies the calculated moments, μ_2 , to those given under μ_3 .

Account must also be taken of the dipole moment induced in the substituent. The moment induced by the primary dipole resulting from hybridisation of the nitrogen atom may be estimated from equations (1), with the numerical values used previously.²³ The moments induced by the net π -electron charges on the unsubstituted atoms in the pyridine and the quinoline ring can be evaluated from equation (2). The absolute values of these charges, and also of ϵ_b , are uncertain; in these calculations the ratio q/ϵ_b was assumed to be 0.05 for the nitrogen atom in pyridine and the remainder scaled according to the ratios in (I) and (II). By taking these factors into account the dipole moments μ_4 were computed from the group moments in toluene and the three methylpyridines.*

Finally in Table 3 are listed the dipole moments μ_5 evaluated when account is taken of the moments induced both by and in the methyl groups.

These various induced moments have only been estimated roughly but it is evident that no single effect, or combination of effects, results in better agreement with the experimental dipole moment in each of the seven positions round the quinoline ring. C-Me group moments are less than expected in all cases except for 4- and 8-methylquinoline, for which they are greater. The last-named result almost certainly arises from interaction of the methyl group and the lone-pair electrons on the nitrogen atom; such an interaction has been suggested for some α -substituted pyridines.²⁴

* Numerically these have comparatively little effect upon the resulting dipole moment but they do influence the magnitude of the apparent group moment and the direction of the resultant moment (cf. ref. 23).

²³ Cumper and Vogel, *J.*, 1960, 4723.

²⁴ Barassin and Lumbruso, *Bull. Soc. chim. France*, 1959, 1947.

The apparently low group moments for substituents in the 5-, 6-, and 7-position of quinoline could arise if the value accepted for the dipole moment of toluene² (0.37 D) were high. If Altshuller's value²⁵ for its atom polarisation is used the dipole moment is reduced to 0.34 D; and microwave absorption by the pure liquid also gives a lower value²⁶ (0.32 D). Dielectric measurements for toluene vapour²⁷ give a dipole moment of 0.37 D and Buckingham and Le Fèvre's equation indicates that the solvent effect with toluene in benzene solution would reduce this by 9%. With substituents in the heterocyclic ring agreement with experiment would be improved for the 3- and the 4-isomer if the effect of the π -electron charge of the substituted carbon atom upon the C-Me group moment were taken into account (cf. I, II); but this factor has an adverse effect with the other isomers.

Another possibility is that the directions of the C-Me bonds differ appreciably from those in the model adopted. This is unlikely since the CCC bond angles in naphthalene and anthracene¹⁶ differ by less than 1° from those in benzene, whereas for the calculated and experimental dipole moments of the methylquinolines to agree the angle between their component moments would need to be altered by 10–20°.

The moments of only two dimethylquinolines were measured but these showed that even when the group moments of the monomethylquinolines are used the predicted dipole moments do not agree exactly with experimental values (2,6-dimethylquinoline, μ_{exp} . 2.02 D, μ_{calc} . 2.06 D; 4,8-dimethylquinoline, μ_{exp} . 2.13 D, μ_{calc} . 2.09 D).

In general, therefore, the apparent methyl-group moments in methylquinolines are less than in toluene or the corresponding pyridine derivative. This seems to be caused by several factors, particularly the π -electron charge on the substituted carbon atom and, in the benzene ring, too great a value for the dipole moment of toluene. The various induced moments in these molecules appear to be only secondary factors, though they are important in determining the relative group moments in the isomers.^{23, 28} These apparent group moments, relative to that of the C-H bond, are in the order 8- (0.47), 2- (0.47), 4- (0.41), 6- (0.33), 5- (0.31), 3- (0.27), and 7- (0.06 D). The high value for 8-methylquinoline has already been discussed; that for 2-methylquinoline is due to its proximity to the electronegative nitrogen atom. The unexpected feature is the low group moment for 7-methylquinoline, a value which was confirmed with a synthetic sample ($\mu = 2.11$ D). The order of these apparent group moments is determined by the balance between the following factors:

(a) The greater the positive charge on the substituted carbon atom in the ring, caused by the distribution of π -electrons and the inductive effect associated with the electronegative nitrogen atom, the larger will be the actual C-Me group moment. This effect will be greatest in 2-methylquinoline. (b) The methyl group reduces the coulombic integral (or electronegativity) of the carbon atom to which it is attached. This reduces the apparent group moments for the 2- and the 7-position, increases them for the 3- and the 6-position, and increases them further for the 4-, 5-, and 8-isomers.²² (c) The moments induced in the methyl group by the primary dipole of quinoline fall off rapidly as their distance from the nitrogen atom increases.

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WOOLWICH POLYTECHNIC, LONDON, S.E.18.

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²⁵ Altshuller, *J. Phys. Chem.*, 1954, **58**, 392.

²⁶ Whiffen and Thompson, *Trans. Faraday Soc.*, 1946, **42**, A, 114, 122; Cripwell and Sutherland, *ibid.*, p. 149.

²⁷ Baker and Groves, *J.*, 1939, 1144.

²⁸ Cumper, *Chem. and Ind.*, 1958, 1628.