225. *Physical Properties and Chemical Constitution. Part XXXIV.*[1] *The Electric Dipole Moments of Chloro- and Nitro-quinolines.*

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The electric dipole moments of the seven monosubstituted chloroquinolines and five nitroquinolines 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 group moments of the electronegative substituents in these compounds are discussed and compared with the values reported previously for chlorobenzene and the chloropyridines, and with recorded values for the corresponding nitro-compounds. The dipole moments of 1- and 2-chloronaphthalene were also determined.

IN the preceding paper [1] the electric dipole moments of methylquinolines were considered. This survey is now extended to two electron-attracting substituents with group moments of about 1·6 D (C–Cl) and 4·0 D ($C–NO_2$). We might therefore expect a greater variation, according to the position of the substituent, than is observed for methylquinolines. Another factor is that these substituents possess π-type electrons which could interact with those of the parent molecule; this is more likely with the nitroquinolines.

EXPERIMENTAL AND RESULTS

The apparatus, experimental techniques, methods of calculation, and presentation are similar to those described in the preceding paper. The measured properties of the benzene solutions are presented in Table 1 and the polarisation data and dipole moments in Table 2.

Preparation of Pure Compounds.—Each compound was extensively purified, the final stage of purification being immediately before its dipole moment was determined. Their physical

TABLE 1.

$100w_2$	ε_{12}	v_{12}	n_{12}	$100w_2$	ε_{12}	v_{12}	n_{12}
	2-Chloroquinoline				*3-Chloroquinoline*		
0·1235	2·2811	1·14407	1·49793	0·1584	2·2777	1·14393	1·49778
0·2024	2·2872	1·14371	1·49806	0·4173	2·2864	1·14302	1·49807
0·3532	2·2986	1·14326	1·49821	0·7755	2·2989	1·14176	1·49841
0·5351	2·3126	1·14255	1·49836	1·0498	2·3089	1·14076	1·49866
0·8119	2·3331	1·14167	1·49865	1·6016	2·3276	1·13880	1·49929
0·9488	2·3438	1·14114	1·49887	1·7349	2·3331	1·13832	1·49944
1·0973	2·3550	1·14056	1·49893	2·3469	2·3538	1·13602	1·50012
	4-Chloroquinoline				*5-Chloroquinoline*		
0·2539	2·2747	1·14357	1·49793	0·1884	2·2742	1·14378	1·49787
0·3787	2·2763	1·14310	1·49807	0·3833	2·2754	1·14295	1·49809
0·7962	2·2801	1·14162	1·49848	0·7545	2·2777	1·14167	1·49837
1·2662	2·2842	1·13987	1·49898	1·2335	2·2803	1·13983	1·49899
1·4469	2·2884	1·13921	1·49912	1·7489	2·2840	1·13804	1·49949
1·8608	2·2898	1·13762	1·49968	1·9332	2·2869	1·13735	1·49972
2·2153	2·2928	1·13635	1·50010	2·3710	2·2808	1·13577	1·50025
	6-Chloroquinoline				*7-Chloroquinoline*		
0·0993	2·2748	1·14411	1·49788	0·1279	2·2813	1·14410	1·49784
0·2538	2·2790	1·14357	1·49803	0·2652	2·2911	1·14357	1·49797
0·5116	2·2862	1·14272	1·49830	0·4950	2·3071	1·14280	1·49815
0·9002	2·2983	1·14123	1·49867	0·8978	2·3348	1·14146	1·49859
1·1788	2·3065	1·14023	1·49911	1·4297	2·3722	1·13941	1·49917
1·2188	2·3080	1·14003	1·49912	1·7098	2·3932	1·13836	1·49950
1·7631	2·3224	1·13815	1·49971	1·7449	2·3947	1·13827	1·49954

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[1] Part XXXIII, preceding paper.

TABLE 1 (*cont.*)

$100w_2$	ε_{12}	v_{12}	n_{12}	$100w_2$	ε_{12}	v_{12}	n_{12}
	8-*Chloroquinoline*				1-*Chloronaphthalene*		
0·1434	2·2842	1·14396	1·49801	0·1180	2·2753	1·14402	1·49760
0·2523	2·2940	1·14353	1·49825	0·3575	2·2799	1·14332	1·49785
0·4216	2·3084	1·14258	1·49839	0·6501	2·2854	1·14239	1·49818
0·7008	2·3324	1·14179	1·49859	1·0236	2·2925	1·14134	1·49859
1·0599	2·3648	1·14037	1·49905	1·3043	2·2981	1·14031	1·49891
1·1881	2·3748	1·13994	1·49916	1·5002	2·3022	1·13965	1·49913
1·3646	2·3908	1·13921	1·49936	1·8652	2·3092	1·13857	1·49957
	2-*Chloronaphthalene*				3-*Nitroquinoline*		
0·1009	2·2753	1·14417	1·49763	0·0608	2·2793	1·14424	1·49758
0·2393	2·2782	1·14377	1·49779	0·1669	2·2912	1·14381	1·49768
0·3750	2·2814	1·14335	1·49791	0·3166	2·3079	1·14320	1·49786
0·7750	2·2902	1·14209	1·49832	0·3881	2·3170	1·14289	1·49796
1·0494	2·2967	1·14125	1·49863	0·5370	2·3330	1·14231	1·49820
1·3025	2·3024	1·14039	1·49895	0·6969	2·3517	1·14164	1·49833
1·6750	2·3108	1·13930	1·49929				
	5-*Nitroquinoline*				6-*Nitroquinoline*		
0·0646	2·2747	1·14427	1·49771	0·0891	2·2817	1·14411	1·49763
0·1877	2·2781	1·14378	1·49786	0·1885	2·2909	1·14368	1·49776
0·3187	2·2822	1·14318	1·49798	0·1924	2·2921	1·14358	1·49777
0·4700	2·2862	1·14265	1·49817	0·3198	2·3044	1·14214	1·49791
0·8811	2·2977	1·14098	1·49865	0·4538	2·3171	1·14259	1·49808
1·1792	2·3061	1·12964	1·49896	0·5305	2·3242	1·14226	1·49820
1·3253	2·3162	1·13896	1·49914	0·5851	2·3300	1·14198	1·49823
	7-*Nitroquinoline*				8-*Nitroquinoline*		
0·0572	2·2838	1·14425	1·49765	0·0737	2·2882	1·14416	1·49765
0·1129	2·2927	1·14404	1·49769	0·1347	2·3003	1·14385	1·49770
0·1802	2·3063	1·14375	1·49774	0·2348	2·3215	1·14351	1·49782
0·2365	2·3181	1·14353	1·49783	0·3778	2·3512	1·14292	1·49807
0·5011	2·3672	1·14247	1·49813	0·4088	2·3572	1·14277	1·49805
0·6855	2·4026	1·14174	1·49831	0·4504	2·3656	1·14261	1·49809
0·9557	2·4533	1·14064	1·49854	0·5846	2·3927	1·14207	1·49823
				0·8852	2·4574	1·14081	1·49851

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-Chloroquinoline ...	7·57$_9$	−0·348$_4$	272·0	47·67	224·3	3·31	3·26[a]
3-Chloroquinoline ...	3·48$_1$	−0·352$_9$	145·7	47·43	98·27	2·19	
4-Chloroquinoline ...	0·90$_7$	−0·362$_9$	65·95	47·33	18·62	0·96	
5-Chloroquinoline ...	0·63$_4$	−0·367$_9$	55·68	47·44	8·24	0·64	
6-Chloroquinoline ...	2·97$_7$	−0·355$_8$	130·0	47·86	82·18	2·02	
7-Chloroquinoline ...	6·99$_7$	−0·347$_0$	254·4	47·21	207·2	3·18	
8-Chloroquinoline ...	8·69$_7$	−0·379$_5$	304·9	47·65	257·2	3·55	
1-Chloronaphthalene	1·94$_5$	−0·316$_0$	99·63	49·72	49·91	1·56	1·59,[b] 1·50,[c] 1·51[d]
2-Chloronaphthalene	2·25$_9$	−0·303$_3$	109·9	49·75	60·10	1·72	1·72,[b] 1·57,[c] 1·65[d]
3-Nitroquinoline	11·3$_7$	−0·397$_4$	411·1	49·53	361·6	4·21	
5-Nitroquinoline	2·81$_1$	−0·393$_3$	131·1	48·35	82·70	2·01	2·55[e]
6-Nitroquinoline	9·66$_5$	−0·412$_6$	354·6	48·88	305·7	3·87	4·12[e]
7-Nitroquinoline	19·1$_8$	−0·393$_1$	660·5	47·98	612·5	5·47	
8-Nitroquinoline	20·5$_3$	−0·408$_9$	710·6	48·87	661·7	5·69	5·67[e]

[a] Rogers and Campbell, *J. Amer. Chem. Soc.*, 1953, **75**, 1209. [b] Parts, *Z. phys. Chem.*, 1930, *B*, **10**, 264. [c] Nakata, *Ber.*, 1931, **64**, 2059; *Bull. Chem. Soc. Japan*, 1935, **10**, 318. [d] Hampson and Weissberger, *J.*, 1936, 393. [e] Le Fèvre and Le Fèvre, *J.*, 1935, 1470.

properties including their infrared and ultraviolet spectra, and those of their derivatives, were in agreement with the best recorded values.

2-*Chloroquinoline.* 2-Chloroquinoline (Eastman-Kodak), purified by recrystallising its picrate from benzene to constant m. p. (123—124°) and then fractionating the regenerated compound, had b. p. 147—148°/15 mm., m. p. 34°, n_D^{35} 1·62923, d_4^{35} 1·2351.

3-*Chloroquinoline.* (i) Chlorination in the 3-position may be achieved by refluxing quinoline with sulphur dichloride.[2] Final purification was effected by fractional distillation and by recrystallising the dichromate from water to constant m. p. (127°). The product, b. p. 83·5—85·3°/0·5 mm., gave a picrate, m. p. 185—186°. (ii) The compound was also prepared by diazotising 3-aminoquinoline, decomposing the product with cuprous chloride, and purifying it as before. This sample had b. p. 132°/30 mm., n_D^{20} 1·63652, d_4^{20} 1·2490 (picrate, m. p. 185°).

4-*Chloroquinoline.* Ochiai's method [3] was used in which quinoline *N*-oxide was nitrated (giving very largely 4-nitroquinoline *N*-oxide), and was followed by chlorination and removal of the oxygen atom with phosphorus trichloride. Several fractional distillations gave the compound of b. p. 81°/0·5 mm., m. p. 30—31°, n_D^{20} 1·63609, d_4^{20} 1·2627 [picrate, m. p. 212—213°; dichromate, m. p. 75° (decomp.)].

5-*Chloroquinoline.* It proved extremely difficult to remove the last trace of 7-chloroquinoline from a mixture of the 5- and the 7-isomer formed in a Skraup reaction from *m*-chloroaniline. The corresponding nitroquinolines, however, can be separated since the 5-isomer is insoluble in dilute nitric acid. This was obtained,[4] purified, reduced to 5-aminoquinoline in a Towers low-pressure hydrogenator, and diazotised, the diazonium chloride being decomposed with cuprous chloride in concentrated hydrochloric acid. Purified by recrystallisation of the perchlorate to a constant m. p. (199°); the base had b. p. 261—263°/755 mm., 127·5°/15 mm., m. p. 31—32° (m. p. of hydrate 42°) (picrate, m. p. 230°; oxalate, m. p. 143·5—144·5°).

6-*Chloroquinoline.*—This was prepared by a Skraup synthesis from *p*-chloroaniline and glycerol, with iodine as oxidising agent.[5] Fractional distillation and crystallisation gave the compound of b. p. 136·5—137·5°/23 mm., m. p. 39°, d_4^{60} 1·2220.

7-*Chloroquinoline.* A Skraup reaction with *m*-chloroaniline and glycerol gave a mixture of the 5- and the 7-isomer. The former was removed by recrystallisation of the dichromates from water [4] to constant m. p. (179—180°). The 7-isomer, b. p. 146·5—147·5°/15 mm., m. p. 30—31°, n_D^{20} 1·63559, d_4^{20} 1·2503, gave a picrate, m. p. 225°

8-*Chloroquinoline.* Eastman-Kodak material, purified by recrystallisation of its zinc chloride complex from aqueous alcohol (m. p. 228°), had b. p. 171—171·5°/26 mm., n_D^{20} 1·64403, d_4^{20} 1·2780.

1-*Chloronaphthalene.* A commercial sample was purified by fractional distillation and through crystallisation of its picrate from alcohol to constant m. p. (132—133°). It boiled at 136·0—136·5°/20 mm.

2-*Chloronaphthalene.* This was prepared from β-naphthylamine by Chattaway and Lewis's method [6] and purified by steam-distillation and crystallisation from ethanol to constant m. p. (57—58°).

2-*Nitroquinoline.* 2-Nitroquinoline does not seem to have been described and attempts to obtain it by oxidising 2-aminoquinoline failed. We were also unsuccessful in obtaining sufficient pure 4-nitroquinoline by oxidising 4-aminoquinoline or by de-oxygenating 4-nitroquinoline *N*-oxide.

3-*Nitroquinoline.* Morley and Simpson's method [7] in which a Schiff's base, formed from aniline and the sodio-derivative of nitromalondialdehyde, is cyclised, was employed. The latter compound was made from αβ-dibromo-β-formylacrylic acid (mucobromic acid) [8] and sodium nitrite. 3-Nitroquinoline, recrystallised from alcohol and then from benzene, had m. p. 129—130°.

5- *and* 7-*Nitroquinoline.* Both isomers were formed by a Skraup reaction from *m*-nitroaniline [4] and glycerol. 5-Nitroquinoline, obtained by recrystallisation of their nitrates from very dilute nitric acid and recrystallised from light petroleum and benzene and dried under a vacuum, had m. p. 71° and gave a picrate, m. p. 214·5—215·5°, and a dichromate, m. p. 129°. 7-Nitroquinoline was obtained by removing the 5-isomer from the mixture with hot light petroleum, and when recrystallised several times from ethanol had a constant m. p. (132—133°). Its picrate had m. p. 217°.

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[2] Baker, Albisetti, Dodson, Lappin, and Riegel, *J. Amer. Chem. Soc.*, 1946, **68**, 1532.

[3] Ochiai, *J. Org. Chem.*, 1953, **18**, 534.

[4] Bradford, Elliott, and Rowe, *J.*, 1947, 437.

[5] Vogel, " Elementary Practical Organic Chemistry," Longmans, Green, London, 1957.

[6] Chattaway and Lewis, *J.*, 1894, **65**, 875.

[7] Morley and Simpson, *J.*, 1948, 2024; cf. Backman, Welton, Jenkins, and Christian, *J. Amer. Chem. Soc.*, 1947, **69**, 365.

[8] Allen and Spangler, *Org. Synth.*, Coll. Vol. III, p. 621.

6-*Nitroquinoline.* Prepared by a Skraup synthesis from *p*-nitroaniline [9] and recrystallisation successively from benzene and from ethanol, this isomer had m. p. 152°.

8-*Nitroquinoline.* (i) 8-Nitroquinoline from B.D.H. was recrystallised from ethanol to constant m. p. (88—89°) and gave a picrate, m. p. 164—165°, and a dichromate, m. p. 160°. (ii) It was also prepared by a Skraup synthesis from *o*-nitroaniline, glycerol, and arsenic acid and, recrystallised from ethanol, had m. p. 88—89°.

DISCUSSION

The geometrical structure of quinoline and some features of the dipole moments of its derivatives, and of the corresponding derivatives of pyridine, were considered in the preceding paper.[1] The dipole moments of chloropyridines have also been discussed.[10]

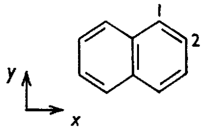
Chloroquinolines.—The chloroquinolines have two primary dipoles of similar magnitude—that of quinoline itself [1] (2·15 D) and that associated with the C–Cl bond (*ca.* 1·6 D). The molecules also have two atoms of comparable electronegativities—the nitrogen atom in the ring structure which participates fully in its π-type bonding, and the chlorine substituent whose *p*-electrons could interact with those in the ring.

TABLE 3.

Dipole moments (D).

Quinoline derivative	$\mu_{exp.}$	μ_1	μ_2	μ_3	μ_4	C–Cl bond moment
2-Chloro-	3·31	3·29	3·19	3·26	3·27	1·61
3-Chloro-	2·19	1·99	1·97	2·06	2·06	2·12
4-Chloro-	0·96	0·56	0·78	0·81	0·81	1·19
5-Chloro-	0·64	0·57	0·57	0·61	0·60	1·51
6-Chloro-	2·02	1·99	1·99	2·08	2·08	1·68
7-Chloro-	3·18	3·29	3·29	3·36	3·37	1·45
8-Chloro-	3·55	3·74	3·74	3·71	3·76	1·40

In Table 3 the experimental dipole moments are compared with those estimated from group and bond moments. The dipole moments μ_1 are those obtained by vector addition of the dipole moment of quinoline and of chlorobenzene,[10] and μ_2 from quinoline and the apparent C–Cl bond moment for the corresponding chloropyridine [10] or chlorobenzene. If it is assumed that the dipole moments of the chloronaphthalenes differ from that of chlorobenzene by the moment induced in the unsubstituted ring, the induced moments may be estimated by the method adopted in the preceding paper. The results are shown below.



	μ_x	μ_y
1-	0·075 D	−0·029 D
2-	0·134	0·019

If the same values apply to the chloroquinolines their calculated moments are modified to those given under μ_3 (Table 3). Finally, the dipole moments μ_4 are obtained when an allowance is also made for the moments induced in the chlorine atom by the primary dipole of quinoline and by the π-electron charges. [These were estimated by using equations (1) and (2) of the preceding paper.]

These corrections to the calculated moments can only be made very approximately but, though their effect is greater than with the methylquinolines, the agreement achieved between calculated and experimental results is not satisfactory. As with the methyl compounds [1] the solvent effect would be expected to increase the apparent C–Cl bond moment above that for chlorobenzene or the corresponding chloropyridine. Three factors, in addition to those mentioned above, should be considered. (*a*) The chlorine

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[9] Le Fèvre and Le Fèvre, *J.*, 1935, 1472; Hashelberg, *J. Org. Chem.*, 1943, **12**, 434.

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

substituent increases the electronegativity of the carbon atom to which it is attached and this consequently changes the π-electron distribution of the quinoline ring, thereby increasing the apparent C–Cl bond moment. This effect is least for the 2- and the 7-isomer, greater for the 4-, 5-, and 8-isomers and greatest for 3- and 6-chloroquinoline.[11] (*b*) The charge asymmetry of the C–Cl σ-bond depends upon the electronegativity of the carbon atom. This is controlled by its closeness to the nitrogen atom (inductive effect) and by the π-electron distribution.[1] (*c*) The *p*-electrons of the chlorine atom are most likely to interact with the π-electrons of the quinoline ring in isomers where the electron charge density of the substituted carbon atom is low. This factor reduces the apparent bond moment and there is evidence, from nuclear quadrupole resonance spectra,[12] that this is particularly great in 2-chloroquinoline, though the interpretation of the results is not unambiguous in view of the shielding from induced circulations of π-electrons.[13]

Factors (*b*) and (*c*) would tend to increase the apparent C–Cl bond moment in the 3- and the 8-isomer above that for 3-chloropyridine or chlorobenzene, respectively, and to decrease them in the other positions.

The net result of the above effects is best seen by examining the apparent C–Cl bond moments for the various positions, relative to that of the C–H bond (Table 3). They vary considerably. For comparison the bond moment in chlorobenzene [10] is 1·59 D, in 1- and 2-chloronaphthalene 1·56 and 1·72 D, respectively, and in 2-, 3-, and 4-chloropyridine [10] 1·47, 1·54, and 1·37 D, respectively. The greatest C–Cl bond moment is in 3-chloroquinoline where factors (*a*), (*b*), and (*c*) all tend to increase its value. In 6-chloroquinoline it seems that factor (*a*) outweighs the effects of (*b*) and (*c*), and in both 2- and 8-chloroquinoline interaction of the nitrogen atom and the C–Cl dipole must more than counteract these factors. The difference between the 4- and the 5-isomer is striking and must reflect the smaller π-electron charge at position 5 in quinoline.[1]

Nitroquinolines.—Unfortunately it was only possible to study five of the seven isomers. Here the C–NO_2 group moment (*ca.* 4·0 D) is greater than that of the C–Cl bond, and the other difference is that any π-electron conjugation, which is probably greater than for the chloroquinolines, would be sterically repressed in the 4-, the 5-, and probably also the 8-isomer (cf. ref. 14). Evidence for a marked difference between the nitroquinoline isomers is provided by an examination of their ultraviolet spectra.[15] Of the five nitroquinolines studied (in ethyl alcohol solution) the 3-, 6-, and 7-isomers had an absorption peak below 210 mμ, a double peak at 250—255 mμ, and another at about 300 mμ. The 5- and the 8-isomer, however, had their first absorption maximum shifted to about 220 mμ, a minimum absorption at 250 mμ, and a weak broad band with a maximum at 300 and 280 mμ, respectively.

The apparent C–NO_2 group moments are 3-, 4·76; 5-, 4·16; 6-, 4·37; 7-, 4·01; and 8-, 3·45 D. As expected, these are in the same order as the apparent C–Cl bond moments. From the published dipole moments the apparent C–NO_2 group moment in nitrobenzene [16] is 4·01, in 1- and 2-nitronaphthalene [17] 3·87 and 4·39, and in 2-, 3-, and 4-nitropyridine [18] 3·59, 3·72, and 3·81 D, respectively.

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[11] Cumper, unpublished calculations.
[12] Dewar and Lucken, *J.*, 1958, 2653.
[13] Cf. Elvidge and Jackman, *Proc. Chem. Soc.*, 1959, 89; *J.*, 1961, 859; Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, London, 1959.
[14] Littlejohn and Smith, *J.*, 1957, 2476.
[15] Unpublished results; cf. Dewar and Maitlis, *J.*, 1957, 2521.
[16] Wesson, "Tables of Electric Dipole Moments," Massachusetts Inst. Technol., 1948.
[17] Nakata, *Ber.*, 1931, **64**, 2059; *Bull. Chem. Soc. Japan*, 1935, **10**, 318; Wassiliew and Syrkin, *Acta Physicochim. U.S.S.R.*, 1941, **15**, 254; Shimozawa and Norino, *J. Chem. Soc. Japan*, 1960, **81**, 20.
[18] Sobczyk, *Roczniki Chem.*, 1959, **33**, 743.