353. *The Dipole Moments and Structures of Some Quinoline Derivatives, and the Orientation of Claus and Hoffmann's* x-*Nitro*iso*quinoline.*

By Catherine G. Le Fèvre and Raymond J. W. Le Fèvre.

In this section measurements of the dipole moments of a number of quinoline derivatives are recorded and discussed in relation to the possible influence of substitution upon the structure of the quinoline skeleton. Little relevant physical evidence is available in the literature.

Results.—The molecular polarisations and refractivities at infinite dilution in benzene solutions of quinoline and seven derivatives at 25° are shown in Table I; from these data the dipole moment in each case (col. 4) has been calculated. The published values for the dipole moment (in Debye units here and throughout) of quinoline are : 2·18 (Le Fèvre and Smith, J., 1932, 2810); 2·25 (Rolinski, *Physikal. Z.*, 1928, **29**, 658); 2·14 (Bergmann, Engel, and Meyer, *Ber.*, 1932, **65**, 446); the present work supports the first value. The data for quinaldine are those of Rau and Narayanaswamy (*Z. physikal. Chem.*, 1934, *B*, **26**, 23).

Table I.

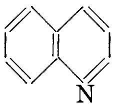
Substance.	Mol. poln., c.c.	Mol. refrty., c.c.	$\mu \times 10^{18}$.
Quinoline	141·1	41·9	2·19
Quinaldine	122·2	50·7	1·86
*6-Methylquinoline	156·2	46·3	2·31
p-Toluquinaldine	134·4	51·5	2·00
2 : 4-Dimethylquinoline	160·6	51·5	2·30
*5-Nitroquinoline	184·4	49·8	2·55
*6-Nitroquinoline	389·1	49·2	4·12
*8-Nitroquinoline	713·0	47·8	5·67

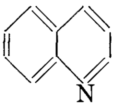
By treating the observed moments of the substituted quinolines as the vector sums of the moments of quinoline and its substituents, the former of which is known as to magnitude and the latter as to magnitude and direction (we have taken Me = 0·37, NO$_2$ = 4·0, and 2 : 4-dimethyl as equivalent to 3-methyl), it is evidently possible to calculate the one unknown quantity, *viz.*, the direction of the moment of quinoline. This has been done, the results being tabulated below as inclinations (counterclockwise denoted by +) to the [(4) –|⟶ (1)] direction :

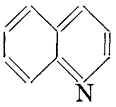
2-Me.	6-Me.	2 : 4-Me$_2$.	5-NO$_2$.	6-NO$_2$.	8-NO$_2$.
+ 35·5°	– 15·5°	+17°·	± 35·5°	– 17·5°	± 49·5°

Of the two possible signs for the 5- and the 8-nitro-derivative, the negative is considered the more correct, by analogy with the 6-nitro-compound, for which there is no ambiguity.

Discussion.—The real structure of any given quinoline compound might be expected, in conformity with recent theory (Ingold, *Chem. Revs.*, 1934, **15**, No. 2), to lie between two extreme forms corresponding in structures to the types (I) or (I*a*) and (II). These would constitute the unreal unperturbed forms from which could arise the real and most stable form by valency exchange degeneracy.


(I.)


(I*a*.)

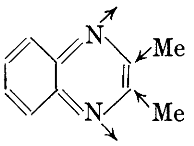

(II.)

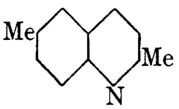
With the aid of the angles now deduced we can assign, qualitatively, the compounds marked with an asterisk in Table I to their places between the extreme types because, in the above two formula types, the –C⁚N– and –C–N⁚ links should have sensibly different moments towards the nitrogen atom, the first having the greater ; and accordingly, in those compounds where the quinoline component moment has an apparent clockwise inclination to the vertical direction (cf. negative signs to above angles), we infer that a quinoline skeleton of type (I) or (I*a*) exists predominantly. A complete decision cannot be made with certainty, but the marked resemblances between quinoline and naphthalene (orientation phenomena, parallelism of the dipole moments of quinoline and *iso*quinoline with α- and β-naphthalene derivatives; cf. Le Fèvre and Smith, *loc. cit.*; Parts, *Z. physikal. Chem.*, 1930, **10**, *B*, 264) definitely favour (I). Naphthalene is commonly assumed to have the two quaternary carbon atoms united by a double bond, a formulation supported by dipole-moment measurements, for this hydrocarbon has a zero moment and must therefore, in the isolated state, contain a symmetrical arrangement of bonds [cf. (I)]: a structure of type (I*a*) would imply a moment of the order of that found for phenanthrene. The present conclusion in the case of quinoline agrees, as far as the heterocyclic ring is concerned, with that reached by Mills and Smith (J., 1922, **121**, 2724) from chemical considerations.

Mesomerism.—Alternatively, the inconstancy of our inclination angle values may be a measure of the departure from true vector additivity of dipole moments occurring in this group of compounds by the operation of " mesomeric " effects (Ingold, J., 1933, 1120); *e.g.*, with 5-substituted quinolines little abnormality is to be expected, in contrast to the 6- or 8-analogues, which constitutionally resemble *p*- and *o*-nitroanilines respectively, and so should similarly display permanent polarisation increments produced by the mechanism of the tautomeric effect. These have been fully discussed by Höjendahl, Sutton, and others (for, references see Ingold, *Chem. Revs.*, *loc. cit.*) and are of obvious application to the present cases.

2-*Methylquinoline and its* 4- *and* 6-*Methyl Derivatives.*—Quinaldine and 2 : 4-dimethylquinoline have inclination angles which are in contrast with those derived from the other compounds. In the α-methylated quinolines the possibility arises of dynamic isomerism of the type $-\mathrm{N{:}\overset{|}{C}{-}CH_3} \rightleftharpoons -\mathrm{NH{-}\overset{|}{C}{:}CH_2}$ and their abnormality is probably to be ascribed to this cause. For this reason we prefer not to apply to the apparent angle values the argument used above, which would indicate the existence of a basal structure of type (II), although such a conception is quite in harmony with the zero moment found by Snoek (*Physikal. Z.*, 1934, **35**, 196) for 2 : 3-dimethylquinoxaline (III). As an indication of the significance of such tautomerism in the interpretation of the second and fifth measurements (Table I), we have examined 2 : 6-dimethylquinoline (IV). By symmetry, if (IV) were correct, the Me–C moments should be identical and in antiparallel alinement. The resultant therefore should equal that of quinoline itself, *viz.*, 2·19; experimentally it is found to be 2·00.

(III.)





(IV.)

Conclusions.—It is concluded that in the quinoline derivatives examined, except the α-methyl-containing compounds, the mobilities, typical of benzene and pyridine, of the single and double linkings are so diminished by ring fusion that the skeleton is best formulated as (I), and that the component electric moment, arising from this structure, acts along directions varying from 15° to 50° to the axis of the 5 : 8-carbon atoms, to meet it at some point outside the molecule on the side of the 8-carbon atom.

EXPERIMENTAL.

Preparation of Materials.—The benzene used was commercial pure material, redistilled and recrystallised, etc., as detailed by Le Fèvre and Smith (J., 1932, 2239).

Quinoline. The commercial " pure " base was fractionated (column), the intermediate one-third, b. p. 238—238·5°/759 mm., being kept over solid potash for a day and then redistilled.

6-Methylquinoline was prepared from *p*-toluidine by Skraup's method (*Monatsh.*, 1881, **2**, 158), a sample of b. p. 258—260°/760 mm. being employed.

p-Toluquinaldine, obtained from *p*-toluidine, paraldehyde, and hydrogen chloride (Döbner and Miller, *Ber.*, 1883, **16**, 2470), had m. p. 60°, b. p. 265—267°.

2 : 4-Dimethylquinoline, prepared from acetylacetone, aniline, and sulphuric acid (Roberts and Turner, J., 1927, 1842), was redistilled; b. p. 264—265°/758 mm.

5-*Nitroquinoline.* This was prepared directly from quinoline by nitration, since the synthetic product from *m*-nitroaniline is liable to be admixed with the 7-isomeride. To quinoline (50 g.), nitric acid (20 c.c., *d* 1·5) was added slowly at 0°. The solid cake formed (75 g.) was powdered and added in five portions to concentrated sulphuric acid (50 c.c., kept at 0°), a small quantity of fuming sulphuric acid (*d* 2·0, 10 c.c.) being run in after each addition. Dilution and neutralisation (caustic soda solution) produced an oil, which solidified over-night. This was dissolved in much hot water (with some dilute nitric acid), and the clear filtrate saturated with sodium acetate. After a time the precipitated 5-nitroquinoline was separated, washed, etc., and finally crystallised from light petroleum; it formed white needles (32 g.), m. p. 72°. Complete neutralisation of the nitration solution led to 8-nitroquinoline (9 g.), which, after crystallisation from dilute alcohol, had m. p. 88—89°.

6-*Nitroquinoline.* This substance was made by the usual Skraup synthesis from arsenic acid (116 g.), concentrated sulphuric acid (220 g.), glycerol (240 g.), and *p*-nitroaniline (112 g.). After 2½—3 hours' heating, the whole was strongly diluted with water and left over-night. Sodium hydroxide solution was added to the filtrate from this, a mass of impure 6-nitroquinoline being obtained. Separation and dissolution of the mass in hydrochloric acid (norit) afforded, on saturation with ammonia, crystalline 6-nitroquinoline; recrystallisation from dilute alcohol (norit) finally gave the pure substance (98 g.), m. p. 148—149°.

8-*Nitroquinoline.* This was similarly obtained (arsenic acid, 51·5 g.; sulphuric acid, 100 g.; glycerol, 110 g.; *o*-nitroaniline, 50 g.). The highly diluted reaction mass was clarified, and neutralised with sodium hydroxide solution; after 1 hour the brown flocky precipitate was filtered off and crystallised from dilute alcohol (norit); m. p. 88—89° (45 g.).

Measurements.—The dielectric constants of dilute solutions of the above compounds in benzene were determined by the resonance method described previously (*loc. cit.*). These measurements were made at 25° and in one case at 45°. The refractive indices of the same solutions were determined at 25° and for the Na_D line with a Pulfrich refractometer. The

Quinoline in benzene at 25°.

$f_1 . 10^6$	0	9101	29020	42910	50501
$M_1f_1+M_2f_2$	78	78·4642	79·4800	80·1884	90·5756
ϵ	2·2725	2·3400	2·4790	2·5771	2·6301
d	0·8738	0·87733	0·88206	0·88594	0·88810
$P_1f_1+P_2f_2$	26·585	27·6136	29·7541	31·1871	31·9423
P_2f_2	26·585	26·3430	25·8135	25·4442	25·2424
P_1f_1	—	1·2706	3·9406	5·7429	6·6999
P_1	—	139·61	135·78	133·84	132·67

Whence extrapolated value of P_1 for $f_1 = 0$ is 141·1 c.c.; $[R_L]_D = 41{\cdot}9$ c.c.; therefore $\mu = 0{\cdot}22\sqrt{141{\cdot}1-41{\cdot}9} = 2{\cdot}19$.

6-*Methylquinoline in benzene at 25°.*

$f_1 . 10^6$	0	16149·4	25013·9	32733·8	43448·0
$M_1f_1+M_2f_2$	78	79·0496	79·6259	80·1277	80·8241
ϵ	2·2725	2·4014	2·4730	2·5341	2·6207
d	0·87380	0·87863	0·88113	0·88341	0·88647
$P_1f_1+P_2f_2$	26·5863	28·6461	29·7590	30·6890	31·9795
P_2f_2	26·5863	26·1569	25·9213	25·7160	25·4312
P_1f_1	—	2·4892	3·8377	4·9730	6·5483
P_1	—	154·14	153·42	151·92	150·72

Whence extrapolated value of P_1 for $f_1 = 0$ is 156·2 c.c.; $[R_L]_D = 46{\cdot}3$ c.c. (Auwers and Kraul, *loc. cit.*); therefore $\mu = 0{\cdot}22\ (109{\cdot}9)^{\frac{1}{2}} = 2{\cdot}31$. Also, $2{\cdot}31 = (2{\cdot}19^2 + 0{\cdot}37^2 \pm 2 \times 2{\cdot}19 \times 0{\cdot}37 \cos\theta)^{\frac{1}{2}}$, whence $\cos\theta = 0{\cdot}2487$, and $\theta = 75{\cdot}6°$.

p-*Toluquinaldine in benzene at 25°.*

$f_1 . 10^6$	0	6751·6	10184·3	17717·0	19714·0
$M_1f_1 + M_2f_2$	78	78·5334	78·8046	79·3996	79·5575
ϵ	2·2725	2·3136	2·3344	2·3812	2·3930
d	0·87380	0·87564	0·87654	0·87862	0·87917
$P_1f_1 + P_2f_2$	26·5863	27·3119	27·6782	28·4892	28·6945
P_2f_2	26·5863	26·4068	26·3155	26·1153	26·0622
P_1f_1	—	0·9051	1·3627	2·3739	2·6323
P_1	—	134·06	133·81	133·99	133·52

Whence extrapolated value of P_1 for $f_1 = 0$ is 134·4 c.c.; $[R_L]_D = 51{\cdot}5$ c.c. (Auwers and Kraul, *loc. cit.*); therefore $\mu = 0{\cdot}22\ (82{\cdot}9)^{\frac{1}{2}} = 2{\cdot}00$.

2 : 4-*Dimethylquinoline in benzene at* 25°.

$f_1 . 10^6$	0	23054·5	25185·2	55016·8	84043·1
$M_1f_1 + M_2f_2$	78	79·8213	79·9897	82·3463	84·6395
ϵ	2·2725	2·4607	2·4737	2·7145	2·9527
d	0·87380	0·88062	0·88122	0·88955	0·89765
$P_1f_1 + P_2f_2$	26·5863	29·6817	29·9014	33·6648	37·1757
P_2f_2	26·5863	25·9733	25·9167	25·1236	24·3519
P_1f_1	—	3·7084	3·9847	8·5412	12·8238
P_1	—	160·85	158·22	155·25	152·59

Whence extrapolated value of P_1 for $f_1 = 0$ is 160·6 c.c.; $[R_L]_D = 51{\cdot}5$ c.c. (Auwers and Kraul, *Z. physikal. Chem.*, 1925, **116**, 438); therefore $\mu = 0{\cdot}22\ (109{\cdot}1)^{\frac{1}{2}} = 2{\cdot}30$. Also, $2{\cdot}30 = (0{\cdot}37^2 + 2{\cdot}19^2 \pm 2 \times 0{\cdot}37 \times 2{\cdot}19 \cos\theta)^{\frac{1}{2}}$, whence $\cos\theta = 0{\cdot}2203$, and $\theta = 77°$.

5-*Nitroquinoline in benzene at* 25°.

$f_1 . 10^6$	0	1066·82	2800·42	3502·14	4568·90
$M_1f_1 + M_2f_2$	78	78·1024	78·2688	78·3362	78·4386
ϵ	2·2725	2·2831	2·3005	2·3075	2·3180
d	0·8738	0·87457	0·87577	0·87625	0·87699
$P_1f_1 + P_2f_2$	26·585	26·7532	27·0264	27·1366	27·2998
P_2f_2	26·585	26·5566	26·5105	26·4919	26·4635
P_1f_1	—	0·1966	0·5159	0·6447	0·8363
P_1	—	184·27	184·22	184·10	183·04
n	1·49733	1·49764	1·49813	—	—
n^2	2·24199	2·24293	2·24439	—	—
$R_1f_1 + R_2f_2$	26·13565	26·16085	26·20218	—	—
R_2f_2	26·13565	26·10782	26·06250	—	—
R_1f_1	—	0·05303	0·13968	—	—
R_1	—	49·7	49·8	—	—

Whence extrapolated value of P_1 for $f_1 = 0$ is 184·4 c.c.; $[R_L]_D = 49{\cdot}8$ c.c.; therefore $\mu = 0{\cdot}220\ (184{\cdot}4 - 49{\cdot}8)^{\frac{1}{2}} = 2{\cdot}55$. Also, $2{\cdot}55 = (4^2 + 2{\cdot}19^2 \pm 2 \times 2{\cdot}19 \times 4 \times \cos\theta)^{\frac{1}{2}}$, from which $\cos\theta = -0{\cdot}8156$, and $\theta = 144\frac{1}{2}°$.

6-*Nitroquinoline in benzene at* 25°.

$f_1 . 10^6$	0	1843·13	4582·86	6000·13	7667·41
$M_1f_1 + M_2f_2$	78	78·1769	78·4399	78·5760	78·7361
ϵ	2·2725	2·3165	2·3822	2·4165	2·4559
d	0·8738	0·87507	0·87699	0·87794	0·87908
$P_1f_1 + P_2f_2$	26·585	27·2475	28·2117	28·7054	29·2651
P_2f_2	26·585	26·5360	26·4632	26·4255	26·3812
P_1f_1	—	0·7115	1·7485	2·2799	2·8839
P_1	—	386·04	381·53	379·98	376·13
n	1·49733	1·49781	1·49854	—	—
n^2	2·24200	2·24343	2·24562	—	—
$R_1f_1 + R_2f_2$	26·1357	26·1782	26·2415	—	—
R_2f_2	26·1357	26·0875	26·0159	—	—
R_1f_1	—	0·0907	0·2256	—	—
R_1	—	49·2	49·2	—	—

Whence extrapolated value of P_1 for $f_1 = 0$ is 389·1 c.c.; $[R_L]_D = 49{\cdot}2$ c.c.; therefore $\mu = 0{\cdot}220\ (389{\cdot}1 - 49{\cdot}2)^{\frac{1}{2}} = 4{\cdot}12$. Also, $4{\cdot}12 = (4^2 + 19^2 \pm 2 \times 2{\cdot}19 \times 4 \times \cos\theta)^{\frac{1}{2}}$, from which $\cos\theta = -\ 0{\cdot}2182$, and $\theta = 102\frac{1}{2}°$.

8-*Nitroquinoline in benzene at* 25°.

$f_1 . 10^6$	0	880·543	2312·94	7009·21	11614·2
$M_1f_1 + M_2f_2$	78	78·0846	78·2221	78·6729	79·1152
ϵ	2·2725	2·3117	2·3788	2·5975	2·8076
d	0·87380	0·87445	0·87547	0·87880	0·88177
$P_1f_1 + P_2f_2$	26·5850	27·1660	28·1344	31·1068	33·7348
P_2f_2	26·5850	26·5616	26·5235	26·3987	26·2763
P_1f_1	—	0·6044	1·6109	4·7081	7·4585
P_1	—	686·38	696·48	671·70	642·19
n	1·49733	—	1·49791	—	1·49998
n^2	2·24200	—	2·24372	—	2·24994
$R_1f_1 + R_2f_2$	26·1357	—	26·1858	—	26·3858
R_2f_2	26·1357	—	26·0753	—	25·8323
R_1f_1	—	—	0·1105	—	0·5535
R_1	—	—	47·77	—	47·66

8-*Nitroquinoline in benzene at* 45°.

ϵ	2·2330	2·2694	2·3282	2·5276	2·7177
d	0·8521	0·85355	0·85450	0·85777	0·86097
$P_1f_1 + P_2f_2$	26·6640	27·2003	28·0919	30·9456	33·4566
P_2f_2	26·6640	26·6405	26·6023	26·4771	26·3544
P_1f_1	—	0·5598	1·4896	4·4685	7·1022
P_1	—	635·74	644·02	637·51	611·51

Whence extrapolated value of P_1 for $f_1 = 0$ is 713 c.c. at 25° and 676 c.c. at 45°; $[R_L]_D = 47{\cdot}8$ c.c.; therefore $\mu = 0{\cdot}220(713—47{\cdot}7)^{\frac{1}{2}} = 5{\cdot}67$. Alternatively, we have, by substituting in $P = A + B/T$, $B = 175313{\cdot}4$, whence $\mu = 5{\cdot}33$. Also, $5{\cdot}67 = (2{\cdot}19^2 + 4^2 \pm 2 \times 2{\cdot}19 \times 4 \times \cos\theta)^{\frac{1}{2}}$, from which $\cos\theta = 0{\cdot}6480$, *i.e.*, $\theta = 49\frac{1}{2}°$.

densities of the solutions were measured at the same temperatures. From these data the molecular polarisations and refractivities were calculated from the well-known modifications of the Clausius–Mosotti and the Lorenz–Lorentz equation. The significant data are in the foregoing tables, in which the symbols M, P, R, refer respectively to the molecular weights, polarisations, and refractions of the components, and f to their mol.-fractions in the solutions, the subscripts 1 and 2 applying to solute and solvent; ε, d, and n are respectively the dielectric constants, densities, and refractive indices of the solutions, and μ the dipole moments of the solutes.

The Orientation of Claus and Hoffmann's x-*Nitro*iso*quinoline.*

Claus and Hoffmann showed (*J. pr. Chem.*, 1893, **47**, 252) that solid *iso*quinolinium nitrate or sulphate could be nitrated to give in high yield a mononitro-derivative, m. p. 110°, permanganate oxidation of which produced α-nitrophthalic acid, showing that either 5- or 8-substitution had taken place. No experimental decision on this point was made, although the authors clearly favoured the latter constitution. This ambiguity cannot be resolved by any conclusive theoretical arguments, but the 5-nitro-structure would be more consistent with analogy. The dipole moments of *iso*quinoline, of its 1-chloro-, and of its unoriented nitro-derivative were therefore measured by the same procedure as above.

Preparation of Materials.—The *iso*quinoline used, after being twice partly frozen and separated from the liquid of lower b. p., had m. p. 24°. We are indebted to Dr. F. M. Hamer for our specimen of 1-chloro*iso*quinoline (cf. Fisher and Hamer, J., 1934, 1908). The benzene was that employed previously.

iso*Quinoline in benzene at* 25°.

$f_1 . 10^6$	0	21012·2	31999·7	43332·9	65041·1
$M_1f_1 + M_2f_2$	78	79·0716	79·6320	80·2100	81·3171
ϵ	2·2725	2·476	2·580	2·681	2·892
d	0·8738	0·88051	0·88370	0·88710	0·89361
$P_1f_1 + P_2f_2$	26·585	29·6129	31·0866	32·4702	35·1951
P_2f_2	26·585	26·0264	25·7343	25·4330	24·8559
P_1f_1	—	3·5865	5·3523	7·0372	10·3392
P_1 (c.c.)	—	170·68	167·26	162·40	158·96

Whence extrapolated value for $f_1 = 0$ is 175·8 c.c.; $[R_L]_D = 41{\cdot}5$ c.c. (Bruhl, *Z. physikal. Chem.*, 1895, **16**, 193); therefore $\mu = 0{\cdot}22\ (175{\cdot}8 - 41{\cdot}5)^{\frac{1}{2}} = 2{\cdot}549$.

1-*Chloro*iso*quinoline in benzene at* 25°.

$f_1 . 10^6$	0	12308·6	17198·3	25162·3	31991·0
$M_1f_1 + M_2f_2$	78	79·0524	79·4705	80·1514	80·7352
ϵ	2·2725	2·4752	2·5594	2·6935	2·8122
d	0·87380	0·88072	0·88342	0·88794	0·89205
$P_1f_1 + P_2f_2$	26·585	29·5880	30·7672	32·5698	34·0829
P_2f_2	26·585	26·2578	26·1278	25·9161	25·7345
P_1f_1	—	3·3302	4·6394	6·6537	8·3484
P_1	—	270·56	269·76	264·43	260·96
n	1·49733	1·49993	—	—	—
n^2	2·24200	2·24979	—	—	—
$R_1f_1 + R_2f_2$	26·1357	26·3965	—	—	—
R_2f_2	26·1357	25·8140	—	—	—
R_1f_1	—	0·5825	—	—	—
$[R_1]_D$	—	47·32	—	—	—

Whence extrapolated value of P_1 for $f_1 = 0$ is 276·4 c.c.; therefore $\mu = 0{\cdot}22(276{\cdot}4 - 47{\cdot}3)^{\frac{1}{2}} = 3{\cdot}33$. Also $3{\cdot}33 = (1{\cdot}52^2 + 2{\cdot}52^2 \pm 2 \times 1{\cdot}52 \times 2{\cdot}52 \cos\theta)^{\frac{1}{2}}$; whence $\cos\theta = 0{\cdot}3170$ and $\theta = 71\frac{1}{2}°$.

x-*Nitro*iso*quinoline in benzene at* 25°.

$f_1 . 10^6$	0	2616·98	3500·21	4540·03	5182·82
$M_1f_1 + M_2f_2$	78	78·2513	78·3360	78·4358	78·4976
ϵ	2·2725	2·3245	2·3420	2·3622	2·3751
d	0·8738	0·87550	0·87609	0·87678	0·87722
$P_1f_1 + P_2f_2$	26·585	27·3748	27·6359	27·9357	28·1260
P_2f_2	26·585	26·5154	26·4919	26·4643	26·4472
P_1f_1	—	0·8594	1·1439	1·4714	1·6788
P_1 (c.c.)	—	328·4	326·8	324·1	323·9
n	1·49733	1·49785	—	—	1·49837
n^2	2·24200	2·24356	—	—	2·24511
$R_1f_1 + R_2f_2$	26·1357	26·1921	—	—	26·2462
R_2f_2	26·1357	26·0673	—	—	26·0003
R_1f_1	—	0·1248	—	—	0·2460
R_1 (c.c.)	—	47·67	—	—	47·46

Whence extrapolated value for $f_1 = 0$ is 333·0 c.c.; $[R_L]_D = 47·7$ c.c.; therefore $\mu = 0·22\,(333·0 - 47·7)^{\frac{1}{2}} = 3·72$. Substitution in $\mu_{\text{Resultant}} = \sqrt{\mu_1{}^2 + \mu^2{}_2 + 2\mu_1\mu_2 \cos\theta}$ gives $3·72^2 = 2·55^2 + 4^2 \pm 2·2 \times 55·4 \cos\theta$, whence $\cos\theta = -\,0·4247$, *i.e.*, $\theta =$ *ca.* 115°.

x-*Nitro*iso*quinoline*. This was first obtained as by Claus and Hoffmann (*loc. cit.*), *viz.*, by addition of the solid nitrate to an excess of well-stirred concentrated sulphuric acid. Later, the following variation was adopted: *iso*quinoline (43 g.) was dissolved in sulphuric acid (200 c.c.) directly; considerable heat was evolved, and the solution was cooled to 0°, stirred, and potassium nitrate (35 g.) in sulphuric acid (200 c.c.) dropped in during 2 hours. After being kept below 50° for 6 hours, the reaction mixture was poured on ice and neutralised by ammonia. Filtration, etc., afforded the required nitro-derivative in quantitative yield (55 g.). The dried substance, crystallised from benzene, had m. p. 110°, as stated by the German authors.

Discussion.—Before discussion of the data, the direction of operation of the moment in the unsubstituted base must be decided. This can be fixed by the consideration of the dipole moment of an *iso*quinoline derivative of known orientation, and for this purpose 1-chloro-*iso*quinoline was used. The dipole moment of this compound has been estimated at 3·33, a figure which (with μC — Cl = 1·52 *) implies that the *iso*quinoline vector makes an angle of 71½° with the C–Cl (vertical) direction. Hence the *iso*quinoline moment has a finite component along the 5 : 8-axis, with the negative end in the direction of the 8-carbon atom.

The substance in question can now be formulated, for consideration of 8-nitro*iso*quinoline shows that the component moments of the nitro-group and the *iso*quinoline nucleus should make an angle of approximately 71°, whereas with the 5-nitro-structure the angle subtended by the vectors should be of the order 109°. The found value is 115°. Hence, we suggest that Claus and Hoffmann's compound should be oriented as 5-nitro*iso*quinoline.

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UNIVERSITY COLLEGE (UNIVERSITY OF LONDON).

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