Molecular Polarisability. Electro-optical Polarisability Tensor Ellipsoids for Pyridine, Quinoline, and iso*Quinoline.*

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The molar Kerr constants of pyridine, quinoline, and *iso*quinoline are now found at infinite dilution in carbon tetrachloride at 25° to be 150×10^{-12}, 149×10^{-12}, and 572×10^{-12}, respectively. Analysis using depolarisation factors in the first two cases, and " shape " factors in all three, yields semi-axes of the molecular polarisability ellipsoids; these semi-axes are not sensitively affected by the particular " factor " employed. The anisotropy of polarisability calculated for pyridine in solution is close to that deduced by Stuart and Volkmann for this substance as a gas. The mean polarisabilities of pyridine, quinoline, and *iso*quinoline are less than those of benzene and naphthalene; the differences are greatest in the direction normal to the molecular plane. The heterocyclic bases are more polarisable than their hydrocarbon relatives only along b_2. An empirical correction to ${}_{\mathrm{m}}K_{\mathrm{liq.}}$, previously suggested by Le Fèvre and Le Fèvre, applies satisfactorily to liquid pyridine and quinoline.

As a result of our work on derivatives of benzene (*J.*, 1954, 1577) and naphthalene (*J.*, 1955, **1641**) it seemed of obvious interest to consider the cases of pyridine, quinoline, and *iso*quinoline. Literature relating to the anisotropic polarisabilities of these bases is scarce. For pyridine, the axes of the molecular polarisability ellipsoids b_1, b_2, and b_3 (shown by broken arrows in the Figure) have been deduced by Stuart and Volkmann (*Ann. Physik*, 1933, **18**, 21) from electric double-refraction measurements on the vapour at 146·3°, while observations of light scattering—confined to gaseous pyridine and quinoline—are summarised by Cabannes (" La Diffusion Moléculaire de la Lumière," Les Presses Universitaires de France, Paris, 1929, pp. 89, 254).

The present paper reports determinations made on solutions in carbon tetrachloride at 25°. Table 1 lists the molar Kerr constants found at infinite dilution, ${}_{\infty}({}_{\mathrm{m}}K_2)$, together with the sum, $(\theta_1 + \theta_2)$, derived therefrom *via* formula (1) of *J.*, 1954, 1577.

TABLE 1. *Molar Kerr constants at infinite dilution.*

Solute	Pyridine	Quinoline	*iso*Quinoline
${}_{\infty}({}_{\mathrm{m}}K_2) \times 10^{12}$	150·0	149·1	571·7
$(\theta_1 + \theta_2) \times 10^{35}$	35·7	35·5	136·0

With the first two solutes, separation of θ_1 from θ_2 is possible by using the molecular anisotropies, δ_0^2, calculated from depolarisation factors (cf. Cabannes, *op. cit.*). With *iso*quinoline, however, the necessary figures are not available and an alternative method must be devised. We accordingly propose the following : a scale drawing, incorporating Stuart's " Wirkungsradien " (*Z. phys. Chem.*, 1935, **27**, *B*, 350), is constructed as described by Barclay and Le Fèvre (*J.*, 1950, 556) and the lengths A, B, and C utilised to divide up $3b_{\mathrm{mean}}$ proportionately ($3b_{\mathrm{mean}}$ is derived from the molecular refraction extrapolated for light of infinite wavelength as $9R_{\infty}/4\pi N$). The numbers so obtained are regarded as rough approximations to the desired half-axes of the molecular polarisability ellipsoid, and inserted into $(b_1 - b_2)^2 + (b_2 - b_3)^2 + (b_3 - b_1)^2 = Z$, whence an estimate of θ_1 follows as ${}_{\mathrm{D}}PZ/(45kT.{}_{\mathrm{E}}P)$. Table 2 compares θ_1 so computed with that obtained *via* depolarisation factors, shown as θ_1 (expt.).

The agreement is adequate, since θ_1 is, with polar substances, usually much smaller than θ_2. Fortunately, among the present three bases, *iso*quinoline has the largest $(\theta_1 + \theta_2)$, so that its analysis for b_1, b_2, and b_3 should be the least affected by errors in θ_1. That this is in fact the case is seen by ignoring θ_1 entirely (*i.e.*, putting $\theta_1 = 0$), whereupon b_1 emerges as $2{\cdot}06 \times 10^{-23}$ (against $2{\cdot}00 \times 10^{-23}$ when $\theta_1 = 17{\cdot}2 \times 10^{-35}$). Table 3 specifies

TABLE 2. *Estimation* * *of* θ₁ *from shape or depolarisation factors.*

	A	B	C	$10^{23} \times 3b_{\text{mean}}$	$10^{35}\theta_1$ (calc.)	$10^{35}\theta_1$ (expt.)
Pyridine	6·1	6·2	2·9	2·74	4·08	3·54
Quinoline	6·1	8·7	2·9	4·68	21·0	18·8
*iso*Quinoline	7·7	7·3	2·9	4·66	17·2	?

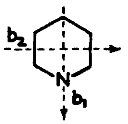
* The $_{\text{E}}P$, $_{\text{D}}P$, and δ_0^2 values required are given in Table 3.

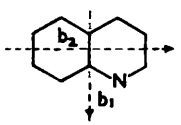
TABLE 3. *Calculation of molecular polarisability ellipsoids.*

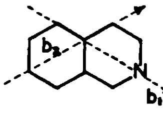
	$_{\text{E}}P$ (c.c.)	$_{\text{D}}P$ (c.c.)	$2\delta_0^2$	μ, D	$10^{23}b_1$	$10^{23}b_2$	$10^{23}b_3$
Pyridine	23·2 [a]	26·5 [b]	0·0792 [c]	2·35	1·06	1·13	$0·55_3$
					1·06	$1·15_5$	$0·52_7$
Quinoline	39·6 [a]	46·1 [b]	0·1444 [c]	2·22	1·65	2·24	$0·79_5$
					1·64	2·29	$0·75_8$
*iso*Quinoline	39·4 [d]	45·6 [b]	?	2·60	—	—	—
					2·00	1·91	$0·75_2$

[a] Extrapolated from refractive indexes given in Landolt–Börnstein's "Tabellen," 1912 Edn. *I.e.*, 1·1R_{D}. [c] From Cabannes, *op. cit.*, p. 254. [d] *I.e.*, 0·95R_{D}.

the molecular polarisability ellipsoids obtained through either θ₁ (expt.) or θ₁ (calc.); results by these routes are entered in the upper and lower lines for each solute respectively. The b_3's from θ₁ (calc.) are seen to be *ca.* 5% below those from θ₁ (expt.), the b_1's scarcely diverge; the position revealed therefore justifies some confidence in the b's now assigned







to *iso*quinoline. Reference to Table 8 of *J.*, 1953, 4041, and to the text following Table 10 of *J.*, 1954, 1577, shows that the differences under comment are less than those often occurring between sets of semi-axes published by separate authors for the same molecule. In this connection we may note that the disparity between our figures for pyridine in solution and those of Stuart and Volkmann for this material as a gas is less than appears at first sight if allowance be made for the greater b_{mean} used by the German workers (*viz.*, 0·950 × 10^{-23} by S. and V.; 0·914 × 10^{-23} by Le Fèvre and Le Fèvre) (see Table 4). Col. 3, which is col. 2 multiplied by 0·914/0·950, accords satisfactorily with col. 1.

TABLE 4. *Polarisabilities of pyridine dissolved or vapourised.*

State	(1) Solute (authors)	(2) Gas (S. and V.)	(3) Gas
$10^{23}b_1$	1·06	1·084	1·043
$10^{23}b_2$	1·13	1·188	1·143
$10^{23}b_3$	$0·55_3$	0·578	0·556

TABLE 5. *Average polarisabilities.*

	$10^{23}b_{\text{mean}}$ *		$10^{23}b_{\text{mean}}$ †	$10^{23}\Delta b_{\text{mean}}$
C_6H_6	0·987	C_5H_5N	0·914	−0·073
$C_{10}H_8$	1·647	C_9H_7N	1·560	−0·087
		iso-C_9H_7N	1·552	−0·095

* From *J.*, 1954, 1577; *J.*, 1955, 1641.
† From $_{\text{E}}P$'s of Table 3.

Comparisons with the Corresponding Ar-*Hydrocarbons.*—The mean polarisability of benzene exceeds that of pyridine, as does that of naphthalene those of quinoline and *iso*quinoline (Table 5). The differences however do not occur uniformly along the three axes, but seem in all cases to be greatest in the direction normal to the molecular plane, intermediate in the dipole (or b_1) direction, and least along b_2; it is notable that the heterocyclic molecules are more polarisable than their hydrocarbon relatives only along b_2 (see Table 6). The last effect is an important sequel to the replacement of a CH by an isoelectronic nitrogen atom: the former having a bond whose b_L is nearly equal to its b_T or b_V (cf. *J.*, 1954, 1577), the latter carrying a lone pair whose contributions to b_2 and b_3 should presumably be the same. For many physical properties, of course, this replacement causes little alteration (*e.g.*, for spectra, see Bowen, *Ann. Reports*, 1943, **40**, 25). Perhaps the contributions of structures such as (d) shown by Coulson (" Valence," Oxford, 1952, p. 241) are not negligible.

TABLE 6. *Values of* b_i^{base} *minus* $b_i^{hydrocarbon}$.

	$10^{23}b_1$	$10^{23}b_2$	$10^{23}b_3$	$10^{23}\Delta b_1$	$10^{23}\Delta b_2$	$10^{23}\Delta b_3$
C_5H_5N	1·06	1·13	0·553	−0·05	$+0{\cdot}01_5$	−0·18
C_6H_6 *	$1{\cdot}11_4$	$1{\cdot}11_4$	0·733.			
C_9H_7N	1·65	2·24	0·795	−0·11	+0·09	$-0{\cdot}23_5$
$C_{10}H_8$ †	1·76	2·15	1·03			
iso-C_9H_7N	2·00	1·91	0·752	−0·05	+0·05	−0·28
$C_{10}H_8$ ‡	2·05	1·86	1·03			

* From *J.*, 1954, 1577.

† From *J.*, 1955, 1641, where b_1 of naphthalene corresponds to the b_2 direction of quinoline.

‡ The b's shown are calculated from those of naphthalene, via $b_1^{\beta} = b_1^{C_{10}H_8} \cos^2 30° + b_2^{C_{10}H_8} \sin^2 30°$, etc.

Molar Kerr Constants of Pure Pyridine and Quinoline.—The B's for these two substances may be deduced from the measurements, relatively to carbon disulphide, reported by Leiser (*Abhand. Deut. Bunsen-gesellschaft*, No. 4, Halle a.S., 1910) and Lippmann (*Z. Elektrochem.*, 1911, **17**, 15), *viz.*, 6·32 and 4·66. The value of $B_{20°}^{CS_2}$ being taken as $3{\cdot}226 \times 10^{-7}$, the B's of pyridine and quinoline are $20{\cdot}4 \times 10^{-7}$ and $15{\cdot}0 \times 10^{-7}$ respectively. The molar Kerr constant of the pure liquid then follows as ${}_mK_{liq.} = 6B\lambda nM/(n^2 + 2)^2(\varepsilon + 2)^2d$; Table 7 contains the necessary data. While ${}_mK_{liq.}$ is considerably smaller than ${}_{\infty}({}_mK_2)$—listed in Table 1—application of the empirical correction suggested by Le Fèvre and Le Fèvre (*J.*, 1953, 4041) produces figures which approach the orders of those now obtained at infinite dilution.

TABLE 7. *Empirical correction of* ${}_mK_{liq.}$.

	10^7B_l	d	n	ε	$10^{12}{}_mK_l$	$(10^{12}{}_mK)\varepsilon/n^2$
Pyridine	20·4	0·978	1·5074	12·01	24·5	130
Quinoline	15·0	1·090	1·625	8·704	43·6	144

EXPERIMENTAL

Materials, Apparatus, and Methods.—The solutes were originally pure commercial samples but were dried and refractionated immediately before preparation of solutions. The carbon tetrachloride was part of the bulk described in *J.*, 1954, 1577. The apparatus, details of procedure, and calculation remain as noted in *J.*, 1953, 4041, wherein the symbols found in the following Tables are defined. Observations are recorded in Table 8, and computations of ${}_{\infty}({}_mK_2)$ summarised in Table 9; λ has been taken as 5893 Å.

TABLE 8. *Kerr constants and refractive indexes of solutions in carbon tetrachloride at* 25°.

Pyridine

10^5w_2	206	628	801	1512	1538	4043
$10^7\Delta B$	0·025	0·128	0·160	0·275	0·293	0·831
n_D	—	—	—	1·4590	1·4591	1·4616

whence $10^7\Delta B = 18{\cdot}1w_2 + 60w_2^2$ and mean $\gamma n_1 = 0{\cdot}102$.

Quinoline

10^5w_2	1174	2209	3708	5157	5641
$10^7\Delta B$	0·113	0·284	0·543	0·759	0·884
n_D	—	—	1·4661	1·4695	1·4706

whence $10^7\Delta B = 11{\cdot}0w_2 + 81w_2^2$ and mean $\gamma n_1 = 0{\cdot}232$.

iso*Quinoline*

10^5w_2	76	530	965	2126	3298
$10^7\Delta B$	0·026	0·217	0·382	0·957	1·510
n_D	—	—	—	1·4625	1·4652

whence $10^7\Delta B = 40{\cdot}3w_2 + 173w_2^2$ and mean $\gamma n_1 = 0{\cdot}234$.

The temperature used throughout was 25°, for which the appropriate solvent constants are: $10^7B = 0{\cdot}070$; $n_D = 1{\cdot}4575$; $d_4^{25} = 1{\cdot}5845$; $\varepsilon = 2{\cdot}2270$; $H = 2{\cdot}060$; $J = 0{\cdot}4731$; $10^{12}{}_sK_1 = 0{\cdot}0749$.

It will be noted that between quinoline and *iso*quinoline, on one hand, and α- and β-naphthyl derivatives, on the other, the relative magnitudes of the molar Kerr constants at infinite dilution show similar trends: $_\infty({}_mK_2)$ of *iso*quinoline is roughly four times that of quinoline, while β-$C_{10}H_7X$—when X = F, Cl, Br, or I—usually has a molar Kerr constant 2—3 times that of its α-isomer (cf. *J.*, 1955, 1641).

TABLE 9. *Calculation of molar Kerr constants at infinite dilution.*

Solute	$a\varepsilon_1$ *	β *	γ	δ	$_\infty({}_mK_2) \times 10^{12}$
Pyridine	13·88	−0·582	0·070	258	150
Quinoline	8·25	−0·443	0·159	157	149
*iso*Quinoline	11·0	−0·424	0·161	576	572

* From unpublished measurements by Freeman, Le Fèvre, Rao, and Tardif.

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