233. *Molecular Polarisability. Ellipsoids of Polarisability for Certain Fundamental Heterocycles.*

By (Mrs.) C. G. Le Fèvre, R. J. W. Le Fèvre, B. Purnachandra Rao, and M. R. Smith.

From the depolarisation factors for light scattered by solutions of pyridine, quinoline, *iso*quinoline, furan, thiophen, and pyrrole in carbon tetrachloride, together with electric double refraction and other measurements on the same systems, the molecular polarisability ellipsoids for these six solutes are specified. With the 5-ring structures a positive exaltation in polarisability is indicated only in the $2:5$ (or $3:4$) directions. Practical new data for pyridine, quinoline, and *iso*quinoline are supplied, but no essential alteration of earlier conclusions is necessitated.

THE polarisability ellipsoids for pyridine, quinoline, and *iso*quinoline published by Le Fèvre and Le Fèvre [1] were derived by making assumptions concerning the "anisotropy" terms [2] incorporated in their respective molar Kerr constants. For pyridine and quinoline, light-scattering observations on the vapours were used to calculate θ_1, while for *iso*quinoline (for which there were no such data) an approximation drawn from molecular dimensions was used. It has since been demonstrated [3] that with molar Kerr constants $_\infty(_mK_2)$ measured at infinite dilution in carbon tetrachloride neither procedure is correct: the light scattering should be studied in the same solvent as that in which $_\infty(_mK_2)$ is determined. This has now been done, with results as given below. Additionally, furan, thiophen, and pyrrole are now examined for the first time.

---

[1] Le Fèvre and Le Fèvre, *J.*, 1955, 2750.
[2] *Idem, Rev. Pure Appl. Chem.*, 1955, **5**, 261.
[3] Le Fèvre and Purnachandra Rao, *J.*, 1957, 3644.

EXPERIMENTAL

Materials were purified as in refs. 1 and 3—6. Apparatus and methods have been described before (*e.g.*, refs. 2, 7, 8). Experimental observations are listed in Tables 1—3, and lead to the information in Table 4. The symbols follow the definitions given in refs. 1—3, and 7—9.

TABLE 1. *Electric double refractions of solutions in carbon tetrachloride* * *at* 25°.

Solute: Furan

$10^5 w_2$	658	2073	2115	2261	2398	3566
$10^7 \Delta B$	0·004	0·016$_5$	0·017$_5$	0·018	0·020	0·029

whence $10^7 \Delta B = 0·778 w_2 + 1·21_5 w_2{}^2$

Solute: Thiophen

$10^5 w_2$	2141	4708	4821	6517	7566	8657
$10^7 \Delta B$	0·026	0·056	0·057	0·070	0·082	0·102

whence $10^7 \Delta B = 1·16_7 w_2 - 0·38_5 w_2{}^2$

Solute: Pyrrole

$10^5 w_2$	621	909	1019	1515	1835	2981
$10^7 \Delta B$	0·040	0·054	0·060	0·081	0·103	0·142

whence $10^7 \Delta B = 6·40_8 w_2 - 54·2 w_2{}^2$

* $B = 0·070 \times 10^{-7}$ when $w_2 = 0$.

TABLE 2. *Depolarisation factors for solutions in carbon tetrachloride.**

Solute: Furan

$10^5 f_2$	3638	7771	11386	15031·5	18541
$10^2 \Delta_{12}$	6·286	9·441	12·21	14·79	17·20

whence $\Delta\Delta_{12} = 0·7981 f_2 - 0·302 f_2{}^2$

Solute: Thiophen

$10^5 f_2$	5225	7503	11250	15021	19625
$10^2 \Delta_{12}$	6·850	8·331	10·62	12·85	15·84

whence $\Delta\Delta_{12} = 0·6484 f_2 - 0·104 f_2{}^2$

Solute: Pyrrole

$10^5 f_2$	4485	9983	13647	18327·5	20834
$10^2 \Delta_{12}$	6·815	10·35	13·12	16·65	17·24

whence $\Delta\Delta_{12} = 0·7542 f_2 - 0·356 f_2{}^2$

Solute: Pyridine

$10^5 f_2$	3170	6548	8515	10293	16006
$10^2 \Delta_{12}$	6·366	9·538	12·59	13·83	20·84

whence $\Delta\Delta_{12} = 0·9106 f_2 + 1·106 f_2{}^2$

Solute: Quinoline

$10^5 f_2$	2168	4020	5952	9109	11895·5
$10^2 \Delta_{12}$	7·627	11·08	14·38	20·48	25·97

whence $\Delta\Delta_{12} = 1·844 f_2 + 0·358 f_2{}^2$

Solute: *iso*Quinoline

$10^5 f_2$	1747	3175	4745	6029	7518
$10^2 \Delta_{12}$	8·122	12·03	16·21	19·70	23·96

whence $\Delta\Delta_{12} = 2·647 f_2 + 0·982 f_2{}^2$

* $\Delta_1 = 0·0346$ for $f_2 = 0$

[4] Buckingham, Chau, Freeman, Le Fèvre, Rao, and Tardif, *J.*, 1956, 1405.
[5] Harris, Le Fèvre, and Sullivan, *J.*, 1935, 1622.
[6] Buckingham, Harris, and Le Fèvre, *J.*, 1953, 1626.
[7] Le Fèvre and Le Fèvre, *J.*, 1953, 4041.
[8] Le Fèvre, " Dipole Moments," Methuen, London, 3rd edn., 1953, p. 45.
[9] Le Fèvre, Le Fèvre, and Oh, *Austral. J. Chem.*, 1957, **10**, 218.

TABLE 3.   *Dielectric polarisation and refraction measurements in carbon tetrachloride at 25°.*

$10^5 w_2$ .... 0 n_D^{25} .... 1·4575 d_4^{25} .... 1·58454 ε^{25} .... 2·2270

Furan

$10^5 w_2$	658	2073	2115	2261	2398	3566
n_D^{25}	1·4573	1·4564	14563	1·4562	1·4561	1·4553
d_4^{25}	1·58451	1·57720	1·56161	1·56060	1·55930	1·55780
ε^{25}		2·2544	2·2545	2·2551	2·2557	2·2714

whence $\Sigma\Delta n/\Sigma w_2 = -0.057$; $\Sigma\Delta d/\Sigma w_2 = -1.115$; $\Sigma\Delta\varepsilon/\Sigma w_2 = 1.258$.

Thiophen

$10^5 w_2$	156	2231	2671	4320	4821	5192	8657
n_D^{25}	—	—	1·4601	1·4617	1·4621	1·4624	1·4661
d^{25}	1·58332	1·56732	1·56388	—	—	1·54463	—
ε^{25}	2·2282	2·2441	2·2472	2·2602	—	2·2667	—

whence $\Sigma\Delta n/\Sigma w_2 = 0.097$; $\Sigma\Delta d/\Sigma w_2 = -0.771$; $\Sigma\Delta\varepsilon/\Sigma w_2 = 0.765$.

Pyrrole

$10^5 w_2$	621	909	1019	1515	1835	2981	3101
n_D^{25}	—	—	—	—	1·4595	1·4605	1·4608
d_4^{25}	1·57838	1·57557	1·57448	1·56953	—	—	—
ε^{25}	2·2842	2·3117	2·3210	2·3648	—	—	—

whence $\Sigma\Delta n/\Sigma w_2 = 0.105$; $\Sigma\Delta d/\Sigma w_2 = -0.989$; $\Sigma\Delta\varepsilon/\Sigma w_2 = 9.19_5$.

TABLE 4.   *Calculations of dipole moments, molar Kerr constants, polarisability semi-axes, etc., for solutes in carbon tetrachloride at 25°.*

	$\alpha\varepsilon_1$	β	γ	δ	$_\infty P_2$ (c.c.)	$_D P$ (c.c.)
Furan	1·25$_8$	−0·708	−0·039	11·1$_1$	30·4	19·6 [a]
Thiophen	0·765	−0·487	0·067	16·6$_7$	29·7	23·8 [a]
Pyrrole	9·19$_5$	−0·624	0·072	91·5$_4$	85·3	20·8 [b]

	$_\infty(_mK_2) \times 10^{12}$	$(\theta_1 + \theta_2) \times 10^{35}$	$_\infty\delta_2^2 \times 10^3$	$_E P$ (c.c.)
Furan	6·2$_6$	1·48$_8$	39·7$_0$	18·2$_4$ [d]
Thiophen	11·1$_9$	2·66$_1$	32·4$_9$	22·7$_0$ [d]
Pyrrole	44·5$_9$	10·6$_0$	37·6$_7$	20·0$_3$ [d]
Pyridine	150·0 [c]	35·6$_7$	44·8$_9$	23·2$_0$ [d]
Quinoline	149·1 [c]	35·4$_9$	88·4$_1$	39·6$_0$ [d]
isoQuinoline	571·7 [c]	135·9$_5$	126·4	39·4$_0$ [d]

	$(b_1 + b_2 + b_3) \times 10^{23}$	$\theta_1 \times 10^{35}$	μ (D)	$10^{23}b_1$	$10^{23}b_2$	$10^{23}b_3$
Furan	2·16$_9$	1·08$_4$	0·72	0·74$_3$	0·88$_9$	0·53$_7$
Thiophen	2·69$_9$	1·34$_{25}$	0·54	1·01$_5$	1·01$_4$	0·67$_0$
Pyrrole	2·38$_2$	1·19$_9$	1·78	0·86$_9$	0·93$_3$	0·57$_9$
Pyridine	2·75$_9$	2·03$_0$	2·37 [e]	1·07$_2$	1·04$_3$	0·64$_5$
Quinoline	4·70$_9$	11·65	2·27 [e]	1·68	2·07$_4$	0·94$_9$
isoQuinoline	4·68$_5$	16·49	2·65 [e]	1·9$_9$	1·91$_4$	0·77$_8$

[a] From ref. 5.   [b] From ref. 6.   [c] From ref. 1.   [d] Extrapolated from refractions given in Landolt and Börnstein's " Tabellen," 1912 Edn., p. 1027.   [e] From ref. 4.

DISCUSSION

Pyridine, Quinoline, and isoQuinoline.—Values of θ_1 calculated from observations on solutions are smaller than those derived from the depolarisation factors of the gases, or from alternatives based on scale-drawings [1] (Table 5).   As expected,[1] the magnitudes of b_1 are little changed by the use of the correct θ_1 but b_2 and b_3 are more affected.

Furan, Thiophen, and Pyrrole.—The dielectric polarisations of these solutes in carbon tetrachloride have not been previously recorded.   The values now found for their dipole moments (0·72, 0·54, and 1·78 D) agree with those (0·71$_5$ ± 0·02, 0·52 ± 0·05, and

1·80 ± 0·07) determined earlier [5,6] in benzene. Marinangeli [10] has since given $\mu = 1\cdot74$ D for pyrrole in benzene.

Ingold [11] has drawn attention to the fact that the mean polarisabilities of these three heterocycles show negative exaltations, thiophen more markedly than furan or pyrrole. Since the semi-axes of the bond ellipsoids are now available for the C–H,[12] C–O,[13] C–C,[14] C–N,[15] N–H,[15] and C=C [16] links, the question as to whether the exaltation is a directional property can be investigated *a priori*. No measurements are yet to hand regarding the

TABLE 5. *Effects of different θ_1 values on the semi-axes calculated therewith.*

	Source of θ_1	$10^{35}\theta_1$	$10^{23}b_1$	$10^{23}b_2$	$10^{23}b_3$
Pyridine	$_\infty\delta_2^2$	2·03	1·07	1·04	0·64$_5$
,,	Δ_{gas}	3·54	1·06	1·13	0·55
,,	Shape factors	4·08	1·06	1·15$_5$	0·53
Quinoline	$_\infty\delta_2^2$	11·6$_5$	1·69	2·07	0·95
,,	Δ_{gas}	18·8	1·65	2·24	0·79$_5$
,,	Shape factors	21·0	1·64	2·29	0·76
*iso*Quinoline *	$_\infty\delta_2^2$	16·5	1·99	1·91	0·78
,,	Shape factors	17·2	2·00	1·91	0·75

* No Δ_{gas} value available.

C–S bond, but for an inter-centre distance of 1·8 Å, b_L^{C-S} should [17] be *ca.* $0\cdot11 \times 10^{-23}$, so that, Vogel's [18] bond refractions being used, b_T^{C-S} appears as *ca.* $0\cdot22 \times 10^{-23}$ c.c.

As a preliminary it may be noted that with $b_L^{C-O} = 0\cdot098_6$, $b_T^{C-O} = 0\cdot027_4$, $b_L^{C=O} = 0\cdot280$, $b_T^{C=O} = 0\cdot077$, $b_V^{C=O} = 0\cdot073$, and $b_i^{C-H} = 0\cdot064$ (all $\times 10^{-23}$ c.c.), the calculated molecular semi-axes for benzene on a regular hexagonal model are: $10^{23}b_1 = 10^{23}b_2 = 1\cdot11$; $10^{23}b_3 = 0\cdot68_5$. The corresponding found values are: $10^{23}b_1 = 10^{23}b_2 = 1\cdot11$; $10^{23}b_3 = 0\cdot73$. The near-agreement between these sets justifies similar calculations for furan, thiophen, and pyrrole. Using $b_L^{C-C} = 0\cdot081$, $b_T^{C-C} = 0\cdot039$, $b_L^{C-N} = 0\cdot057$, $b_T^{C-N} = 0\cdot069$, $b_L^{N-H} = 0\cdot050$, $b_T^{N-H} = 0\cdot083$ and b's for other bonds as above, in conjunction with the valence angles given by Allen and Sutton,[19] we forecast semi-axes as follow:

		$10^{23}b_1$	$10^{23}b_2$	$10^{23}b_3$
Furan	calc.	0·92	0·67	0·51$_5$
	obs.	0·74	0·89	0·54
	obs. − calc.	−0·18	+0·22	+0·02$_5$
Thiophen	calc.	1·11	0·89	0·88
	obs.	1·01$_5$	1·01	0·67
	obs. − calc.	−0·09$_5$	+0·12	−0·21
Pyrrole	calc.	0·98	0·75	0·67
	obs.	0·87	0·93	0·58
	obs. − calc.	−0·11	+0·18	−0·09

In all three cases exaltations are predicted as positive in the b_2 direction, and as negative along b_1. On the estimates just quoted, exaltations of mean polarisabilities should be most negative for thiophen, less so for pyrrole, and a little positive for furan and benzene. The change in algebraic sign is contrary to experience, since benzene and furan actually exhibit small negative exaltations (ref. 11, p. 184). Numerically however the discrepancies are slight; they are probably due to minor errors in the bond and geometrical data used for prediction.

[10] Marinangeli, *Ann. Chim. (Italy)*, 1954, **44**, 211, 219.
[11] Ingold, " Structure and Mechanism in Organic Chemistry," Cornell Univ. Press, New York, 1953.
[12] Le Fèvre and Le Fèvre, *Chem. and Ind.*, 1955, 1121.
[13] *Idem, J.*, 1956, 3549.
[14] *Idem, Chem. and Ind.*, 1956, 54.
[15] Aroney and Le Fèvre, *J.*, 1958, 3002.
[16] Bramley, Le Fèvre, Le Fèvre, and Rao, preceding paper.
[17] Le Fèvre, *Proc. Chem. Soc.*, 1958, 283.
[18] Vogel, *J.*, 1952, 514.
[19] Allen and Sutton, *Acta Cryst.*, 1950, **3**, 46.

It is noteworthy that this work reveals one more point of resemblance between benzene and thiophen: the ratios of their semi-axes of polarisability are practically the same ($1 \cdot 52 : 1 \cdot 52 : 1$, and $1 \cdot 51_5 : 1 \cdot 51_3 : 1$ respectively).

UNIVERSITY OF SYDNEY, N.S.W., AUSTRALIA.