360. *Molecular Polarisability. The Molar Kerr Constant of Ferrocene.*

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From the viewpoint of polarisability ferrocene is equivalent to a krypton atom sandwiched between two planar regular-pentagonal $(CH)_5$ rings in each of which the carbon–carbon bond ellipsoids have the same semi-axes as those of the C_{Ar}–C_{Ar} bonds in benzene. On this basis the predicted molar Kerr constant is $20{\cdot}1 \times 10^{-12}$, against a measured value of $19{\cdot}9 \times 10^{-12}$.

The molar Kerr constants and total dielectric polarisations of ferrocene dissolved in carbon tetrachloride have been measured by standard methods [1] at 25°. The observations listed below show the two properties mentioned to have values at infinite dilution of $19{\cdot}8_7 \times 10^{-12}$ and $52{\cdot}4_6$ c.c. respectively. Since the molecular refraction (Na-D line) of ferrocene is 50·4 c.c. (so that ${}_\infty P_2$ is slightly less than $1{\cdot}05R_D$) the non-polarity of this molecule is confirmed.[2]

The molar Kerr constant is therefore controlled [3] by the terms θ_1 and θ_3; θ_3 cannot be estimated *a priori* and, being probably small, will be neglected. From ${}_\infty({}_{m}K_2) = 19{\cdot}87 \times 10^{-12}$ we have,[4] therefore, $\theta_1 = 4{\cdot}72_5 \times 10^{-35}$, whence (with ${}_{D}P/{}_{E}P = 1{\cdot}1$), $b_1 - b_3 = \pm 0{\cdot}631 \times 10^{-23}$. It is assumed from the *X*-ray analyses of ferrocene [5] that

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[1] (*a*) Le Fèvre and Le Fèvre, *J.*, 1953, 4041; 1954, 1577; (*b*) *Rev. Pure Appl. Chem.*, 1955, **5**, 261; (*a*) Le Fèvre, " Dipole Moments," Methuen, London, 3rd edn., 1953, Chap. 2.

[2] Wilkinson, Rosenblum, Whiting, and Woodward, *J. Amer. Chem. Soc.*, 1952, **74**, 2125.

[3] Ref. 1(*b*), pp. 286, 309.

[4] Ref. 1(*b*), p. 270.

[5] Pauson, *Quart. Rev.*, 1955, **9**, 391.

the appropriate polarisability ellipsoid will be one of rotation, with semi-axes $b_1 = b_2$, and b_3. Taking the electronic polarisation as $0\cdot95R_D$ gives $2b_1 + b_3 = 5\cdot691 \times 10^{-23}$. By experiment two alternative solutions thus become available:

	$10^{46}(b_1 - b_3)^2$	$10^{23}b_1$	$10^{23}b_3$
Solution A	0·398	2·107	1·476
Solution B	0·398	1·687	2·318

According to A, ferrocene is more polarisable in planes parallel to the pentagonal rings than in directions perpendicular to them; according to B, the reverse is true.

No direct evidence exists to guide a choice between A and B. Previously [6] it has been noted that the dimensions of the " cavity " created by a solute in its solvent often provide data with which to divide $(b_1 + b_2 + b_3)$ into the separate components. Using the distances C–C = 1·40 Å, C–Fe = 2·044 Å (as cited in Pauson's review [5]), and C–H = 1·04 Å, and adopting 108° as the C–C–C angle, together with " Wirkungsradien " from Stuart [7] (*i.e.*, following the procedures of past studies [8] of the dielectric polarisation–medium effect), gives a model containable within a cylinder of height 6·2 Å and diameter 6·3 Å. Solution A is thus favoured, although the anisotropy forecast is much less than that observed.

A more satisfactory approach is to note that the C–C distance is equal to that which occurs in benzene, so that—since bond lengths and bond polarisabilities are connected [9]—C_{Ar}–C_{Ar} ellipsoids may be applied to the C_5 rings of ferrocene. As the C–H link is isotropically polarisable,[10] an ellipsoid for the $(CH–CH)_{aromatic}$ unit may be used. Benzene [11] has $_\infty({}_mK_2) = 7\cdot2_4 \times 10^{-12}$ at 20°; this with $_EP = 25\cdot0_3$ c.c. gives $b_1^{C_6H_6} = b_2^{C_6H_6} = 1\cdot12_0 \times 10^{-23}$, and $b_3^{C_6H_6} = 0\cdot73_6 \times 10^{-23}$; $b_V^{(CH\cdot CH)Ar}$ therefore is $0\cdot123 \times 10^{-23}$. By Le Fèvre's equation,[9] $10^{23}b_L^{(CH\cdot CH)Ar}$ is 0·288; $b_L + b_T + b_V$ for $(CH\cdot CH)_{Ar}$ is 1/6 of $2b_1 + b_3$ for benzene; by difference $b_T^{(CH\cdot CH)Ar}$ is therefore $0\cdot085 \times 10^{-23}$. Utilising these semi-axes for a regular pentagonal $(CH)_5$ ring gives 0·932, 0·932, and $0\cdot615 \times 10^{-23}$ respectively for $b_1^{(CH)_5}$, $b_2^{(CH)_5}$, and $b_3^{(CH)_5}$. As there are two parallel $(CH)_5$ rings in ferrocene, the θ_1 for this molecule should contain a contribution from these rings of $(b_1 - b_3)^2 = 0\cdot402 \times 10^{-46}$; this is very close to the quantity ($0\cdot398 \times 10^{-46}$) observed; the calculated $_mK$ from this factor alone is $20\cdot1 \times 10^{-12}$; the $_mK$ from experiment is $19\cdot9 \times 10^{-12}$.

The implication is that the iron atom is nearly isotropic in its polarisability. Algebraically positive semi-axes for the iron atom can be estimated only from solution A (which is therefore preferable to B); they are:

$$\text{Across the } (CH)_5 \text{ planes: } 2\cdot107 - 2 \times 0\cdot932 = 0\cdot243 \times 10^{-23}$$

$$\text{At } 90° \text{ to the } (CH)_5 \text{ planes: } 1\cdot476 - 2 \times 0\cdot615 = 0\cdot246 \times 10^{-23}$$

Such values for iron are of interest in regard to suggestions [5] that the iron atom in ferrocene has the electronic configuration of krypton, for which gas Watson and Ramaswamy [12] (from refractivity-dispersion measurements) recorded an electronic polarisation of 6·26 c.c; from this, treating krypton as an isotropically polarisable atom, we obtain $b_1^{Kr} = b_2^{Kr} = b_3^{Kr} = 0\cdot248 \times 10^{-23}$. To emphasise the significance of these conclusions: had we assumed *a priori* that ferrocene is equivalent to a krypton atom sandwiched between two parallel $(CH)_5$ planes, the b_1 and b_3 expected would have been $2\cdot112 \times 10^{-23}$ and $1\cdot478 \times 10^{-23}$, and the $_mK_{calc.}$ only *ca.* $0\cdot2 \times 10^{-12}$ higher than that in fact found.

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[6] Ref. 2, p. 287; Le Fèvre and Le Fèvre, *J.*, 1955, 2750; Le Fèvre, Le Fèvre, Rao, and Smith, *J.*, 1959, 1188.

[7] Stuart, *Z. phys. Chem.*, 1935, *B*, **27**, 350.

[8] Ref. 1(*c*), Chap. 3.

[9] Le Fèvre, *Proc. Chem. Soc.*, 1958, 283.

[10] Le Fèvre and Le Fèvre, *Chem. and Ind.*, 1955, 1121; cf. ref. 1(*b*), p. 299.

[11] Ref. 1(*a*), 1954; cf. ref. 1(*b*), p. 284.

[12] Watson and Ramaswamy, *Proc. Roy. Soc.*, 1936, *A*, **156**, 144.

EXPERIMENTAL

Ferrocene, m. p. 173—174°, was prepared as described by Wilkinson [13] except that the crude product was distilled in steam and recrystallised from aqueous methanol.

Measurements of the following properties of solutions containing weight fractions w_2 of solute in carbon tetrachloride have been made at 25°: ΔB, differences between Kerr constants of solution and solvent, Δn, differences between refractive indexes (Na light) of solution and solvent, ε_{12} and d_{12}, the dielectric constants and densities respectively. For $w_2 = 0$, $B = 0{\cdot}070 \times 10^{-7}$, $n_D = 1{\cdot}4575$, $\varepsilon = 2{\cdot}2270$, and $d = 1{\cdot}58454$. Details concerning procedures, calculations, etc., are given in ref. 1.

Observations on ferrocene–carbon tetrachloride solutions at 25°.

$10^5 w_2$	1046	1292	1426	1434	1671	1909	1924
$10^7 \Delta B$	$0{\cdot}011_5$	$0{\cdot}014_5$	$0{\cdot}015_8$	$0{\cdot}016_1$	$0{\cdot}019_4$	$0{\cdot}022_5$	$0{\cdot}023_3$
$10^4 \Delta n$	22	27	29	30	35	40	41
ε_{12}	$2{\cdot}2335$	$2{\cdot}2349$	$2{\cdot}2360$	$2{\cdot}2363$	$2{\cdot}2374$	$2{\cdot}2388$	$2{\cdot}2392$
d_{12}	$1{\cdot}58124$	$1{\cdot}58104$	$1{\cdot}58086$	$1{\cdot}58030$	$1{\cdot}57979$	$1{\cdot}57956$	$1{\cdot}57902$

whence $10^7 \Delta B = 0{\cdot}947 w_2 + 12{\cdot}7 w_2^2$; $\sum \Delta n / \sum w_2 = 0{\cdot}209$; $\sum \Delta \varepsilon / \sum w_2 = 0{\cdot}627$; $\sum \Delta d / \sum w_2 = -0{\cdot}280$; so that $_\infty({}_mK_2) = 19{\cdot}8_7 \times 10^{-12}$ and $_\infty P_2 = 52{\cdot}4_6$ c.c. ($= 1{\cdot}041\ R_D$ c.c. consistently with $\mu = 0$).

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[13] Wilkinson, *Org. Synth.*, 1956, **36**, 31.