

## SHORT COMMUNICATIONS

### THE PRINCIPAL MOLECULAR POLARIZABILITIES OF FERROCENE

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The molar Kerr constant of ferrocene in carbon tetrachloride has been determined using visual methods by Aroney, Le Fèvre, and Somasundaram<sup>1</sup> and found to be  $19.9 \times 10^{-12}$ . Used in conjunction with an estimate of the total electronic polarization, this value of  $\alpha_{(m)K_2}$  led to two alternative sets of principal molecular polarizabilities:§

$$\text{Solution A: } b_1 = b_2 = 21.07, b_3 = 14.76$$

$$\text{Solution B: } b_1 = b_2 = 16.87, b_3 = 23.18$$

Although solution A was favoured, no direct evidence existed at that time to guide a choice between A and B. The present communication shows how a measurement of the molar Cotton-Mouton constant,  $\alpha_{(m)C_2}$ , enables this choice to be made with certainty.

Using methods described previously<sup>2,3</sup> solutions of ferrocene in carbon tetrachloride have been found to exhibit magnetic birefringences as follows ( $w_2$ , weight fraction of solute;  $\Delta C$ , incremental Cotton-Mouton constant):

$10^5 w_2$	604	630	665	740	782
$10^{15} \Delta C$	3.1	3.5	3.7	4.3	4.4

(whence  $\Sigma \Delta C / \Sigma w_2 = 0.56 \times 10^{-12}$ )

Because the earlier Kerr effect results were obtained visually and involved a non-linear extrapolation to infinite dilution, it was felt advisable to repeat these measurements using a more accurate photometric technique.<sup>4</sup> All the values now reported for the incremental Kerr constant ( $\Delta B$ ) are for solutions more dilute than those used in the previous work.

$10^5 w_2$	531	699	765	948	1030
$10^{11} \Delta B$	42	51	46	81	90

(whence  $\Sigma \Delta B / \Sigma w_2 = 0.78 \times 10^{-7}$ )

These measurements on ferrocene lead to a value of  $2.0 \times 10^{-15}$  for the molar Cotton-Mouton constant and to a new estimate of  $16.8 \times 10^{-12}$  for the molar Kerr

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§ Polarizabilities are quoted in Å<sup>3</sup> units throughout.

<sup>1</sup> Aroney, M. J., Le Fèvre, R. J. W., and Somasundaram, K. M., *J. chem. Soc.*, 1960, 1812.

<sup>2</sup> Le Fèvre, R. J. W., Williams, P. H., and Eckert, J. M., *Aust. J. Chem.*, 1965, **18**, 1133.

<sup>3</sup> Le Fèvre, R. J. W., and Murthy, D. S. N., *Aust. J. Chem.*, 1966, **19**, 179; 1969, **22**, 1415.

<sup>4</sup> Le Fèvre, R. J. W., and Ritchie, G. L. D., *J. chem. Soc.*, 1963, 4933.

constant. The latter value gives rise to two sets of molecular polarizabilities differing only slightly from those quoted above.

$$\text{Solution A: } b_1 = b_2 = 20.90, b_3 = 15.11$$

$$\text{Solution B: } b_1 = b_2 = 17.04, b_3 = 22.84$$

Substitution of these semi-axes into the following equation leads to two estimates of  $k_1 + k_2 - 2k_3$  and hence the molar diamagnetic anisotropy  $\Delta K = [K_3 - \frac{1}{2}(K_1 + K_2)]$ :

$$\chi_{\text{m}}(C_2) = (2\pi N/45kT)[(k_1 - k_2)(b_1 - b_2) + (k_2 - k_3)(b_2 - b_3) + (k_3 - k_1)(b_3 - b_1)]$$

where  $k_1$ ,  $k_2$ , and  $k_3$  are the principal diamagnetic susceptibilities of the ferrocene molecule,  $N$  is Avogadro's number,  $k$  is Boltzmann's constant, and  $T$  is the absolute temperature.

$$\text{Solution A: } k_1 + k_2 - 2k_3 = +16.61, \Delta K = -50.0 \times 10^{-6} \text{ CGS units}$$

$$\text{Solution B: } k_1 + k_2 - 2k_3 = -16.58, \Delta K = +49.9 \times 10^{-6} \text{ CGS units}$$

The magnetic anisotropy ( $\Delta K$ ) of single crystals of ferrocene has been found to be  $-56.0 \times 10^{-6}$  CGS units by Mathis, Sweeney, and Fox.<sup>5</sup> An earlier estimate was  $-49.5 \times 10^{-6}$  CGS units by Mulay and Fox.<sup>6</sup> These values are in reasonable agreement with solution A above and hence the polarizabilities of ferrocene are best taken as:  $b_1 = b_2 = 20.90$ ,  $b_3 = 15.11$ .

<sup>5</sup> Mathis, R., Sweeney, M., and Fox, M. E., *J. chem. Phys.*, 1964, **41**, 3652.

<sup>6</sup> Mulay, L. N., and Fox, M. E., *J. chem. Phys.*, 1963, **38**, 760.