

## SHORT COMMUNICATIONS

### THE PRINCIPAL MOLECULAR POLARIZABILITIES OF DIPHENYL\*

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For the evaluation of the principal polarizabilities,  $b_1$ ,  $b_2$ , and  $b_3$ , of a *non-polar* molecule, three independent observational equations are needed in the general case when  $b_1 \neq b_2 \neq b_3$ . Usually only two are available, namely (1) and (2), which expand respectively the electronic polarization and the molar Kerr constant of the species under investigation:

$${}_EP = 4\pi N(b_1 + b_2 + b_3)/9 \quad (1)$$

$${}_mK = 2\pi N({}_DP/{}_EP)[(b_1 - b_2)^2 + (b_2 - b_3)^2 + (b_3 - b_1)^2]/405kT \quad (2)$$

(Here,  $N$  is Avogadro's number,  ${}_DP$  and  ${}_EP$  the distortion and electronic polarizations,  $k$  is Boltzmann's constant, and  $T$  the absolute temperature.) A number of such situations have been noted before,<sup>1-4</sup> and possible sources of a third relationship examined.

The present communication concerns diphenyl, and illustrates the usefulness of measurements of diamagnetic anisotropies in problems of the above type.

For this hydrocarbon a molar Kerr constant of  $40.5 \times 10^{-12}$  at infinite dilution in carbon tetrachloride at 25° has been recorded;<sup>5</sup> the electronic polarization is 49.5 c.c.<sup>6</sup> and the distortion polarization is 52.0 c.c.<sup>5</sup> From (1) and (2) we obtain:

$$b_1 + b_2 + b_3 = 58.86 \times 10^{-24} \quad (3)$$

$$b_1^2 + b_2^2 + b_3^2 - b_1b_2 - b_2b_3 - b_3b_1 = 84.76 \times 10^{-48} \quad (4)$$

Five solutions of diphenyl in carbon tetrachloride at 20° have now been found to exhibit magnetic birefringence as follows ( $w_2$ , weight fraction of solute;  $C_{12}$ , Cotton-Mouton constant of solution):

$10^6 w_2$	3296	3977	4472	4873	6426
$10^{16} C_{12}$	79.1	96.3	110.0	109.6	155.5
whence $\Sigma C_{12}/\Sigma w_2 = 2.39 \times 10^{-12}$					

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<sup>2</sup> Le Fèvre, R. J. W., and Sundaram, K. M. S., *J. chem. Soc.*, 1963, 4442.

<sup>3</sup> Le Fèvre, R. J. W., Radom, L., and Ritchie, G. L. D., *J. chem. Soc. (B)*, 1967, 595.

<sup>4</sup> Le Fèvre, R. J. W., and Radom, L., *J. chem. Soc. (B)*, in press.

<sup>5</sup> Chau, J. Y. A., Le Fèvre, C. G., and Le Fèvre, R. J. W., *J. chem. Soc.*, 1959, 2666.

<sup>6</sup> Le Fèvre, R. J. W., and Narayana Rao, D. A. A. S., *Aust. J. Chem.*, 1955, **8**, 39.

(For explanations of techniques used, see Le Fèvre, Williams, and Eckert,<sup>7</sup> and Le Fèvre and Murthy;<sup>8</sup> the quoted observations were made photometrically as described in the last reference.<sup>8</sup>) Accordingly, since the magnetic birefringence of the solvent is beneath detectability, the molar Cotton-Mouton constant,  ${}_{\infty}(mC_2)$ , of diphenyl at infinite dilution emerges<sup>7</sup> as  $6.99 \times 10^{-15}C$ . Therefore by equation (15) of Le Fèvre *et al.*<sup>7</sup> we have:

$$(k_1 - k_2)(b_1 - b_2) + (k_2 - k_3)(b_2 - b_3) + (k_3 - k_1)(b_3 - b_1) = 336.1 \times 10^{-53} \quad (5)$$

(Here,  $k_1$ ,  $k_2$ , and  $k_3$  are the principal diamagnetic susceptibilities of the diphenyl molecule.)

Lasheen<sup>9</sup> has recently published the *molar* anisotropies of this hydrocarbon as  $-67.7$ ,  $-61.7$ , and  $-183.8$  (all times  $10^{-6}$ )—these being obtained by the Krishnan-Banerjee<sup>10</sup> method together with a knowledge of the molecular orientations in the crystal.<sup>11</sup> In molecular units,  $k_1 = -11.24_0 \times 10^{-29}$ ,  $k_2 = -10.24_4 \times 10^{-29}$ , and  $k_3 = -30.51_6 \times 10^{-29}$ ; by insertion into (5) they produce:

$$18.280b_1 + 21.268b_2 - 39.548b_3 = 336.1 \times 10^{-24} \quad (6)$$

Equations (3), (4), and (6), involving a quadratic during solution, yield alternative sets of values, A or B:

	A	B
$10^{24}b_1$	19.6 <sub>5</sub>	24.7 <sub>4</sub>
$10^{24}b_2$	25.1 <sub>2</sub>	20.2 <sub>8</sub>
$10^{24}b_3$	14.0 <sub>9</sub>	13.8 <sub>4</sub>

Set B is preferred since<sup>5</sup> it is obvious that the molecule should be most polarizable in the direction parallel to the 1,1'-carbon-carbon bond.

The results under B are the first for diphenyl to be deduced from observable physical properties without any assumptions of an empirical kind. They are consistent with the suppositions made by Chau *et al.*<sup>5</sup> concerning the inadequate estimate of  $b_1$  then reached from bond and group polarizabilities without allowances for conjugative effects.<sup>12</sup> The conclusion<sup>5</sup> that diphenyl as a solute adopts a near-flat conformation is also supported by the new values and the smallness of  $b_3$  compared with  $b_2$  (twisting the structure towards orthogonality would increase  $b_3$  and diminish  $b_2$ ). It is of interest that a relationship between the "vertical" polarizabilities  $b_v$  and the inter-centre distances  $r$  of C...C bonds, lately advanced by Le Fèvre and Radom,<sup>4</sup> predicts  $b_3$  for a fully coplanar form as  $14.2 \times 10^{-24}$  c.c. if the  $r$  values given by Hargreaves and Hasan Rizvi<sup>11</sup> are used, or as 13.8 and  $14.0 \times 10^{-24}$  c.c. if the alternative bond lengths given in Sutton's tables<sup>13</sup> are taken.

<sup>7</sup> Le Fèvre, R. J. W., Williams, P. H., and Eckert, J. M., *Aust. J. Chem.*, 1965, **18**, 1133.

<sup>8</sup> Le Fèvre, R. J. W., and Murthy, D. S. N., *Aust. J. Chem.*, 1966, **19**, 179.

<sup>9</sup> Lasheen, M. A., *Phil. Trans. R. Soc. A*, 1964, **256**, 357.

<sup>10</sup> Krishnan, K. S., and Banerjee, S., *Phil. Trans. R. Soc. A*, 1935, **234**, 265.

<sup>11</sup> Trotter, J., *Acta crystallogr.*, 1961, **14**, 1135; Hargreaves, A., and Hasan Rizvi, S., *Acta crystallogr.*, 1962, **15**, 365.

<sup>12</sup> Le Fèvre, R. J. W., *Adv. phys. org. Chem.*, 1965, **3**, 1.

<sup>13</sup> Sutton, L. E., "Tables of Interatomic Distances and Configuration in Molecules and Ions." Spec. Publ. Chem. Soc., No. 11, entry M 232, 1958.