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:

\[
\varepsilon P = 4\pi N (b_1 + b_2 + b_3)/9 \quad (1)
\]

\[
mK = 2\pi N (\rho P/\varepsilon P) [(b_1 - b_2)^2 + (b_2 - b_3)^2 + (b_3 - b_1)^2]/405kT \quad (2)
\]

(Here, \( N \) is Avogadro's number, \( \rho P \) and \( \varepsilon P \) the distortion and electronic polarizations, \( k \) is Boltzmann's constant, and \( T \) the absolute temperature.) A number of such situations have been noted before,1-4 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 \( 25^\circ \) has been recorded;5 the electronic polarization is \( 49.5 \text{ c.c.} \) and the distortion polarization is \( 52.0 \text{ c.c.} \). From (1) and (2) we obtain:

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

\[
\sum b_i^2 + b_2^2 + b_3^2 - b_1b_2 - b_2b_3 - b_3b_1 = 84.76 \times 10^{-48} \quad (4)
\]

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

\[
\begin{array}{cccccc}
10^6w_2 & 3296 & 3977 & 4472 & 4873 & 6426 \\
10^6C_{12} & 79.1 & 96.3 & 110.0 & 109.6 & 155.5
\end{array}
\]

whence \( \Sigma C_{12}/\Sigma w_2 = 2.39 \times 10^{-11} \)

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4 Le Fèvre, R. J. W., and Radom, L., J. chem. Soc. (B), in press.

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

\[
(k_1 - k_2)(b_1 - b_2) + (k_3 - k_2)(b_2 - b_3) + (k_2 - k_1)(b_3 - b_1) = 336.1 \times 10^{-23}
\] (5)

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

Lasheen9 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–Banerjee10 method together with a knowledge of the molecular orientations in the crystal.11 In molecular units, \( k_1 = -11.24_3 \times 10^{-26}, k_2 = -10.24_4 \times 10^{-26}, \) and \( k_3 = -30.51_8 \times 10^{-26}; \) by insertion into (5) they produce:

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

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

\[
\begin{array}{ccc}
\text{A} & \text{B} \\
10^{24}b_1 & 19.6 & 24.7 \\
10^{24}b_2 & 25.1 & 20.2 \\
10^{24}b_3 & 14.0 & 13.8
\end{array}
\]

Set B is preferred since 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.5 concerning the inadequate estimate of \( b_1 \) then reached from bond and group polarizabilities without allowances for conjugative effects.12 The conclusion 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 \( b_2 \) and the inter-centre distances \( r \) of C···C bonds, lately advanced by Le Fèvre and Radom,4 predicts \( b_2 \) for a fully coplanar form as \( 14.2 \times 10^{-24} \) c.c. if the \( r \) values given by Hargreaves and Hasan Rizvi11 are used, or as \( 13.8 \) and \( 14.0 \times 10^{-24} \) c.c. if the alternative bond lengths given in Sutton’s tables13 are taken.

9 Lasheen, M. A., Phil. Trans. R. Soc. A, 1964, 256, 357.