# 294. *Molecular Polarisability. The Anisotropies of Seven Monosubstituted Benzenes and of Nitromethane as Solutes in Carbon Tetrachloride.*

By R. J. W. LE FÈVRE and B. PURNACHANDRA RAO.

The molecular anisotropies at infinite dilution in carbon tetrachloride of $CH_3{\cdot}NO_2$ and $C_6H_5X$ (with X = $CH_3$, F, Cl, Br, I, $NO_2$, and CN) have been determined, by measurements of the depolarisation factors of light scattered by solutions, and these data, in combination with molecular refractions and Kerr constants previously recorded, are used to calculate the semi-axes of the polarisability ellipsoids of these molecules. Such semi-axes are entirely based upon experiment and are free from certain assumptions made formerly; the indications they provide regarding the directed exaltations of polarisability in the Ar-structures are summarised in Table 5(*B*).

LE FÈVRE and LE FÈVRE,[1, 2] when computing semi-axes for the molecular polarisability ellipsoids of a number of monosubstituted benzenes, were handicapped in two respects: (*a*) by scattered light-depolarisation factors being available only for toluene and chloro-, bromo-, and nitro-benzene, and (*b*) by the absence of evidence showing whether or not depolarisation data for gaseous substances were appropriate for use in conjunction with molar Kerr constants and refractions determined from observations on solutions. Consequently, certain of the polarisabilities listed then and since (*e.g.*, in Table 4 of ref. 1, or Table 9 of ref. 2) have been perforce derived by methods which involved empirical assumptions concerning the smallest of the three semi-axes in each case. The problem mentioned in (*b*) above, however, has recently been solved by measurements by Le Fèvre and Rao,[3] which indicate depolarisation factors of *solutions* as the correct source in the circumstances stated. There thus occurs an opportunity to check or amend earlier results.

*Present Work.*—Accordingly, the molecular anisotropies at infinite dilution, ${}_{\infty}\delta_2^{\,2}$, of toluene, the four halogenobenzenes, nitrobenzene, and benzonitrile, have been determined in carbon tetrachloride; also that for nitromethane has been ascertained, since this datum was needed but was lacking when our earlier papers [1, 2] were prepared.

Experimental methods, symbols, and calculation procedures have been explained before.[3] All materials were redistilled, dry specimens; solvent and solutions were made

---

[1] Le Fèvre and Le Fèvre, *J.*, 1954, 1577.

[2] Le Fèvre and Le Fèvre, *Rev. Pure Appl. Chem.*, 1955, **5**, 261.

[3] Le Fèvre and Rao, *J.*, 1957, 3644.

equally dust-free as described before;[3] with iodobenzene it was found necessary to remove traces of free iodine by passage through an alumina-packed column immediately before use, otherwise a general scattering prevented accurate readings. Essential observations are recorded in Tables 1 and 2; densities of mixtures are not included since in all cases these are available from published dielectric polarisation measurements.[4]

TABLE 1. *Depolarisation factors for solutions in carbon tetrachloride.**

| | *Solute*: *toluene* | | | | | *Solute*: *fluorobenzene* | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| $10^5 f_2$ ...... | 3759 | 10,776 | 15,986 | 21,039 | 22,503 | 2944 | 5345 | 8790 | 11,367·5 | 14,541 |
| $10^2 \Delta_{12}$ ... | 6·124 | 10·94 | 14·63 | 17·62 | 18·91 | 5·903 | 7·836 | 10·33 | 12·14 | 14·48 |
| | *Solute*: *chlorobenzene* | | | | | *Solute*: *bromobenzene* | | | | |
| $10^5 f_2$ ...... | 2582 | 4507 | 5881 | 8502 | 9969 | 1333 | 2736·5 | 4487 | 6260·5 | 8236 |
| $10^2 \Delta_{12}$ ... | 6·041 | 7·942 | 9·441 | 11·18 | 12·54 | 5·246 | 6·882 | 8·194 | 10·42 | 11·71 |
| | *Solute*: *iodobenzene* | | | | | *Solute*: *nitrobenzene* | | | | |
| $10^5 f_2$ ...... | 2037 | 4597 | 6828 | 8288 | 11,733 | 1905 | 3249 | 4929 | 7105 | 10,818 |
| $10^2 \Delta_{12}$ ... | 6·195 | 9·722 | 12·33 | 13·87 | 17·35 | 5·694 | 7·181 | 9·341 | 10·91 | 13·32 |
| | *Solute*: *benzonitrile* | | | | | *Solute*: *nitromethane* | | | | |
| $10^5 f_2$ ...... | 2465 | 4937 | 7542 | 9559 | 14,643 | 5666 | 10,035 | 13,181 | 18,117 | 22,723 |
| $10^2 \Delta_{12}$ ... | 7·114 | 10·56 | 12·97 | 14·90 | 18·49 | 4·177 | 4·675 | 5·019 | 5·683 | 6·032 |

* $\Delta_1 = 0·0346$ for $f_2 = 0$.

TABLE 2. *Calculation of molecular anisotropies of solutes at infinite dilution.*

| Solute | R.H.S. of equation giving $\Delta\Delta_{12}$ | $D$ * | ${}_\infty\delta_2{}^2 \times 10^3$ |
|---|---|---|---|
| $C_6H_5{\cdot}CH_3$ ............................ | $0{\cdot}7156f_2 - 0{\cdot}155f_2{}^2$ | −0·7505 | 35·27 |
| $C_6H_5F$ ................................... | $0{\cdot}8448f_2 - 0{\cdot}631f_2{}^2$ | −0·5874 | 41·52 |
| $C_6H_5Cl$ .................................. | $1{\cdot}087_5f_2 - 1{\cdot}85f_2{}^2$ | −0·4475 | 52·94 |
| $C_6H_5Br$ .................................. | $1{\cdot}292f_2 - 3{\cdot}46f_2{}^2$ | −0·0921 | 62·49 |
| $C_6H_5I$ ................................... | $1{\cdot}449f_2 - 2{\cdot}26f_2{}^2$ | +0·2929 | 69·79 |
| $C_6H_5{\cdot}NO_2$ ............................. | $1{\cdot}324f_2 - 3{\cdot}80f_2{}^2$ | −0·3607 | 64·09 |
| $C_6H_5{\cdot}CN$ .............................. | $1{\cdot}561f_2 - 3{\cdot}68f_2{}^2$ | −0·6304 | 75·22 |
| $CH_3{\cdot}NO_2$ .............................. | $0{\cdot}1298f_2 - 0{\cdot}066f_2{}^2$ | −0·2707 | 8·38 |

* $D$ is a density coefficient given by $d_{12} = d_1 + Df_2$

*Discussion.*—(*a*) The values of ${}_\infty\delta_2{}^2$ given in Table 2 are considerably smaller than $\delta^2_{\text{gas}}$ but approximately equal to $\delta^2_{\text{liquid}}$ in the four cases where $\Delta_{\text{gas}}$, $\Delta_{\text{liquid}}$, and $\beta$ (the isothermal compressibility) are all known (see Table 3). Since Le Fèvre and Rao[3] have already found the same relation among a number of non-polar solutes, it may therefore be recognised as a general principle.

TABLE 3. *Values of* $\delta^2 \times 10^3$ *for the gaseous, liquid, and dissolved states.*

| Substance | $10^3\delta^2_{\text{gas}}$ | $10^3\delta^2_{\text{liquid}}$ | $10^3\,{}_\infty\delta_2{}^2$ | Substance | $10^3\delta^2_{\text{gas}}$ | $10^3\delta^2_{\text{liquid}}$ | $10^3\,{}_\infty\delta_2{}^2$ |
|---|---|---|---|---|---|---|---|
| $C_6H_5Cl$ ...... | 86·6 | 61·2 | 52·9 | $C_6H_5{\cdot}CH_3$ ... | 75·4 | 40·8 | 35·3 |
| $C_6H_5Br$ ...... | 94·2 | 63·7 | 62·5 | $C_6H_5{\cdot}NO_2$ ... | 109·4 | 71·6 | 64·1 |

Data for $\delta^2_{\text{gas}}$ and $\delta^2_{\text{liquid}}$ are values selected from the literature by Bhagavantam.[5]

(*b*) We can now recalculate the semi-axes of the polarisability ellipsoids for the mono-substituted benzenes from the molar Kerr constants and electronic polarisations recorded previously.[1,2] The result is in Table 4; it may be claimed for the *b*'s listed on the right-hand side of Table 4(*C*) that they are based entirely on experiment and do not depend upon any assumptions such as Le Fèvre and Le Fèvre made on an earlier occasion.[1] For toluene, $b_2$ emerges as greater than $b_1$, and for fluorobenzene $b_1$ and $b_2$ are roughly the same, but with the remainder of the substances no serious differences are seen between the

[4] Le Fèvre and Le Fèvre, *Australian J. Chem.*, 1954, **7**, 33.

[5] Bhagavantam, "Scattering of Light and the Raman Effect," Andhra Univ., Waltair, 1940.

TABLE 4. *Calculation of polarisability semi-axes for molecules of type* $C_6H_5X$.

(*A*) *Basic data*

| Group X | $T$ | $(\theta_1 + \theta_2) \times 10^{34}$ | ${}_{\mathrm{D}}P$ (c.c.) | ${}_{\mathrm{E}}P$ (c.c.) | $\mu$ (D) | ${}_{\infty}\delta_2{}^2 \times 10^3$ |
|---|---|---|---|---|---|---|
| Me | 25° | $3{\cdot}04_4$ | 32·7 | 29·9 | 0·34 | $35{\cdot}2_7$ |
| F | 20 | $13{\cdot}5_1$ | 31·3 | 24·9 | 1·38 | $41{\cdot}5_2$ |
| Cl | 20 | $34{\cdot}4_8$ | 34·9 | 29·9 | 1·59 | $52{\cdot}9_4$ |
| Br | 25 | $40{\cdot}6_6$ | 35·6 | 32·6 | 1·51 | $62{\cdot}4_9$ |
| I | 20 | $42{\cdot}2_3$ | 41·4 | 38·3 | 1·39 | $69{\cdot}7_9$ |
| $NO_2$ | 20 | 255·2 | 36·2 | 30·9 | 3·95 | $64{\cdot}0_9$ |
| CN | 20 | 272·8 | 33·1 | 30·2 | 4·02 | $75{\cdot}2_2$ |

(*B*) *Calculations of* $\theta_1$ *and* $\theta_2$

| Group X | $(b_1 + b_2 + b_3) \times 10^{23}$ | $\sum(b_i - b_j)^2 \times 10^{46}$ | ${}_{\mathrm{D}}P/{}_{\mathrm{E}}P$ | $\theta_1 \times 10^{35}$ | $\theta_2 \times 10^{35}$ |
|---|---|---|---|---|---|
| Me | 3·555 | 0·4457 | 1·094 | 2·634 | 0·410 |
| F | 2·961 | 0·3640 | 1·257 | 2·514 | 11·00 |
| Cl | 3·555 | 0·6691 | 1·167 | 4·290 | 30·19 |
| Br | $3{\cdot}876_5$ | 0·9391 | 1·092 | 5·540 | 35·12 |
| I | 4·554 | 1·4474 | 1·081 | 8·596 | 35·63 |
| $NO_2$ | 3·674 | 0·8651 | 1·172 | 5·570 | 249·6 |
| CN | 3·591 | 0·9700 | 1·096 | 5·743 | 267·0 |

(*C*) *Semi-axes obtained by using* ${}_{\infty}\delta_2{}^2$ *compared with those* (*in parentheses*) *given in J.*, 1954, 1577

| Group X | $10^{23}b_1$ | $10^{23}b_2$ | $10^{23}b_3$ | $10^{23}b_1$ | $10^{23}b_2$ | $10^{23}b_3$ |
|---|---|---|---|---|---|---|
| Me | $(1{\cdot}37_7)$ | $(1{\cdot}25_3)$ | (0·904) | $1{\cdot}27_5$ | $1{\cdot}40_1$ | $0{\cdot}87_9$ |
| F | $(1{\cdot}12_6)$ | $(1{\cdot}10_6)$ | (0·711) | $1{\cdot}12_9$ | $1{\cdot}13_0$ | $0{\cdot}70_3$ |
| Cl | $(1{\cdot}47_2)$ | $(1{\cdot}24_4)$ | (0·818) | $1{\cdot}47_8$ | $1{\cdot}25_5$ | $0{\cdot}82_1$ |
| Br | $(1{\cdot}68_4)$ | $(1{\cdot}21_3)$ | (0·956) | $1{\cdot}68_3$ | $1{\cdot}30_1$ | $0{\cdot}89_2$ |
| I | $(1{\cdot}98_4)$ | $(1{\cdot}40_7)$ | (1·136) | $1{\cdot}97_1$ | $1{\cdot}58_8$ | $0{\cdot}99_6$ |
| $NO_2$ | $(1{\cdot}60_4)$ | $(1{\cdot}38_6)$ | (0·662) | $1{\cdot}61_7$ | $1{\cdot}20_0$ | $0{\cdot}86_2$ |
| CN | $(1{\cdot}63_8)$ | $(1{\cdot}21_1)$ | (0·849) | $1{\cdot}61_6$ | $1{\cdot}16_0$ | $0{\cdot}81_5$ |

bracketed and unbracketed figures; $b_1$ and $b_3$ for nitrobenzene are now closer to the corresponding values obtained from Stuart and Volkmann's measurements on the vapour than was formerly the case.[6]

Tables 5(*A*) and 5(*B*) are replacements, from the new data of Table 4(*C*), for those published before (pp. 300 and 301 of ref. 2). The semi-axes, not hitherto available, of the polarisability ellipsoid of nitromethane, are also involved; these follow from ${}_{\infty}({}_{\mathrm{m}}K_2) = 89{\cdot}0 \times 10^{-12}$, ${}_{\mathrm{D}}P = 18{\cdot}3$ c.c., ${}_{\mathrm{E}}P = 12{\cdot}0$ c.c., $\mu = 3{\cdot}14$ D (Le Fèvre and Le Fèvre[1]) and ${}_{\infty}\delta_2{}^2 = 8{\cdot}38 \times 10^{-3}$ (Table 2 of this paper) as:

TABLE 5. *Recalculation of Tables* 12 *and* 15 *of reference* 2.

(*A*) *Principal axes * for* C–X *links in various methyl and phenyl compounds*

| C–X in | $b_{\mathrm{L}}{}^{\mathrm{CX}}$ | $b_{\mathrm{T}}{}^{\mathrm{CX}}$ | $b_{\mathrm{V}}{}^{\mathrm{CX}}$ | C–X in | $b_{\mathrm{L}}{}^{\mathrm{CX}}$ | $b_{\mathrm{T}}{}^{\mathrm{CX}}$ | $b_{\mathrm{V}}{}^{\mathrm{CX}}$ |
|---|---|---|---|---|---|---|---|
| $CH_3F$ | $0{\cdot}12_5$ | 0·04 | 0·04 | $C_6H_5F$ | 0·08 | 0·08 | 0·03 |
| $CH_3Cl$ | 0·32 | 0·22 | 0·22 | $C_6H_5Cl$ | 0·43 | $0{\cdot}20_5$ | 0·15 |
| $CH_3Br$ | $0{\cdot}46_5$ | 0·31 | 0·31 | $C_6H_5Br$ | 0·63 | 0·25 | 0·22 |
| $CH_3I$ | 0·68 | 0·47 | 0·47 | $C_6H_5I$ | 0·92 | 0·54 | 0·33 |
| $CH_3{\cdot}CN$ | 0·35 | 0·18 | 0·18 | $C_6H_5{\cdot}CN$ | 0·57 | 0·11 | $0{\cdot}14_5$ |
| $CH_3{\cdot}NO_2$ | 0·34 | 0·28 | 0·23 | $C_6H_5{\cdot}NO_2$ | 0·57 | 0·15 | 0·19 |
| $CH_3{\cdot}CH_3$ | 0·30 | 0·22 | 0·22 | $C_6H_5{\cdot}CH_3$ | $0{\cdot}22_5$ | 0·35 | 0·21 |

* In units $= 10^{-23}$ c.c.

(*B*) *Directed exaltations * in* $C_6H_5X$ *shown as* $b_i = (b_i{}^{\mathrm{CX}})_{\mathrm{aryl}}$ *minus* $(b_i{}^{\mathrm{CX}})_{\mathrm{alphyl}}$

| Substituent | $b_{\mathrm{L}}$ | $b_{\mathrm{T}}$ | $b_{\mathrm{V}}$ | Substituent | $b_{\mathrm{L}}$ | $b_{\mathrm{T}}$ | $b_{\mathrm{V}}$ |
|---|---|---|---|---|---|---|---|
| F | $-0{\cdot}04_5$ | +0·04 | −0·01 | CN | +0·22 | −0·07 | $-0{\cdot}03_5$ |
| Cl | +0·11 | $-0{\cdot}01_5$ | −0·07 | $NO_2$ | +0·23 | −0·13 | −0·04 |
| Br | $+0{\cdot}16_5$ | −0·06 | −0·09 | $CH_3$ | $-0{\cdot}07_5$ | +0·13 | −0·01 |
| I | +0·24 | +0·07 | −0·14 | | | | |

* In units $= 10^{-23}$ c.c.

$$10^{23}b_1 = 0{\cdot}530,\ 10^{23}b_2 = 0{\cdot}474,\ 10^{23}b_3 = 0{\cdot}423$$

The argument used in compiling Tables 5(*A*) and (*B*) has been set out in refs. 1 and 2. For methyl, $b_1 = b_2 = b_3 = 0{\cdot}190_5$; for phenyl, $b_1 = b_2 = 1{\cdot}050_5, b_3 = 0{\cdot}669_5$ (all $\times 10^{-23}$ c.c.).

---

[6] See ref. 2, p. 289.

Conclusions reached in refs. 1 and 2 are not qualitatively affected by these recalculations except in the case of toluene, for which the chief (positive) exaltation now appears in the $b_2$ (transverse) direction. On a simple view this seems a resonable consequence of hyperconjugation between $H^+$ and $^-CH_2{\cdot}C_6H_5$, since in the redistribution of charge within the benzyl structure there are two *ortho*-positions, but only one *para*-position, at which electron excesses are to be expected. An interesting coincidence is that F and the united atom group $CH_3$, which both show negative exaltation in the longitudinal direction and very little exaltation in the direction perpendicular to the Ar-ring, are isoelectronic and have the same electronic configuration ($1s^22s^22p^5$), deformation of the orbitals in $CH_3$ presumably being the main difference.

The authors acknowledge with gratitude finanical assistance received from the Chemical Society and the award of a Scholarship by the Nuffield Foundation (to B. P. R.).

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

[*Received, July* 15*th*, 1957.]