# Dipole Moments of α-, β-, γ-, and δ-Hexachlorocyclohexane and of Tetrachlorocyclohexane (m.p. 174° C)

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The following is a report of measurements of dipole moments of α-, β-, γ- and δ-hexachlorocyclohexane and of tetrachlorocyclohexane in benzene at 25°.

The measurements of the dielectric constant differences were carried out in an oil thermostat regulated to 25.00 ± 0.02° using the heterodyne beat method. The solvent was purified by fractional distillation, the middle fraction only being used for the measurements.

## EXPERIMENTAL

*The oscillator.* The oscillator consisted of two generators capable of producing electric vibrations of frequency of the order of 5 megacycles per second. The second harmonic was always used and the precision obtained in the reading was about one per cent.

*The cell condenser.* The test condenser contained in the glass vessel shown in Fig. 1A, in the following referred to as the cell condenser, consists of concentric gold-plated brass cylinders which were held in position by glass rods, indicated in Fig. 1B. Solute could be added to the cell through the opening H from a weighing tube Fig. 1C, the bent form of which made the transfer easy.

The level of the solution can, generally without difficulty, be adjusted to coincide with the marks MM owing to the fact that the mixing procedure intensely increases the evaporation which further causes a lowering of the miniscus. If a rising of the miniscus is desired pure benzene may simply be added.

*Reference condenser.* It was found very helpful to use a reference condenser with a capacity which could be set very close to that of the cell condenser when filled with pure benzene. It consisted of a precision air condenser in a glass vessel placed in the thermostat. The oscillator could be connected either to the cell condenser or to the reference condenser. Small changes in the stability of the oscillator could thus be detected and corrected for.

*The measuring condenser.* The measuring condenser consisted of a small variable precision air condenser which was wired parallel to the cell. A difference in the capacity
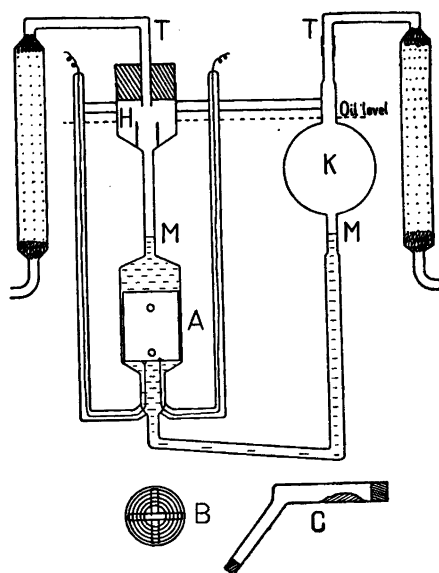
*Fig. 1. Cell condenser (test condenser). The pressure inside the cell could be varied using the glass tubes filled with calcium chloride, and, by aid of the bulb K, mixing of the solution obtained.*

of the cell condenser, due to an increment of the concentration, could thus be compensated and measured. The measuring condenser was adjusted by means of a variable high precision air condenser manufactured by H. W. Sullivan Ltd., London, two settings of which had been determined by comparison with a high precision condenser belonging to the Norwegian Broadcasting Station. The variation of the capacity of the measuring condenser could with sufficient accuracy be regarded as linear.

*Procedure.* Successively increasing concentrations were made up in the cell and the differences in the scale readings between that of pure benzene and that of the respective solutions in a series were found. The stability of the oscillator was always checked with the reference condenser.

*Symbols and formulae* [1] used in the calculations:

$c = 99.57$ picofarads, capacity of air-filled cell condenser.

$k = 0.025813$ sensitivity of measuring condenser (picofarads/scale divisions).

$\Delta c = k \cdot d$, increment of capacity due to dissolved solute.

$d =$ reading of the measuring condenser due to dissolved solute.

$\varepsilon = 2.2727$ dielectric constant of benzene at 25° [2].

$$\Delta \varepsilon = \frac{\Delta c}{c}$$

$$\varepsilon_1 = \varepsilon + \Delta \varepsilon$$

$$p = \frac{\varepsilon - 1}{\varepsilon + 2} = 0.29786 \text{ for benzene}$$

$$p' = \frac{\varepsilon_1 - 1}{\varepsilon_1 + 2}$$

$Q$ = weight of solvent in cell (33.110 g benzene sp. w. 0.8739).

$q$ = weight of solute added, in grams.

$M_1$ = molecular weight of solvent (78.108 for benzene).

$M_2$ = molecular weight of solute.

$f_2$ = mole fraction of solute.

$\Delta n_E$ = difference in refractive index, extrapolated. ($\Delta n_E = f_2 \cdot 0.1085$ used, for hexachloro-cyclohexane; $\Delta n_E = f_2 \cdot 0.0404$, used for tetrachlorocyclohexane).

$p_E = \dfrac{n^2 - 1}{n^2 + 2}$

$\Delta p_E = \dfrac{6n}{(n^2 + 2)^2} \Delta n_E$. Obtained by derivation of $p_E$.

$n = 1.5024$ refractive index used.

$V = 37.888$ cm$^3$, volume of the cell condenser at 25°.

$C = \dfrac{1000 \, \Sigma \, q}{M_2 \, V}$ concentration of solution in grammol/litre at 25°.

$P_{A+O} = \dfrac{1000}{C} (p - p' - \Delta p_E)$ sum of atomic and orientation polarization.

$P_{A+O}^{\infty}$ = sum of atomic and orientation polarization, extrapolated.

$\mu$ = dipole moment = $1.273 \cdot 10^{-20} \sqrt{T \cdot P_{A+O}^{\infty}}$

$T = 298.2$ ° absolute temperature.


## RESULTS

Fig 2. gives the observed values $d$ as a function of the weights $q$ of the solute added to the cell.

Tables 1 and 2 is based on data taken from the graph Fig. 2. In the determination of $P_{A+O}^{\infty}$ a greater number of points were used than given in the tables.


*Table 1.*

Hexachlorocyclohexane, M = 290.8.

| $d$ | $\varepsilon_1$ | $p'$ | $\Delta p_E$ | $C$ | $P_{A+O}$ |
|---|---|---|---|---|---|
| | | $\alpha$-isomere (m. p. 156.3°). | | | |
| 50 | 2.2857 | 0.3000 | 0.00010 | 0.2015 | 100.7 |
| 100 | 2.2986 | 0.3021 | 0.00020 | 0.4021 | 100.7 |

$P_{A+O}^{\infty} = 100.6$; $\mu = 2.20 \cdot 10^{-18}$ e. s. u.

$\beta$-isomere (m. p. 308°).

$P_{A+O}^{\infty} \sim 0$; $\mu = 0$.

| $d$ | $\varepsilon_1$ | $p'$ | $\Delta p_E$ | $C$ | $P_{A+O}$ |
|---|---|---|---|---|---|
| | | $\gamma$-isomere (m. p. 113.3 °). | | | |
| 100 | 2.2986 | 0.30210 | 0.00012 | 0.02388 | 172.6 |
| 200 | 2.3246 | 0.30629 | 0.00023 | 0.04784 | 171.4 |

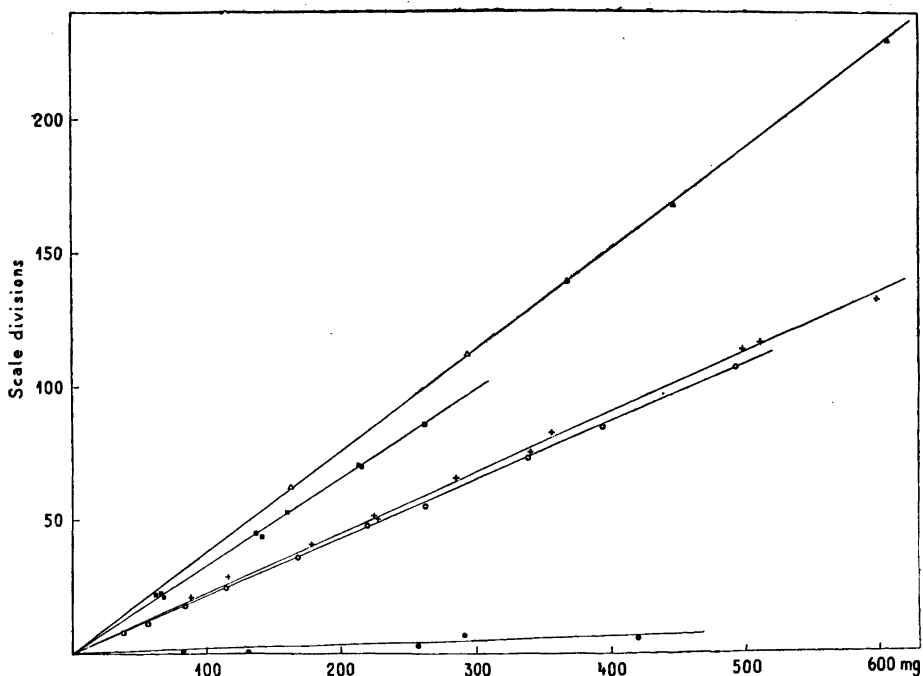$P_{A+O}^{\infty} = 173.3$; $\mu = 2.89 \cdot 10^{-18}$ e. s. u.

*Fig. 2. Observed values (scale divisions) of the measuring condenser plotted agains
the weights of solute added to the cell.*

■ *Tetrachlorocyclohexane*               △ *γ-Hexachlorocyclohexane*
\+ *a-Hexachlorocyclohexane*             ○ *δ-Hexachlorocyclohexane*
● *β-Hexachlorocyclohexane*

$\delta$-isomere (m. p. 138.2°).

| 50  | 2.2857 | 0.3000 | 0.00010 | 0.02097 | 97.3 |
| 100 | 2.2986 | 0.3021 | 0.00020 | 0.04193 | 96.3 |

$$P_{A+O}^{\infty} = 97.2; \ \mu = 2.17 \cdot 10^{-18} \ \text{e.s.u.}$$

*Table 2.*

Tetrachlorocyclohexane, M = 221.95 (m. p. 174°).

| $d$ | $\varepsilon_1$ | $p'$ | $\Delta p_E$ | $C$ | $P_{A+O}$ |
|-----|------|------|------|------|------|
| 50  | 2.2857 | 0.3000 | 0.00003 | 0.01813 | 116.3 |
| 100 | 2.2986 | 0.3021 | 0.00006 | 0.03621 | 115.4 |

$$P_{A+O}^{\infty} = 115.6; \ \mu = 2.36 \cdot 10^{-18} \ \text{e.s.u.}$$

$\Delta p_E$ is found from the experimental values of $\Delta n$ (difference between the refractive index of solution and solvent) for different wave lenghts. By plotting the experimental $\Delta n$ values against the corresponding frequencies the value $\Delta n_E$ at zero frequency may be obtained by graphical extrapolation. A Pulfrich refractometer, fitted with a divided cell was used for the determination of $\Delta n$ [3].

The $\gamma$- and $\delta$-compounds were plased at our disposal by Imperial Chemical Industries Ltd.

The obtained values for $\alpha$- and $\beta$-hexachlorocyclohexane show good agreement with those of Hassel and Næshagen [4] and also with those of Williams [5] for the $\alpha$-isomere. B. Melander [6] reports $\mu = 3.6 \cdot 10^{-18}$ for the $\gamma$-isomere and $\mu \sim 0$ for the $\alpha$-isomere at $17°$.

## SUMMARY

A cell, convenient for dielectric constant measurements of solutions, has been described.

Measurements of the sum $P^{\infty}_{A+O}$ of the atomic and orientation polarization at infinite dilution of $\alpha$-, $\beta$-, $\gamma$- and $\delta$-hexachlorocyclohexane and of tetrachlorocyclohexane (m. p. $174°$ C) have been carried out on solutions in benzene at $25°$, and the corresponding dipole moments have been computed.

## REFERENCES

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