## 303. *Properties of Conjugated Compounds. Part XVII.* The Determination of the Dipole Moments of the Monomethyl- and Dimethyl-butadienes (continued).*

By Ernest H. Farmer and Frank L. Warren.

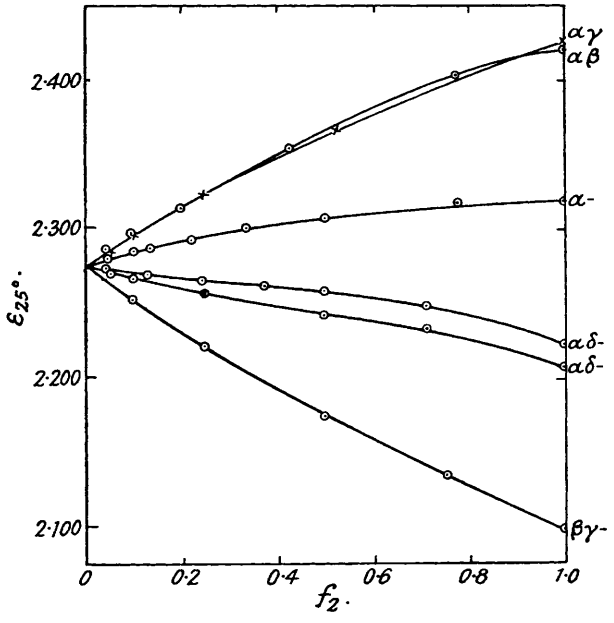
In the preceding paper the dipole moments of three monomethyl- and dimethyl-butadienes have been calculated from density and dielectric constant data relating to the hydrocarbons and their solutions in a non-polar solvent. The dipole moments of the remaining four hydrocarbons of the same series, *viz.*, α-methyl-, and αβ-, αγ-, and αδ-dimethyl-butadiene (all of which can display geometrical isomerism), have now been calculated. The new density and dielectric constant data on which the computations are based refer, however, to one temperature only, 25°, and the synthetic *n*-hexane formerly employed as non-polar solvent has been replaced by carefully purified benzene.† It has been necessary, accordingly, to make the assumption, which is probably correct within the limits of experimental error, that substances of the same type and molecular weight, such as the monomethyl- or the dimethyl-butadienes, have the same atom polarisation, $P_A$: actually, the values of $P_A$ already recorded for isoprene and βγ-dimethylbutadiene have been utilised.

### Experimental.

The circuit and cell used for the observations were those formerly employed (*loc. cit.*); the pyknometer was of the Hartley pattern and had a capacity of 25 c.c.; the temperature of the

Fig. 1.

*Dielectric constants in benzene.*




water thermostat remained constant within 0·01°. The whole apparatus was calibrated in the

* Part XVIII, J., 1932, 2072.

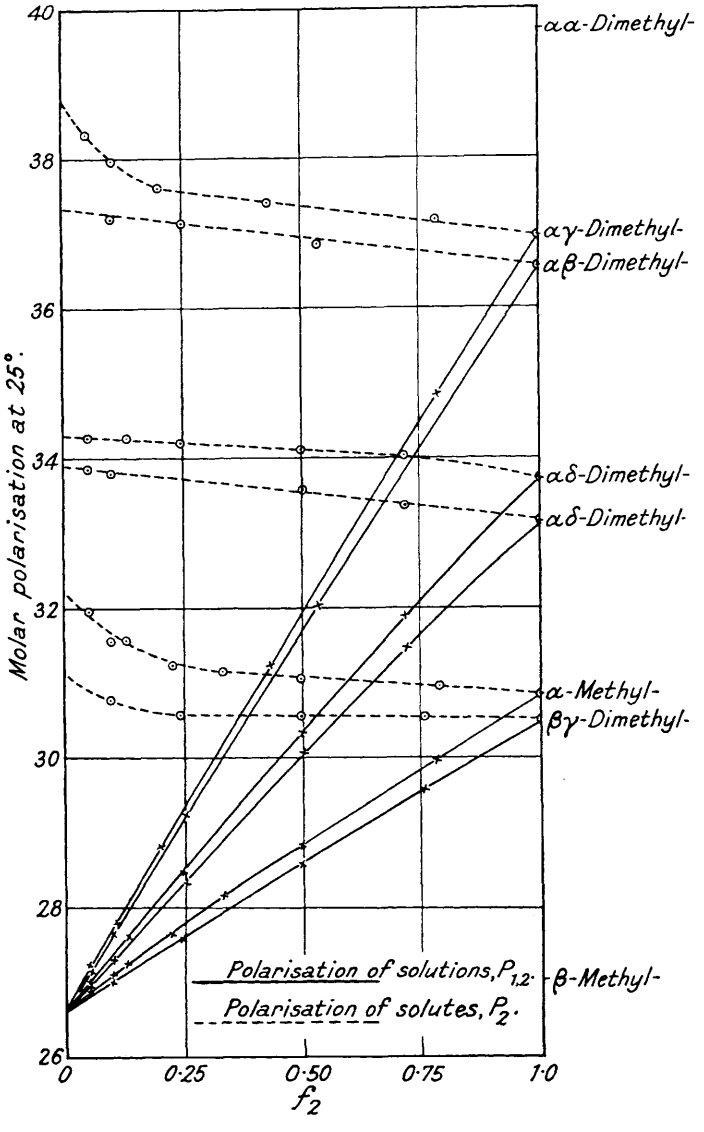
† Discontinuance of the use of synthetic *n*-hexane was necessitated by the great expense of preparing the requisite large quantities of this substance in a high state of purity. Petroleum *n*-hexane was thoroughly tested as a substitute but was unsatisfactory for the purpose. At 25°, however, benzene and synthetic *n*-hexane proved to be equally satisfactory as solvents in determining the molar polarisation of the butadienes in solution ($P_\infty$).

way previously described, the capacity of the dielectric cell, including a small capacity (2·6 μμF) due to the leads, etc., being 99 μμF in air and 224 μμF in benzene.

The hydrocarbons were prepared by methods which had previously been found to yield chemically, although not configurationally, homogeneous products (Farmer and Warren, J., 1931, 3229). With the αδ-hydrocarbon, owing to the large range of boiling point resulting from

FIG. 2.

*Polarisations of alkylbutadienes in benzene.*




the presence of (presumably) *cis-cis-*, *cis-trans-*, and *trans-trans*-isomerides, the same division into lower- and higher-boiling fractions was made which was previously employed in studying the refractivity of this substance; this division doubtless resulted in some measure of separation of the geometrically isomeric forms (Farmer and Warren, *loc. cit.*, pp. 3227, 3228).

In the tables below, the symbols are those used in the preceding paper. The variation of the dielectric constant of the benzene–hydrocarbon solutions with concentration is represented in Fig. 1; the corresponding variation of the molar polarisation of the solutions and of the solutes

is shown in Fig. 2. It is remarkable that the polarisations of α-methyl-, αγ-dimethyl-, and βγ-dimethyl-butadiene (unlike those of the αβ- and the αδ-compound) show a rapid increase with diminution in concentration at low dilutions.

*Dielectric constant, density, and molar polarisations.*

*α-Methylbutadiene.*

| $f_2$. | $\epsilon^{25°}$. | $d_4^{25°}$. | $P_{1,2}$. | $P_2$. |
|---|---|---|---|---|
| 0·0000 | 2·274 | 0·8731 | 26·62 | — |
| 0·0497 | 2·280 | 0·8626 | 26·89 | 31·99 |
| 0·1014 | 2·284 | 0·8514 | 27·12 | 31·56 |
| 0·1292 | 2·287 | 0·8454 | 27·26 | 31·58 |
| 0·2241 | 2·292 | 0·8252 | 27·65 | 31·24 |
| 0·3370 | 2·300 | 0·8017 | 28·16 | 31·19 |
| 0·5007 | 2·307 | 0·7686 | 28·84 | 31·06 |
| 0·7752 | 2·317 | 0·7154 | 29·98 | 30·96 |
| 1·0000 | 2·319 | 0·6738 | 30·85 | 30·85 |

*αβ-Dimethylbutadiene.*

| | | | | |
|---|---|---|---|---|
| 0·0524 | 2·284 | 0·8634 | 27·16 | 37·30 |
| 0·0995 | 2·293 | 0·8541 | 27·67 | 37·19 |
| 0·2507 | 2·324 | 0·8273 | 29·26 | 37·14 |
| 0·5288 | 2·367 | 0·7838 | 32·02 | 36·84 |
| 1·0000 | 2·426 | 0·7233 | 36·56 | 36·56 |

*βγ-Dimethylbutadiene.*

| | | | | |
|---|---|---|---|---|
| 0·0984 | 2·252 | 0·8546 | 27·03 | 30·79 |
| 0·2462 | 2·220 | 0·8279 | 27·60 | 30·58 |
| 0·5018 | 2·173 | 0·7871 | 28·60 | 30·57 |
| 0·7554 | 2·134 | 0·7519 | 29·59 | 30·55 |
| 1·0000 | 2·099 | 0·7215 | 30·50 | 30·50 |

*αγ-Dimethylbutadiene.*

| $f_2$. | $\epsilon^{25°}$. | $d_4^{25°}$. | $P_{1,2}$. | $P_2$. |
|---|---|---|---|---|
| 0·0496 | 2·284 | 0·8632 | 27·20 | 38·31 |
| 0·0985 | 2·296 | 0·8532 | 27·74 | 37·97 |
| 0·1997 | 2·314 | 0·8336 | 28·81 | 37·61 |
| 0·4281 | 2·354 | 0·7941 | 31·24 | 37·42 |
| 0·7784 | 2·404 | 0·7429 | 34·84 | 37·18 |
| 1·0000 | 2·422 | 0·7139 | 36·97 | 36·97 |

*αδ-Dimethylbutadiene* (b. p. <80°/764·3 mm.).

| | | | | |
|---|---|---|---|---|
| 0·0493 | 2·271 | 0·8624 | 27·00 | 34·28 |
| 0·1310 | 2·269 | 0·8458 | 27·62 | 34·28 |
| 0·2434 | 2·264 | 0·8233 | 28·46 | 34·18 |
| 0·4953 | 2·259 | 0·7800 | 30·34 | 34·12 |
| 0·7138 | 2·249 | 0·7457 | 31·90 | 34·02 |
| 1·0000 | 2·224 | 0·7052 | 33·73 | 33·73 |

*αδ-Dimethylbutadiene* (b. p. 79·4—81·6°/765 mm.).

| | | | | |
|---|---|---|---|---|
| 0·0499 | 2·270 | 0·8627 | 26·98 | 33·87 |
| 0·1003 | 2·267 | 0·8522 | 27·34 | 33·80 |
| 0·2471 | 2·256 | 0·8237 | 28·32 | 33·51 |
| 0·4997 | 2·242 | 0·7812 | 30·10 | 33·58 |
| 0·7173 | 2·233 | 0·7493 | 31·46 | 33·35 |
| 1·0000 | 2·207 | 0·7105 | 33·15 | 33·15 |

*The Dipole Moments.*—The values for the electron polarisation ($P_E$) (determined as previously described, Part XVI, p. 1297) and atom polarisation ($P_A$) of the different hydrocarbon molecules, together with those for the polarisation of the molecules (in benzene) at infinite dilution ($P_\infty$), are given in the table below. From these values the values shown for the dipole moment, $\mu \times 10^{18} = 0{\cdot}0127\sqrt{(P_\infty - P_A - P_E)T}$, of the different molecules have been calculated.

| Alkylbutadiene. | $P_\infty$, c.c. | $P_E$, c.c. | $P_A$,* c.c. | $\mu \times 10^{18}$. | Alkylbutadiene. | $P_\infty$, c.c. | $P_E$, c.c. | $P_A$,* c.c. | $\mu \times 10^{18}$. |
|---|---|---|---|---|---|---|---|---|---|
| α-Methyl | 32·27 | 24·65 | (2·34) | 0·50 | αδ-Dimethyl I† | 34·30 | 29·24 | (2·50) | 0·36 |
| αβ-Dimethyl | 37·27 | 29·01 | (2·50) | 0·53 | αδ- ,, II† | 33·87 | 29·39 | (2·50) | 0·31 |
| αγ- ,, | 38·80 | 29·09 | (2·50) | 0·59 | βγ- ,, | 31·00 | 28·50 | 2·50 | 0 |

* The values shown in parentheses are assumed (see p. 1302).

† I = low-boiling fraction; II = high-boiling fraction.

The authors thank the Chemical Society for a grant which has defrayed a part of the cost of this investigation.

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[*Received, October 1st*, 1931.]