

302. Properties of Conjugated Compounds. Part XVI. The Dipole Moments and Atomic Polarisation of the Monomethyl- and Dimethyl-butadienes.

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THE paraffin hydrocarbons whether normal or branch-chained possess zero dipole moment (Smyth and Zahn, *J. Amer. Chem. Soc.*, 1925, **47**, 2501; Sanger, *Physikal. Z.*, 1926, **27**, 556; Williams and Ogg, *J. Amer. Chem. Soc.*, 1928, **50**, 94; Smyth and Morgan, *ibid.*, p. 1547; Smyth and Stoops, *ibid.*, p. 1883); unsaturated ethylene and acetylene also have zero moment (Smyth and Zahn, *loc. cit.*). The unsymmetrical olefin, Δ^a -butylene, on the other hand, is reported to have a small dipole moment, 0.37×10^{-18} e.s.u. (Smyth and Zahn, *loc. cit.*), whilst the symmetrical dihalogen olefins, dichloro-, dibromo-, and di-iodo-ethylene would seem to fulfil expectation in having zero or an appreciable moment according to their possession of *trans*- or *cis*-configuration respectively (Errera, *J. Phys. Radium*, 1925, **6**, 390). The investigations described in this and the succeeding paper represent attempts to discover whether the considerable difference in additive properties which exists between the two monomethyl- and the five dimethyl-butadienes corresponds to a discernible permanent difference in the polar condition of the individual molecules. Of course, in these instances the molecules are relatively complex, permitting of the rotation of two halves of each molecule about a single bond, and (in some cases) have possibilities of geometrical isomerism centred at one or both of the unsaturated positions of the chain. There is, therefore, no necessity for the dipole moment of the molecule to be entirely dependent upon those of the groups present, or indeed to constitute a fixed magnitude * at all. The determination of the dipole moment of simple butadiene, a knowledge of which is requisite for comparison, has been omitted for practical reasons, but in the group of three hydrocarbons now dealt with (β -methyl-, $\alpha\alpha$ -dimethyl-, and $\beta\gamma$ -dimethyl-butadiene) the complication arising from geometrical isomerism is absent.

EXPERIMENTAL.

The dielectric constant, ϵ' , and density, d_4^{20} , of the pure hydrocarbons (prepared and purified as previously described by the authors, *J.*, 1931, 3221) and of their dilute solutions in synthetic *n*-hexane were measured over a range of 100° (-75° to 25°), and the value of the molar polarisation of the solution, $P_{1,2}$, calculated from the formula $P_{1,2} = (\epsilon - 1)/(\epsilon + 2) \cdot (M_1 f_1 + M_2 f_2)/d$, where M_1 and M_2 , and f_1 and f_2 , are the molecular weights and molar fractions of the solvent and solute respectively. The molar polarisation at infinite dilution (P_∞) of the different butadienes was obtained either by graphical extrapolation of the P_2 - f_2 curves (P_2 , the molar polarisation of the solute, being calculated for the different concentrations from the expression $P_2 = [P_{1,2} - P_1 f_1]/f_2$) or by similar extrapolation of the $P_{1,2}$ - f_2 curves; for β -methyl- and $\alpha\alpha$ -dimethyl-butadiene the extrapolation could be effected with greater certainty by the latter procedure, and the values of P_∞ quoted below for these hydrocarbons were obtained in this way (see Williams and Krichma, *J. Amer. Chem. Soc.*, 1927, **49**, 1676; also Smyth, Morgan, and Boyce, *ibid.*, 1928, **50**, 1536).

The value of P_∞ , determined for different temperatures, was plotted against $1/T$, where T is the absolute temperature, and from the curve of the general equation $P = a + b/T$, the following were calculated (see Debye, "Polar Molecules," p. 37; also Smyth and Morgan, *loc. cit.*): (i) the dipole moment, $\mu = 0.0127\sqrt{b} \times 10^{-18}$ e.s.u.; (ii) the atomic polarisation, $P_A = a - P_E$, where P_E , the electronic polarisation, is equal to the molecular refraction for light of infinite wave-length (see Part XV; *J.*, 1932, 430).

Apparatus, and Method of Calibration.—A circuit diagram of the apparatus used for measuring the dielectric constants of the hydrocarbons and of their solutions is shown in Fig. 1. The arrangement is similar in essentials to that employed by Whiddington (*Phil. Mag.*, 1920, **40**, 634), except that a dielectric cell of fixed dimensions is employed. *A* is a valve oscillator comprising a Marconi DEL 210 valve with 2.0 volts applied to the filament and 100 volts to the

* Owing both to rotation (with possible dependence of the average spatial configuration on existing experimental conditions) and to the variability of the proportion of geometrical isomerides in different specimens.

anode; a_1 and b_1 are inductances, and c_1 a variable condenser, the maximum capacity of which is $500 \mu\text{F}$. The frequency of the oscillations generated is 2×10^5 p.p.s. B is a similar oscillator, the condenser c_2 being a Sullivan standard condenser of maximum capacity $1200 \mu\text{F}$ with a vernier adjustment permitting a rough estimate of the second decimal place with the aid of a lens. In order to eliminate the effect of the capacity of the operator, c_2 is controlled by an insulated handle about 4' long. The moving plates of this condenser are connected to the case of the condenser and to the filament end of the inductance a_2 . The dielectric cell, d , can be connected in parallel with the standard condenser by the switch, s , which is virtually a mercury contact connexion to the inside silver film of the cell, and this can be made by very slight movement of the wire so that the change in capacity is independent of external effects. A valve amplifier, C , is used to amplify the heterodyne note, so that a comfortably audible signal is produced by the loud speaker, l . The thermostat and all clamps, etc., are earthed.

With the switch, s , open, the oscillator is tuned by the condenser, c_2 , until the heterodyne note in the loud speaker (the frequency of which increases with an increase in capacity of c_2) becomes identical in pitch with that of a valve-maintained tuning fork of 1000 p.p.s. The reading of c_2 is noted. The switch is then closed and the oscillator again tuned by means of the condenser, c_2 , to the same frequency as before. The reading of c_2 is again noted. The capacity of c_1 is then slightly changed, and another similar pair of readings taken: this procedure is repeated 6—8 times. The average decrease in the capacity of c_2 (calibration corrections being made for all readings) gives the capacity of the dielectric cell, d , together with a small capacity Σc due to the leads, etc.

By using benzene ($n_D^{20} 1.5012_4$; $n_D^{25} 1.4979_6$) purified by the method of Williams and Krchma

FIG. 1

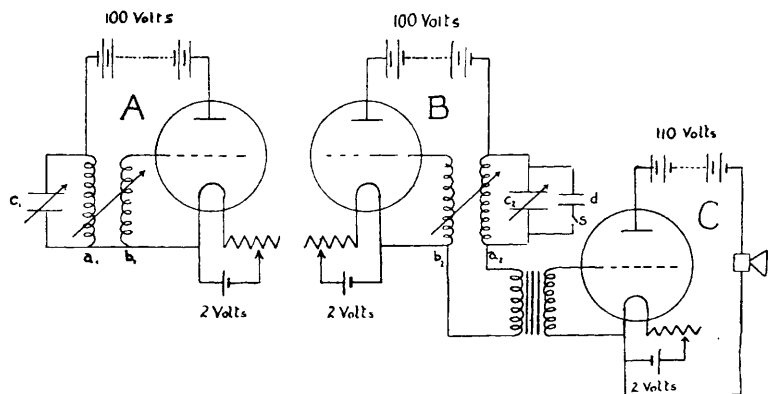
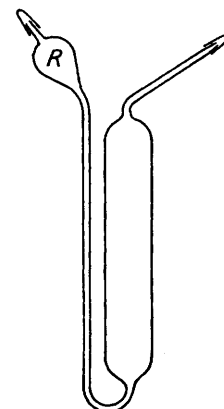


FIG. 2.



(*loc. cit.*) as a standard ($\epsilon^{25} = 2.273$; Hartshorn, *Proc. Roy. Soc.*, 1929, A, 123, 664), the value of the capacity, Σc , was ascertained and allowed for in all subsequent measurements.

Capacity (μF) of dielectric cell containing

Cell.	air.	benzene.	Σc , μF .
I	87	186	1.2
II	89	190	1.5
III	120	280	0.9

The assumption that this value was constant over the range employed appeared justified from the determined value of the dielectric constant for petroleum hexane ($\epsilon^{25} = 1.911$) which is in agreement with that found by Ball (J., 1930, 570) for the same sample.

Density Determination.—The type of pycnometer found to be most reliable for low-temperature determinations of density is shown in Fig. 2. It had a capacity of 25 c.c., and its two ends were closed with well-ground glass stoppers, and the axis of the pear-shaped reservoir R was inclined at such an angle to the vertical that the liquid ran down completely into the capillary tube. Final adjustment of the liquid under examination was made after the pycnometer had been in the thermostat for about 50 minutes, the steadiness of the liquid on the mark indicating that the temperature of the bath had been attained. The position of the reservoir R at the head of a long capillary tube conduced to rapid adjustment since the liquid which necessarily descended

into the capillary from the reservoir during adjustment rapidly attained the temperature of the bath.

The pycnometer was calibrated with boiled-out distilled water, and the coefficient of expansion of the glass (3.1×10^{-5}) determined by filling with pure mercury and weighing at a series of temperatures (compare Sugden, "The Parachor and Valency," p. 204).

The density determinations gave values which were accurate to 0.0001 for temperatures below 0°, but at higher temperatures the probable error was never greater than ± 0.00005 .

Low-temperature Thermostat.—The thermostat was of the type described by Walters and Loomis (*J. Amer. Chem. Soc.*, 1925, **47**, 2302), modified as follows: (1) The Dewar flask was made of glass and not spun copper. (2) A head of mercury was used instead of a head of water, the level of mercury being sufficiently adjustable to give the desired flow of liquid air through the cooling worm of the thermostat whilst at the same time permitting relief of excess pressure by the escape of air through the mercury; a small rubber press-bulb attached to the liquid-air container allowed the desired internal pressure to be attained rapidly. (3) The enamelled copper wire used for the electrical heating coil was wound round a piece of glass rod, the turns of wire being separated by cotton thread. This was found to be a much safer device than that afforded by winding the wire round a strip of mica, since the latter arrangement tended to produce kinks in the wire which occasionally produced arcing.

The Dielectric Cell.—The cell used in these determinations, illustrated in Fig. 3, is based on that used by Dr. A. O. Ball (*loc. cit.*, Fig. 5), to whom the authors are indebted for invaluable advice and initial help. The cell was thoroughly cleaned with fuming nitric acid, washed with grease-free distilled water, and, without being allowed to dry, immediately silvered by allowing the silvering solution * to run in down the side tube *A* until the cell was filled to the mark *B*.

DISCUSSION OF RESULTS.

$\beta\gamma$ -Dimethylbutadiene.—The curve $P_{\infty} = a + b/T$ gives a negative value for *b*, and this finds no interpretation in Debye's equation for the calculation of the polar moment; but at very low temperatures the increase of P_{∞} with temperature ($P_{\infty} = 30.97$ c.c. at -75° ; 31.00 c.c. at -50°) is very small and lies within the limits of experimental error, whilst the actual values are almost identical, as is shown in Fig. 4, with that observed in benzene solution at 25° ($P_{\infty} = 31.02$ c.c.; see following paper). It is concluded that the anomaly is due to the polymerisation of the hydrocarbon during the heating of the solution from -75° to 25° (a time interval of about 10 hours, since approximately 2 hours were required for measurements at each temperature), and that within the limits of the experiment, the polarisation at infinite dilution is independent of temperature.

β -Methylbutadiene.—The curves obtained by plotting $P_{1,2}$ against f_2 are nearly straight lines over the range of temperature -75° to -25° , so it is justifiable to use the polarisation values of the pure hydrocarbon for the calculation. Increase in P_{∞} is again observed at the higher temperatures, and on the assumption that these increases also are due to polymerisation, the high-temperature values are rejected.

$\alpha\alpha$ -Dimethylbutadiene.—The analysis of the data in this instance is less obvious even after recalculation on the assumption, justified by the curve representing experimental observations, that over the range of dilution measured, the dielectric constant is a linear function of dilution. It is apparent from the $P_{1,2}$ - f_2 curve, however, that there is very little association, and values for the polarisation of the hydrocarbon in the pure state and at infinite dilution lead to the same figure for the polar moment. The extrapolation, however, of the line $P = a + b/T$ in the derivation of *a* is of more doubtful character and gives an atomic polarisation twice that found for $\beta\gamma$ -dimethylbutadiene; but this extrapolation must be less accurate than that of the latter hydrocarbon for which *b* is zero. As the difference in P_A between β -methyl- and $\beta\gamma$ -dimethyl-butadiene is of the same low order of magnitude as

* The silvering solution was that in use at Leiden University for silvering Dewar vessels. **Solution A.** Pure silver nitrate (6 g.) is dissolved in water (70 c.c.) and ammonia added until the precipitate is redissolved. Then 3% caustic potash solution (70 c.c.) is added and the precipitate again redissolved by addition of ammonia; the whole is diluted to 500 c.c. and a few drops of dilute silver nitrate solution added to render the liquid slightly turbid. **Solution B.** Glucose (6 g.) is dissolved in water (30 c.c.), and the solution boiled after addition of 4 drops of concentrated nitric acid. After cooling, alcohol (12.5 c.c.) is added and the whole is diluted to 500 c.c. with water. 10 Parts of solution A are mixed with 1 part of solution B, and allowed to stand.

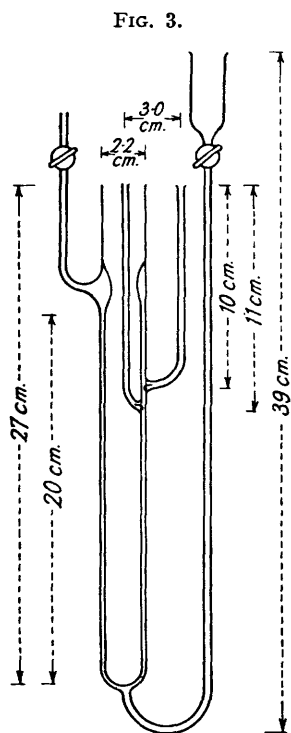


FIG. 3.

Dielectric constant, density, and polarisation data for solutions of the hydrocarbons in synthetic n-hexane.

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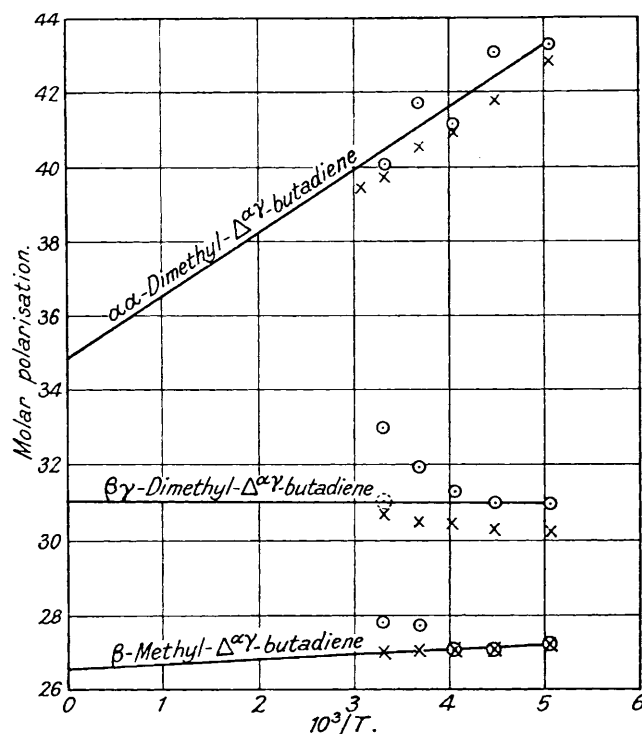
the difference found by Dornte and Smyth (*J. Amer. Chem. Soc.*, 1930, **52**, 3546) to hold between the members of the paraffin-hydrocarbon series, the value of P_A obtained for $\beta\gamma$ -dimethylbutadiene is used in preference to that derived from the doubtful value of a , referred to above, in calculating the dipole moment of other dialkylbutadienes (succeeding paper).

The following table gives the characteristic constants :

Butadiene.	a , c.c.	P_E , c.c.	P_A , c.c.	b .	$\mu \times 10^{18}$, e.s.u.
β -Methyl-	26.54	24.20	2.34	130	0.15
$\alpha\alpha$ -Dimethyl-	(34.9)	29.36	(5.5)	1700	0.52
$\beta\gamma$ -Dimethyl-	31.00	28.50	2.50	0	0.0

The values obtained for the dipole moment would seem to indicate that alkyl substitution at the α -carbon atom of a butadiene chain causes a greater permanent polarisation of

FIG. 4.
Polarisation-temperature curves of hydrocarbons in synthetic n-hexane.



Values of the polarisation of the hydrocarbons at infinite dilution (P_∞) are indicated by \odot and values of the polarisation of the pure hydrocarbons (P_2) by \times . The point \odot represents a value of P_∞ measured in benzene solution.

the molecule than similar substitution at the β -carbon atom. In addition, any small permanent moments which may characterise the two halves of the molecule in $\beta\gamma$ -dimethylbutadiene (in the sense that $\text{CHEt}:\text{CH}_2$ possesses a small moment) must be opposed directionally or otherwise neutralised, since this hydrocarbon has zero moment.

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