251. *The Determination of Dipole Moments in the Vapour Phase. Part I. An Improved Apparatus.* By L. G. Groves. *Part II. The Moments of Alkylbenzenes and Alkyl*cyclo*hexanes.* By J. W. Baker and Leslie G. Groves.

(Part I.) A heterodyne apparatus is described which employs stabilised matched Hartley oscillators, electronically coupled, the resultant frequencies of which are constant over extended periods to within about 5 parts per million.

The gas cell is vapour-jacketed, and the changes in capacity due to introduction of dielectric gases and vapours are measured by direct parallel replacement on a specially constructed micrometer variable condenser.

The beat frequency is observed as a simple Lissajous figure on a cathode-ray oscillograph using the 50-cycle mains as time base.

(Part II.) The dipole moments of toluene, ethyl-, *iso*propyl-, and *tert.*-butylbenzene, accurately determined in the vapour phase by the method described in Part I, are, respectively, 0·37, 0·58, 0·65, and 0·70 D; that of *p-tert.*-butyltoluene is 0·39 D, in good agreement with the value (0·33) deduced from the moments of toluene and *tert.*-butylbenzene. All the corresponding alkyl*cyclo*hexanes have zero moments in the vapour phase.

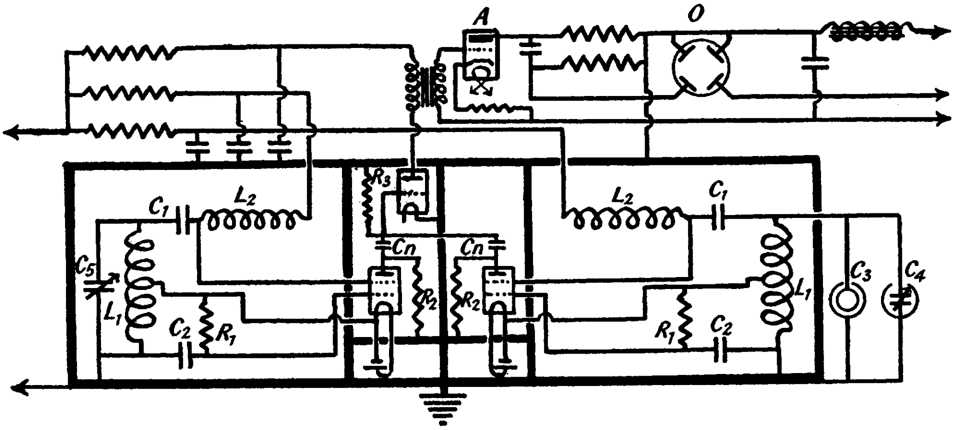
Part I.

Experience of the measurement by high-frequency methods of the small changes in capacity normally associated with determinations of the dielectric constants of gases and vapours has shown that the limiting factor for accurate measurement is the " drift " of frequency (and in some cases, amplitude) of the emitted oscillations during the time occupied in making one measurement. Such variations may be limited to two main sources, *viz.*, temperature coefficients of components of the oscillating circuits and variations in supply voltages to the valves.

Owing to the extreme difficulty of eliminating amplitude variation, attention has been confined to the heterodyne method, and in an attempt to eliminate the first of the above two factors, it has been the aim to co-ordinate lay-out rather than to incorporate components of low temperature coefficent, as the latter procedure is of little value unless temperature compensation of every component is uniform. There is no gain in over-all stability by crystal-controlling, or otherwise stabilising, the fixed-frequency oscillator alone. The two oscillators have been constructed as mirror images of one another and of as closely identical components as possible except for the rough tuning capacity (C_5) and the gas cell (C_3), and with the exception of the valves they are contained in similar aluminium boxes. The valves are housed in perforated zinc boxes, sandwiched in between the aluminium boxes, and are of 2-volt battery type to keep heat production low. The perforated valve-screening boxes are excellent heat dissipators by ventilation, and lateral conduction to the main components is negligible. Filament accumulators are stood on ebonite in biscuit tins which, together with the oscillator and valve screening boxes, rigidly interconnected, are covered with expanded rubber heat-insulating material. The apparatus is situated on a stone bench in a basement room which is virtually an air thermostat, and local temperature gradients in the gas cell have been eliminated by jacketing with vapour from liquids boiling under atmospheric pressure.

The almost complete removal of factors affecting purely electrical stability, *viz.*, the effect of supply voltage variations on the characteristics of the valves and the effect of load conditions on the functioning of the oscillators, has been obtained by incorporating the principles developed by Llewellyn (*Proc. Inst. Rad. Eng.*, 1931, **19**, 2063) and Dow (*ibid.*, p. 2095). Llewellyn considers the network formed by various oscillating circuits of the Hartley and Colpitts type, and derives an expression for the natural frequency of oscillation such that no physical constants of the valve other than the interelectrode capacities appear in it. The practical implication of this is that variations of amplification factor or of grid- or plate-circuit resistance in the valve do not affect the frequency of oscillation, and these principles are brought into action by the insertion of stabilising condensers in the plate and grid circuits, the magnitudes of which require to be calculated from values from the inductance and capacity in the tuned circuit.

Fig. 1.



L_1 = 170 μH. (104 *turns of* 26 *S.W.G. copper wire,* 4 *cm. diam.*). L_2 = H.F. *choke.* C_1 = 0·0003 μF. C_2 = 0·001 μF. C_3 = *Gas cell.* C_4 = *Micrometer condenser.* C_5 = 0·00015 μF. (*max.*). R_1 = 25,000 *ohms.* R_2 = 10^5 *ohms.* R_3 = 1 *megohm.* C_n = *Electron coupling condenser.* A = *Amplifier.* O = *Oscillograph.*

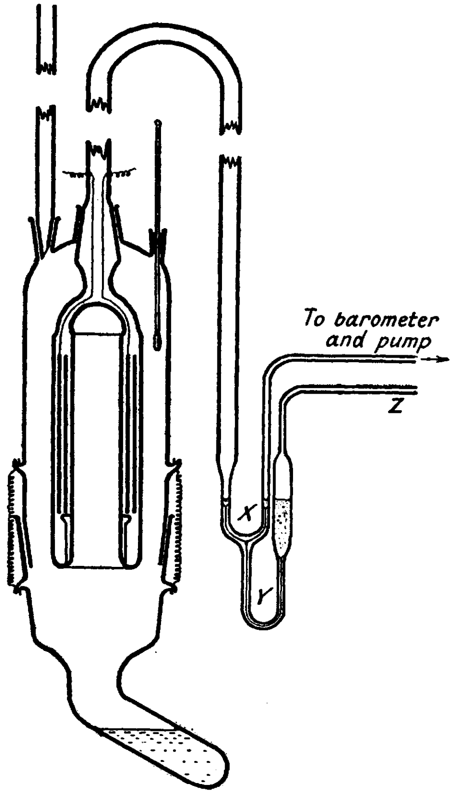
A modification of Dow's electron-coupling system serves to mix the two high-frequency oscillations in the grid circuit of the rectifier. The distinctive feature of this arrangement is that the load is applied in the anode circuit of a screened-grid valve, the screening grid of which is functioning as anode of a triode oscillator formed with the remaining two electrodes, and in Dow's original arrangement an accelerating potential is applied to the anode.

The H.F. voltage is fed to the rectifier through a small condenser C_n which should satisfy the relation $C_n = C_r \, . \, C_g/C_p$, where C_r = capacity between the screening grid and anode, and C_g and C_p are the grid and the plate circuit capacities. Adequate pick-up from each osicillator may be obtained, however, by dispensing with the accelerating voltage and joining the anodes to earth through resistances, the connexions to the grid of the rectifier then being made through two small condensers as in the original Dow arrangement. This method of coupling reduces the tendency for the oscillators to lock, and eliminates effects due to load variation.

The high-frequency feed leads from the small condensers are directly connected to the grid of a triode rectifier which is situated in one of the perforated screening boxes, the output from which, after one stage of amplification, is fed to one pair of deflecting plates of the oscillograph. Time base is supplied to the other pair from the 50-cycle A.C. mains, and any conveniently recognised Lissajous figure may be used as zero point. In practice the circle or ellipse from a 50-cycle beat frequency is the most suitable figure to use, but it is noteworthy that a heterodyne of 10 cycles can be reached before tendency to locking between the two oscillators sets in.

The complete apparatus gives remarkable frequency stability provided the temperature of the room remains sensibly constant, the normal variation between the two oscillators (of natural frequency about 1 megacycle) being ± *ca.* 3 cycles over periods of several hours, and being indicated by occasional slow rotation of the pattern in alternate directions.

FIG. 2.



The oscillators are quite insensitive to deliberately imposed variations in screening grid voltages which are derived directly, through decoupling, from the D.C. mains. The oscillograph is supplied from the A.C. mains by means of a Westinghouse rectifier used as voltage doubler, the higher-potential half of which also supplies the amplifier valve. The circuit, complete except for standard technical details, is shown in Fig. 1.

The original gas cell as used by Groves and Sugden (J., 1934, 1094) has been modified to permit of accurate thermostatic control and is shown in Fig. 2. The liquids employed, *viz.*, chloroform, carbon tetrachloride, *n*-heptane, *n*-butyl alcohol, xylene, *cyclo*hexanol, aniline, benzyl alcohol, and thymol, are boiled electrically at the bottom of the outer vessel, which is heavily lagged, and the tip of the air condenser is disposed so that refluxed liquid runs down the inside of the outer jacket. An electrically heated tube connects the cell to the source of vapour, which is similar to that used by Groves and Sugden (*loc. cit.*) except that the additional U tube (*Y*) allows the liquid under investigation to be withdrawn from the U tube (*X*) by reduction of pressure *via Z*.

Direct pneumatic connexion is thus obtained between the vapour in the cell and air in the barometer, and no correction is necessary for difference in liquid levels at *X*.

Condensation does not occur with this procedure as the bend of *X* (1 mm. capillary) becomes filled with air, which, however, does not diffuse into the body of the cell because of the volume and length of the connecting tube.

Change in capacity of the gas cell is measured directly by parallel replacement with the micrometer variable condenser (Fig. 3), which is constructed from a micrometer head (Brown and Sharpe) and precision-turned brass tubing; these two components, of external and internal diameter respectively 5·969 and 8·044 mm., and insulated from one another with amber, form the electrodes and are enclosed in an earthed screen, the micrometer head and rod being also earthed. Change in capacity is thus directly proportional to micrometer reading, provided that the end of the moving rod be always remote from the open end of the tube.

The condenser was calibrated by measurement of the relevant diameters and lengths, the internal diameter of the brass tube being further checked for uniformity by a determination of its volume by weighing in water. Proof of linearity was provided by checking the capacity change required to compensate for change in heterodyne frequency from circle to circle on the oscillograph (*i.e.*, 100 cycles) at different parts of the condenser scale.

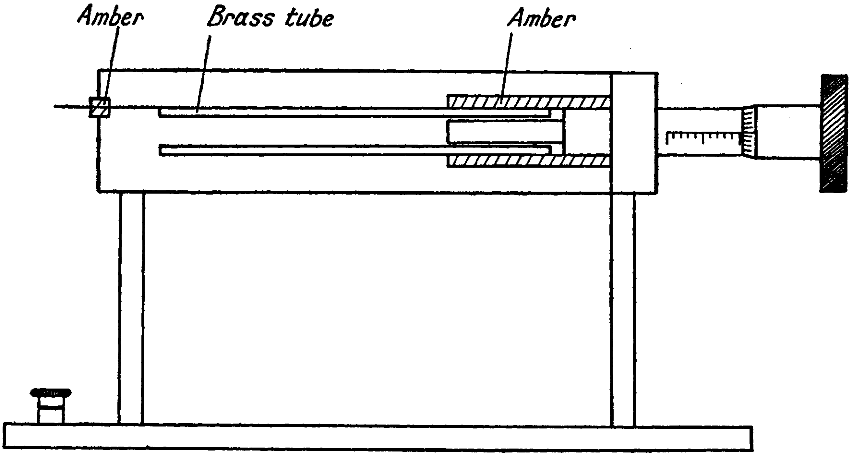
The condenser constant was 1·862 μμF. cm.$^{-1}$, and the micrometer reading can be estimated to 10^{-4} cm., equivalent to 2×10^{-4} μμF.

The method of making measurements is similar to that used by Groves and Sugden (*loc. cit.*) except that, before each pressure reading, the liquid is just withdrawn from *X* by a slight reduction in pressure through *Z* (Fig. 2).

PART II.

ACCURATE values of the dipole moments of the various alkylbenzenes have great significance in relation to the complicated problem of the relative electron-release capacities of alkyl groups. Since the differences in polarisation between the various alkylbenzenes are likely to be small, it is important that any complications which arise in solution measurements should be avoided. Advantage has accordingly been taken of the greatly improved technique, described by one of us in Part I, to obtain reliable values for the dipole moments of the alkylbenzenes (and the corresponding alkyl*cyclo*hexanes) in the vapour phase. The values obtained are tabulated below:

FIG. 3.



Dipole moments of PhR *in the vapour phase.*

R	Me	Et	Pr$^{\beta}$	Bu$^{\gamma}$
μ, D........................	0·37	0·58	0·65	0·70

Methyl-, ethyl-, *iso*propyl- and *tert.*-butyl-*cyclo*hexanes all have zero moment.

EXPERIMENTAL.

Purification of Materials.—*Toluene.* The pure sample used by Ingold, Rothstein, Lapworth, and Ward (J., 1931, 1959) was again dried over sodium for 3 days and fractionated over sodium through a long column in an all-glass apparatus; the fraction, b. p. 111·0°/761·7 mm., was again distilled over sodium to give the sample used, b. p. 110·9°/756·5 mm.; $n_D^{20^\circ}$ 1·4951 (lit.; b. p. 110·8°/760 mm.; $n_D^{20^\circ}$ 1·4962).

Ethylbenzene. A commercial sample (Messrs. British Drug Houses, Ltd.) was repeatedly shaken with concentrated sulphuric acid until the acid was no longer coloured, well washed with water, aqueous sodium carbonate, and again with water, and dried over calcium chloride. The fraction, b. p. 136—137°/767 mm., obtained by fractionation through a column in an all-glass apparatus was twice frozen with liquid air, partly melted, and the liquid fraction decanted and rejected. The crystalline material (25% of the whole) was dried over calcium chloride, refluxed over sodium for one hour, and fractionated. The portion, b. p. 136·1°/745 mm., was again refluxed and fractionated over sodium, a column and bath being used, and a sample, b. p. 135·5°/737·4 mm., $n_D^{20°}$ 1·4959, was thus obtained. Repetition of this treatment gave the sample used, b. p. 136·0°/740·5 mm. with unchanged refractive index (lit.; $n_D^{20·2°}$ 1·4959).*

iso*Propylbenzene.* A sample obtained from Messrs. Boots Ltd. was similarly treated except that the earlier distillations were carried out under reduced pressure. The fraction, b. p. 44°/15 mm., was purified as above by freezing (twice) and distillation over sodium to give, finally, a sample, b. p. 152·5°/750·6 mm., $n_D^{20°}$ 1·4914 (lit.; b. p. 152·6—152·8°/759 mm., $n_D^{20°}$ 1·4930), unchanged by further treatment.

tert.-*Butylbenzene.* Similar purification of a sample from Messrs. Kodak Ltd. gave a fraction, b. p. 54·5—56°/15 mm., which, by subsequent treatment as above, afforded the sample used, b. p. 170·0°/772 mm., $n_D^{20°}$ 1·4929 (lit.; $n_D^{20°}$ 1·4969).

p-tert.-*Butyltoluene.* A sample, b. p. 74°/14 mm., prepared (by Verley's method) for previous investigations (Baker and Nathan, J., 1935, 1840) was similarly purified to give, finally, a sample, b. p. 189·8°/746 mm.; $n_D^{20°}$ 1·4922.

*Methyl*cyclo*hexane.* A sample from Schuchardt, distilled over sodium, b. p. 101°/730 mm., was hydrogenated in emulsion in dilute acetic acid by means of Adams's catalyst. No appreciable absorption of hydrogen occurred in 24 hours. After removal of the catalyst, the product was neutralised with sodium carbonate, extracted with pure ether, and the extract well washed with aqueous sodium carbonate and water, and dried over anhydrous potassium carbonate. The residue obtained after removal of the ether through a column was repeatedly fractionated over sodium, a short column and a bath being used, to give finally a sample, b. p. 101·2°/746 mm., $n_D^{20°}$ 1·4230 (lit.; $n_D^{20°}$ 1·4235).

*Ethyl*cyclo*hexane.* Ethyl*cyclo*hexylcarbinol, b. p. 65—68°/10 mm., prepared in the usual manner from 39·2 g. of pure *cyclo*hexanone, 44 g. of ethyl bromide, and 9·6 g. of magnesium in 150 c.c. of ether, was dehydrated by heating with 10—20 g. of powdered zinc chloride on a water-bath for 0·5 hour. 1-Ethyl-Δ^1-*cyclo*hexene, isolated in the usual manner by ether extraction, was obtained (22 g.) with b. p. 135°/747 mm. after fractionation over sodium. The unsaturated hydrocarbon (11 g.) was readily reduced by hydrogen and Adams's catalyst in an emulsion with a few c.c. of aqueous acetic acid at room temperature (H_2 absorbed, 2300 c.c. Calc.: 2240 c.c.). The united products from two runs, obtained by ether extraction from the neutralised reaction mixture after removal of the catalyst and drying with potassium carbonate, were fractionated over sodium (column and bath). The fraction, b. p. 130·5—131°/731 mm. (15 g.), was shaken with aqueous sodium carbonate and 3% potassium permanganate and, after standing for several days, was extracted with ether, washed, dried, and repeatedly fractionated over sodium. The sample used had b. p. 131·2°/742 mm., $n_D^{20°}$ 1·4332 (lit.; $n_D^{20°}$ 1·4324).

iso*Propyl*cyclo*hexane.* This was obtained by catalytic reduction of *iso*propylbenzene (12 g.) in an equal volume of dilute acetic acid, Adams's catalyst being used. The product, isolated as above, was rehydrogenated with fresh catalyst (no appreciable absorption of hydrogen) and purified in the same manner. The sample used had b. p. 151°/753·5 mm., $n_D^{20°}$ 1·4440.

tert.-*Butyl*cyclo*hexane.* The sample, b. p. 55°/14 mm., obtained by the initial hydrogenation of *tert.*-butylbenzene was again hydrogenated and isolated and purified in the same manner to give a specimen, b. p. 168·2°/752 mm., $n_D^{20°}$ 1·4468 (lit.; b. p. 166—167°, $n_D^{16°}$ 1·4556).

In all cases before determination of the dipole moments the final specimens were left sealed over fresh sodium for approximately two years, during which period the sodium remained bright.

Calibration of Gas Cell Capacity.—The cell was calibrated with dry air and carbon dioxide, and the value for the replaceable capacity (C_0) further checked by a measurement with chlorobenzene vapour derived from some of the material used in the determination of its polarisation in the vapour state. The values taken for the three polarisations were 4·368, 7·317, and 82·55 c.c. (at 369·9° K.) for air, carbon dioxide, and chlorobenzene respectively (cf. Groves and Sugden, J., 1934, 1095).

From the relations $\varepsilon - 1 = \delta C/C_0$, where δC = increase in capacity of the cell upon

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* Determination of $n_D^{20°}$ (Abbé refractometer) was used as a joint control, with the b. p., in the final stages of purification. The final values sometimes differ slightly from those in the literature, but since no corresponding redeterminations of $d_D^{20°}$ were carried out, they have not been employed in the calculation of P_E. In any case the differences which would be introduced in the value of μ are of the same order as the experimental error.

admission of a dielectric of constant ε, and $P = (\varepsilon - 1)\mathbf{R}T/3p$, where T = absolute temperature and p = pressure of the dielectric vapour, we have $C_0 = 10^5 T.\delta C/4{\cdot}81Pp$, and as $\delta C = 0{\cdot}1862x$ μμF., where x = micrometer reading in mm. (cf. Part I), $C_0 = 3871xT/Pp$.

Gas.	T, °K.	p (mm.).	x (mm.).	C_0 (μμF.).
Air	292·0	764·2	0·364 *	123·6
Carbon dioxide	292·0	764·7	0·611 †	123·6
Chlorobenzene	369·9	165—190	1·169—1·345 ‡	123·2

* Mean of 8 determinations. † Mean of 6 determinations. ‡ 4 Determinations within this range.

The value taken for C_0 is 123·6 μμF., and substitution in the last equation gives $P = 31{\cdot}32Tx/p$, which is the equation used for all subsequent calculations of the total polarisations.

In the determinations which follow, all the vapour pressures used gave readings for x in excess of 0·250 mm. This figure was approximately that required to give the 100-cycle change in frequency quoted in Part I and was known to be reproducible to ± 0·001 on any part of the condenser scale. It is therefore a suitable minimum permissible reading, as its determining accuracy for P is still slightly better than 1%.

The following is a summary of the data obtained, all values of μ being in Debye units (e.s.u. × 10^{-18}).

Alkylbenzenes.

Toluene.

T, °K.	Pressure range, mm.	Mean P, c.c.	μ.
349·4°	80—105	33·2	
370·2	165—175	33·1	0·37
412·0	185—285	32·8	
456·0	175—210	32·7	

The Debye-curve equation calculated by the method of zero sum gives μ = 0·37 and P_{A+E} = 30·8 c.c.

*iso*Propylbenzene.

T, °K.	Pressure range, mm.	Mean P, c.c.	μ.
349·2 *	—	—	—
369·0	55— 80	52·8	(0·75)
411·0	135—230	49·7	0·66
455·0	90—135	48·7	0·64
		Mean	0·65

The moments are calculated individually, it being assumed that P_{A+E} = 1·05, P_E(D) = 43·1 c.c. (Groves and Sugden, J., 1935, 971). The result at 369·0° is probably too high on account of saturation pressure effect.

Ethylbenzene.

T, °K.	Pressure range, mm.	Mean P, c.c.	μ.
349·0°	70— 80	41·8	
369·6	80—100	41·5	0·58
411·5	110—130	40·9	
455·0	110—135	40·4	

The Debye-curve equation calculated by the method of zero sum gives μ = 0·58 and P_{A+E} = 35·8 c.c.

tert.-Butylbenzene.

T, °K.	Pressure range, mm.	Mean P, c.c.	μ.
412·0	75— 95	58·1	(0·85)
456·0	100—170	54·5	0·73
477·0	70—135	53·5	0·68
		Mean	0·70

P_{A+E} (calc. as for $PhPr^{\beta}$) = 47·3 c.c. The result at 412·0° is probably too high for the same reason.

p-tert.-Butyltoluene.

T, °K.	Pressure range, mm.	Mean P, c.c.	μ.
477·0	128·1	63·5	
,,	116·9	60·5	
,,	102·3	58·1	
477·0	75·8	56·0	
,,	Zero pressure	54·4 (Extrapolated)	0·39

P_{A+E} (calc. as above) = 52·4 c.c. Results at lower temperatures showed pronounced saturation pressure effect.

*Alkyl*cyclo*hexanes.*

Methyl*cyclo*hexane.

370·0	100—140	33·0	0
455·5	110—165	33·0	

Ethyl*cyclo*hexane.

369·7	95—140	39·9	0
455·5	95—140	40·0	

*iso*Propyl*cyclo*hexane.

390·5	70	43·3	0
455·5	100—115	43·3	

tert.-Butyl*cyclo*hexane.

411·0	65— 95	49·9	0
455·5	80—110	49·9	

* Smallest pressure giving satisfactory x was too near saturation.

Discussion of Results.

Our value of μ for toluene agrees exactly with that obtained in the vapour phase by McAlpine and Smythe (*J. Amer. Chem. Soc.*, 1933, **55**, 453). No previous data are available for the values of μ of the other alkylbenzenes in the vapour phase. Le Fevre, Le Fèvre, and Robertson (J., 1935, 480), from measurements in solution, obtained $\mu = 0{\cdot}53$ for *tert.*-butylbenzene, a value considerably lower than that (0·70) which we have obtained in the vapour phase. The higher value is in better agreement with that observed for *p-tert.*-butyltoluene, for which these authors obtained $\mu = 0{\cdot}35$, in good agreement with our value of 0·39 in the vapour phase and with the value calculated from our data for toluene and *tert.*-butylbenzene, *viz.*, $0{\cdot}70 - 0{\cdot}37 = 0{\cdot}33$. The value of μ for *p-tert.*-butyltoluene is thus not " unexpectedly high " and requires no special explanation such as that suggested by Le Fèvre *et al.* The validity of the additive principle in this case justifies its application to other *p*-dialkylbenzenes, and its application gives the values $\mu = 0{\cdot}28$ $(0{\cdot}65 - 0{\cdot}37)$ and $\mu = 0{\cdot}21$ $(0{\cdot}58 - 0{\cdot}37)$ for *p*-cymene and *p*-ethyltoluene, respectively. These values are again somewhat higher than those observed by Le Fèvre *et al.*, *viz.*, 0·15 and 0·12 (or " zero within the experimental error ") in solution.

As expected, the corresponding alkyl*cyclo*hexanes all possess a zero moment, thus indicating that the dipoles in the alkylbenzenes arise from the polar effect of the alkyl groups upon the aromatic electronic system.

The significance of the new data in the elucidation of the polar effects of alkyl groups is discussed by one of us in the following paper.

One of us (L. G. G.) wishes to thank Dr. A. E. Martin, of the Government Laboratory, for advice in connexion with the development of the design of the apparatus, Dr. A. Müller, of the Royal Institution, for the loan of a condenser which led to the design finally adopted, and Dr. J. J. Fox, C.B., O.B.E., for facilities to carry out the work. The other (J. W. B.) thanks the Royal Society for a grant.

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