107. *The Dipole Moments of* p-*Cymene ; 2- and 3-Halogeno*-p-*cymenes, Carvacrol, and Thymol ;* p-*Ethyltoluene ;* p-tert.-*Butyltoluene, 1 : 3-Dimethyl-5-*tert.-*butylbenzene,* tert.-*Butylbenzene and its* p-*Nitro-derivative.*

By CATHERINE G. LE FÈVRE, RAYMOND J. W. LE FÈVRE, and (in part) KATHLEEN W. ROBERTSON.

PREVIOUSLY (*Nature*, 1933, **131**, 655 ; *Chem. and Ind.*, 1933, **52**, 505) the following *a priori* conditions were regarded as sufficient to cause a 1 : 4-disubstituted benzene derivative to exhibit substitution phenomena at variance with expectations based on current theories alone : (*a*) that a marked difference in volume between the two groups should exist, (*b*) that the inductive effects of the competing groups should roughly compensate one another or be not very dissimilar, and (*c*) that electromerisations should not be unequally initiated or facilitated by the two radicals concerned.

A suitable compound for examination being a 1 : 4-dialkylbenzene, *p*-cymene was chosen (J., 1933, 680) rather than *p*-ethyl- or *p-tert.*-butyl-toluene because, although condition (*b*) most probably held for all three hydrocarbons, it was not certain that conditions (*a*) and (*c*) applied respectively to the second and the third. The following four sections deal with points of interest which arose when making this selection.

Section I. The Dipole Moment of p-*Cymene.*—In the preceding communications (*locc. cit.*), aromatic substitution, with particular reference to *p*-cymene, has been viewed in the manner commonly adopted in this country, *viz.*, that electrophilic (kationoid) reagents are effective by virtue of a constitutional affinity for electrons, and therefore attack most fruitfully those nuclear carbon atoms at which the necessary high electron densities can be developed; and that the electron-supply mechanisms, by which such alterations of electron distribution are achieved at the various points, can be, in the first analysis, subdivided into *permanent* and *temporary* polarisation effects within the molecule undergoing substitution.

In the absence of external activating influences (such as the fields of reagent molecules), a molecule will exhibit only the former effect, which can therefore be assessed by a determination of the dipole moment of the substance concerned.

The application to the case of cymene is easy, for if in this compound all electronic displacements arising from the methyl group are neutralised by those from the *iso*propyl radical, the resultant dipole moment should be zero * and the 2 : 6- and 3 : 5-positions equally activated. Whether or not this is the case cannot be decided owing particularly to the uncertainty of the dielectric constant data, reproduced in the following table. In col. 4 are shown the total polarisations, calculable by the usual Clausius–Mosotti formula from the appropriate values in cols. 2 and 3. These, combined with the calculated molecular refractivity (for Na_D light) of cymene would correspond to moments ranging from 0 to 1 Debye unit.

Dielectric Constant and Molecular Polarisation of p-*Cymene from Data in the Literature.*

Temp.	$d_{4^\circ}^{t^\circ}$.	ϵ.	P, c.c.	Temp.	$d_{4^\circ}^{t^\circ}$.	ϵ.	P, c.c.
15·58°	0·86004 [1]	2·231 [1]	45·31	18·00°	0·85875 [6]	2·43 [3]	50·37
17·24	0·85913 [1]	2·230 [1]	45·36			2·25 [4]	45·89
17·00	0·85949 [6]	2·26 [2]	46·11	176·5	0·7248 [5]	2·27 [2]	54·99

[1] Landolt and Jahn, *Z. physikal. Chem.*, 1892, **10**, 289. [2] Grimm and Patrick, *J. Amer. Chem. Soc.*, 1923, **45**, 2794. [3] Mathews, *J. Physical Chem.*, 1905, **9**, 641. [4] Nernst, *Z. physikal. Chem.*, 1894, **14**, 622. [5] Schiff, *Annalen*, 1883, **220**, 94. [6] Present work.

In view of these disagreements, we made the series of redeterminations recorded below.

Measurements.—The dielectric constants were measured by the resonance method described

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* The possibility of polarisation *within* the Pr^β group is small in view of the zero moment recorded for 1 : 4-diethylbenzene (Weissberger and Sängewald, *Physikal. Z.*, 1929, **30**, 792).

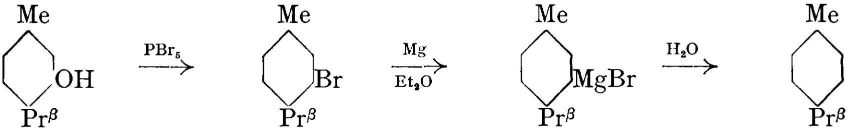
by J. W. Smith (*Proc. Roy. Soc.*, 1932, *A*, **136**, 251), modified in the one detail that a high tension voltage of 220 v. can be substituted satisfactorily for the 900 v. specified in this reference. We wish to acknowledge our indebtedness to Dr. J. W. Smith for help and advice in setting up the apparatus. A cell of the Sayce–Briscoe type, silvered by the recipe of Sugden—whose statements regarding the permanency of the silver film produced by this and other methods we confirm—was used in preference to other types. The experimental procedure followed is fully described in Smith's paper, where the methods of calculation are illustrated.

The refractive indexes were determined with a Pulfrich refractometer, a Phillips " Neron " lamp affording a convenient source of yellow light.

For the density determinations the Perkin modification of Sprengel's pyknometer (J., 1884, **45**, 421) was found to give better results than the usual Ostwald–Sprengel type, which could not be wiped so easily prior to weighing. The pyknometers were of *ca.* 10 c.c. capacity; the final densities should be accurate to 0·00001.

Materials.—The benzene and carbon tetrachloride were purified as described by Le Fèvre and Smith (J., 1932, 2239). The purity of the *p*-cymene used would appear to require comment. Von Auwers (*Annalen*, 1919, **419**, 114) has pointed out that certain physical properties (notably the refractive index) of this hydrocarbon vary according to the mode of preparation, so we therefore had to eliminate impurities which might themselves have a moment. Probable contaminants of this nature are (in synthetic products) *m*-cymene and (in commercial supplies from spruce turpentine) certain compounds (? terpenic hydrocarbons) which sometimes cause a slight optical activity. *m*-Cymene must have constituted a large part of the sample of " *p*-cymene " prepared by the Friedel–Crafts method examined by von Auwers (cf. Kelbe, *Annalen*, 1881, **210**, 25), and is probably never entirely absent from specimens obtained by the action of phosphoric oxide on camphor (cf. Armstrong and Miller, *Ber.*, 1883, **16**, 2259; these, in addition, are exceedingly difficult to free from the last traces of phosphorus compounds). Owing to their close b. p.'s, separation of the *m*- and the *p*-isomeride by fractional distillation is impossible.

We therefore first used material prepared from crystalline thymol by the following sequence :



This gave the pure hydrocarbon quite satisfactorily; but later we found that identical results were obtained by purifying a commercial specimen as described subsequently.

(a) *Preparation of Cymene from Thymol.*—Thymol (100 g.) was heated under reflux for 2 hrs. with phosphorus pentabromide (70 g.); water was then added, the mixture steam-distilled, the distillate extracted with ether, and the extract washed, dried (sodium sulphate), and distilled, 30 g. of 3-bromocymene, b. p. 130°/35 mm., being obtained. This compound (48 g.), dry ether (500 c.c.), and magnesium (6 g.) were refluxed together until solution was complete. Water in excess was then added slowly, followed by dilute sulphuric acid. The ethereal layer was separated, dried (calcium chloride), and distilled. The crude *p*-cymene obtained was once redistilled (column); b. p. 177—178°/760 mm. (yield, 22 g.).

(b) *Purification of Technical Cymene.*—Several litres (obtained from Messrs. Hopkin and Williams) were refluxed over powdered sulphur for 2 days, shaken with successive quantities of concentrated sulphuric acid until the latter was no longer coloured, then twice treated with a little chlorosulphonic acid, and subsequently (after a rough washing with water) with potassium permanganate solution, followed by dilute aqueous sodium hydroxide. Finally, the material was dried (sodium sulphate) and fractionated through a Dufton column; b. p. 177—177·5°/760 mm.; $d_{4^\circ}^{25^\circ}$ 0·85341, $n_D^{25^\circ}$ 1·48878.

Results.—The symbols used in the tables below have the usual significance, subscripts 1 and 2 referring to solute and solvent in cases where this is possible.

Molecular Polarisation of Liquid Cymene.

Temp.	$d_{4^\circ}^{t^\circ}$.	ϵ.	*P*, c.c.	Temp.	$d_{4^\circ}^{t^\circ}$.	ϵ.	*P*, c.c.
4°	0·87013	2·2653	45·68	40°	0·83970	2·1992	45·57
18	0·85875	2·2451	45·77	45	0·83588	2·1950	45·67
20·9	0·85643	2·2409	45·78	50	0·83205	2·1828	45·54
25	0·85341	2·2322	45·72	60	0·82439	2·1684	45·56

Molecular Polarisation of Cymene in Benzene Solution.

Temperature 25°.

$10^6 f_1$.	$M_1f_1 + M_2f_2$.	ϵ.	d.	$P_1f_1 + P_2f_2$.	P_2f_2.	P_1f_1.	P_1.
0	78	2·2725	0·87380	26·585	26·585	—	—
11,457	78·6416	2·2717	0·87351	26·802	26·280	0·522	45·57
18,188	79·0186	2·2713	0·87337	26·929	26·101	0·828	45·52
21,001	79·1761	2·2710	0·87335	26·979	26·027	0·952	45·32
24,011	79·3447	2·2708	0·87330	27·035	25·947	1·087	45·28
89,922	83·0357	2·2660	0·87320	28·221	24·194	4·027	44·78
195,086	88·9248	2·2583	0·87213	30·129	21·399	8·730	44·75

Whence P_1 extrapolated to $f_1 = 0$ is 45·62 c.c.

Temperature 45°.

$10^6 f_1$.	$M_1f_1 + M_2f_2$.	ϵ.	d.	$P_1f_1 + P_2f_2$.	P_2f_2.	P_1f_1.	P_1.
0	78	2·2333	0·85210	26·664	26·664	—	—
11,457	78·6416	2·2327	0·85199	26·882	26·359	0·523	45·62
18,188	79·0186	2·2325	0·85198	27·008	26·179	0·829	45·57
24,011	79·3447	2·2317	0·85170	27·116	26·024	1·092	45·47
89,922	83·0357	2·2270	0·84788	28·428	24·266	4·072	45·28
195,086	88·9248	2·2193	0·84840	30·290	21·462	8·828	45·25

Whence P_1 extrapolated to $f_1 = 0$ is 45·79 c.c.

Molecular Polarisation of Cymene in Carbon Tetrachloride.

Temperature 0°.

0	154	2·2748	1·63170	28·116	28·116	—	—
22,432	153·5514	2·2744	1·60598	28·507	27·485	1·0212	45·52
55,486	152·8903	2·2714	1·56491	29·081	26·556	2·5246	45·50
80,878	152·3824	2·2732	1·53818	29·517	25·842	3·6750	45·44
121,662	151·5668	2·2735	1·49489	30·214	24·695	5·5187	45·36

Whence P_1 extrapolated to $f_1 = 0$ is 45·61 c.c.

Temperature 20°.

0	154	2·2345	1·59402	28·1368	28·1368	—	—
22,432	153·5514	2·2350	1·56957	28·529	27·506	1·0234	45·62
55,486	152·8903	2·2371	1·53386	29·103	26·576	2·5269	45·54
80,878	152·3824	2·2385	1·50731	29·540	25·861	3·6792	45·49
121,662	151·5668	2·2402	1·46577	30·244	24·714	5·5307	45·46

Whence P_1 extrapolated to $f_1 = 0$ is 45·62 c.c.

The Dipole Moment of p-*Cymene.*—From the above results the total polarisation of *p*-cymene is 45·66 ± 0·04 c.c. According to accepted theories, this is the sum of the electronic, atomic, and orientation polarisations. The first of these equals the molecular refractivity for light of infinite wave-length, $[M_L]_\infty$, which is calculated as 43·6 c.c. from the following data (Landolt–Börnstein–Roth, 4th Edn., p. 1039) : M_α, 44·87 ; M_D, 45·18 ; M_β, 45·96 ; M_γ, 46·62 c.c. The atomic polarisation cannot be stated with certainty. If, following Debye (" Polar Molecules," 1929, p. 43), $P_E + P_A$ is assumed equal to the molecular refractivity for the D line, then $P_O = 45·66 - 45·18 = 0·48$ c.c., and $\mu = 0·01273(0·48 \times 298)^{1/2} = 0·15 \times 10^{-18}$ e.s.u.

A probably more accurate result can be obtained if the atomic polarisation of cymene be taken as equal to that of *p*-xylene (*i.e.*, 2 c.c. ; Smyth, *J. Amer. Chem. Soc.*, 1929, **51**, 2051 ; *J. Chem. Physics*, 1933, **1**, 247) rather than to 15% of P_E ; that such an estimate is evidently of the right order, follows from the fact that, although the atomic polarisation increases roughly with the number of atomic nuclei in a given series of molecules, yet the change from benzene to *p*-xylene is only 0·5 c.c. Thus $P_O = 45·66 - (43·6 + 2) =$ *ca.* 0, and μ is also zero. A similar conclusion must be drawn from the temperature invariance of the polarisation.

Confirmation of this value can be obtained from a comparison of the Kerr constant of cymene with that of benzene, because in such molecules where the electric moments lie along the axes of maximum polarisability, a parallelism is generally observed between the magnitudes of their Kerr constants (B) and their moments (cf. Briegleb and Wolf, *Fortsch. Chem.*, 1931, **21**, Part 3). Now B = (term due to anisotropy) + (dipole term)

(Debye, "Handbuch der Radiologie," **6**, Leipzig, 1925) and *p*-cymene, which has almost certainly * a greater anisotropy term than benzene, has a Kerr constant which is only slightly greater ($B = 15{\cdot}7$ instead of 12·1). The contrast with, *e.g.*, toluene is marked—even so small a moment as that found for this hydrocarbon ($\mu = 0{\cdot}4 \times 10^{-18}$ e.s.u.) corresponds to a Kerr constant ($B = 24{\cdot}3$) nearly double that of benzene. By inference, therefore, *p*-cymene must have a vanishingly small moment.

Section II. The Dipole Moments of 2- *and* 3-*Halogeno*-p-*cymenes, Carvacrol, and Thymol.*—The extent to which activation of the various nuclear carbon atoms by temporary polarisation effects can become operative during aromatic substitution will obviously vary with the reaction and other factors, and always be difficult to estimate. Cymene, however, offers a simplification in that not more than two pairs of equal positions are available for substitution, and information regarding only their *relative* activation is desired. An attempt was therefore made to deduce this from observations of the dipole moments of 2- and 3-chloro-, -bromo-, and -hydroxy-*p*-cymenes.

In these isomeric compounds the substituents are regarded as corresponding, in their polarising actions on the attached hydrocarbon structures, to the effective parts of the reagent molecules engaged in attacking the 2 : 6- and the 3 : 5-positions of cymene at some comparable stage, *before* substitution is completed *but* when propinquity has caused the polarisability of the hydrocarbon towards the particular point of address to become developed. Since the unsubstituted cymene molecule is non-polar (Section I), any observable differences of dipole moment between the 2- and 3-isomerides must be held to imply that during electrophilic reagent action either the 2- or the 3-nuclear position is likely to become more polarised, and hence achieve a greater activation, depending on which of each isomeric pair has the greater moment.

Materials.—2-Chlorocymene (for preparation, see J., 1933, 983), b. p. 216—217°/761 mm., $d_{4^\circ}^{17^\circ}$ 1·0208, $n_{\mathrm{D}}^{17^\circ}$ 1·51776, whence $[R_L]_{\mathrm{D}}$ 50·0 (Calc., 49·6). 3-Chlorocymene (for preparation, see J., 1934, 848), b. p. 120—122°/20 mm., $d_{4^\circ}^{18^\circ}$ 1·01799, $n_{\mathrm{D}}^{18^\circ}$ 1·51796, whence $[R_L]_{\mathrm{D}}$ 50·15. 2-Bromocymene (from direct halogenation of the hydrocarbon, see J., 1933, 981), b. p. 229—230°/765 mm., $d_{4^\circ}^{18^\circ}$ 1·26889, $n_{\mathrm{D}}^{18^\circ}$ 1·54162, whence $[R_L]_{\mathrm{D}}$ 52·8 (Calc., 52·5). 3-Bromocymene (from thymol, see J., 1934, 848), b. p. 235°/760 mm., $d_{4^\circ}^{18^\circ}$ 1·26865, $n_{\mathrm{D}}^{18^\circ}$ 1·54275, whence $[R_L]_{\mathrm{D}}$ 52·9. The thymol used had m. p. 50° and was not further purified.

Carvacrol was available only as commercial products obtained from an *Origanum* oil from Asia Minor; the most probable impurity would appear to be thymol, the separation of which from carvacrol is exceedingly difficult owing to close similarities in physical properties. The material used in the following determinations was prepared as follows: the commercial, completely alkali-soluble phenol, b. p. 230—240°/760 mm., was kept at − 10° for a day, a certain quantity of thymol crystallising, and the liquor was distilled through a long column, only the condensate of b. p. 237—237·5°/760 mm. being collected. That the substance still contained impurities was indicated by the fact that when a mixture of it (15 g.) with ethyl alcohol (250 c.c.), sodium hydroxide (8 g.), and *p*-nitrobenzoyl chloride (17 g.) was heated under reflux for an hour, the *p*-nitrobenzoyl ester afforded by the usual procedure solidified only after standing in a vacuum for some weeks, and then required crystallisation from alcohol before the m. p. reached the constant value, 50°. Hydrolysis of this purified ester afforded carvacrol which solidified in a freezing mixture (Jahns, *Ber.*, 1882, **15**, 815, gives m. p. 0·5—1·0°) and gave a phenylurethane as radiating bunches of needles, m. p. 132—133° (Goldschmidt, *Ber.*, 1893, **26**, 2086, gives 134—135°, and Gildemeister, *Arch. Pharm.*, 1895, **233**, 188, m. p. 140°). Similar treatment of the carvacrol used in the following work gave a phenylurethane, m. p. *ca.* 110°, not raised by several recrystallisations from various solvents. A rough mixed m. p. curve for the urethanes of carvacrol and thymol showed that this specimen would contain 20—30% of the thymol derivative.

Measurements.—These are given in the following tables, being summarised in the last.

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* Cymene cannot be regarded as less anisotropic than benzene. Experiments on the scattering of light show that benzene and toluene have practically the same anisotropy terms, the former possibly being slightly the smaller; for *p*-xylene, however, a definitely larger term is indicated (Ramakrishna Rao, *Indian J. Physics*, 1927, **2**, 61; Ramachandra Rao, *ibid.*, 1928, **3**, 21). The actual case of *p*-cymene does not appear to have been investigated.

Molecular Polarisation of 2-Chlorocymene in Benzene Solution.

10^6f_1.	$M_1f_1 + M_2f_2$.	ϵ.	$d_{4^\circ}^{25^\circ}$.	$P_1f_1 + P_2f_2$.	P_2f_2.	P_1f_1.	P_1.
0	78	2·2725	0·87380	26·5850	26·5850	—	—
8,432·1	78·7631	2·3041	0·87593	27·2447	26·3608	0·8839	104·82
22,181·5	80·0075	2·3548	0·87924	28·3094	25·9953	2·3141	104·33
32,803·6	80·9687	2·3939	0·88180	29·1292	25·7129	3·4163	104·14
34,993·0	81·1669	2·4022	0·88230	29·3024	25·6547	3·6477	104·24

Whence extrapolated P_1 for $f_1 = 0$ is 105·3 c.c.

Molecular Polarisation of 3-Chlorocymene in Benzene Solution.

1,842·4	78·1667	2·2785	0·87385	26·7298	26·5360	0·1938	105·19
5,168·3	78·4677	2·2906	0·87483	26·9799	26·4476	0·5323	102·99
11,245·7	79·0177	2·3096	0·87588	27·4147	26·2860	1·1286	100·36
17,063·3	79·5442	2·3301	0·87783	27·8347	26·1314	1·7034	99·83

Whence extrapolated P_1 for $f_1 = 0$ is 106·0 c.c.

Molecular Polarisation of 2-Bromocymene in Benzene Solution.

1,574·2	78·0802	2·2828	0·87498	26·7277	26·5445	0·1832	116·38
3,111·6	78·4199	2·2865	0·87618	26·8625	26·5036	0·3590	115·36
5,059·6	78·6826	2·2946	0·87721	27·0385	26·4518	0·5867	115·96
8,373·5	79·1297	2·3098	0·88025	27·3196	26·3637	0·9559	114·16

Whence extrapolated P_1 for $f_1 = 0$ is 116·6 c.c.

Molecular Polarisation of 3-Bromocymene in Benzene Solution.

2,383·0	78·3215	2·2826	0·87551	26·7913	26·5229	0·2684	112·63
5,179·0	78·6988	2·2943	0·87754	27·0291	26·4486	0·5805	112·09
6,246·2	78·8428	2·2985	0·87831	27·1170	26·4202	0·6968	111·56
6,991·0	78·9431	2·3017	0·87884	27·1821	26·4004	0·7817	111·82

Whence extrapolated P_1 for $f_1 = 0$ is 113·1 c.c.

*Molecular Polarisation of Carvacrol in Benzene Solution.**

13,258	78·9548	2·3169	0·87586	27·4994	26·2325	1·2669	95·56
14,037	79·0107	2·3193	0·87597	27·5496	26·2118	1·3378	95·30
18,668	79·3442	2·3344	0·87671	27·8623	25·0887	1·7736	95·01
28,902	80·0809	2·3680	0·87831	28·5554	25·8167	2·7387	94·76

Whence extrapolated P_1 for $f_1 = 0$ is 95·7 c.c.

*Molecular Polarisation of Thymol in Benzene Solution.**

13,256·3	78·9544	2·3158	0·87585	27·4837	26·2326	1·2511	94·75
16,096·6	79·1589	2·3275	0·87631	27·7103	26·1571	1·5532	96·49
21,143·0	79·5222	2·3417	0·87711	28·0175	26·0229	1·9946	94·34
30,006·5	80·1646	2·3705	0·87850	28·6146	25·7857	2·8289	94·28

Whence extrapolated P_1 for $f_1 = 0$ is 95·4 c.c.

*Refractivity Data for Carvacrol and Thymol in Benzene Solution at 25°.**

10^6f_1.	n.	n^2.	$R_1f_1 + R_2f_2$.	R_2f_2.	R_1f_1.	R_1.
0	1·49733	2·24200	26·1357	26·1357	—	—
			Carvacrol.			
13,258	1·49773	2·24320	26·4114	25·7891	0·6223	46·94
14,037	1·49775	2·24326	26·4283	25·7688	0·6595	46·98
18,668	1·49789	2·24367	26·5230	25·6478	0·8752	46·88
			Thymol.			
21,143·0	1·49791	2·24372	26·5711	25·5831	0·9880	46·73
30,006·5	1·49815	2·24444	26·7543	25·3499	1·4044	46·80

* With (Miss) K. W. Robertson.

Summary of Results.

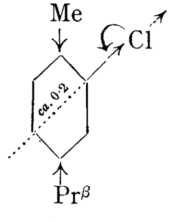
Substance.	Total polarisation, c.c.	Distortion polarisation, c.c.	P_O, c.c.	$\mu \times 10^{18}$.
2-Chlorocymene	105·3	50·0	55·3	1·64
3-Chlorocymene	106·0	50·15	56·85	1·66
2-Bromocymene	116·6	52·8	63·8	1·76
3-Bromocymene	113·1	52·9	60·2	1·71
Carvacrol..............................	95·7	47	48·7	1·54
Thymol	95·4	46·8	48·6	1·54

Discussion.—From the identity of the moments of the pairs of isomeric substances in the foregoing summary, we conclude that during the substitution of *p*-cymene itself preferential activation of either the 2- or the 3-position is unlikely to occur. In general, polarisability differences, such as were here sought for in cymene, would appear to be little developed in aromatic nuclei where the lower alkyl radicals are concerned, although, at the same time, the *possibility* that such effects might arise if a sufficiently strong polar influence were to approach the nucleus is illustrated by their obvious presence in, *e.g.*, the homologous alkyl halides, where a greater juxtaposition of the polar halogen and the polarisable alkyl occurs.

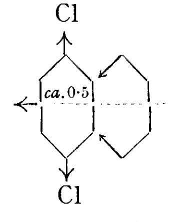
A point of interest arising out of the above measurements is that the moments of the chloro-, bromo-, and to a less extent the hydroxy-cymenes are not identical with those of the appropriate monosubstituted aryl compounds, but differ from them in the directions of the corresponding aliphatic analogues. This is easily explicable when the moment of a given aryl halide is regarded as the vector sum of the following three factors: (1) the unknown natural moment of a C–Cl link, (2) the additional moment caused by the inductive ($-I$) effect of the halogen on the electronic distribution in the aromatic nucleus, and (3) the further superimposed moment originating by the (mesomerising) action of the benzenoid system on the polarisable halogen atom. In proceeding from, say, a phenyl to a cymyl halide, the relative significances of these three effects are changed. In the latter, the presence of the methyl and the *iso*propyl group (these radicals having, in the unsubstituted hydrocarbon, equal $+I$ inductive actions opposed at 180°) will operate to increase the electron density in the nucleus and thus make it more polarisable; this, in the halogen derivatives of cymene, will allow the additional moment (2) to become more developed and/or cause a diminution of the mesomeric polarisation contribution, with the effect that the resultant molecular moments will numerically approach the figures for typically aliphatic halogeno-compounds. It is also noteworthy that these cymyl halides have moments of the same order as the *p*-tolyl halides. It therefore follows that the reversed moments in the benzene halides due to the $+M$ effects of the halogen atoms must be, in magnitude, not far removed from those caused by the (inductive, $+I$) action of the methyl group, a relationship which causes $\mu_{p\text{-Cl}\cdot\text{C}_6\text{H}_4\text{Me}}$, etc., to tend to increase to the full aliphatic values in the measure in which the M polarisation is cancelled out.

Finally, it may be pointed out that the situation in the halogeno-cymenes is an inversion of that observed in, *e.g.*, 1 : 4-dichloronaphthalene [cf. (I) and (II)], where the $-I$ effects of the chlorine atoms have so depleted the nucleus holding them of electrons that the C–C linkings attaching the second nucleus become permanently polarised—this induced polarisation corresponding to the whole of the measured moment, *i.e.*, to a resultant of *ca.* 0·5 × 10^{-18} e.s.u. (Weissberger, Sängewald, and Hampson, *Trans. Faraday Soc.*, 1934, **30**, 884) acting in the transverse direction depicted in the formula.

(I.)



(II.)



Relative Activity of p-*Cymene.*—The raising of the electron density and the polarisability of the aromatic nucleus should be reflected in an enhanced activity of those carbon atoms available for substitution, leading to a greater velocity and ease of replacement of nuclear hydrogen by electrophilic reagents in the case of cymene than in that of benzene. Evidence that this is true can be found in the qualitatively observable greater vigour of nitration and ease of halogenation of the former than of the latter. No relevant quantitative data are available, but we have often noticed during iodination and bromination of benzene solutions of cymene, that it is the latter and not the benzene which is principally attacked.

Section III. The Dipole Moment of p-*Ethyltoluene.*—The identical values for the dipole moments of toluene (Williams, *Physikal. Z.*, 1928, **29**, 174) and of ethylbenzene (Smyth, *J. Amer. Chem. Soc.*, 1924, **46**, 2151) lead one to conclude that the dipole moment of *p*-ethyltoluene should be zero and that the condition of polarisation of this molecule resembles that of *p*-cymene. The following results substantiate this.

p-Ethyltoluene was prepared from redistilled commercial *p*-methylacetophenone by Clemmensen's reduction (Brady and Day, J., 1934, 114); b. p. 162—163°/760 mm., $d_{4°}^{17°}$ 0·8644; $n_{D}^{25°}$ 1·492505, whence $[R_L]_D = 40·64$. A test with 2 : 4-dinitrophenylhydrazine sulphate in alcohol indicated the absence of unreduced *p*-methylacetophenone.

Molecular Polarisation of Liquid p-*Ethyltoluene.*

Temp.	$d_{4°}^{t°}$.	ε.	*P*, c.c.	Temp.	$d_{4°}^{t°}$.	ε.	*P*, c.c.
25°	0·85740	2·23952	40·92	45°	0·83838	2·20225	40·95

Molecular Polarisation of p-*Ethyltoluene in Benzene Solution.*

$10^6 f_1$.	$M_1f_1 + M_2f_2$.	ε.	$d_{4°}^{25°}$.	$P_1f_1 + P_2f_2$.	P_2f_2.	P_1f_1.	P_1.
0	78	2·2725	0·87380	26·5850	26·5850	—	—
40,175·4	79·6873	2·2709	0·87267	27·1726	25·5170	1·6556	41·21
98,639·2	82·1429	2·2666	0·87104	27·9956	23·9627	4·0329	40·89
130,007·1	83·4603	2·2634	0·87016	28·4227	23·1288	5·2939	40·72
150,478·5	84·3201	2·2575	0·86958	28·6401	22·5271	6·1130	40·62

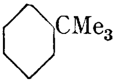
Whence extrapolated P_1 for $f_1 = 0$ is 41·4 c.c.

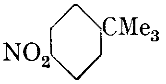
From the data given by Auwers and Müller (*Ber.*, 1911, **44**, 1607) the molecular refraction for light of infinite wave-length is deduced to be 39·12 c.c. ; if the same allowance (2 c.c.) for atomic polarisation be made as in Section I, then $P_E + P_A = 41·12$ c.c., and $P_O = 41·4—41·12 = 0·28$ c.c. The moment therefore becomes $0·22 \times (0·28)^{1/2} = 0·12 \times 10^{-18}$ e.s.u., which is zero within the limits of experimental error.

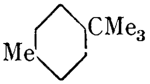
However, for the purposes of the substitution experiments previously cited, the methyl and the ethyl group were not thought to have sufficiently contrasted space requirements to produce a marked steric orientation capable of operating against the various polar factors. From other data, the forecast can be made that this hydrocarbon will give on mononitration the 2- and the 3-nitro-derivative in the proportions 57 : 43 (cf. J., 1933, 980), *i.e.*, a much closer approximation to the ideal 50 : 50 ratio than is observed with cymene.

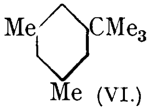
Section IV. The Dipole Moments of tert.-*Butylbenzene and its* p-*Nitro-*, p-*Methyl-*, *and* 3 : 5-*Dimethyl-derivatives.*—As stated on p. 480, reasons also exist to suggest that *p*-*tert.*-butyltoluene would not obey all the three conditions there mentioned. For instance, the recorded value of the dipole moment of *tert.*-butyl chloride shows a marked exaltation over that for methyl, ethyl, or propyl chloride (Parts, *Z. physikal. Chem.*, 1930, *B*, **7**, 327), indicating that the C–Cl bond in the first compound is considerably more polarised than is the corresponding covalency in the last three compounds, presumably because the *tert.*-butyl has a greater polarisability than the other three groups.

Therefore in *p*-*tert.*-butyltoluene it seemed possible that, in a substitution process of the type defined in Section I, the 3-position could be more activated by an inductive and/or a tautomeric mechanism originating at the butyl group than the 2-position could be by analogous displacements initiated at the methyl radical; *i.e.*, conditions (*b*) and (*c*) might not hold, and the steric might not entirely outweigh the polarisation effects. Relevant cases where this evidently happens are, *e.g.*, the ready formation of a Grignard complex from *o*-bromo- and -iodo-*tert.*-butylbenzenes (Shoesmith and Mackie, J., 1928, 2334), and the preparations of the common artificial musks (trinitro-*tert.*-butyl-toluene or -xylene, etc.), during which nitration ortho to the *tert.*-butyl group is effected without great difficulty; but it is impossible to conclude from Battegay and Haeffely's account of the mononitration of *p*-*tert.*-butyltoluene (*Bull. Soc. chim.*, 1924, **35**, 981) whether or not this substitution is as unidirectional as the analogous reaction with *p*-cymene (Le Fèvre, *loc. cit.*). At the outset we had hoped to obtain information on the foregoing points from dielectric polarisation measurements of the types utilised in Sections I and II for the related case of *p*-cymene, but, owing to the fact that the necessary 2- and 3-monosubstituted derivatives of (V) are unknown (cf. Brady and Lahiri, J., **1934**, 1954), this proved impossible; we have therefore undertaken a comparison of the moments of the four *tert.*-butyl compounds (III)—(VI) instead.


(III.)


(IV.)


(V.)


(VI.)

Materials.—tert.-*Butylbenzene* (III). This was prepared from *tert.*-butyl chloride, benzene, and aluminium chloride (Schramm, *Monatsh.*, 1888, **9**, 615); b. p. 167—169°/760 mm., $n_D^{20°}$ 1·50168, $d_{4°}^{20°}$ 0·86733, whence $[R_L]_D$ is 45·57. Richards and Shipley (*J. Amer. Chem. Soc.*, 1919, **41**, 2008) found 2·4 for the dielectric constant of this substance in bulk at 20° and with $\lambda = \infty$; this, combined with $d_{4°}^{20°}$ 0·8671, corresponds to $P = 49·2$ c.c.

p-*Nitro*-tert.-*butylbenzene* (IV). From (III) by direct nitration (Seňkowski, *Ber.*, 1890, **23**, 2416; cf. also Malherbe, *Ber.*, 1919, **52**, 319); b. p. 140—142°/15 mm.

p-tert.-*Butyltoluene* (V). We are indebted to Dr. O. L. Brady and Mr. J. K. Lahiri for a specimen (prepared by Verley's method; *Bull. Soc. chim.*, 1898, **19**, 68); b. p. 76°/15 mm., $d_{4°}^{19°}$ 0·86272, $n_D^{25°}$ 1·489008, $d_{4°}^{25°}$ 0·85968, whence $[R_L]_D$ is 50·3.

5-tert.-*Butyl*-m-*xylene* (VI). From *m*-xylene, *tert.*-butyl chloride, and aluminium chloride (Baur, *Ber.*, 1891, **24**, 2840); b. p. 203—206°/756 mm.

Measurements.—The following tables, except the third, relate to solutions in benzene at 25°.

Molecular Polarisation of tert.-*Butylbenzene.*

$10^6 f_1$.	$M_1f_1 + M_2f_2$.	ϵ.	$d_{4°}^{25°}$.	$P_1f_1 + P_2f_2$.	P_2f_2.	P_1f_1.	P_1.
0	78	2·2725	0·87380	26·5850	26·5850	—	—
14,323·1	78·8021	2·2768	0·87332	26·9382	26·2042	0·7340	51·25
17,882·0	79·0013	2·2778	0·87323	27·0239	26·1096	0·9143	51·13
28,002·1	79·5681	2·2809	0·87296	27·2725	25·8406	1·4319	51·14
36,462·3	80·0419	2·2834	0·87275	27·4790	25·6157	1·8633	51·10

Whence extrapolated value of P_1 for $f_1 = 0$ is 51·39 c.c.

Molecular Polarisation and Refractivity of p-*Nitro*-tert.-*butylbenzene.*

5,426·7	78·5481	2·4363	0·87624	29·0225	26·4407	2·5818	475·76
21,667·5	80·1884	2·9265	0·88378	35·4812	26·0090	9·4722	437·16
30,012·1	81·0313	3·1781	0·88771	38·3963	25·7872	12·6091	420·13
39,794·8	82·0193	3·4801	0·89234	41·5974	25·5271	16·0703	403·83

Whence extrapolated value of P_1 for $f_1 = 0$ is 490 c.c.

$10^6 f_1$.	$M_1f_1 + M_2f_2$.	n.	n^2.	$R_1f_1 + R_2f_2$.	R_2f_2.	R_1f_1.	R_1.
0	78	1·49733	2·2400	26·1357	26·1357	—	—
21,667·5	80·1884	1·50002	2·25006	26·69	25·57	1·12	51·7
39,794·8	82·0193	1·50243	2·2573	27·15	25·10	2·05	51·5

Molecular Polarisation of p-tert.-*Butyltoluene.*

Temp.	$d_{4°}^{t°}$.	ϵ.	P, c.c.	Temp.	$d_{4°}^{t°}$.	ϵ.	P, c.c.
0°	0·87940	2·3728	52·83	40°	0·84781	2·2931	52·58
10	0·87160	2·3522	52·76	45	0·84392	2·2824	52·52
20	0·86370	2·3240	52·47	60	0·83204	2·2565	52·51

Molecular Polarisation of p-tert.-*Butyltoluene.*

$10^6 f_1$.	$M_1f_1 + M_2f_2$.	ϵ.	$d_{4°}^{25°}$.	$P_1f_1 + P_2f_2$.	P_2f_2.	P_1f_1.	P_1.
0	78	2·2725	0·87380	26·5850	26·5850	—	—
11,362·8	78·7954	2·2734	0·87346	26·8813	26·2829	0·5984	52·66
30,077·0	80·1054	2·2749	0·87277	27·3724	25·7854	1·5870	52·76
30,407·5	80·1285	2·2749	0·87276	27·3806	25·7766	1·6040	52·75
36,008·1	80·5206	2·2754	0·87255	27·5287	25·6277	1·9010	52·79

Whence extrapolated P_1 for $f_1 = 0$ is 52·8 c.c.

Molecular Polarisation and Refractivity of 5-tert.-*Butyl*-m-*xylene*.

$10^6 f_1$.	$M_1 f_1 \times M_2 f_2$.	ϵ.	$d_{4°}^{25°}$.	$P_1 f_1 \times P_2 f_2$.	$P_2 f_2$.	$P_1 f_1$.	P_1.
6,896·4	78·5793	2·2723	0·87347	26·7909	26·4017	0·3892	56·44
22,496·4	79·8897	2·2719	0·87270	27·2557	25·9869	1·2688	56·40
12,001·4	79·0081	2·2721	0·87321	26·9422	26·2659	0·6763	56·35
17,999·9	79·5120	2·2720	0·87292	27·1216	26·1065	1·0151	56·39

Whence extrapolated P_1 for $f_1 = 0$ is 56·5 c.c.

$10^6 f_1$.	n.	n^2.	$R_1 f_1 + R_2 f_2$.	$R_2 f_2$.	$R_1 f_1$.	R_1.
0	1·49733	2·2400	26·1357	26·1357	—	—
6,896·4	1·49724	2·24173	26·3358	25·9554	0·3804	55·2
22,496·4	1·49705	2·24116	26·7899	25·5477	1·2422	55·2

Summary of Results.

	P.	$[R_L]_D$.	$\mu \times 10^{18}$.
tert.-Butylbenzene	51·4	45·6	0·53
Nitrobenzene	355	32·7	3·95
p-Nitro-*tert.*-butylbenzene	490	51·7	4·61
Toluene	33·5	31·1	0·34
p-*tert.*-Butyltoluene	52·8	50·3	0·35
5-*tert.*-Butyl-*m*-xylene	56·5	55·2	0·25

In the calculation of the above results no attempt has been made to allow accurately for the atomic polarisation, but, as on p. 482, $P_E + P_A$ has been taken as the molecular refraction for D light, and, in order to give these figures a comparative significance, the moments of nitrobenzene and of toluene, computed from some earlier polarisation measurements made in benzene solution at 25° with our apparatus, are included.

Discussion.—These results appear to indicate that inductive effects are, in fact, operative in this group of compounds. For instance, the higher moment of *tert.*-butylbenzene than of toluene parallels the relationship between the corresponding halides, and illustrates how even the weak (— *I*) polarising influence of the phenyl group is sufficient to demonstrate the greater ease with which polarisation can be induced in *tert.*-butyl than in methyl; when to this action is added the relayed (— *I*) effect of a nitro-group in the *p*-position, a further slight exaltation of the moment found over that required by vector addition can be discerned, such superimposition leading, of course, to a moment for 4-nitro-*tert.*-butylbenzene greater than any yet advanced for *p*-nitrotoluene (Williams and Schwingel, *J. Amer. Chem. Soc.*, 1928, **50**, 362; Højendahl, *Physikal. Z.*, 1929, **30**, 391).

The moments of the last two hydrocarbons are difficult to understand, for, not only are they not equal (as required by vectorial principles), but they are unexpectedly high. The possibility that the samples used were mixtures of isomerides is rather small in the first case, in view of the high yields of substitution products, etc., obtained by Brady and Lahiri (*loc. cit.*) on identical material; and in the second instance it is absolutely ruled out by a trinitration of part of the sample of butylxylene used, for this afforded a crude product which, as long boiling with piperidine showed (cf. Le Fèvre and Turner, J., 1927, 1113), certainly did not contain *o*- or *p*-dinitro-groups (as it would have done had the initial hydrocarbon been admixed with 4-butyl-*m*-xylene).

A possible explanation lies in the suggestion (Ingold, J., 1933, 1125) that, during attack on a suitably constituted alkyl compound by a nucleophilic reagent, the alkyl group could be caused to exhibit a — *I* inductomeric effect (or at least, suffer a diminution of its normal + *I* character). If in, say, *p*-*tert.*-butyltoluene, the latter group is regarded as standing permanently towards the rest of the molecule in the same relation as the effective part of a nucleophilic reagent would be during a reaction temporarily towards toluene, a possible mechanism can be envisaged by which the normal Me–C moment becomes depressed; the resultant molecular moment therefore becoming this much larger than would otherwise be the case.

The authors thank Professor F. G. Donnan, F.R.S., for the loan of apparatus.

UNIVERSITY COLLEGE (UNIVERSITY OF LONDON). [*Received, February 6th,* 1935.]
