720. *Physical Properties and Chemical Constitution. Part XXVI.*[1] *The Dipole Moments of Alkylbenzenes.*

By C. W. N. Cumper, A. I. Vogel, and S. Walker.

The orientation polarisations and dipole moments of seven alkylbenzenes have been calculated from measurements of the dielectric constants and specific volumes of their solutions in benzene. The dipole moments were analysed quantitatively into primary and induced bond moments and these values compared with those of the corresponding alkylpyridines. The dipole moments in benzene solutions are compared with those for the gaseous and liquid states.

Dipole moments of some alkylpyridines have been analysed in terms of their component moments.[1] The same method has now been applied to alkylbenzenes. As the dipole moments are comparatively small (<0·5 D), it is difficult to allow adequately for the distortion polarisation in the alkylbenzene molecules. Any error introduced by this factor will, however, have little effect on the relative dipole moments of the compounds investigated.

Experimental

The apparatus and techniques have been described.[1] Measurements were made in benzene at 25·00° ± 0·01° C.

Materials.—Methyl-, ethyl-, *iso*propyl-, and *tert.*-butyl-benzenes were high-grade commercial products; *sec.*-butylbenzene was a gift from the Koninklijke/Shell-Laboratorium, Amsterdam. *n*-Propylbenzene was prepared here from benzyl chloride, magnesium, and pure ethyl sulphate,[2] and *n*-butylbenzene from benzylsodium and *n*-propyl bromide.[3] Ethyl-, *iso*propyl-, and *tert.*-butyl-benzenes contained traces of sulphur compounds which were removed by repeatedly washing with 10% of their volume of concentrated sulphuric acid until the washings were colourless, then successively with water, 10% sodium carbonate solution, and water. Finally they were dried ($MgSO_4$). Before use, the hydrocarbons were fractionated from sodium two or three times in an all-glass 20 in. column packed with Fenske helices and provided with a variable take-off head, a middle fraction being collected. All the measurements were completed within 24 hr. of the final distillation and the solutions were kept in the dark when not in use. To check their purity the boiling points, densities, and refractive indices of the alkylbenzenes were determined (Table 1) and found to agree satisfactorily with values in the literature.[2, 4, 5]

Table 1.

	B. p.	n_D^{25}	d_4^{25}		B. p.	n_D^{25}	d_4^{25}
Toluene	110·5°	1·4941	0·8622	*n*-Butylbenzene	183°	1·4875	0·8560
Ethylbenzene	136	1·4933	0·8627	*sec.*-Butylbenzene	173	1·4878	0·8580
n-Propylbenzene	159	1·4896	0·8577	*tert.*-Butylbenzene	169	1·4903	0·8624
*iso*Propylbenzene	152	1·4887	0·8577				

Results

Dielectric constants (ε_{12}) and specific volumes (v_{12}) of the solutions in benzene, with weight fractions w_2, are recorded in Table 2. Since the dipole moments of these compounds are small it was necessary to use weight fractions up to 0·1; the simple relation between dielectric constant and weight fraction used previously was extended by the inclusion of a "square" term, *viz.*, $\varepsilon_{12} = \varepsilon_1 (1 + \alpha w_2 + \alpha' w_2^2)$. The specific volumes, over the range studied, were linear functions

---

[1] Part XXV, Cumper, Vogel, and Walker, *J.*, 1956, 3621.

[2] Vogel, *J.*, 1948, 607.

[3] Vogel, "Practical Organic Chemistry," 3rd Edn., Longmans, London, 1956, p. 934.

[4] National Bureau of Standards, American Petroleum Project 44, NBS Circular C461, United States Government Printing Office, Washing, D.C., 1947.

[5] Forsiati, *J. Res. Nat. Bur. Stand.*, 1950, **44**, 373.

of w_2, *i.e.*, $v_{12} = v_1\,(1 + \beta w_2)$, and were used in preference to the densities of the solutions, which showed a slight curvature when plotted against w_2. The values obtained for ε_1, α and α' by a method of least squares, and of β, are also given in Table 2.

The total polarisation of the solutes, when extrapolated to infinite dilution $({}_{\infty}P_2)_2$, were calculated from the values [1] of α and β and are shown in Table 3. The distortion polarisation which is subtracted from ${}_{\infty}P_2$ to evaluate the orientation polarisation (${}_{\mathrm{O}}P$), was deduced in two ways: (i) it was assumed equal to the molar refraction for sodium light (R_{D}); (ii) Forsiati's value [5] for the molar refraction (R_{∞}), obtained by extrapolating the refractive indices of the compound in the visible region to infinite wavelength, was taken as the electron polarisation (${}_{\mathrm{E}}P$) and Altshuller's [6] approximate results for the atom polarisation (${}_{\mathrm{A}}P$) added to ${}_{\mathrm{E}}P$.

TABLE 2.

Toluene

w_2	v_{12}	ε_{12}
0·00156	1·14448	2·2729
0·00295	1·14452	2·2730
0·006526	1·14458	2·2735
0·016224	1·14478	2·2745
0·034326	1·14513	2·2766
0·052271	1·14550	2·2785
0·074698	1·14596	2·2808

$\varepsilon_{12} = 2{\cdot}2726_8(1 + 0{\cdot}0508w_2 - 0{\cdot}039w_2^2)$
$v_{12} = 1{\cdot}14445(1 + 0{\cdot}0176w_2)$

Ethylbenzene

w_2	v_{12}	ε_{12}
0·00194	1·14450	2·2728
0·006165	1·14458	2·2733
0·017770	1·14479	2·2744
0·043021	1·14525	2·2772
0·058059	1·14553	2·2786
0·081610	1·14597	2·2808
0·093062	1·14620	2·2821

$\varepsilon_{12} = 2{\cdot}2725_9(1 + 0{\cdot}0472w_2 - 0{\cdot}030w_2^2)$
$v_{12} = 1{\cdot}14445(1 + 0{\cdot}0164w_2)$

n-*Propylbenzene*

w_2	v_{12}	ε_{12}
0·00164	1·14448	2·2727
0·004928	1·14457	2·2731
0·013662	1·14484	3·2738
0·024591	1·14515	2·2749
0·036116	1·14544	2·2760
0·052027	1·14586	2·2774
0·073837	1·14649	2·2794

$\varepsilon_{12} = 2{\cdot}2726_0(1 + 0{\cdot}0408w_2 - 0{\cdot}001w_2^2)$
$v_{12} = 1{\cdot}14445(1 + 0{\cdot}0238w_2)$

iso*Propylbenzene*

w_2	v_{12}	ε_{12}
0·00170	1·14449	2·2727
0·004883	1·14457	2·2730
0·012780	1·14478	2·2738
0·025478	1·14510	2·2751
0·032970	1·14529	2·2758
0·051908	1·14580	2·2777
0·081837	1·14658	2·2803
0·096484	1·14694	2·2817

$\varepsilon_{12} = 2{\cdot}2725_4(1 + 0{\cdot}0447w_2 - 0{\cdot}033w_2^2)$
$v_{12} = 1{\cdot}14445(1 + 0{\cdot}0225w_2)$

n-*Butylbenzene*

w_2	v_{12}	ε_{12}
0·00165	1·14452	2·2727
0·005990	1·14467	2·2730
0·012219	1·14484	2·2735
0·022230	1·14516	2·2742
0·032528	1·14547	2·2750
0·053750	1·14613	2·2763
0·078502	1·14690	2·2782
0·105359	1·14773	2·2801

$\varepsilon_{12} = 2{\cdot}2726_0(1 + 0{\cdot}0313w_2)$
$v_{12} = 1{\cdot}14445(1 + 0{\cdot}0274w_2)$

sec.-*Butylbenzene*

w_2	v_{12}	ε_{12}
0·00244	1·14452	2·2727
0·005357	1·14460	2·2730
0·011211	1·14473	2·2735
0·019898	1·14501	2·2743
0·029075	1·14526	2·2750
0·038538	1·14550	2·2759
0·062476	1·14617	2·2780
0·089103	1·14686	2·2800

$\varepsilon_{12} = 2{\cdot}2725_1(1 + 0{\cdot}0397w_2 - 0{\cdot}026w_2^2)$
$v_{12} = 1{\cdot}14445(1 + 0{\cdot}0238w_2)$

tert.-*Butylbenzene*

w_2	v_{12}	ε_{12}
0·00161	1·14448	2·2728
0·005737	1·14457	2·2731
0·010531	1·14466	2·2737
0·020527	1·14487	2·2747
0·029232	1·14506	2·2754
0·054348	1·14555	2·2774
0·071845	1·14590	2·2788
0·087701	1·14620	2·2799

$\varepsilon_{12} = 2{\cdot}2726_2(1 + 0{\cdot}0447w_2 - 0{\cdot}094w_2^2)$ $v_{12} = 1{\cdot}14445(1 + 0{\cdot}0176w_2)$

The values of R_{D}, R_{∞} (*i.e.*, ${}_{\mathrm{E}}P$), ${}_{\mathrm{A}}P$ and the two values of ${}_{\mathrm{O}}P$ [*viz.*, $({}_{\infty}P_2 - R_{\mathrm{D}})$ and $({}_{\infty}P_2 - R_{\infty} - {}_{\mathrm{A}}P)$] are also presented in Table 3. It appears that R_{D} for these compounds includes about 60—70% of their atom polarisations.

The dipole moments were calculated from the usual formula $\mu = 0{\cdot}01281\sqrt{({}_{\mathrm{O}}PT)}$, and are listed under μ_1 (with ${}_{\mathrm{O}}P = {}_{\infty}P_2 - R_{\mathrm{D}}$) and μ_2 (with ${}_{\mathrm{O}}P = {}_{\infty}P_2 - R_{\infty} - {}_{\mathrm{A}}P$) in Table 3. Earlier values (where available) are also given. When complete allowance is made for the atom polarisation, the calculated dipole moments are naturally somewhat smaller (*i.e.*, $\mu_2 < \mu_1$).

---

[6] Altshuller, *J. Phys. Chem.*, 1954, **58**, 392.

TABLE 3.

Benzene derivative	$_{\infty}P_2$ (cm.^{3})	R_D (cm.^{3})	R_{∞} (cm.^{3})	$_AP$ (cm.^{3})	$_0P$ (cm.^{3})		μ_1 (D)	μ_2 (D)	μ (calc.) (D)
					$_{\infty}P_2 - R_D$	$_{\infty}P_2 - R_{\infty} - {}_AP$			
Methyl	33·96	31·11	29·88 *	1·78 †	2·85	2·30	0·37 ‡	0·34	$0{\cdot}36_8$
Ethyl	38·92	35·78	34·43 §	2·00	3·14	2·49	0·39	0·35	$0{\cdot}39_5$
n-Propyl ...	44·04	40·48	39·02	2·22	3·56	2·80	0·42	0·37	$0{\cdot}42_0$
*iso*Propyl ...	44·18	40·43	39·00	2·22	3·75	2·96	0·43	0·38	$0{\cdot}42_3$
n-Butyl	48·80	45·11	43·55	2·44	3·69	2·81	0·43	0·37	$0{\cdot}42_7$
sec.-Butyl ...	49·11	45·05	43·49	2·44	4·06	3·18	0·45	0·39	$0{\cdot}44_7$
tert.-Butyl ...	49·12	45·00	43·45	2·44	4·12	3·23	0·45 ‖	0·40	$0{\cdot}45_0$

Other literature values: * ($R_{\infty} + {}_AP$) = 30·8.[a] † 2·5,[b] 1·0.[c] ‡ 0·34,[d] 0·39.[e] § ($R_{\infty} + {}_AP$) = 35·8.[a] ‖ 0·53.[d]

[a] Baker and Groves, *J.*, 1939, 1144. [b] McAlpine and Smyth, *J. Amer. Chem. Soc.*, 1933, **55**, 453. [c] Cartwright and Errera, *Proc. Roy. Soc.*, 1936, *A*, **154**, 138. [d] Le Fèvre, Le Fèvre, and Robertson, *J.*, 1935, 480. [e] Tiganik, *Z. phys. Chem.*, 1931, *B*, **13**, 425.

DISCUSSION

Comparison with the Dipole Moments of 4-*Alkylpyridines.*—The dipole moments of the alkylbenzenes can be expressed by an empirical equation analogous to that suggested for the alkylpyridines, *viz.*,

$$\mu = -\mu_{C-H} + \mu_R + I$$

where μ_{C-H} is the bond moment of hydrogen attached to the benzene ring, I the moment induced in the benzene ring when its hydrogen atom is replaced by the alkyl group R and μ_R the dipole moment associated with the alkyl group itself. μ_R can be expressed in terms of a primary moment " a ", the C–H bond moment in saturated aliphatic hydrocarbons " b ", and the moment induced by $(a - b)$ in the C–H bonds (μ_H) and in the other C–C bonds in the substituent chain. The last is assumed to decrease in a geometrical progression with constant ratio " x " as the chain-length increases. μ_H will include any moment arising through hyperconjugation with the ring,

e.g.,
$$\mu_R = 3\,\mu_H + (a - b) \text{ for PhMe}$$
$$= 2\,\mu_H + (a - b)(1 + x + x^2) \text{ for PhPr}^n\text{, etc.}$$

Some variation is possible amongst these parameters but probably the best set (obtained from the dipole moments μ_1, calculated to 0·001D) are: $(a - b) = 0{\cdot}25$ D, $\mu_{C-H} - I = 0{\cdot}03_2$ D, $\mu_H = 0{\cdot}05$ D, and $x = 0{\cdot}31$. By employing these values the moment shown under μ (calc.) in Table 3, are obtained and the agreement with the measured values supports this method of analysis.

The values of the above parameters can be compared with the corresponding figures for the 4-alkylpyridines[1] [$(a - b) = 0{\cdot}53$ D, $\mu_H = 0{\cdot}11$ D, $\mu_{C-H} - I = 0{\cdot}48$ D, and $x = 0{\cdot}31$]. x, a property of the side-chain alone, is given the same value in both series and μ_H, as expected, is seen to depend on the value of $(a - b)$.

Since b is thought[7] to be about 0·30 D the primary moment a is about 50% greater in the pyridine than in the benzene series and this, together with the actual magnitude of a (corresponding in the alkylbenzenes to formal electronic charges of ±0·074 at a distance apart of 1·54 Å) means that part of the electric field polarising the side-chain must reside in the ring system. This field would naturally be greater in a pyridine than in a benzene ring. Cahill and Mueller's approximate wave-mechanical calculations indicate that the moment of the bond from the α-carbon atom of the side-chain to the ring, arising from the different states of hybridisation of the carbon atoms, is only 0·14 D.[8] The magnitudes of a and μ_H

---

[7] Smith, " Electric Dipole Moments," Butterworths, London, 1955.

[8] Cahill and Mueller, *J. Chem. Phys.*, 1956, **24**, 513.

seem to agree somewhat better with Pullman and Pullman's [9] calculated charge distribution in toluene than with that suggested by Crawford.[10]

Reasons have been advanced for taking μ_{C-H} as 0·40 D in benzene and 0·54 D in pyridine.[1] These are necessarily very approximate, but the change in the moment of the ring itself when an alkyl group is introduced (*i.e.*, *I*) seems to be greater in benzene than in pyridine. This is probable in view of the electron drift towards the nitrogen atom which is already present in the unsubstituted pyridine molecule.

Comparison of the Values for the Dipole Moments of Alkylbenzenes in Benzene Solution with those for the Liquid and the Gaseous State.—In Table 4 the dipole moments of the alkylbenzenes obtained in benzene solutions are compared with Altshuller's values for the pure liquids [6] (the subscripts i and ii refer to the two values assumed previously for the distortion polarisation) and Baker and Groves's [11] moments for the compounds in the gaseous state. On the whole the agreement between the values in solution and in the pure liquid is reasonable, except for *tert.*-butylbenzene where the figure for the pure liquid seems somewhat low, particularly since its moment is less than that reported for *iso*propylbenzene.

The moments in the last two columns of Table 4, $(\mu')_B$ and $(\mu')_L$, are the values of the moments in the gaseous phase calculated by means of Buckingham and Le Fèvre's empirical equations (numbers 3 and 5 in ref. 12) from the experimental moments in benzene solutions and in the liquid state respectively. Except for toluene the agreement with the experimental gas values is less satisfactory than is usually obtained with these equations; the experimental dipole moments in the gaseous phase should be confirmed in order to establish whether the deviations from Buckingham and Le Fèvre's equations are real.

TABLE 4.

	Benzene solution		Liquid		Gas		
Benzene derivative	μ_1	μ_2	μ_1	μ_2	μ	$(\mu_1')_B$	$(\mu_1')_L$
Methyl	0·37	0·34	0·35	0·31	0·37 [a]	0·41	0·39
Ethyl	0·39	0·35	0·40 [b]	0·36	0·58	0·43	0·44
n-Propyl	0·42	0·37	0·40	0·35	—	—	—
*iso*Propyl	0·43	0·38	0·42	0·37	0·65	0·47	0·46
n-Butyl	0·43	0·37	0·42	0·36	—	—	—
sec.-Butyl	0·45	0·39	0·42	0·37	—	—	—
tert.-Butyl	0·45	0·40	0·41	0·36	0·70	0·48	0·44

Other literature values: [a] 0·37, McAlpine and Smyth, *J. Amer. Chem. Soc.*, 1933, **55**, 453; [b] 0·35, van Arkel, Meerburg, and van der Handel, *Rec. Trav. chim.*, 1942, **61**, 767.

The authors thank Mr. R. Grzeskowiak, B.Sc., of this Laboratory, for assistance in preparing the compounds, and Imperial Chemical Industries Limited for a grant.

WOOLWICH POLYTECHNIC, LONDON, S.E.18.

[*Received, March 29th,* 1957.]

---

[9] Pullman and Pullman, "Les Théories Electroniques de la Chimie Organique," Masson et Cie., Paris, 1952.

[10] Crawford, *J.*, 1953, 2058.

[11] Baker and Groves, *J.*, 1939, 1144.

[12] Buckingham and Le Fèvre, *J.*, 1952, 1932.