

370. *The Apparent Polarities of a Number of Substituted Chloro-, Nitro-, Methyl-, Methoxy-, and Acetyl-benzenes.*

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The apparent dipole moments, in benzene at 25° (refractivity method), of some 19 substances are recorded. When the aromatic nucleus has three or more substituent groups the molecular polarities cannot be predicted accurately or explained generally by any one alone of a number of qualitative treatments, already described in, or indicated by, the literature.

The Barclay-Le Fèvre relation (*J.*, 1950, 556) is found to provide, from data for benzene solutions, a satisfactory estimate of the moments, as measured in the gaseous state, of anisole and acetophenone.

KADESCH AND WELLER (*J. Amer. Chem. Soc.*, 1941, **63**, 1310) have reported the dipole moment of acetylmesitylene as 2.71 D. and attributed the difference between this figure and that found by them for acetophenone, *viz.*, 2.88 D., to steric inhibition of mesomerism (cf. Birtles and Hampson, *J.*, 1937, 10; Ingham and Hampson, *J.*, 1939, 981). The purpose of the present communication is to put on record a number of determinations, of which that for acetylmesitylene was one, started at University College, London, during 1935—39, to compare the moments of various monosubstituted benzene derivatives with those of derivatives which, by crude vectorial arguments based on a regular hexagonal C₆ skeleton, should have had the same values. The work was originally suggested by suppositions (Le Fèvre and Le Fèvre, *J.*, 1935, 957) which,

after the appearance of Hampson's papers, seemed much less necessary. Our results may, however, have a residual usefulness. They are given in Table I below, together with figures for a few related substances. Benzene has been the solvent throughout.

TABLE I.

Compound.	∞P_1 (c.c.).	$[RL]_D$.	$-\infty P_1$ $[RL]_D$.	μ_{apparent} D.	Source.
(A) <i>Anisole series.</i>					
Anisole	67.4	33.0 *	34.4	1.3 ₀	Present work.
3-Methyl-6- <i>tert.</i> -butylanisole.....	96.0	56.6 †	39.4	1.3 ₉	"
<i>p</i> -Nitroanisole	515.0	39.6 †	475.4	4.8 ₂	"
2 : 4 : 6-Trinitroanisole	134.6	50.6 †	84.0	2.0 ₃	"
"Musk Ambrette"	315.3	67.3 †	248.0	3.4 ₈	"
(B) <i>Toluene series.</i>					
Toluene	33.5	31.1 *	2.4	(0.3 ₄)	<i>J.</i> , 1935, 480.
2 : 4 : 6-Trichlorotoluene	54.9	46.1 †	8.8	0.6 ₈	Present work
2 : 4 : 6-Trinitrotoluene	87.2	48.7 †	38.5	1.3 ₇	"
Mesitylene	41.8	40.6 *	1.2	(0.2 ₄)	"
Nitromesitylene	329.4	47.0 †	282.4	3.7 ₁	"
Trinitromesitylene	70.5	59.2	11.3	(0.7 ₄)	<i>J.</i> , 1935, 957
5- <i>tert.</i> -Butyl- <i>m</i> -xylene	56.5	55.2	1.3	(0.2 ₅)	<i>J.</i> , 1935, 488
2 : 4 : 6-Trinitro-5- <i>tert.</i> -butyl- <i>m</i> -xylene ...	98.5	72.2	26.3	1.1 ₃	<i>J.</i> , 1935, 957
(C) <i>Chlorobenzene series.</i>					
Chlorobenzene.....	83.3	31.1 *	52.2	1.60	<i>Trans. Faraday Soc.</i> , 1950, 46, 1
1 : 4-Dichlorobenzene	37.7	36.2 †	1.5	(0.27)	<i>J.</i> , 1936, 487
1 : 3 : 5-Trichlorobenzene	42.8 ₅	40.9 †	1.9 ₅	(0.31)	Present work
1-Chloro-2 : 4-dinitrobenzene	258.2	43.0 †	215.2	3.2 ₄	"
Picryl chloride	74.8	48.8 †	26.0	1.1 ₃	"
(D) <i>Acetophenone series.</i>					
Acetophenone	217.1	36.3 *	170.8	2.8 ₉	"
4-Methylacetophenone	255.2	40.9	214.3	3.2 ₃	"
2 : 4 : 6-Trimethylacetophenone	209.9	50.8 †	159.1	2.7 ₉	"
3 : 5-Dinitro-2 : 6-dimethyl-4- <i>tert.</i> -butyl- acetophenone	228.2	74.8	153.4	2.7 ₄	"
3-Nitro-4-methylacetophenone	298.9	46.8	152.1	2.7 ₃	"
(E) <i>Nitrobenzene series.</i>					
Nitrobenzene	356.1	32.7 *	323.4	3.97	<i>Trans. Faraday Soc.</i> , 1950, 46, 1
1 : 3-Dinitrobenzene	344.7	38.6	306.1	3.8 ₆	Present work
1 : 3 : 5-Trinitrobenzene	54.3	44.7	9.6	(0.6 ₈)	<i>J.</i> , 1935, 957
2 : 5-Dichloronitrobenzene	290.0	42.5(2)	247.5	3.48	Present work

* From Landolt-Börnstein-Roth, "Tabellen," 4th Edn., p. 1027. † Calc. from the preceding asterisked datum, by using the group refractivities listed by Vogel, *J.*, 1948, 1842.

¹ Calc. from figures for anisole and nitrobenzene, together with $C_6H_6 = 26.2$ and $H = 1.1$.
² Thomson, *J.*, 1944, 404. ³ Tiganik, *Z. physikal. Chem.*, 1931, B, 13, 425.

Comparison with Previous Measurements.—Nitro- and chloro-benzene have been frequently studied (cf. Cleverdon and Smith, *Trans. Faraday Soc.*, 1949, 45, 109; Le Fèvre, *ibid.*, 1950, 46, 1, for references). Where several of the remaining compounds are concerned previous data were not always consistent; these cases are summarised in Table II and may be compared with our values, shown by asterisks. It should be noted that, in our calculations, we have used the latest values for Avogadro's number and Boltzmann's constant (Birge, *Reports Prog. Physics*, 1941, 8, 126; *J.*, 1946, 219). The conversion of earlier dipole-moment values to our basis requires multiplication by 1.006.

Discussion.—In a general way it is obvious that substitution in the positions *ortho*- to groups such as methoxy, nitro, etc., may effect the configurations of the latter and so, by induction, inhibition of resonance, or valence deflection, influence the resultant molecular moment of the derivative. Much more experimental evidence will be needed before the "weights" of these causes can be assessed, and the position at present is still as stated by Watson (*Ann. Reports*, 1939, 36, 215; 1942, 38, 124) in the concluding paragraph of his review of the various manifestations of the "*ortho*-effect." Indeed, where the polarities now recorded are concerned there are two further complications: (a) that recent work (Bastiansen and Hassel, *Acta Chem.*

Scand., 1947, 1, 489; cf. Angus, Bailey, Hale, Ingold, Leckie, and Raison, *J.*, 1936, 971) suggests that valency deflections above or below—as well as in—the C_6 plane may occur when adjacent positions are highly crowded, and (b) that, especially with *s*-trinitro-derivatives, the "refractivity" method of calculation, applied in Table I, fails to make adequate allowance for the atomic polarisations (cf. Sutton, *Ann. Reports*, 1940, 37, 57), so that for the 1 : 3 : 5-trinitro-derivatives of benzene and mesitylene apparent moments *ca.* 0.7 D. are indicated. Yet if this figure be applied as a "correction" in the cases of picryl chloride, T.N.T., trinitrobutylxylene, and trinitroanisole, only with the last is there no excess over the moment of the un-nitrated compound.

Solvent Influences with Anisole and Acetophenone.—The moments of these two molecules have been determined in the gaseous state by Groves and Sugden (*J.*, 1937, 1782; *J.*, 1935, 971) as 1.35 and 3.00 D. respectively. From the worked example (ether) shown in the 1937 paper it seems that these figures, before incorporation with our present data into $\mu^2_{\text{solution}}/\mu^2_{\text{gas}}$ ratios, should also (see above) be multiplied by 1.006. After this adjustment, they become 1.36 and 3.02 D.

TABLE II.

Anisole.	0.8 ¹ , 1.16 ² , 1.23 ³ , 1.22 ⁴ , 1.28 ⁵ , 1.30 [*] .
<i>p</i> -Nitroanisole.	4.36 ⁶ , 4.78 ⁷ , 4.74 ⁸ , 4.82 [*] .
2 : 4 : 6-Trichlorotoluene.	0.57 ⁹ , (0.6 ₆) [*] .
Nitromesitylene.	3.67 ¹⁰ , 3.64 ¹¹ , 3.7 [*] .
1 : 3 : 5-Trichlorobenzene.	0.28 ¹² , 0.31 [*] .
1-Chloro-2 : 4-dinitrobenzene.	3.29 ¹³ , 3.00 ¹⁴ , 3.2 [*] .
Acetophenone.	2.97 ¹⁵ , 2.88 ¹⁷ , 2.96 ¹⁸ , 2.96 ¹⁹ , 2.89 [*] .
4-Methylacetophenone.	3.23 ¹⁹ , 3.2 ₈ [*] .
2 : 4 : 6-Trimethylacetophenone.	2.71 ¹⁷ , 2.81 ¹⁸ , 2.79 [*] .
1 : 3-Dinitrobenzene.	4.02 ²⁰ , 3.70 ²⁰ , 3.81 ²¹ , 3.78 ²² , 3.96 ²³ , 3.86 [*] .
2 : 5-Dichloronitrobenzene.	3.45 ²⁴ , 3.45 ²⁵ , 3.4 ₈ [*] .

¹ Estermann, *Z. physikal. Chem.*, 1928, B, 1, 134. ² Højendahl, Thesis, Copenhagen, 1928, p. 105. ³ Donle and Volkert, *Z. physikal. Chem.*, 1930, B, 8, 60. ⁴ Phadke, Gokhale, Phalniker, and Bhide, *J. Indian Chem. Soc.*, 1945, 22, 235. ⁵ Everard and Sutton, *J.*, 1949, 2312. ⁶ Ref. 2, p. 106. ⁷ Donle and Gehrckens, *Z. physikal. Chem.*, 1932, B, 13, 316. ⁸ Cowley and Partington, *J.*, 1933, 1258, ⁹ Maryott, Hobbs, and Gross, *J. Amer. Chem. Soc.*, 1940, 62, 2320. ¹⁰ Hammick, New, and Williams, *J.*, 1934, 29. ¹¹ Brown, de Bruyne, and Gross, *J. Amer. Chem. Soc.*, 1934, 56, 1291. ¹² Tiganik, *Z. physikal. Chem.*, 1931, B, 13, 425. ¹³ Hassel and Naeshagen, *ibid.*, p. 79. ¹⁴ Lütgert, *ibid.*, 1932, B, 17, 460. ¹⁵ Hassel and Naeshagen, *ibid.*, 1929, B, 4, 217; Hassel and Uhl, *ibid.*, 1930, B, 8, 187. ¹⁶ Fuchs and Donle, *ibid.*, 1933, B, 22, 1. ¹⁷ Kadesch and Weller, *J. Amer. Chem. Soc.*, 1941, 63, 1310. ¹⁸ Cherrier, *Compt. rend.*, 1947, 225, 1306. ¹⁹ Bentley, Everard, Marsden, and Sutton, *J.*, 1949, 2957. ²⁰ Ref. 2, pp. 85—89. ²¹ Williams, *Physikal. Z.*, 1928, 29, 174; Williams and Schwingel, *J. Amer. Chem. Soc.*, 1928, 50, 362. ²² Ref. 12. ²³ Higasi, *Bull. Inst. Phys. Chem. Res. Japan*, 1941, 20, 218. ²⁴ Ref. 13. ²⁵ Thomson, *J.*, 1944, 404.

TABLE III.

	n_D^{25}	Exp. χ^2	$\mu_{C_6H_5}$	(μ_{gas}) , calc.	(μ_{gas}) , found.
Anisole	1.5147	0.664	1.30	1.36	1.36
Acetophenone	1.5308	0.590	2.89	3.06	3.02

As a further test of its usefulness, the Barclay-Le Fèvre relation (*J.*, 1950, 556) has been applied (Table III) to anisole and acetophenone on the assumptions that both molecules are planar and that $\mu_{\text{resultant}}$ bisects a C—O—Me angle of 110° in one case and acts collinearly with the C=O link in the other. Details are explained in the reference just cited; $(n_D^{25})_{C_6H_5}^{25}$ is taken as 2.2417.

Agreement between prediction and experiment is satisfactory. With the exception of certain amines (cf. Barclay and Le Fèvre, *Trans. Faraday Soc.*, in the press) these are the first structures having moments off an axis of symmetry, upon which the new equation has been tried.

It will be noted that $\delta\mu (= \mu_{\text{soln.}} - \mu_{\text{gas}})$ is, for anisole, -0.06 , and for acetophenone, -0.13 D., *viz.*, approximately as 1 : 2. According to Leiser (*Abh. Dtsch. Bunsen-Ges.*, 1910, 67) these two substances have electric double refractions related as *ca.* 1 : 57, so that—as with aniline (Le Fèvre, Roberts, and Smythe, *J.*, 1949, 902) or methylene dichloride (Barclay and Le Fèvre, *J.*, 1950, 556)—neither the sign nor the magnitude of this property is necessarily a good guide to the type of solvent action to be expected (cf. also, Le Fèvre and Ross, *J.*, 1950, 283).

EXPERIMENTAL.

Materials.—Unless otherwise stated, these were commercial specimens. Anisole was dried over phosphoric oxide and distilled; it had b. p. 153—154°/*ca.* 750 mm. 3-Methyl-5-*tert.*-butylanisole, from

isobutyl bromide, *m*-tolyl methyl ether, and aluminium chloride (Baur, *Ber.*, 1894, **27**, 1616), was collected at 220—225°/758 mm. *p*-Nitroanisole, crystallised from light petroleum, had m. p. 51°. 2 : 4 : 6-Trinitroanisole, from picryl chloride and sodium methoxide (Brady and Horton, *J.*, 1925, 2230), had m. p. 68° after two crystallisations (methyl alcohol). "Musk Ambrette" (Baur, D.R.P. 62,362/1891; for constitution see Fuson *et al.*, *J. Org. Chem.*, 1947, **12**, 587), recrystallised several times from alcohol, had m. p. 83°. 2 : 4 : 6-Trichlorotoluene, prepared following Cohen and Dakin (*J.*, 1902, **81**, 1335), had m. p. 33° after distillation. Mesitylene was purified as described by Le Fèvre (*J.*, 1933, 980) for *p*-cymene and had b. p. 163—164°, d_4^{25} 0.8595, n_D^{25} 1.4969. Nitromesitylene, prepared by the method of *Org. Synth.*, **14**, 68, had m. p. 44° (from methyl alcohol). T.N.T., recrystallised from nitric acid and subsequently from a benzene-ethanol mixture, melted at 82°. Baur's directions (*Ber.*, 1891, **24**, 2840) afforded 5-*tert*-butyl-*m*-xylene, b. p. 203°/759 mm. Trichlorobenzene, m. p. 63—64°, was obtained from 2 : 4 : 6-trichloroaniline (Jackson and Lamar, *Amer. Chem. J.*, 1896, **18**, 667). 1-Chloro-2 : 4-dinitrobenzene had m. p. 50—51° (from ether). Picryl chloride, prepared from picric acid by the method of Gazzolo and Jackson (*Amer. Chem. J.*, 1900, **23**, 384; cf. Brady and Horton, *loc. cit.*) and recrystallised from ligroin, had m. p. 83°. Acetophenone, dried over calcium chloride, was distilled immediately before use, and had b. p. 200°/758 mm. 4-Methylacetophenone, from toluene, etc. (cf. Adams and Noller, *J. Amer. Chem. Soc.*, 1924, **46**, 1889), was treated similarly to the previous substance, and had b. p. 225°/736 mm. Trimethylacetophenone (Noller and Adams, *loc. cit.*) had b. p. 123°/20 mm. Dinitrodimethyl-*tert*-butylacetophenone was a specimen of "Musk ketone" with m. p. 135—136° (Baur, *Ber.*, 1898, **31**, 1344, gives 136°) after successive crystallisations from acetic acid and alcohol. 3-Nitro-4-methylacetophenone, prepared by direct nitration (cf. Errera, *Gazzetta*, 1891, **21**, 92), had m. p. 61° (from light petroleum). 1 : 3-Dinitrobenzene had m. p. 89—90°, and 2 : 5-dichloronitrobenzene, m. p. 55—56° (both from alcohol; cf. Cohen and Bennett, *J.*, 1905, **87**, 322, for the second compound). Benzene (as solvent) was AnalaR material to which sodium wire had been added, and one-third frozen, decanted, remelted, and left for 2 days before use.

Measurements.—These have involved the resonance circuits of Le Fèvre and Russell (*Trans. Faraday Soc.*, 1947, **43**, 374), and the simpler arrangement now in use in Sydney (cf. Calderbank and Le Fèvre, *J.*, 1948, 1949). Data are set out below under the usual symbols (cf. "Dipole Moments," Methuen, 1938, Chap. II). Those cases where the concentrations are shown as molar fractions (f_1) are our earliest observations, taken in 1935—36. For uniformity, we have calculated dielectric constants and densities relatively to benzene ($\epsilon_2^{25} = 2.2725$ and $d_4^{25} = 0.87378$). When $\alpha\epsilon_2$ or βd_2 has appeared non-rectilinear with composition, the extrapolation procedure of Le Fèvre (*Trans. Faraday Soc.*, 1950, **46**, 1) has been adopted.

Anisole.					<i>p</i> -Nitroanisole.					
$10^6 w_1$...	1223	1891	2551	5692	9148	1025	1046	2543	3114	3186
ϵ_2^{25}	2.2933	2.3067	2.3171	2.3727	2.4389	2.4434	2.4471	2.7001	2.7982	—
d_4^{25}	0.87533	0.87618	0.87705	0.88107	0.88540	0.87619	0.87625	0.87976	0.88110	0.88128
P_1 (c.c.) ...	65.8 ₈	67.9 ₁	66.5 ₃	66.1 ₇	66.7 ₀	498.2	498.3	475.0	467.2	—
Mean $\alpha\epsilon_2 = 1.76_8$; mean $\beta d_2 = 0.127_4$.						$(\alpha\epsilon_2)_{w_1=0} = 16.5_8$ (graphically); βd_2 is approximately constant, mean = 0.2353.				

2 : 4 : 6-Trinitroanisole.					3-Methyl-5- <i>tert</i> -butylanisole.					
$10^6 f_1$	2622.5	8002.3	13,160	14,501	11,462	15,144	19,244	29,593	29,593	29,593
ϵ_2^{25}	2.2882	2.3211	2.3532	2.3608	2.3053	2.3166	2.3269	2.3564	2.3564	2.3564
d_4^{25}	0.87680	0.88345	0.88993	0.89164	0.87608	0.87694	0.87789	0.87996	0.87996	0.87996
P_1 (c.c.) ...	134.5	134.2	134.1	133.2	96.8	96.1	95.9	94.1	94.1	94.1
∞P_1 (graphically) = 134.6 c.c.						Mean $\alpha\epsilon_2 = 2.85_2$; mean $\beta d_2 = 0.208_8$.				

2 : 4-Dinitro-3-methyl-6- <i>tert</i> -butylanisole ("Musk Ambrette").					2 : 4 : 6-Trichlorotoluene.					
$10^6 w_1$	27,224	46,115	48,947	69,547	9861	12,135	20,661	20,661	20,661	20,661
ϵ_2^{25}	2.4116	2.5121	2.5278	2.6411	2.2757	2.2765	2.2793	2.2793	2.2793	2.2793
d_4^{25}	0.88102	0.88570	0.88650	0.89168	0.87686	0.87756	0.88022	0.88022	0.88022	0.88022
P_1 (c.c.) ...	311.3	309.4	309.2	306.1	54.8	55.0	55.0	55.0	55.0	55.0
$(\alpha\epsilon_2)_{w_1=0} = 4.98$ graphically; mean $\beta d_2 = 0.260_4$.						$\Sigma(\epsilon_{12} - \epsilon_2)/\Sigma w_1 = 0.3281$; $\Sigma(d_{12} - d_2)/\Sigma w_1 = 0.311_8$.				

2 : 4 : 6-Trinitrotoluene.					Mesitylene.					
$10^6 f_1$	1883	3220	5420	5420	5420	32,061	54,882	54,882	54,882	54,882
ϵ_2^{25}	2.2786	2.2822	2.2886	2.2886	2.2886	2.2710	2.2703	2.2703	2.2703	2.2703
d_4^{25}	0.87596	0.87750	0.88001	0.88001	0.88001	0.87250	0.87158	0.87158	0.87158	0.87158
P_1 (c.c.) ...	90.6	86.8	86.2	86.2	86.2	41.7	41.9	41.9	41.9	41.9
$\Sigma(P_{12} - P_2)/\Sigma f_1 = 60.64$, whence $\infty P_1 = 87.2_2$ c.c.										

Nitromesitylene.					2 : 4 : 6-Trichlorobenzene.					
$10^6 w_1$	1012	2591	2613	2613	2613	1019	1130	2098	2098	2098
ϵ_2^{25}	2.3658	2.5090	2.5111	2.5111	2.5111	2.2737	2.2739	2.2750	2.2750	2.2750
d_4^{25}	0.87545	0.87805	0.87809	0.87809	0.87809	0.87711	0.87747	0.88063	0.88063	0.88063
P_1 (c.c.) ...	325.1	312.8	312.7	312.7	312.7	42.8	43.1	42.7	42.7	42.7
Mean $\alpha\epsilon_2 = 9.14_4$; mean $\beta d_2 = 0.164_2$.						Mean $\alpha\epsilon_2 = 0.120_1$; mean $\beta d_2 = 0.326_4$.				

1-Chloro-2 : 4-dinitrobenzene.

$10^6 w_1$...	6215	7316	8241	9918
ϵ_4^{25}	2.3080	2.3149	2.3205	2.3303
d_4^{25}	0.87624	0.87669	0.87705	0.87771
P_1 (c.c.)	253.1	296.5	256.3	255.9

Mean $\alpha\epsilon_2 = 5.79$; mean $\beta d_2 = 0.396_8$.

Picryl chloride.

$10^6 f_1$...	2245	3216	6197	6205
ϵ_4^{25}	2.2768	2.2796	2.2883	2.2869
d_4^{25}	0.8769	0.8784	0.8828	0.8829
P_1 (c.c.)	71.0	73.6	77.6	73.8

$\Sigma(P_{12} - P_2)/\Sigma f_1 = 48.2$, whence $\infty P_1 = 74.8$ c.c.

Acetophenone.

$10^6 w_1$...	801.2	1986	2113	3202	3301
ϵ_4^{25}	2.3342	2.4314	2.4394	2.5255	2.5333
d_4^{25}	0.87389	0.87649	0.87666	0.87815	0.87829
P_1 (c.c.)	211.7	208.3	205.7	202.2	201.9

Mean $\alpha\epsilon_2 = 8.08$; mean $\beta d_2 = 0.136_5$.

4-Methylacetophenone.

$10^6 w_1$...	8135	11,312	16,215
ϵ_4^{25}	2.3421	2.3692	2.4111
d_4^{25}	0.87474	0.87511	0.87569
P_1 (c.c.)	251.6	250.1	247.8

$\Sigma(\epsilon_{12} - \epsilon_2)/\Sigma w_1 = 8.55$;
 $\Sigma(d_{12} - d_2)/\Sigma w_1 = 0.117_7$.

2 : 4 : 6-Trimethylacetophenone.

$10^6 w_1$...	9981	11,561	12,889	13,102	21,951	32,501
ϵ_4^{25}	2.3225	2.3335	2.3415	2.3426	2.3823	2.4448
d_4^{25}	0.87432	0.87460	0.87473	0.87475	0.87538	0.87628
P_1 (c.c.)	202.6	209.1	211.1	210.9	199.0	205.3

$\Sigma(\epsilon_{12} - \epsilon_2)/\Sigma w_1 = 5.22$; $\Sigma(d_{12} - d_2)/\Sigma w_1 = 0.072_4$.

3 : 5-Dinitro-2 : 6-dimethyl-4-tert.-butylacetophenone.

$10^6 f_1$...	3801.0	8525.0	12,777	15,119
ϵ_4^{25}	2.3126	2.3622	2.4058	2.4302
d_4^{25}	0.87728	0.88161	0.88550	0.88762
P_1 (c.c.)	226.8	225.5	223.5	223.1
n_D^* ...	—	—	1.49828	1.49875
R_1 (c.c.)	—	—	74.9	74.8

∞P_1 (graphically) = 228.2 c.c.

* The benzene used had $n_D = 1.49733$.

3-Nitro-4-methylacetophenone.

$10^6 f_1$...	3695.4	4352.1	7689.6	8155.4
ϵ_4^{25}	0.3348	2.3451	2.3991	2.4065
d_4^{25}	0.87560	0.87593	0.87758	0.87777
P_1	920.9	287.8	282.0	281.4

∞P_1 (graphically) = 298.9 c.c.

1 : 3-Dinitrobenzene.

$10^6 w_1$...	6176	9018	10,299	16,927	19,957
ϵ_4^{25}	2.3333	2.3614	2.3741	2.4402	2.4705
d_4^{25}	0.87590	0.87689	0.87733	0.87967	0.88075
P_1 (c.c.)	340.8	338.3	338.1	333.9	331.8

$(\alpha\epsilon_2)_{w_1=0} = 9.80$; $(\beta d_2)_{w_1=0} = 0.340_2$.

(Both by graphical extrapolation.)

2 : 5-Dichloronitrobenzene.

$10^6 w_1$	10,123	12,105	17,501	25,131	30,021
ϵ_4^{25}	2.3416	2.3548	2.3898	2.4376	2.4673
d_4^{25}	0.87764	0.87840	0.88046	0.88337	0.88524
P_1 (c.c.)	278.4	276.6	270.9	263.1	258.5

$(\alpha\epsilon_2)_{w_1=0} = 7.01$ (graphically); βd_2 (average) = 0.381₈.

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