442. *Dielectric Polarisation of 1-Nitronaphthalene, 9-Nitroanthracene, and 4-Nitrodiphenyl in Various Solvents.*

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The magnitudes of the apparent orientation polarisations of the solutes in the title in dioxan, carbon tetrachloride, or benzene are not in the order predicted by earlier empirical equations for solvent effects.

THE dielectric polarisations now reported were observed in connection with the work of the preceding paper. We present them separately because of their bearing on the problem of solvent effects in dipole moment measurements.

Barclay and Le Fèvre[1] and Buckingham and Le Fèvre[2] tested their equations (connecting the ratios ${}_{\mathrm{O}}P_{\mathrm{soln.}}/{}_{\mathrm{O}}P_{\mathrm{gas}}$ between the apparent and true orientation polarisations of a dissolved species with shape and solvent properties) with the ${}_{\mathrm{O}}P_{\mathrm{soln.}}$ figures published by Cleverdon and Smith[3] for nitrobenzene in various media. A minor disagreement was noted. In benzene, carbon tetrachloride, and dioxan, the observed orientation polarisations increased from dioxan to benzene, whereas predictions based on equations numbered 1 to 4 by Buckinghan and Le Fèvre[2] suggested the reverse, as annexed.

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[1] Barclay and Le Fèvre, *J.*, 1950, 556.
[2] Buckingham and Le Fèvre, *J.*, 1952, 1932.
[3] Cleverdon and Smith, *Trans. Faraday Soc.*, 1949, **45**, 109.

Ratios ${}_0P_{\text{soln.}}/{}_0P_{\text{gas}}$ *for nitrobenzene.*

Reqd. by equation	1	2	3	4	Expt.
Dioxan	0·88	0·91	0·90	0·89	0·85
Carbon tetrachloride	0·86	0·88	0·87	0·89	0·86
Benzene	0·85	0·87	0·85	0·88	0·87

It was therefore of interest to ascertain how the orientation polarisations of other nitroaryls are graded in these three solvents. The results are given in Tables 1—3.

TABLE 1. *Solvent constants at 25°.*

	ε	d_4^{25}	p_1 (c.c.)	$C = 3M_1/d_1(\varepsilon_1 + 2)^2$
Carbon tetrachloride	2·2270	1·58454	0·18319	0·10596
Dioxan	2·2090	1·0280	0·2794	0·1647
Benzene	2·2725	0·87378	0·34086	0·18809
Toluene	2·3661	0·8622	0·3629	0·1825

TABLE 2. *Dielectric constant and density measurements.*

10^5w_2	ε_{25}	d_4^{25}	10^5w_2	ε_{25}	d_4^{25}
		1-Nitronaphthalene in dioxan			
840	2·3029	1·0295	1173	2·3392	1·0300
954	2·3154	1·0296	1174	2·3441	1·0301
990	2·3226	1·0299			
		1-Nitronaphthalene in carbon tetrachloride			
343	2·2901	1·5828	579	2·3325	1·5815
510	2·3205	1·5820	1057	2·4209	—
563	2·3309	1·5819	1844	2·5653	—
		1-Nitronaphthalene in benzene			
800	2·3555	0·8763	945	2·3698	0·8770
864	2·3628	0·8766	965	2·3705	0·8771
908	2·3665	0·8768	1140	2·3919	0·8774
		1-Nitronaphthalene in toluene			
555	2·4201	0·8639	1248	2·4904	0·8656
814	2·4464	0·8644	1390	2·5041	0·8660
1058	2·4722	0·8650	1553	2·5210	0·8665

10^5w_2	ε_{25}	d_4^{25}	10^5w_2	ε_{25}	d
		9-Nitroanthracene in carbon tetrachloride			
75	2·2353	1·58320	94	2·2379	1·58286
84	2·2367	1·58306	128	2·2415	—
94	2·2374	1·58291			
		9-Nitroanthracene in benzene			
268	2·2890	—	481	2·3020	0·8750
275	2·2894	—	493	2·3034	0·8751
312	2·2915	0·8746	566	2·3079	0·8753
325	2·2920	0·8746	836	2·3251	0·8761
384	2·2959	0·8747			
		4-Nitrodiphenyl in dioxan			
270	2·2395	1·0283	519	2·2665	1·0286
317	2·2441	1·0284	579	2·2731	1·0287
475	2·2612	1·0285	588	2·2740	1·0288
		4-Nitrodiphenyl in carbon tetrachloride			
121	—	1·58368	204	—	1·58310
123	2·2503	—	207	2·2654	—
136	—	1·58343	209	2·2657	—
139	2·2530	—	227	2·2702	1·58284
188	2·2630	—	302	2·2838	1·58216
190	2·2635	—	303	2·2853	—

TABLE 3. *Calculations of dipole moments.*

Solute	Solvent	$d\varepsilon_1$	β	${}_\infty P_2$ (c.c.)	R_D (c.c.)	μ (D)
1-Nitronaphthalene	Dioxan	11·29	0·172$_5$	362·1	50·1 *	3·90
,,	CCl_4	18·33$_5$	−0·315	378·2	,,	4·00
,,	Benzene	10·35	0·378	373·9	,,	3·98
,,	Toluene	9·93$_7$	0·319	356·9	,,	3·87
9-Nitroanthracene	CCl_4	(11·33)	(−1·111)	(354·3)	72·7 *	(3·71)
,,	Benzene	6·18$_5$	0·301	312·9	,,	3·43
4-Nitrodiphenyl	Dioxan	11·08	0·117	412·7	58·1 *	4·16
,,	CCl_4	18·92	−0·477$_5$	453·3	,,	4·39$_5$

* Computed from R_D of the parent hydrocarbon by taking R_D values of 1·03 and 6·71 c.c. respectively for H and NO_2 (see Vogel, *J.*, 1948, 1833; Campbell, Le Fèvre, Le Fèvre, and Turner, *J.*, 1938, 404).

1-Nitronaphthalene and 4-nitrodiphenyl have been examined hitherto only in benzene; Wesson[4] gives $\mu = 3{\cdot}62$ or 3·88 D for the former and 4·17 or 4·28 D for the latter. Our figures for 1-nitronaphthalene (3·98 D) in benzene is identical with one reported by Vassiliev and Sirkin.[5] No previous determinations of the moment of 9-nitroanthracene appear to be recorded; the material is sparingly soluble in carbon tetrachloride and our

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[4] Wesson, "Tables of Electric Dipole Moments," Technology Press, Massachusetts Institute of Technology, 1948.

[5] Vassiliev and Sirkin, *Acta Physicochim. U.S.S.R.*, 1941, **14**, 414.

results (Table 3, and below) in this medium, being therefore somewhat uncertain, are shown in parentheses.

Littlejohn and Smith [6] have published data for 4-nitrodiphenyl in benzene ($_{\infty}P_2 = 447{\cdot}7$ c.c. at 25°, $\mu = 4{\cdot}36$ D) which seem concordant with ours in carbon tetrachloride.

The following solvent actions on μ_{apparent} can accordingly be discerned: for 1-nitronaphthalene and 4-dinitrodiphenyl μ increases in order dioxan < benzene < carbon tetrachloride and for nitrobenzene the order is dioxan < carbon tetrachloride < benzene (for 9-nitroanthracene μ is less in benzene than in carbon tetrachloride). The order for nitrobenzene is contrary to that predicted. Since no information is available for n_2 for the present solutes at 25°, Buckingham and Le Fèvre's equations cannot be applied. As an approximation, however, the shape factors A, B, and C from the previous paper have been applied in the rough form: $\mu_s^2/\mu_g^2 = 1 + (\varepsilon_1 - 1)(\exp x^2 - 1)/(\varepsilon_1 + 2)$ to compute ratios μ_{s1}^2/μ_{s2}^2. Predictions for 1-nitronaphthalene, 9-nitroanthracene, or 4-nitrodiphenyl, however, again resemble those for nitrobenzene, *viz.*, the apparent moments should be greatest in dioxan and least in benzene: by experiments the expected order is observed only in carbon tetrachloride and benzene, being less in dioxan than either of the others.

Experimental.—The solutes were recrystallised specimens with m. p.s given in Beilstein's "Handbuch." Experimental procedures and methods of calculation were those described by Le Fèvre; [7] the circuit used to determine ε was that noted by Buckingham *et al.*[8] For symbols used see ref. 7.

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[6] Littlejohn and Smith, *J.*, 1953, 2456.
[7] Le Fèvre, "Dipole Moments," Methuen, London, 3rd Edn., 1953, Chap. 2.
[8] Buckingham, Freeman, Le Fèvre, Narayana Rao, and Tardif, *J.*, 1956, 1405.