363. *Molecular Polarisability. The Molar Kerr Constants of Phenol and its* p-*Methyl, Chloro-, Bromo-, and Nitro-derivatives.*

By R. J. W. Le Fèvre and A. J. Williams.

The apparent dipole moments, molar Kerr constants, and certain other properties of the compounds mentioned in the title have been measured at 25° in carbon tetrachloride or benzene. Semi-axes of the corresponding polarisability ellipsoids are calculated, various bond data being used from previous work, and compared with results from experiment. Measurement and prediction are reconcilable if (*a*) in phenol and *p*-cresol the O–H link lies effectively slightly out of the plane of the Ar ring (either vibrating above or below this plane, or adopting fixed conformations, thus making the solutes mixtures of conformational isomers), and the resultant moments act at 60° or more to the C–O directions; and (*b*) in the other three compounds the molecules are effectively flat, and the resultant moments act at angles of *ca.* 45°, 37°, and 5° to the C–O direction.

As a result of recent work[1] on the n-alcohols it became of interest to enquire whether conclusions drawn therefrom regarding the polarisation and polarisability of the C–O–H unit could be applied satisfactorily to phenols. Accordingly, appropriate measurements were instituted on the five solutes named in Tables 1—3, and are here reported and discussed.

Experimental.—Materials and procedures. The solutes were redistilled or recrystallised immediately before use, steps being taken to keep them anhydrous. Benzene and carbon tetrachloride, as solvents, were also dry, being stored over sodium wire or calcium chloride respectively. Apparatus, procedures, methods of calculation, etc., were those standard among the Sydney group.[2,3]

Results.—These are recorded under usual headings (see refs. 2—4 for definitions, explanations, etc.) in Tables 1—3.

Table 1. *Kerr constants, refractivities, dielectric constants, and densities of mixtures containing weight fractions w_2 of solute at 25°.**

Phenol in carbon tetrachloride

$10^5 w_2$	253	448	507	644	802	887	1118
ε^{25}	2·2398	2·2496	2·2524	2·2591	2·2665	2·2710	2·2814
d_4^{25}	1·58228	1·58107	1·58045	1·57952	1·57833	1·57780	1·57594
$10^4 \Delta n_D$ ...	4	6	6	7	10	13	—
$10^5 w_2$	1556	2470	2863	2879	3715	5541	
ε^{25}	2·3021	2·3469	2·3678	2·3682	2·4124	2·5164	
d_4^{25}	1·57289	1·56632	1·56340	1·56222	1·55718	1·54442	
$10^4 \Delta n_D$ ...	22	—	41	42	53	76	

whence $\Delta\varepsilon = (5{\cdot}15 \pm 0{\cdot}02)w_2 + 24{\cdot}3w_2^2$; $\Delta d = (-0{\cdot}82 \pm 0{\cdot}02)w_2 + 5{\cdot}23w_2^2$; $\sum\Delta n/\sum w_2 = 0{\cdot}1394$

$10^5 w_2$	474	492	757	983	1076	1228	1525	1789
$10^7 \Delta B$ ...	0·018	0·015	0·027	0·036	0·040	0·051	0·062	0·068

whence $\sum(\Delta B \,.\, w_2)/\sum w_2^2 = 3{\cdot}86_0$; $\sum\Delta B/\sum w_2 = 3{\cdot}80_8$

p-*Cresol in carbon tetrachloride*

$10^5 w_2$	549	709	786	1075	1277	1286	1567
ε^{25}	2·2508	2·2577	2·2624	2·2745	2·2829	2·2830	2·2964
d_4^{25}	1·57981	1·57848	1·57767	1·57523	1·57364	1·57364	1·57107
$10^4 \Delta n_D$ ...	7	8	—	—	18	18	—
$10^5 w_2$	1734	2133	2210	2391	3022	3112	4041
ε^{25}	2·3040	2·3209	2·3259	2·3323	2·3619	2·3662	2·4118
d_4^{25}	1·56992	1·56648	1·56574	1·56446	1·55927	1·55865	1·55109
$10^4 \Delta n_D$ ...	23	28	—	29	39	40	52

whence $\Delta\varepsilon = (4{\cdot}36 \pm 0{\cdot}02)w_2 + 3{\cdot}38w_2^2$; $\Delta d = (-0{\cdot}872 \pm 0{\cdot}003)w_2 + 1{\cdot}24w_2^2$; $\sum\Delta n/\sum w_2 = 0{\cdot}1294$

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[1] (*a*) Le Fèvre and Williams, *J.*, 1960, 108; (*b*) *ibid*, p. 115; (*c*) Le Fèvre and Rao, *J.*, 1960, 119; (*d*) Le Fèvre, Le Fèvre, Rao, and Williams, *J.*, 1960, 123; (*e*) Le Fèvre and Williams, *J.*, 1960, 128.

[2] Le Fèvre and Le Fèvre, *J.*, 1953, 4041.

[3] Le Fèvre and Le Fèvre, *Rev. Pure Appl. Chem.*, 1955, **5**, 261.

[4] Le Fèvre, Le Fèvre, and Oh, *Austral. J. Chem.*, 1957, **10**, 218.

TABLE 1. (*Continued.*)

10^5w_2	923	963	1099	1514	1551	1973	2153	3086	3129	3937	3939
$10^7\Delta B$	0·021	0·025	0·028	0·041	0·038	0·047	0·054	0·075	0·076	0·093	0·095

whence $\sum(\Delta B\,.\,w_2)/\sum w_2^2 = 2{\cdot}425$; $\sum\Delta B/\sum w_2 = 2{\cdot}444$.

p-*Chlorophenol in carbon tetrachloride*

10^5w_2	522	728	1128	1142	1153	1378	1427
ε^{25}	2·2647	2·2788	2·3079	2·3075	2·3086	2·3257	2·3286
d_4^{25}	1·58253	1·58167	1·58039	1·58020	1·58025	1·57930	1·57938
$10^4\Delta n_D$	—	—	15	—	15	—	21
10^5w_2	1629	1704	2440	2727	2754	3484	4333
ε^{25}	2·3414	2·3472	2·3888	2·4078	2·4089	2·4508	2·4958
d_4^{25}	1·57851	1·57820	1·57535	1·57456	1·57431	1·57188	1·56864
$10^4\Delta n_D$	22	23	—	39	—	50	—

whence $\Delta\varepsilon = (7{\cdot}41 \pm 0{\cdot}03)w_2 - 28{\cdot}2w_2^2$; $\Delta d = (-0{\cdot}376 \pm 0{\cdot}003)w_2 + 0{\cdot}23w_2^2$; $\sum\Delta n/\sum w_2 = 0{\cdot}1408$

10^5w_2	346	516	780	937	1008	1180	1374	1483	2272	2594
$10^7\Delta B$	0·057	0·071	0·094	0·120	0·132	0·153	0·173	0·181	0·278	0·305

whence $\sum(\Delta B\,.\,w_2)/\sum w_2^2 = 12{\cdot}2_6$; $\sum\Delta B/\sum w_2 = 12{\cdot}5_2$

p-*Chlorophenol in benzene*

10^5w_2	1637	2074	3131	3863
ε^{25}	2·3466	2·3681	2·4188	2·4570
d_4^{25}	0·87839	0·87963	0·88267	0·88477

whence $\Delta\varepsilon = (4{\cdot}37 \pm 0{\cdot}04)w_2 + 10{\cdot}4w_2^2$; $\Delta d = (0{\cdot}2795 \pm 0{\cdot}004)w_2 + 0{\cdot}13w_2^2$

p-*Bromophenol in carbon tetrachloride*

10^5w_2	468	960	1064	1216	1316	1573	1972
ε^{25}	2·2516	2·2764	2·2822	2·2906	2·2940	2·3081	2·3289
d_4^{25}	1·58485	1·58527	1·58530	1·58541	1·58552	1·58574	1·58600
$10^4\Delta n_D$	3	—	13	15	—	—	29
10^5w_2	2278	2311	2635	3026	4030	5504	
ε^{25}	2·3438	2·3442	2·3580	2·3768	2·4222	2·4869	
d_4^{25}	1·58638	1·58616	1·58652	1·58683	1·58757	1·58887	
$10^4\Delta n_D$	33	—	—	—	—	—	

whence $\Delta\varepsilon = (5{\cdot}31 \pm 0{\cdot}02)w_2 - 10{\cdot}79w_2^2$; $\Delta d = (0{\cdot}071 \pm 0{\cdot}001)w_2 + 0{\cdot}12_5w_2^2$; $\sum\Delta n/\sum w_2 = 0{\cdot}1330$

10^5w_2	312	691	713	966	981	1194	1274	1553
$10^7\Delta B$	0·040	0·082	0·085	0·115	0·118	0·138	0·155	0·193
$10^4\Delta n_D$	—	—	9	11	11	17	18	20

whence $\sum(\Delta B\,.\,w_2)/\sum w_2^2 = 12{\cdot}0_7$; $\sum\Delta B/\sum w_w = 12{\cdot}0_5$

10^5w_2	575	589	625	708	922	1108	1446
ε^{25}	2·2926	2·2922	2·2936	2·2970	2·3053	2·3099	2·3238
d_4^{25}	0·87624	0·87622	0·87638	0·87649	0·87731	0·87841	0·87982
$10^4\Delta n_D$	4	2	4	5	8	8	9
10^5w_2	1504	1527	1636	2142	2542	2742	4420
ε^{25}	2·3249	2·3254	2·3279	2·3491	2·3648	2·3683	2·4272
d_4^{25}	0·88012	0·88015	0·88070	0·88241	0·88414	0·88530	0·89269
$10^4\Delta n_D$	7	9	8	12	14	17	22

whence $\Delta\varepsilon = (3{\cdot}50 \pm 0{\cdot}03)w_2 + 0{\cdot}61w_2^2$; $\Delta d = (0{\cdot}403 \pm 0{\cdot}004)w_2 + 0{\cdot}53w_2^2$; $\sum\Delta n/\sum w_2 = 0{\cdot}0574$

p-*Nitrophenol in benzene*

10^5w_2	347	424	517	532	643	701	712	748	759
ε^{25}	2·3390	2·3563	2·3716	2·3759	2·4000	2·4085	2·4112	2·4228	2·4202
d_4^{25}	0·87496	0·87497	0·87550	0·87527	0·87599	0·87611	0·87611	0·87598	0·87620
$10^4\Delta n_D$	4	—	—	—	6	7	—	—	—
10^5w_2	908	943	979	1073	1077	1113	1118	1151	
ε^{25}	2·4537	2·4532	2·4707	2·4877	2·4883	2·4984	2·4964	2·5102	
d_4^{25}	0·87682	0·87672	0·87707	0·87730	0·87728	0·87745	0·87732	0·87766	
$10^4\Delta n_D$	7	—	8	9	10	10	—	—	

whence $\Delta\varepsilon = (18{\cdot}6 \pm 0{\cdot}6)w_2 + 144{\cdot}9w_2^2$; $\Delta d = (0{\cdot}305 \pm 0{\cdot}001)w_2 + 2{\cdot}01w_2^2$; $\sum\Delta n/\sum w_2 = 0{\cdot}0617$

10^5w_2	58	106	125	136	213	336	348	373
$10^7\Delta B$	0·050	0·109	0·120	0·130	0·209	0·347	0·380	0·376
$10^4\Delta n_D$	—	—	—	—	—	—	3	—

whence $\sum(\Delta B\,.\,w_2)/\sum w_2^2 = 102{\cdot}9$; $\sum\Delta B/\sum w_2 = 101{\cdot}5$.

* Values at 25° when $w_2 = 0$ are (*a*) for carbon tetrachloride, $\varepsilon = 2{\cdot}2270$, $d = 1{\cdot}58454$, $n_D = 1{\cdot}4575$, $B = 0{\cdot}070 \times 10^{-7}$; (*b*) for benzene, $\varepsilon = 2{\cdot}2725$, $d = 0{\cdot}87378$, $n_D = 1{\cdot}4973$, $B = 0{\cdot}410 \times 10^{-7}$.

TABLE 2. *Total polarisations at infinite dilution, molecular refractions, and dipole moments calculated from Table* 1.

Solute	Solvent	$(\alpha\varepsilon_1)_{w_2=0}$	$(\beta)_{w_2=0}$	$_{\infty}P_2$ (c.c.)	R_D (c.c.)	μ (D) *	μ (D) †
$C_6H_5{\cdot}OH$	CCl_4	5·15	−0·517	77·5	28·0	$1{\cdot}5_6$	$1{\cdot}5_3$
$Me{\cdot}C_6H_4{\cdot}OH$	CCl_4	4·36	−0·550	$80{\cdot}6_5$	33·4	$1{\cdot}5_2$	$1{\cdot}4_9$
$Cl{\cdot}C_6H_4{\cdot}OH$	CCl_4	7·41	−0·237	130·1	33·3	$2{\cdot}1_7$	$2{\cdot}1_6$
,,	C_6H_6	4·37	0·320	135·5	32·7	$2{\cdot}2_4$	$2{\cdot}2_2$
$Br{\cdot}C_6H_4{\cdot}OH$	CCl_4	5·31	0·045	127·6	36·0	$2{\cdot}1_2$	$2{\cdot}0_{95}$
,,	C_6H_6	3·50	0·461	145·7	37·5	$2{\cdot}3_0$	$2{\cdot}2_8$
$NO_2{\cdot}C_6H_4{\cdot}OH$	C_6H_6	18·6	0·349	517·5	$37{\cdot}7_5$	$4{\cdot}8_4$	$4{\cdot}8_3$

* The distortion polarisation being taken as R_D, or † as $1{\cdot}05R_D$.

TABLE 3. *Molar Kerr constants at infinite dilution calculated from Tables* 1 *and* 2.

Solute	Solvent	γ	δ *	δ **	$_{\infty}(_{m}K_2)$ * $\times 10^{12}$	$_{\infty}(_{m}K_2)$ ** $\times 10^{12}$
$C_6H_5{\cdot}OH$	CCl_4	0·095	55·14	$54{\cdot}4_1$	38·1	37·6
$Me{\cdot}C_6H_4{\cdot}OH$	,,	0·088	$34{\cdot}6_4$	$34{\cdot}9_1$	27·6	27·7
$Cl{\cdot}C_6H_4{\cdot}OH$	,,	0·096	175·2	178·9	166·4	170·0
$Br{\cdot}C_6H_4{\cdot}OH$	,,	0·091	172·4	172·2	221·3	221·0
$NO_2{\cdot}C_6H_4{\cdot}OH$	C_6H_6	0·062	$250{\cdot}9_5$	247·7	2559	2524

* $(1/B_1)\Sigma(\Delta B\,.\,w_2)/\Sigma w_2^{\,2}$; ** $(1/B_1)\Sigma\Delta B/\Sigma w_2$; corresponding values of $_{\infty}(_{m}K_2)$ are similarly asterisked.

DISCUSSION

Dipole Moments.—Earlier reported values for the present five solutes are not numerous and differ among themselves. They mostly refer to solutions in benzene, none to carbon tetrachloride as solvent. The M.I.T. Tables [5] list ranges as follows:

	μ (D)		μ (D)
Phenol	1·4—1·7	*p*-Chlorophenol	2·1—2·68
p-Cresol	1·57—1·64	*p*-Bromophenol	$2{\cdot}12_5$—2·86
		p-Nitrophenol	$5{\cdot}01_6$—5·05

In particular, our results may be compared with those of Donle and Gehrekens [6] who quote 1·57, 1·57, 2·22, $2{\cdot}12_5$, and 5·02 D, respectively, for the above molecules. Anzillotti and Curran [7] give $\mu = 2{\cdot}25$ D for *p*-bromophenol. Both Fogelberg and Williams [8] and Donle and Gehrckens [6] record the moment of *p*-nitrophenol as slightly over 5 D.

Molar Kerr Constants.—An analysis of the observed values of $_{m}K$ is difficult because the conformation of the hydroxyl group and the direction of action of the molecular resultant moment (*vis-à-vis* the principal semi-axes of polarisability) are not known with certainty. The following approach to the problem leads to conclusions which roughly fit the data from experiment.

Le Fèvre and Rao [9] listed semi-axes for benzene, toluene, chloro- and bromo-benzene, and nitrobenzene. Since $b_L^{C-H} = b_T^{C-H} = b_V^{C-H} = 0{\cdot}064 \times 10^{-23}$ c.c., the corresponding semi-axes for "phenyl" or "*p*-X-phenyl" are known. Le Fèvre, Le Fèvre, Rao, and Williams determined the semi-axes of methanol [1(d)] as 0·315, 0·363, and 0·278 × 10^{-23}; subtraction of $3b_i^{C-H}$ gives for the C–O–H fragment $b_1 = 0{\cdot}123$, $b_2 = 0{\cdot}171$, and $b_3 = 0{\cdot}086 \times 10^{-23}$. If it is assumed that the respective semi-axes of the aryl group and the C–O–H unit are parallel, then estimates for the phenols emerge as in Table 4.

The totals, $\sum b_i$ (calc.) $= b_1 + b_2 + b_3$, computed on this basis, show satisfactory agreement in the first four cases with $\sum b_i$ (obs.) drawn from electronic polarisations taken as

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[5] Wesson, "Tables of Electric Dipole Moments," Technology Press, Massachusetts Inst. Technology, 1948.

[6] Donle and Gehrckens, *Z. phys. Chem.*, 1932, *B*, **18**, 316.

[7] Anzillotti and Curran, *J. Amer. Chem. Soc.*, 1943, **65**, 607.

[8] Fogelberg and Williams, *J. Amer. Chem. Soc.*, 1930, **52**, 1356.

[9] Le Fèvre and Rao, *J.*, 1958, 1465.

TABLE 4. *Predicted polarisability semi-axes.*

	$10^{23}b_1$	$10^{23}b_2$	$10^{23}b_3$	$10^{23}\sum b_i$ (calc.)	$10^{23}\sum b_i$ (obs.)
$H{\cdot}C_6H_4{\cdot}OH$	1·18	1·23	0·76	3·17	3·16
$Me{\cdot}C_6H_4{\cdot}OH$	1·33	1·51	0·90	3·74	3·78
$Cl{\cdot}C_6H_4{\cdot}OH$	1·54	1·36	0·84	3·74	3·76
$Br{\cdot}C_6H_4{\cdot}OH$	1·74	1·41	0·91	4·06	4·07
$NO_2{\cdot}C_6H_4{\cdot}OH$	1·68	1·31	0·88	3·87	4·26
$NO_2{\cdot}C_6H_4{\cdot}OH$	(2·07)	1·31	0·88	4·26	4·26

$0{\cdot}95R_D$, the values of R_D being those in Table 2. For *p*-nitrophenol $\sum b_i$ (obs.) — $\sum b_i$ (calc.) $= 0{\cdot}39 \times 10^{-23}$ c.c. If, as previous work[9-11] suggests, such exaltation of polarisability occurs predominantly along the 1,4 direction, then the semi-axes in the last line of Table 4 are probably more appropriate. The data of Table 4 correspond to values of $10^{35}\theta_1$ (the " anisotropy " term in the molar Kerr constant) as follow:

$C_6H_5{\cdot}OH$	2·4
$C_7H_7{\cdot}OH$	3·5
$Cl{\cdot}C_6H_4OH$	4·7
$Br{\cdot}C_6H_4{\cdot}OH$	6·2
$NO_2{\cdot}C_6H_4{\cdot}OH$	5·7
$NO_2{\cdot}C_6H_4{\cdot}OH$	12·9

The problem now is the estimation of the θ_2's (the " dipole " terms in the $_mK$'s). When the resultant moment μ_r acts in the plane containing b_1 and b_2, and makes an angle $\alpha°$ with the b_1 direction, θ_2 is given by

$$\theta_2 = (1/45k^2T^2)[(b_1 - b_2)(\mu_r^2 \cos^2 \alpha - \mu_r^2 \sin^2 \alpha) + (b_2 - b_3)(\mu_r^2 \sin^2 \alpha) - (b_3 - b_1)(\mu_r^2 \cos^2 \alpha)]$$

At the outset we thought α in phenol and *p*-cresol might be *ca.* 60° as in alcohols;[1(d)] however, this led to values of θ_2 which were too large (the *sums*, $\theta_1 + \theta_2$, from experiment being *ca.* 9×10^{-35} for phenol and 7×10^{-35} for *p*-cresol). Angles less than 60° diminished the disagreement:

	α	60°	50°	40°	30°	0°
Phenol	$10^{35}\theta_2$ (calc.)	15	14	13·3	12·5	11·4
p-Cresol	,,	19	16·5	13·8	11	7·3

The nearest approach to the observed values of θ_2 is given when $\alpha = 0°$, but from the natures of the two molecules concerned this cannot be a correct result. With the more polar *para*-substituted derivatives the dependence of θ_2 on α is marked, θ_2 increasing as α is diminished. Values of α in harmony with our measurements are as follows:

	$\alpha°$	$10^{35}\theta_2$ (calc.)	$10^{35}(\theta_1 + \theta_2)$ (calc.)	$10^{35}(\theta_1 + \theta_2)$ (expt.) *
$Cl{\cdot}C_6H_4{\cdot}OH$	45°	37	42	40—41
$Br{\cdot}C_6H_4{\cdot}OH$	37	46	52	53
$NO_2{\cdot}C_6H_4{\cdot}OH$	5	592	605	600—609

* *I.e.*, $(9/2\pi N) \times {}_\infty({}_mK_2)$.

That α might have such magnitudes in these three molecules seems credible; they are notably acidic, so that their $X{\cdot}C_6H_4{\cdot}O$ portions are predisposed to become anions; two effects of this are predictable: the C–O–H angle may be increased (presumably in $C{-}O^-\}H^+$ the three atoms are collinear) and resonance of the kind $X{\cdot}C_6H_4{\cdot}O^- \longleftrightarrow X{\cdot}C_6\overset{-}{H}_4{=}O$ will be favoured. Both effects will tend to move μ_{res} towards the 1,4 line; the presence in the 4-positions of groups having $-M$ character will also assist the resonance mentioned.

With all five solutes we have initially assumed that contributions from forms such as $^-C_6H_5{=}\overset{+}{O}H$ cause the O–H bond to be coplanar with the Ar ring. Were this not so, however, for phenol and *p*-cresol an explanation of the foregoing unsuccessful calculations of θ_2 for these substances would be forthcoming. As an illustration, suppose the C–O–H

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[10] Le Fèvre and Le Fèvre, *J.*, 1954, 1577.

[11] Ref. 3, p. 301.

unit to be in a plane normal to the Ar ring in phenol and *p*-cresol, then with μ_r at 60° to b_1, $10^{35}\theta_2$ becomes $-17{\cdot}7$ and $-20{\cdot}9$ respectively; it is clear therefore that, as the O–H link is rotated about the C–O bond, out of the Ar plane, θ_2 will become less and less positive, and ultimately negative. There is of course no firm evidence that in these two molecules μ_{res} is acting at 60° to b_1. A simple vector calculation shows that the moment of phenol (1·53 D) needs to interact at 77° with the moment of toluene (0·34 D) to produce the resultant observed (1·49 D) for *p*-cresol. Use of 77° instead of 60° increases the negativities of the θ_2's quoted. The observation of values of θ_2 lower than those calculated can thus be easily understood. Parallel considerations for the *p*-halogeno- and *p*-nitro-phenols are unnecessary because the quantities from experiment agree well enough with those from prediction and in no way suggest any need to reduce the latter.

UNIVERSITY OF SYDNEY, N.S.W., AUSTRALIA.

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