

638. Molecular Polarisability: The Molar Kerr Constants of Mono- and Di-methoxy-, -acetoxy-, and -ethoxycarbonyl-benzenes.

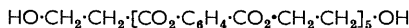
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From considerations involving both dipole moments and molar Kerr constants the effective conformations of the molecules named in the title are deduced. In no case does a single coplanar structure fit the observed properties. With anisole a form in which the $C_{ar}-O-Me$ triangle is twisted 18° out of the C_6 -plane is satisfactory. For phenyl acetate a corresponding angle of *ca.* 90° is indicated, and for ethyl benzoate, one of 23° . Measurements on the di-derivatives can only be explained if mixtures of non-planar forms are assumed; compositions of mixtures compatible with experiment are suggested.

THE measurements now reported were made as a preliminary to studies of certain condensation polymers of the poly-ester type.¹ Subsequently, it became clear that solubilities were in general too low in non-polar solvents to permit useful work, even on polymeric esters of low molecular weights, by extant methods involving the Kerr effect.² The programme has therefore been suspended pending the development of techniques using polar media. Meanwhile, results already to hand for the mono- and di-benzene derivatives named in the title will now be examined for evidence bearing on the effective (or average) conformations adopted by these molecules when present as solutes in carbon tetrachloride at 25° .

EXPERIMENTAL

Materials.—The twelve simple substances were prepared and/or purified until m. p.s or b. p.s agreed with those recorded in the literature (Beilstein's "Handbuch," Chattaway,³ and Timmermans⁴). Poly(ethylene *o*-phthalate) (P.E.O.P. in the following Tables) was obtained from ethylene glycol and diethyl phthalate by the method given by Hardy⁵ for poly(ethylene terephthalate); the white powder resulting did not have a definite m. p. Analysis showed C, 61.3; H, 4.3%; since the molecular weight (in camphor) was *ca.* 1020 the product was regarded as consisting mainly of the polymer



(Calc.: C, 61.1; H, 4.5%; *M*, 1022). Carbon tetrachloride and benzene, as solvents, were commercial supplies treated as in ref. 6, p. 45.

Measurements and Results.—These are listed in Tables 1—3 under headings which, with other symbols used, are defined in refs. 2 and 6. The observations of Table 1 constitute the data from which molar Kerr constants are deduced in Table 2, and dipole moments in Table 3; μ_R and μ are respectively the moments obtained when R_D and $1.05R_D$ are taken as the distortion polarisation of a particular solute.

Previous Measurements.—Since 1948, dipole moments (in D units) have been recorded as follows: anisole, 1.3₀ (C_6H_6 ⁷), 1.25 (CCl_4 ⁸), 1.2₈ (C_6H_6 ⁹); veratrole, 1.3₈ (CCl_4 ⁸); resorcinol dimethyl ether, 1.6₂ (CCl_4 ⁸); quinol dimethyl ether, 1.7₅ (CCl_4 ⁸), 1.7₃ (C_6H_6 ⁹); *m*-phenylene diacetate, 2.1₀ (C_6H_6 ¹⁰).

¹ Carothers, "Collected Papers," Vol. 1 of "High Polymers," Interscience Publ. Inc., New York, 1940.

² Le Fèvre and Le Fèvre, *J.*, 1953, 4041; 1954, 1577; *Rev. Pure Appl. Chem.*, 1955, 5, 261.

³ Chattaway, *J.*, 1931, 2495.

⁴ Timmermans, "Physico-chemical Constants of Pure Organic Compounds," Elsevier, Amsterdam, 1950.

⁵ Hardy, *J. Soc. Chem. Ind.*, 1948, 67, 426.

⁶ Le Fèvre, "Dipole Moments," Methuen, London, 3rd edn., 1953.

⁷ Le Fèvre and Le Fèvre, *J.*, 1950, 1829.

⁸ Klages and Klöpping, *Z. Elektrochem.*, 1953, 57, 369.

⁹ Everard and Sutton, *J.*, 1949, 2312.

¹⁰ Rogers, *J. Amer. Chem. Soc.*, 1955, 77, 3681.

TABLE I. Values of ϵ , d , ΔB , and Δn observed for solutions having weight-fractions w_2 of solute in carbon tetrachloride at 25°.

$10^5 w_2$	$10^7 \Delta B$	$10^4 \Delta n$	ϵ	d	$10^5 w_2$	$10^7 \Delta B$	$10^4 \Delta n$	ϵ	d
0	—*	—*	2.2270	1.5845					
<i>Solute: anisole</i>									
1014	0.023	10	2.2576	1.5751	2638	0.069	26	2.3074	1.5599
1492	0.035	15	2.2730	—	3185	0.084	—	2.3241	1.5553
1557	0.040	—	2.2742	1.5701	4288	0.113	43	2.3561	1.5452
1867	0.051	—	2.2839	1.5671					
whence $10^7 \Delta B = 2.486w_2 + 3.96w_2^2$, $\sum \Delta n / \sum w_2 = 0.100$, $\sum \Delta \epsilon / \sum w_2 = 3.04$, $\sum \Delta d / \sum w_2 = -0.9253$									
<i>Solute: o-dimethoxybenzene</i>									
320	—	—	2.2363	1.5822	2617	-0.004	31	2.3031	1.5657
853	—	—	2.2520	1.5783	3586	-0.006	42	2.3317	1.5588
1142	-0.002	—	2.2598	1.5762	4080	-0.007	—	—	—
1568	-0.003	—	2.2730	1.5732	5216	-0.009	59	2.3757	1.5478
whence $10^7 \Delta B = -0.1634w_2 - 0.159w_2^2$, $\sum \Delta n / \sum w_2 = 0.1153$, $\sum \Delta \epsilon / \sum w_2 = 2.912$, $\sum \Delta d / \sum w_2 = -0.7222$									
<i>Solute: m-dimethoxybenzene</i>									
975	0.035	—	2.2651	1.5771	2865	0.118	31	2.3372	1.5628
1352	0.051	—	2.2794	1.5742	3709	0.153	40	2.3680	1.5566
1637	0.064	18	2.2886	1.5720	3907	0.165	42	2.3773	1.5544
whence $10^7 \Delta B = 3.627w_2 + 14.8w_2^2$, $\sum \Delta n / \sum w_2 = 0.1085$, $\sum \Delta \epsilon / \sum w_2 = 3.84$, $\sum \Delta d / \sum w_2 = -0.760$									
<i>Solute: p-dimethoxybenzene</i>									
1007	0.014	—	2.2738	1.5769	2083	0.028	—	—	1.5691
1137	0.015	—	2.2803	1.5760	2379	0.034	27	2.3396	1.5669
1342	0.018	15	2.2908	1.5744	3253	0.044	36	2.3824	1.5601
1614	0.022	18	2.3040	1.5722	4972	—	—	2.4638	1.5477
whence $10^7 \Delta B = 1.368w_2 - 0.011w_2^2$, $\sum \Delta n / \sum w_2 = 0.1118$, $\sum \Delta \epsilon / \sum w_2 = 4.73$, $\sum \Delta d / \sum w_2 = -0.749$.									
<i>Solute: phenyl acetate</i>									
852	-0.029	—	—	—	5303	—	34	2.4408	1.5468
1094	-0.038	—	—	—	5634	-0.198	—	—	—
1518	-0.052	—	—	—	6063	—	38	—	—
2245	-0.078	—	—	—	6933	—	44	2.5080	1.5345 ₅
3489	—	22	2.3758	1.5583 ₅	8009	—	51	2.5456	1.5280
3656	—	23	—	—	8469	—	55	2.5716	1.5235
4149	-0.145	—	—	—	8639	—	—	2.5744	—
4326	—	—	2.4048	1.5538					
whence $10^7 \Delta B = -3.42w_2 - 1.62w_2^2$, $\sum \Delta n / \sum w_2 = 0.064$, $\sum \Delta \epsilon / \sum w_2 = 4.05$, $\sum \Delta d / \sum w_2 = -0.714$.									
<i>Solute: o-phenylene diacetate</i>									
885	-0.019	—	2.2757	1.5796	1510	-0.034	8	2.3105	1.5762
1102	-0.024	6	2.2880	1.5785	1615	-0.035	—	2.3158	1.5757
1180	-0.026	—	2.2914	1.5781	1717	-0.038	9	2.3216	1.5751
whence $10^7 \Delta B = -2.15w_2 - 2.86w_2^2$, $\sum \Delta n / \sum w_2 = 0.053$, $\sum \Delta \epsilon / \sum w_2 = 5.51$, $\sum \Delta d / \sum w_2 = -0.550$.									
<i>Solute: m-phenylene diacetate</i>									
825	-0.026	—	2.2657	1.5804	4479	-0.145	27	2.4390	1.5621
1779	-0.054	—	2.3111	1.5755	6440	-0.225	40	2.5320	1.5523 ₅
3110	-0.105	—	2.3745	1.5689	8002	-0.282	52	2.6064	1.5447
whence $10^7 \Delta B = -3.07w_2 - 5.79w_2^2$, $\sum \Delta n / \sum w_2 = 0.062$, $\sum \Delta \epsilon / \sum w_2 = 4.73$, $\sum \Delta d / \sum w_2 = -0.503$.									
<i>Solute: p-phenylene diacetate</i>									
426	-0.021	—	2.2465	1.5823	590	-0.028	3	2.2533	1.5814
446	-0.023	—	2.2473	1.5822 ₅	717	-0.036	4	2.2595	1.5809
482	-0.024	—	2.2490	1.5820	852	-0.044	—	2.2661	1.5802 ₅
whence $10^7 \Delta B = -4.72w_2 - 46.3w_2^2$, $\sum \Delta n / \sum w_2 = 0.053$, $\sum \Delta \epsilon / \sum w_2 = 4.54$, $\sum \Delta d / \sum w_2 = -0.516$.									
<i>Solute: ethyl benzoate</i>									
903	0.050	—	2.2730	1.5774	4170	0.228	30	2.4390	1.5518
1587	0.089	12	2.3085	1.5719	5521	0.300	—	—	—
2550	0.136	19	2.3568	1.5644	5978	0.319	—	—	—
3366	0.187	25	2.3991	1.5580 ₅	8039	0.443	57	2.6358	1.5221
whence $10^7 \Delta B = 5.39w_2 + 1.02w_2^2$, $\sum \Delta n / \sum w_2 = 0.074$, $\sum \Delta \epsilon / \sum w_2 = 5.10$, $\sum \Delta d / \sum w_2 = -0.788$.									

TABLE 1. (Continued.)

$10^2 w_2$	$10^7 \Delta B$	$10^4 \Delta n$	ϵ	d	$10^5 w_2$	$10^7 \Delta B$	$10^4 \Delta n$	ϵ	d
<i>Solute: diethyl phthalate</i>									
982	0.008	—	2.2992	—	4005	0.040	26	2.5189	1.5595
1616	0.016	11	2.3450	1.5743	4300	0.045	—	—	1.5573
2666	0.029	—	—	1.5674	6936	0.074	45	2.7378	1.5414
3677	0.037	23	2.4942	1.5618	9447	—	59	2.9126	—
whence $10^7 \Delta B = 0.974w_2 + 1.32w_2^2$, $\Sigma \Delta n / \Sigma w_2 = 0.065$, $\Sigma \Delta \epsilon / \Sigma w_2 = 7.30$, $\Sigma \Delta d / \Sigma w_2 = -0.629$.									
<i>Solute: diethyl isophthalate</i>									
275	0.030	—	—	—	1153	—	—	2.2897	1.5773
502	0.052	—	—	1.5813	1161	—	8	—	—
630	0.066	—	2.2613	1.5805	1242	0.147	—	—	—
737	0.080	—	—	—	1484	—	10	2.3084	1.5753
893	—	—	2.2758	1.5788	1560	0.169	—	—	—
1075	0.118	—	—	—	1728	—	12	2.3211	—
1145	0.125	—	—	—	2736	—	19	2.3782	1.5675
whence $10^7 \Delta B = 10.7w_2 + 24.9w_2^2$, $\Sigma \Delta n / \Sigma w_2 = 0.069$, $\Sigma \Delta \epsilon / \Sigma w_2 = 5.46$, $\Sigma \Delta d / \Sigma w_2 = -0.631$.									
<i>Solute: diethyl terephthalate</i>									
960	0.030	—	2.2812	1.5784	2910	0.090	23	2.3934	1.5655
1238	0.041	—	2.2972	1.5766	4265	0.134	33	—	—
2413	0.076	19	2.3638	1.5689	4302	—	—	2.4728	1.5570
2782	0.084	22	2.3850	1.5668	4850	0.154	37	2.4951	1.5540
whence $10^7 \Delta B = 3.06w_2 + 2.01w_2^2$, $\Sigma \Delta n / \Sigma w_2 = 0.078$, $\Sigma \Delta \epsilon / \Sigma w_2 = 5.68$, $\Sigma \Delta d / \Sigma w_2 = -0.640$.									
<i>Solute: poly(ethylene o-phthalate). Solvent: benzene</i>									
0	— †	— †	2.2725	0.8738	2316	0.042	—	2.3689	0.8809
1632	0.028	—	—	—	2450	—	13	2.3758	0.8817
1781	0.032	—	2.3497	0.8793	2782	0.050	—	2.3919	0.8826
2030	0.038	11	2.3615	0.8804	2952	0.053	16	2.4003	0.8833
2110	0.040	12	—	—	3370	—	—	2.4167	0.8844
whence $10^7 \Delta B = 1.827w_2 - 0.561w_2^2$, $\Sigma \Delta n / \Sigma w_2 = 0.054$, $\Sigma \Delta \epsilon / \Sigma w_2 = 4.29$, $\Sigma \Delta d / \Sigma w_2 = 0.317$.									
* For $w_2 = 0$, $B_1 = 0.070 \times 10^{-7}$, $n_1 = 1.4575$. † $B_1 = 0.410 \times 10^{-7}$, $n_1 = 1.4973$.									

TABLE 2. Molar Kerr constants at infinite dilution in carbon tetrachloride at 25°.

	$\alpha \epsilon_1$	β	γ	δ	$\infty (mK_2) \times 10^{12}$
PhOMe	3.04	-0.584	0.069	35.5 ₁	28.8
<i>o</i> -C ₆ H ₄ (OMe) ₂	2.91	-0.456	0.079	-2.33 ₄	-2.4 ₂
<i>m</i> - "	3.84	-0.480	0.074	51.8 ₁	53.2
<i>p</i> - "	4.73	-0.473	0.077	19.5 ₄	19.3 ₅
PhOAc	4.05	-0.451	0.044	-48.9 ₃	-50.4
<i>o</i> -C ₆ H ₄ (OAc) ₂	5.51	-0.347	0.036	-30.7 ₁	-46.6
<i>m</i> - "	4.73	-0.317	0.043	-43.8 ₆	-65.2
<i>p</i> - "	4.54	-0.326	0.036	-67.4 ₃	-99.3
BzOEt	5.10	-0.497	0.051	77.0 ₁	85.5
<i>o</i> -C ₆ H ₄ (CO ₂ Et) ₂	7.30	-0.397	0.045	13.9 ₁	19.6
<i>m</i> - "	5.46	-0.398	0.047	153.4	253.3
<i>p</i> - "	5.68	-0.404	0.054	43.7 ₁	70.5
P.E.O.P.*	4.29	0.363	0.036	4.46	235 †

* Determined in benzene. † Calc. by using $M_2 = 1022$.

TABLE 3. Polarisations and dipole moments.

	∞P_2 (c.c.)	R_D (c.c.)	μ_R (D)	μ (D)		∞P_2 (c.c.)	R_D (c.c.)	μ_R (D)	μ (D)
PhOMe	66.2	32.9	1.27	1.24 ₅	<i>p</i> -C ₆ H ₄ (OAc) ₂ ...	140.6	47.7	2.13	2.1 ₀
<i>o</i> -C ₆ H ₄ (OMe) ₂	79.5	39.8	1.39	1.3 ₆	BzOEt	122.3	42.3	1.98	1.9 ₅
<i>m</i> - "	93.7	40.1	1.62	1.5 ₉	<i>o</i> -C ₆ H ₄ (CO ₂ Et) ₂	228.8	58.0	2.89	2.8 ₆
<i>p</i> - "	106.5	40.0	1.80	1.7 ₈	<i>m</i> - "	185.5	58.4	2.49	2.4 ₆
PhOAc	94.6	36.8	1.68	1.6 ₅	<i>p</i> - "	190.9	59.3	2.53	2.5 ₁
<i>o</i> -C ₆ H ₄ (OAc) ₂	161.3	48.4	2.35	2.3 ₂	P.E.O.P.*	1047 †	250	6.2	6.2
<i>m</i> - "	144.2	47.9	2.17	2.1 ₄					

* Determined in benzene. † Calc. by using $M_2 = 1022$.

Measurements made before 1948 are listed by Wesson¹¹ but his tables contain no entries for the diacetates of veratrole and resorcinol, or for diethyl isophthalate.

Lippmann,¹² Leiser,¹³ and Becker¹⁴ have noted the Kerr constant of pure anisole, and Lippmann has also reported the Kerr effects (relatively to carbon disulphide) of three mixtures with benzene, but for none of the present thirteen solutes is a molar Kerr constant available in the literature.

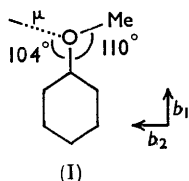
DISCUSSION

Anisole and the Three Dimethoxybenzenes.—From the molecular refractions for anisole given by Vogel,¹⁵ the electronic polarisation follows as 31.58 c.c., whence $b_1 + b_2 + b_3 = 3.755 \times 10^{-23}$ c.c. Krishnan¹⁶ has reported a depolarisation factor (for light scattered at 90° to an incident beam) which, with an isothermal compressibility of 63×10^{-6} per atm., yields 28.6×10^{-3} as the molecular anisotropy δ^2 (cf. ref. 17), so that

$$(b_1 - b_2)^2 + (b_2 - b_3)^2 + (b_3 - b_1)^2 = 0.4033 \times 10^{-46}$$

From the molar Kerr constant (Table 2), $\theta_1 + \theta_2$ is 6.85×10^{-35} . Accordingly, if the resultant moment acts along one of the principal axes of the polarisability ellipsoid, this axis has the magnitude 1.32×10^{-23} and the two associated axes have magnitudes 1.47 and 0.96×10^{-23} . Since the moment¹⁸ of dimethyl ether is 1.25 D and the Me-O-Me angle is 110°, 1.10 D seems a reasonable value for $\mu_{\text{Me-O}}$; despite the estimates of mesomeric moments in anisole by Lumbroso²⁰ and Groves and Sugden,²¹ $\mu_{\text{Ph-O}}$ cannot be greatly less than 1.1 D to produce $\mu_{\text{anisole}} = 1.24_5$ D by the interaction of components at *ca.* 110° (the assumed Ph-O-Me angle in this molecule). Lumbroso²⁰ considers that the resultant acts at 104° to the Ph-O axis; we shall accept this in what follows.

When account is taken of the anisotropic polarisabilities of benzene² ($10^{23}b_1 = 10^{23}b_2 = 1.12$, $10^{23}b_3 = 0.73_5$), and of the C-O bond ($10^{23}b_L = 0.081$, $10^{23}b_T = 10^{23}b_V = 0.039$), together with the isotropic² polarisability of the C-H link (0.064×10^{-23} c.c.), it becomes evident that b_{max} in anisole can justifiably be taken as nearly parallel to the Ph-O bond direction. Calculation for a flat molecule as (I) provides the following specifications



for the polarisability ellipsoid: $10^{23}b_1 = 1.37_2$, $10^{23}b_2 = 1.36_3$, $10^{23}b_3 = 0.94_2$; $\theta_1 + \theta_2$ is therefore 10.57×10^{-35} , which corresponds to an mK of 44.4×10^{-12} . The observed value is less than this (28.8×10^{-12}). The difference between the found and calculated sums $b_1 + b_2 + b_3$, *viz.*, $(3.755 - 3.677 = 0.078) \times 10^{-23}$, indicates a small exaltation in the total polarisability; this Δb may (in the light of previous conclusions, cf. p. 301 of ref. 2) be added to b_1 , thus making the "predicted" semi-axes for anisole 1.45₀, 1.36₃, and 0.94₂

(all $\times 10^{-23}$ c.c.). These produce a calculated mK of 40×10^{-12} which still considerably exceeds the value from experiment.

Because Lumbroso²⁰ in 1950 and Everard and Sutton⁹ in 1949 had previously noted that interactions between the methoxy-group and hydrogen atoms *ortho* to it could reduce the probability of the existence of flat forms, the effects to be expected if the molecule were non-planar have been investigated. The most satisfactory result is obtained by supposing that the effective conformation of anisole is one in which the planes containing

¹¹ Wesson, "Tables of Electric Dipole Moments," Technology Press, M.I.T., 1948.

¹² Lippmann, Diss., Dresden, 1912.

¹³ Leiser, Abh. Bunsen Ges., No. 4, 1910.

¹⁴ Becker, Ann. Physik, 1925, 76, 849.

¹⁵ Vogel, J., 1948, 616.

¹⁶ Krishnan, Phil. Mag., 1925, 50, 697.

¹⁷ Le Fèvre and Rao, J., 1957, 3644; 1958, 1465.

¹⁸ Barclay and Le Fèvre, J., 1952, 1643.

¹⁹ Sutton and Brockway, J. Amer. Chem. Soc., 1935, 57, 473; Pauling and Brockway, *ibid.*, p. 2684.

²⁰ Lumbroso, Bull. Soc. chim. France, 1950, 812; 1955, 643; Lumbroso and Dumas, *ibid.*, p. 655.

²¹ Groves and Sugden, J., 1937, 1992.

the $C_{ar}-O-Me$ triangle and the benzene ring are at about 18° to one another; then $10^{23}b_1 = 1.45$, $10^{23}b_2 = 1.36$, and $10^{23}b_3 = 0.94$, giving mK calc. = 29.8×10^{-23} .

The situations with the three dimethoxybenzenes are less clear. It seems reasonable to argue that if anisole does not have a flat configuration, none of the dimethoxybenzenes will have one either. In this analysis, for each isomer intervalency angles and component moments have been assumed to be the same as in anisole. Predictions, and various details underlying them, are summarised against the formulæ (IIa—d) for veratrole, (IIIa—f) for *m*-dimethoxybenzene, and (IVa—h) for the *p*-isomer.

In no case does a single effective conformation agree with both the dipole moment and molar Kerr constant as measured (cf. Tables 2 and 3).

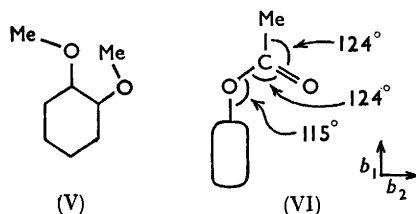
(II) (a) (b) (c) (d)
 $p = 30^\circ$ up; $q = 30^\circ$ down. $r = 40^\circ$ up; $s = 40^\circ$ down.

(III) (a) (b) (c) (d) (e) (f)
 $t = 18^\circ$ up; $u = 18^\circ$ down

(IV) (a) (b) (c) (d) (e) (f) (g) (h)

	(IIa)	(IIb)	(IIc)	(IId)	(IIIa)	(IIIb)	(IIIc)	(IIId)	(IIIe)	(IIIf)
$10^{23}b_1$	1.617	1.617	1.603	1.603	1.619	1.619	1.640	1.640	1.598	1.598
$10^{23}b_2$	1.597	1.597	1.597	1.597	1.606	1.606	1.585	1.585	1.627	1.627
$10^{23}b_3$	1.167	1.167	1.180	1.180	1.156	1.156	1.156	1.156	1.156	1.156
μ (D).....	1.5 ₈	1.9 ₇	1.4 ₄	2.1 ₁	1.1 ₈	1.4 ₁	2.2 ₇	2.3 ₉	1.7 ₀	1.8 ₈
$mK \times 10^{12}$	66	-6	2.1 ₁	-56	46	17	116	87	90	60
	(IVa)	(IVb)	(IVc)	(IVd)	(IVe)	(IVf)	(IVg)	(IVh)		
$10^{23}b_1$	1.626	1.626	1.626	1.626	1.626	1.626	1.626	1.626	1.626	1.626
$10^{23}b_2$	1.600	1.600	1.600	1.600	1.588	1.588	1.588	1.588	1.588	1.588
$10^{23}b_3$	1.156	1.156	1.156	1.156	1.167	1.167	1.167	1.167	1.167	1.167
μ (D)	0	0.74	2.2 ₉	2.4 ₁	0	1.2 ₀	2.0 ₈	2.0 ₈	2.4 ₀	2.4 ₀
$mK \times 10^{12}$	10	-18	131	103	9	-61	101	101	31	31

With *o*-dimethoxybenzene we are confronted with the special problem that none of the structures (IIa—d) should have a $\mu_{\text{resultant}}$ as low as that observed; therefore, neither a single form nor any mixture of these four forms can correctly describe this solute. Curran²³ supposed the existence of an "appreciable number" of *cis-trans*-molecules (V), but inspection of Fig. *b* on p. 2316 of Everard and Sutton's paper⁹ indicates that a coplanar arrangement for (V) is sterically impossible. One is thus driven to the conclusion that in this *ortho*-compound the two oxygen atoms cannot be coplanar with the Ar-ring. If, however, we assume the oxygen atoms to be situated one above and one below the C_6 plane (as are the chlorine atoms in *o*-dichlorobenzene²⁴ or *cis*-dichloroethylene²⁵), then the individual group moment directions can be approximately at right angles to the projections of the $C_{\text{ar}}-\text{O}$ longitudinal axes in the C_6 plane. Calculations then show that an equimolecular mixture of the two sterically allowable isomers in which the group moments are disposed at *ca.* 30° to this C_6 plane would correspond to a dipole moment and molar Kerr constant close to those actually recorded (Tables 2 and 3). Such a hypothesis is advanced with diffidence, since the "Wirkungsradius" of oxygen is usually considered to be less than that of chlorine²⁶ and no obvious steric cause can be cited in justification.



With *m*-dimethoxybenzene it is clear that, since $\mu_{\text{obs.}}$ is 1.5₉ D, there must be some participation by forms (IIIa) and/or (IIIb). A mixture of equal parts of (IIIa—d) would produce $\mu = 1.88$ D and ${}_mK = 66 \times 10^{-12}$, and a similar mixture of all six forms, $\mu = 1.85$ D and ${}_mK = 69 \times 10^{-12}$. Mixtures in which forms *a* and *b* predominate seem most likely from a study of models, and are easily reconcilable with our measurements; *e.g.*, a mixture having forms *a*, *b*, *c*, and *d* in the proportions 3 : 3 : 1 : 1 would have $\mu_{\text{calc.}} = 1.6_2$ D and ${}_mK_{\text{calc.}} = 49 \times 10^{-12}$; agreement with experiment can be made closer by minor alterations in the proportions assumed.

With *p*-dimethoxybenzene the non-polar form (IVa) (or IVe) cannot only be accompanied by (IVb) (or IVf), because the observed resultant moment is 1.7₈ D. Equimolecular mixtures of (IVa—d) or (IVe—h) (the latter group having a greater non-planarity than the former) require $\mu_{\text{resultant}}$ and ${}_mK$ of 1.70 D and 57×10^{-12} or 1.70 D and 20×10^{-12} , respectively; since the observed data are 1.7₈ D and 19.4×10^{-12} , the conformations (IVe—IVh) are preferred.

Phenyl Acetate and the Three Diacetoxybenzenes.—In addition to the bond polarisabilities mentioned above, those for C—C and C=O are now needed. For the former bond, the values (*viz.*, $b_L^{\text{C-C}} = 0.098_6$, $b_T^{\text{C-C}} = b_V^{\text{C-C}} = 0.027_4$; all as units 10^{-23} c.c.) extracted from cyclohexane²² will be used; for the latter, those (*viz.*, $b_L^{\text{C=O}} = 0.230$, $b_T^{\text{C=O}} = 0.140$, $b_V = 0.046$) from acetone.²⁷

For a completely flat conformation of phenyl acetate we calculate $b_1 = 1.63$, $b_2 = 1.58$, and $b_3 = 1.01$, which, with $\mu_{\text{resultant}}$ acting parallel to the C=O bond, should give a positive ${}_mK$ of about 100×10^{-12} . This is in marked disagreement with -50.4×10^{-12} actually observed. Inspection of scale models shows such a flat structure to be sterically impossible. For (VI), in which the plane of the benzene ring is perpendicular to that of the rest of the

²² Le Fèvre and Le Fèvre, *J.*, 1956, 3549.

²³ Curran, *J. Amer. Chem. Soc.*, 1945, **67**, 1835.

²⁴ Bastiansen and Hassel, *Acta Chem. Scand.*, 1947, **1**, 489.

²⁵ Bramley, Le Fèvre, Le Fèvre, and Rao, *J.*, 1959, 1183.

²⁶ Stuart, *Z. phys. Chem.*, 1935, *B*, **27**, 350.

²⁷ Le Fèvre, Le Fèvre, and Rao, *J.*, 1959, 2340.

molecule, we forecast $b_1 = 1.63_8$, $b_2 = 1.20_9$, and $b_3 = 1.39_9$, so that θ_1 calc. is 1.65×10^{-35} and the precise magnitude of θ_2 depends on the angle $\mu_{\text{resultant}}$ makes with the principal polarisability axes. For simplicity we consider $\mu_{\text{resultant}}$ to act in the b_1b_2 plane and at an angle ϕ to the b_2 axis; ${}_mK_{\text{calc.}}$ is sensitively affected by ϕ :

Angle ϕ	0°	20°	25°	31°
$10^{12} {}_mK_{\text{calc.}}$	-86	-63	-52	-35

Small variations could, of course, be made in these calculations by taking inter-valency angles different from those shown in (VI), which were selected from data for related molecules listed in refs. 28(a) and (b). The "trans"-conformation of this ester has not been considered, in view of its moment and the arguments (concerning aliphatic esters) used by Marsden and Sutton,²⁹ but it is possible that $\mu_{\text{resultant}}$ for (VI) does not act exactly parallel to the C=O bond direction [*i.e.*, $\phi = 31^\circ$ in (V)]; obviously, for a given Ph-O-C angle, the larger the O-C=O angle the more will ϕ be reduced, and that ϕ might have a value of *ca.* 25° is not surprising. Calculations for conformations having partial rotations about the Ph-O or O-C bonds are not reproduced, since in general they lead to predicted values of ${}_mK$ which are less negative than the ${}_\infty({}_mK_2)$ actually observed.

With the isomeric diacetoxybenzenes, therefore, we foresee only two possible conformations in each case: one in which both $\text{CH}_3\text{CO-O}$ units lie in planes at 90° to the central C_6 ring ("both up"), and the other in which they are on opposite sides ("up-down"). Calculations are listed in Table 4; b_1 and b_2 are throughout located along the 1,4 and 6,2 directions of the C_6 ring.

TABLE 4. Predicted semi-axes, dipole moments, and molar Kerr constants for the diacetoxybenzenes.

Conformation	$10^{23}b_1$	$10^{23}b_2$	$10^{23}b_3$	μ (D)	${}_mK \times 10^{12}$
<i>1,2-Diacetoxybenzene</i>					
Both up	1.971	1.850	1.673	3.1 ₉	-175
Up-down	"	"	"	1.4 ₂	+40
<i>1,3-Diacetoxybenzene</i>					
Both up	1.971	1.850	1.673	2.9 ₇	-206
Up-down	"	"	"	0.82	+9
<i>1,4-Diacetoxybenzene</i>					
Both up	2.152	1.670	1.673	2.8 ₆	-204
Up-down	"	"	"	0	+11

Since in no instance does prediction for a single form agree *both* with the observed moment *and* with the molar Kerr constant, we suggest that these compounds exist in solution as mixtures as follow:

	Proportions	μ_{mixture}		${}_mK_{\text{mixture}}$	
	Both up : up-down	Calc.	Obs.	Calc.	Obs.
1,2-Isomer	1 : 2	2.2	2.3	-32	-47
1,3- ,,	1 : 2	1.9	2.1	-63	-65
1,4- ,,	1 : 1	2.0	2.1	-97	-99

Ethyl Benzoate and the Three Diethoxycarbonylbenzenes (Diethyl Phthalates).—As a preliminary, we reconsider the case of ethyl formate, for which Le Fèvre, Le Fèvre, and Oh³⁰ have reported ${}_\infty({}_mK_2) = 54.6 \times 10^{-12}$ and $\mu_{\text{resultant}} = 2.0_1$ (D). Taking the structure of this ester as (VII), with $\alpha = 110^\circ$, $\beta = 110^\circ$, and $\gamma = 120^\circ$, we calculate, respectively for b_1 directed as shown in (VII) or for b_2 directed parallel to the C=O bond, the two following sets of molecular semi-axes:

$$\left. \begin{array}{l} 10^{23}b_1 = 0.724 \\ 10^{23}b_2 = 0.778 \\ 10^{23}b_3 = 0.533 \end{array} \right\} \text{or} \left\{ \begin{array}{l} 0.740 \\ 0.762 \\ 0.533 \end{array} \right.$$

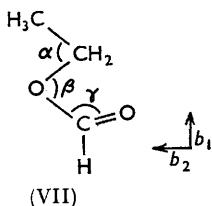
²⁸ (a) Allen and Sutton, *Acta Cryst.*, 1950, **3**, 46; (b) *Chem. Soc. Spec. Publ.*, No. 11, 1958.

²⁹ Marsden and Sutton, *J.*, 1936, 1383.

³⁰ Le Fèvre, Le Fèvre, and Oh, *Austral. J. Chem.*, 1957, **10**, 218.

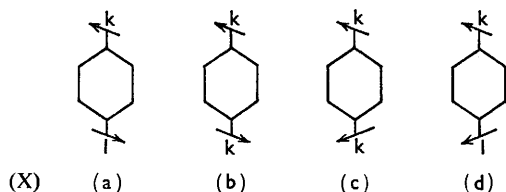
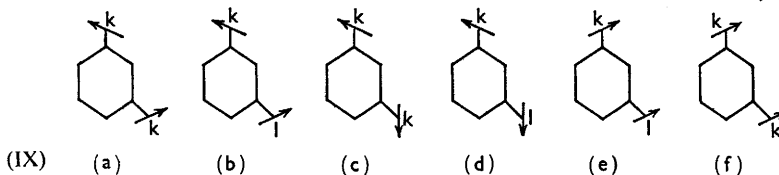
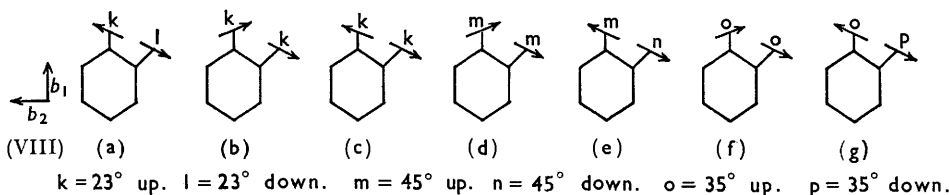
In ref. 30 the second of these assumptions was made and the observational equations were solved to give apparent semi-axes of 0.755×10^{-23} , 0.764×10^{-23} , and 0.541×10^{-23} , but since it is now clear that axial locations as in (VII) lead to a larger value of b_2 —and therefore to a better recognition of the greatest principal axis—than do those of Le Fèvre, Le Fèvre, and Oh,³⁰ we shall adopt (VII) as a basis for subsequent calculations. [Incidentally, the semi-axes calculated for (VII) correspond to an mK of 59.3×10^{-12} , in reasonable accord with the value from experiment—a fact which further justifies the C-O, C=O, C-C, and C-H bond polarisability data used in this paper.]

With regard to ethyl benzoate, it is clear that a structure in which the C_6H_5 and the EtO·C:O groups are coplanar is unsatisfactory; good agreement with measurement is, however, achieved if the ethoxycarbonyl plane is twisted 23° out of that of the benzene ring:



	$10^{23}b_1$	$10^{23}b_2$	$10^{23}b_3$	$10_m^{12}K$ (calc.)	$10_m^{12}K$ (expt.)
Coplanar	1.840	1.778	1.174	143	} 85.5
Planes at 23°	1.840	1.744	1.207	86	

The calculations for the three esters are summarised under formulæ in which arrows indicate the EtO·C:O resultant moments (taken as acting parallel to the C=O direction, cf. Marsden and Sutton²⁹) and the expressions "up x° " or "down x° " refer to the twists assumed for the EtO·C:O plane above or below the C_6 -plane.



	(VIIIa)	(VIIIb)	(VIIIc)	(VIIId)	(VIIIe)	(VIIIf)	(VIIIg)
$10^{23}b_1$	2.495	2.495	2.495	2.436	2.436	2.465	2.465
$10^{23}b_2$	2.446	2.446	2.446	2.349	2.349	2.397	2.397
$10^{23}b_3$	1.680	1.680	1.680	1.837	1.837	1.761	1.761
μ (D)	0.13	3.4_4	1.3_3	3.5_3	0.50	3.5_3	0.30
$mK \times 10^{12}$	31	279	-121	-165	24	13	25

	(IXa)	(IXb)	(IXc)	(IXd)	(IXe)	(IXf)	(Xa)	(Xb)	(Xc)	(IXd)
$10^{23}b_1$	2.495	2.495	2.495	2.495	2.495	2.495	2.566	2.566	2.566	2.566
$10^{23}b_2$	2.446	2.446	2.446	2.446	2.446	2.446	2.374	2.374	2.374	2.374
$10^{23}b_3$	1.680	1.680	1.680	1.680	1.680	1.680	1.681	1.681	1.681	1.681
μ (D)	2.2_6	1.8_4	2.1_7	1.7_3	3.6_7	3.9_0	0	1.3_2	3.3_8	3.1_1
$mK \times 10^{12}$	39	191	1	153	590	438	31	-121	146	299

In each instance we started by adopting the degree of non-planarity deduced above for ethyl benzoate. As with the two previous groups of compounds, no single conformation

appeared to be simultaneously compatible with the two properties measured; again therefore we conclude that these solutes exist as mixtures. The following, into which the components enter in 1 : 1 ratios, are suggested for the three di-esters:

	Components	μ_{mixture}		mK_{mixture}	
		Calc.	Obs.	Calc.	Obs.
1,2-Ester	(VIIIf and g)	2.5	2.9	19	20
1,3- ,,	(IXa—f)	2.7	2.5	235	253
1,4- ,,	(Xa—d)	2.4	2.5	89	71

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