568. *Molecular Polarisability. The Dipole Moments, Molar Kerr Constants, and Conformations of Eleven Phosphate and Phosphite Triesters as Solutes in Benzene.*

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Dipole moments, molar Kerr constants, and refractivities are recorded for the molecules $(RO)_3PO$ (R = Me, Et, Pr^n, Pr^i, n-C_5H_{11},Ph) and $(RO)_3P$ (R = Me, Et, Pr^i, n-$C_{10}H_{21}$, Ph) as solutes in benzene. The principal polarisability semi-axes have been calculated from the observational data, assuming C_3 symmetry. The polarities and polarisabilities of the solutes are interpreted in terms of equivalent molecular conformations, using known bond and group parameters. The polarisability specifications of the groups O_3P and O_3PO, derived from previously documented measurements on the constrained phosphite ester 4-methyl-2,6,7-trioxa-1-phosphabicyclo[2,2,2]-octane and its oxide, are shown to be inapplicable.

This Paper is concerned with the measurement of the polarities and the electric bire-fringences of eleven phosphate and phosphite triesters, and the extraction from such data of information on the configurations of these molecules as solutes in benzene. The experimental quantities are listed in Tables 1 and 2.

TABLE 1.

Incremental Kerr constants, refractive indices, dielectric constants, and densities for solutions in benzene at 25°.

Solute: Trimethyl phosphate

10^5w_2	3931	4391	4893	5005	8694
$10^7\Delta B$	—	−0·097	−0·109	−0·116	−0·194
$10^4\Delta n$	−29	−32	−36	−38	—
ε^{25}	2·5726	2·6088	2·6507	2·6572	—
$d_4{}^{25}$	0·88348	0·88461	0·88594	0·88614	—

whence $\Sigma 10^7\Delta B/\Sigma w_2 = -2\cdot25$; $\Sigma\Delta n/\Sigma w_2 = -0\cdot074$; $\Sigma\Delta\varepsilon/\Sigma w_2 = 7\cdot68$; $\Sigma\Delta d/\Sigma w_2 = 0\cdot247$.

Solute: Triethyl phosphate

10^5w_2	3151	3335	3546	5523	5655
$10^7\Delta B$	−0·099	−0·116	−0·114	−0·179	−0·189

whence $\Sigma 10^7\Delta B/\Sigma w_2 = -3\cdot29$.

10^5w_2	1474	1818	2528	3132	3335	5523
$10^4\Delta n$	−10	−14	−19	—	−26	−41
ε^{25}	2·3557	2·3737	2·4141	2·4472	2·4595	2·5831
$d_4{}^{25}$	0·87611	0·87666	0·87783	0·87878	0·87896	0·88241

whence $\Sigma\Delta n/\Sigma w_2 = -0\cdot075$; $\Sigma\Delta\varepsilon/\Sigma w_2 = 5\cdot61$; $\Sigma\Delta d/\Sigma w_2 = 0\cdot158$.

Solute: Tri-n-propyl phosphate

10^5w_2	2737	3642	4828	5263	6334	6589
$10^7\Delta B$	−0·106	−0·136	−0·183	−0·211	−0·254	−0·265
$10^4\Delta n$	−21	−26	−36	−38	−48	−52
ε^{25}	2·4006	2·4423	2·4975	2·5203	2·5695	2·5821
$d_4{}^{25}$	0·87701	0·87813	0·87955	0·88007	0·88141	0·88174

whence $\Sigma 10^7\Delta B/\Sigma w_2 = -3\cdot93$; $\Sigma\Delta n/\Sigma w_2 = -0\cdot075$; $\Sigma\Delta\varepsilon/\Sigma w_2 = 4\cdot69$; $\Sigma\Delta d/\Sigma w_2 = 0\cdot120$.

Solute: Tri-isopropyl phosphate

10^5w_2	2677	3626	4728	5183	6094	7164
$10^7\Delta B$	−0·069	−0·096	−0·134	—	−0·166	−0·211
$10^4\Delta n$	−24	−31	−44	−49	−51	−67
ε^{25}	2·3706	2·4044	2·4504	2·4606	2·4924	2·5334
$d_4{}^{25}$	0·87626	0·87730	0·87820	0·87864	0·87998	0·88065

whence $\Sigma 10^7\Delta B/\Sigma w_2 = -2\cdot78$; $\Sigma\Delta n/\Sigma w_2 = -0\cdot090$; $\Sigma\Delta\varepsilon/\Sigma w_2 = 3\cdot65$; $\Sigma\Delta d/\Sigma w_2 = 0\cdot096$.

TABLE 1. (*Continued.*)

Solute: *Tri-n-pentyl phosphate*

$10^5 w_2$	2450	3094	4514	5742	6698	8663
$10^7 \Delta B$ ...	−0·085	—	−0·145	—	−0·234	—
$10^4 \Delta n$	−15	−24	−35	−40	−45	−55
ε^{25}	2·3523	2·3752	2·4189	2·4626	2·4945	2·5615
d_4^{25}	0·87548	0·87592	0·87694	0·87775	0·87846	0·87989

whence $\Sigma 10^7 \Delta B / \Sigma w_2 = -3\cdot40$; $\Sigma \Delta n / \Sigma w_2 = -0\cdot069$; $\Sigma \Delta \varepsilon / \Sigma w_2 = 3\cdot31$; $\Sigma \Delta d / \Sigma w_2 = 0\cdot070$.

Solute: *Triphenyl phosphate*

$10^5 w_2$	2687	3407	3447	4093	4504
$10^7 \Delta B$ ...	−0·046	−0·065	−0·064	−0·082	−0·086

whence $\Sigma 10^7 \Delta B / \Sigma w_2 = -1\cdot89$.

$10^5 w_2$	1682	2024	2513	3174	3407	4255
$10^4 \Delta n$	11	12	14	20	20	26

whence $\Sigma \Delta n / \Sigma w_2 = 0\cdot060$.

$10^5 w_2$	1018	1533	1682	1893	2024	3174
ε^{25}	2·3039	2·3181	2·3239	2·3289	2·3345	2·3690
d_4^{25}	0·87649	0·87778	0·87831	0·87869	0·87925	0·88213

whence $\Sigma \Delta \varepsilon / \Sigma w_2 = 3\cdot03$; $\Sigma \Delta d / \Sigma w_2 = 0\cdot265$.

Solute: *Trimethyl phosphite*

$10^5 w_2$	2180	3196	3557	3786
$10^7 \Delta B$ ...	0·046	0·052	0·067	0·065

whence $\Sigma 10^7 \Delta B / \Sigma w_2 = 1\cdot81$.

$10^5 w_2$	3077	3878	5026	5789	7398	8453
$10^4 \Delta n$	−24	−28	−41	−46	−58	−67
ε^{25}	2·3519	2·3732	2·4037	2·4306	2·4691	2·5053
d_4^{25}	0·87824	0·87945	0·88118	0·88233	0·88467	0·88623

whence $\Sigma \Delta \varepsilon / \Sigma w_2 = 2\cdot67$; $\Sigma \Delta d / \Sigma w_2 = 0\cdot147$; $\Sigma \Delta n / \Sigma w_2 = -0\cdot079$.

Solute: *Triethyl phosphite*

$10^5 w_2$	1527	2240	2358	2588	3831	5071	5278	5673	5854	7178
$10^7 \Delta B$ ...	—	—	—	—	−0·005	—	—	−0·010	−0·012	−0·013
$10^4 \Delta n$	—	−20	—	—	—	—	−44	−47	—	−58
ε^{25}	2·3022	2·3139	2·3178	2·3222	2·3446	2·3669	—	—	—	2·4129
d_4^{25}	—	0·87562	0·87565	0·87578	—	0·87767	—	0·87843	—	0·87908

whence $\Sigma 10^7 \Delta B / \Sigma w_2 = -0\cdot177$; $\Sigma \Delta n / \Sigma w_2 = -0\cdot083$; $\Sigma \Delta \varepsilon / \Sigma w_2 = 1\cdot91$; $\Sigma \Delta d / \Sigma w_2 = 0\cdot078$.

Solute: *Tri-isopropyl phosphite*

$10^5 w_2$	3105	3564	4201	4365	5683	6076	6644	7172	8453	8619
$10^7 \Delta B$ ...	—	—	−0·062	−0·058	−0·073	−0·083	—	−0·104	−0·109	—
$10^4 \Delta n$	—	−29	—	−41	—	−53	−56	−60	−76	—
ε^{25}	2·3198	2·3264	—	—	—	2·3644	—	2·3783	2·3999	—
d_4^{25}	0·87484	0·87491	—	0·87528	—	0·87578	0·87620	0·87610	0·87655	0·87671

whence $\Sigma 10^7 \Delta B / \Sigma w_2 = -1\cdot36$; $\Sigma \Delta n / \Sigma w_2 = -0\cdot087$; $\Sigma \Delta \varepsilon / \Sigma w_2 = 1\cdot50$; $\Sigma \Delta d / \Sigma w_2 = 0\cdot034$.

Solute: *Tri-n-decyl phosphite*

$10^5 w_2$	2599	3225	3864	4607	5386	6670	7414	8282
$10^7 \Delta B$ ...	—	—	—	—	−0·116	−0·138	−0·146	−0·146
$10^4 \Delta n$	−13	—	−19	−20	−27	−35	—	−41
ε^{25}	2·2892	2·2905	2·2943	2·2983	2·3067	2·3084	2·3104	2·3177
d_4^{25}	0·87396	—	0·87406	0·87410	0·87416	0·87426	—	0·87438

whence $\Sigma 10^7 \Delta B / \Sigma w_2 = -1\cdot97$; $\Sigma \Delta n / \Sigma w_2 = -0\cdot049$; $\Sigma \Delta \varepsilon / \Sigma w_2 = 0\cdot56$; $\Sigma \Delta d / \Sigma w_2 = 0\cdot007$.

Solute: *Triphenyl phosphite*

$10^5 w_2$	2370	2833	3559	4757	5202	5328	6280	8369
$10^7 \Delta B$ ...	−0·020	—	−0·034	—	−0·051	—	−0·068	−0·083
$10^4 \Delta n$	15	19	22	29	35	35	39	55
ε^{25}	2·2979	2·3027	2·3098	—	2·3264	2·3300	2·3379	2·3601
d_4^{25}	0·87948	0·88059	0·88242	0·88537	0·88645	0·88666	0·88905	0·89336

whence $\Sigma 10^7 \Delta B / \Sigma w_2 = -0\cdot99$; $\Sigma \Delta n / \Sigma w_2 = 0\cdot064$; $\Sigma \Delta \varepsilon / \Sigma w_2 = 1\cdot05$; $\Sigma \Delta d / \Sigma w_2 = 0\cdot24$.

TABLE 2.

Polarisations, dipole moments, and molar Kerr constants (from observations on solutions in benzene at 25°).

Solute	$\alpha\varepsilon_1$	β	γ	δ	$_\infty P_2$ (c.c.)	R_D (c.c.)	μ (D) *	$10^{12} {}_\infty({}_mK_2)$
(MeO)$_3$PO	7·68	0·283	−0·049	−5·49	237	27·8	3·18	−88
(EtO)$_3$PO	5·61	0·181	−0·050	−8·02	243	42·1	3·12	−135
(Pr^{n}O)$_3$PO	4·69	0·137	−0·050	−9·59	264	54·9	3·18	−184
(Pr^{i}O)$_3$PO	3·65	0·110	−0·060	−6·78	222	54·8	2·84	−128
(n-C$_5$H$_{11}$O)$_3$PO	3·31	0·080	−0·046	−8·29	289	82·5	3·14	−207
(PhO)$_3$PO	3·03	0·303	+0·040	−4·61	263	87·4	2·89	−133
(MeO)$_3$P................	2·67	0·168	−0·053	4·41	97·5	28·8	1·81	+38
(EtO)$_3$P	1·91	0·089	−0·055	−0·43	111	42·8	1·80	−4·4
(Pr^{i}O)$_3$P	1·50	0·039	−0·058	−3·32	127	56·3	1·82	−47
(n-C$_{10}$H$_{21}$O)$_3$P	0·56	0·008	−0·033	−4·80	223	152	1·75	−153
(PhO)$_3$P................	1·05	0·275	+0·043	−2·41	138	87·2	1·51	−52

* Calculated assuming $_DP = 1·05R_D$.

EXPERIMENTAL

Materials, Apparatus, etc.—The esters were prepared and/or purified, to give trimethyl phosphate (b. p. 197—198°), triethyl phosphate (b. p. 215—216°), tri-n-propyl phosphate (b. p. 115—117°/8 mm.), tri-isopropyl phosphate (b. p. 123—125°/19—20 mm.), tri-n-pentyl phosphate (b. p. 220—224°/38—40 mm.), triphenyl phosphate (m. p. 50°), trimethyl phosphite (b. p. 111—113°), triethyl phosphite (b. p. 156—158°), tri-isopropyl phosphite (b. p. 76—78°/21—22 mm.), tri-n-decyl phosphite (b. p. 220—222°/0·7 mm.), triphenyl phosphite (b. p. 200—203°/5—6 mm.).

Details of procedures, apparatus, computational methods, symbols used, etc., are given in refs. 1—3. For pure benzene (*i.e.*, when $w_2 = 0$ in Table 1) at 25°, the properties indicated have values as follows: ε (dielectric constant) = 2·2725; d (density) = 0·87378; n (refractive index) = 1·4973; B (Kerr constant) = 0·410 × 10^{-7}.

Previous Measurements.—The following dipole moments (in D units) have been recorded: trimethyl phosphate, 3·02 (CCl$_4$); [4] triethyl phosphate, 3·07 (CCl$_4$),[4] 3·08 (C$_6$H$_6$),[5] 3·07 (C$_6$H$_6$),[6] 3·00 (C$_6$H$_6$); [7] tri-n-propyl phosphate, 3·09 (CCl$_4$); [4] tri-isopropyl phosphate, 2·85 (CCl$_4$); [4] triphenyl phosphate, 2·79 (C$_6$H$_6$),[8] 2·81 (C$_6$H$_6$),[9] 2·89 (CCl$_4$); [4] trimethyl phosphite, 1·83 (CCl$_4$); [4] triethyl phosphite, 1·96 (CCl$_4$); [4] tri-isopropyl phosphite, 1·98 (CCl$_4$); [4] triphenyl phosphite, 2·02 (C$_6$H$_6$),[9] 1·59 (CCl$_4$),[4] 1·71 (C$_6$H$_6$).[10]

DISCUSSION

Polarities and Polarisabilities of the Phosphate and Phosphite Groups.—The electric moment of the phosphate ester, 4-methyl-2,6,7-trioxa-1-phosphabicyclo[2,2,2]octane 1-oxide can be resolved as μ[MeC(CH$_2$O)$_3$PO] (= 7·10 D from Brown, Verkade, and Piper [11]) = μ(O$_3$PO) + 3μ(C–O), where each μ(C–O), acting parallel to the molecular symmetry axis,[12] reinforces the phosphate group moment [see (I)]. The magnitude of μ(C–O), which includes the C–H bond contributions, is calculable as 1·1$_7$ D from μ(Me$_2$O) =

[1] Le Fèvre, " Dipole Moments," Methuen, London, 3rd edn., 1953.
[2] Buckingham, Chau, Freeman, Le Fèvre, Rao, and Tardif, *J.*, 1956, 1405.
[3] Le Fèvre and Le Fèvre, (*a*) *J.*, 1953, 4041; (*b*) *Rev. Pure Appl. Chem. (Australia)*, 1955, **5**, 261; (*c*) in " Physical Methods of Organic Chemistry," ed. Weissberger, Interscience, New York and London, 3rd edn., vol. 1, ch. XXXVI, p. 2459.
[4] Arbuzov and Rakov, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1950, 237.
[5] Estok and Wendlandt, *J. Amer. Chem. Soc.*, 1955, **77**, 4767.
[6] Svirbely and Lander, *J. Amer. Chem. Soc.*, 1948, **70**, 4121.
[7] Ketelaar, Gersmann, and Hartog, *Rec. Trav. chim.*, 1958, **77**, 982.
[8] Cowley and Partington, *Nature*, 1935, **136**, 643.
[9] Lewis and Smyth, *J. Amer. Chem. Soc.*, 1940, **62**, 1529.
[10] French and Tomlinson, *J.*, 1961, 311.
[11] Brown, Verkade, and Piper, *J. Phys. Chem.*, 1961, **65**, 2051.
[12] Aroney, Le Fèvre, and Saxby, *J.*, 1963, 4938.

1·32 D [13] together with an angle C–O–C of 111° (ref. 14, $M = 138$). It follows that $\mu(O_3PO) = 3\cdot6$ D and is directed in the $+X$ direction in (I). Similarly, we calculate, from $\mu[MeC(CH_2O)_3P] = 4\cdot15$ D,[11] that $\mu(O_3P) = 0\cdot6$ D, and this also acts in the $+X$ direction.

Aroney, Le Fèvre, and Saxby [12] have estimated, from electric birefringence data, the anisotropic polarisabilities of molecules $MeC(CH_2O)_3X$ (X = PO or P) as solutes in dioxan.

(I)
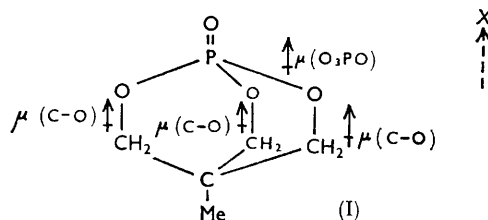
Deduction of the C–C, C–H, and C–O bond contributions [3,15] $[b_L(C–C) = 0\cdot099;\ b_T(C–C) = b_V(C–C) = 0\cdot027;\ b_L(C–H) = b_T(C–H) = b_V(C–H) = 0\cdot064;\ b_L(C–O) = 0\cdot089,\ b_T(C–O) = b_V(C–O) = 0\cdot046]$,* by way of equations (3) and (4) in ref. 12, leads to the following polarisability specifications for the phosphate and the phosphite groups: $b_1(O_3PO) = 0\cdot419$, $b_2(O_3PO) = b_3(O_3PO) = 0\cdot275;\ b_1(O_3P) = 0\cdot413;\ b_2(O_3P) = b_3(O_3P) = 0\cdot350$. These differ slightly from the values recorded in Table 4 of ref. 12, as we now use recently revised estimates [15] of the C–O bond polarisabilities.

Molecular Conformations of Trimethyl Phosphate and Trimethyl Phosphite.—Molecular models indicate that there can only be restricted rotation about the P–O–Me bonds. Initially we consider five conformations of trimethyl phosphate (IIa—e). In (IIa) and (IIb) each P–O–C plane includes the P=O bond axis [the methyl groups can then be above the XY plane (that of the three oxygen atoms) as in (IIa) or below as in (IIb); in (IIc) the carbon atoms are located symmetrically in the XY plane; in (IId), two methyl groups are
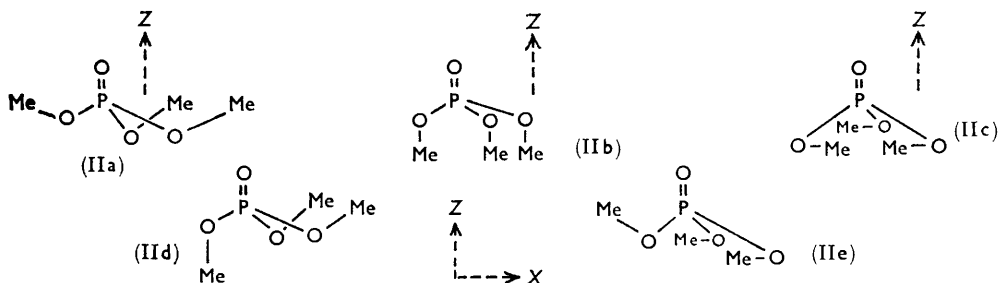
as in (IIa) and one as in (IIb); (IIe) is generated from (IIa) by rotation, in opposite senses, of two O–Me groups about their respective P–O bonds as axes until the carbons are in the XY plane. In the following calculations we assume that $\angle O=P=O = 115°$ (see refs. 16 and 17), and $\angle P–O–C = 110°$. Theoretical values of the polarisability semi-axes, dipole moments, and molar Kerr constants for structures (IIa—e) of trimethyl phosphate were calculated by the method outlined in ref. 3c, p. 2486. These are listed in Table 3, together with the computed values for analogous conformations of trimethyl phosphite. Comparison

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* Bond and molecular polarisabilities are quoted throughout in 10^{-23} c.c. units.

[13] Aroney, Le Fèvre, and Saxby, *J.*, 1962, 2886.
[14] Sutton, " Tables of Interatomic Distances and Configuration in Molecules and Ions," *Chem. Soc. Spec. Publ.* No. 11, 1958.
[15] Le Fèvre, Sundaram, and Pierens, *J.*, 1963, 479.
[16] Davies and Stanley, *Acta Cryst.*, 1962, **15**, 1092.
[17] Kraut and Jensen, *Acta Cryst.*, 1963, **16**, 79.

with the experimental quantities of Table 2 shows that although an " effective " conformation, or, alternatively, a mixture of conformations, can be found for trimethyl phosphite which will have the required dipole moment and molar Kerr constant, no such correlation

TABLE 3.

Calculated polarisabilities, dipole moments, and molar Kerr constants.

Conformation		Trimethyl phosphate			Trimethyl phosphite		
		b_l	μ (D)	$10^{12}\,{}_mK$	b_l	μ (D)	$10^{12}\,{}_mK$
(IIa)	$\begin{cases} b_1 = 1{\cdot}198 \\ b_2 = 1{\cdot}021 \\ b_3 = 1{\cdot}021 \end{cases}$		1·1	+26	$\begin{cases} 1{\cdot}192 \\ 1{\cdot}096 \\ 1{\cdot}096 \end{cases}$	1·9	+38
(IIb)	$\begin{cases} b_1 = 1{\cdot}261 \\ b_2 = 0{\cdot}990 \\ b_3 = 0{\cdot}990 \end{cases}$		7·1	+1512	$\begin{cases} 1{\cdot}255 \\ 1{\cdot}065 \\ 1{\cdot}065 \end{cases}$	4·1	+354
(IIc)	$\begin{cases} b_1 = 1{\cdot}133 \\ b_2 = 1{\cdot}054 \\ b_3 = 1{\cdot}054 \end{cases}$		3·6	+114	$\begin{cases} 1{\cdot}127 \\ 1{\cdot}129 \\ 1{\cdot}129 \end{cases}$	0·6	0
(IId)	$\begin{cases} b_1 = 0{\cdot}999 \\ b_2 = 1{\cdot}021 \\ b_3 = 1{\cdot}220 \end{cases}$		3·3	+197	$\begin{cases} 1{\cdot}073 \\ 1{\cdot}096 \\ 1{\cdot}215 \end{cases}$	0·9	−7
(IIe)	$\begin{cases} b_1 = 1{\cdot}039 \\ b_2 = 1{\cdot}043 \\ b_3 = 1{\cdot}159 \end{cases}$		3·6	+19	$\begin{cases} 1{\cdot}107 \\ 1{\cdot}118 \\ 1{\cdot}160 \end{cases}$	2·3	−5

can be attained for trimethyl phosphate. Without greatly altering any of the basic assumptions, it is not possible to calculate for any rotational isomer a molar Kerr constant which is sufficiently negative to agree with experiment. We offer no explanation for this; it may be that the polarisability specifications of the phosphate group, and most likely of the phosphite group also, in the open-chain compounds are significantly different from those for the " cage " structure.

The Trialkyl Phosphates as Ellipsoids of Revolution.—If the assumption is made that the anisotropies of trimethyl phosphate and its homologues can be represented by ellipsoids of revolution, then $b_1 \neq b_2 = b_3$, $\mu_1 = \mu_{\text{obs.}}$, and $\mu_2 = \mu_3 = 0$. The usual expressions for the molar Kerr constant and the electronic polarisation simplify to

$$_mK[(RO)_3PO] = 4\pi N[_DP(b_1 - b_2)^2/_EPkT + \mu^2(b_1 - b_2)/k^2T^2]/405 \qquad (1)$$

$$_EP[(RO)_3PO] = 4\pi N(b_1 + 2b_2)/9, \qquad (2)$$

where $_DP$ and $_EP$ are the distortion and the electronic polarisations, respectively.

TABLE 4.

The electronic polarisations and principal polarisability semi-axes of the molecules $(RO)_3PO$.

| R	Me	Et	Pr^n	Pr^i	n-C_5H_{11}
$_EP$ (c.c.)	27·4 *	41·0 †	54·7 †	54·7 †	81·9 †
b_1	1·033	1·541	2·057	2·071	3·118
$b_2 = b_3$	1·112	1·667	2·223	2·216	3·310

* By extrapolation of the refractivities listed by Vogel and Cowan, *J.*, 1943, 16. † By addition to $_EP[(MeO)_3PO] = 27\cdot4$ c.c. of the appropriate number of C–C and C–H bond equivalents (from Le Fèvre and Steel, *Chem. and Ind.*, 1961, 670).

Now, $\mu[(MeO)_3PO] = +3\cdot18$ D (from Table 2) $= +\mu(O_3PO) \pm 3\mu(C\text{–}O)\cos\phi$, where ϕ, the inclination of each O–C bond with the symmetry axis, can only be 83° and such that the methyl groups are above the plane of the oxygen atoms [see (III)]. It follows then that

$$b_1[(MeO)_3PO] = b_1(O_3PO) + 9b_L(C\text{–}H) + 3b_L(C\text{–}O)\cos^2 83 + 3b_T(C\text{–}O)\sin^2 83 \qquad (3)$$

and

$$\Sigma b[(MeO)_3PO] = \Sigma b(O_3PO) + 9\Sigma b(C\text{–}H) + 3\Sigma b(C\text{–}O), \qquad (4)$$

from which we estimate $b_1(O_3PO)/b_2(O_3PO) = 0.95$. The above conclusions are not seriously affected by small variations in our estimate of $\mu(O_3PO)$. If, for example, each C–O bond moment in the molecule $MeC(CH_2O)_3PO$ were to contribute 1·3 D, then $\mu(O_3PO)$ would be 3·2 D; ϕ for trimethyl phosphate would then be 90° and $b_1(O_3PO)/b_2(O_3PO)$ would be 0·96.

(IIIa)   (IIIb)
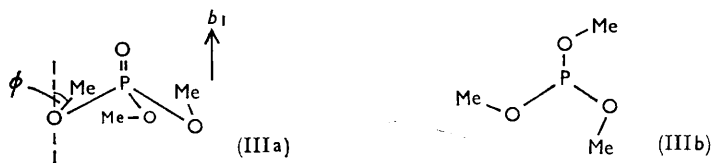
The four tri-n-alkyl phosphates examined have almost identical moments (all lie within the range 3.15 ± 0.03 D). This suggests that the effective dispositions of the C–O bond dipoles with respect to $\mu(O_3PO)$ must be similar throughout. If we assume that the group $(H_2CO)_3PO$ in triethyl phosphate has a trimethyl phosphate-like structure (less three C–H bonds), then the inclination η of each C–C bond with the symmetry axis is calculable, by way of the following relation, as 78°.

$$b_1[(EtO)_3PO] = b_1[(MeO)_3PO] + 6b_L(C-H) + 3b_L(C-C) \cos^2 \eta + 3b_T(C-C) \sin^2 \eta \quad (5)$$

In an analogous manner we calculate that the terminal C–C links in tri-n-propyl phosphate make 61° with the b_1 direction, whilst in tri-n-pentyl phosphate the mean inclination of the C–C links γ and δ ($\overset{\delta}{CH_3}-\overset{\gamma}{CH_2}-\overset{\beta}{CH_2}-\overset{\alpha}{CH_2}-CH_2-O$) with $b_1[(n-C_5H_{11}O)_3PO]$ is 57°.

The Trialkyl Phosphites.—Polarisability specifications for the molecules $(RO)_3P$, where R = Me, Et, Pr^i, and $n-C_{10}H_{21}$, are listed in Table 5. For trimethyl phosphite the

TABLE 5.

The electronic polarisations and principal polarisability semi-axes of the molecules $(RO)_3P$.

R	Me	Et	Pr^i	$n-C_{10}H_{21}$
$_EP$ (c.c.) *	28·6	42·2	55·9	151·3
b_1	1·203	1·665	2·129	5·672
$b_2 = b_3$	1·100	1·677	2·259	6·160

* Calculated from the electronic polarisation of the corresponding phosphate by subtraction of one P=O bond equivalent $[_EP(P=O) = 0.95R_D(P=O) = 1.2$ c.c., Gillis, *Rev. Pure Appl. Chem. (Australia)*, 1960, **10**, 21].

observed dipole moment ($= 1.81$ D from Table 2) could be directed in the $+Z$ or $-Z$ directions [where Z is disposed as in (IIa) for trimethyl phosphate] and we have $\pm\mu[(MeO)_3P] = +\mu(O_3P) \pm 3\mu(C-O) \cos \phi$, where ϕ is the inclination of each C–O bond with the symmetry axis. Solution yields $\phi = 47°$ or 70° dependent on whether the carbon atoms lie, respectively, above or below the plane of the oxygen atoms. It follows also, from equations similar to (3), (4), and (5), that $b_1(O_3P)/b_2(O_3P) = 1.22$ ($\phi = 47°$) or 1·44 ($\phi = 70°$); each C–C link in triethyl phosphite is perpendicular to the b_1 direction (*i.e.*, $\eta = 90°$); for tri-n-decyl phosphite the mean inclination with the b_1 direction of the C–C links beyond a triethyl phosphite (less two C–H bonds) nucleus is 66°.

Triphenyl Phosphate and Triphenyl Phosphite.—The principal polarisability semi-axes for these molecules, which are calculable (if $b_1 \neq b_2 = b_3$) from their respective molar Kerr constants and electronic polarisations, are listed in Table 6. We can equate $b_1[(PhO)_3PO]$ to the component bond and group polarisabilities in the following manner:

$$b_1[(PhO)_3PO] = b_1(O_3PO) + 3\{[b_L(C-O) + b_L(Ph)] \cos^2 \alpha$$
$$+ [b_T(C-O) + b_T(Ph) \cos^2 \beta + b_V(Ph) \sin^2 \beta] \sin^2 \alpha\}, \quad (6)$$

TABLE 6.

The electronic polarisations and principal polarisability semi-axes of triphenyl phosphate and triphenyl phosphite.

Solute	$_{\mathrm{E}}P$ (c.c.)	b_1	$b_2 = b_3$
(PhO)$_3$PO	83·1 *	3·197	3·342
(PhO)$_3$P	84·3 †	3·197	3·413

* Calculated as $_{\mathrm{E}}P[(\mathrm{MeO})_3\mathrm{PO}] - 9\,_{\mathrm{E}}P(\mathrm{C-H}) + 3\,_{\mathrm{E}}P(\mathrm{Ph})$.   † Equals $_{\mathrm{E}}P[(\mathrm{PhO})_3\mathrm{PO}] - \,_{\mathrm{E}}P(\mathrm{P=O})$.

where $b_1(\mathrm{O_3PO})$ is derived from $b_1[(\mathrm{MeO})_3\mathrm{PO}]$ by way of equation (3); $b_\mathrm{L}(\mathrm{Ph})$ (which is located along the 1,4-axis) $= b_\mathrm{T}(\mathrm{Ph}) = 1\cdot056$, $b_\mathrm{V}(\mathrm{Ph}) = 0\cdot672$; α is the angle which each $\mathrm{C_{Ar}-O}$ bond makes with the normal (through O) to the $b_2 b_3$ plane; β is the angle between $b_\mathrm{T}(\mathrm{Ph})$ and its projection in the plane defined by its $b_\mathrm{L}(\mathrm{Ph})$ and a line parallel to the b_1 direction. If, for example, the benzene ring planes are parallel to b_1 then $\beta = 0°$. In this calculation we assume $\alpha = 83°$ (as in trimethyl phosphate). This appears reasonable from Leybold models, and is supported qualitatively by the evidence of Ketelaar *et al.*[7] who state that the dipole moment of tri-*p*-nitrophenyl phosphate is larger than that of triphenyl phosphate. They do not quote $\mu[(p\text{-}\mathrm{O_2N\cdot C_6H_4\cdot O})_3\mathrm{PO}]$ but they provide data for the corresponding thiophosphates, from which the difference $\Delta\mu = \mu[(p\text{-}\mathrm{O_2N\cdot C_6H_4\cdot O})_3\mathrm{PS}] - \mu[(\mathrm{PhO})_3\mathrm{PS}]$ is equal to 0·75 D   This is equivalent to three nitrobenzene moments [3a] inclined 86° to the three-fold symmetry axis such that they reinforce $\mu(\mathrm{O_3PS})$. Solution of equation (6) yields $\beta = 38°$. With triphenyl phosphite it seems unlikely, from an examination of scale models, that the phenyl 1,4-axes would be more than 20° above or below the plane of the oxygen atoms. Taking into account the two possible values of $b_1(\mathrm{O_3P})$ (from trimethyl phosphite), we calculate that for $\alpha = 90 \pm 20°$, β lies in the range $46 \pm 4°$.