

Physical Properties and Chemical Constitution. Part XLIX.¹ The Refractivities, Densities, and Surface Tensions of some Organophosphorus Compounds

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Pure samples of tri-*n*-alkyl phosphites, di-*n*-alkyl phosphonates, di-*n*-propyl *n*-alkylphosphonates, di-*n*-alkyl ethylphosphonates (methyl to octyl) of tri-*n*-alkyl orthophosphates (butyl to heptyl), of tri-2-*n*-alkoxyethyl phosphites (methoxy- to hexyloxy-), of di-2-*n*-alkoxyethyl phosphonates (methoxy- to heptyloxy-) and of 2-*n*-alkoxy-4-methyl-1,3,2-dioxaphospholans (methoxy- to hexyloxy-) have been prepared and their refractive indices at 20° and densities and surface tension over a range of temperatures determined: the infrared spectra were measured in detail for a number of representative compounds. The parachors, refractions, and molecular refraction coefficients for the bonds (P=O), (P-O), (P-C), (P-H) and for the 1,3,2-dioxaphospholan ring have been evaluated from the new experimental data.

THE present investigation was undertaken to secure trustworthy data on some physical properties of pure tri-*n*-alkyl phosphites, tri-2-*n*-alkoxyethyl phosphites, tri-*n*-alkyl orthophosphates, di-*n*-alkyl phosphonates, di-2-*n*-alkoxyethyl phosphonates, di-*n*-alkyl ethylphosphonates, di-*n*-propyl *n*-alkylphosphonates, and 2-*n*-alkoxy-4-methyl-1,3,2-dioxaphospholans, and to evaluate the refractions, molecular refraction coefficients, and parachors for the bonds (P-H), (P-C), (P-O), and (P=O) and for the 1,3,2-dioxaphospholan ring. The mean values for the CH₂ increments of the molecular refractions and of the molecular refraction coefficients are generally in good agreement with those previously found,² but the parachor increment (38.2 for tri-*n*-alkyl orthophosphates and 39.2 for the other esters) is appreciably lower. The refraction and molecular refraction coefficient constants for the P-O bond were calculated as follows:

$$3(P-O) = E - R \text{ (phosphites)}$$

where E is the observed molar refractivity or molecular refraction coefficient and R the sum of the bond constants³ of all the (C-C), (C-H), and (C-O)_{acetal} bonds in the molecule (alkyl phosphites), and also of (C-O)_{ether}

bonds (2-*n*-alkoxyethyl phosphites). The constants for the other bonds were then calculated from the equations:

- (i) $(P=O) = E - \{R + 3(P-O)\}$, (orthophosphates);
- (ii) $(P-H) = E - \{R + 2(P-O) + (P=O)\}$,
(phosphonates);
- (iii) $(P-C) = E - \{R + 2(P-O) + (P=O)\}$, (di-propyl
alkylphosphonates).

The molar refraction and molar refraction coefficient for the 1,3,2-dioxaphospholan ring were calculated from the results for the 2-*n*-alkoxy-4-methyl-1,3,2-dioxaphospholans using the equation:

$$\text{Ring constant} = E - \{R' + (P-O) + (C-C) + (C-O)_{\text{acetal}} - (C-H)\};$$

R' is the sum of the refractivities of the alkyl groups attached to positions 2 and 4.

The method of calculation of the parachor constants was modified so as to utilise the observed CH₂ increment for each series of compounds; thus the (P-O) bond parachor was obtained from the results with the tri-*n*-alkyl phosphites by means of the expression:

$$(P-O) = \left\{ \frac{1}{3} P_{\text{obs}} - n(\text{CH}_2)_{\text{obs}} - (\text{CH}_3) - (C-O)_{\text{acetal}} \right\};$$

¹ Part XLVIII, preceding Paper.

² Part XXIII, A. I. Vogel, *J. Chem. Soc.*, 1948, 1842.

³ Part XXIV, A. I. Vogel, W. T. Cresswell, G. H. Jeffery, and J. Leicester, *J. Chem. Soc.*, 1952, 514.

similar equations were used to calculate the parachor constants of the other bonds, and also of the 1,3,2-dioxaphospholan ring.

The constants for the various bonds are summarised in Table 1. The values for the (P-C) bond are based on

TABLE 1

Mean constants for various bonds involving phosphorus, and for the 1,3,2-dioxaphospholan ring

Compounds	P	[R] _O	[R] _D	[R] _F	[R] _G	Mn _D ²⁰
Phosphites (P-O)						
Tri-alkyl	23.6	3.22	3.22	3.33	3.38	28.53
s	0.5	0.03	0.05	0.03	0.06	0.04
Tri-2-alkoxyethyl	21.6	3.21	3.21	3.33	3.36	29.49
s	0.5	0.01	0.01	0.02	0.02	0.09
Mean values	22.6	3.22	3.22	3.33	3.37	29.01
Orthophosphates (P=O)						
Tri-alkyl*	24.8	-1.24	-1.26	-1.46	-1.60	21.03
s	2.2	0.05	0.06	0.09	0.07	0.36
Phosphonates (P-H)						
Di-alkyl	21.9	4.20	4.22	4.28	4.32	17.24
s	1.3	0.04	0.05	0.02	0.04	0.18
Di-2-alkoxyethyl	19.2	4.26	4.27	4.38	4.39	16.77
s	1.1	0.01	0.02	0.04	0.02	0.18
Mean values	20.6	4.23	4.24	4.33	4.35	17.01
n-Alkylphosphonates (P-C)						
Dipropyl	-2.0	3.69	3.71	3.84	4.04	25.52
s	0.4	0.01	0.01	0.02	0.01	0.16
1,3,2-Dioxaphospholan ring †						
2-Alkoxy-4-methyl-1,3,2-dioxaphospholans	152.7	17.09	17.19	17.42	17.54	116.3

s = Standard deviation.

* Including previous results.^{16a} † Preliminary values.

the results for the di-n-propyl n-alkylphosphonates RPO(OC₃H₇)₂ (R = C₃H₇ to C₈H₁₇) only. In this series of compounds the CH₂ increments (Et-Me) and (Pr-Et) are abnormal, indicating that the anomalies frequently associated with a methyl group are here also encountered with an ethyl group; for this reason, the results for the

TABLE 2

Comparison of [R]_D values for various bonds

Authors	(P-O)	(P=O)	(P-H)	(P-C)
Fehér and Blümcke (ref. 4)	3.12	+1.22	4.27	3.64
Gillis, Horwood, and White (ref. 5)	3.18	-1.22	—	3.60
Keeber and Post (ref. 6).....	3.04	+0.91	2.26	1.29
Sayre (ref. 7)	3.102	-1.032	4.010	3.575
This Paper	3.22	-1.26	4.24	3.71

di-n-alkyl ethylphosphonates have been ignored in evaluating the (P-C) bond constants.

In Table 2 the [R]_D values deduced for the various bonds are compared with values given by other workers.⁴⁻⁷

⁴ F. Fehér and A. Blümcke, *Chem. Ber.*, 1957, **90**, 1934.

⁵ R. G. Gillis, J. E. Horwood, and G. L. White, *J. Amer. Chem. Soc.*, 1958, **72**, 2999; R. G. Gillis, *Rev. Pure Appl. Chem. (Australia)*, 1960, **10**, 21.

⁶ W. H. Keeber and K. W. Post, *J. Org. Chem.*, 1956, **21**, 509.

⁷ R. Sayre, *J. Amer. Chem. Soc.*, 1958, **80**, 5438.

The results of Fehér and Blümcke and of Keeber and Post are based on the bond constants evaluated by Denbigh,⁸ the remainder are based on the constants given in Part XXIV.³

In Table 3 the [R]_D values for some typical compounds, calculated by using the constants given in Table 1 and in Part XXIV,³ are compared with the values deduced from the experimental results.

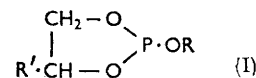
TABLE 3

Comparison of calculated and observed [R]_D values

Compound	Observed	Calculated
(C ₄ H ₉ O) ₃ P	71.09	70.96
(C ₄ H ₉ O) ₃ PO	69.67	69.70
HPO(OC ₄ H ₉) ₂	50.25	50.28
C ₄ H ₉ PO(OC ₃ H ₇) ₂	59.39	59.43

The agreement between observed and calculated values is satisfactory. Tolkmith⁹ has pointed out that negative values for bond refractivities are untenable on theoretical grounds. Although a negative value for a bond refractivity is unsatisfactory from a theoretical standpoint, the evaluation of refractivity constants for bonds involving phosphorus is desirable so that the extensive system of bond constants already developed can also be applied to phosphorus compounds.

The constants given above for the 1,3,2-dioxaphospholan ring are regarded as preliminary. The values of



this ring constant calculated using our bond constants, from the measurements of (a) Lucas, Mitchell, and Scully¹⁰ on a series of 2-n-alkoxy-1,3,2-dioxaphospholans (I) and also some 4-methyl compounds, and of (b) Arbuzov, Zoroastrova, and Rizpolozhensky¹¹ with a similar series of 4-methoxy and 4-ethoxy compounds, differ markedly from those in Table 1. Some of the compounds (I) described by Lucas and his co-workers were prepared and found to be very easily oxidised and very sensitive to atmospheric moisture; the 4-methyl compounds which we investigated are relatively stable.

EXPERIMENTAL

Physical Measurements.—Details of experimental methods are given in Part XXVIII.¹² Unless otherwise stated, b. p.s are corrected. The compounds were re-fractionated immediately before the measurements were made; they were examined for impurities by vapour-phase chromatography and by ultraviolet and infrared spectroscopy, but none was found.

Compounds Investigated.—Tri-n-alkyl phosphites (RO)₃P. A modification of the procedures described by Ford-Moore

⁸ K. G. Denbigh, *Trans. Faraday Soc.*, 1940, **36**, 936.

⁹ H. Tolkmith, *Ann. New York Acad. Sci.*, 1959, **79**, 187.

¹⁰ H. J. Lucas, F. W. Mitchell, and C. N. Scully, *J. Amer. Chem. Soc.*, 1950, **72**, 5491.

¹¹ A. E. Arbuzov, V. M. Zoroastrova, and N. I. Rizpolozhensky, *Izvest. Akad. Nauk, S.S.S.R., Otdel. Khim. Nauk*, 1948, 208.

¹² Part XXVIII, C. T. Kyte, G. H. Jeffery, and A. I. Vogel, *J. Chem. Soc.*, 1960, 4454.

TABLE 4

No.	Compound (R)	B. p./mm.	d_4^{20}	d_4^{40}	d_4^{60}	d_4^{85}	γ^{20}	γ^{40}	γ^{60}	γ^{85}	P	Note
<i>Tri-n-alkyl phosphites (RO)₃P</i>												
902	Methyl	111°	1.0512	1.0286	—	—	27.18	24.88	—	—	269.5	a
903	Ethyl	55.5/20	0.9591	0.9388	0.9161	0.8882	24.06	22.03	20.51	18.30	384.8	a
904	n-Propyl	67/25	0.9300	0.9126	0.8955	0.8726	25.04	23.32	21.52	19.30	500.6	a
905	n-Butyl	120.5/3.0	0.9146	0.8986	0.8814	0.8606	26.07	23.84	22.28	20.37	617.2	a
906	n-Pentyl	128/2.2	0.9047	0.8903	0.8741	0.8551	27.04	25.15	23.37	21.56	736.0	a
907	n-Hexyl	131/0.7	0.8975	0.8828	0.8688	0.8504	27.54	25.94	24.28	22.32	854.4	a
908	n-Heptyl	180.5/0.7	0.8917	0.8778	0.8643	0.8469	28.19	26.62	24.86	23.04	973.0	a
909	n-Octyl	178/0.2	0.8858	0.8729	0.8590	0.8416	28.18	26.98	25.35	23.36	1092.5	a
<i>Tri-2-n-alkoxyethyl phosphites (ROC₂H₄O)₃P</i>												
910	Methyl	123.5/2.0	1.0874	1.0699	1.0516	1.0282	33.92	31.91	26.75	27.28	569.1	b
911	Ethyl	121.5/0.75	1.0300	1.0127	0.9953	0.9740	30.54	28.83	26.71	24.45	681.5	b
912	n-Propyl	146.5/0.25	0.9966	0.9802	0.9631	0.9427	29.04	27.30	25.67	23.85	795.2	b
913	n-Butyl	155.5/0.2	0.9744	0.9590	0.9444	0.9253	29.33	27.70	26.07	24.12	913.5	b
914	n-Pentyl	171/0.3	0.9595	0.9449	0.9297	0.9109	29.60	27.89	26.26	24.01	1032.7	b
915	n-Hexyl	208/0.3	0.9469	0.9332	0.9182	0.9005	29.93	28.18	26.43	24.50	1152.5	b
<i>Di-n-alkyl phosphonates HPO(OR)₂</i>												
916	Methyl	94.5/64	1.1997	1.1783	1.1566	1.1284	37.60	35.24	32.76	29.92	227.6	c
917	Ethyl	71.5/10	1.0739	1.0549	1.0346	1.0095	30.87	28.96	26.86	24.11	303.5	c
918	n-Propyl	77.5/5.0	1.0212	1.0029	0.9842	0.9616	29.23	27.48	25.56	23.36	379.3	c
919	n-Butyl	119.5/8.0	0.9870	0.9700	0.9529	0.9281	28.26	26.20	25.31	23.59	455.8	c
920	n-Pentyl	96.5/0.25	0.9659	0.9501	0.9343	0.9145	28.46	26.98	25.31	23.26	533.0	c
921	n-Hexyl	116/0.2	0.9509	0.9356	0.9206	0.9026	28.70	27.19	25.74	23.70	611.0	c
922	n-Heptyl	131.5/0.25	0.9361	0.9219	0.9077	0.8898	28.67	27.38	25.73	24.04	689.3	c
923	n-Octyl	155.5/0.4	0.9285	0.9146	0.9004	0.8856	29.00	27.57	26.11	24.44	768.4	c
<i>Di-2-n-alkoxyethyl phosphonates HPO(OC₂H₄OR)₂</i>												
924	Methyl	111/1.0	1.1617	1.1435	1.1256	1.1020	37.68	35.96	33.97	30.96	423.9	c
925	Ethyl	110.5/0.4	1.0919	1.0734	1.0568	1.0343	33.78	32.09	30.56	26.92	502.0	c
926	n-Propyl	128/0.5	1.0507	1.0337	1.0180	0.9967	31.07	29.38	28.51	26.59	578.6	c
927	n-Butyl	150/0.4	1.0222	1.0058	0.9895	0.9680	31.10	29.69	28.26	27.56	656.3	c
928	n-Pentyl	167.5/0.4	1.0004	0.9852	0.9704	0.9521	31.04	29.35	28.48	26.57	735.5	c
929	n-Hexyl	174/0.3	0.9853	0.9707	0.9563	0.9358	31.17	28.93	28.48	26.73	814.9	c
930	n-Heptyl	183.5/0.2	0.9715	0.9568	0.9426	0.9236	30.96	29.40	28.26	26.22	894.6	c
<i>Orthophosphates (RO)₃PO</i>												
931	n-Butyl	114/0.8	0.9770	0.9613	0.9444	0.9245	27.55	25.96	24.44	23.25	630.0	d
932	n-Pentyl	139.0/1.0	0.9545	0.9394	0.9241	0.9051	27.60	26.19	25.00	23.46	744.3	d
933	n-Hexyl	160.8/0.9	0.9398	0.9290	0.9114	0.8933	28.11	26.50	25.03	23.24	860.0	d
934	n-Heptyl	186.9/0.4	0.9272	0.9128	0.8990	0.8825	28.11	26.53	25.37	23.57	978.2	d
935	MeOC ₂ H ₄	139.1/0.4	1.1642	1.1472	1.1290	1.1063	36.61	34.66	32.53	30.14	575.9	d
936	EtOC ₂ H ₄	141.0/0.35	1.0903	1.0737	1.0567	1.0354	32.24	30.30	28.69	26.40	687.7	d
<i>Di-n-alkyl ethylphosphonates C₂H₅PO(OR)₂</i>												
937	Methyl	73.5/15	1.1500	1.1300	1.1096	1.0837	36.77	33.89	31.58	28.48	295.1	e
938	Ethyl	93/19	1.0224	1.0048	0.9865	0.9661	28.68	26.73	24.78	22.34	375.8	e
939	n-Propyl	105/18	0.9918	0.9756	0.9578	0.9355	28.36	26.29	24.66	22.45	452.1	e
940	n-Butyl	129.5/15	0.9682	0.9520	0.9354	0.9147	28.05	26.37	24.81	22.67	529.5	f
941	n-Pentyl	112/1.0	0.9502	0.9342	0.9192	0.8978	27.97	26.25	24.85	22.60	607.1	f
942	n-Hexyl	117/0.2	0.9394	0.9247	0.9095	0.8902	28.11	26.74	25.15	23.71	685.2	f
943	n-Heptyl	142.5/0.4	0.9282	0.9138	0.8992	0.8815	28.46	27.13	25.65	23.93	765.7	f
944	n-Octyl	160/0.4	0.9211	0.9073	0.8836	0.8662	28.87	27.63	25.14	23.45	846.1	f
<i>Di-n-propyl alkyl phosphonates RPO(OC₃H₇)₂</i>												
945	Methyl	115.5/0.25	1.0092	1.0019	0.9739	0.9512	28.64	26.66	24.89	22.72	415.2	g
946	n-Propyl	118.5/12	0.9724	0.9552	0.9384	0.9170	27.98	26.20	24.37	22.21	491.9	g
947	n-Butyl	98.5/1.7	0.9634	0.9469	0.9296	0.9100	27.98	26.27	24.59	22.24	531.2	h
948	n-Pentyl	104.5/0.5	0.9543	0.9469	0.9229	0.9026	28.25	27.04	24.64	22.70	570.7	h
949	n-Hexyl	110/1.0	0.9475	0.9318	0.9163	0.8966	28.07	26.59	25.21	23.35	610.8	h
950	n-Heptyl	112.5/0.4	0.9412	0.9262	0.9112	0.8920	28.58	26.83	25.19	23.17	649.8	h
951	n-Octyl	155.5/0.4	0.9355	0.9205	0.9053	0.8861	28.83	26.97	25.34	23.26	689.7	h
<i>2-n-Alkoxy-4-methyl-1,3,2-dioxaphospholans (I; R' = Me)</i>												
952	Methyl	63.5/30	1.1304	0.9893	—	—	29.65	—	—	—	280.7	i
953	Ethyl	69/27	1.0797	1.0605	1.0416	1.0194	27.75	25.67	24.42	22.34	319.2	i
954	n-Propyl	82/25	1.0550	1.0368	1.0213	0.9990	28.13	26.53	24.64	23.48	356.9	i
955	n-Butyl	93/21	1.0349	1.0172	1.0006	0.9789	28.30	26.57	23.94	22.48	396.9	i
956	n-Pentyl	89/12	1.0318	1.0160	1.0008	0.9814	28.07	26.98	25.34	23.40	435.1	i
957	n-Hexyl	82.5/6.0	1.0043	0.9893	0.9740	0.9551	28.31	26.96	25.23	23.28	474.5	i

TABLE 5

No.	$n_{C^{20}}$	$n_{D^{20}}$	$n_{F^{20}}$	$n_{G^{20}}$	$[R]_C$	$[R]_D$	$[R]_F$	$[R]_G$	$Mn_{D^{20}}$	Note
<i>Tri-n-alkyl phosphites</i>										
902	1.40591	1.40843	1.41483	1.41968	28.99	29.15	29.55	29.85	119.46	a
903	1.41061	1.41306	1.41906	1.42392	42.98	43.20	43.76	44.20	234.79	a
904	1.42259	1.42493	1.43104	1.43589	56.98	57.25	57.97	58.53	296.25	a
905	1.43029	1.43263	1.42869	1.44347	70.75	71.09	71.79	72.63	358.06	a
906	1.43772	1.44010	1.44441	1.44919	84.50	84.91	85.91	86.72	419.91	a
907	1.44056	1.44286	1.44894	1.45375	98.34	98.77	99.95	101.64	481.90	a
908	1.44406	1.44642	1.45244	1.45720	112.20	112.72	114.03	115.07	544.65	a
909	1.44603	1.44836	1.45430	1.45900	126.06	126.63	128.08	129.22	606.32	a
<i>Tri-2-n-alkoxyethyl phosphites</i>										
910	1.43964	1.44207	1.44821	1.45312	62.06	62.35	63.11	63.71	369.51	b
911	1.43775	1.44014	1.44612	1.45100	75.99	76.35	77.25	77.98	429.62	b
912	1.43904	1.44145	1.44740	1.45212	89.81	90.23	91.29	92.12	490.44	a
913	1.44131	1.44373	1.44962	1.45438	103.68	104.17	105.37	106.33	551.97	a
914	1.44433	1.44666	1.45261	1.45738	117.61	118.14	119.51	120.59	614.18	a
915	1.44591	1.44825	1.45412	1.45875	131.41	132.00	133.50	134.67	675.80	a
<i>Di-n-alkyl phosphonates</i>										
916	1.40092	1.40282	1.40749	1.41148	22.29	22.38	22.61	22.80	154.39	c
917	1.40588	1.40785	1.41264	1.41651	31.58	31.72	32.05	32.31	194.44	c
918	1.41590	1.41791	1.42289	1.42702	40.82	41.00	41.42	41.78	235.60	c
919	1.42239	1.42446	1.42955	1.43378	50.04	50.25	50.78	51.21	276.44	c
920	1.42847	1.43065	1.43589	1.44021	59.26	59.52	60.15	60.67	317.98	c
921	1.43336	1.43546	1.44077	1.44509	68.48	68.77	69.50	70.09	359.29	c
922	1.43649	1.43868	1.44407	1.44843	77.67	78.01	78.84	79.51	400.49	c
923	1.44006	1.44224	1.44770	1.45208	86.97	87.35	88.28	89.03	441.93	c
<i>Di-2-n-alkoxyethyl phosphonates</i>										
924	1.43254	1.43460	1.43983	1.44410	44.29	44.48	44.94	45.32	284.28	a
925	1.43115	1.43323	1.43850	1.44276	53.64	53.87	54.44	54.90	324.21	a
926	1.43299	1.43514	1.44040	1.44471	62.90	63.17	63.83	64.37	364.93	a
927	1.43539	1.43750	1.44286	1.44718	72.13	72.43	73.20	73.82	405.85	a
928	1.43830	1.44041	1.44589	1.45028	81.49	81.85	82.72	83.42	447.11	a
929	1.44110	1.44330	1.44872	1.45314	90.72	91.15	92.08	92.86	488.46	a
930	1.44276	1.44502	1.45051	1.45493	100.01	100.45	101.52	102.38	529.59	a
<i>Orthophosphates</i>										
931	1.42278	1.42478	1.42974	1.43386	69.38	69.67	70.38	70.93	379.45	d
932	1.42886	1.43093	1.43601	1.44019	83.27	83.62	84.48	85.18	441.29	d
933	1.43424	1.43637	1.44155	1.44582	97.15	97.57	98.58	99.40	503.39	d
934	1.43768	1.43979	1.44511	1.44941	111.06	111.53	112.70	113.64	565.18	d
935	1.43268	1.43471	1.43791	1.44384	60.74	60.98	61.59	62.10	390.59	a
936	1.43115	1.43321	1.42828	1.44246	74.65	74.96	75.72	76.35	450.49	a
<i>Di-n-alkyl ethylphosphonates</i>										
937	1.41253	1.41449	1.41916	1.42323	29.91	30.04	30.34	30.60	195.36	a
938	1.41454	1.41651	1.42137	1.42547	40.40	40.57	40.83	41.38	235.28	e
939	1.41944	1.42146	1.42645	1.43057	49.60	49.81	50.33	50.75	276.06	a
940	1.42521	1.42733	1.43256	1.43683	58.72	58.98	59.61	60.21	317.24	f
941	1.42947	1.43159	1.43680	1.44109	67.98	68.27	68.99	69.58	358.36	a
942	1.43457	1.43666	1.44200	1.44633	77.26	77.58	78.41	79.08	399.92	a
943	1.43722	1.43942	1.44480	1.44906	86.53	86.90	87.83	88.56	441.10	a
944	1.44046	1.44264	1.44812	1.45253	95.79	96.21	97.24	98.06	482.52	a
<i>Di-n-propyl alkylphosphonates</i>										
945	1.41898	1.42098	1.42597	1.43015	45.02	45.27	45.67	46.06	256.05	g
946	1.42410	1.42616	1.43127	1.43549	54.42	54.67	55.25	55.72	296.97	h
947	1.42638	1.42846	1.43358	1.43785	59.14	59.39	60.01	60.52	317.49	a
948	1.42856	1.43062	1.43584	1.44007	63.78	64.04	64.71	65.27	338.04	a
949	1.43118	1.43327	1.43848	1.44277	68.41	68.69	69.41	70.00	358.76	a
950	1.43332	1.43544	1.44073	1.44500	73.04	73.55	74.13	74.75	379.44	a
951	1.43500	1.43716	1.44244	1.44677	77.64	77.98	78.80	79.47	400.06	a
<i>2-n-Alkoxy-4-methyl-1,3,2-dioxaphospholans</i>										
952	1.43423	1.43672	1.44313	1.44829	31.37	31.52	31.93	32.25	195.52	i
953	1.43187	1.43433	1.44061	1.44554	36.05	36.23	36.69	37.04	215.32	i
954	1.43557	1.43806	1.44426	1.44926	40.64	40.84	41.34	41.74	236.15	i
955	1.43854	1.44099	1.44718	1.45205	45.24	45.46	46.05	46.45	256.76	i
956	1.44227	1.44474	1.45099	1.45609	49.85	50.09	50.70	51.2	277.61	a
957	1.44334	1.44579	1.45199	1.45699	54.47	54.74	55.39	55.9	297.88	a

^a A. E. Arbutov and V. S. Vinogradova (*Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1947, 455; 1951, 733) give methyl $d_{0^{20}}$ 1.0520, $n_{D^{20}}$ 1.4095, γ^{20} 26.52; ethyl $d_{0^{20}}$ 0.9687, $n_{D^{20}}$ 1.4134, γ^{20} 24.46; n-propyl $d_{0^{20}}$ 0.9522, $n_{D^{20}}$ 1.4265, γ^{20} 25.91; n-butyl $d_{0^{20}}$ 0.9133, $n_{D^{20}}$ 1.4327, γ^{20} 27.67; n-hexyl $d_{0^{20}}$ 0.9002, $n_{D^{20}}$ 1.4105, γ^{20} 27.86; n-octyl $d_{0^{20}}$ 0.8936, $n_{D^{20}}$ 1.4489, γ^{20} 28.67. ^b V. S. Abramov and N. F. Tryapitsina (*Zhur. obshchei Khim.*, 1949, 19, 929) give methoxy- $d_{0^{20}}$ 1.096, $n_{D^{20}}$ 1.4402; ethoxy- $d_{0^{20}}$ 1.034, $n_{D^{20}}$ 1.4377. ^c A. E. Arbutov and V. S. Vinogradova (*Doklady Akad. Nauk S.S.S.R.*, 1947, 55, 31) give methyl $d_{0^{20}}$ 1.2004, $n_{D^{20}}$ 1.4036, γ^{20} 37.21; ethyl $d_{0^{20}}$ 1.0742, $n_{D^{20}}$ 1.4080, γ^{20} 30.79; n-propyl $d_{0^{20}}$ 1.0184, $n_{D^{20}}$ 1.4175, γ^{20} 21.21; n-butyl $d_{0^{20}}$ 0.9888, $n_{D^{20}}$ 1.4320, γ^{20} 28.53; n-hexyl $d_{0^{20}}$ 0.9846, $n_{D^{20}}$ 1.4325, γ^{20} 28.38; n-heptyl $d_{0^{20}}$ 0.9363, $n_{D^{20}}$ 1.4382, γ^{20} 28.51; n-octyl $d_{0^{20}}$ 0.9286, $n_{D^{20}}$ 1.4420, γ^{20} 29.25. ^d Cf. Part VII (*J. Chem. Soc.*, 1943, 16) butyl, pentyl; A. E. Arbutov and V. S. Vinogradova (ref. a) give butyl $d_{0^{20}}$ 0.9731, $n_{D^{20}}$ 1.4247; hexyl $d_{0^{20}}$ 0.9396, $n_{D^{20}}$ 1.4340. ^e A. E. Arbutov and V. S. Vinogradova (*Doklady Akad. Nauk S.S.S.R.*, 1946, 54, 787) give $d_{0^{20}}$ 1.0272, $n_{D^{20}}$ 1.4165; A. H. Ford-Moore and J. H. Williams (*J. Chem. Soc.*, 1947, 1465) give $d_{25^{21}}$ 1.032, $n_{D^{20}}$ 1.4172. ^f G. M. Kosolapoff (*J. Amer. Chem. Soc.*, 1945, 67, 1180) gives $d_{4^{25}}$ 0.9623, $n_{D^{25}}$ 1.4258. ^g A. E. Arbutov and G. Kamai (*Zhur. obshchei Khim.*, 1947, 17, 2149) give $d_{0^{20}}$ 1.0683, $n_{D^{18}}$ 1.4082. ^h A. E. Arbutov and V. S. Vinogradova (ref. a) give $d_{0^{20}}$ 0.9776, $n_{D^{20}}$ 1.4245. ⁱ H. J. Lucas, F. W. Mitchell, and C. N. Scully (*J. Amer. Chem. Soc.*, 1950, 72, 5491) give methoxy $d_{0^{25}}$ 1.1374, $n_{D^{25}}$ 1.4354; ethoxy $d_{0^{25}}$ 1.0814, $n_{D^{25}}$ 1.4330; propoxy $d_{0^{25}}$ 1.0540, $n_{D^{25}}$ 1.4357; butoxy $d_{0^{25}}$ 1.0307, $n_{D^{25}}$ 1.4380.

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and Perry¹³ and by McCombie, Saunders, and Stacey¹⁴ was used; details are given for triethyl phosphite. Freshly distilled phosphorus trichloride (44.5 g.) dissolved in dry ether (50 ml.) was slowly added to a well-stirred mixture of anhydrous ethanol (50 g.), redistilled diethylaniline (150 g.), and dry ether (300 ml.) maintained at 5–10° in an ice-bath. After addition of the phosphorus trichloride, the ice-bath was removed and stirring continued (1 hr.). The reaction mixture was rapidly filtered through a sintered glass funnel, the precipitate washed with six portions of dry ether (50 ml.), and the ether distilled from the filtrate. The residue was fractionated at low pressure in a current of dry nitrogen using a modified Claisen flask with side arm packed with Fenske helices, to yield triethyl phosphite (43 g.), b. p. 55–56°/15 mm. Infrared spectroscopy and vapour phase chromatography indicated the presence of a small amount of diethyl ester; this was removed by keeping the product over sodium wire (24 hr.) and then redistilling over sodium in a current of dry nitrogen; pure triethyl phosphite (39 g.) b. p. 55.5°/20 mm. was obtained.

Tri-2-n-alkoxyethyl phosphites (ROC₂H₄O)₃P. These were prepared from 2-n-alkoxyethanols in similar manner to that employed for the trialkyl phosphites except that, after addition of the phosphorus trichloride, the reaction mixture was heated under reflux (3 hr.) and then cooled before filtration. Of the n-alkoxyethanols employed, the methoxy-, ethoxy-, butoxy-, and hexyloxy- were redistilled commercial samples; the remainder were prepared from ethanediol as described by Cooper and Partridge.¹⁵

Tri-n-alkyl orthophosphates (RO)₃PO. The procedure used for preparation of the 2-n-alkoxyethyl phosphites was adapted by substituting phosphoryl chloride for phosphorus trichloride and by employing light petroleum (b. p. 60–80°) as solvent; a reflux period of 6 hr. was used. A similar procedure was used for the two tri-alkoxyethyl phosphates investigated; the higher alcohols yielded purer products by this method than were produced by interaction of phosphoryl chloride with sodium alkoxides.¹⁶

Di-n-alkyl phosphonates HPO(OR)₂; *di-2-n-alkoxyethyl phosphonates* HPO(OC₂H₄OR)₂. Phosphorus trichloride (0.33 moles) was caused to react with excess of the appropriate alcohol (1.1–1.5 moles); no tertiary base was added, and care was taken to remove hydrogen chloride from the reaction mixture as completely as possible:¹⁴ details are given for diethyl phosphonate. Anhydrous ethanol (50 g.) and light petroleum (b. p. 40–60°) (150 ml.) were cooled (ice-bath) in a three-necked flask, and after evacuation (water-pump), phosphorus trichloride (44.5 g.) was slowly added to the well-stirred mixture (30 min.). The ice-bath was removed, and after stirring (6 hr.) with the flask still connected to the water-pump, the pump was disconnected, the stirrer replaced by a gas inlet tube, and dry nitrogen was bubbled through the liquid to complete the removal of hydrogen chloride. The residual solvent was evaporated on a water-bath and the residue distilled under

reduced pressure to give diethyl phosphonate (38 g.), b. p. 70–73°/10 mm.; if hydrogen chloride is not completely removed, pronounced decomposition occurs during distillation. The product was redistilled using a modified Claisen flask with side-arm packed with glass helices to give pure diethyl phosphonate (30 g.), b. p. 72.5°/10 mm. With the higher alcohols (n-butanol upwards) and with the 2-alkoxyethanols, no solvent was employed.

Di-n-alkyl ethylphosphonates C₂H₅PO(OR)₂; *di-n-propyl n-alkylphosphonates* RPO(OC₃H₇)₂. These compounds were prepared by treating a benzene solution of the appropriate di-alkyl phosphonate with sodium, and then causing the resulting sodio-compound to react with an alkyl halide.¹⁷ For dimethyl and diethyl ethylphosphonates, dioxan was used as solvent, since the corresponding sodio-compounds are insoluble in benzene; furthermore, the sodium halide produced was removed by filtration, whereas with the higher members the sodium halide was removed by washing the benzene solution with water. The dimethyl and diethyl phosphonates employed were redistilled commercial samples (Albright and Wilson); all others were prepared as described above. The alkylphosphonates prepared in this manner were found to be purer than the products obtained by treating trialkyl phosphites with alkyl halides.¹⁸

2-Alkoxy-4-methyl-1,3,2-dioxaphospholans (I; R' = Me). The procedure described by Lucas and his co-workers¹⁹ was adapted by treating propane-1,2-diol with phosphorus trichloride in chloroform solution; the 2-chloro-4-methyl-1,3,2-dioxaphospholan, distilled in a current of nitrogen, had b. p. 59–60°/25 mm. An ethereal solution of the chloro-compound was treated with the appropriate alcohol in presence of diethylaniline and in an atmosphere of dry nitrogen; the product was distilled under reduced pressure in a current of nitrogen.

Tables 4 and 5 summarise the physical properties of all the pure compounds investigated; the numbering of compounds in Clarendon type follows from Part XLI.¹⁹ Table 4 contains the b. p. (at 760 mm. unless otherwise stated), rounded values of the density and surface tension at various temperatures, and the mean parachor, whilst Table 5 gives the refractive indices, molar refractivities, and the molar refraction coefficients. Compounds not previously reported in the literature were analysed for carbon, hydrogen and phosphorus, and in all cases gave satisfactory results.

Infrared Spectra.—The infrared absorption spectra (capillary film) were measured using a Perkin-Elmer Infracord spectrophotometer; typical spectra are incorporated in ref. 20. Where overlap occurs, our results agree well with previously published spectra, and the absorption frequencies observed for P=O, P–O–C (alkyl), P–H, and P–C all lie within the generally accepted limits.²¹

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