77. *Physical Properties and Chemical Constitution. Part XXXIX.* The Electric Dipole Moments of Some Tri-n-alkylphosphines, of Triphenylphosphine, and of their Oxides.*

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THE electric dipole moments of triethyl-, tri-n-propyl-, tri-n-butyl-, tri-n-pentyl- and triphenyl-phosphine, and of their oxides, have been calculated from measurements of the dielectric constants, specific volumes, and refractive indices of the solutions in benzene at 25·00°. The results are discussed in terms of the conformation of the phosphines and the moment associated with the phosphorus–oxygen bond.

A COMPARISON of the electric dipole moments of trialkylphosphines with those of their corresponding oxides does not seem to have been reported. The apparent moment of the P–O bond in triphenylphosphine oxide has been measured previously[1-3] but it seemed desirable to ascertain if this is influenced by interaction between the phosphorus or oxygen atom and the π-electrons of the phenyl groups. Klages and Langpape[4] reported that in

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* Part XXXVIII, *J.*, 1963, 1731.

[1] Phillips, Hunter, and Sutton, *J.*, 1945, 146.

[2] Jensen, *Z. anorg. Chem.*, 1943, **250**, 268.

[3] Subbarayan, Ph.D. Thesis, Annamalai University, S. India, 1961.

[4] Klages and Langpape, *Z. Elektrochem.*, 1959, **63**, 533.

cyclohexane solution the dipole moment of triphenylphosphine is intermediate between those of tri-n-alkylphosphines and phosphines with mixed alkyl-phenyl residues. This would be unusual. Their moments for the trialkylphosphines, however, are substantially greater than the values found in this investigation. The dipole moments of esters of phosphoric, phosphorous, and phosphinic acids have been measured,[5] but reliable figures for the P–O moment cannot be obtained from these results because of complications associated with internal rotations.

EXPERIMENTAL AND RESULTS

The apparatus for measuring dielectric constants has been rebuilt since our previous communications; in particular the electronic circuits have been modified to improve the stability and ease of operation. The dielectric constants (ε_{12}), specific volumes (v_{12}), the square of the refractive indices (n^2_{12}), and the specific refractions of the solutions were linear functions of their weight fractions (w_2) over the concentration range investigated. Each was fitted to a straight-line relationship by a least-squares procedure, and any results which deviated from the line by more than about twice the probable error were rejected. From the slopes of these lines the electric dipole moment was computed by the method described earlier [6] and also by the method of Guggenheim [7] and Smith.[8] The results from the two methods agreed within 0·001 D. Calculations were preformed on a Stantec Zebra computer. The values of the dielectric constant, specific volume, and refractive index taken for the solvent benzene at 25·00° were [9] $\varepsilon_1 = 2{\cdot}2741$, $v_1 = 1{\cdot}14445$, and $n_1 = 1{\cdot}49790$.

The alkylphosphines were oxidised very rapidly on exposure to air. The final distillation of the compounds was performed in an atmosphere of oxygen-free (" white spot ") nitrogen; the benzene solutions were prepared and kept throughout the measurements under pure nitrogen. Their dipole moments were each measured several times to ensure that the results were completely reproducible. The phosphine oxides are hygroscopic and consequently were also handled under a pure-nitrogen atmosphere in a dry-box.

The measured physical properties of the benzene solutions at 25·00° for one determination on each compound are presented in Table 1; the slopes of the linear graphs of dielectric constant and specific volume, α and β, respectively, against weight fraction, together with the polarisation data and dipole moments (μ) are given in Table 2.

Preparation and Purification of Compounds.—The dipole moment of each compound was measured immediately it had been purified.

Trialkylphosphines. The tri-n-alkylphosphines were prepared by the method of Davies and Jones.[10] A solution of phosphorus trichloride in ether was added dropwise at 0° to a Grignard solution prepared from magnesium and the appropriate alkyl bromide. The mixture was refluxed for about 8 hr., then cooled aqueous ammonium chloride was added to decompose the Grignard complex and to dissolve the magnesium salts, and the organic layer was separated and dried ($MgSO_4$). The ether was distilled off and the alkylphosphine fractionated. All the operations, including transfers from one vessel to another, were performed in an atmosphere of pure nitrogen. Thus were obtained:

Triethylphosphine, b. p. 127·0°/745 mm. (Found: C, 60·7; H, 12·8; P, 26·0. Calc. for $C_6H_{15}P$: C, 61·0; H, 12·7; P, 26·3%).

Tri-n-propylphosphine, b. p. 81·8—81·9°/20 mm. (Found: C, 67·5; H, 12·9; P, 19·0. Calc. for $C_9H_{21}P$: C, 67·5; H, 13·1; P, 19·4%).

Tri-n-butylphosphine, b. p. 77°/0·85 mm. (Found: C, 71·0; H, 13·3; P, 15·1. Calc. for $C_{12}H_{27}P$: C, 71·3; H, 13·4; P, 15·3%).

Tri-n-pentylphosphine, b. p. 100°/0·6 mm., m. p. 29°.

Triphenylphosphine. A pure commercial sample (B.D.H. Organic Analytical Standard) was recrystallised from ethanol to constant m. p. (80°).

[5] Arbuzov and Rakov, *Izvest. Akad. Nauk S.S.S.R., Otdel, khim. Nauk*, 1950, 237; Arbuzov and Shavsha-Tolkachera, *ibid.*, 1954, 812.

[6] Cumper, Vogel, and Walker, *J.*, 1956, 3621; Cumper, Redford, and Vogel, *J.*, 1962, 1176.

[7] Guggenheim, *Trans. Faraday Soc.*, 1949, **45**, 714.

[8] Smith, *Trans. Faraday Soc.*, 1950, **45**, 394.

[9] Hartshorn, Parry, and Essen, *Proc. Phys. Soc.*, 1955, **68**, *B*, 422; Timmermans, "Physico-Chemical Constants of Pure Organic Compounds," Elsevier, Amsterdam, 1950.

[10] Davies and Jones, *J.*, 1929, 33; Davies, Pearse, and Jones, *J.*, 1929, 1262.

TABLE 1.

100 w_2	ε_{12}	v_{12}	n_{12}	100 w_2	ε_{12}	v_{12}	n_{12}
	Triethylphosphine				*Tri-n-propylphosphine*		
0·16770	2·27458	1·14454	1·49770	0·10670	2·27458	1·14472	1·49746
0·21086	2·28560	1·14457	1·49765	0·17980	2·27548	1·14487	1·49746
0·31757	2·27747	1·14467	1·49754	0·21157	2·27662	1·14499	1·49734
0·50700	2·28005	1·14480	1·49746	0·36907	2·27722	1·14517	1·49727
0·54560	2·28083	1·14485	1·49743	0·43847	2·27812	1·14524	1·49722
0·54760	2·28107	1·14487	1·49743	0·55645	2·27993	1·14535	1·49713
0·58400	2·28234	1·14491	1·49739	0·59164	2·28053	1·14545	1·49708
0·80320	2·28618	1·14511	1·49727				
	Tri-n-butylphosphine				*Tri-n-pentylphosphine*		
0·07236	2·27510	1·14447	1·49771	0·15551	2·27621	1·14453	1·49769
0·19037	2·27667	1·14452	1·49765	0·32784	2·27726	1·14469	1·49759
0·48783	2·28056	1·14479	1·49755	0·52054	2·27926	1·14487	1·49754
0·90868	2·28151	1·14494	1·49732	0·77584	2·28115	1·14522	1·49736
0·92976	2·28377	1·14527	1·49726	0·95210	2·28263	1·14541	1·49731
1·15026	2·28592	1·14547	1·49712	1·31612	2·28621	1·14557	1·49713
1·25378	2·28697	1·14558	1·49705	1·50035	2·28715	1·14594	1·49703
	Triphenylphosphine				*Triethylphosphine oxide*		
0·08733	2·27570	1·14420	1·49800	0·11640	2·29295	1·14429	1·49763
0·24661	2·27760	1·14379	1·49823	0·21440	2·30916	1·14418	1·49759
0·49923	2·28094	1·14321	1·49853	0·29560	2·32113	1·14405	1·49755
0·67471	2·28313	1·14271	1·49889	0·37200	2·33370	1·14393	1·49750
0·91273	2·28628	1·14204	1·49907	0·50420	2·35439	1·14375	1·49746
1·09575	2·28865	1·14155	1·49936	0·62900	2·37249	1·14357	1·49740
1·49443	2·29384	1·14055	1·49984	0·99500	2·42848	1·14298	1·49728
	Tri-n-propylphosphine oxide				*Tri-n-butylphosphine oxide*		
0·10550	2·28591	1·14439	1·49755	0·03973	2·27724	1·14442	1·49772
0·18840	2·29489	1·14433	1·49753	0·08925	2·28212	1·14438	1·49769
0·33560	2·31215	1·14417	1·49742	0·26084	2·29791	1·14433	1·49761
0·56810	2·33932	1·14406	1·49728	0·57172	2·32680	1·14416	1·49750
0·61590	2·34430	1·14394	1·49723	0·81735	2·35007	1·14404	1·49740
0·89490	2·37614	1·14383	1·49715	1·01124	2·36758	1·14395	1·49732
1·12000	2·40387	1·14360	1·49701	1·10856	2·03898	1·14393	1·49729
	Tri-n-pentylphosphine oxide				*Triphenylphosphine oxide*		
0·03344	2·27771	1·14442	1·49766	0·15145	2·28754	1·14393	1·49774
0·17674	2·28794	1·14436	1·49762	0·25342	2·29652	1·14356	1·49799
0·36757	2·30277	1·14426	1·49752	0·38136	2·30723	1·14313	1·49814
0·48229	2·31196	1·14423	1·49745	0·60460	2·32433	1·14239	1·49841
0·70327	2·32873	1·14418	1·49739	0·83266	2·34322	1·14166	1·49872
0·91450	2·34508	1·14415	1·49734	1·10235	2·36525	1·14069	1·49910
1·00290	2·34711	1·14412	1·49727	1·19362	2·37227	1·14040	1·49915

TABLE 2.

Compound	α	β	$_\infty P_2$ (cm.^{3})	R_D (cm.^{3})	$_0P$ (cm.^{3})	μ (D)
Triethylphosphine	1·76$_7$	0·088$_5$	82·66	38·16	44·51	1·48 *
Tri-*n*-propylphosphine	1·19$_5$	0·142$_7$	97·46	52·99	44·47	1·48
Tri-n-butylphosphine	0·98$_8$	0·096$_7$	112·44	67·17	45·27	1·49 †
Tri-n-pentylphosphine	0·82$_2$	0·107$_6$	125·80	80·81	44·99	1·48
Triphenylphosphine	1·28$_4$	−0·260$_1$	132·45	87·00	45·06	1·49 ‡
Triethylphosphine oxide	15·3$_1$	−0·149$_6$	425·9	36·05	389·8	4·37
Tri-n-propylphosphine oxide	11·6$_0$	−0·075$_1$	440·0	50·91	389·1	4·36
Tri-n-butylphosphine oxide	9·2$_7$	−0·046$_5$	452·0	65·28	386·7	4·35
Tri-n-pentylphosphine oxide	7·7$_4$	−0·029$_5$	465·3	78·93	386·3	4·35
Triphenylphosphine oxide	8·0$_5$	−0·338$_3$	488·1	85·55	402·5	4·44 §

* 1·84 D in cyclohexane.[4] † 2·22 D in cyclohexane. ‡ 1·39,[1] 1·45,[2] 1·50,[12] 1·52 [3] D in benzene, 1·44 D in cyclohexane.[4] § 4·28,[1] 4·31,[2] 4·49[3] D in benzene.

Trialkylphosphine oxides. Freshly distilled samples of the trialkylphosphines were heated and oxidised [11] to their corresponding oxides by drawing a stream of dry air through them for ~8 hr. The products were fractionated (Fenske column) three times under reduced pressure.

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[11] Jackson and Jones, *J.*, 1931, 575.

[12] Aroney, Le Fèvre, and Saxby, *J.*, 1963, 1739.

Stringent precautions were taken to exclude moisture in all the operations and in the analyses. Thus were obtained:

Triethylphosphine oxide, b. p. 124·5—124·7°/18 mm., m. p. 47·3° (Found: C, 53·7; H, 11·1; P, 23·4. Calc. for $C_6H_{15}PO$: C, 53·7; H, 11·2; P, 23·1%).

Tri-n-propylphosphine oxide, b. p. 120·3—120·5°/7 mm., m. p. 38·7° (Found: C, 62·5; H, 11·1; P, 17·5. Calc. for $C_9H_{21}PO$: C, 62·1; H, 10·9; P, 17·8%).

Tri-n-butylphosphine oxide, b. p. 108°/0·2 mm., b. p. 69° (Found: C, 66·5; H, 11·7; P, 14·7. Calc. for $C_{12}H_{27}PO$: C, 66·7; H, 11·6; P, 14·4%).

Tri-n-pentylphosphine oxide, b. p. 136°/0·4 mm., m. p. 84° (Found: C, 68·9; H, 12·6; P, 11·6. Calc. for $C_{15}H_{33}PO$: C, 69·2; H, 12·8; P, 11·9%).

Triphenylphosphine oxide. The corresponding phosphine, dissolved in acetone, was oxidised with hydrogen peroxide. Addition of water gave a precipitate which was collected and converted into anhydrous triphenylphosphine oxide by heating it at 120—130° for several hours. The product was crystallised from light petroleum–benzene to constant m. p. (158°).

DISCUSSION

Phosphines.—The trialkylphosphines studied have virtually identical dipole moments. This is also the case for the corresponding n-alkyl sulphides[13] and implies that the hydrocarbon chains tend, as a mean conformation, to be nearly perpendicular to the direction of the primary moment in the molecules. A " folded " conformation has been suggested as the predominant one for the chains of alkyl esters of phosphorous, phosphoric, and alkanephosphoric acids,[14] though this has been denied in other investigations.[15] In a folded conformation the dipole moments of the phosphines and their oxides would be expected to decrease slightly as the chain length is increased.

Phosphine Oxides.—The alkylphosphine oxides measured also have very similar dipole moments, so that the change in moment which accompanies the formation of the P–O bond is nearly constant (Table 3).

TABLE 3.

Substituents	Phosphine	Phosphine oxide	Difference
Triethyl-	1·48	4·37	2·89
Tri-n-propyl-	1·48	4·36	2·88
Tri-n-butyl-	1·49	4·35	2·86
Tri-n-pentyl-	1·48	4·35	2·87
Triphenyl-	1·49	4·44	2·95

The bond angles of the phosphorus trihalides increase by about 4° when their oxyhalides are formed.[16] If a similar increase in the CPC angle occurred upon oxidation of the phosphines, the apparent P–O bond moment calculated from the experimental values in Table 3 would be increased by 0·15 D. The apparent bond moment of 2·88 D is a little lower than the value of 2·95 D calculated from the moments[17] of the phosphite ester, 4-methyl-2,6,7-trioxa-1-phosphabicyclo[2,2,2]octane and its oxide. In this ester rotation about the C–O bonds is not possible. The experimental data in Table 3 refer to measurements in benzene solution; if it were possible to determine the dipole moments of these compounds in the vapour phase, the values would differ slightly because of a solvent effect, but it is highly unlikely that the near-constancy of the values in each series would be appreciably affected.

The dipole moment of triphenylphosphine oxide, and its apparent P–O moment, are slightly greater than in the aliphatic compounds. This could be due to a reduction of the CPC angle when the aromatic phosphine is oxidised, or to a change in the interaction

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[13] Cumper, Read, and Vogel, unpublished work.

[14] Arbuzov and Vinogradova, *Compt. rend. Acad. Sci. U.R.S.S.*, 1946, **54**, 787; *Izvest. Akad. Nauk S.S.S.R., Otdel, khim. Nauk*, 1951, 733; Kosolapoff, *J. Amer. Chem. Soc.*, 1954, **76**, 615.

[15] Arbuzov and Vinogradova, *Izvest. Akad. Nauk S.S.S.R., Otdel, khim. Nauk*, 1952, 507; Kosolapoff, *J.*, 1954, 3222; 1955, 2964.

[16] Brockway and Beach, *J. Amer. Chem. Soc.*, 1938, **60**, 1836.

[17] Brown, Verkade, and Piper, *J. Phys. Chem.*, 1961, **65**, 2051.

between the phosphorus atom and the π-electrons of the phenyl groups. It seems more likely, however, that it arises from polarisation of the phenyl rings by the high moment associated with the P–O bond and the consequently increased electronegativity of the phosphorus atom. A similar difference is observed between the S–O bond moment in phenyl and tolyl sulphoxides and in aliphatic sulphoxides; the difference is greater with the corresponding sulphones.

It is interesting that the apparent P–O bond moment is very similar to that of the S–O moment in aliphatic sulphoxides (2·90 D) and sulphones (3·00 D) [13,18] in spite of the phosphorus atom's being less electronegative and slightly larger than the sulphur atom. The dipole moment of trimethylamine and of its oxide indicate that the apparent moment of the corresponding N–O bond is greater (*ca.* 4 D).[1,19]

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[18] Cumper and Walker, *Trans. Faraday Soc.*, 1956, **52**, 193; Lumbroso and Passerini, *Bull. Soc. chim. France*, 1955, 1179.

[19] Le Fèvre and Russell, *Trans. Faraday Soc.*, 1947, **43**, 374; Cumper and Walker, *ibid.*, 1955, **52**, 193.