Dipole Moments of the Lower Dialkyl Alkylphosphonates.

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The calculation of dipole moments of several lower members of the dialkyl alkylphosphonate series was made from the determinations on the pure liquids, of the dielectric constants of these esters. The values of the dipole moments obtained through the use of the empirical formula proposed by Buckingham and Le Fèvre seem to indicate a low probability of the " folded structure " of such esters, which has been proposed by other workers to explain deviations found among the parachor values in this series of substances.

There is a scarcity of experimental data on the dipole moments of esters of aliphatic phosphonic acids. Until a recent publication by the author (*J. Amer. Chem. Soc.*, 1954, **76**, 615) for some diethyl esters of the higher alkylphosphonic acids, the only other determinations were those by Arbuzov and Rakov (*Izvest. Akad. Nauk S.S.S.R.*, *Otdel. Khim. Nauk*, 1950, 237) with five substances in which all three aliphatic radicals (methyl, ethyl, propyl, *iso*propyl, and butyl) were identical in each ester. Their results on solutions in various solvents were converted into the calculated dipole-moment data by extrapolation. The five esters gave extremely close grouping of the dipole moments (2·86—2·92 D), which seems to indicate a lack of dependence of the resultant moment on molecular constitution.

Since it is well-substantiated that the dipole moments of solute molecules obtained by translation of dielectric-constant data for their solutions often deviate considerably from the " true " values obtainable from measurements in the gaseous state, it was felt that dielectric data obtained for the pure liquids may be at least as useful in calculations of dipole moments as those data for solutions. The same idea has been explored recently by many workers and has resulted in several formulæ of both the theoretically derived and the empirical type. Kosolapoff (*loc. cit.*) used the Onsager formula for computation of dipole moments from dielectric data on the higher diethyl alkylphosphonates. This formula, *viz.*,

$$\mu^2 = \frac{9kTM}{4\pi Nd} \times \frac{(\varepsilon - n^2)(2\varepsilon + n^2)}{\varepsilon(n^2 + 2)^2}$$

has been used with success with numerous anisotropic substances by Böttcher (" Theory of Electric Polarisation," Elsevier Publ. Co., Amsterdam, 1952, pp. 186—187, 298, 323—328). The results thereby obtained showed a smooth variation of the dipole moments of the phosphonates with the molecular weight, a decline of the moment with increasing molecular weight tending to an apparent limit of about 2·5 D for esters with an alkyl group greater than 16 carbon atoms in length. As pointed out at that time, such a trend could be real or it could be the result of incomplete validity of the above equation.

In the present series of determinations the dielectric data were obtained for several phosphonates which carry short radicals, and dipole moments were then calculated by Onsager's equation. It was seen that the trend, mentioned above, continued for the lower members of the series, and for a group of diethyl esters resulted in continuation of the smooth curve of dipole moment against molecular weight of the phosphonate alkyl radical. It appeared that such data might be employed for estimation of the link moment for the P–O group by graphic vector addition of the remaining moments in the simple molecules. This determination would be of interest since the link-moment data for this group had been previously estimated only for aromatic compounds (Phillips, Hunter, and Sutton, *J.*, 1945, 146). For such a computation it was necessary to formulate the possible atomic configurations of these esters which would involve rotation of groups about the single bonds. Rotation of either the R or the OR groups, among the lower members of this group, can produce the extreme cases of either the " folded " or the " extended " structures. In the former, the third atom of each chain, attached to the phosphorus atom, would approach the singular O–P link in such a way that an attraction might be postulated between this oxygen and the hydrogen atom that is connected to the third atom of the chain. Such an attraction could lead to hindrance of free rotation of the side chain and could cause the assumption of a bulb-like form of the molecule. A conclusion of this nature was reached by previous workers in the field of parachor measurements with these compounds (Arbuzov and Vinogradova, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk,* 1952, 882, 865, 505; 1951, 733; 1947, 459). Such an interpretation of the structure of the phosphonates, also employed for other esters of phosphorus acids, was attractive from the purely chemical point of view. It afforded a simple explanation for the great increase of reactivity in hydrolysis, ester-exchange reactions, and others, in passing from esters that contain ester groups with two or more carbon atoms, to those esters whose side chains, *in toto*, contain one or two atoms only, *i.e.*, side chains which are too short to " reach " the singular oxygen. Compounds of the second class would lack a screening effect, therefore, which is present in compounds of the first group—a screening effect afforded by the CH_2 or CH_3 groups around the highly polar singular oxygen which is expected to be the point of protonic attack in acid-catalysed reactions. Accordingly, graphic vector addition was performed for the various esters that were examined in this group. In each case the " folded " and the " extended " form were taken as the extreme cases of group rotation, employing for the computations the normally expected component values of: C–P moment 0·9 D, P–O (in ester link) moment 1·2 D, O–P–O angle 118°, C–O–P angle 110°, P–O distance (ester link) 1·84 Å, C–O distance 1·51 Å, C–C distance 1·54 Å, and P–O (singular oxygen) distance 1·5 Å (Arbuzov and Shavsha, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk,* 1952, 875). The vectorial addition of the moments, the singular P–O link being omitted, gave resultant vector sums which were closely grouped for all esters in either the folded or the extended form: the former gave a range of 2·9—3·4 D, the latter 0·5—1·0 D. However, the " folded " models had the resultant vector directed essentially along the singular P–O link and in the same directiomas, but in opposite sense from, the expected polarity of the P–O link. Coupled with the actual calculated values of the total molecular moment (by Onsager's equation), the assumption of the " folded " structure would call for the P–O moment link of some 6·3—6·7 D, a value that is more than twice the expected one. The " extended " structures gave the resultant moments (lacking the P–O link moment) which were directed in the same sense as the expected vector of the singular P–O moment, and the P–O link moments calculated on this basis ranged closely at 2·2—2·8 D for the various esters. This value is somewhat smaller than the value of 3·5 D assumed by Arbuzov and Shavsha (*loc. cit.*). Thus, the results secured through Onsager's equation appear to make it clear that, although the " folded " structure is not completely excluded, yet it is certainly not the predominant form that is assumed by the alkylphosphonates at room temperature.

Although the comparison previously obtained of the molecular dipole moment of diethyl ethylphosphonate as calculated by the Onsager equation and as obtained by extrapolation method from dilute-solution data in *n*-heptane appeared to indicate a satisfactory agreement of the two sets of data (Kosolapoff, *loc. cit.*), yet it was felt that the wide spread of the total molecular moments as estimated by the Onsager equation in this family of compounds might indicate an apparent spread only, and not reflect the true electric dipoles of the molecules. Accordingly, we applied the empirical formula proposed recently by Buckingham and Le Fèvre [*J.*, 1952, 1932; formula (5)] for the estimation of dipole moments from dielectric and dimensional data on pure liquids of anisotropic character, *viz.* (for notation, see *idem, ibid.*):

$$\frac{\mu^2{}_1}{\mu^2{}_g} = 1 + \frac{\varepsilon - 1}{\varepsilon + 2}(e^{x^2} - 1) - \frac{1{\cdot}69\, e^{x^2}(\varepsilon - 1)(n^2 + 1)(\varepsilon - n^2)}{\varepsilon^2 n^2 (e^{x^2} + 1)\, e^{M/dABC}}$$

In view of the considerable success with which this formula was applied to a varied group of anisotropic materials, it was felt that the results obtained with it may be a better indication of the true dipole moments of the phosphonates than is afforded by the Onsager formula. The results of this set of calculations showed a much closer grouping of the dipole moments among the esters than was obtained through Onsager's formula, with general lowering, the extent of which varied with different compounds. In the computations we made use of dimensions of the molecules that would be expected of the " folded " and the " extended " forms. This was necessary because the formula contains an implicit function of molecular shape (or area) which, of course, differs for the two possible extreme forms. The root-mean-square values of these data were then derived, it being deemed reasonable to use them for the representation of the moments of molecules in which rotation of groups leads to constant variation of one form to the other. For the propyl derivative, three positions of the alkyl group were taken into consideration. No attempt was made to apply Buckingham and Le Fèvre's formula to the higher alkylphosphonates, owing to the very great number of possible chain configurations caused by rotation in the long chains.

The values of the dipole moments calculated by the two formulæ are listed in Table 1. In addition, the dipole moment of diethyl *p*-tolylphosphonate is included for an example of the effect produced by the interposition of the phenyl group between the ester and the methyl radicals; only the Onsager formula was used for this computation.

TABLE 1. *Dipole moments of dialkyl alkylphosphonates.*

		μ, in D.			
		From Onsager's formula	From Buckingham and Le Fèvre's formula		
No.	Ester		" Folded "	" Extended "	R.M.S.
1	MeP(O)(OMe)$_2$	3·62	3·04	2·48	2·78
2	EtP(O)(OMe)$_2$	3·38	2·51	2·42	2·47
3	MeP(O)(OEt)$_2$	3·33	2·82	3·39	3·11
4	EtP(O)(OEt)$_2$	2·95	2·46	2·64	2·55
5	PrP(O)(OEt)$_2$	2·94	2·58	2·86, 3·39	2·96
6	Pr^{i}P(O)(OEt)$_2$	2·85	2·50	2·98	2·75
7	MeP(O)(OPr^i)$_2$	2·83	2·70	2·86	2·78
8	*p*-MeC$_6$H$_4$·P(O)(OEt)$_2$	3·53	—	—	—

Since the calculation of the root-mean-square values listed in Table 1 implies the constant variation of the shape and dimensions of the molecules, no attempt at estimation of the P–O link moments from these values was made, since such computation necessitates assumptions as to definite vector directions of the components.

EXPERIMENTAL

Preparation of Compounds.—The methylphosphonates were prepared by the Arbuzov reaction of methyl iodide with tri*iso*propyl phosphite, which yielded 90% of very pure di*iso*propyl methylphosphonate. This method avoids the possible contamination of the methylphosphonate which would be expected in a reaction of methyl halide with a trialkyl phosphite containing primary alkyl radicals, other than methyl. The resulting ester was hydrolysed by refluxing overnight with concentrated hydrochloric acid. The solution was dehydrated by azeotropic distillation with benzene–toluene, after which the mixture was cooled, yielding a nicely crystalline layer of methylphosphonic acid, which was rinsed with dry benzene and treated with a slight excess of phosphorus pentachloride. Distillation gave an 85% yield of methylphosphonyl dichloride, b. p. 163°/756 mm., which was dissolved in dry benzene, and the solution was slowly added with stirring to a solution of slightly more than 2 equivs. of metallic sodium in either methanol or ethanol (dry). The slight excess of the alkoxide ensured the isolation of halogen-free esters, which were obtained in 78—84% yields.

Ethylphosphonates were obtained similarly from diethyl ethylphosphonate, which in turn was prepared conventionally from ethyl iodide and triethyl phosphite. Ethylphosphonyl dichloride, used as the intermediate, was obtained in 89% yield and boiled at 179°/756 mm.

Propyl- and the *iso*propyl-phosphonates were prepared (75—84% yield) by reaction of the corresponding bromides with diethyl sodiophosphonate in dry benzene solution by conventional procedure.

Diethyl *p*-tolylphosphonate was prepared by treatment of the pure *p*-tolylphosphonic acid (m. p. 195°) with phosphorus pentachloride, followed by conventional esterification of the resulting dichloride with absolute ethanol under slightly reduced pressure.

All the esters were carefully distilled through an efficient ring-packed column and only the middle cuts were employed for the determination of the physical constants, although the entire specimens showed a constant b. p.

Determination of Dipole Moments.—The values of the physical constants, determined at 30°, are shown in Table 2. The measurements of the dielectric constants were made as described previously (Kosolapoff, *loc. cit.*).

TABLE 2. *Physical constants of the phosphonates.*

Ester *	B. p./mm.	n_D^{30}	d_4^{30}	ε^{30}	$[R_D]$, found	calc.†
1	79·5°/20	1·4099	1·1507	20·68	26·69	26·92
2	82°/18	1·4128	1·1029	15·89	31·19	31·54
3	85°/15	1·4101	1·0406	13·405	36·20	36·16
4	86°/14	1·4108 ‡	1·0158 ‡	10·653 ‡	40·56	40·77 §
5	104°/17	1·4169	0·9937	9·452	45·54	45·39
6	94°/17	1·4130	0·9914	8·481	45·27	45·39
7	89°/18	1·4062	0·9734	8·061	45·44	45·39
8	100°/0·4	1·4931	1·0834	11·18	61·17	60·26 †

* See Table 1.

† The atomic refraction of phosphorus for the phosphonates was taken at the accepted value of 4·27; this has been established only for the aliphatic compounds thus far. It appears that a higher value is in order for the aromatic members.

‡ At 32°.

§ Reported earlier (*loc. cit.*).

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