DIPOLE MOMENTS
AND CONFORMATION OF DIALKYLPHOSPHINIC ESTERS

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The dipole moments of six dialkylphosphinic esters, measured in benzene solution, agree with the gauche conformation of the alkoxy group with respect to the P=O bond (*C*). In derivatives of methylphenylphosphinic acid the conformation *D* is preferred from the two possibilities.

In a series of papers[1-3] conformation on functional groups of the general formula *A* (where Y = O or S, and Z = O, S, Se, Te) was investigated by the dipole moment approach. For X = C the whole molecule is planar[1] and possesses the Z conformation while for X = S or P the configuration on these atoms is tetrahedral (with an additional lone electron pair or an additional alkyl group, respectively), and the conformation on the X—Z bond is synclinal[2,3] (gauche). A previous communication[3] was confined to derivatives with X = P and Y, Z = S, *i.e.* dialkyldithiophosphinic acids and their derivatives; in this paper we are dealing with the corresponding oxygen derivatives, dialkylphosphinic esters (*B* or *C*), much less extensively.
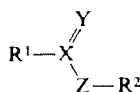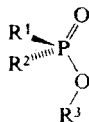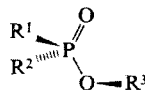
It is because these compounds have already been studied[4], even using dipole moments[5-7], and their conformation may be considered as essentially known. Our approach differs from the papers quoted[5-7] in using substituents in the *para* position of a benzene nucleus and comparing the results graphically[8] (Fig. 1). In this way the information obtained from dipole moments is enhanced, but the compounds studied are restricted to aromatic derivatives.

EXPERIMENTAL AND RESULTS

Materials: Dialkylphosphinic esters *I—VI* (Table I) were prepared according to the literature[9-12] or by applying known methods. Their purity was checked by vapor-phase chromatography or by determining the physical constants (m.p., b.p., n_D^{20}). All the values agreed with literature data[9-13], except those of compound *VI*, which is a crystalline substance, m.p. 81—82°C, and not a liquid as described previously[13]. For $C_6H_{13}Cl_2O_2P$ (315·1) calculated: 53·35% C, 4·16% H, 9·83% P; found: 53·56% C, 3·99% H, 9·81% P.

Physical measurements: The method used has been described[1-3]. Molar refractions were determined experimentally with one exception (compound *VI*). The dipole moment data listed in Table I are internally consistent and agree well with some literature data[6,7] on these and similar compounds (in particular methyl dimethylphosphinate[6] in tetrachloromethane —3·29 D, butyl dibutylphosphinate[14] in dioxan —3·29 D, pentyl dipentylphosphinate[14] in dioxan —3·25 D). The little dependence on solvent is also apparent from these comparisons.

Calculations of theoretical dipole moments: All the calculations were carried out graphically with an accuracy of $\pm 0·03$ D. The bond moments C—P (0·8 D), O—P (0·55 D), P=O (2·85 D) are mentioned in the Discussion, the remaining ones were the same as previously[2,3]. The bond angles adopted were $\measuredangle$ C—P—C 108°, $\measuredangle$ O=P—O 112°, $\measuredangle$ P—O—C 113°; they are essentially based on an X-ray study of dimethylphosphinic acid[16] although diphenylphosphinic acid[17] shows larger deviations from the tetrahedral arrangement.

DISCUSSION

The choice of suitable bond moments has some special problems in the case of phosphorus compounds; they were discussed in detail in the previous communication[3]. The essential feature is the presence of a lone pair moment in 3-covalent compounds which enters implicitly the values of bond moments derived. Hence the bond moment[3] $C^{(+)}$—$P^{(-)}$ of 0·8 D is mainly due by this contribution and is not immediately related to the electronegativities of the two atoms. This is still more apparent in the unexpected direction of the moment $O^{(+)}$—$P^{(-)}$ which has been confirmed from several sources[18-20]. The numerical value of 0·55 D chosen by us is intermediate between those given in the literature[18-20]. On the other hand, the $P^{(+)}$=$O^{(-)}$ moment is lessened by the lone pair contribution since it is determined as the difference between a 3-covalent and a 4-covalent derivatives[21]. Instead of the recommended values[21] 2·88 or 2·95 D, we used the insignificantly lower value of 2·85 D in order to correlate it to the P=S bond moment[3] (2·90 D). The mesomeric dipole moment $C_6H_5^{(+)}$—$P^{(-)}$ has been given the same value (0·6 D) as in the case of diaryldithiophosphinic acids[3], although the difference between the experimental moments of aromatic and aliphatic derivatives seems to be slightly smaller in the present case (Table I). No mesomeric moment was applied for the conjugation O—C_6H_5 in the compound *II* since the latter is assumed to be sterically repressed[20].

In Fig. 1 the experimental dipole moments are plotted together with those calculated for various dihedral angles $\tau = \measuredangle$ O=P—O—C; the graphical method[8] used is based on the comparison of a *para*-substituted and the corresponding unsubstituted

derivative. There are two such pairs among our compounds, *III* − *IV* and *V* − *VI*; both give concordant results. The *sc* (gauche) conformation of the compounds *V*, *VI* is unambiguous according to the upper part of Fig. 1. In the case of *III* and *IV*, two *sc* conformations are possible (D and E); according to Fig. 1, lower part, the form D with OCH_3 on the side of the phenyl group is favoured. Hence the purely steric effects are clearly not deciding. The conformation of aliphatic derivatives (*I*, *II*) can be assigned less safely since the graphical method is not applicable. Nevertheless similar values of the experimental dipole moments of all the compounds *I*, *II*, *III*, *V* suggest their similar conformations. This is substantiated by the values computed for the *sc* conformation, listed in Table I (last column).
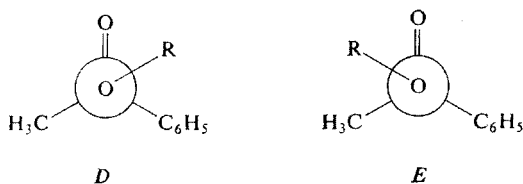

D   *E*

TABLE I

Polarization Data of Dialkylphosphinic Esters $R^1R^2P(=O)OR^3$ (Benzene, 25°C)

Compound	R^1	R^2	R^3	n_D^{20} d^{20}	R_D^{20}, cm^3 ∞P_2 cm^3	$\mu(5)^a$, D $\mu(15)^a$	$\mu_{calc}{}^b$ D
I	C_2H_5	C_2H_5	C_2H_5	1·4312 1·0047	38·71 280·7	3·41 3·39	3·54
II	C_2H_5	C_2H_5	C_6H_5	1·5055 1·0939	53·78 312·5	3·52 3·49	3·58
III	C_6H_5	CH_3	CH_3	1·5253 1·1498	45·37 346·0	3·82^c 3·79	3·74
IV	$4\text{-}ClC_6H_4$	CH_3	CH_3	1·5380 1·2708	50·37 249·9	3·10 3·06	3·11
V	C_6H_5	C_6H_5	C_2H_5	1·5665 1·1547	69·61 353·6	3·70^d 3·65^d	3·75
VI	$4\text{-}ClC_6H_4$	$4\text{-}ClC_6H_4$	C_2H_5	— —	79·2^c 290·1	3·18 3·12	3·05

^{a} Calculated with a correction of 5% or 15% of the R_D value, respectively, for the atomic polarization; ^{b} calculated from bond moments for the gauche conformation, $\tau = 60°$; ^{c} ref.[7] gives 3·80 D in tetrachloromethane; ^{d} another determination on a sample supplied by Dr H. R. Hays, gave the values of 3·68 or 3·63 D, respectively; ^{e} calculated from the R_D value of *V* and Vogel's increment[15] for chlorine.

In previous dipole moment studies of dialkylphosphinates the free rotation around the P—O bond was assumed first[5], but the finding was based upon unreliable bond moments. In Fig. 1 the points for the free rotation (denoted F) clearly disagree with experiments. Later studies found the sc conformation[7] for III and other esters of methyl-phenylphosphinic acid but the decision between the two possibilities $(D$ or $E)$ could not be reached without introducing substituents. Methyl dimethyl-phosphinate was claimed[6] to exist in sp (cis) conformation $(\tau = 0°)$ in addition to the less populated sc form (C). In our opinion the IR spectral proof is not quite convincing and a decision on the basis of dipole moments is impossible $(e.g.$ in the case of compound I the calculated value would be 3.02 D for the sp conformation and 3.18 D for a $70 : 30$ mixture). The sp form is very improbable $a\ priori$, the less is the co-existence of two forms separated only by an angle of $60°$. Using the ^{1}H NMR spectro-scopy, the sc conformation D of $(-)$-menthyl methyl-phenylphosphinate was esta-blished[4] like in III and IV. The sc conformation was also invariantly found[3] for dialkyldithiophosphinic acids and their esters and seems thus to be a general feature in phosphorus stereochemistry. In all the mentioned compounds it may be explained in terms of the gauche effect[22] arising between the polar bonds P=O and O—R (or P=S and S—R, respectively). New theoretical interpretations of the gauche effect have been advanced[23,24].

From the molar refraction of liquid derivatives $I - V$ we derived the increments of the P(O)O group: 7.66 cm^3 for the aliphatic derivatives and 8.68 cm^3 for the aro-
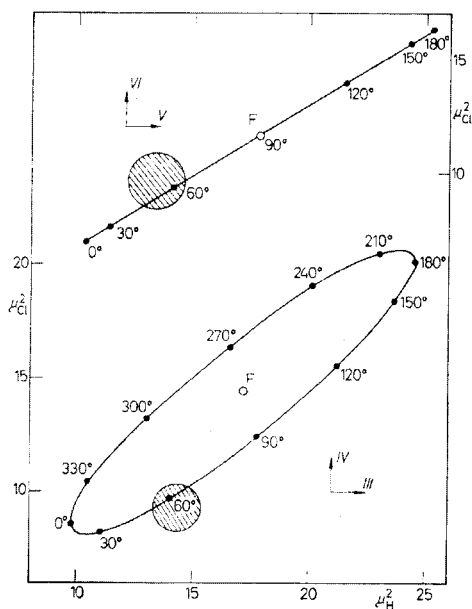

Fɪɢ. 1

Comparison of Squared Dipole Moments of Dialkylphosphinates Experimental (hatch-ed circles) and Calculated for Various Dihedral Angles $\tau = \sphericalangle$ O=P—O—C

The values for unsubstituted compounds III, V are plotted on the x-axis, for the chloro derivatives IV, VI on the y-axis.

matic derivatives. These are based on Vogel's atomic and group increments[15]. Our values are not very precise since the individual calculations scatter, nevertheless, the exaltation due to the conjugation C_6H_5—P is evident $(1\cdot0\text{ cm}^3)$. An additional benzene nucleus bonded to the same P atom seems to be without effect. When the bond increments of Gillis[25] are recalculated from the bond system to the atom system, the value of $8\cdot74\text{ cm}^3$ is obtained for the P(O)O group; hence this is more probably an "aromatic" value.

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