945. *Molecular Polarisability. Specification of the Phosphite, Phosphate, Thiophosphate, and Arsenite Group Polarisability Ellipsoid Semi-axes.*

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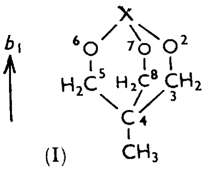
On the basis of polarisability ellipsoids of revolution, major and minor semi-axes for groups O_3X, where X = P, PO, PS, or As, appear as 0·410 and 0·359, 0·416 and 0·284, 0·869 and 0·492, and 0·535 and 0·421 (all in 10^{-23} c.c. units), respectively. "Effective" longitudinal and transverse polarisabilities of the O–P and O–As bonds are estimated as $b_{\rm L}^{\rm O-P} = 0{\cdot}086$, $b_{\rm T}^{\rm O-P} = 0{\cdot}145$, $b_{\rm L}^{\rm O-As} = 0{\cdot}066$, and $b_{\rm T}^{\rm O-As} = 0{\cdot}196$ (also in 10^{-23} c.c. units).

Our investigation of the configurations of molecules $(RO)_3X$ (where X is P, PO, PS, and As), as solutes in non-polar media, requires a knowledge of the anisotropic polarisabilities of each bond or group in the system. Accordingly the present work has been undertaken to determine the polarisability specifications of the groups O_3P, O_3PO, O_3PS, and O_3As, to supplement previous data[1,2] for the bonds C–C, C–O, and C–H ($b_{\rm L}^{\rm C-C} = 0{\cdot}099$, $b_{\rm T}^{\rm C-C} = b_{\rm V}^{\rm C-C} = 0{\cdot}027$; $b_{\rm L}^{\rm C-O} = 0{\cdot}090$, $b_{\rm T}^{\rm C-O} = b_{\rm V}^{\rm C-O} = 0{\cdot}043$; $b_{\rm L}^{\rm C-H} = b_{\rm T}^{\rm C-H} = b_{\rm V}^{\rm C-H} = 0{\cdot}064$).*

Experimental

Materials, Apparatus, etc.—The solutes were prepared and purified by the method of Verkade and Reynolds.[3] Apparatus, techniques, symbols used, and methods of calculation have been described before.[1,4] Measurements, taken in all cases at 25°, are listed in Table 1; ΔB is the difference found between the Kerr constant of the solvent and those of solutions containing weight fractions w_2 of solute. Estimates of δ ($= \sum 10^7 \Delta B / B_1 \sum w_2$) deduced from Table 1 are given in Table 2 together with the various other data required for the calculation of the molar Kerr constants listed therein. The following constants apply at 25° to dioxan: $\varepsilon_1 = 2{\cdot}2090$; $d_1 = 1{\cdot}0280$; $(n_1)_{\rm D} = 1{\cdot}4202$; $10^7 B_1 = 0{\cdot}068$; $10^{12}{}_{\rm s}K_1 = 0{\cdot}0116$.



(I)

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* Polarisabilities are expressed throughout this paper as 10^{-23} c.c. units.

[1] Le Fèvre and Le Fèvre, *Rev. Pure Appl. Chem.*, 1955, **5**, 261.

[2] Le Fèvre, unpublished data.

[3] Verkade and Reynolds, *J. Org. Chem.*, 1960, **25**, 663.

[4] Le Fèvre and Le Fèvre, Chap. XXXVI in "Physical Methods of Organic Chemistry," ed. Weissberger, Interscience Publ., Inc., New York, London, 3rd edn., Vol. I, p. 2459.

TABLE 1.

Incremental Kerr constants of solutions in dioxan at 25°.

4-*Methyl*-1-*phospha*-2,6,7-*trioxabicyclo*[2,2,2]*octane* (I; X = P).

10^6w_2	2831	3060	3420	3528	3997	4472	4505
$10^7\Delta B$	0·043	0·048	0·051	0·054	0·059	0·066	0·065

whence $\sum 10^7\Delta B/\sum w_2 = 15{\cdot}0$.

4-*Methyl*-1-*phospha*-2,6,7-*trioxabicyclo*[2,2,2]*octane* 1-*oxide* (I; X = PO).

10^6w_2	672	704	762	763	881	967
$10^7\Delta B$	0·037	0·037	0·042	0·043	0·050	0·054

whence $\sum 10^7\Delta B/\sum w_2 = 55{\cdot}4$.

4-*Methyl*-1-*phospha*-2,6,7-*trioxabicyclo*[2,2,2]*octane* 1-*sulphide* (I; X = PS)

10^6w_2	562	644	645	682	714	761	829
$10^7\Delta B$	0·048	0·054	0·055	0·057	0·064	0·068	0·073

whence $\sum 10^7\Delta B/\sum w_2 = 86{\cdot}6$.

4-*Methyl*-1-*arsa*-2,6,7-*trioxabicyclo*[2,2,2]*octane* (I; X = As)

10^5w_2	1049	1594	1740	2189	2209	2501
$10^7\Delta B$	0·050	0·090	0·093	0·113	0·096	0·116

whence $\sum 10^7\Delta B/\sum w_2 = 4{\cdot}95$.*

* Solutions of this substance, when placed in the Kerr cell, quickly became yellow, so that the measurements of ΔB were made very rapidly; this results in a greater uncertainty in δB_1 than for the other solutes.

TABLE 2.

Polarisations, dipole moments, and molar Kerr constants.

Solute	$\alpha\varepsilon_1$ *	β †	γ ‡	δ	${}_{\mathrm{E}}P$ (c.c.) §	μ (D) *	$10^{12}{}_{\infty}({}_{\mathrm{m}}K_2)$
$\mathrm{CH_3{\cdot}C}\leqslant[\mathrm{CH_2{\cdot}O}]_3\geqslant\mathrm{P}$	14·6	0·184	0·034	220	33·6	4·15	368
$\mathrm{CH_3{\cdot}C}\leqslant[\mathrm{CH_2{\cdot}O}]_3\geqslant\mathrm{PO}$	38·6	0·320	0·044	814	32·4	7·10	1519
$\mathrm{CH_3{\cdot}C}\leqslant[\mathrm{CH_2{\cdot}O}]_3\geqslant\mathrm{PS}$	32·0	0·244	0·054	1274	39·7	6·77	2637
$\mathrm{CH_3{\cdot}C}\leqslant[\mathrm{CH_2{\cdot}O}]_3\geqslant\mathrm{As}$	3·72	0·350	0·042	73	35·7	2·36	160

* Quoted from Brown, Verkade, and Piper (*J. Phys. Chem.*, 1961, **65**, 2051). † Calc. from data of Brown *et al.* (*loc. cit.*). ‡ Calc. from R_{D} (cf. Brown *et al.*, *loc. cit.*) and β. § Extrapolation of the refractivities listed by Vogel and Cowan (*J.*, 1943, 16) for trimethyl phosphate leads to ${}_{\infty}R(\mathrm{Me_3PO_4}) = {}_{\mathrm{E}}P(\mathrm{Me_3PO_4}) = 27{\cdot}4$ c.c., from which we obtain, after addition of four ${}_{\mathrm{E}}P$(C–C) equivalents (cf. Le Fèvre and Steel, *Chem. and Ind.*, 1961, 670), ${}_{\mathrm{E}}P(\mathrm{CH_3{\cdot}C}\leqslant[\mathrm{CH_2{\cdot}O}]_3\geqslant\mathrm{PO}) = 32{\cdot}4$ c.c. Gillis [*Rev. Pure Appl. Chem.* (*Australia*), 1960, **10**, 21] gives $R_{\mathrm{D}}(\mathrm{P{=}O}) = -1{\cdot}22$ c.c. and $R_{\mathrm{D}}(\mathrm{P{=}S}) = 6{\cdot}4$ c.c., from which we estimate the electronic polarisation of the molecules $\mathrm{CH_3{\cdot}C}\leqslant[\mathrm{CH_2{\cdot}O}]_3\geqslant\mathrm{P}$ and $\mathrm{CH_3{\cdot}C}\leqslant[\mathrm{CH_2{\cdot}O}]_3\geqslant\mathrm{PS}$ as 33·6 and 39·7 c.c., respectively [assuming that ${}_{\mathrm{E}}P(\mathrm{P{=}O}) = 0{\cdot}95\ R_{\mathrm{D}}(\mathrm{P{=}O})$ and that ${}_{\mathrm{E}}P(\mathrm{P{=}S}) = 0{\cdot}95\ R_{\mathrm{D}}(\mathrm{P{=}S})$]. From the dispersion data of Gryszkiewicz-Trochimowski and Sikorski (*Bull. Soc. chim. France*, 1927, **41**, 1570), ${}_{\mathrm{E}}P[(\mathrm{MeO})_3\mathrm{As}]$ is calculated as 30·7 c.c.; addition to this of four ${}_{\mathrm{E}}P$(C–C) equivalents yields ${}_{\mathrm{E}}P(\mathrm{CH_3{\cdot}C[CH_2{\cdot}O]_3As}) = 35{\cdot}7$ c.c.

DISCUSSION

The ellipsoid of polarisability for each of the molecules $\mathrm{CH_3{\cdot}C[CH_2{\cdot}O]_3X}$ can be regarded as one of revolution with $b_1 \neq b_2 = b_3$, *i.e.*, b_1 is located along the symmetry axis (see I); it follows that $\mu_1 = \mu_{\mathrm{obs}}$, $\mu_2 = \mu_3 = 0$. The equations relating the electronic polarisation and molar Kerr constant with the principal polarisabilities simplify to:

$${}_{\mathrm{E}}P = 4\pi\boldsymbol{N}(b_1 + 2b_2)/9; \tag{1}$$

$${}_{\mathrm{m}}K = 4\pi\boldsymbol{N}\{{}_{\mathrm{D}}P(b_1 - b_2)^2/\boldsymbol{k}T\,{}_{\mathrm{E}}P + \mu^2_{\mathrm{obs}}(b_1 - b_2)/\boldsymbol{k}^2T^2\}/405. \tag{2}$$

Substitution in equations (1) and (2) of μ_{obs}, ${}_{\mathrm{E}}P$, and ${}_{\infty}({}_{\mathrm{m}}K_2)$, from Table 2, and of ${}_{\mathrm{D}}P$ (which we take as 1·05 times the corresponding R_{D} of ref. 5) leads to the molecular polarisability semi-axes listed in Table 3.

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

TABLE 3.

Polarisability semi-axes of the molecules $CH_3{\cdot}C{<}[CH_2{\cdot}O]_3{>}X$.

Compound	b_1	$b_2 = b_3$	b_1/b_2
$CH_3{\cdot}C[CH_2{\cdot}O]_3P$	1·460	1·268	1·15
$CH_3{\cdot}C[CH_2{\cdot}O]_3PO$	1·466	1·193	1·23
$CH_3{\cdot}C[CH_2{\cdot}O]_3PS$	1·919	1·401	1·37
$CH_3{\cdot}C[CH_2{\cdot}O]_3As$	1·585	1·330	1·19

Now b_1 and b_2 can be equated with the component bond and group polarisabilities through the following expressions:

$$b_1 = b_1^{O_3X} + 3b_L^{C-O}\cos^2\phi + 3b_T^{C-O}\sin^2\phi + 3b_L^{C-C}\cos^2\lambda + 3b_T^{C-O}\sin^2\lambda + b_L^{C-C} + 9b_L^{C-H}, \quad (3)$$

and
$$b_1 + 2b_2 = b_1^{O_3X} + 2b_2^{O_3X} + 3b_L^{C-O} + 6b_T^{C-O} + 4b_L^{C-C} + 8b_T^{C-C} + 27b_L^{C-H}, \quad (4)$$

where ϕ and λ are the angles of inclination of each b_L^{C-O} and each non-terminal carbon–carbon bond axis, respectively, with the b_1 direction. For the phosphorus compounds it seems reasonable to assume the following geometrical specifications: $r^{C-C} = 1{\cdot}54$ Å, $r^{C-O} = 1{\cdot}43$ Å, $\angle CCC = \angle CCO = \angle COP =$ tetrahedral, $r^{O-P} = 1{\cdot}57$ Å, and $\angle OPO = 106°$ (from an *X*-ray study[6] of phosphoric acid), from which we deduce $\phi = 0°$ and $\lambda = 70°$. Very few analogous data exist for the arsenite: r^{O-As} in As_4O_6 is given in ref. 7 as 1·78 Å, and it seems likely that $0 < \phi < 10°$; the polarisability semi-axes given below for the O_3As group have been calculated by using the same values of ϕ and λ as for the phosphorus compounds.

Tables 2 and 3 show the following information: (*a*) The ratios $b_1 : b_2$ are of the same order of magnitude, since the molecules are sterically very similar. (*b*) Electronic polarisation for the phosphate is smaller than for the phosphite, so that $\sum b(\text{phosphate}) < \sum b(\text{phosphite})$; the addition to the phosphite of an oxygen atom does not significantly change the polarisability along the b_1 direction: $\Delta b_1 = b_1(\text{phosphate}) - b_1(\text{phosphite}) = +0{\cdot}006$, $\Delta b_2 = -0{\cdot}075$ (cf. Hacket and Le Fèvre's conclusions[8] for phosphorus trichloride and oxychloride, where $\Delta b_1 = -0{\cdot}012$ to $+0{\cdot}044$, and $\Delta b_2 = -0{\cdot}032$ to $-0{\cdot}060$). (*c*) Addition of a sulphur atom to the phosphite results in an increase of polarisability directed predominantly along the symmetry axis: $\Delta b_1 = +0{\cdot}459$, $\Delta b_2 = +0{\cdot}133$.

Verkade and Reynolds[3] record that in the infrared spectra of these compounds the P=O and P=S stretching frequencies occur at 1325 and 800 cm.$^{-1}$, respectively. Substitution of these values into the empirical equation[9] of Le Fèvre (1959) together with the intercentre distances, $r^{P=O} = 1{\cdot}45$ and $r^{P=S} = 1{\cdot}85$ (from Williams *et al.*[10]), leads to the following predicted longitudinal polarisabilities: $b_L^{P=O}(\text{calc.}) = 0{\cdot}484$, $b_L^{P=S}(\text{calc.}) = 0{\cdot}928$. Significantly the difference ($b_L^{P=S}$calc. $-$ $b_L^{P=O}$calc.) equals $+0{\cdot}444$ in good agreement with that found from experiment $\{b_1(CH_3{\cdot}C{<}[CH_2{\cdot}O]_3{>}PS) - b_1(CH_3{\cdot}C{<}[CH_2{\cdot}O]_3{>}PO) = +0{\cdot}453\}$.

TABLE 4.

Polarisability semi-axes of the groups O_3X.

	O_3P	O_3PO	O_3PS	O_3As
b_1	0·410	0·416	0·869	0·535
$b_2 = b_3$	0·359	0·284	0·492	0·421

The "effective" longitudinal and transverse polarisabilities of the O–P and O–As

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[6] Furberg, *Acta Chem. Scand.*, 1955, **9**, 1557.

[7] Sutton *et al.*, "Tables of Interatomic Distances and Configuration in Molecules and Ions," *Chem. Soc. Spec. Publ.* No. 11, 1958.

[8] Hacket and Le Fèvre, *J.*, 1961, 2612.

[9] Le Fèvre, *Proc. Chem. Soc.*, 1959, 363.

[10] Williams, Sheridan, and Gordy, *J. Chem. Phys.*, 1952, **20**, 164.

bonds in the phosphite and arsenite can be deduced from the O_3P and O_3As group values of Table 4 by means of the equations:

$$b_1^{O_3X} + 2b_2^{O_3X} = 3b_L^{O-X} + 6b_T^{O-X}, \tag{5}$$

and

$$b_1^{O_3X} = 3b_L^{O-X}\cos^2\psi + 3b_T^{O-X}\sin^2\psi, \tag{6}$$

where ψ, the angle which the longitudinal O–P or O–As axis makes with the b_1 direction, is taken as 68° (by analogy with Furberg's data). Solution yields $b_L^{O-P} = 0{\cdot}086$, $b_T^{O-P} = 0{\cdot}145$, $b_L^{O-As} = 0{\cdot}066$, $b_T^{O-As} = 0{\cdot}196$. The "effective" bond semi-axes thus resolved include, of course, the polarisability contributions of the "lone-pair" electrons.

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[*Received, March* 15*th*, 1963.]