

**1182.** *Molecular Polarisability. Polarities, Polarisabilities, and Conformations of the Oxides and Sulphides of the Group VB Triphenyls.*

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Dipole moments ( $D$ ) and molar Kerr constants ( $\times 10^{12}$ ) are reported for  $\text{Ph}_3\text{PO}$  (4.49; -828),  $\text{Ph}_3\text{PS}$  (4.79; -446),  $\text{Ph}_3\text{AsO}$  (5.41; -1300),  $\text{Ph}_3\text{AsS}$  (5.31; -447), and  $\text{Ph}_3\text{SbS}$  (5.66; -523) as solutes in benzene at 25°. The data are analysed in terms of apparent molecular conformations. The phenyl rings in  $\text{Ph}_3\text{PO}$  and  $\text{Ph}_3\text{PS}$  are rotated (in the same sense to preserve  $C_3$  symmetry) through angles of 60° and 62°, respectively, from a theoretical model in which the Ph planes are parallel to the molecular symmetry axis. The conformations of  $\text{Ph}_3\text{As}$  and  $\text{Ph}_3\text{Sb}$  appear to be not greatly affected by the formation of As-O, As-S, or Sb-S bonds.

THIS paper deals with relationships between the anisotropies of polarisability and the apparent conformations of the oxides and sulphides of the triphenyl derivatives of the Group VB elements, examined as solutes at high dilution in benzene at 25°. The experimental results are summarised under usual<sup>1,2</sup> headings in Tables 1 and 2.

<sup>1</sup> Le Fèvre, "Dipole Moments," Methuen, London, 3rd edn., 1953.

<sup>2</sup> Le Fèvre and Le Fèvre, (a) *Rev. Pure Appl. Chem. (Australia)*, 1955, **5**, 261; (b) Chap. XXXVI in "Physical Methods of Organic Chemistry," ed. Weissberger, Interscience, New York and London, 3rd edn., vol. I, p. 2459.

TABLE 1.

Incremental Kerr constants, dielectric constants, densities, and refractive indices for solutions in benzene at 25°.

<i>Triphenylphosphine oxide</i>							
$10^5 w_2$	503	917	970	1074	1433	1712	1970
$-10^7 \Delta B$	0.073	0.148	0.134	0.161	0.212	0.248	—
$10^4 \Delta n$	6	—	12	13	18	—	24
$\epsilon^{25}$	—	2.3491	2.3523	2.3605	2.3938	2.4149	2.4366
$d_4^{25}$	0.87512	0.87636	—	0.87642	0.87754	0.87809	0.87883
whence $\Sigma 10^7 \Delta B / \Sigma w_2 = -14.8$ ; $\Sigma \Delta n / \Sigma w_2 = 0.123$ ; $\Sigma \Delta \epsilon / \Sigma w_2 = 8.32$ ; $\Sigma \Delta d / \Sigma w_2 = 0.259$							
<i>Triphenylphosphine sulphide</i>							
$10^5 w_2$	548	779	1100	1408	1846	2859	—
$-10^7 \Delta B$	0.039	0.040	0.085	0.110	0.122	0.178	—
whence $\Sigma 10^7 \Delta B / \Sigma w_2 = -6.72$							
$10^5 w_2$	751	900	970	1049	1462	1490	2252
$10^4 \Delta n$	11	14	15	16	23	24	34
$\epsilon^{25}$	2.3406	—	2.3601	—	2.4039	2.4069	2.4764
$d_4^{25}$	—	0.87615	0.87631	0.87653	—	0.87774	0.87961
whence $\Sigma \Delta n / \Sigma w_2 = 0.154$ ; $\Sigma \Delta \epsilon / \Sigma w_2 = 9.03$ ; $\Sigma \Delta d / \Sigma w_2 = 0.262$							
<i>Triphenylarsine oxide</i>							
$10^5 w_2$	387	521	630	720	815	982	1261
$-10^7 \Delta B$	—	0.102	0.122	0.142	0.174	0.190	0.262
$10^4 \Delta n$	5	—	7	8	9	9	16
$\epsilon^{25}$	2.3104	2.3285	2.3344	2.3476	—	2.3765	—
$d_4^{25}$	0.87517	—	0.87596	0.87629	0.87651	0.87704	0.87823
whence $\Sigma 10^7 \Delta B / \Sigma w_2 = -20.1$ ; $\Sigma \Delta n / \Sigma w_2 = 0.113$ ; $\Sigma \Delta \epsilon / \Sigma w_2 = 10.3$ ; $\Sigma \Delta d / \Sigma w_2 = 0.345$							
<i>Triphenylarsine sulphide</i>							
$10^5 w_2$	347	380	604	850	1017	—	—
$-10^7 \Delta B$	0.017	0.020	0.034	0.047	0.059	—	—
$10^4 \Delta n$	6	5	8	12	15	—	—
$\epsilon^{25}$	2.3067	2.3090	2.3311	2.3521	2.3699	—	—
$d_4^{25}$	0.87494	0.87503	0.87571	0.87658	0.87716	—	—
whence $\Sigma 10^7 \Delta B / \Sigma w_2 = -5.54$ ; $\Sigma \Delta n / \Sigma w_2 = 0.144$ ; $\Sigma \Delta \epsilon / \Sigma w_2 = 9.58$ ; $\Sigma \Delta d / \Sigma w_2 = 0.329$							
<i>Triphenylstibine sulphide</i>							
$10^5 w_2$	440	441	544	729	864	1119	1185
$-10^7 \Delta B$	0.028	0.024	—	—	0.054	0.061	—
$10^4 \Delta n$	5	—	7	8	11	14	15
whence $\Sigma 10^7 \Delta B / \Sigma w_2 = -5.83$ ; $\Sigma \Delta n / \Sigma w_2 = 0.124$							
$10^5 w_2$	541	544	729	982	1185	1733	—
$\epsilon^{25}$	2.3205	2.3221	2.3392	2.3627	2.3784	2.4255	—
$d_4^{25}$	0.87586	0.87584	0.87647	0.87733	0.87824	0.88029	—
whence $\Sigma \Delta \epsilon / \Sigma w_2 = 8.99$ ; $\Sigma \Delta d / \Sigma w_2 = 0.374$							

TABLE 2.

Dielectric polarisations, dipole moments, and molar Kerr constants (from observations on solutions at 25°).

Solute	$\alpha \epsilon_1$	$\beta$	$\gamma$	$\delta$	$\infty P_2$ (c.c.)	$R_D$ (c.c.)	$\mu$ (D)*	$10^{12} \infty (mK_2)$
Ph <sub>3</sub> PO	8.32	0.296	0.082	-36.1	502.3	85.2	4.49	-828
Ph <sub>3</sub> PS	9.03	0.300	0.103	-16.4†	570.1	95.0	4.79	-446
Ph <sub>3</sub> AsO	10.3	0.395	0.075	-49.0	690.6	86.2	5.41	-1300
Ph <sub>3</sub> AsS	9.58	0.377	0.096	-13.5†	681.4	98.5	5.31	-447
Ph <sub>3</sub> SbS	8.99	0.428	0.083	-14.2†	726.4	101.2	5.66	-523

\* Calculated assuming  $D_P = 1.05 R_D$ .

† Some difficulty was experienced in the measurement of the electric birefringences of the sulphides; these were determined, in part, photometrically with the assistance of Mr. G. L. D. Ritchie.

## EXPERIMENTAL

*Materials, Apparatus, etc.*—Substances were presented to us by the Metal and Thermit Corporation, U.S.A. (triphenylphosphine oxide and sulphide, and triphenylstibine sulphide) and Messrs. R. Armstrong and D. C. Weatherburn, University of Sydney (triphenylarsine oxide and sulphide). Recrystallisation (solvent given in parentheses), and drying over phosphorus pentoxide *in vacuo*, yielded: triphenylphosphine oxide, m. p. 158° (benzene); triphenylphosphine sulphide, m. p. 166° (ethanol); triphenylarsine oxide, m. p. 197° (ethanol); triphenylarsine sulphide, m. p. 162° (ethanol); triphenylstibine sulphide, m. p. 111–112° (attempts to recrystallise this resulted in partial decomposition, but the melting point of the commercial sample agreed very closely with that given by Lile and Menzies<sup>3</sup>). Apparatus, techniques, symbols used, and methods of calculation have been described before.<sup>1,2</sup> The quantities  $\Delta\epsilon$ ,  $\Delta d$ ,  $\Delta n$ , and  $\Delta B$  are the differences found between the dielectric constants, densities, refractive indices, and Kerr constants, respectively, of benzene as solvent and of solutions in benzene containing weight fractions  $w_2$  of solute. The following data apply at 25° to benzene:  $\epsilon_1 = 2.2725$ ;  $d_1 = 0.87378$ ;  $(n_D)_1 = 1.4973$ ;  $10^7 B_1 = 0.410$ .

*Previous Measurements.*—The following dipole moments (D) have been recorded: triphenylphosphine oxide, 4.31 (in benzene),<sup>4</sup> 4.28 (in benzene),<sup>5</sup> 4.49 (in benzene),<sup>6</sup> 4.40 (in *p*-xylene),<sup>7</sup> 4.44 (in benzene);<sup>8</sup> triphenylphosphine sulphide, 4.74 (in benzene),<sup>4</sup> 4.73 (in benzene);<sup>5</sup> triphenylarsine oxide, 5.50 (in benzene);<sup>4</sup> triphenylstibine sulphide, 5.40 (in benzene).<sup>4</sup>

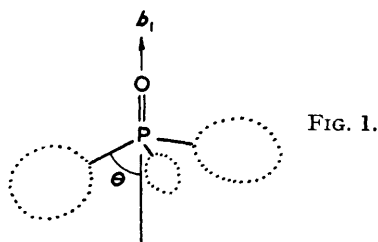
## DISCUSSION

*Triphenylphosphine Oxide and Sulphide.*—The dipole moments and molar Kerr constants of the triphenyl derivatives of the Group VB elements ( $\text{Ph}_3\text{M}$  where  $\text{M} = \text{N}, \text{P}, \text{As}, \text{Sb}, \text{Bi}$ ) have been analysed by Aroney, Le Fèvre, and Saxby,<sup>9,10</sup> to indicate that, in benzene solution, the phenyl groups in each molecule are rotated (in the same sense to preserve  $\text{C}_3$  symmetry) through angles  $\phi$ , equal to 62°, 59°, 50°, 41°, and 23° or 51°, respectively, from a model, having  $\phi = 0$ , in which the Ph planes intersect along the symmetry axis. Similar considerations are now applied to determining the preferred molecular conformations of triphenylphosphine oxide and sulphide. Theoretical models have been examined for which  $0 < \phi < 90^\circ$ . The principal polarisability semi-axes ( $b_1 \neq b_2 = b_3$ ) are calculable from the component group parameters through relationships similar to (1) and (2)

$$b_1(\text{Ph}_3\text{PO}) = 3\{b_1(\text{Ph}) \cos^2 \theta + [b_2(\text{Ph}) \cos^2 \phi + b_3(\text{Ph}) \sin^2 \phi] \sin^2 \theta\} + b_1(\text{C}_3\text{PO}) \quad (1)$$

$$\Sigma b_i(\text{Ph}_3\text{PO}) = 3\Sigma b_i(\text{Ph}) + \Sigma b_i(\text{C}_3\text{PO}) \quad (2)$$

where  $\theta$ , the angle between a C–P longitudinal direction and the symmetry axis (see Fig. 1) has been taken, in each case, as 63°, in common with that calculated for triphenylphosphine



<sup>3</sup> Lile and Menzies, *J.*, 1950, 617.

<sup>4</sup> Jensen, *Z. anorg. Chem.*, 1943, 250, 268.

<sup>5</sup> Phillips, Hunter, and Sutton, *J.*, 1945, 146.

<sup>6</sup> Subbarayan, Ph.D. Thesis, Annamalai University, S. India, 1961.

<sup>7</sup> Fischer, Laulicht, and Pinchas, *J. Phys. Chem.*, 1962, 66, 2708.

<sup>8</sup> Cumper, Foxton, Read, and Vogel, *J.*, 1964, 430.

<sup>9</sup> Aroney, Le Fèvre, and Saxby, *J.*, 1963, 1739.

<sup>10</sup> Aroney, Le Fèvre, and Saxby, *Canad. J. Chem.*, 1964, 42, 1493.

from a C-P-C bond angle of  $101^\circ$  (ref. 9, Table 5). Group polarisability specifications\* ( $b_1, b_2, b_3$ ) used in the subsequent calculations are: Ph 10·56, 10·56, 6·72;<sup>11</sup> C<sub>3</sub>PO 4·17, 3·36, 3·36 (see text); C<sub>3</sub>PS 8·70, 5·44, 5·44 (see text). The polarisability semi-axes of the group C<sub>3</sub>P: are estimated as  $b_1 = b_2 = b_3 = 4·11$  by addition of the apparent C-P bond polarisabilities of ref. 9 ( $b_L = b_T = b_V = 1·37$ ; the derivation of these values is such that they include contributions from the phosphorus lone-pair electrons). Specification of the C<sub>3</sub>PO group ellipsoid can be effected through equations (3) and (4).

$$b_1(\text{C}_3\text{PO}) = b_1(\text{C}_3\text{P:}) + b_L(\text{PO}) - b_L(\text{lone pair}) \quad (3)$$

$$b_2(\text{C}_3\text{PO}) = b_3(\text{C}_3\text{PO}) = b_2(\text{C}_3\text{P:}) + b_T(\text{PO}) - b_T(\text{lone pair}) \quad (4)$$

Though the individual quantities  $b_L(\text{PO})$  and  $b_L(\text{lone pair})$  are not known, the differences  $b_L(\text{PO}) - b_L(\text{lone pair})$  and  $b_T(\text{PO}) - b_T(\text{lone pair})$  can be evaluated from the principal molecular polarisabilities recorded (in Table 4 of ref. 12) for 4-methyl-1-phospha-2,6,7-trioxabicyclo[2,2,2]octane and for the corresponding 1-oxide. An analogous procedure is used to specify  $b_L(\text{PS}) - b_L(\text{lone pair})$  and  $b_T(\text{PS}) - b_T(\text{lone pair})$ , and hence  $b_1$  and  $b_2 = b_3$  for the C<sub>3</sub>PS group. Calculations of the molecular polarisabilities and molar Kerr constants (by way of equation 5, assuming  ${}_D P/{}_E P = 1·1$ ) for the various conformations considered are summarised in Table 3.

$${}_m K = 2\pi N [2{}_D P(b_1 - b_2)^2 / 45{}_E P k T + 2\mu^2(\text{obs.}) (b_1 - b_2) / 45 k^2 T^2] / 9 \quad (5)$$

The observed molar Kerr constants are  $-828 \times 10^{-12}$  (Ph<sub>3</sub>PO) and  $-446 \times 10^{-12}$  (Ph<sub>3</sub>PS), in good agreement with the calculated values for rotations of  $60^\circ$  and  $62^\circ$ , respectively.

TABLE 3.

Polarisability semi-axes and molar Kerr constants calculated for conformations of (a) triphenylphosphine oxide and (b) triphenylphosphine sulphide.

(a)	$\phi$	$0^\circ$	$50^\circ$	$60^\circ$	$70^\circ$	$90^\circ$	
	$b_1$	35·85	30·48	28·99	27·77	26·70	
	$b_2 = b_3$	29·28	31·97	32·71	33·32	33·86	
	$10^{12}{}_m K$ (calc.)	+1484	-331	-821	-1220	-1568	
(b)	$\phi$	$0^\circ$	$50^\circ$	$60^\circ$	$62^\circ$	$70^\circ$	$90^\circ$
	$b_1$	40·38	35·01	33·52	33·25	32·30	31·23
	$b_2 = b_3$	31·36	34·05	34·79	34·93	35·40	35·94
	$10^{12}{}_m K$ (calc.)	+2325	+244	-321	-424	-780	-1182

Utilisation in the above calculations of the alternative set of C-P bond semi-axes ( $b_L = 1·16$ ;  $b_T = b_V = 1·47$ ), which were derived, in ref. 9, from the empirical relationship of Le Fèvre,<sup>13</sup> leads to  $\phi = 61^\circ$  (Ph<sub>3</sub>PO) and  $63^\circ$  (Ph<sub>3</sub>PS). The corresponding value ( $\phi$ ) for triphenylphosphine is given as  $59^\circ$  (ref. 9). Thus we may conclude that the apparent conformations of triphenylphosphine, its oxide, and its sulphide are closely similar in benzene solution.

*Conformations of the Molecules Ph<sub>3</sub>AsO, Ph<sub>3</sub>AsS, and Ph<sub>3</sub>SbS.*—The analytical procedure described previously for Ph<sub>3</sub>PO and Ph<sub>3</sub>PS cannot now be applied, as polarisability data (analogous to those quoted from ref. 12 and used subsequently in equations 3 and 4) are unavailable, so that we are unable to specify the anisotropic polarisabilities of the groups C<sub>3</sub>AsO, C<sub>3</sub>AsS, and C<sub>3</sub>SbS. However, it is possible to derive the molecular polarisability

\* Polarisability semi-axes of bonds,  $b_L$ ,  $b_T$ , or  $b_V$ , or of groups or molecules,  $b_1$ ,  $b_2$ , or  $b_3$ , are quoted throughout in  $10^{-24}$  c.c. units.

<sup>11</sup> Aroney and Le Fèvre, *J.*, 1960, 3600.

<sup>12</sup> Aroney, Le Fèvre, and Saxby, *J.*, 1963, 4938.

<sup>13</sup> Le Fèvre, *Proc. Chem. Soc.*, 1958, 283.

semi-axes for each of these molecules from the observed molar Kerr constant and the  ${}_E P$  (taken as  $0.95 R_D$ ) by way of equations (5) and (6):  $b_1 = 29.76$ ,  $b_2 = b_3 = 33.81$  ( $\text{Ph}_3\text{AsO}$ );

$${}_E P = 4\pi N(b_1 + 2b_2)/9 \quad (6)$$

$b_1 = 36.14$ ,  $b_2 = b_3 = 37.58$  ( $\text{Ph}_3\text{AsS}$ );  $b_1 = 37.10$ ,  $b_2 = b_3 = 38.58$  ( $\text{Ph}_3\text{SbS}$ ). Table 4 lists the ratios  $b_1/b_2$  found for the Group VB triphenyls (calculated from the data of ref. 9) and for their oxides and sulphides.

TABLE 4.  
Values of the ratio  $b_1/b_2$ .

M	N	P	As	Sb	Bi
$\text{Ph}_3\text{M}$	0.75	0.87	0.93	0.97	1.11
$\text{Ph}_3\text{MO}$	—	0.89	0.88	—*	(0.90)
$\text{Ph}_3\text{MS}$	—	0.95	0.96	0.96	—

\* Triphenylstibine oxide though preparable<sup>14</sup> ( $\text{H}_2\text{O}_2$  and  $\text{Ph}_3\text{Sb}$ ; m. p.  $295^\circ$ ) was not sufficiently soluble in benzene to allow accurate determination of the dipole moment and molar Kerr constant. Measurements on very dilute solutions ( $< 0.05\%$ ) appear to indicate that  $\mu(\text{Ph}_3\text{SbO}) \sim 2$  D, in agreement with Jensen's values<sup>4</sup> for  $\mu(\text{tri-}i>p\text{-tolylstibine oxide}) = 2.0$  D (in benzene) and  $2.3$  D (in dioxan). The present results support the conclusions of Jensen and Nielsen,<sup>15</sup> gained from infrared spectral evidence, that  $\text{Ph}_3\text{SbO}$  does not exist as individual molecules but as a pseudo-ionic polymeric form.

Within the group of molecules  $\text{Ph}_3\text{P}$ ,  $\text{Ph}_3\text{PO}$ , and  $\text{Ph}_3\text{PS}$ , for which the angle  $\phi$  is effectively invariant ( $60 \pm 2^\circ$ ), the  $b_1/b_2$  ratios appear also to be fairly constant ( $0.91 \pm 0.04$ ); cf. values of  $b_1/b_2$  for the extreme forms corresponding, respectively, to  $\phi = 0^\circ$  and  $\phi = 90^\circ$ :  $1.19$ — $0.77$  ( $\text{Ph}_3\text{P}$ );  $1.22$ — $0.79$  ( $\text{Ph}_3\text{PO}$ );  $1.29$ — $0.87$  ( $\text{Ph}_3\text{PS}$ ). For  $\text{Ph}_3\text{As}$ ,  $\text{Ph}_3\text{AsO}$ , and  $\text{Ph}_3\text{AsS}$  the ratios ( $b_1/b_2$ ) lie within the range  $0.92 \pm 0.04$ , while for  $\text{Ph}_3\text{Sb}$  and  $\text{Ph}_3\text{SbS}$  they are practically identical. It may thus be inferred that  $\text{Ph}_3\text{AsO}$  and  $\text{Ph}_3\text{AsS}$  are conformationally similar to  $\text{Ph}_3\text{As}$  (for which  $\phi = 50^\circ$ )<sup>10</sup> and that  $\text{Ph}_3\text{SbS}$  resembles  $\text{Ph}_3\text{Sb}$  ( $\phi = 41^\circ$ ).<sup>9</sup>

*Apparent MO and MS Bond Polarity and Polarisability Increments.*—The apparent MO or MS bond moments (defined as the change in the moment of  $\text{Ph}_3\text{M}$  which accompanies the formation of the MO or MS bond) and the corresponding incremental changes in the molecular polarisability semi-axes are listed in Table 5. The appropriate parameters for the  $\text{Ph}_3\text{M}$

TABLE 5.  
Bond moments and incremental changes in molecular polarisability semi-axes.

	PO-P:	PS-P:	AsO-As:	AsS-As:	SbS-Sb:
$\Delta_1\mu$ (D)	2.99	3.29	4.18	4.08	4.89
$\Delta b_1$	0.06*	4.59*	-1.67	4.71	3.79
$\Delta b_2 = \Delta b_3$	-0.75*	1.33*	-0.05	3.72	4.17

\* Quoted from ref. 12 and applied to  $\text{Ph}_3\text{PO}$  and  $\text{Ph}_3\text{PS}$  in the previous discussion.

molecules have been taken from ref. 9. The present estimate of the apparent PO moment agrees well with that ( $2.95$  D) recorded by Cumper *et al.*,<sup>8</sup> and both values are slightly higher than the mean PO moment ( $2.88$  D) found<sup>8</sup> in the tri-*n*-alkylphosphine oxides. This small difference has been attributed in most part to induced polarisation effects (see ref. 8, p. 434). The apparent moments of the P=O and P=S bonds in the phosphate and the thiophosphate "cage" molecules of ref. 12 are calculable, from the data of Brown, Verkade, and Piper,<sup>16</sup> as  $2.95$  and  $2.62$  D, respectively. The latter value is somewhat lower than that ( $3.29$ ) now found for the P=S bond in  $\text{Ph}_3\text{PS}$ , and this may be indicative of contributions to the structure of

<sup>14</sup> Goodgame and Cotton, *J. Amer. Chem. Soc.*, 1960, **82**, 5774.

<sup>15</sup> Jensen and Nielsen, *Acta Chem. Scand.*, 1963, **17**, 1875.

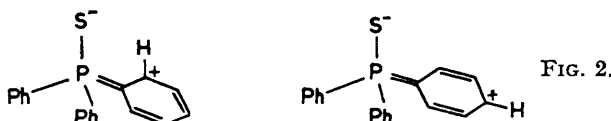
<sup>16</sup> Brown, Verkade, and Piper, *J. Phys. Chem.*, 1961, **65**, 2051.

Ph<sub>3</sub>PS from the resonance forms shown in Fig. 2. Conjugative interactions of the benzene ring  $\pi$ -electrons with P=O in Ph<sub>3</sub>PO are known to be very weak (refs. 17 and 18).

Calculation of the MO or MS bond refractions using classical valence-bond formulations (equation 7) results in negative values for PO and AsO ( $-1.4$  and  $-2.0$  c.c., respectively;

$$R_D(\text{MO or MS}) = R_D(\text{Ph}_3\text{MO or Ph}_3\text{MS}) - R_D(\text{Ph}_3\text{M}) \quad (7)$$

cf. Gillis<sup>19</sup> who quotes the refraction of P=O in phosphates as  $-1.22$  c.c.), from which it may be deduced that  $\alpha(\text{P=O}) < \alpha(\text{phosphorus lone pair})$ , and  $\alpha(\text{As=O}) < \alpha(\text{arsenic lone pair})$ . The mean polarisability ( $\alpha$ ) is defined as  $(b_L + b_T + b_V)/3$ . Aroney, Le Fèvre, and Saxby<sup>12</sup> have proposed that  $b_L(\text{P=O}) \approx b_L(\text{phosphorus lone pair})$  and that a P=O bond is significantly less polarisable than the phosphorus lone-pair electrons only in the transverse directions.



Changes in the arsenic lone-pair polarisabilities on the formation of an As=O bond cannot, however, be accurately predicted from the molecular increments  $\Delta b_1(\text{AsO-As})$  of Table 5, since the dispositions of the phenyl groups in the molecules Ph<sub>3</sub>AsO and Ph<sub>3</sub>As, though similar, may not be identical. The empirical equation of Le Fèvre<sup>20</sup> can be used to relate the quantity  $b_L(\text{As=S}) - b_L(\text{As=O})$  to the As=S and As=O stretching frequencies ( $495$  and  $881$  cm.<sup>-1</sup>, respectively, from ref. 15) and the internuclear distances ( $r(\text{As=S})$  and  $r(\text{As=O})$ ). An estimate ( $1.69$  Å) of  $r(\text{As=O})$  is available from the crystal-structure determination<sup>21</sup> of HgCl<sub>2</sub>·2Ph<sub>3</sub>AsO. If then we assume that the phenyl groups in Ph<sub>3</sub>AsS and Ph<sub>3</sub>AsO are inclined equally to the molecular  $b_1$  directions, it follows that  $b_L(\text{AsS}) - b_L(\text{AsO}) = b_1(\text{Ph}_3\text{AsS}) - b_1(\text{Ph}_3\text{AsO}) = 6.38$ . Substitution of these values into Le Fèvre's equation<sup>20</sup> leads to a predicted As=S bond length of  $2.16$  Å.

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<sup>17</sup> Halmann and Pinchas, *J.*, 1958, 3264.

<sup>18</sup> Kabachnik, *Tetrahedron*, 1964, 20, 655.

<sup>19</sup> Gillis, *Rev. Pure Appl. Chem. (Australia)*, 1960, 10, 21.

<sup>20</sup> Le Fèvre, *Proc. Chem. Soc.*, 1959, 363.

<sup>21</sup> Bränden, *Acta Chem. Scand.*, 1963, 17, 1363.