

**324.** *Molecular Polarisability. Conformations and Polarities of Triphenyl Derivatives of Group VB Elements.*

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As solutes in benzene, the molecules  $\text{NPh}_3$ ,  $\text{PPh}_3$ ,  $\text{AsPh}_3$ ,  $\text{SbPh}_3$ , and  $\text{BiPh}_3$  show, respectively, dipole moments of 0.52, 1.50, 1.23, 0.77, and ca. 0 D, and molar Kerr constants ( $\times 10^{12}$ ) of 33.3, -100, -37.6, -6.6, and +7.1. These data are interpreted as indicating rotations of the phenyl groups by angles  $\phi$  from conformations, having  $\phi = 0$ , in which the Ph planes intersect along the lines of action of the resultant moments; values of  $\phi$  for the five derivatives named appear as  $62^\circ$ ,  $59^\circ$ ,  $53^\circ$ ,  $41^\circ$ , and  $23^\circ \pm 4^\circ$  or  $51^\circ \pm 3^\circ$ .

MEASUREMENTS, here recorded, of the molar Kerr constants, refractivities, and dipole moments for the series  $\text{NPh}_3$ ,  $\text{PPh}_3$ ,  $\text{AsPh}_3$ ,  $\text{SbPh}_3$ , and  $\text{BiPh}_3$  as solutes in benzene were started in the hope that, through considerations of anisotropic polarisabilities, information on the structures and conformations of these molecules would be provided.

EXPERIMENTAL

*Materials, Apparatus, etc.*—Substances were presented to us by the following: Metal and Thermit Corporation, U.S.A. (triphenyl-phosphine, -stibine, and -bismuthine); Dr. B. O. West, University of Adelaide (triphenyl-phosphine and -arsine); Dr. N. A. Gibson, Mr. J. W. Hosking, and Mr. D. C. Weatherburn, University of Sydney (triphenylarsine). Recrystallisation from

alcohol yielded: triphenylphosphine (m. p. 78—79°), triphenylarsine (m. p. 60—61°), triphenylstibine (m. p. 53—54°), triphenylbismuthine (m. p. 78°). Thiophen-free benzene, as solvent, was dried (Na) for 1 week before use. Symbols, methods of calculation, and headings used in

TABLE 1.

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

<i>Triphenylphosphine</i>										
$10^5 w_2$ .....	1607	3383	3717	4296	4813					
$10^7 \Delta B$ .....	-0.033	-0.062	-0.086	-0.080	-0.109					
whence $\sum 10^7 \Delta B / \sum w_2 = -2.08$										
$10^5 w_2$ .....	1372	2203	2324	2462	2551	2806				
$10^4 \Delta n$ .....	—	26	29	33	—	—				
$\epsilon^{25}$ .....	2.2914	2.3019	2.3054	—	2.3082	—				
$d_4^{25}$ .....	—	0.87838	0.87855	—	0.87899	0.87985				
$10^5 w_2$ .....	3010	3938	4127	4133	5081					
$10^4 \Delta n$ .....	35	—	—	55	—	—				
$\epsilon^{25}$ .....	—	2.3276	—	2.3285	2.3439	—				
$d_4^{25}$ .....	—	0.88207	0.88225	0.88215	0.88425	—				
whence $\sum \Delta n / \sum w_2 = 0.126$ ; $\sum \Delta \epsilon / \sum w_2 = 1.39$ ; $\sum \Delta d / \sum w_2 = 0.207$										
<i>Triphenylarsine</i>										
$10^5 w_2$ ...	1394	1578	2028	2278	2523	2664	2778	3626	4034	4280
$10^7 \Delta B$ ..	-0.010	-0.011	—	—	—	—	-0.022	-0.027	-0.030	-0.028
$10^4 \Delta n$ ...	—	—	—	—	—	30	31	—	—	48
$\epsilon^{25}$ .....	—	2.2874	—	—	2.2945	2.2981	2.2995	2.3082	—	2.3106
$d_4^{25}$ .....	0.87775	—	0.87966	—	0.88116	0.88152	—	—	0.88536	0.88624
whence $\sum 10^7 \Delta B / \sum w_2 = -0.724$ ; $\sum \Delta n / \sum w_2 = 0.112$ ; $\sum \Delta \epsilon / \sum w_2 = 0.93$ ; $\sum \Delta d / \sum w_2 = 0.290$										
<i>Triphenylstibine</i>										
$10^5 w_2$ ...	1083	2762	3017	3260						
$10^7 \Delta B$ ...	-0.003	—	-0.005	-0.007						
$10^4 \Delta n$ ...	—	30	33	38						
whence $\sum 10^7 \Delta B / \sum w_2 = -0.20$ ; $\sum \Delta n / \sum w_2 = 0.112$										
$10^5 w_2$ ...	2500	2762	2813	3004	3017	3206	3260	3918	5147	5368
$\epsilon^{25}$ .....	—	2.2894	2.2889	2.2896	2.2880	—	2.2901	—	2.3032	—
$d_4^{25}$ .....	0.88243	0.88393	0.88363	0.88449	—	0.88488	—	0.88780	—	0.89297
whence $\sum \Delta \epsilon / \sum w_2 = 0.571$ ; $\sum \Delta d / \sum w_2 = 0.355$										
<i>Triphenylbismuthine</i>										
$10^5 w_2$ .....	1068	2476	2781	3084	3936	4718				
$10^4 \Delta n$ .....	—	29	32	33	40	50				
$\epsilon^{25}$ .....	2.2762	2.2817	2.2830	2.2837	2.2876	2.2903				
$d_4^{25}$ .....	0.87861	0.88503	0.88676	0.88823	0.89210	0.89590				
whence $\sum \Delta n / \sum w_2 = 0.108$ ; $\sum \Delta \epsilon / \sum w_2 = 0.374$ ; $\sum \Delta d / \sum w_2 = 0.465$										
$10^7 \Delta B = 0$ for concentrations up to $w_2 = 4718 \times 10^{-5}$										

TABLE 2.

Polarisations, dipole moments, and molar Kerr constants (from observations on solutions in benzene at 25°).

Solute	$\alpha_{\epsilon_1}$	$\beta$	$\gamma$	$\delta$	$\infty P_2$ (c.c.)	$R_D$ (c.c.)	$R_D$ (calc.) (c.c.) <sup>a</sup>	$\mu_D$ <sup>b</sup>	$\infty (mK_2) \times 10^{12}$
NPh <sub>3</sub>	0.609 <sup>c</sup>	0.222 <sup>c</sup>	0.110 <sup>c</sup>	1.42 <sub>4</sub> <sup>c</sup>	93.0 <sup>c</sup>	83.2 <sup>c</sup>	81.1	0.52 <sup>c</sup>	+33.3 <sup>c</sup>
PPh <sub>3</sub>	1.39	0.236	0.084	-5.07	136.7	86.6	87.3	1.50	-100
AsPh <sub>3</sub>	0.935	0.332	0.075	-1.77	123.5	88.2	89.9	1.23	-37.6
SbPh <sub>3</sub>	0.571	0.406	0.075	-0.49	109.4	92.8	92.6	0.77	-6.6
BiPh <sub>3</sub>	0.374	0.532	0.072	0	101.1	96.3	97.1	0	+7.1

<sup>a</sup> Calculated by addition of bond refractions in Vogel (ref. 2, p. 531) and Gillis (ref. 3, p. 24).  
<sup>b</sup> Calculated on the assumption that  ${}_D P^2 = 1.05 R_D$ . <sup>c</sup> Quoted from Aroney and Le Fèvre (ref. 4, p. 3602).

the Tables are explained in ref. 1, pp. 280—283. For benzene at 25°,  $\epsilon_1 = 2.2725$ ,  $d_1 = 0.87378$ ,  $(n_D)_1 = 1.4973$ , and  $B_1 = 0.410 \times 10^{-7}$  (Na light).

*Previous Measurements.*—Dipole-moment determinations made before 1948 as listed by Wesson<sup>5</sup> in the M.I.T. Tables (solvent in each case, benzene) have been recalculated on the basis  ${}_D P = 1.05R_D$ : NPh<sub>3</sub>, 0;<sup>6</sup> PPh<sub>3</sub>, 1.40;<sup>6</sup> 1.39;<sup>7</sup> AsPh<sub>3</sub>, 0.98;<sup>6</sup> SbPh<sub>3</sub>, 0.34;<sup>6</sup> BiPh<sub>3</sub>, 0.<sup>6</sup> Since 1948 the following additional moments (recomputed on the same basis) have been recorded (also in benzene): NPh<sub>3</sub>, 0.55,<sup>8</sup> 0.47,<sup>9</sup> 0.47;<sup>10</sup> PPh<sub>3</sub>, 1.36.<sup>10</sup> No determinations of molar Kerr constants for these substances appear in the literature.

## DISCUSSION

The ellipsoid of polarisability for each molecule MPh<sub>3</sub> (where M = N, P, As, Sb, Bi) is specified completely by the three principal half-axes,  $b_1$ ,  $b_2$ , and  $b_3$ . If  $b_1$  is located along the three-fold symmetry axis (the direction of action of the permanent dipole moment), then  $b_2 = b_3$ ,  $\mu_1 = \mu_{\text{obs.}}$ ,  $\mu_2 = \mu_3 = 0$ , and the usual expressions for the molar Kerr constant and the electronic polarisation simplify to<sup>1,11</sup>

$${}_M K^{\text{MPh}_3} = 2\pi N [2{}_D P (b_1 - b_2)^2 / 45 {}_E P k T + 2\mu^2 (b_1 - b_2) / 45 k^2 T^2] / 9 \quad (1)$$

$${}_E P^{\text{MPh}_3} = 4\pi N (b_1 + 2b_2) / 9, \quad (2)$$

where  ${}_D P$  and  ${}_E P$  are the distortion and the electronic polarisations, respectively.

TABLE 3.

Principal polarisability semi-axes of the molecules MPh<sub>3</sub>.\*

	NPh <sub>3</sub>	PPh <sub>3</sub>	AsPh <sub>3</sub>	SbPh <sub>3</sub>	BiPh <sub>3</sub>
A { $b_1$ .....	2.537	2.908	3.143	3.331	3.825
{ $b_2 (= b_3)$ .....	3.405	3.351	3.386	3.441	3.448
B { $b_1$ .....	3.652	0.184	1.237	2.604	3.322
{ $b_2 (= b_3)$ .....	2.847	4.714	4.338	3.804	3.699

\* Bond and molecular polarisabilities are quoted throughout in  $10^{-23}$  c.c. units.

Aroney and Le Fèvre<sup>4</sup> give  $R_\infty (= {}_E P)$  for triphenylamine as 78.6 c.c. from extrapolation of the  $R_D$  and  $R_G$  values. As the literature contains no dispersion data for the other molecules or for the bonds M-C, the electronic polarisations have been estimated *via* the equation

$${}_E P^{\text{MPh}_3} = 3({}_E P^{\text{C-H}} - {}_E P^{\text{C-H}} + 0.95R_D^{\text{M-C}}),$$

where  ${}_E P^{\text{C-H}}$  and  ${}_E P^{\text{C-H}}$  are as listed by Le Fèvre and Steel<sup>12</sup> and  $R_D^{\text{M-C}}$  as by Gillis (ref. 3, p. 24). Values of  ${}_E P^{\text{MPh}_3}$  thus derived are: 80.8 (PPh<sub>3</sub>), 83.4 (AsPh<sub>3</sub>), 85.9 (SbPh<sub>3</sub>), 90.2 (BiPh<sub>3</sub>). Solution of the simultaneous equations (1) and (2) leads to two sets of polarisability semi-axes,  $b_1$  and  $b_2$ , for each molecule; these are listed in Table 3.

*Component Bond and Group Polarisability Semi-axes.*—The phenyl group semi-axes, derived by subtracting the contribution of one C-H link (for which  $b_L^{\text{C-H}} = b_T^{\text{C-H}} = b_V^{\text{C-H}} = 0.064$ ) from the anisotropic polarisabilities of benzene, are  $b_1^{\text{Ph}} = b_2^{\text{Ph}} = 1.056$ ,  $b_3^{\text{Ph}} = 0.672$ . Aroney and Le Fèvre<sup>13</sup> have specified the "effective" N-C bond polarisability semi-axes

<sup>1</sup> Le Fèvre and Le Fèvre, *Rev. Pure Appl. Chem.*, 1955, **5**, 261.

<sup>2</sup> Vogel, Cresswell, Jeffery, and Leicester, *J.*, 1952, 514.

<sup>3</sup> Gillis, "Bond Refractions of Single Covalencies," Tech. Note 51, Defence Standards Laboratories, Maribyrnong, Vic., Australia; *Rev. Pure Appl. Chem.*, 1960, **10**, 21.

<sup>4</sup> Aroney and Le Fèvre, *J.*, 1960, 3600.

<sup>5</sup> Wesson, "Tables of Electric Dipole Moments," Technology Press, M.I.T., Cambridge, Mass., 1948.

<sup>6</sup> Bergmann and Schütz, *Z. phys. Chem.*, 1932, **B**, **19**, 401.

<sup>7</sup> Phillips, Hunter, and Sutton, *J.*, 1945, 146.

<sup>8</sup> Leonard and Sutton, *J. Amer. Chem. Soc.*, 1948, **70**, 1564.

<sup>9</sup> Cowley, *J.*, 1952, 3557.

<sup>10</sup> Klages and Langpape, *Z. Elektrochem.*, 1959, **63**, 533.

<sup>11</sup> Le Fèvre, "Dipole Moments," 3rd edn., Methuen, London, 1953.

<sup>12</sup> Le Fèvre and Steel, *Chem. and Ind.*, 1961, 670.

<sup>13</sup> Aroney and Le Fèvre, *J.*, 1958, 3002.

TABLE 4.

Estimated longitudinal and transverse polarisabilities of the bonds M-C.

	P-C	As-C	Sb-C	Bi-C
A $b_L^{M-C}(=b_T^{M-C}=b_V^{M-C})$ .....	0.137	0.170	0.202	0.262
B $\left\{ \begin{array}{l} b_L^{M-C} \\ b_T^{M-C}(=b_V^{M-C}) \end{array} \right.$ .....	0.116	0.130	0.165	0.187
	0.147	0.190	0.221	0.299

in trimethylamine as  $b_L^{N-C} = 0.057$ ,  $b_T^{N-C} = b_V^{N-C} = 0.069$ , the method of resolution of the molecular polarisabilities into N-C and C-H bond components alone being such that the nitrogen "lone-pair" contribution is included in the N-C bond estimates; the assumption is made that the N-C bond ellipsoids thus described are axially symmetric about the intercentre line. For the other bonds M-C only one equation in  $b_L^{M-C}$  and  $b_T^{M-C}$  is available:

$$E^{PM-C} = 0.95R_D^{M-C} = 4\pi N(b_L^{M-C} + 2b_T^{M-C})/9$$

so that a direct evaluation cannot be effected. Table 4 lists possible values of the M-C bond polarisabilities; the estimates in line A follow if we take each M-C link to be isotropically polarisable; the longitudinal polarisabilities in line B are derived *via* the empirical relation of Le Fèvre:<sup>14</sup>

$$10^{24}b_L^{M-C} = 0.140 + 0.156d^3$$

where  $d$ , the internuclear distance, is the sum of the covalent radii listed in ref. 15, p. 246 (cf. ref. 16, M 154 and M 157). Estimates of  $b_L^{M-C}$  obtained by substitution of the M-C stretching frequencies listed in refs. 17 and 18 into Le Fèvre's 1959 equation<sup>19</sup> are improbably high.

TABLE 5.

Polarisability semi-axes and molar Kerr constants calculated for models 1 and 2 of the molecules MPh<sub>3</sub>.

	$\angle C-M-C$	Model 1 ( $\phi = 0^\circ$ )			Model 2 ( $\phi = 90^\circ$ )		
		$b_1$	$b_2(=b_3)$	$10^{12}{}_mK$	$b_1$	$b_2(=b_3)$	$10^{12}{}_mK$
NPh <sub>3</sub> .....	116° <sup>a</sup>	3.392 <sup>f</sup>	2.978 <sup>f</sup>	+20.9	2.287 <sup>f</sup>	3.530 <sup>f</sup>	+40.2
PPh <sub>3</sub> .....	101° <sup>b</sup>	3.578	3.017	+155	2.663	3.474	-169
AsPh <sub>3</sub> .....	96° <sup>c</sup>	3.678	3.118	+109	2.830	3.542	-93.6
SbPh <sub>3</sub> .....	113° <sup>d</sup>	3.775	3.219	+51.8	2.707	3.753	-13.8
BiPh <sub>3</sub> .....	120° <sup>e</sup>	3.953	3.384	+16.2	2.801	3.960	+67.1

<sup>a</sup> From electron-diffraction measurements on triphenylamine vapour<sup>20</sup> at 200°. <sup>b</sup> From dipole-moment determinations<sup>7</sup> (an alternative, but less credible value of 117° is also quoted in ref. 7). <sup>c</sup> By electron diffraction.<sup>21</sup> <sup>d</sup> By dipole moments.<sup>22</sup> <sup>e</sup> From an X-ray analysis of triphenylbismuthine.<sup>23</sup> <sup>f</sup> These differ from the calculated values (Va) and (Vb) given in ref. 4, which were derived by using a bond angle C-N-C of 114° as in ref. 8 and which contain no allowance for exaltation (the  $\Delta b_{\text{observed}}$  was subsequently resolved along the three principal axes in the following manner:  $\Delta b_1 = 0$ ,  $\Delta b_2 = \Delta b_3 = \Delta b_{\text{obs.}}/2$ ); we prefer to regard  $\Delta b_{\text{obs.}}/3$  as an incremental increase in the longitudinal polarisability of each N-C link; the overall effect of these refinements is negligible.

*Molecular Conformations.*—Initially we examine, for each molecule MPh<sub>3</sub>, the extreme conformations represented by  $\phi = 0^\circ$  (see Fig. 1, in which the planes of the benzene rings intersect along the line of action of  $\mu_{\text{resultant}}$ ), and  $\phi = 90^\circ$ , where the benzene rings have been rotated about the M-C bonds  $90^\circ$  respectively from their dispositions in Fig. 1.

<sup>14</sup> Le Fèvre, *Proc. Chem. Soc.*, 1958, 283.<sup>15</sup> Pauling, "The Nature of the Chemical Bond," 3rd edn., Cornell University Press, 1960.<sup>16</sup> Sutton, "Tables of Interatomic Distances and Configuration in Molecules and Ions," *Chem. Soc. Special Publ.* No. 11, 1958.<sup>17</sup> Halmann, *Spectrochim. Acta*, 1960, **16**, 407.<sup>18</sup> Rosenbaum, Rubin, and Sandberg, *J. Chem. Phys.*, 1940, **8**, 366.<sup>19</sup> Le Fèvre, *Proc. Chem. Soc.*, 1959, 363.<sup>20</sup> Sasaki, Kimura, and Kubo, *J. Chem. Phys.*, 1959, **31**, 477.<sup>21</sup> Kuz Min and Kamai, *Doklady Akad. Nauk S.S.S.R.*, 1950, **73**, 709.<sup>22</sup> Campbell, *J.*, 1955, 3116.<sup>23</sup> Wetzel, *Z. Krist.*, 1942, **104**, 305.

Molecular polarisabilities can be calculated for these models by addition of component bond and group semi-axes (providing the bond angles C-M-C are known), thence we can evaluate  ${}_m K_{\text{calc.}}$  for each model on the assumption that the resultant dipole moment in each case is equal to  $\mu_{\text{obs.}}$  and acts along the symmetry axis. Table 5 summarises the results.

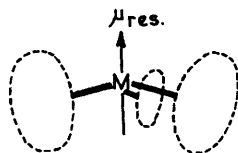


FIG. 1.

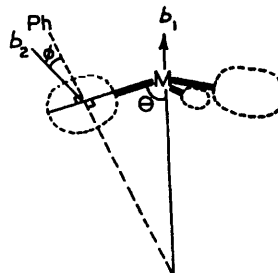


FIG. 2.

Comparison of the calculated values of Table 5 with those of Tables 2 and 3 shows that none of the models so far examined correctly describes the solute species.

We next consider structures, intermediate between models 1 and 2, for which  $0^\circ < \phi < 90^\circ$  (see Fig. 2); for these

$$b_{1\text{obs.}} = 3[(b_1^{\text{Ph}} + b_L^{\text{M-C}} + \Delta b_{\text{obs.}}/3)\cos^2 \theta + (b_T^{\text{M-C}} + b_2^{\text{Ph}} \cos^2 \phi + b_3^{\text{Ph}} \sin^2 \phi) \sin^2 \theta] \quad (3)$$

The angle  $\theta$  in each case is calculable from the corresponding bond angle C-M-C as set out in Table 5;  $\Delta b_{\text{obs.}}$  is zero for all molecules  $\text{MPh}_3$  except triphenylamine. If now the M-C links (apart from N-C for which we know  $b_L^{\text{N-C}} = 0.057$  and  $b_T^{\text{N-C}} = 0.069$ ) are assumed to be isotropic with  $b_{\text{mean}}^{\text{M-C}}$  having the values of line A in Table 4, then the two sets of experimental  $b_1^{\text{MPh}_3}$ 's of Table 3 (A and B) lead to two estimates of  $\phi$  for each molecule.

TABLE 6.

Values of  $\phi$  calculated from equation (3).

	$\text{NPh}_3$	$\text{PPh}_3$	$\text{AsPh}_3$	$\text{SbPh}_3$	$\text{BiPh}_3$
$\phi$ (from results A in Table 3)	$61.5^\circ$	$59^\circ$	$52.5^\circ$	$40^\circ$	$19.5^\circ$
$\phi$ (from results B in Table 3)	No solution <sup>a</sup>	No solution	No solution	No solution	$48^\circ$

<sup>a</sup> Equation (3) reduces to  $\sin^2 \phi > 1$ ; the values of  $b_{1\text{obs.}}$  leading to such a solution are either impossibly small or impossibly great and do not correspond to any conformation between the limits of  $\phi = 0^\circ$  and  $\phi = 90^\circ$ .

TABLE 7.

Calculated values of  $\phi$ , assuming anisotropic M-C link polarisabilities.

	$\text{PPh}_3$	$\text{AsPh}_3$	$\text{SbPh}_3$	$\text{BiPh}_3$
$\phi$ (from results A in Table 3) .....	$59.5^\circ$	$53.5^\circ$	$42.5^\circ$	$27^\circ$
$\phi$ (from results B in Table 3) .....	No solution	No solution	No solution	$53.5^\circ$

Alternatively, if we substitute in equation (3) the M-C link polarisability specifications of line B in Table 4 (as predicted by Le Fèvre's 1958 rule),<sup>14</sup> then the corresponding estimates of  $\phi$  are as in Table 7. Only in the case of triphenylbismuthine is  $\phi$  sensitively dependent on the anisotropy of the M-C links. If we average out the values  $\phi$  in Tables 6 and 7 we obtain:  $62^\circ$  ( $\text{NPh}_3$ ),  $59^\circ$  ( $\text{PPh}_3$ ),  $53^\circ$  ( $\text{AsPh}_3$ ),  $41^\circ$  ( $\text{SbPh}_3$ ),  $23^\circ \pm 4^\circ$  or  $51^\circ \pm 3^\circ$  ( $\text{BiPh}_3$ ). Wetzel<sup>23</sup> has shown from an X-ray analysis of triphenylbismuthine that, in the solid state,  $\phi = 31^\circ \pm 4^\circ$ , which suggests that our smaller estimate is the more correct. An uncertainty of  $\pm 0.1$  D in each of the dipole moments listed in Table 2 leads to a maximum error ( $\pm$ ) in  $\phi$  of  $7^\circ$ ,  $4^\circ$ ,  $3^\circ$ ,  $2^\circ$ , and  $1^\circ$ , respectively. In triphenylamine, delocalisation of the nitrogen "lone-pair" electrons accounts for the almost non-basic nature of this

molecule (see ref. 24, p. 46), for the observed exaltation of refraction, and for the small dipole moment ( $\mu_{\text{obs.}}^{\text{NPh}_3}$  can be regarded as the vector sum of  $\mu_a$  and  $\mu_m$ , where  $\mu_a$  approximates to  $\mu^{\text{NMe}_3}$  and  $\mu_m$  is the mesomeric moment). For substances  $\text{MPh}_3$  ( $\text{M} = \text{P to Bi}$ ) the bond lengths  $\text{M-C}$  increase and the benzene-ring orientations tend towards that in Fig. 1; so that inter-ring resonance effects ( $\mu_m^{\text{MPH}_3}$ ) are less significant than in triphenylamine. Cullen and Hochstrasser<sup>25</sup> have concluded, from a study of the ultraviolet spectra of these substances, that "nitrogen is the only member of the series which has a fully conjugated triphenyl derivative." Significantly, the observed dipole moment diminishes from 1.50 D ( $\text{PPh}_3$ ) to zero ( $\text{BiPh}_3$ ) with increase of electropositivity of the central metalloid atom.

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<sup>24</sup> Kemmitt, Nuttall, and Sharp, *J.*, 1960, 46.

<sup>25</sup> Cullen and Hochstrasser, *J. Mol. Spectroscopy*, 1960, 5, 118.

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