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An Electron Diffraction Investigation of the Molecular Structures of Gaseous Trimethylphosphine Oxide, Trimethylphosphine Sulfide, Trimethylarsine Oxide, and Trimethylarsine Sulfide

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Abstract: The molecular structures of (CH₃)₃PO, (CH₃)₃PS, (CH₃)₃AsO, and (CH₃)₃AsS have been determined by gaseous electron diffraction at nozzle-tip temperatures of 150–160, 160, 190, and 170–175°C, respectively. The values of the principal distances (r_a) and angles with estimated uncertainties of 2σ are: $r_{P-O} = 1.476$ (0.002) Å, $r_{P-C} = 1.809$ (0.002) Å, $\angle OPC = 114.4$ (0.7)° for (CH₃)₃PO; $r_{P-S} = 1.940$ (0.002) Å, $r_{P-C} = 1.818$ (0.002) Å, $\angle SPC = 114.1$ (0.2)° for (CH₃)₃PS; $r_{As-O} = 1.631$ (0.003) Å, $r_{As-C} = 1.937$ (0.002) Å, $\angle OAsC = 112.6$ (1.3)° for (CH₃)₃AsO; $r_{As-S} = 2.059$ (0.003) Å, $r_{As-C} = 1.940$ (0.003) Å, $\angle SAsC = 113.4$ (0.4)° for (CH₃)₃AsS. The sulfur bond lengths lie close to values expected for classical double bonding, but the P–O and As–O distances are especially short corresponding to even higher bond orders. It is shown that the polarities and force constants of the M–Y bonds in these MX₃Y-type molecules confirm a bond type having σ and π components with oppositely directed transfer of charge. Rotational freedom of the methyl group appears to increase in the order (CH₃)₃PO < (CH₃)₃PS ≃ (CH₃)₃AsO < (CH₃)₃AsS.

Elements from central groups of the periodic table, such as silicon or phosphorus, form bonds to more electronegative elements which are characteristically short and strong. The distances between atoms of a given type are found to vary, with differences reflecting both the number and electronegativities of other atoms bonded to the same central atom. Thus, the P–O bond in POCl₃ is longer than in POF₃[1] and the P–F bonds in the latter are shorter than in PF₃.[2]

The nature of the bonding involving central-group atoms has been much discussed.[1,3-6] Phosphorus compounds of the types PX₃ and PX₃Y have attracted interest particularly because there exists the possibility of charge transfer within the P–Y linkages, and recently several SCF–MO calculations have been made for PX₃ and PX₃Y molecules with X = H, CH₃, F, Cl, and Y = O or BH₃.[7-13] Although a considerable amount of the structural information necessary either for theoretical or semiempirical descriptions of the bonding in MX₃Y-type molecules is available, there is very little on the type (CH₃)₃MY with M = P or As and Y = O or S. In these molecules the M–Y bonds presumably experience minimal, and in any case very similar, interaction with

adjacent bonds; intercomparison of structural details thus offers special opportunity for better understanding the M–Y bonding. Knowledge of these (CH₃)₃MY structures could conceivably also be of help in understanding the metal–ligand interactions in complexes[14-16] formed between the molecules and metals.

The present report describes results of electron-diffraction investigations of the structures of the four (CH₃)₃MY molecules mentioned. Of the phosphorus compounds, trimethylphosphine oxide has been studied earlier by electron diffraction,[17] but refinement of the structure was not done and no error limits were reported for the parameter values. There is also a brief report on the structure of trimethylphosphine sulfide in the crystal.[16] No structural information seems to be available for the arsenic compounds.

Experimental Section

The oxides and sulfides were obtained from trimethylphosphine and trimethylarsine by published methods.[18] The compounds were freshly resublimed before use and the hygroscopic oxides handled out of contact with atmospheric moisture. The behavior of the vapor pressure curve for trimethylphosphine oxide[19] suggests asso-

ciation in the gas phase up to 110°. The nozzle-tip temperatures were considerably higher [(CH$_3$)$_3$PO, 150–160°; (CH$_3$)$_3$PS, 160°; (CH$_3$)$_3$AsO, 190°; (CH$_3$)$_3$AsS, 170–175°] and could be expected in all cases to exclude the possibility of residual association.

Diffraction photographs were made in the Oregon State apparatus using a sector with an angular opening proportional to r^3 and 8 × 10 in. plates (Kodak Projector Slide, medium). Nozzle-to-plate distances (nominal) were 70 and 30 cm, and for trimethylphosphine sulfide also 12 cm. The experimental conditions were: beam currents, 0.4–0.5 μA; exposure times, 1–5 min; ambient apparatus pressure during exposures, 0.3–2.0 × 10^{-5} Torr; electron wavelength, 0.05738–0.05746 Å as determined by measurement of the accelerating voltage calibrated against diffraction patterns from gaseous CO$_2$ (r_a(C=O) = 1.1646 Å and r_a(O···O) = 2.3244 Å).

For each molecule three or four plates from each of the nozzle-to-plate distances were selected for analysis, which was carried out as described previously.[20] A smooth background was calculated[21] and subtracted from the reduced data leading to molecular intensity distributions from individual plates in a form corresponding to the formula

$$sI_m(s) = k \sum_{i \neq j} n_{ij} A_i A_j r_{ij}^{-1} V_{ij} \cos |\eta_i - \eta_j| \sin r_{ij}s \qquad (1)$$

where the A's are electron scattering amplitudes multiplied by s^2 and the other symbols have their usual significances. The ranges of the data from the long, intermediate, and short nozzle-to-plate distances were $2.00 < s < 12.75$, $8.00 < s < 31.00$, and $25.00 < s < 44.00$, respectively, and the data interval was $\Delta s = 0.25$. For each molecule the individual intensity distributions from each nozzle-to-plate distance were combined to give an averaged distribution for that distance[22] to be used in the structure refinements; these curves are shown in Figure 1.

Structure Analysis

Radial Distribution Curves. For purposes of calculating radial distribution curves the average distributions from the long and intermediate distances[23] were combined by scaling and averaging them in the overlap region to give the composite intensity curves. Experimental radial distribution curves (Figure 2) were calculated according to the expression

$$D(r) = \frac{2}{\pi} \Delta s \sum_{s_{min}}^{s_{max}} I_m'(s) \exp(-Bs^2) \sin rs \qquad (2)$$

The $I_m'(s)$'s were obtained by multiplying the composite intensity curves with $Z_M Z_Y A_M^{-1} A_Y^{-1}$ to produce "constant coefficient" curves.[24] The summations included data from the unobserved or uncertain inner region taken from theoretical curves for models close to the final ones. The convergence coefficient B was given the value 0.0025.

Each radial distribution curve is consistent with a model of C_{3v} heavy-atom symmetry (Figure 3) having distances as indicated by the vertical lines in Figure 2.

Choice of Models for Refinement. If one assumes C_{3v} heavy-atom symmetry for the molecules and ignores all distances to hydrogen atoms dependent on the torsion angle of the methyl groups, five parameters are required to describe the geometries. Convenient choices are r_{M-Y}, r_{M-C}, r_{C-H}, $\angle$YMC, and $\angle$MCH. However, there was evidence from the radial distribution curves that some information about the torsion angles could be obtained and accordingly we decided to compare results for models in which the methyl groups assumed an average position defined by a sixth parameter, the torsion angle $\delta = \angle$YMCH (taken as equal to zero for the eclipsed conformation of the C–H and M–Y bonds), with models in which the methyl groups were freely rotating. Refinements of the torsion-angle models (hereafter symbolized by TA) were restricted to those having overall symmetry C_3; these models differ from models in which the different methyl groups are arbitrarily rotated clockwise or counterclockwise by the same amount only in
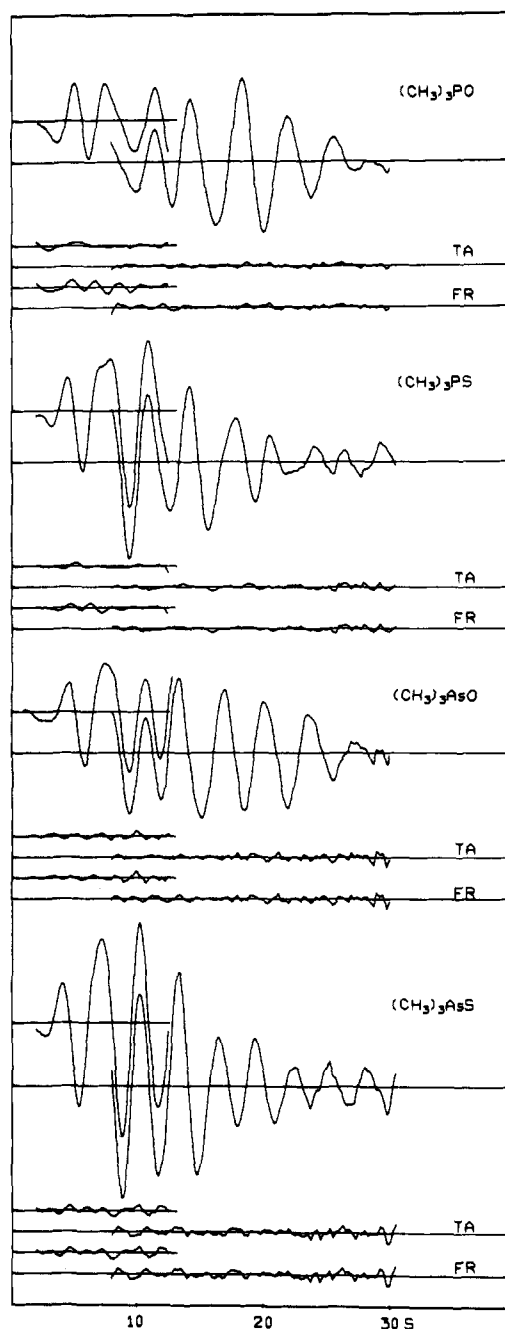

Figure 1. Experimental and difference intensity curves. The difference curves are experimental minus theoretical for the models of Table II.

the values of the relatively unimportant H···H distances between methyl groups. Such models have 16 different interatomic distances (excluding H···H distances between methyl groups) many of which overlap, requiring some assumptions about the root-mean-square amplitudes. These assumptions included the usual groupings of certain amplitudes and assignments of some assumed values. The amplitude parameters were chosen to be l_{M-Y}, l_{M-C}, l_{C-H}, $l_{C···C} = l_{C···Y} + \Delta_1$, $l_{M···H}$, $l_{C···H} = l_{Y···H} + \Delta_2$ (the C···H distances between methyl groups and the Y···H distances were treated as groups each having one amplitude value), and $l_{H···H}$ (within a methyl group) = 0.13 (assumed). The free rotation (FR) models were simulated by discarding the torsion parameter δ used for the TA models and placing one-third of a proton at nine equally spaced positions on the circle of rotation arranged so that one of the fractional atoms was trans to the M–Y bond. The total number of different interatomic dis-
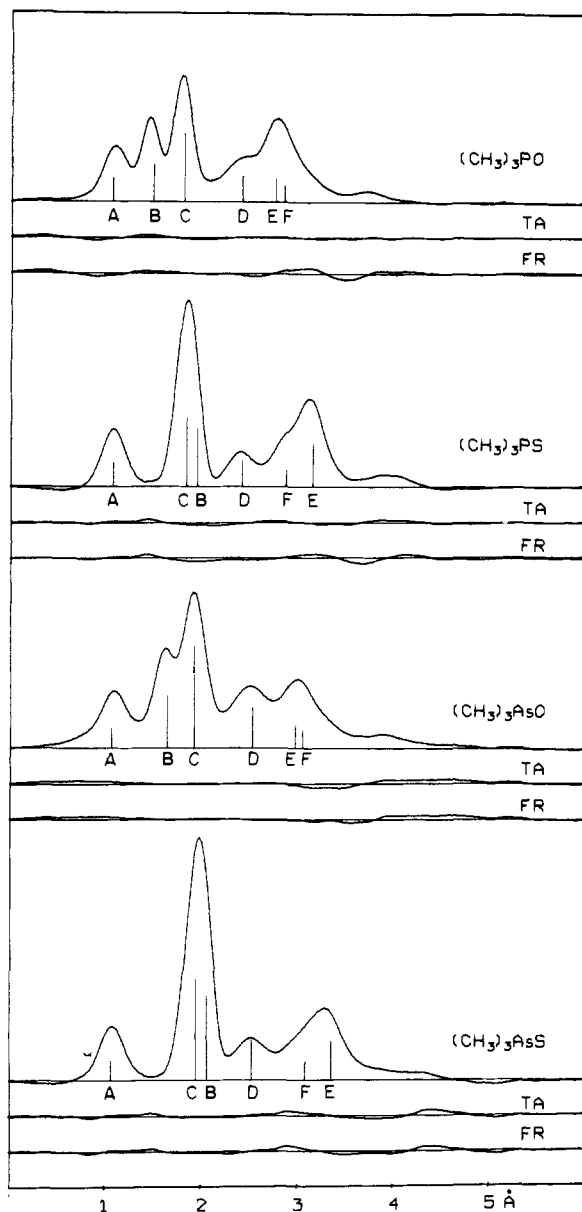
Figure 2. Experimental and difference radial distribution curves. The difference curves are experimental minus theoretical calculated for the models of Table II. The experimental curves are normalized to give equal weight to the C-H peaks. The vertical lines designate the weights and values of the important distances in the TA models: A, C-H; B, M-Y; C, M-C; D, M···H; E, C···Y; F, C···C. The unlabeled features at $r > 3.5$ Å arise from long H···Y, H···C, and H···H distances.

Figure 3. Model of $(CH_3)_3MY$ molecules.

Table I. Calculated Values of Vibrational Amplitudes for $(CH_3)_3MY$ Molecules

	$(CH_3)_3PO$	$(CH_3)_3PS$	$(CH_3)_3AsO$	$(CH_3)_3AsS$
l_{M-Y}, Å	0.048	0.051	0.041	0.047
l_{M-C}, Å	0.053	0.054	0.053	0.053
$l_{C...C}$, Å	0.126	0.104	0.121	0.122
$l_{Y...C}$, Å	0.092	0.104	0.095	0.112

tances was thus 21, again ignoring H···H interactions between methyl groups. The parameters, aside from the ignored δ, were as for the TA models.

Refinement Results. The structures of the molecules were refined by the method of least squares based on intensity curves,[25] adjusting in each case a single theoretical curve simultaneously to the average experimental curves from each camera distance. Since short-camera distance data were available only for trimethylphosphine sulfide, refinements of this molecule usually omitted these data in order that the results might be more meaningfully compared with those for the other molecules. The harmonic-vibration approximation $V_{ij} = \exp(-l_{ij}^2 s^2/2)$ was assumed. A unit weight matrix was used.

In the case of each sulfur compound, refinements based on both the TA and FR models in which all parameters were allowed to va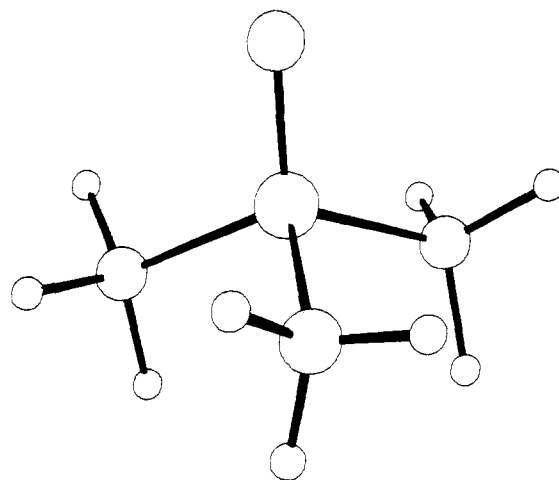ry simultaneously converged quickly to approximately the same parameter values. For the oxides, however, similar refinements were unsuccessful in respect to the parameters $\angle OMC$, $l_{O...C}$, and $l_{C...C}$ which were found to be highly correlated.[26] Restricted refinements of trimethylphosphine oxide in which the assumption $l_{O...C} = l_{C...C}$ was introduced led to a value of $\angle OPC$ for the FR model about equal to the SMC angles in the sulfur compounds; however, the same assumption applied to the TA model led to an OPC angle 5° larger. Similar restricted refinements of the TA and FR models of trimethylarsine oxide gave for each an OAsC angle 5° larger than the corresponding angles in the sulfur compounds. Further tests showed, as expected, that for the oxygen compounds the values of $\angle OMC$ were sensitive functions of the assumptions regarding $l_{O...C}$ and $l_{C...C}$. The problem arises from the distances $r_{O...C}$ and $r_{C...C}$ which are determined by $\angle OMC$. As may be seen by the vertical lines labeled E and F in Figure 2, these distances are of similar weight and magnitude whereas their counterparts in the sulfur compounds are quite different. As it turns out, the values of $\angle OMC$ differing by the 5° mentioned above correspond to approximate exchanges of the positions of $r_{O...C}$ and $r_{C...C}$.

Since the correlations among the O···C and C···C distances and amplitudes in the oxygen compounds prevented an accurate determination of their values from the diffraction data alone, we sought a basis for plausible assumptions which would make possible determinations of at least some of them. Because vibrational amplitudes can be rather easily calculated from force fields and molecular geometries, we turned our attention to them. A vibrational potential function of the form

$$2V = f_R R^2 + 3f_r r^2 + 3f_\alpha \alpha^2 + 3f_\beta \beta^2 + 6f_{Rr} Rr + 6f_{rr'} rr' + 6f_{\alpha\alpha} \alpha\alpha' + 6f_{\beta\beta'} \beta\beta' \quad (3)$$

where R, r, α, and β are the changes in r_{M-Y}, r_{M-C}, $\angle YMC$, and $\angle CMC$, was assumed. The force-constant values were calculated[27] for each molecule by fitting six of

Table II. Final Results from Structure Refinements[a,b]

	(CH₃)₃PO		(CH₃)₃PS[c]		(CH₃)₃AsO		(CH₃)₃AsS	
	TA[d]	FR[e]	TA	FR	TA	FR	TA	FR
r_{M-Y}	1.476 (0.002)	1.477 (0.003)	1.940 (0.002)	1.940 (0.002)	1.631 (0.003)	1.631 (0.003)	2.059 (0.003)	2.059 (0.003)
r_{M-C}	1.809 (0.002)	1.809 (0.002)	1.818 (0.002)	1.818 (0.002)	1.937 (0.002)	1.937 (0.003)	1.940 (0.003)	1.940 (0.003)
r_{C-H}	1.107 (0.004)	1.106 (0.006)	1.106 (0.005)	1.105 (0.005)	1.107 (0.006)	1.106 (0.006)	1.105 (0.008)	1.105 (0.008)
$r_{C...C}$	2.854 (0.016)	2.865 (0.040)	2.874 (0.007)	2.872 (0.006)	3.097 (0.030)	3.092 (0.029)	3.083 (0.012)	3.080 (0.012)
$r_{Y...C}$	2.767 (0.011)	2.760 (0.027)	3.154 (0.005)	3.156 (0.005)	2.973 (0.022)	2.977 (0.021)	3.344 (0.009)	3.346 (0.010)
$r_{M...H}$	2.425 (0.011)	2.435 (0.021)	2.410 (0.010)	2.413 (0.011)	2.518 (0.011)	2.521 (0.012)	2.520 (0.022)	2.518 (0.022)
∠YMC	114.4 (0.7)	113.9 (1.8)	114.1 (0.2)	114.2 (0.2)	112.6 (1.3)	112.8 (1.3)	113.4 (0.4)	113.6 (0.5)
∠CMC	104.1 (0.8)	104.7 (2.0)	104.5 (0.3)	104.4 (0.2)	106.2 (1.4)	105.9 (1.4)	105.2 (0.5)	105.1 (0.5)
∠MCH	110.3 (0.8)	111.0 (1.6)	108.6 (0.8)	108.8 (0.9)	108.6 (0.9)	108.8 (1.0)	108.6 (1.7)	108.5 (1.7)
δf	44.1 (3.4)		42.7 (7.3)		36.8 (3.8)		27.5 (7.6)	
l_{M-Y}	0.039 (0.003)	0.040 (0.005)	0.036 (0.004)	0.036 (0.004)	0.046 (0.004)	0.047 (0.004)	0.052 (0.004)	0.051 (0.004)
l_{M-C}	0.054 (0.003)	0.054 (0.004)	0.045 (0.003)	0.045 (0.004)	0.057 (0.004)	0.057 (0.004)	0.051 (0.007)	0.051 (0.007)
l_{C-H}	0.079 (0.005)	0.079 (0.007)	0.078 (0.005)	0.078 (0.005)	0.074 (0.006)	0.075 (0.006)	0.074 (0.007)	0.074 (0.007)
$l_{C...C}$	⎡0.110 (0.008)	0.112 (0.041)	0.094 (0.009)	0.091 (0.009)	⎡0.132 (0.017)	⎡0.130 (0.015)	0.133 (0.036)	0.127 (0.037)
$l_{Y...C}$	⎣0.085	0.087 (0.012)	0.088 (0.005)	0.087 (0.005)	⎣0.107	⎣0.105	0.116 (0.014)	0.115 (0.013)
$l_{M...H}$	0.134 (0.010)	0.125 (0.012)	0.116 (0.009)	0.114 (0.009)	0.121 (0.011)	0.120 (0.011)	0.147 (0.017)	0.146 (0.017)
$l_{C...H}$	⎡0.167 (0.028)	⎡0.142 (0.047)	⎡0.147 (0.064)	⎡0.108 (0.036)	⎡0.159 (0.038)	⎡0.194 (0.087)	⎡0.125 (0.081)	⎡0.145 (0.090)
$l_{Y...H}$	⎣0.117	⎣0.092	⎣0.147	⎣0.108	⎣0.109	⎣0.144	⎣0.125	⎣0.145
$l_{H...H}$[g]	0.130	0.130	0.130	0.130	0.130	0.130	0.130	0.130
R[h]	0.052	0.081	0.048	0.052	0.071	0.076	0.065	0.067

[a] Distances (r_a) and amplitudes (l) in ångströms, angles in degrees. [b] Parenthesized quantities are 2σ values and include estimates of systematic error and correlation among the observations; bracketed quantities were refined as a group. [c] Short-camera data, available only for this compound, were omitted. [d] Models including the average torsion angle ∠YMCH as a parameter. [e] Models simulating free rotation of the methyl groups. [f] The methyl-group torsion angle, taken equal to zero for eclipsed M–Y and C–H bonds. [g] Values assumed. [h] $R = [\Sigma w_i \Delta_i^2 / \Sigma w_i l_i^2 (\text{obsd})]^{1/2}$; $\Delta_i = l_i(\text{obsd}) - l_i(\text{calcd})$.

Table III. Correlation Matrix for the Parameters of (CH₃)₃PO[a]

	r_{P-O}	r_{P-C}	r_{C-H}	∠OPC	∠PCH	δ[c]	l_{P-O}	l_{P-C}	l_{C-H}	$l_{C\cdot\cdot\cdot C}$	$l_{P\cdot\cdot\cdot H}$	$l_{O\cdot\cdot\cdot H}$
σ[b]	0.0005	0.0004	0.0014	0.24	0.29	1.22	0.0010	0.0007	0.0015	0.0022	0.0030	0.0095
	1.000	0.021	0.128	-0.178	0.009	-0.030	0.198	0.329	0.137	-0.025	0.071	-0.028
		1.000	-0.137	-0.096	0.025	-0.071	-0.251	-0.169	-0.188	-0.153	0.080	-0.037
			1.000	-0.032	-0.246	0.046	0.129	0.157	0.045	0.035	0.010	0.015
				1.000	0.125	0.461	-0.057	-0.104	-0.037	0.678	0.157	0.417
					1.000	0.099	-0.002	-0.023	0.014	-0.238	0.099	-0.116
						1.000	0.048	0.027	0.021	0.101	0.268	0.643
							1.000	0.740	0.504	0.160	0.203	0.053
								1.000	0.449	0.157	0.198	0.055
									1.000	0.102	0.151	0.020
										1.000	0.126	0.347
											1.000	0.062
												1.000

[a] Distances (r) and root-mean-square amplitudes of vibration (l) in ångströms, angles in degrees. [b] Standard deviations from least squares. [c] δ is the OPCH torsion angle.

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Table IV. Parameter Values for Some X_3M and X_3MY Molecules[a,b]

X		X_3M^c	X_3MS	X_3MO
		M = P		
CH_3	r_{P-C}, Å	1.844 (0.003)	1.818 (0.002)	1.809 (0.002)
	r_{P-Y}, Å		1.940 (0.002)	1.476 (0.002)
	$\angle YPC$, deg	118.9 (0.2)	114.1 (0.2)	114.4 (0.7)
Cl	r_{P-Cl}, Å	2.039 (0.002)	2.010 (0.003)	1.992 (0.003)
	r_{P-Y}, Å		1.884 (0.005)	1.447 (0.005)
	$\angle YPCl$, deg	117.6 (0.1)	116.3 (0.2)	115.1 (0.2)
F	r_{P-F}, Å	1.569 (0.001)	1.53 (0.02)	1.523 (0.003)
	r_{P-Y}, Å		1.87 (0.03)	1.435 (0.006)
	$\angle YPF$, deg	119.6 (0.2)	117.6 (1.6)	116.8 (0.2)
		M = As		
CH_3	r_{As-C}, Å	1.959 (0.010)	1.940 (0.003)	1.937 (0.002)
	r_{As-Y}, Å		2.059 (0.003)	1.631 (0.003)
	$\angle YAsC$, deg	120.9 (2.3)	113.4 (0.4)	112.6 (1.3)

[a] Distances are r_a. [b] Sources of the data are as follows. $(CH_3)_3P$: L. Bartell and L. O. Brockway, *J. Chem. Phys.* 32, 512 (1960). $(CH_3)_3PS$ and $(CH_3)_3PO$: this work. Cl_3P: M. Iwasaki and K. Hedberg, *J. Chem. Phys.* 36, 589 (1962). Cl_3PS and Cl_3PO: ref 1. F_3P: ref 2. F_3PS: Q. Williams, J. Sheridan, and W. Gordy, *J. Chem. Phys.*, 20, 164 (1952). F_3PO: ref 1. $(CH_3)_3As$: D. R. Lide, Jr., *Spectrochim. Acta*, 15, 473 (1959). $(CH_3)_3AsS$ and $(CH_3)_3AsO$: this work. [c] The angles for these molecules are between the bonds and C_3 axis.

Table V. Properties of $(CH_3)_3MY$ Molecules

	n_{M-Y}^a	δ_{M-Y}^b	f_{M-Y}^c	f_{M-C}^c
$(CH_3)_3PO$	2.68	0.45	8.03	3.04
$(CH_3)_3PS$	2.00	0.40	3.37	3.06
$(CH_3)_3AsO$	2.29	0.51	5.68	2.85
$(CH_3)_3AsS$	1.94	0.43	3.16	2.76

[a] Pauling bond orders. [b] Charge transfer. [c] Stretching force constant in mdyn Å^{-1}. Values from ref 27 except those for $(CH_3)_3PS$ which were calculated from a frequency assignment by H. Rojhantalab, J. W. Nibler, and C. J. Wilkins, *Spectrochim. Acta*, in press.

the more important frequencies using a minimum deviation criterion, assuming $f_{Rr} = f_{rr'}$ and $f_{\alpha\beta} = f_{\beta\beta'}$, and treating the methyl groups as pseudo-atoms of mass 15.035 located at the center of mass of the group. Vibrational amplitudes were then calculated[28] for distances not involving hydrogen atoms, again treating the methyl groups as pseudo-atoms. The results (Table I) show $l_{C...C}$ to be greater than $l_{O...C}$ by about the same amount for each oxygen compound, and it was decided to base the final refinements of these compounds on the assumption $l_{C...C} = l_{O...C} + 0.025$. These refinements converged nicely, yielding values of $\angle OMC$ for both the TA and FR models comparable to those obtained for the sulfur compounds. The final results are shown in Table II together with error estimates derived from formulas given previously.[29] The correlation matrix for the TA model of trimethylphosphine oxide is given as Table III; the other TA model correlation matrices will appear as Tables VI-VIII in the microfilm edition of the journal.[22] The correlation matrices for the FR models are similar to those for the TA models.

For the sulfur compounds, comparisons of the bond lengths and bond angles derived from refinements under various conditions as described above show them to be nearly invariant; accordingly the values given in Table II may be accepted with confidence. For the oxygen compounds all geometrical parameters except $\angle OMC$ are similarly invariant, but the accuracy of the $\angle OMC$ value depends on the assumption that the C···C amplitude is greater than the O···C by about 0.025 Å as suggested by vibrational analysis. The assumption would appear to be a good one since the calculated and observed values of the important amplitudes for the oxygen compounds are in good agreement (Tables I and II). However, confidence in this comparison as a criterion of reliability is somewhat weakened by the poor agree-

ment between the calculated and observed values of l_{P-S}, even though the amplitude assumption was unnecessary in the case of either sulfur compound. We are presently unable to account for this discrepancy, which, incidentally, is also found in trichlorophosphine sulfide[1] where the observed and calculated values of l_{P-S} are 0.0325 ± 0.005 Å and 0.0465 Å. All in all, we feel our experimental values for the parameters of the four molecules are accurate, but that errors in the amplitudes are more likely than in the geometrical quantities.

Discussion

The M-C bond lengths in our four compounds are about equal to the sum of the Schomaker-Stevenson single-bond radii corrected for electronegativity difference ($r_{P-C} = 1.84$ Å; $r_{As-C} = 1.94$ Å).[30] The P-C bonds are about 0.03 Å longer than those in triphenylphosphine oxide (1.76 Å)[31] and the As-C bonds about 0.04 Å longer than in triphenylarsine oxide monohydrate (1.907 Å),[32] both measured in the crystal. An M-C(aryl) bond shorter than an M-C(alkyl) may be ascribed to the usual hybridization effects (sp^2 bonds are shorter than sp^3) or to conjugation of the ring system orbitals with d orbitals from the M atom. Despite their apparently unexceptional character, however, P-C(alkyl) and As-C(alkyl) bond lengths do vary slightly in a consistent way. Table IV summarizes parameter values for some X_3M and X_3MY-type molecules. The M-C bond lengths are seen to decrease in the series $(CH_3)_3P$, $(CH_3)_3PS$, $(CH_3)_3PO$ and in the series $(CH_3)_3As$, $(CH_3)_3AsS$, $(CH_3)_3AsO$. Since these M-C bonds can hardly possess significant π character, the decreases may be attributed to changes in the polarity of the M atom which alter the σ bond lengths. Similar decreases in the P-F and P-Cl bond lengths are seen for the two series F_3P, F_3PS, F_3PO and Cl_3P, Cl_3PS, Cl_3PO (Table IV) and have been interpreted[1] in terms of the electron-pair repulsion theory.[33] The same theoretical arguments applied to the M-C bonds in our compounds predict smaller values as the M atom extra electron pair is increasingly drawn away by more electronegative Y atoms.

The M-S bond lengths in our compounds are close to the double-bond values and the M-O bonds are even shorter. It is generally considered that a terminal P-O bond involves a σ-component in which there is charge transfer from the phosphorus to the oxygen atom together with a π contribution arising from $p_\pi \rightarrow d_\pi$ charge transfer in the reverse direction. Since two p_π orbitals and at least two d orbitals are

available, formal bond orders greater than 2.0 are possible. These views apply as well to the other M–Y bonds in our molecules and, as we shall show, they provide a simple and satisfying picture of the M–Y bonding. First, however, we take note of variations in the lengths of P–O and P–S bonds similar to those mentioned for M–C bonds. From Table IV, P–O and P–S bond lengths are seen to decrease over the series $(CH_3)_3PO$, Cl_3PO, F_3PO and $(CH_3)_3PS$, Cl_3PS, F_3PS. These shortenings again suggest a polarity effect rather than the effect of competitive π bonding; if the latter were to dominate, the P–Y bonds should lengthen through each series rather than shorten because the available π orbitals on the M atoms would be increasingly involved with the other ligands. This deduction from the structures is supported by the results of MO treatments[10-13] which do not suggest large differences in the orbitals contributing to the P–Y π bonding. As expected from the polarity argument, the linking of other electronegative ligands to a phosphorus atom leads to a short terminal P–O bond, for example as in P_4O_{10} where this bond is found to be 1.40 Å.[34]

In our group of trimethyl compounds the absence of π bonding between the carbon and phosphorus or arsenic atoms and the similar polarities of the M–C σ bonds means minimal, and in any case very similar, effects from the methyl groups on the M–Y bonds. The bond lengths, force constants, and polarities of these M–Y bonds should therefore provide a clear picture of the extent to which π bonding and charge transfer are involved. Table V shows data calculated for the four compounds of interest. The bond orders were obtained from Pauling's formula $r(n) = r(1) - a \log n$, using his single-bond radii and $a = 0.665$.[35] The net charge transfers were estimated from the formula $\delta_e = |\mu - \mu^0|/|er_{M-Y} \times 10^{18}|$, where μ is the observed dipole moment of the compound in question,[36] μ^0 is the dipole moment of $(CH_3)_3P$ for the phosphorus compounds and $(CH_3)_3As$ for the arsenic compounds (respectively equal to 1.19 D[37] and 1.10 D[38]), and $er_{M-Y} \times 10^{18}$ is the hypothetical moment corresponding to the transfer of one electronic charge over the length of the bond.[39] The source of the force constant values has been described.[40]

The bond orders indicate that the sulfur links are essentially double bonds, whereas the oxygen links have considerable triple-bond character. Extensive π bonding is therefore suggested for each. The net charge transfers are substantial, but they are each less than the value 0.62 estimated for trimethylamine oxide[41] in which the N–O bond is essentially a single σ bond. One may interpret this comparison as evidence of a partially compensating back-flow of charge within the additional π components of the phosphorus and arsenic bonds, i.e., that $p_\pi \rightarrow d_\pi$ bonds are formed using d orbitals from the phosphorus and arsenic atoms; the argument is simply that in the absence of $p_\pi \rightarrow d_\pi$ bonding, one would expect charge transfer values for P–Y and As–Y bonds greater than for N–O arising from their greater polarizabilities[41] and from electronegativity differences equal to or greater than that for N–O. The force constants for the M–Y bonds vary rather widely while those for the M–C bonds, as expected, are quite similar. These similar M–C values suggest bonding of similar type. The values for As–O and P–O suggest lower π bond order for the former in accordance with the bond orders themselves, whereas the P–S and As–S bonds appear to be more nearly alike. The bonds from phosphorus or arsenic to oxygen are clearly stronger than are their counterparts to sulfur.

The M–Y bond orders and force constants show similar trends, but the charge transfers are correlated with neither. Taking the former as an index of bond strength and assuming that reduced transfer of charge reduces bond strength,[4] it is possible to distinguish differences in charge transfer

within the individual σ and π components of the bonds. Thus, since the strength of the P–O bond is much greater than those of P–S and As–S while the bond polarities are similar, it may be inferred that there is greater charge transfer within both components of the stronger P–O bond. Similarly, the P–O bond has lower polarity and higher strength than the As–O bond, indicating that the compensating back-flow of charge through the π system is larger.

It is tempting to view the trend in the values of the parameter δ (Table II) as having significance. However, since the TA model is somewhat artificial in regard to methyl-group rotation, and since some of the error limits on δ are large, any interpretations would be highly speculative. Comparison of the R values for the final TA and FR models for each molecule together with comparison of the difference curves in Figure 2 suggests that the barriers to methyl-group rotation have relative magnitudes $(CH_3)_3PO > (CH_3)_3PS \simeq (CH_3)_3AsO > (CH_3)_3AsS$.

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Synthesis and Structure of Metallic Polymeric Sulfur Nitride, $(SN)_x$, and Its Precursor, Disulfur Dinitride, S_2N_2

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Abstract: The synthesis of analytically pure single crystals, suitable for solid state studies, of the covalent, polymeric, metallic conductor, polymeric sulfur nitride, $(SN)_x$ (polythiazyl), is described. The $(SN)_x$ crystals were obtained by slowly growing crystals of S_2N_2 at 0° from the vapor phase during 48 hr followed by room temperature solid state polymerization over a period of 60 hr. Polymerization was completed by heating at 75° for 2 hr. The initially colorless tabular monoclinic crystals of S_2N_2 turned at first dark blue-black and became paramagnetic (g = 2.005) and then finally changed to lustrous golden, diamagnetic crystals which were pseudomorphs of, and had the same space group ($P2_{1/C}$) as, the S_2N_2 crystals from which they were derived. The $(SN)_x$ crystals are composed of an ordered array of parallel $(SN)_x$ fibers which consist of an almost planar chain of alternating sulfur and nitrogen atoms. The cell constants are a = 4.153 (6) Å, b = 4.439 (5) Å, c = 7.637 (12) Å and β = 109.7 (1)° with ρ_c = 2.30 g/cm³ for four SN units per unit cell. The refined structure (R = 0.11) shows nearly equal S–N bond lengths, 1.593 (5) and 1.628 (7) Å. The S–N–S angle is 119.9 (4) and the N–S–N angle is 1.2 (2)°. Crystals of $(SN)_x$ show little reactivity toward oxygen or water at room temperature. In order to attempt to understand the solid state polymerization of S_2N_2 to $(SN)_x$, a single-crystal X-ray structural study of S_2N_2 was performed at −130°. Disulfur dinitride, S_2N_2, has the cell constants (R = 0.03) a = 4.485 (2) Å, b = 3.767 (1) Å, c = 8.452 (3) Å, and β = 106.43 (4)° with ρ_c = 2.23 g/cm³ with two S_2N_2 molecules per unit cell. The molecule is square planar with essentially equal S–N bond lengths (1.657 (1) and 1.651 (1) Å). The S–N–S angle is 90.4 (1)° and the N–S–N angle is 89.6 (1)°. The mode of polymerization of S_2N_2, the nature of the bonding in $(SN)_x$, and a possible source of the metallic conduction band are discussed.

The study of organic metals and inorganic conductors whose electronic properties are quasi-one-dimensional has become a subject of broad interest.[2] Solids such as the organic charge transfer salts NMP-TCNQ[3] (*N*-methylphenazinium-7,7,8,8-tetracyanoquinodimethan), TTF-TCNQ[3] (tetrathiafulvalene-7,7,8,8-tetracyanoquinodimethan), and the mixed valence platinum salt $K_2Pt(CN)_4Br_{0.30}\cdot3H_2O$[4] are experimental systems that exhibit a rich variety of many-body instabilities associated with their quasi-one-dimensionality.

The phenomena and concepts discovered and developed in the organic metals can be carried over directly to other potentially conducting solids such as polymers. Using specific chemical methods, whole new classes of materials might be anticipated that exhibit exciting electronic or magnetic properties.[2]

Of fundamental importance to attaining the metallic state is the presence of unpaired electrons in the primary molecular units.[2,5] In the case of the polymeric solid, polythiazyl, $(SN)_x$, commonly known as polymeric sulfur

nitride, a single polymer chain can be considered schematically as a collection of covalently bonded monomeric NS free radicals each of which is the sulfur analog of NO. The NS molecule, like NO, contains an unpaired electron in the lowest occupied π^*-antibonding molecular level. In principle in a polymer of this type this π^* level may form the basis of the metallic conduction band.

Recently, $(SN)_x$ has been proposed as another example of a quasi-one-dimensional metal.[6] Labes et al.[6] prepared $(SN)_x$ *directly from the vapor phase* by passing S_4N_4 vapor over silver wool at 200° and allowed the resulting vapor to impinge upon a cold finger at 8°. Shiny bronze-colored crystalline bundles of $(SN)_x$ fibers formed directly on the cold finger during 4 hr. The resulting $(SN)_x$ material contained impurities ranging from 1.3 to 5.5%. Measurements of the dc electrical conductivity gave room temperature values ranging from (0.01 to 1.7) × 10³ $(\Omega\ cm)^{-1}$ and a negative temperature coefficient suggestive of metallic behavior. For comparison, the room temperature conductivity of a metal such as mercury is 10.4 × 10³ $(\Omega\ cm)^{-1}$.[7] How-