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Contribution from the Departments of Chemistry, Iowa State University, Ames, Iowa 50011,
Southern Methodist University, Dallas, Texas 75275, and University of Texas at Austin, Austin, Texas 78712

Molecular Photoelectron Spectroscopic Investigation of Some Polycyclic Group 5A Compounds and Related Acyclic Species. 2. Free and Coordinated Phosphite, Thiophosphite, and Arsenite Esters

A. H. COWLEY,[1a] M. LATTMAN,*[1b] R. A. MONTAG,[1c] and J. G. VERKADE[1c]

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He I molecular photoelectron (PE) spectra have been obtained for $XP(SCH_2)_3CCH_3$ (X = lone pair (lp) (**1**), O (**1a**), S (**1b**)), $\overline{P(SCH_2)_2CHS}$ (**2**), $P(OCH_2)_3CH$ (**3**), $XP(OCH_2)_3CCH_3$ (X = lp (**4**), S (**4b**), Se (**4c**), BH_3 (**4d**)), and $OP(OCH_2)_3CC_2H_5$ (**5**) and the adamantane-like molecules $XP(OCH)_3(CH_2)_3$ (X = lp (**6**), O (**6a**), S (**6b**)), $As(OCH_2)_3CCH_3$ (**7**), $As(OCH)_3(CH_2)_3$ (**8**), and $XP(SCH_3)_3$ (X = lp (**10**), O **10a**)), and $P(S\text{-}i\text{-}Pr)_3$ (**11**). These data are compared with those of $XP(OCH_3)_3$ (X = lp (**9**), O (**9a**), S (**9b**), Se (**9c**)). The spectra for the thiophosphite ester cages support the deduced structures. The presence of four ionization bands in the "lone pair" region of **10** strongly suggests a symmetry lower than C_3. Extraction of structural evidence from PE spectroscopy for the phosphite ester molecules is hampered by overlapping ionizations in the oxygen lone-pair region. Besides use of the ionization energy (IE) of the phosphorus lone-pair orbital as an indication of phosphorus base strength, the IE of the sulfur e orbitals can be employed in a similar manner for **4b**, **6b**, and **9b**. The basicity ordering **9** > **6** > **4** is consistent with proton affinity data for these compounds from ion cyclotron resonance measurements.

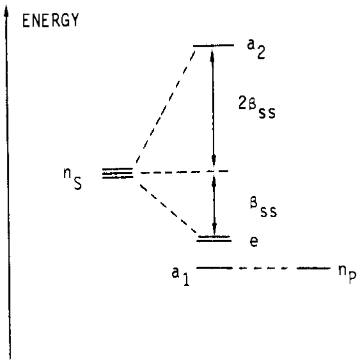
Introduction

As described in a previous paper,[2] molecular photoelectron (PE) spectroscopy is very useful for the study of conformation and bonding in aminophosphines in the gas phase. We now extend these investigations to acyclic and polycyclic thiophosphite, phosphite, and arsenite esters and several of their derivatives in which the group 5 atom is coordinated to a chalcogen atom or a CH_3 group.

Experimental Section

Materials. Compounds **1**,[3] **1a**,[3] **1b**,[3] **3**,[4] **4**,[5] **4b**,[6] **4c**,[7] **4d**,[8] **6**,[9] **6a**,[9] **6b**,[9] **7**,[6] **8**,[10] **9c**,[11] **10**,[12] **10a**,[12] and **11**[12] were prepared as described earlier. Compounds **9**, **9a**, and **9b** were obtained from Aldrich, and **5** was made with use of a preparation for an analogous compound.[6] The PE spectral data for **4**,[13] **7**,[14] **9**,[14] **9a**,[14] **9b**,[14] and **9c**[14] were taken from our previous reports. New PE spectra described herein were recorded as described earlier.[2]

Scheme I



$\overline{P(SCH_2)_2CHS}$ (2). The starting material, $BrCH_2CHCH_2$ (Aldrich), was converted to $BrCH_2CHBrCH_2Br$ by following a standard preparation.[15] The tribromide was treated with NaS_xH[16] by following a method reported earlier[17] to give $HSCH_2CH(SH)CH_2SH$. A mixture of 22 mL of DC550 silicone oil and 3.00 g (21.4 mmol) of the trithiol was heated under nitrogen to 70 °C. Freshly distilled $P(NMe_2)_3$ (2.60 g, 22.0 mmol) was added dropwise. When the evolution of Me_2NH subsided, the temperature was raised to 150 °C. The reaction mixture was then allowed to cool and stand overnight. Insertion of a cold finger into the flask followed by evacuation to 0.1 torr and heating to 100 °C afforded crude **2**, which was sublimed twice to give the pure product in 12% yield (^1H NMR δ, $CDCl_3$) 5.58 dm (1 CH, $^{3,4}J_{PH}$ = 10, 3.15 m (2 CH_2), ^{31}P NMR (δ, $CDCl_3$) 77.9).

Spectroscopic Measurements. All UV PES data were recorded on a Perkin-Elmer Model PS-18 photoelectron spectrometer using a He I photon source (21.22 eV). When necessary, the heated inlet probe was used to obtain suitable sample vapor pressures. Each spectrum was calibrated with a mixture of xenon (12.130 eV) and argon (15.759 eV), which was used as an internal standard. Resolution was maintained between 20 and 50 meV for the argon line. All ionization energies were read as the band maxima unless noted otherwise and are the average of at least three different runs. Ionization energy data are accurate to ca. ±0.02 eV when reported to two decimal places.

Results and Discussion

The UV PES data for the compounds studied are summarized in Table I. The data and assignments pertain primarily to lone-pair ionizations; however, other ionizations have been assigned when feasible. For convenience, formulas (structures when relevant) for the compounds are presented in Table I along with pertinent reference numbers in the text. The compound numbering system is such that the free (uncomplexed) base is given only a number while the various com-

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(1) (a) University of Texas at Austin. (b) Southern Methodist University. (c) Iowa State University.
(2) Cowley, A. H.; Lattman, M.; Stricklen, P. M.; Verkade, J. G. *Inorg. Chem.* **1982**, *21*, 543.
(3) Vandenbroucke, A. C.; Boros, E. J.; Verkade, J. G. *Inorg. Chem.* **1968**, *7*, 1469.
(4) Boros, E. J.; Coskran, K. J.; King, R. W.; Verkade, J. G. *J. Am. Chem. Soc.* **1966**, *88*, 1140.
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(8) Heitsch, C. W.; Verkade, J. G. *Inorg. Chem.* **1962**, *1*, 863.
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(11) Nuretdinov, I. A.; Grechkin, N. P. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1968**, 2831.
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(14) Cowley, A. H.; Goodman, D. W.; Kuebler, N. A.; Sanchez, M.; Verkade, J. G. *Inorg. Chem.* **1977**, *16*, 854 and references therein.
(15) Johnson, J. R.; McEwen, W. L. "Organic Syntheses"; Gilman, H., Blatt, A. H., Eds.; Wiley: New York, 1941; Collect. Vol. I, p 521.
(16) Brauer, G. "Handbuch der Präparativen Anorganischen Chemie"; Ferdinand Enke: Stuttgart, West Germany, 1954; p 269.
(17) Doering, W. v.; Levy, L. K. *J. Am. Chem. Soc.* **1955**, *77*, 509.

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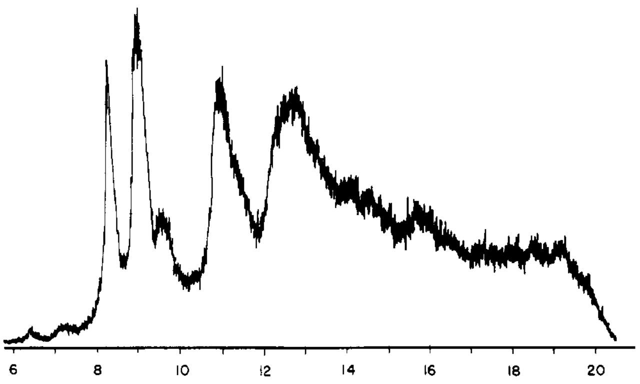


Figure 1. PE spectrum of $P(SCH_2)_3CCH_3$ (**1**).

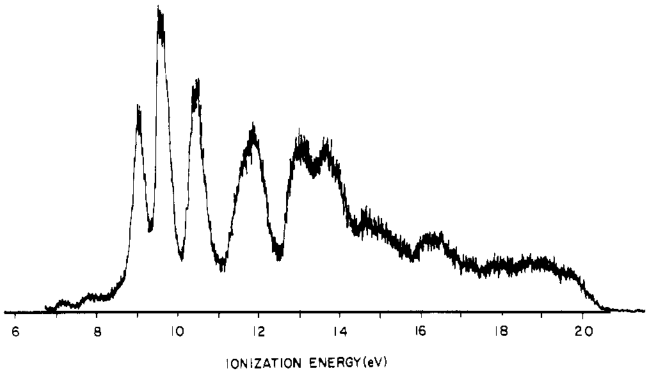


Figure 2. PE spectrum of $OP(SCH_2)_3CCH_3$ (**1a**).

plexes are given a number and letter. Each letter represents a specific complex, thus **a** = oxygen, **b** = sulfur, **c** = selenium, and **d** = borane.

Polycyclic Thiophosphite and Phosphite Esters. The spectra of the polycyclic thiophosphite esters **1**, **1a**, **1b**, and **2** will be discussed before the corresponding phosphite molecules since the former species exhibit sharp, well-defined bands in the low ionization energy (IE) region of the PE spectrum. Though bond angles and lengths for **1**, **1a**, and **1b** are unknown, the solid-state structures of $OP(OCH_2)_3CCH_3$[18] and $P(OCH_2)_3CH_2Br$[19] have been determined by X-ray diffraction techniques. The atoms in the POCC bridges in the latter molecules are found to lie in a plane, and the bicyclic skeletons are essentially C_{3v} with one set of oxygen 2p "lone pairs" lying in a plane perpendicular to the 3-fold axis. The same conformation obtains for the nitrogen lone pairs in $P(NMeCH_2)_3CMe$, whose PE spectrum was analyzed earlier.[2] A similar arrangement is assumed for one set of sulfur lone pairs in **1**, **1a**, and **1b**. Thus, the sulfur lone pairs (n_S) transform as a_2 and e, while the phosphorus lone pair (n_P) is of a_1 symmetry. In general, dicoordinate sulfur lone pair IE bands are quite sharp and intense,[20] while phosphorus lone pairs exhibit much broader IE bands of lower intensity.[21] The PE spectrum of **1** is shown in Figure 1, and the first three IE's are easily assigned as a_2, e, and a_1, respectively, according to the qualitative molecular orbital (MO) diagram in Scheme I. The approximate 1:2 ratio of peak areas for the first two IE bands is consistent with the orbital degeneracies, and the IE ordering $a_2 < e$ is expected from the nodal properties of

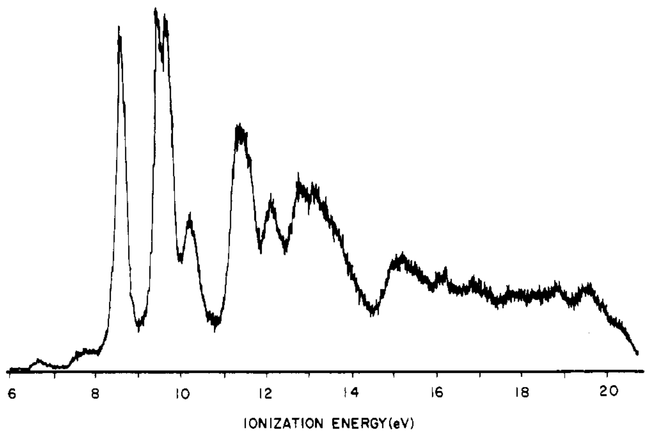


Figure 3. PE spectrum of $\overline{P(SCH_2)_2CHS}$ (**2**).

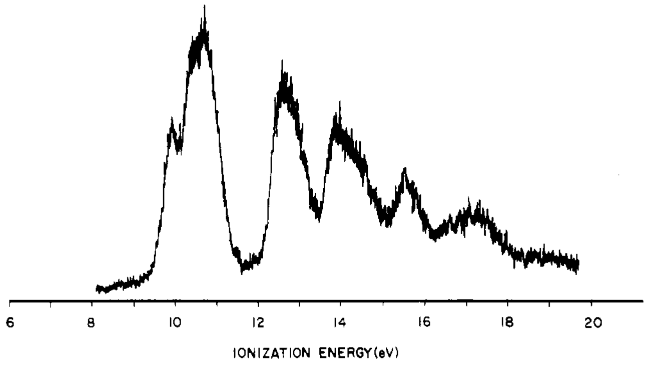
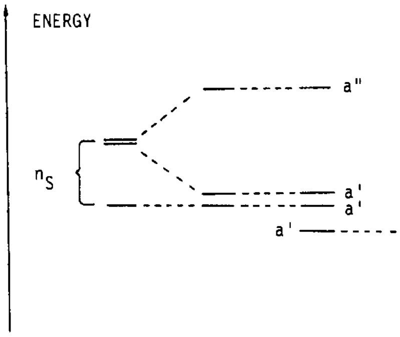


Figure 4. PE spectrum of $P(OCH_2)_3CH$ (**3**).

Scheme II



the MO's.[22] The next IE band with a maximum at 11.0 eV arises from ionization of the orbitals composed of the 3p orbital on sulfur which lie in the plane of the PSC atoms and which bisect the PSC angle. These are primarily bonding MO's, but they have some sulfur "lone pair" character[13,23] and transform as a_1 + e. These orbitals will be denoted as σ/n_S (or σ/n_O in the case of oxygens). Note that the interactions in Scheme I (as reflected by the β parameter) may contain a contribution from $p_\pi \rightarrow d_\pi$ bonding.

Upon coordination, the a_1 (n_P) orbital becomes σ bonding and moves to lower energy (higher IE). This is illustrated in the PE spectrum of **1a** (Figure 2), where the first two IE's are assigned as a_2 and e (n_S), respectively. The third IE is attributed to electron ejection from the oxygen e orbitals (n_O), consistent with the expected IE position.[2] For **1b**, ionization from the exocyclic sulfur e orbitals completely masks the a_2

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(18) Nimrod, D. M.; Fitzwater, D. R.; Verkade, J. G. *J. Am. Chem. Soc.* **1968**, *90*, 2780.

(19) Milbrath, D. S.; Springer, J. P.; Clardy, J. C.; Verkade, J. G. *J. Am. Chem. Soc.* **1976**, *98*, 5493.

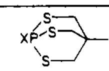
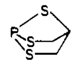
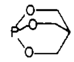
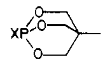
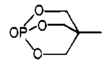
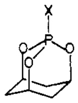
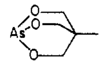
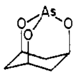
(20) See, for example: Cradock, S.; Whiteford, R. A. *J. Chem. Soc., Faraday Trans. 2* **1972**, *68*, 281.

(21) See, for example: Elbel, S.; Bergmann, H.; Ensslin, W. *J. Chem. Soc., Faraday Trans. 2* **1974**, *70*, 555.

(22) Hoffman, R. *Acc. Chem. Res.* **1971**, *4*, 1.

(23) See, for example: (a) Weiner, M. A.; Lattman, M. *Inorg. Chem.* **1978**, *17*, 1084. (b) Bock, H.; Mollère, P. D. *J. Chem. Educ.* **1974**, *51*, 506. (c) Wagner, G.; Bock, H. *Chem. Ber.* **1974**, *107*, 68. (d) Frost, D. C.; Herring, F. G.; Katrib, A.; McDowell, C. A.; McLean, R. A. N. *J. Phys. Chem.* **1972**, *76*, 1030. (e) Bock, H.; Ramsey, B. G. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 734.

Table I. Ionization Energies and Interaction Parameters[a]

compd	X	no.	$IE_{S/O}$	$\overline{IE}_{S/O}$	$IE_{P/As}$	IE_X	other IE	interaction parameters
	lp	**1**	8.32 (a_2)[b] 9.05 (e)	8.81	9.65 (a_1)		11.0 11.4 sh[c] (σ/n_S)[d]	β_{SS} = 0.24
	O	**1a**	8.94 (a_2) 9.51 (e)	9.32	13.0 (a_1)[e]	10.4 (e)	11.8 (σ/n_S)	β_{SS} = 0.19
	S	**1b**	8.89 (a_2)[f] 9.48 (e)	9.28[g]	12.4 (a_1)[e]	8.89 (e)[f]	11.5 (σ/n_S)	β_{SS} = (0.20)
		**2**	8.48 (a'') 9.36 (a') 9.55 (a')	9.13	10.11 (a')		11.3 12.0 (σ/n_S)	
		**3**	10.7 (a_2,e)[f]	10.7	9.9 (a_1)		12.6 (σ/n_O)	
	lp	**4**[h]	10.4 sh (a_2) 10.6 (e)	10.5	9.95		12.4 (σ/n_O)	β_{OO} = 0.1
	S	**4b**	11.0 (a_2,e)[f]	11.0	12.6 (a_1)[e]	9.31 (e)	12.9 (σ/n_O)	
	Se	**4c**[i]				8.68 (e)		
	BH_3	**4d**	11.0[f]				12.8 (σ/n_O)	
		**5**	11.0[f]					
	lp	**6**	10.2[f]					
	O	**6a**	11.0[f]					
	S	**6b**	10.9[f]			9.25 (e)		
		**7**	9.9 (a_2,e)[f]	9.9	11.0 (a_1)		11.7 (σ/n_O)	
		**8**	9.9 (a_2,e)[f]	9.9	10.6 (a_1)		11.4 (σ/n_O)	
$XP(OCH_3)_3$	lp	**9**[j]	10.54 11.1 11.3		9.22		12.3 13.0 (σ/n_O)	
	O	**9a**[j]	11.36 11.9 12.1		12.4[e]	10.82	12.9 (σ/n_O)	
	S	**9b**[j]	11.15 11.56 11.8		12.0[e]	9.16	12.7 (σ/n_O)	
	Sc	**9c**[j]	10.93 11.5		[f]	8.67		
$XP(SCH_3)_3$	lp	**10**	8.76 (a'') 9.16 (a') 9.84 (a')[k]		8.33 (a')[f]		11.0 sh 11.3 (σ/n_S)	
	O	**10a**	9.13 9.5	9.38		10.3	11.8 sh 12.1 (σ/n_S)	
P(S-*i*-Pr)$_3$		**11**	8.48 (a'') 8.79 (a') 9.36 (a')[k]		7.91 (a')[k]			

[a] In eV. [b] Orbital assignments in parentheses. [c] Shoulder. [d] See text. [e] σ_{PX} ionization. [f] Overlapping bands. [g] Value uncertain due to overlapping bands. [h] Data from ref 14. [i] PE spectrum contained large amounts of 4; see text. [j] Data from ref 13. [k] Interacting n_S/n_P orbitals.

(n_S) IE band.[24] The next IE band of **1a** in Figure 2 is attributed to the a_1 + e σ/n_S MO's. The slight lowering of β_{SS} upon complexation most likely reflects the opening of the SPS angles as found for coordination of the bicyclic phosphite esters.[18,19] The fact that this trend was not observed in XP-$(NMeCH_2)_3CMe$ (X = lone pair (lp), S, Se, BH_3) may mean that there is little change in NPN angle upon coordination of the parent aminophosphine.[2]

In **2**, the n_S orbital symmetry is lowered to C_s and these lone pairs therefore transform as 2a' + a'', while the n_p orbital is of a' symmetry. Although the reduced symmetry allows additional interactions, a qualitative MO diagram (Scheme II) can be developed with the assumption that the presence of the methylene groups inductively raises the lone-pair energies of the two equivalent sulfurs relative to that of the unique lone pair. Nodal rule considerations[22] place the a'' MO as the HOMO. The exact ordering of the two primarily n_S a' orbitals is, of course, speculative, but the fourth IE is unambiguously assigned to the n_p a' MO on intensity considerations (Figure 3).

We turn now to the bicyclic phosphite ester systems **3**, **4–4d**, and **5**, which are of C_{3v} symmetry. In the PE spectrum of **3** in Figure 4, the first ionization envelope is split into two major bands, the more intense of which exhibits a definite shoulder. On the basis of MO calculations[14,25,26] the first peak is assigned

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(24) The PE spectrum of **1b** could not be obtained free of small quantities of **1**.

(25) Yarbrough, L. W.; Hall, M. B. *J. Chem. Soc., Chem. Commun.* **1978**, 161.

(26) Because of the closeness in IE's of the n_P and n_O MO's, these bands for **4** were misassigned in ref 14. The calculations described in ref 25 suggest the assignments shown in Table I for **3** and the assignments for **4** have been corrected in this table and are included for comparison.

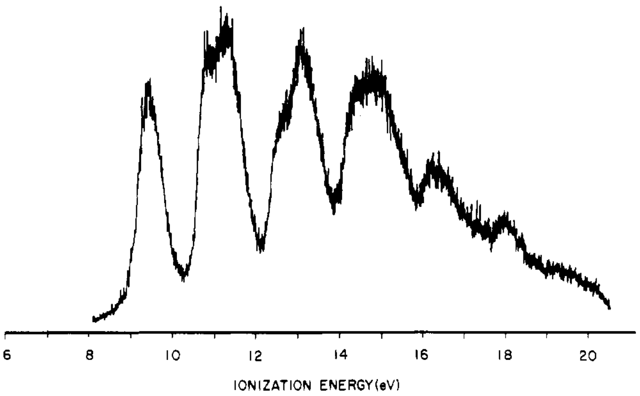


Figure 5. PE spectrum of $SP(OCH_2)_3CCH_3$ (**4b**).

to a_1 (n_p), while the more intense peak contains the n_O, a_2, and e ionizations. The splitting of the n_O orbitals should be analogous to that of the n_S orbitals (Scheme I), but the interaction parameter, β, is too small to be obtained with confidence. Due to the higher effective nuclear charge, the n_O orbitals lie at lower energies (higher IE's) than the n_S orbitals. As expected, the n_P a_1 orbital moves to lower energy upon complexation and ionization from the e orbitals of the Lewis acid moiety appears, as is illustrated in the PE spectrum of **4b** in Figure 5. The first IE band arises from the n_S e orbitals while the two maxima observed in the next ionization envelope are attributed to the n_O a_2 and e orbitals, respectively. The PE spectrum of the selenium adduct, **4c**, exhibited a high concentration of the free ligand **4** so that only the first IE is reported. The spectra of **4d** and **5** were virtually uninterpretable due to overlapping ionizations; thus, only the first ionization maximum is reported in each case. The apparent smaller β_{OO} values compared to β_{SS} and β_{NN}[2] probably arise from the higher effective nuclear charge, which permits relatively poor spatial overlap of oxygen lone pairs in the C_{3v} orientation.

Comparison of the trends in ionization energies from C_{3v} to C_s symmetry, i.e., **1** and **2**, is informative. Even though mixing of the n_P and n_S orbitals of a′ symmetry is possible in **2**, the similarity of the spectra of **1** (where such mixing is not possible) and **2** argue against significant n_S/n_P interaction as is implied in Scheme II. The value of $\overline{\mathrm{IE}}_S$ increases by 0.32 eV from **1** to **2**, probably as the result of the changes of inductive effect due to one less methylene bridge and the absence of the bridgehead methyl group. The PSC bond angle should have little effect on the n_S orbital IE's since this 3p AO is perpendicular to the PSC plane.[23] IE_P increases by 0.46 eV on going from **1** to **2**, primarily because of the smaller bond angles about phosphorus in **2**,[27] leading to more s character in the n_P orbitals. Here the inductive effects mentioned above probably play a minor role.

The n_O and n_P IE bands in the spectra of **6**, **6a**, and **6b** overlap too greatly to be interpreted with confidence. The only definitive assignment is the band at 9.25 eV in **6b**, which is attributed to the n_S e orbitals. This value is very close to the corresponding ionization in **4b**, which is expected considering the similar $P(OC)_3$ skeletal geometries.

Polycyclic Arsenite Esters. An interesting trend in IE's is observed when phosphorus is replaced by arsenic in **7** and **8**. Though arsenic is less electronegative than phosphorus, the smaller bond angles about arsenic increase the s character in its lone pair, thus stabilizing the n_{As} orbital. These opposing trends cancel in the PE spectra of $P(CH_3)_3$ and $As(CH_3)_3$, where the observed lone-pair IE's are almost identical.[21] The PE spectra of **9** and $As(OCH_3)_3$[13] reveal that the n_{As} IE is 0.51 eV greater than the n_P IE. Moreover, the n_O IE's are 0.4–0.6 eV less in the arsenic compounds, probably as a consequence of changes in inductive effects. The observed trends in these ionization energies from phosphite to arsenite ester molecules may be enhanced by poorer $p_\pi \rightarrow d_\pi$ bonding in the arsenic compounds. In the spectrum of **7** (Figure 6), $\overline{\mathrm{IE}}_O$ is 0.6 eV lower than the corresponding value in **4** (Table I). However, the n_{As} IE appears at 11.0 eV, more than 1 eV greater than the IE of n_P in **4**. This large shift is attributable to (i) bond angle changes, (ii) diminution in $p_\pi \rightarrow d_\pi$ bonding when phosphorus is replaced by arsenic, or (iii) a combination of these effects. Unfortunately, as in the case of the corresponding phosphites, the n_O e and a_2 IE's overlap in the arsenites **7** and **8**.

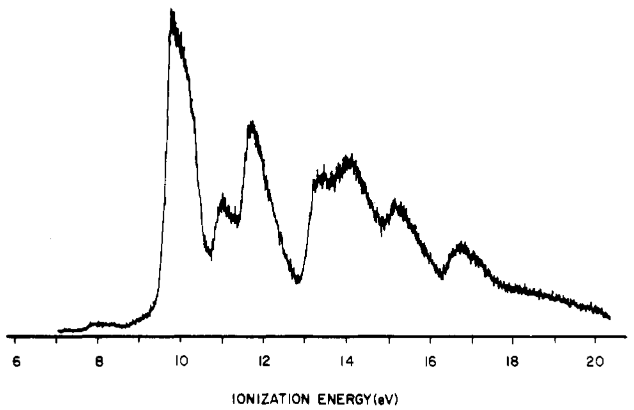
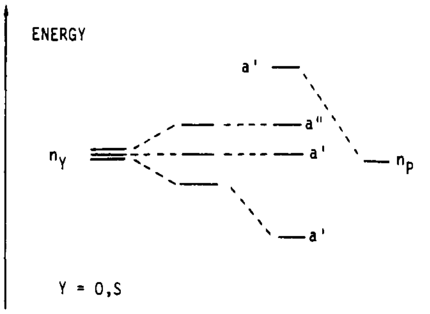
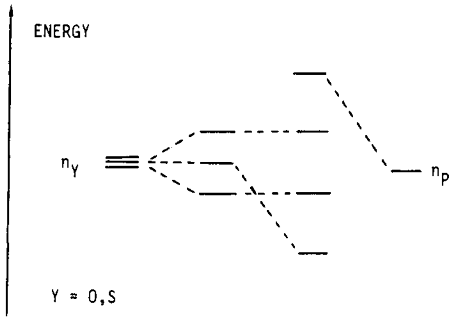


Figure 6. PE spectrum of $As(OCH_2)_3CCH_3$ (**7**).

Scheme III



Scheme IV



Acyclic Species. The conformations of **9**–**9c** in the gas phase have been difficult to ascertain by PE spectroscopy because of overlapping ionization bands (Table I).[13] For example, the third and fourth ionization bands in **9** lie within 0.2 eV of one another, which is consistent with the Jahn–Teller splitting of the n_O e band in C_3 symmetry.[14] A conformation of C_s symmetry such as A shown below (Scheme III) cannot be ruled out; however, a conformation of C_1 symmetry symmetry such

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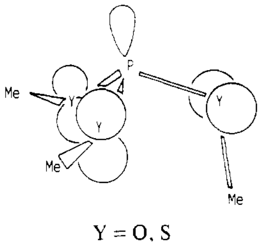
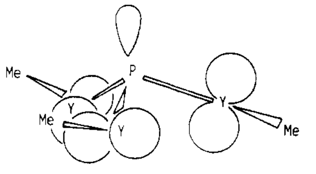
[27] Though the structures of **1** and **2** are unknown, those of $OP(OCH_2)_3CCH_3$ and $OP(OCH_2)_2CCH_3O$ are not.[16,17] The sum of the OPO bond angles in the latter is 12° smaller. Similar bond angle differences are assumed for the uncoordinated phosphites **4** and **6**, as well as the thiophosphites **1** and **2**.



Y = O, S
A



Y = O, S
B

as B (Scheme IV) could also be responsible for the PE spectrum of **9**. It is believed that **9** in the liquid and gas phases comprises a mixture of conformers, although their symmetries are not known with certainty.[28,29] The same is believed to be true for **9a**.[30a] In a recent PE spectral and MNDO calculational study it was concluded that the two conformations of lowest energy are C_3 and C_s.[30b] The assignments of the IE's based on these calculations were essentially the same as ours. Structural determinations of solid complexes of $P(OMe)_3$[31] also reveal a variety of conformations for the ligand. In the majority of cases, however, one OMe group is directed away from the metal (i.e., the O–C bond is trans to the P–M link with the oxygen p orbital orthogonal to the P–M axis)[31k] while the other two OMe substituents are oriented such that their oxygen p orbital axes are nearly coplanar with the P–M bond (see A above). Also, trivalent aminophosphines and their selenium adducts adopt approximate C_s conformations in the solid state.[32] It is therefore anticipated that **9** and its adducts **9a–c** also adopt the C_s structure represented by A above.

The spectrum of **10** clearly exhibits four IE bands in the lone-pair region (Figure 7), implying C_s symmetry at best (see A above and Scheme III). Upon coordination to oxygen in **10a**, the n_P orbital is removed from interaction and all the n_S MO's are inductively stabilized by the oxygen. The observed spectrum (Figure 8) shows two band maxima in the n_S IE region, the second of which is of greater intensity. This could mean a C_3 arrangement of the n_S orbitals leading to the assignment a and e (n_S) in increasing IE order, respectively. However, there is little reason to postulate a C_3 arrangement in **10a**, and it is likely that the symmetry is less than C_3 with an accidental degeneracy occurring in the PE spectrum. Therefore, no detailed n_S assignments are given. The n_O e orbitals ionize at 10.26 eV in **10a**. The PE spectrum of **11** is quite similar to that of **10** and is assigned analogously (Table I). It may be mentioned in this connection that $As(OCH_3)_3$ has been shown to possess a symmetry lower than C_3.[33]

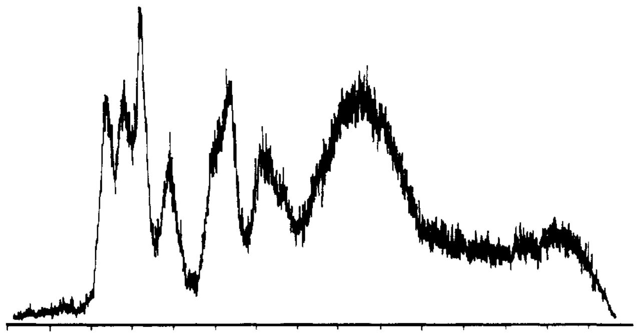


Figure 7. PE spectrum of $P(SCH_3)_3$ (**10**).

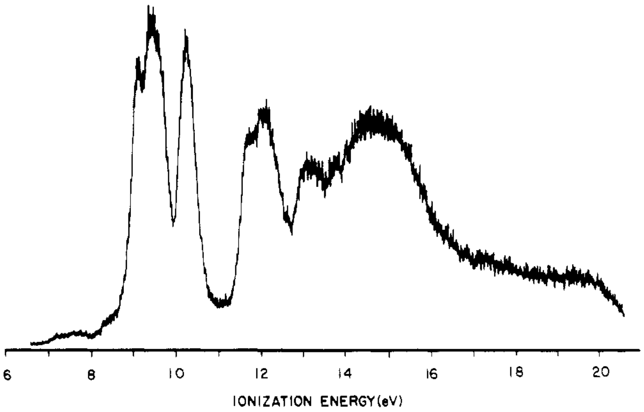
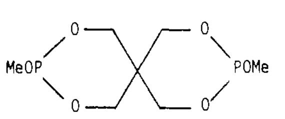


Figure 8. PE spectrum of $OP(SCH_3)_3$ (**10a**).

Basicities of Phosphites and Thiophosphites. Equilibrium studies[34] have revealed the order of basicity of phosphites toward BH_3 to be **9** > **4**, which is supported by the higher energy (lower IE) of the phosphorus lone pair in **9**. In **4** the n_O orbitals are orthogonal to the n_P orbital, while in **9** a strong interaction can occur between the n_P and n_O orbitals of a′ symmetry. Since the n_O orbital is of lower energy, the net effect will be to raise the energy of the n_P orbital. (See Scheme III, bearing in mind the n_O orbitals will be lower in energy than the n_P orbital.)

Another factor that could influence basicity is the OPO angle about phosphorus. The smaller this angle, the more s character will be accumulated in the orbital and the lower will be its energy and donor ability. The sum of the OPO angles ($\sum$OPO) opens from 300.3° in $P(OCH_2)CCH_2Br$[5] to 310.0° in $OP(OCH_2)_3CCH_3$.[16] Similarly $\sum$OPO in **12** (302.2°)[35] rises 11° in the related BH_3 adduct **13** (313.0°).[36] The exact conformation of **9** has not been determined, but $\sum$OPO appears to be between 300.6 and 302.4°,[28] which is quite close to the value in $P(OCH_2)_3CCH_2Br$ (300.3°).[5] This information, taken along with the value of $\sum$OPO in $OP(OCH_2Ph)_2OH$ (311.4°)[37] and **6b** (313.5°),[38] suggests that the OPO bond angle opening in strainless phosphite esters



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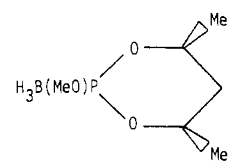

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when coordinated to main-group acids involves ca. 12° increases in $\sum$OPO. Since the OPO angle enlargements upon coordination of **4** and **9** are approximately the same, there appears to be no substantial evidence for the basicity order **9** > **4** to arise from OPO angle differences.

A detailed σ/π analysis for phosphates as presented for the aminophosphine oxides[2] is precluded by the fact that the phosphoryl and ester n_O IE's overlap. However, the simple σ-donor model appears to hold for X = S, where the n_S e orbitals ionize in order of energies **9b** < **4b**. The corresponding IE in **6b** implies that **6** lies between **4** and **9** in base strength, a conclusion reached independently from gas-phase proton affinity data obtained from ion cyclotron resonance experiments.[39] For X = Se, the basicity trend also seems to hold except that the IE range spanned is much smaller and the difference between **9c** and **4c** is negligible.

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Registry No. **1**, 18818-32-1; **1a**, 18818-34-3; **1b**, 18818-33-2; **2**, 91711-76-1; **3**, 280-45-5; **4**, 1449-91-8; **4b**, 3196-56-3; **4c**, 67471-54-9; **4d**, 6867-41-0; **5**, 1005-93-2; **6**, 281-33-4; **6a**, 875-12-7; **6b**, 58299-37-9; **7**, 22223-55-8; **8**, 536-97-0; **9**, 121-45-9; **9a**, 512-56-1; **9b**, 152-18-1; **9c**, 152-19-2; **10**, 816-80-8; **10a**, 681-71-0; **11**, 3862-19-9; $BrCH_2CH{=}CH_2$, 106-95-6; $BrCH_2CHBrCH_2Br$, 96-11-7; $HSCH_2CH(SH)CH_2SH$, 4756-13-2; $P(NMe_2)_3$, 1608-26-0.

Supplementary Material Available: PE spectra of **1b**, **4c**, **4d**, **5**, **6**, **6a**, **6b**, **8**, and **11** (9 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry and Laboratory for Molecular Structure and Bonding,
Texas A&M University, College Station, Texas 77843

Preparation of the Crystalline β (Bridged) Isomer of $Mo_2Cl_4(dppe)_2$ and Determination of Its Crystal Structure

PRADYOT A. AGASKAR and F. ALBERT COTTON*

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It has been found that the α and β isomers of $Mo_2Cl_4(dppe)_2$, dppe = $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$, can be prepared by the reaction of $Mo_2(O_2CCF_3)_4$ with $(CH_3)_3SiCl$ and dppe. The isomer obtained is controlled by reaction conditions, primarily the solvent. It has also been found possible to obtain both isomers in crystalline form. The crystal structure of the β isomer, in which the dppe ligands bridge the $\mathrm{Mo}\overset{4}{-}\mathrm{Mo}$ unit, has been determined. It forms crystals in space group $P2_1/n$ with a = 23.103 (45) Å, b = 13.258 (75) Å, c = 16.792 (62) Å, β = 107.19 (7)°, V = 4913 (11) Å^3, and Z = 4. The midpoints of the Mo–Mo quadruple bonds reside on a set of general positions. At each position there are two orientations, a principal one (87%) and a minor one (13%). In the principal orientation the helical molecule consists of two fused rings with chair conformations and a mean angle of twist about the Mo–Mo axis of 30.5°. In the minor orientation, the fused rings have twist conformations and the sense of the helix about the Mo–Mo bond is opposite to the one in the principal molecule with an angle of 27.7°. In the principal molecule, the Mo–Mo distance is 2.183 (3) Å and the mean Mo–P and Mo–Cl distances are 2.579 (8) and 2.385 (7) Å, respectively.

Introduction

It is now well established that in compounds of the type $M_2X_4(R_2EYE'R_2)_2$, where M may be Mo, W, or Re, R may be phenyl or methyl, E and E′ are usually P but in one instance we have E = P and E′ = As, and Y may be CH_2CH_2, CH_2CHMe, CHMeCHMe, or $(CH_2)_3$, there are two isomers and that in most cases both isomers are formed. The two isomers have the chelated, α, and bridged, β, structures, shown schematically in Figure 1. The pioneering work on these systems was done by Walton and his students who first discovered that there are isomeric forms of $Re_2Cl_4(dppe)_2$, dppe = $Ph_2PCH_2CH_2PPH_2$, and who offered a correct conjecture as to their nature.[1] Since then, structural assignments based on X-ray crystallography have been made for several compounds. The detailed structural results heretofore published are collected in Table I.

Table I. Previously Reported Crystal Structures for Compounds of the Type $M_2X_4(R_2ECH_2CH_2E'R_2)$

M	X	$R_2EXE'R_2$	M-M dist, Å	% minor orientation	ref
Re	Cl	$Ph_2PCH_2CH_2PPh_2$	2.244 (1)	6.5	*a*
Mo	Br	$Ph_2PCH_2CH_2AsPh_2$	2.167 (4)	23	*b*
W	Cl	$Ph_2PCH_2CH_2PPh_2$	2.314 (1)	7	*c*
Mo	Cl	$Me_2PCH_2CH_2PMe_2$	2.183 (3)	8	*d*

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With all of these compounds, perhaps most severely with those of molybdenum, one encounters difficulties because of insolubility. This makes it difficult to control the course of the syntheses so as to obtain the desired products and frequently denies access to useful single crystals unless these form directly from the synthetic reaction, which, by good fortune, is sometimes the case.

In this paper we report the successful result of a deliberate effort to isolate the β (bridged) isomer of $Mo_2Cl_4(dppe)_2$ in crystalline form and determine its structure. From this prototypal compound in the field it was expected that lessons could be learned about both the synthesis and structure that would have wider implications. Since the original synthetic method of Best, Smith, and Walton[2,3] is not appropriate for the pro-

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