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Dipole Moments of Several Tertiary Phosphine Oxides, Sulfides, and Selenides and of Some Tertiary Arsine Oxides and Sulfides

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Dipole moments of thirteen phosphine and two arsine chalcogenide derivatives were determined in benzene solution at 20°. The results show that (1) the arsine compounds are more polar than the corresponding phosphine compounds, (2) the polarity of tertiary phosphine derivatives increases in the series oxide < sulfide < selenide, and (3) electronegative groups decrease the polarity of the derivative. Group bond moments, which were calculated from the net dipole moments of the molecule and the known structural parameters, give trends that follow electronegativities of the group and permit calculation of chemically reasonable M–X charge separations. Within a derivative series, *e.g.*, the oxides, the magnitude of $\delta\pm$ decreases with increasing electronegativity of the group. For a given group, *e.g.*, C_6H_5, the charge separation produces the trend oxide > sulfide ≈ selenide. The trends in the M–X bond moments and charge separations are discussed in terms of the relative amounts of double-bond character in the different M–X bonds.

Introduction

A great deal of controversy exists in the literature concerning the nature of the M–X bond (where M = P or As, and X = O, S, or Se). It has been argued that the M–X bond is (1) a dative bond,[1] (2) a double bond, or (3) a bond possessing a character intermediate between a single bond and a double bond, depending upon the extent of $p\pi$–$d\pi$ bonding between M and X.[2] Physical measurements such as (1) dissociation energies of the M–X bond,[3] (2) infrared stretching frequencies of the M–X group,[4–15] (3) nmr studies,[6b,15–21] and (4) donor properties of the M–X group toward Lewis acids such as phenol, chloroform, and iodine[22–28] indicate that the M–X bond is more accurately described by type (3) above. However, the determination of the amount of π bonding in the M–X group by these physical methods is

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qualitative at best, and often the trend in the amount of π bonding indicated by one method is contradicted by another. Accurate dipole moments of a number of phosphine oxides, sulfides, and selenides and arsine oxides and sulfides were determined in this study to obtain a quantitative measure of the polarity of the M–X group, from which the amount of multiple-bond character in the M–X bond could be evaluated.

Experimental Section

Reagents.[29] Commercial samples of triphenylphosphine oxide and triphenylphosphine sulfide were recrystallized from benzene–petroleum ether and absolute ethanol, respectively; oxide mp 156.0° (lit.[30] mp 156°); sulfide mp 157.5° (lit.[31] mp 157.5°). Triphenylphosphine selenide[32] was recrystallized from absolute ethanol; mp 187.5–188.0° (lit.[33] mp 187–188°). Triphenylarsine oxide and sulfide (Eastman Organic Chemicals) were recrystallized from benzene–petroleum ether; oxide mp 192.5–193.8° (lit.[34] mp 194.5–196°); sulfide mp 165.8–166.3° (lit.[35] mp 166°). Ethyldiphenylphosphine oxide and sulfide were recrystallized from benzene–petroleum ether; oxide mp 122.5–123.5° (lit.[36] mp 123–124°); sulfide mp 63.0–64.0° (lit.[37] mp 65.5–66.0°). Dimethylphenylphosphine sulfide and dimethylpentafluorophenylphosphine sulfide were recrystallized from benzene-pentane; nonfluorinated compound mp 43.8–44.4° (lit.[38] mp 45.0–46.3°); pentafluoro derivative mp 71.2°.[29] Diphenyl(dimethylamino)phosphine selenide was recrystallized from ether–hexane; mp 85.0–85.5°.[29] Tris(dimethylamino)phosphine oxide (Aldrich Chemical Co.) was refluxed over barium oxide and then vacuum distilled; bp 51.0–51.5° (0.1 Torr). Tris(dimethylamino)phosphine sulfide was vacuum distilled; bp 64–66° at (~1 Torr) [lit.[39] bp 63° (1.2 Torr)]. Diphenyl(dimethylamino)phosphine sulfide was vacuum distilled; bp 116–120° (1 Torr) [lit. bp 123° (0.1 Torr),[40] 112° (2 Torr)[41]]. This compound solidifies upon standing; mp 91.0–91.5° (lit.[42] mp 88–90°). Methyldiphenylphosphine sulfide was vacuum distilled; bp 157–159° (0.1 Torr) [lit.[38] bp 157–159° (0.1 Torr)]. Trimethoxyphosphine sulfide was vacuum distilled; bp 73.0–73.5° (12 Torr) [lit.[43] bp 80° (20 Torr)].

Calibration Liquids. Cyclohexane (Fisher Spectranalyzed reagent) was refluxed over phosphorus pentoxide for 1.5 days and distilled through a 50-cm column packed with glass helices; a middle fraction boiling at 80° was collected. Carbon tetrachloride (Fisher Spectranalyzed reagent) was refluxed over phosphorus pentoxide for 1 day and distilled as above; a middle fraction boiling at 76° was collected. Benzene (Matheson Coleman and Bell Spectroquality reagent) was shaken over phosphorus pentoxide, filtered, refluxed over molten potassium for 2 days, and distilled as above; a middle fraction boiling at 79° was collected. *n*-Butyl ether (Matheson Coleman and Bell Quality Control reagent) was refluxed over molten sodium for 1 day and distilled through a 50-cm Vigreux column wrapped with asbestos tape; a middle fraction boiling at 140° was collected. Benzene, which was purified as above, was also used as the solvent for the dielectric constant measurements on dilute solutions of the compounds whose dipole moments were to be determined. All calibration liquids were stored under a dry nitrogen atmosphere until used. Just prior to calibration of the dipolemeter, the calibration liquids were passed over specially treated molecular sieves (Linde, Type 4A, $^1/_{16}$-in. pellets) as a final drying step.[44] Transfers of solutions were accomplished in a dry nitrogen atmosphere.

The dielectric constants assumed for the calibration liquids were as follows: cyclohexane, 2.0229; carbon tetrachloride, 2.2368; benzene, 2.2833; *n*-butyl ether, 3.0922.[45]

Instrumentation. The dielectric constants of dilute benzene solutions of the compounds studied and the calibration liquids were measured with a Dipolemeter DM 01 (Wissenshaftlich-Technische Werkstatten) equipped with a 20-ml jacketed gold-plated DFL1 cell. The refractive indices of the solutions were measured with a Bausch and Lomb Abbe 3L refractometer. Both the dipolemeter cell and refractometer were thermostated with a circulating water bath in conjunction with a heat exchanger which allowed cooling below ambient temperatures. The temperature was maintained at 20 ± 0.07° by an electronic control relay and a 100°-range contact thermometer.

The temperature of the water bath was measured with a 100°-range thermometer calibrated in 0.1° scale divisions.

Solution Preparation. All solutions were prepared by weight on an analytical balance under a dry nitrogen atmosphere within a large polyethylene glove bag. Approximately 20 solutions were prepared for each measurement; weight fractions for the dielectric constant measurements ranged from zero to an upper limit of 3×10^{-3}–8×10^{-3}; weight fractions for refractive indices ranged from zero to an upper limit of 2×10^{-2}–24×10^{-2}.

Calculations. The dipole moments were calculated according to the Guggenheim–Smith method.[46] No correction was made for the atomic polarization; the molar refraction, R_D, was assumed equal to the sum of the atomic and electronic polarizations. A program written for the IBM 7094 computer applied linear least-squares equations to the solution data *vs.* the weight fraction of the solute and calculated the dipole moments directly. The program also calculated precision limits of the dipole moments.

Results

The results of the dipole moment determinations are presented in Table I together with any previously reported dipole moments of the compounds studied. The standard error limits for this work represent precision, not accuracy. One can see the rather wide range in the reported dipole moments of a compound that has been measured a number of times. Factors that contribute to the differences in these values are (1) solvent effects, (2) temperature effects, (3) differences in measurement technique, and (4) the method of calculation of the dipole moment from the experimental data.

Calculation of the MX Bond Moment. Nuclear magnetic resonance coupling constant data indicate that the P–H bond in phosphine, PH_3, has almost pure p character.[47] Thus, the lone pair electrons on phosphorus reside principally in the 3s orbital and are spherically distributed around the phosphorus nucleus. Consequently, one expects the lone-pair contribution to the dipole moment of phosphine (and other phosphines and arsines) to be very small, in contrast

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(29) A number of the compounds studied in this work were prepared by other workers in these laboratories. We thank P. E. Nicpon for a sample of $(C_6H_5)_3PSe$; S. C. Cummings for samples of $C_2H_5(C_6H_5)_2PO$ and $C_2H_5(C_6H_5)_2PS$; E. C. Alyea for samples of $(CH_3)_2C_6H_5PS$ and $(CH_3)_2C_6F_5PS$; and W. E. Slinkard for samples of $[(CH_3)_2N]_3PS$, $[(CH_3)_2N](C_6H_5)_2PS$, $[(CH_3)_2N](C_6H_5)_2PSe$, $CH_3(C_6H_5)_2PS$, and $(CH_3O)_3PS$. Apparently, $(CH_3)_2C_6F_5PS$ and $[(CH_3)_2N](C_6H_5)_2PSe$ had not been previously prepared. Melting points observed were 71.2 and 85.0–85.5°, respectively. All solid compounds were dried *in vacuo* over P_4O_{10} overnight after recrystallization and stored under a dry nitrogen atmosphere. Melting points of the solid compounds were determined on a Nalge-Axelrod melting point apparatus.

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Table I. Dipole Moments of Several Phosphine and Arsine Chalcogenides

Compd	Dipole moment (D) (this work, benzene soln, 20°)	Reported dipole moment (D), solv,[a] temp
$C_2H_5(C_6H_5)_2PO$	4.51 ± 0.01	
$(C_6H_5)_3PO$	4.51 ± 0.01	4.49,[b] 4.34,[c,d] 4.31,[c,e] 4.44,[f] all B, 25°; 4.55,[g] D, 20°; 4.61,[h] CCl_4, 20°; 4.40,[i] *p*-xylene soln, 30°
$[(CH_3)_2N]_3PO$	4.47 ± 0.01	5.54,[j] 4.30,[k] both B, 25°; 4.29,[k] D, 25°; 4.47,[l] CCl_4, 20°; 5.39,[j] L-O, 20°; 5.38,[j] 4.31,[m] both L-O, 25°
$(CH_3)_2C_6H_5PS$	4.80 ± 0.01	
$(CH_3)_2C_6F_5PS$	4.43 ± 0.01	
$CH_3(C_6H_5)_2PS$	4.80 ± 0.01	
$C_2H_5(C_6H_5)_2PS$	4.67 ± 0.02	
$(C_6H_5)_3PS$	4.88 ± 0.01	4.89,[n] B, 20°; 4.79,[b] 4.78,[c,d] 4.73,[e] all B, 25°; 5.02,[g] D, 20°
$[(CH_3)_2N](C_6H_5)_2PS$	4.46 ± 0.01	
$[(CH_3)_2N]_3PS$	4.47 ± 0.02	
$(CH_3O)_3PS$	2.85 ± 0.02	
$[(CH_3)_2N](C_6H_5)_2PSe$	4.71 ± 0.01	
$(C_6H_5)_3PSe$	5.17 ± 0.02	4.87,[c,d] B, 25°
$(C_6H_5)_3AsO$	5.51 ± 0.03	5.41,[b] 5.54,[c,d] 5.53,[n] all B, 25°
$(C_6H_5)_3AsS$	5.43 ± 0.01	5.31,[b] B, 25°

[a] B, benzene solution; D, dioxane solution; L–O, pure liquid measurement, calculation by Onsager equation: L. Onsager, *J. Amer. Chem. Soc.*, **58**, 1486 (1936). [b] M. J. Aroney, R. J. W. Le Fevre, and J. D. Saxby, *J. Chem. Soc., Suppl.*, 6180 (1964). [c] Dipole moments reported prior to 1948 have been recalculated to account for changes in the value of Avogadro's number and Boltzmann's constant: A. L. McClellan, "Tables of Experimental Dipole Moments," Freeman, San Francisco, Calif., 1963. [d] Reference 1. [e] G. M. Phillips, J. S. Hunter, and L. E. Sutton, *J. Chem. Soc.*, 146 (1945). [f] C. W. N. Cumper, A. A. Foxton, J. Read, and A. I. Vogel, *ibid.*, 430 (1964). [g] H. Goetz, F. Nerdel, and K.-H. Wiechel, *Justus Liebigs Ann. Chem.*, **665**, 1 (1963). [h] Reference 26i. [i] E. Fischer, I. Laulicht, and S. Pinchas, *J. Phys. Chem.*, **66**, 2708 (1962). [j] J.-E. DuBois and H. Viellard, *J. Chim. Phys. Physicochim. Biol.*, **62**, 699 (1965). [k] J.-P. Fayet, *C. R. Acad. Sci., Ser. C*, **270**, 9 (1970). [l] Reference 26g. [m] M. Schafer and C. Curran, *Inorg. Chem.*, **4**, 623 (1965). [n] V. D. Chernokal'skii, A. S. Gel'fond, and G. Kamai, *Zh. Obshch. Khim.*, **39**, 829 (1969); *J. Gen. Chem. USSR*, **39**, 792 (1969).

to the large lone-pair moment on ammonia.[48,49] If the lone-pair moment is considered as zero, then the net dipole moments of symmetrical phosphines and arsines may be resolved into their respective M–R group moments.[49] The group moments of a number of these compounds were calculated from the experimental dipole moments and are given in Table II.[50]

Parry and coworkers considered the P–H group moment to be directed toward and the P–F group moment directed away from phosphorus in PHF_2[49c,51] and the alkyl-phosphorus group moments to be directed toward phosphorus in the alkylphosphines.[49]

The dipole moment of tris(*p*-chlorophenyl)phosphine is 0.65 D;[52] that of triphenylphosphine is 1.49 D.[53] As the chlorine–carbon moment can be assumed to be directed away from the phosphorus atom, these net dipole moments can be rationalized by assuming that the phenyl–phosphorus group moment is directed toward the phosphorus atom. Similarly, Chernokal'skii, *et al.*,[54] argued that the phenyl to arsenic moment is directed toward the arsenic atom in arylarsines and -arsine oxides.

The structures and dipole moments of several unsymmetrical phosphines of the type $R_2R'P$ have been determined by microwave spectroscopy. For eight of these, the perpendicular components of the dipole moments along the axes of rotation have been reported. For these molecules it is possible to calculate the P–R and P–R′ group moments using the structural parameters, the dipole moment data, and the directions of the P–R group moments established above. These calculated group moments are tabulated in Table III. Note that the variation of a particular group moment from compound to compound prevents simply adding the group moments in compounds of this type. Apparently, only if

Table II. Experimental Dipole Moments, Interatomic Angles, Bond Distances, and Calculated Group Moments of Some Phosphines and Arsines

Compd	Dipole moment, D	Interatomic angles RMR, deg	Calcd group moment, D
PH_3	0.57395[a]	93.45[b]	0.35
PF_3	1.025[c]	97.8[d]	0.69
PCl_3	0.56[e]	100.27[f]	0.40
$(CH_3)_3P$	1.192[g]	99.1[g]	0.83
$(C_6H_5)_3P$	1.49[h]	102.99[i]	1.16
$CH_3C(CH_2O)_3P$	4.15[j]		
$(CH_3)_3As$	1.10[k]	96[l]	0.71
$(C_6H_5)_3As$	1.36[m]	102.0[n]	1.03

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(53) See ref *f* of Table I.

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Table III. Net Dipole Moments, Component Dipole Moments along Rotational Axes, Interatomic Angles, and Calculated Group Moments of Some Unsymmetrical Phosphines, $R_2R'P$

Compd	Net dipole moment, D	Component dipole moments, D	Interatomic angles, deg		Calcd group moments, D	
			RMR	R'MR	μ_{PR}	$\mu_{PR'}$
PHF_2[a]	1.32	$\vert\mu_b\vert = 1.21$, $\vert\mu_c\vert = 0.52$	99.0	96.3	0.83	0.61
PF_2Cl[b]	0.890	$\vert\mu_a\vert = 0.103$, $\vert\mu_c\vert = 0.884$	97.3	99.2	0.63	0.58
PF_2CN[c]	2.39	$\vert\mu_a\vert = 2.03$, $\vert\mu_c\vert = 1.27$	99.2	96.9	0.49	2.43
PF_2NH_2[d]	2.576	$\vert\mu_a\vert = 2.570$, $\vert\mu_c\vert = 0.18$	94.6	100.6	1.07	1.76
CF_3PH_2[e]	1.92	$\vert\mu_a\vert = 1.77$, $\vert\mu_c\vert = 0.74$	96.7	91.9	0.56	1.73
$C_3H_5PH_2$[f]	1.158	$\vert\mu_a\vert = 0.810$, $\vert\mu_c\vert = 0.828$	93.7	98.3	0.32	1.17
CH_3PH_2[g]	1.100	$\vert\mu_a\vert = 0.958$, $\vert\mu_c\vert = 0.541$	93.35	97.50	0.38	1.06
$(CH_3)_2PH$[h]	1.23	$\vert\mu_b\vert = 1.15$, $\vert\mu_c\vert = 0.44$	99.72	96.95	0.96	0.38

[a] R. L. Kuczkowski, *J. Amer. Chem. Soc.*, 90, 1705 (1968). [b] A. H. Brittain, J. E. Smith, and R. H. Schwendeman, *Inorg. Chem.*, 11, 39 (1972). [c] P. L. Lee, K. Cohn, and R. H. Schwendeman, *ibid.*, 11, 1917 (1972). [d] A. H. Brittain, J. E. Smith, P. L. Lee, K. Cohn, and R. H. Schwendeman, *J. Amer. Chem. Soc.*, 93, 6772 (1971). [e] I. Y. M. Wang, C. O. Britt, A. H. Cowley, and J. E. Boggs, *J. Chem. Phys.*, 48, 812 (1968). [f] L. A. Dinsmore, C. O. Britt, and J. E. Boggs, *ibid.*, 54, 915 (1971). [g] T. Kojima, E. L. Breig, and C. C. Lin, *ibid.*, 35, 2139 (1961). [h] R. Nelson, *ibid.*, 39, 2382 (1963).

the polarizabilities of the groups on phosphorus are similar can additivity be assumed.[49c]

The structures and dipole moments of $F_3P{\cdot}BH_3$,[55] $HF_2P{\cdot}BH_3$,[56] $(CH_3)_3P{\cdot}BH_3$, and $CH_3PH_2{\cdot}BH_3$[57] have been determined from microwave spectroscopy. Since the perpendicular components of the dipole moments along the axes of rotation of these compounds are available, the group and bond moments of these molecules may be determined if one assumes that the $P\text{-}BH_3$ group moment is the same in the two fluorophosphine-boranes, $F_3P{\cdot}BH_3$ and $HF_2P{\cdot}BH_3$, and the same in the two methylphosphine-boranes, $(CH_3)_3P{\cdot}BH_3$ and $CH_3PH_2{\cdot}BH_3$; also, we need to assume that the P-H bond moment in $HF_2P{\cdot}BH_3$ is the same as in PHF_2 and that the P-H bond moment in $CH_3PH_2{\cdot}BH_3$ is the same as in CH_3PH_2. Use of the same value for the $P\text{-}BH_3$ group moments for $(CH_3)_3P{\cdot}BH_3$ and $CH_3PH_2{\cdot}BH_3$ is based upon the assumption of nearly equal charges on the phosphorus atoms as a result of the small electronegativity differences between the methyl and hydrogen groups on phosphorus and on the essentially equal P-B bond distances in the two molecules (1.901 ± 0.007 Å for $(CH_3)_3P{\cdot}BH_3$ and 1.906 ± 0.006 Å for $CH_3PH_2{\cdot}BH_3$).[57] A similar argument is made for assuming equivalent $P\text{-}BH_3$ group moments in $F_3P{\cdot}BH_3$ and $HF_2P{\cdot}BH_3$ (P-B bond distances are 1.836 ± 0.012[55] and 1.832 ± 0.009 Å,[56] respectively). The assumption of equal P-H bond moments in PHF_2 and $HF_2P{\cdot}BH_3$ is justified by the nearly equal P-H bond distances in the two molecules (1.412 ± 0.006[58] and 1.409 ± 0.004 Å, respectively); hence, essentially equivalent electronic charge separations between phosphorus and hydrogen should exist in both molecules. Contrast this P-H situation with the unequal P-F bond distances in the same two molecules, *e.g.*, P-F = 1.582 ± 0.002[58] and 1.552 ± 0.006 Å in PHF_2 and $HF_2P{\cdot}BH_3$, respectively. The P-H bond moment equivalency in CH_3PH_2 and $CH_3PH_2{\cdot}BH_3$ is justified with the same arguments (in CH_3PH_2, $d_{P\text{-}H} = 1.414$ Å, $d_{P\text{-}C} = 1.863$ Å;[59] in $CH_3PH_2{\cdot}BH_3$, $d_{P\text{-}H} = 1.404 \pm 0.006$ Å, $d_{P\text{-}C} = 1.809 \pm 0.006$ Å).

Using the above structural data a $P\text{-}BH_3$ group moment of 2.58 D for $F_3P{\cdot}BH_3$ and $HF_2P{\cdot}BH_3$ may be calculated; a $P\text{-}BH_3$ group moment of 3.69 D was calculated for $(CH_3)_3P{\cdot}BH_3$ and $CH_3PH_2{\cdot}BH_3$. P-F bond moments of 0.665 and 0.703 D were obtained for $F_3P{\cdot}BH_3$ and $HF_2P{\cdot}BH_3$, respectively, and $P\text{-}CH_3$ group moments of 1.08 and 1.30 D were calculated for $(CH_3)_3P{\cdot}BH_3$ and $CH_3PH_2{\cdot}BH_3$, respectively.

The P-C bond distances in $(CH_3)_3P$, $(CH_3)_3P{\cdot}BH_3$, and $(CH_3)_3PO$ are 1.841 ± 0.003,[60] 1.819 ± 0.010,[57] and 1.813 ± 0.010 Å,[61] respectively. The P-F bond distances in PF_3, $F_3P{\cdot}BH_3$, and F_3PO are 1.5700 ± 0.0012,[62] 1.538 ± 0.008,[55] and 1.5240 ± 0.003 Å,[63] respectively; and the P-F bond distances in PHF_2, $HF_2P{\cdot}BH_3$, and HF_2PO are 1.582 ± 0.002,[58] 1.552 ± 0.006,[56] and 1.539 ± 0.003 Å,[64] respectively. These data show that the P-R bond distances in the boranes and their corresponding oxides are the same within (or nearly within) experimental error, whereas the differences in the P-R bond distances of the parent phosphines and their borane or oxide derivatives vary. If one assumes that the P-R bond distance varies from compound to compound largely as a result of the charge separation between phosphorus and the oxygen or borane group on phosphorus, then it follows that the corresponding P-R bond and group moments in the borane and oxide derivatives of a given phosphine are approximately equal. Assuming that the P-F or $P\text{-}CH_3$ group moments of the oxides are the same as in the corresponding boranes,[65] a knowledge of the structures and dipole moments of F_3PO,[63,66] HF_2PO,[64] and $(CH_3)_3PO$,[61,67] permits calculation of the P-O bond moment of each compound. From a knowledge of the P-O bond distance in each molecule, the P-O charge separation, $\delta\pm$, may be calculated as

$$\mu_{PO} = \text{charge of separation} \times \text{distance of separation}$$

$$\mu_{PO} = (\delta\pm)(4.80)(r_{PO} \text{ in Å})$$

The resulting $P^{\delta+}\text{-}O^{\delta-}$ charge separations in these molecules are presented in Table IV.

At present, it is possible to calculate the $M^{\delta+}X^{\delta-}$ charge separation in the above manner only for the three molecules

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(55) R. L. Kuczkowski and D. R. Lide, Jr., *J. Chem. Phys.*, 46, 357 (1967).

(56) J. P. Pasinski and R. L. Kuczkowski, *J. Chem. Phys.*, 54, 1903 (1971).

(57) P. S. Bryan and R. L. Kuczkowski, *Inorg. Chem.*, 11, 553 (1972).

(58) Reference *a* of Table III.

(59) Reference *g* of Table III.

(60) Reference *g* of Table II.

(61) H. K. Wang, *Acta Chem. Scand.*, 19, 879 (1965).

(62) Reference *d* of Table II.

(63) T. Moritani, K. Kuchitsu, and Y. Morino, *Inorg. Chem.*, 10, 344 (1971).

(64) L. F. Centofanti and R. L. Kuczkowski, *Inorg. Chem.*, 7, 2582 (1968).

(65) The P-F bond moment in HF_2PO was assumed to be the same as in $HF_2P{\cdot}BH_3$. The P-H bond moment along with the PO bond moment could then be calculated from the microwave data of ref 64.

(66) S. J. Senatore, *Phys. Rev.*, 78, 293 (1950).

(67) R. S. Armstrong, M. J. Aroney, R. J. W. Le Fevre, R. K. Pierens, J. D. Saxby, and C. J. Wilkins, *J. Chem. Soc. A*, 2735 (1969).

Table IV. Experimental Dipole Moments, Interatomic Angles, Interatomic Distances, M-X Bond Moments, and M-X Charge Separations of Some Phosphine and Arsine Chalcogenides

Compd	Dipole moment, D	Interatomic angles RMR, deg	M-X bond dist, Å	M-X bond moment, D	M-X charge sepn, δ±
F_3PO	1.735[a]	101.3[b]	1.4356[b]	2.63 (2.67)	0.38 (0.39)
F_2HPO	2.65[c]	HPF = 101.9[c] [RMX: HPO = 117.9[c]] FPF = 99.8[c] [RMX: FPO = 116.3[c]]	1.437[c]	2.43	0.35
Cl_3PO	2.42_5[d]	103.3[b]	1.4487[b]	2.93	0.42
$CH_3C(CH_2O)_3PO$	7.10[e]	103.7[f]	1.464[f]	2.95	0.42
$(C_6H_5)_3PO$	4.51[g]	107.1[h]	1.46[h]	3.27	0.47
$(CH_3)_3PO$	4.29[i]	106.0[j]	1.47_9[j]	3.04 (3.32)	0.43 (0.47)
F_3PS	0.633[k]	100.3[l]	1.87[l]	1.57	0.18
Cl_3PS	1.42[m]	101.8[b]	1.8851[b]	1.95	0.22
$CH_3C(CH_2O)_3PS$	6.77[e]		1.90[n]	2.62	0.29
$(C_6H_5)_3PS$	4.88[g]	106[o]	1.96[p]	3.55	0.38
$(CH_3)_3PS$	4.73[i]	105.93[q]	1.959[q]	3.78	0.40
$(C_6H_5)_3PSe$	5.17[g]	106[r]	2.10[s]	3.73	0.37
$(C_6H_5)_3AsO$	5.51[g]	108[t]	1.644[t]	4.77	0.57
$(CH_3)_3AsO$	5.12[i]	108[u]	1.64[u]	4.38	0.55
$(C_6H_5)_3AsS$	5.43[g]	108[u]	2.24[v]	4.70	0.41
$(CH_3)_3AsS$	5.28[i]	108[u]	2.24[v]	4.54	0.42

[a] Reference 66. [b] Reference 63. [c] Reference 64. [d] N. Hacket and R. J. W. Le Fevre, *J. Chem. Soc.*, 2612 (1961). [e] Reference *j* of Table II. [f] D. M. Nimrod, D. R. Fitzwater, and J. G. Verkade, *J. Amer. Chem. Soc.*, **90**, 2780 (1968). [g] This work. [h] G. Bandoli, G. Bortolozzo, D. A. Clemente, U. Croatto, and C. Panattoni, *J. Chem. Soc. A*, 2778 (1970). [i] Reference 67. [j] Reference 61. [k] N. J. Hawkins, V. W. Cohen, and W. S. Koski, *J. Chem. Phys.*, 20, 528 (1952). [l] Q. Williams, J. Sheridan, and W. Gordy, *ibid.*, 20, 164 (1952). [m] C. P. Smith, A. J. Grossman, and F. B. Jennings, *J. Amer. Chem. Soc.*, 62, 1219 (1940). [n] Assumed the same as in cyclohexane-1(a),3(a),5(a)-thiophosphoric acid ester: P. Andersen and K. E. Hjortaas, *Acta Chem. Scand.*, **14**, 829 (1960). [o] W. W. Schweikert and E. A. Meyers, *J. Phys. Chem.*, 72, 1561 (1968). [p] Assumed to be the same as in $(CH_3)_3PS$. [q] P. G. Eller and P. W. R. Corfield, *Chem. Commun.*, 105 (1971). [r] Assumed to be the same as in $(C_2H_5)_3PSe$: M. Van Meerssche and A. Leonard, *Acta Crystallogr.*, 12, 1053 (1959). [s] Assumed to be the same as in $[(C_2H_5)_2PSe_2]Se$: S. Husbeye and G. Helland-Madsen, *Acta Chem. Scand.*, 23, 1398 (1969). [t] G. Ferguson and E. W. Macaulay, *J. Chem. Soc. A*, 1 (1969). [u] Assumed to be the same as in $(C_6H_5)_3AsO$. [v] Average of 2.23, exocyclic As-S in As_4S_4, and 2.25, exocyclic As-S in As_4S_6: L. E. Sutton, *Chem. Soc., Special Publ.*, No. 11 (1958); *Chem. Soc., Spec. Publ., Suppl.*, No. 11 (1956-1959).

F_3PO, HF_2PO, and $(CH_3)_3PO$. However, it is possible to calculate the M-X bond moments and $M^{\delta+}X^{\delta-}$ charge separations in a number of phosphine and arsine chalcogenides possessing C_{3v} symmetry, provided that their structural parameters and those of their parent phosphine or arsine are known and provided one assumes that the M-R bond or group moments in the parent phosphine or arsine are identical with the corresponding group moments in the chalcogenide derivative. M-X bond moments and $M^{\delta+}X^{\delta-}$ charge separations of several such molecules are presented in Table IV. The μ_{MX} and δ±(MX) values given in Table IV in parentheses are the values of F_3PO and $(CH_3)_3PO$ calculated by the latter method for purposes of comparison with the μ_{MX} and δ±(M-X) values obtained by the former calculation method.

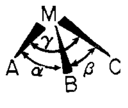
Included in Tables II and IV are the dipole moments of the constrained cage phosphite ester 1-methyl-4-phospha-3,5,8-trioxabicyclo[2.2.2]octane and its phosphate and thiophosphate derivatives.[68] Since the internal bond angles can be assumed to be virtually the same in all three compounds, the PO and PS bond moments are obtained simply from the differences in dipole moments of the phosphate and phosphite and of the thiophosphate and phosphite, respectively.

Despite the electronegativity of oxygen, the dipole moment of $CH_3C(CH_2O)_3P$ is directed toward phosphorus, apparently because of pπ-dπ electron donation from the oxygen atoms to phosphorus.[69] In a like manner a $P-BH_3$ group moment of 4.45 D in $CH_3C(CH_2O)_3P \cdot BH_3$ may be obtained from the difference between its dipole moment (8.60 D)[69] and that of $CH_3C(CH_2O)_3P$. Compare this value with the $P-BH_3$ group moments of $F_3P \cdot BH_3$ (2.58 D) and $(CH_3)_3P \cdot BH_3$ (3.69 D) calculated earlier. With no pπ-dπ back-bonding from B to P possible, the $P-BH_3$ group moment is affected greatly by the electron-withdrawing or -releasing character of the R groups on phosphorus.

Discussion

The trends in the magnitudes of δ± in Table IV could have been predicted on the basis of electronegativity considerations. Note the large differences in δ± among $(C_6H_5)_3AsO$, $(C_6H_5)_3PO$, and $(C_6H_5)_3AsS$ and the small differences in δ± among $(C_6H_5)_3AsS$, $(C_6H_5)_3PSe$, and $(C_6H_5)_3PS$. Note, also, the large effect that the substituent groups have on δ± of the P-O and P-S bonds. Increasing electronegativity of the substituent groups causes the charge separation of these bonds to decrease markedly, indicating an increase in pπ-dπ (X→P) bonding. Although the magnitude of charge separation in a thiophosphoryl compound is smaller than the charge separation in its phosphoryl analog, the decrease in δ± from R_3PS to R'_3PS is more than double the decrease in δ± from R_3PO to R'_3PO in all cases. The decreased magnitude of charge may result from the fact that the PS bond is more easily polarized than the PO bond.

Although it was noted that additivity of group moments does not hold in compounds of the type in Table III, it probably is a valid assumption in the case of unsymmetrical alkyl-, aryl-, or alkylarylphosphines or -arsines, owing to the small changes in electronegativities of the groups. If the bond angles are known, or can be assumed, and group moments from the symmetrical molecules are used (Table II), then the net dipole moment of a molecule of the type



I

is given by the equation[70,71]

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(68) Reference *j* of Table II.

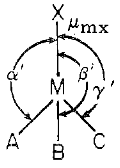
(69) J. G. Verkade, *Coord. Chem. Rev.*, 9, 1 (1972).

(70) J. E. Mackey, Jr., personal communication, Department of Physics, The Ohio State University.

$$\mu_T^2 = \mu_1^2 + \mu_2^2 + \mu_3^2 + 2\mu_1\mu_2 \cos\alpha + 2\mu_2\mu_3 \cos\beta + 2\mu_1\mu_3 \cos\gamma$$

where μ_T is the net dipole moment of the molecule; μ_1, μ_2, and μ_3 are the MA, MB, and MC group moments, respectively; and α, β, and γ are the AMB, BMC, and AMC angles, respectively.

For a molecule of the type XM(ABC)



II

a similar vector equation can be obtained[70]

$$\mu_T^2 = \mu_{MX}^2 + \mu_1^2 + \mu_2^2 + \mu_3^2 + 2\mu_{MX}\mu_1 \cos\alpha' + 2\mu_{MX}\mu_2 \cos\beta' + 2\mu_{MX}\mu_3 \cos\gamma' + 2\mu_1\mu_2 \cos\alpha + 2\mu_2\mu_3 \cos\beta + 2\mu_1\mu_3 \cos\gamma$$

where the terms defined above still apply and where μ_{MX} is the bond moment of the M-X bond and α', β', and γ' are the XMA, XMB, and XMC angles, respectively.

Thus if $(CH_3)_2C_6H_5PS$ and $CH_3(C_6H_5)_2PS$ are assumed to have the same interatomic angles as $(CH_3)_3PS$,[72] application of the vector equation yields values of 3.70 and 3.59 for μ_{PS}, respectively. Thus μ_{PS} for the series $(C_6H_5)_3PS$, $CH_3(C_6H_5)_2PS$, $(CH_3)_2C_6H_5PS$, and $(CH_3)_3PS$ are 3.55, 3.59, 3.70, and 3.78 D, respectively, suggesting that the P-S bond becomes more polar as the phenyl groups are replaced by methyl groups.

The dipole moments measured for $(CH_3)_2C_6F_5PS$ and $(CH_3)_2C_6H_5PS$ are 4.43 and 4.80 D, respectively. Is the difference in the dipole moments of these two compounds due essentially to the replacement of five hydrogen atoms on the phenyl ring with five fluorine atoms? The following calculation suggests that this is the case. The bond moments of the fluorine atoms in the ring positions 2, 3, 5, and 6 cancel vectorially owing to their spatial orientations. Hence, one needs to consider only the effect of replacing the para hydrogen with a fluorine. A common practice of assigning group moments in aryl compounds is to assume that the CH bond moments are zero.[73] If this is done, then the C-F bond moment in aromatic compounds can be assigned from the experimental dipole moment of fluorobenzene. Several values for the dipole moment of fluorobenzene are reported,[74] the average being 1.46 D. If this value is taken as the difference between $\mu_{CF(aromatic)}$ and $\mu_{CH(aromatic)}$ and $(CH_3)_2C_6H_5PS$ and $(CH_3)_2C_6F_5PS$ are assumed to have the same interatomic angles as $(CH_3)_3PS$[72] *and* if the net moment of $(CH_3)_2C_6H_5PS$ is taken to be along the PS group moment [this is a good assumption, since the μ_{PS} moment is the predominant moment of the molecule], then replacement of the para hydrogen with a fluorine results in a vector of magnitude 1.46 D acting at an angle of 113.2° to a vector of 4.80 D, which is the experimentally measured dipole moment of $(CH_3)_2C_6H_5PS$. Resolution gives a net vector of 4.43 D, exactly the measured moment of $(CH_3)_2C_6F_5PS$.

The values of μ_{PO} and μ_{PS} for $C_2H_5(C_6H_5)_2PO$ and $C_2H_5(C_6H_5)_2PS$ were calculated to be 3.82 and 3.45 D, respectively, using the interatomic angles of $(C_6H_5)_3PO$ and $(CH_3)_3PS$ (Table IV) and the value of $\mu_{EtP} = 0.94$ D as determined by Parry and coworkers.[51] This value for $C_2H_5(C_6H_5)_2PO$ is quite large compared to the values of μ_{PO} obtained for $(C_6H_5)_3PO$ (3.27 D) and $(CH_3)_3PO$ (3.04 D). On the other hand, the μ_{PS} for $C_2H_5(C_6H_5)_2PS$ is low compared to that observed for $(C_6H_5)_3PS$ (3.55 D) and $(CH_3)_3PS$ (3.78 D). Perhaps these anomalous values for μ_{PO} and μ_{PS} result from rotational conformers of the ethyl group. If preferred conformers of this group vary significantly from molecule to molecule, then application of the vector equation as described in this paper will be inappropriate.

A meaningful vector calculation of the dipole moments in the molecules $[(CH_3)_2N]_3PS$, $[(CH_3)_2N](C_6H_5)_2PS$, $[(CH_3)_2N](C_6H_5)_2PSe$, $[(CH_3)_2N]_3PO$, and $(CH_3O)_3PS$ has been precluded by insufficient data on the dipole moments and/or structural parameters of these molecules and their parent phosphines. However, in view of the fact that all of these compounds have substituent groups which could be expected to have rotational conformers as well, interpretation of the calculations on these molecules would be tenuous at best.

Conclusions

The experimental moments of the tertiary phosphine and arsine chalcogenides used in this work and in previous studies cited earlier show that (1) the arsine compounds are more polar than the corresponding phosphine compounds, (2) the polarity of tertiary phosphine derivatives increases in the series oxide < sulfide < selenide, and (3) electronegative groups decrease the polarity of the derivative. Group bond moments, which were calculated from the net dipole moments of the molecule and the known structural parameters, give trends that follow electronegativities of the group and permit calculation of chemically reasonable M-X charge separations. Within a derivative series, *e.g.*, the oxides, the magnitude of $\delta\pm$ decreases with increasing electronegativity of the group. For a given group, *e.g.*, C_6H_5, the charge separation produces the trend oxide > sulfide ≈ selenide.

The observed dipole moments and the calculated charge separations give consistent correlations with previous chemical and physical studies that have been concerned with the donor properties, bond orders, and bond energies of the M-X bond. For example, infrared studies and bond energies of phosphoryl and thiophosphoryl compounds suggest much greater double-bond character in the phosphorus-oxygen bond than in the phosphorus-sulfur bond, which is consistent with the fact that the electronegativity of the R group on phosphorus has a greater effect on the $\delta\pm$ values of the sulfides than on the $\delta\pm$ values of the corresponding oxides. Proton and phosphorus-31 nmr data can also be interpreted in terms of a lower bond order (and concomitant less π bonding) in analogous thiophosphoryl compounds. Also, the donor properties of phosphoryl compounds decrease as the electronegativity of the substituents on phosphorus increase, which suggests more π bonding and less negative charge on oxygen, as observed in this study.

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[71] For a symmetrical trigonal-pyramidal molecule (A = B = C, $\alpha = \beta = \lambda$), this equation simplifies to that of G. Kodama, J. R. Weaver, J. La Rochelle, and R. W. Parry, *Inorg. Chem.*, **5**, 710 (1966).

[72] Reference *q* of Table IV.

[73] Reference 46c, p 96.

[74] A. L. McClellan, "Tables of Experimental Dipole Moments," Freeman, San Francisco, Calif., 1963.

discussions with Professor P. W. R. Corfield concerning the vector calculations.

Registry No. $C_2H_5(C_6H_5)_2PO$, 1733-57-9; $(CH_3)_2C_6H_5PS$, 1707-00-2; $(CH_3)_2C_6F_5PS$, 19100-54-0; $CH_3(C_6H_5)_2PS$, 13639-74-2; $C_2H_5(C_6H_5)_2PS$, 1017-98-7; $[(CH_3)_2N](C_6H_5)_2PS$, 17513-68-7; $[(CH_3)_2N]_3PS$, 3732-82-9; $(CH_3O)_3PS$, 152-18-1; $[(CH_3)_2N](C_6H_5)_2PSe$, 23486-86-4; F_3PO, 13478-20-1; F_2HPO, 14939-34-5; Cl_3PO, 10025-87-3; $CH_3C(CH_2O)_3PO$, 1449-89-4; $(C_6H_5)_3PO$, 791-28-6; $(CH_3)_3PO$, 676-96-0; F_3PS, 2404-52-6; Cl_3PS, 3982-91-0; $CH_3C(CH_2O)_3PS$, 3196-56-3; $(C_6H_5)_3PS$, 3878-45-3; $(CH_3)_3PS$, 2404-55-9; $(C_6H_5)_3PSe$, 3878-44-2; $(C_6H_5)_3AsO$, 1153-05-5; $(CH_3)_3AsO$, 4964-14-1; $(C_6H_5)_3AsS$, 3937-40-4; $(CH_3)_3AsS$, 26386-93-6.

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Electronic Structures of Phosphorus Pentafluoride and Tetrafluorophosphorane

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Ab initio LCAO-MO-SCF calculations were carried out on the PF_5 and PF_4H molecules, employing moderately small gaussian basis sets. Using the resulting wave functions, it was found that the molecular orbitals of these two molecules are readily interrelated with respect to their detailed electron density distributions. A further such interrelationship was carried out between the molecular orbitals of PF_5 and those of the PF_3 and OPF_3 molecules.

Introduction

According to the standard valence-bond picture used by chemists, it is necessary to employ d atomic orbitals (the sp^3d hybrid[1]) to describe pentacoordinate phosphorus. However, it has been known[2] for a number of years that such structures may alternatively be described using only s and p atomic orbitals, and this approach has been delineated in a recent semiempirical study.[2b] In the study reported herein, we have carried out *ab initio* calculations of the wave functions of the PF_5 and PF_4H molecules using a small number of s and p functions in the basis set. Further calculations were made by adding to these s and p functions sufficient d functions so that adequate d character was allotted to the phosphorus atom to permit the d atomic orbitals to participate in the basic σ structure of the molecular orbitals in addition to allowing charge feedback to the phosphorus and polarization of its s and p orbitals. The resulting wave functions were employed to evaluate the similarity between the orbitals of PF_5 and PF_4H. A further inquiry was made into the possible interrelationships of the PF_5 molecular orbitals with those of the related compounds OPF_3 and OPF_2H, the orbitals of which have previously been correlated[3] with each other and with the orbitals of PF_3 and PF_2H. After this paper had been completed, another *ab initio* study of phosphorus pentafluoride appeared in the literature.[4]

Calculational Details

The bond distances in the PF_5 molecule of D_{3h} symmetry were taken to be 1.534 Å for the equatorial fluorine atoms and 1.577 Å for the axial, as determined by electron diffraction.[5] For the PF_4H molecule with the hydrogen in the equatorial position to give C_{2v} symmetry, the following geometry based on microwave spectroscopy[6] was employed: $P\text{-}F_{eq} = 1.550$ Å, $P\text{-}F_{ax} = 1.594$ Å, $P\text{-}H = 1.360$ Å, $\angle F_{eq}PH = 124°$, $\angle F_{ax}PH = 90°$. The *ab initio* calculations were carried out with an atom-optimized uncontracted gaussian basis set using nine s- and five p-type exponents to describe the phosphorus atom,[7] five s- and two p-type for each fluorine,[8] and three s-type for the hydrogen;[7] *i.e.*, the PF_5 molecule without d orbitals was described in a (95/52) and the PF_4H in a (95/52/3) basis set. These basis sets were expanded to (952/52) for PF_5 and (952/52/3) for PF_4H, using exponents[9] of 0.27 and 1.55 for the added pair of spherically harmonic fivefold sets of d functions. Note that the (52) description of fluorine was employed even though it was recognized to be only marginally adequate for such an electrophilic atom. Since 10 individual functions were added to a set of only 24 such functions by going from a (95) to a (952) basis set for the phosphorus, the d orbitals placed on this atom may possibly substitute for a paucity of s and p character in the molecule.

The SCF calculations were carried out using an uncontracted basis set with the program POLYATOM.[10] The electron densities were first calculated[11] and then converted into computer-made three-dimensional cross-sectional plots by a subsidiary program.[12] The Mulliken populations were separately calculated[13] for each molecular orbital with respect to (a) all of the individual gaussian basis functions, (b) the basis functions of each symmetry, and (c) the atomic centers.

Results and Discussion

Overall Properties of PF_5 and PF_4H. The total energy and

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