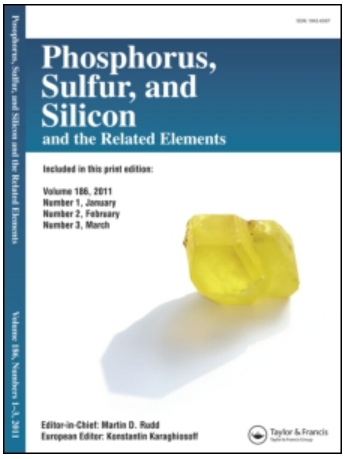

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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Online publication date: 19 November 2010

To cite this Article Gökçınar, Elif , Karaghiosoff, Konstantin , Klapötke, Thomas M. , Evangelisti, Camilla and Rotter, Christiane(2010) 'Structure and Bonding in the Trichalcogenometaphosphate-Pyridine Anions $[PX_3 - Py]^-$ (X = O, S, Se, Te)', Phosphorus, Sulfur, and Silicon and the Related Elements, 185: 12, 2527 — 2534
To link to this Article: DOI: 10.1080/10426501003724913
URL: http://dx.doi.org/10.1080/10426501003724913

Phosphorus, Sulfur, and Silicon, 185:2527–2534, 2010

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426501003724913

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STRUCTURE AND BONDING IN THE TRICHALCOGENOMETAPHOSPHATE–PYRIDINE ANIONS $[PX_3 - Py]^-$ (X = O, S, Se, Te)

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The structures, bonding, NMR chemical shifts, and Lewis acid/base behavior of the trichalcogenometaphosphate–pyridine anions $[PX_3 - Py]^-$ (X = O, S, Se, Te) have been evaluated theoretically on the basis of B3LYP/ECP(Se,Te) + cc-pVTZ//PM3 calculations using quasirelativistic pseudopotentials for Se and Te. The molecular and electronic structures of the trichalcogenometaphosphate–pyridine adducts $[PX_3 - Py]^-$ (X = O, S, Se, Te) were calculated, and the bonding was analyzed and discussed on the basis of natural bond orbital (NBO) analyses and qualitative valence bond (VB) considerations. The $(\sigma(p_x)$-LP(N)) → $(\sigma(p_x)$-LP*(P)) donor–acceptor interaction increases, and, consequently, the P—N bond length decreases from $PO_3 - Py^-$ (weak interaction, long P—N bond) to $PTe_3 - Py^-$ (strong interaction, short P—N bond). This theoretical finding is in good accord with the measured P—N bond lengths in $[PSe_3 - Py]^-$ and $[PTe_3 - Py]^-$. In the gas phase, all four $[PX_3 - Py]^-$ (X = O, S, Se, Te) adducts are unstable with respect to dissociation into free PX_3^- and pyridine.

Keywords Acidity/basicity; calculations; NMR shifts; trichalcogenometaphosphate anions; VB structures

INTRODUCTION

In the series of the trichalcogenometaphosphate anions PX_3^- (X = O, S, Se, Te), only the sulfur and, quite recently, the selenium species have been synthesized and characterized experimentally. Although the trithiometaphosphate PS_3^- was mentioned first in 1986,[1] it was not until 2005 that its structure was determined by X-ray diffraction.[2] In 2009, two of us (Rotter and Karaghiosoff) then reported on the synthesis and structural characterization of the selenium analogue.[3] Both trichalcogenometaphosphate anions exist in the crystal as a pyridine adduct of the type $[X_3P - Py]^-$ (X = S, Se). The experimental observation

Received 27 January 2010; accepted 23 February 2010.

Financial support of this work by the Ludwig-Maximilian University of Munich (LMU) and the U.S. Army Research Laboratory (ARL) under contract no. W911NF-09-2-0018 is gratefully acknowledged. E.G. acknowledges financial support by TÜBİTAK (PhD studies in Ankara) and the EU ERASMUS program (study leave in Munich).

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that the P—N bond length in the Se species [1.853(2) Å] is significantly shorter than in the sulfur anion [1.906(2)–1.922(2) Å][2,3] gave rise to the question about the structure and bonding within the trichalcogenometaphosphate–pyridine anions $[PX_3 - Py]^-$ (X = O, S, Se, Te). For the neutral and isovalent-electronic boron species BY_3 (Y = F, Cl, Br, I), it is well known that the acidity increases from BF_3 to BI_3.[4] However, this effect is often attributed to the decrease in the π bond strength from BF_3 to BI_3 and hence the energetically easier pyramidalization of the heavier homologues. The strong π bonds in BF_3 in turn are rationalized by the similar p_π-orbital size centered at B and F since both elements are in the same (second) period of the periodic table. For the above mentioned trichalcogenometaphosphate anions PX_3^- (X = O, S, Se, Te), which are the subject of this study, the situation is not as clear as it is for the boron halides. In terms of the covalent radius, the central P atom ($r_{cov.} = 1.10$ Å) is closest to sulfur and selenium [$r_{cov.} =$ 0.66 (O), 1.04 (S), 1.17 (Se), 1.37 (Te) Å],[4] whereas positive partial charge at the P atom is expected to decrease from PO_3^- to PTe_3^- due to the decreasing electronegativity from oxygen to tellurium [$\chi_M = 7.6$ (O), 6.3 (S), 5.9 (Se), 5.5 (Te) eV; χ_M = Mulliken electronegativity; $\chi_P = 3.5$ (O), 2.4 (S), 2.5 (Se), 2.0 (Te); χ_P = Pauling electronegativity].[4] This prompted us to investigate computationally the bonding situation in the series of the trichalcogenometaphosphate–pyridine anions $[PX_3 - Py]^-$ (X = O, S, Se, Te), of which only the S and Se species have been prepared, whereas, as far as we are aware, neither the oxygen nor the tellurium derivatives have been reported (neither as free PX_3^- nor as the pyridine adducts $[PX_3 - Py]^-$ with X = O, Te).

RESULTS AND DISCUSSION

Computational Results

Semiempirical molecular orbital methods have a long history. They serve to tackle larger systems. Although their setup is derived from Hartree–Fock theory, the design of approximate energy expressions and the empirical parameters are used to achieve higher accuracy than the underlying ab initio theory.[5,6] In this way, the effect of electron correlation can be partially simulated. All widely used semiempirical methods establish their accuracy by error statistics for molecular properties with experimental and high-level ab initio or density functional theory calculations as a reference. The PM3 method has very successfully been applied for S, Se, and Te containing systems.[7–9] We therefore decided to also use this semiempirical method to calculate the structures of the trichalcogenometaphosphate–pyridine anions $[PX_3 - Py]^-$ (X = O, S, Se, Te). The trichalcogenometaphosphate–pyridine anions $[PX_3 - Py]^-$ (X = O, S, Se, Te) are bound at PM3 level of theory (Table I, *NIMAG* = 0); however, they are not bound at the B3LYP level, and coupled cluster methods are too expensive to treat the 10 heavy electron systems. This again shows the suitability of semiempirical methods for rather large (many heavy atoms) systems where electron correlation plays an important role.

The computational results (point groups, electronic energies, NBO charges, and bond lengths between P and N) for PX_3^- and $[PX_3 - Py]^-$ (X = O, S, Se, Te) are summarized in Table I. The B3LYP/ECP(Se,Te)+cc-pVTZ//PM3 calculations clearly reproduce the experimentally observed (for S and Se) decrease in the unexpected P—N bond length from $[PO_3 - Py]^-$ (2.44 Å) to $[PTe_3 - Py]^-$ (1.87 Å). The computed positive NBO charges at P increase from +0.3 e ($[PTe_3 - Py]^-$) to 2.39 e ($[PO_3 - Py]^-$), as expected.

Table I Computational results for PX_3^- and $[PX_3 - Py]^-$ (X = O, S, Se, Te)

	Pg	E^{PM3}/Au	zpe^{PM3}/kcal mol^{-1} [kJ mol^{-1}]	*NIMAG*	$-E^{B3LYP}$/Au	NBO^{B3LYP} charge/e X	P	N	*d*(P—N)/Å calcd./exptl.
Py	C_{2v}	+0.048249	54.3 [227.2]	0	248.371118	—	—	−0.43	—
PO_3^-	D_{3h}	−0.314336	5.6 [23.4]	0	567.289610	−1.11	2.32	—	—
PS_3^-	D_{3h}	−0.065301	3.4 [14.2]	0	1536.211181	−0.59	0.78	—	—
PSe_3^-	D_{3h}	−0.054862	2.4 [10.0]	0	369.619332	−0.47	0.40	—	—
PTe_3^-	D_{3h}	−0.094669	1.3 [5.4]	0	365.794340	−0.29	−0.14	—	—
$[O_3P - Py]^-$	C_s	−0.244443	60.2 [251.9]	0	815.659732	−1.15	2.39	−0.43	2.44
$[S_3P - Py]^-$	C_s	−0.002639	58.2 [243.5]	0	1784.567719	−0.69	0.95	−0.48	2.11/1.92
$[Se_3P - Py]^-$	C_s	−0.027876	57.5 [240.6]	0	617.956199	−0.58	0.69	−0.53	1.93/1.85
$[Te_3P - Py]^-$	C_s	−0.095788	56.7 [237.2]	0	614.123404	−0.47	0.30	−0.55	1.87

In order to rationalize the observed and computed trends in the P—N bond lengths, we also calculated the energy lowering due to a donor ($\sigma(p_x)$-LP(N)) → acceptor ($\sigma(p_x)$-LP*(P)) interaction via NBO analysis. As it is apparent from Table II that the ($\sigma(p_x)$-LP(N)) → ($\sigma(p_x)$-LP*(P)) interaction increases steadily and significantly from $[PO_3 - Py]^-$ (23.9 kcal mol^{-1}, 100.0 kJ mol^{-1}) to $[PTe_3 - Py]^-$ (223.8 kcal mol^{-1}, 936.4 kJ mol^{-1}). This already accounts for the shorter P—N bond in the Te species. Moreover, the $\sigma(p_x)$-LP*(P) acceptor orbital at the P atom decreases in energy from the O compound (+0.12) to the Te species (−0.05), which allows a better (stronger) interaction with the donating ($\sigma(p_x)$-LP(N)) orbital at the pyridine N atom.

In terms of qualitative valence bond (VB) considerations (Figure 1) out of the three resonance structures **I**–**III**, structure **II** with four σ bonds should have highest weight followed by structure **III** (three times) with three σ and one π bond and structure **I** having the lowest weight (sextet structure). From the NBO analysis (partial charges, Table I; occupancies, Table II) it is also apparent that the *no-bond* Lewis-type structures **III** (three times) and much less so the sextet structure **I** (Figure 1) are relatively more important for the anion $[PO_3 - Py]^-$ than for the heavier S, Se, and Te analogues, for which Lewis-type structures of type **II** are even more important contributors to the resonance scheme.

Although at the level of theory applied, all four $[PX_3 - Py]^-$ anions (X = O, S, Se, Te) are weakly bound species in the gas phase, they all are unstable with respect to

Table II NBO donor–acceptor interaction energy: LP(1)N5 → LP*(1)P1

	$E^{(2)}$ [a]/kcal mol^{-1} [kJ mol^{-1}]	Valence p_x @ P (in PX_3 unit) E/eV	Occupancy/e	Valence p_x @ N (in NC_5H_5 unit) E/eV	Occupancy/e
$[O_3P - Py]^-$	23.9 [100.0]	+0.12	0.65	−0.12	1.65
$[S_3P - Py]^-$	106.5 [445.6]	0.00	0.82	−0.17	1.56
$[Se_3P - Py]^-$	198.8 [831.8]	0.01	0.80	−0.20	1.53
$[Te_3P - Py]^-$	223.8 [936.4]	−0.05	1.07	−0.20	1.37

[a]Energy according to a second-order perturbation theory analysis of the Fock matrix in the NBO basis.

Table III Reaction profile for $[PX_3 - Py]^-$ (X = S, Se, Te)

	$[PS_3 - Py]^-$		$[PSe_3 - Py]^-$		$[PTe_3 - Py]^-$	
d(P—N)/Å	$-E^{B3LYP//PM3}$/ Au	$E_{rel.}$/kcal mol^{-1} [kJ mol^{-1}]	$-E^{B3LYP//PM3}$/ Au	$E_{rel.}$/kcal mol^{-1} [kJ mol^{-1}]	$-E^{B3LYP//PM3}$/ Au	$E_{rel.}$/kcal mol^{-1} [kJ mol^{-1}]
1.90	—	—	617.954813	0.0 [0.0]	614.124921	0.0 [0.0]
2.10	1784.567685	0.0 [0.0]	617.961733	−4.3 [−18.0]	614.125226	0.2 [0.8]
2.30	1784.570715	−1.9 [−7.9]	617.965953	−6.9 [−28.9]	614.135418	−6.6 [−27.6]
2.50	1784.572222	−2.8 [−11.7]	617.973290	−11.6 [−48.5]	614.144871	−12.5 [−52.3]
2.70	1784.574073	−4.0 [−16.7]	617.977916	−14.5 [−60.7]	614.149298	−15.3 [−64.0]
2.90	1784.575359	−4.8 [−20.1]	617.979846	−15.7 [−65.7]	−614.153871	−18.2 [−76.1]
3.10	1784.576060	−5.3 [−22.2]	617.980811	−16.3 [−68.2]	614.156363	−19.7 [−82.4]
3.30	1784.576470	−5.5 [−23.0]	617.981592	−16.8 [−70.3]	614.158119	−20.8 [−87.0]
3.5	1784.576820	−5.7 [23.8]	617.982327	−17.3 [−72.4]	614.158920	−21.3 [89.1]

Table IV *zpe* corrected dissociation energies according to Eq. (1)

Eq. (1)	$\Delta E^{zpe\ corrected}$/kcal mol^{-1} [kJ mol^{-1}]
O	−0.97 [−4.1]
S	−9.73 [−40.7]
Se	−22.27 [−93.2]
Te	−27.56 [−115.3]

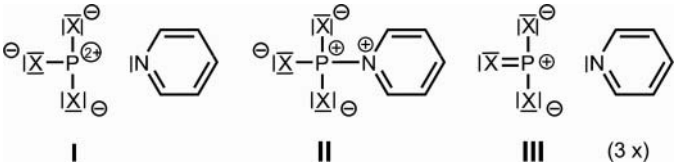

Figure 1 Lewis-type VB structures for $[PX_3 - Py]^-$ (X = O, S, Se, Te).

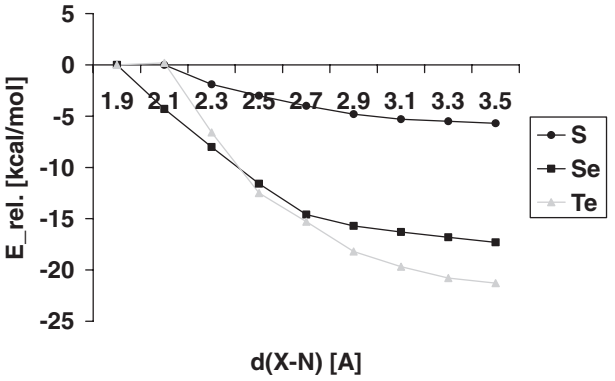

Figure 2 Reaction profile for the dissociation of $[PX_3 - Py]^-$ into PX_3^- and Py (X = S, Se, Te).

dissociation, according to Eq. (1).

$$PX_3 - Py^- \text{ (g)} \rightarrow PX_3^- \text{ (g)} + Py \text{ (g)} \quad (1)$$

The two-dimensional dissociation potentials are shown in Figure 2 (and Table III), and the corresponding *zpe* (zero point energy) corrected dissociation energies are summarized in Table IV.

The fact that the $[PTe_3 - Py]^-$ anion is the least stable compound with respect to dissociation but possesses the shortest P—N bond and the highest ($\sigma(p_x)$-LP(N)) → ($\sigma(p_x)$-LP*(P)) donor–acceptor interaction energy is only an apparent contradiction. If we "force" the $[PX_3 - Py]^-$ anion to be bound (very shallow minimum, see above), the Lewis-type structure **II** is more important for the Te anion, whereas the structure **III** has a relatively higher weight for the O containing anion (see above). Hence, in the bound pyridine adduct, the P—N bond interaction is stronger in the Te- than in the O-containing species. In contrast, dissociation of $[PTe_3 - Py]^-$ into PTe_3^- and pyridine releases the most energy because of the more favorable re-hybridization of the P atom from $[PTe_3 - Py]^-$ to PTe_3^- [Eqs. (2a) and (2b)]. In other words, in $[PO_3 - Py]^-$, the interaction energy is weaker (P—N bond longer) and the PO_3^- moiety resembles more the dissociated (more favorable) species, but therefore less energy is released upon dissociation.

$$[PTe_3 - Py]^- \text{ (Lewis-type structure } \mathbf{II}) \rightarrow PTe_3^- + Py \quad (2a)$$

$$[PO_3 - Py]^- \text{ (Lewis-type structure } \mathbf{III}) \rightarrow PO_3^- + Py \quad (2b)$$

$$|\Delta E(2a)| > |\Delta E(2b)|$$

The generally remarkably reduced acidity of the trichalcogenometaphosphate anions PX_3^- (X = O, S, Se, Te) compared with the formally valence isoelectronic boron trihalides BY_3 (Y = F, Cl, Br, I) can be attributed to the fact that in the predominant Lewis structure of the free acid (one double bond, two single bonds) one of the Y halogen atom carries one positive formal charge, whereas two of the X chalcogen atoms carry one negative charge each. This is less favorable for the electropositive halogen atoms than for the chalcogen atoms. Therefore the Lewis base adduct Y_3B-Py with formally neutral halogen atoms is much more favorable than the free acid BY_3, whereas in the case of the trichalcogenometaphosphate anions with respect to formal charge separation, the free acid PX_3^- and the Lewis base adduct $[PX_3 - Py]^-$ are equally favorable; hence the boron adducts are relatively speaking more preferred.

We also calculated the ^{31}P NMR chemical shifts for free PX_3^- and the $[PX_3 - Py]^-$ adducts (X = O, S, Se, Te) in order to compare the values with the experimental data for the

Table V Computed isotropic magnetic shieldings (GIAO method,[25–28] MPW1PW91/aug-cc-pVTZ) and relative ^{31}P NMR chemical shifts δ (ppm) referenced to H_3PO_4

	Abs. isostropic shielding	Rel. shift, δ	Exptl. δ[34]
H_3PO_4	+330.3	0.0	0.0
PS_3^-	+14.1	+316.2	+297.5
PSe_3^-	−75.7	+405.3	+212.2
$[PS_3 - Py]^-$	+91.0	+239.3	+223.9 (25°C)
$[PSe_3 - Py]^-$	+96.0	+234.3	+200.6 (25°C)

S and Se species. (Unfortunately, there have been no ^{15}N NMR shifts reported in the literature.) The qualitatively reasonable agreement between the computed and experimentally observed chemical shifts (Table V) provides further credence that the applied electronic models for free PX_3^- and the $[PX_3 - Py]^-$ adducts describe the systems reasonably well.

CONCLUSIONS

From this computational study the following conclusions can be drawn:

(i) The molecular and electronic structures of the trichalcogenometaphosphate pyridine adducts $[PX_3 - Py]^-$ (X = O, S, Se, Te) were calculated at the B3LYP/ECP(Se, Te)+cc-pVTZ//PM3 level of theory, and the bonding was analyzed and discussed on the basis of natural bond orbital (NBO) analyses and qualitative valence bond (VB) considerations.

(ii) The $(\sigma(p_x)\text{-LP(N)}) \rightarrow (\sigma(p_x)\text{-LP}^*(P))$ donor–acceptor interaction increases and consequently the P—N bond length decreases from $PO_3 - Py^-$ (weak interaction, long P—N bond) to $PTe_3 - Py^-$ (strong interaction, short P—N bond). This theoretical finding is in good accord with the measured P—N bond lengths in $[PSe_3 - Py]^-$ and $[PTe_3 - Py]^-$.

(iii) In the gas phase, all four $[PX_3 - Py]^-$ (X = O, S, Se, Te) adducts are unstable with respect to dissociation into free PX_3^- and pyridine.

(iv) Since in $[PO_3 - Py]^-$ the P—N donor–acceptor interaction is the weakest, the PO_3 moiety in the adduct resembles free PO_3^- more than do the heavier PX_3 units resemble free PX_3^- (X = S, Se, Te); therefore the dissociation of $[PO_3 - Py]^-$ is less exothermic than that of the heavier chalcogen congeners.

(v) The computed ^{31}P NMR chemical shifts are in good agreement with the experimentally observed values (where available), which gives credence to the reliability of the applied electronic model.

EXPERIMENTAL

All calculations were performed using the G03W code.[10] The structures were fully optimized without symmetry constraints at the PM3 level of theory. True minima (*NIMAG* = 0) were established, and zero point energies calculated via frequency analyses. The PM3 method differs from AM1 only by the values of the parameters in such a way that non-bonded interactions are less repulsive in PM3 than in AM1.[11,12] For this reason, we chose PM3 as the self-consistent field (SCF) method for the structure calculations. In order to obtain more reliable energies, single-point calculations were carried out using the gradient-corrected hybrid three-parameter B3LYP[13,14] functional, because previous theoretical calculations have shown that B3LYP in combination with quasirelativistic energy consistent MWB pseudopotentials of the Stuttgart–Dresden group is a cost-effective and reliable method for studying heavy chalcogen-containing systems;[15] cc-pVTZ basis set for the elements H, C, N, P, and S[16–19] and MWB for selenium and tellurium;[20,21] Se: ECP28MWB + (14s10p2d1f)/[3s3p2d1f] valence basis set, Te: ECP46MWB + (15s11p3d1f)/[3s3p2d1f] valence basis set. The natural bond orbital analyses (NBO analyses) were performed using the NBO 3.0 program by Weinhold and colleagues.[22–29] In order to calculate the NMR chemical shifts for ^{31}P, the isotropic magnetic shieldings were computed using the GIAO

(gauge-independent atomic orbital) method implemented in G03.[10,30–33] The NMR shielding tensors were calculated at the MPW1PW91/aug-cc-pVTZ level of theory using the GIAO method.[30–33] Table V summarizes the computed isotropic magnetic shieldings and relative ^{31}P NMR chemical shifts (ppm) referenced to H_3PO_4.

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