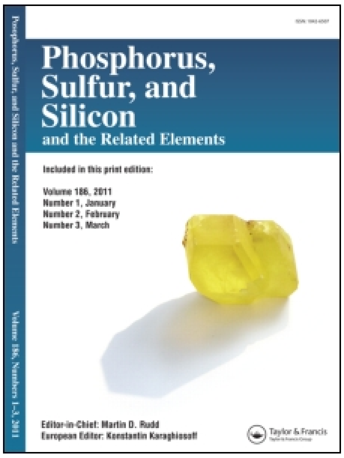

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Timoshkin, Alexey Y.(2001) 'Comparative DFT Study of Group 13-15 Rings: Structure, Bonding and Thermochemistry', Phosphorus, Sulfur, and Silicon and the Related Elements, 168: 1, 275 — 280

To link to this Article: DOI: 10.1080/10426500108546567

URL: http://dx.doi.org/10.1080/10426500108546567

Phosphorus Sulfur and Silicon, 2001, Vol. 168, pp. 275-280
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Comparative DFT Study of Group 13–15 Rings: Structure, Bonding and Thermochemistry

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Dimeric inorganic rings $[X_2MYH_2]_2$ and $[XMYH]_2$ (X=H,F,Cl,Br,I; M=Al,Ga,In; Y=N,P,As) and related monomer compounds X_2MYH_2, XMYH were theoretically investigated at B3LYP /LANL2DZP level of theory. Optimized structures and standard thermodynamic parameters of gas phase dissociation reactions were obtained. Nitrogen and Al-containing rings have higher stability compared to P,As and Ga,In systems; substituents x have minor effect on M-Y dissociation energy. $[X_2MNH_2]_2$ dimers are stable in the gas phase up to 1100–1300K.

Keywords: inorganic rings; quantum-chemical study; gas phase thermochemistry

INTRODUCTION

Formation of group 13-15 rings, clusters and cages is well known in organometallic chemistry [1,2]. Oligomer species are easily formed via elimination reactions from the source X_3MYH_3 adduct, this path eventually leads to the binary pnictide MY:

$$X_3MYH_3 \xrightarrow{-HX} {}^1/_n\,[X_2MYH_2]_n \xrightarrow{-HX} {}^1/_m\,[XMYH]_m \xrightarrow{-HX} MY$$

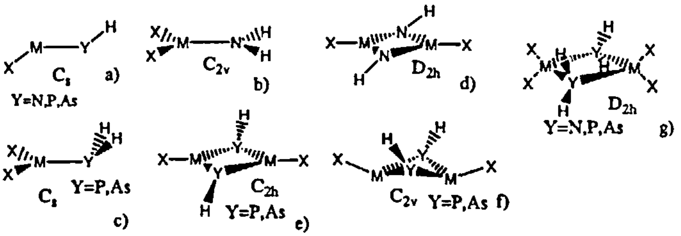
The association degree n, m in $[X_2MYH_2]_n$ and $[XMYH]_m$ compounds is strongly influenced by the bulkiness of the ligand X, the more bulky organic ligands result in low association degree. In case of inorganic ligands (X=H or halogen), highly polymeric species $[XMYH]_m$ are usually formed in the solid state [3,4]. Despite the numerous reports on synthesis and identification of group 13-15 oligomer compounds in the solid state and non-aqueous solutions [1,2], experimental reports on their thermochemistry are rather rare. Yet less is known about their gas-phase behavior. Quantum-chemical methods allow one to obtain a consistent set of structural and thermodynamic properties to model gas phase reactions of ring and cluster compounds [5,6]. The influence of the terminal atoms X on the bonding in the source donor-acceptor complexes X_3MYH_3 has been recently investigated [7]. Herein structures and thermodynamic characteristics of dimeric inorganic rings and related monomer compounds $[X_2MYH_2]_n$ and $[XMYH]_n$ n=1,2 (M=Al,Ga,In; Y=N,P,As; X=H,F,Cl,Br,I) are reported.

COMPUTATIONAL DETAILS

All computations have been carried out in the Center of the Computational Quantum Chemistry, University of Georgia, USA. Gaussian 94 set of programs was used throughout [8]. The three parameter exchange functional of Becke [9] with the gradient-corrected functional of Lee, Yang and Parr [10] (B3LYP) was used in conjunction with effective core potential basis set of Hay and Wadt [11] augmented by *d* and *p* polarization functions [7] (LANL2DZP). As was shown before [7] this level of theory gives adequate description for the dissociation energy of the parent donor-acceptor compounds X_3MYH_3. All structures were fully optimized with subsequent vibrational analysis and correspond to the minimum of potential energy surface. The standard reaction enthalpies (298.15 K, 1 atm) were calculated with account of the zero point vibrational energy (ZPVE) and thermal correction. ZPVE was obtained from unscaled vibrational frequencies.

RESULTS AND DISCUSSION

Structures of investigated compounds are presented in the Figure 1. All XMYH and $[X_2MYH_2]_2$ species posses symmetric geometries (C_s and D_{2h} point group, Figure 1 (*a,g*), respectively). Pyramidalization of



FUGURE 1 Structures of investigated compounds

3-coordinated P and As centers was found for X_2MYH_2 and $[XMYH]_2$, in agreement with previous experimental [12] and theoretical [13,14] works. These compounds are planar in case of Y=N (Figure 1 *b,d*) but adopt distorted structures for Y=P,As (Figure 1 *c,e,f*). For the distorted $[XMYH]_2$ species two stable isomers of C_{2h} and C_{2v} symmetry were obtained, in all cases C_{2v} isomer has the lowest energy, but the C_{2h}-C_{2v} energy difference is very small (mean 5, maximum 15 kJ mol^{-1}). Predicted metal-pnictide bond distances for the $[X_2MYH_2]_{1,2}$ and $[XMYH]_{1,2}$ species are presented in Tables 1 and 2, respectively.

M-Y bond lengths exhibit expected decreasing trend with decreasing coordination number on M and Y centers. The most pronounced changes are found for the nitrogen species (11% increase of M-Y bond length in dimer compared to monomer), while only 5-6% bond elongation is observed for P,As compounds. For all species, M-Y bond length is not very sensitive toward the nature of the halogen atom X, the mean difference between F and I compounds is less than 0.01 Å.

Standard enthalpies and entropies for the dissociation processes $[X_2MYH_2]_2 = 2\ X_2MYH_2$ and $[XMYH]_2 = 2\ XMYH$ are given in Tables 3 and 4, respectively. Nitrogen-containing rings have significantly higher dissociation enthalpies compared to P,As. Temperature, at which equilibrium constant of dissociation reaction $[X_2MYH_2]_2 = 2\ X_2MYH_2$ is equal 1, can be estimated from the standard enthalpies and entropies as $T=\Delta H^0_{(298)}/\Delta S^0_{(298)}$. This value may serve as a criterion of gas-phase ring stability. Aluminum containing rings are stable up to 1300-1500K (Y=N), 700-800K (Y=P), 500-600K(Y=As), gallium and indium rings are by 200-250 K less stable for all Y.

Dimeric $[XMYH]_2$ species exhibit even higher stability toward the dissociation (Table 4). However, since they bear unsaturated Y, M centers, further association processes are expected to be favorable.

TABLE 1 Calculated M-Y bond lengths (in Å) for $[X_2MYH_2]_n$ n=1,2 compounds

M	X	X_2MYH_2			$[X_2MYH_2]_2$		
		Y=N	Y=P	Y=As	Y=N	Y=P	Y=As
Al	H	1.774	2.345	2.461	1.977	2.483	2.591
	F	1.752	2.325	2.435	1.945	2.454	2.557
	Cl	1.752	2.329	2.440	1.948	2.455	2.559
	Br	1.755	2.333	2.445	1.952	2.457	2.562
	I	1.757	2.338	2.450	1.955	2.459	2.565
Ga	H	1.804	2.355	2.470	2.021	2.503	2.606
	F	1.773	2.330	2.438	1.983	2.474	2.573
	Cl	1.775	2.334	2.445	1.986	2.470	2.570
	Br	1.779	2.341	2.452	1.991	2.473	2.574
	I	1.783	2.346	2.458	1.997	2.476	2.578
In	H	1.969	2.539	2.643	2.196	2.691	2.788
	F	1.936	2.507	2.609	2.162	2.657	2.750
	Cl	1.933	2.513	2.615	2.159	2.651	2.744
	Br	1.938	2.521	2.621	2.163	2.656	2.751
	I	1.942	2.526	2.628	2.167	2.660	2.755

TABLE 2 Calculated M-Y bond lengths (in Å) for XMYH, and C_{2v} and C_{2h} (in parentheses) isomers of $[XMYH]_2$

M	X	XMYH			$[XMYH]_2$		
		Y=N	Y=P	Y=As	Y=N	Y=P	Y=As
Al	H	1.616	2.157	2.258	1.806	2.339 (2.323)	2.459 (2.492)
	F	1.659	2.181	2.292	1.795	2.342 (2.330)	2.467 (2.480)
	Cl	1.651	2.157	2.280	1.796	2.341 (2.328)	2.464 (2.480)
	Br	1.653	2.164	2.281	1.797	2.343 (2.330)	2.466 (2.483)
	I	1.652	2.162	2.279	1.798	2.344 (2.331)	2.467 (2.485)
Ga	H	1.678	2.167	2.272	1.846	2.365 (2.349)	2.480 (2.481)
	F	1.706	2.194	2.283	1.834	2.381 (2.393)	2.501 (2.508)
	Cl	1.706	2.175	2.282	1.836	2.377 (2.385)	2.497 (2.507)
	Br	1.706	2.176	2.284	1.837	2.378 (2.385)	2.498 (2.509)
	I	1.707	2.185	2.285	1.839	2.378 (——)	2.498 (2.511)
In	H	1.847	2.346	2.447	2.011	2.553 (2.541)	2.664 (2.685)
	F	1.876	2.375	2.486	2.002	2.577 (2.584)	2.687 (2.687)
	Cl	1.877	2.356	2.470	2.001	2.573 (2.582)	2.684 (2.686)
	Br	1.878	2.359	2.468	2.003	2.574 (2.584)	2.686 (2.688)
	I	1.879	2.355	2.473	2.005	2.574 (2.584)	2.687 (2.689)

TABLE 3 Calculated standard dissociation enthalpies $\Delta H^0_{(298)}$, kJ mol^{-1} and entropies $\Delta S^0_{(298)}$, J mol^{-1} K^{-1} for $[X_2MYH_2]_2$

M	X	Y=N		Y=P		Y=As	
		$\Delta H^0_{(298)}$	$\Delta S^0_{(298)}$	$\Delta H^0_{(298)}$	$\Delta S^0_{(298)}$	$\Delta H^0_{(298)}$	$\Delta S^0_{(298)}$
Al	H	226.0	183.8	148.0	175.4	116.1	176.6
	F	282.3	191.7	131.8	194.6	92.1	194.2
	Cl	262.3	192.9	128.3	193.2	89.9	196.9
	Br	251.2	193.0	122.4	193.5	84.5	194.6
	I	240.2	193.9	119.6	196.8	82.3	197.7
Ga	H	192.1	184.5	115.4	176.3	90.3	179.7
	F	241.0	197.6	76.2	189.4	41.0	189.1
	Cl	223.7	195.6	76.9	191.5	42.8	193.2
	Br	214.9	196.3	74.3	190.4	41.4	191.8
	I	204.2	196.2	73.4	193.0	41.3	193.8
In	H	211.8	183.2	116.8	180.5	89.5	180.8
	F	252.4	214.8	81.8	187.3	44.9	184.3
	Cl	242.6	204.4	81.4	189.4	45.8	188.8
	Br	234.6	211.5	78.2	189.9	43.9	189.9
	I	225.9	204.5	75.9	190.0	42.9	190.1

TABLE 4 Calculated standard dissociation enthalpies $\Delta H^0_{(298)}$, kJ mol^{-1} and entropies $\Delta S^0_{(298)}$, J mol^{-1} K^{-1} for $[XMYH]_2$ (C_{2v})

M	X	Y=N		Y=P		Y=As	
		$\Delta H^0_{(298)}$	$\Delta S^0_{(298)}$	$\Delta H^0_{(298)}$	$\Delta S^0_{(298)}$	$\Delta H^0_{(298)}$	$\Delta S^0_{(298)}$
Al	H	563.3	131.8	331.0	187.6	303.1	186.6
	F	640.6	196.3	413.8	188.4	420.8	190.4
	Cl	623.8	196.3	345.8	188.9	357.0	188.2
	Br	610.0	195.4	335.6	186.7	338.9	187.9
	I	597.2	194.8	326.7	185.3	310.5	183.2
Ga	H	455.1	185.9	331.6	181.1	336.4	181.5
	F	494.2	191.6	309.3	181.1	264.3	173.6
	Cl	491.2	192.2	273.1	176.6	258.7	175.1
	Br	481.5	191.0	268.9	177.7	254.2	175.7
	I	473.6	190.2	270.4	181.0	248.8	175.4
In	H	425.6	183.8	300.2	175.9	310.8	177.9
	F	435.2	186.4	313.2	184.8	323.9	190.1
	Cl	440.6	189.6	265.6	174.3	280.5	184.3
	Br	434.8	188.7	262.4	177.4	264.4	180.6
	I	430.4	188.1	254.1	173.9	249.6	159.9

Indeed, it was predicted [5] that dimer-trimer reorganization energy of $[ClAlNH]_2$ is highly exothermic and clusters $[ClAlNH]_{4,6}$ are the most stable gas phase species. Theoretical study of trimers and tetramers $[XMYH]_{3,4}$ is underway and will be the subject of further publications.

Acknowledgements
This research was conducted in close collaboration with Center for Computational Quantum Chemistry, University of Georgia, USA (Director Prof. H.F. Schaefer) and in part was supported by the Center for Fundamental Natural Science, Russia, Grant M99-2.5П-160.

References

[1] C.E. Housecroft, Ed. Comprehensive Organometallic Chemistry II, Vol. 1. Pergamon, London (1995).
[2] I. Haiduc, F.T. Edelmann, Supramolecular Organometallic Chemistry, Wiley VCH, New York, (1999).
[3] J.A. Jegier, S. McKernan, W.L. Gladfelter, Inorg. Chem. **38**, 2726 (1999).
[4] W.G. Woods, A.L. McCloskey, Inorg. Chem. **2**, 861 (1963).
[5] A.Y. Timoshkin, H.F. Bettinger, H.F. Schaefer, J. Amer. Chem. Soc. **119**, 5668 (1997).
[6] H. Ni, D.M. York, L. Bartolotti, R.L. Wells, W. Yang, J. Amer. Chem. Soc. **118**, 5732 (1996).
[7] A.Y. Timoshkin, A.V. Suvorov, H.F. Bettinger, H.F. Schaefer, J. Amer. Chem. Soc. **121**, 5687 (1999).
[8] Frisch, M.J.; Trucks, G.W.; Schlegel, H.B.; Gill, P.M.W.; Johnson, B.G.; Robb, M.A.; Cheeseman, J.R.; Keith, T.; Petersson, G.A.; Montgomery, J.A.; Raghavachari, K.; Al-Laham, M.A.; Zakrzewski, V.G.; Ortiz, J.V.; Foresman, J.B.; Cioslowski, J.; Stefanov, B.B.; Nanayakkara, A.; Challacombe, M.; Peng, C.Y.; Ayala, P.Y.; Chen, W.; Wong, M.W.; Andres, J.L.; Replogle, E.S.; Gomperts, R.; Martin, R.L.; Fox, D.J.; Binkley, J.S.; Defrees, D.J.; Barker, J.; Stewart, J.P.; Head-Gordon, M.; Gonzalez, C.; and Pople, J.A. GAUSSIAN 94 Revision C.3, Gaussian, Inc., Pittsburgh PA, 1995.
[9] A.D. Becke, J. Chem. Phys. **98**, 5648. 1993,.
[10] C. Lee, W. Yang, R.G. Parr, Phys. Rev. B. **37**, 785 (1988).
[11] P.J. Hay, W.R. Wadt, J. Chem. Phys. **82**, 270 (1985).
[12] P.P. Power, R.J. Wehmshulte, J. Am. Chem. Soc. **118**, 791 (1996).
[13] R.D. Davy, H.F. Schaefer, J. Phys. Chem. A **101**, 5707 (1997).
[14] R.D. Davy, H.F. Schaefer, J. Phys. Chem. A **101**, 3135 (1997).